



Soot black carbon concentration and isotopic composition in soils from an arid urban ecosystem

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ABSTRACT

Black carbon (BC) is a poorly understood type of organic carbon but it is present in almost all environmental systems (i.e., atmosphere, soil and water). This work focuses on soot BC in desert soils and, in particular, urban soils from the Phoenix, Arizona metropolitan area. Soot BC is that fraction of black carbon formed from the condensation of gas phase molecules produced during burning. Soot BC in Phoenix area soils exhibits a range in both concentration and isotopic composition. Soot BC concentration in 52 soils (desert, agricultural and urban) ranges from 0.02–0.54 wt% and comprises from < 1 to as much as 89% of the soil organic carbon (OC). Soot BC concentrations are higher in urban soils than in desert or agricultural soils. The average isotopic composition of soot BC is $-18‰ \pm 3‰$; this is an enrichment of 5.5‰ relative to bulk soil organic carbon. The distribution in concentration and variation in isotopic composition across the study area suggests soot BC in this arid-land city has multiple sources, including a significant fossil fuel component.

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1. Introduction

Black carbon (BC) is the product of incomplete combustion of fossil fuels and biomass. It is traditionally thought to be the most refractory, aromatic substance remaining after combustion (Goldberg, 1985). Black carbon refers to a continuum of combustion products that range from slightly charred, degradable biomass to highly condensed, refractory soot (Masiello, 2004). Because BC is operationally defined, differences in the precision and accuracy of the various quantification methods have led to a wide range in reported BC concentrations. The different methods isolate or detect different parts of the BC continuum and different methods reflect greater or lesser degrees of interference (such as the presence of false positives). Thus, BC can be difficult to define and to quantify.

The term “soot BC” was first used by Schmidt and Noack (2000) to describe the aromatic byproduct of carbon combustion that forms in the gas phase at high temperatures. Soot BC is <1 μm in size and smaller than other combustion products that are sometimes called black carbon (i.e., char and charcoal). Soot BC, like all sub-categories of the BC continuum, is an operational definition that defines the material using a specific process to determine its identity (here soot BC is defined by its method of quantification; see methods, Section 2.2). Soot BC is known to be produced during fossil fuel burning (Widory, 2006; Lopez-Veneroni, 2009). More recent work has shown that biomass burning can also produce soot

BC; soot BC is produced from combustion by intense fire, for instance during stubble burning (Rivas et al., 2012). Soot produced from biomass burning has also been identified in lake sediments based on elemental carbon measurements using thermal/optical methods (Han et al., 2012). Furthermore, studies of pinewood charring using ¹³C NMR have shown that increasing the charring temperature enhances signal intensity in the aryl carbon regions due to increased aromaticity in the chemical structure. At charring temperatures of 250 °C, more than 60% of the signal intensity is attributed to the aryl carbon region (Baldock and Smernik, 2002). Natural fires have been shown to reach temperatures of 800 °C (Johnson and Miyanishi, 2001) suggesting that forest fires are more than hot enough to generate soot BC. We note that fuel and oxygen concentrations are also important for soot BC production; the molar ratio of oxygen:fuel for complete combustion is 25:4 and soot particles are typically formed under conditions of reduced oxygen content (Johnson and Miyanishi, 2001). Our work focuses specifically on the soot BC fraction of the soil organic carbon in the Phoenix metropolitan area.

In recent years, black carbon has been increasingly studied because it is found in both marine and terrigenous systems, it plays an important role in the long term carbon cycle and it is a global warming agent (Menon et al., 2002; Masiello, 2004). Despite a considerable range in BC estimates due to measurement uncertainties (Mannino and Harvey, 2004; Ramanathan and Carmichael, 2008), sources of BC, especially those from fossil fuel burning, are fairly well known (Penner et al., 1993). Much less is known about the magnitude and distribution of BC sinks (Masiello and Druffel,

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1998; Masiello, 2004). Black carbon generally comprises roughly 1–8% of soil organic carbon (Gonzalez-Perez et al., 2004), but can be as much as 35% of soil organic carbon (OC) in frequently burned soils (Skjemstad et al., 2002). Traditionally, due to its aromatic content, BC was deemed to be highly refractory. Results from Preston and Schmidt (2006) indicate that BC decomposes very slowly, with turnover on millennial timescales (5–7 ky). However, Bird et al. (1999) compared savannah soils that were protected from natural burning to sites that had been burned continually over time and were able to calculate a half-life for oxidation-resistant elemental carbon of < 100 years. Others results demonstrate that BC can be degraded by microbes on relatively short timescales (10–100 s of years; Solomon et al., 2007; Hilscher et al., 2009; Steinbeiss et al., 2009; Zimmerman, 2010) and suggest BC is more reactive in the terrigenous environment than it has been considered previously.

Most soil studies present only BC concentration data, [BC], with very few reports of soil BC isotopic composition ($\delta^{13}\text{C}_{\text{BC}}$). Early studies from the fire literature generally reported that charred plant material has an isotopic composition similar to that of the biomass from which it derived (Leavitt et al., 1982; Bird and Grocke, 1997). However, other data indicate some burned materials are isotopically distinct from their unburned sources (Cachier et al., 1995; Czimczik et al., 2002; Krull et al., 2003; Das et al., 2010) and that certain changes in isotopic composition are unique to the combustion of specific types of starting material (Table 1). For example, burned C_4 plant material is isotopically depleted in ^{13}C by -4% to -6% relative to the unburned C_4 material (Krull et al., 2003; Das et al., 2010). In contrast, burned fossil fuel is enriched in ^{13}C by $+1\%$ to $+8\%$ relative to the starting material (Widory, 2006; Lopez-Veneroni, 2009). Generally, C_3 plant material shows little or no fractionation as a result of burning (Das et al., 2010) and, to the best of our knowledge, there are no studies of the fractionation during the burning of CAM plants or cactus. These fractionation patterns between starting material and burned byproduct are just one tool that can help distinguish among C_3 and C_4 plants, fossil fuels and their respective combustion byproducts.

Our primary objective was to quantify soot BC concentrations, soot [BC], in central Arizona soils and determine the distribution of soot BC across various land use types (i.e., rural-desert, agricultural and urban). Soils are a potentially important sink for soot BC, and this study quantifies soot BC in a previously unstudied reservoir, desert soils. We hypothesize that soot BC is a significant fraction of the bulk soil OC because desert soils typically have very low OC content. In addition, inputs of soot BC to central AZ are likely high, since urban systems can export large amounts of pyrogenic

carbon (mostly from the burning of fossil fuels; Yan et al., 2006). Elevated carbon inputs in the form of soot BC to the desert soils of central AZ may have the potential to affect soil biogeochemistry. We show that soot BC is a significant fraction of soil OC in central AZ and that soot BC is not evenly distributed across the region, suggesting soot BC derives from local as opposed to distant sources. A secondary objective was to quantify soot BC isotopic composition ($\delta^{13}\text{C}_{\text{soot BC}}$) and assess differences between $\delta^{13}\text{C}_{\text{soot BC}}$ and $\delta^{13}\text{C}_{\text{OC}}$. By investigating patterns in both concentration and soot BC isotopic composition across the region, we can begin to assess the sources of soot BC in central AZ soils.

2. Method

2.1. Study site

The Central Arizona-Phoenix Long-Term Ecological Research (CAP-LTER) program studies the urban ecosystem of metropolitan Phoenix and the surrounding Sonoran desert (Fig. 1). Central AZ is semi-arid (< 18 cm annual rainfall) and the area comprises a high density urban core, rapidly developing suburbs, agricultural lands of various ages and undeveloped native desert. Over the last 10 years the Phoenix metropolitan population increased by about 30% to its current population of 4.2 million (2010 US Census). Between 2000 and 2004, this rapid growth expanded the footprint of the Phoenix metropolitan area by 225 km², or 154,110 m²/day (Maricopa Association of Governments), making Phoenix one of the fastest growing areas in the United States.

We analyzed samples collected in 2005 during CAP-LTER's semi-decadal field survey of urban, agricultural and rural-desert sites. The rural-desert sites hereafter will be referred to as 'desert' sites. At each site (a 30 × 30 m plot) samples were collected from four 10 cm soil cores taken at the cardinal points (NSEW). The cores were homogenized, dried and stored in the dark, dry at 20 °C. Soils in central AZ are classified by the USDA-NRCS (United States Department of Agriculture – National Resource Conservation Service) as aridisols (soils that are too dry for mesophytic plant life and that have low OC content) and entisols (soils that have little or no evidence for the development of pedogenic horizons; Bohn et al., 2001; USDA-NRCS, <http://soils.usda.gov/>). Soils collected in this study are heterogeneous and generally large grained; the average soil size fractions are 45.0% sand, 37.5% silt, and 17.4% clay (<http://caplter.asu.edu/data/?id=281>). The plant life in the study area can be classified, generally, as typical arid land or desert vegetation. The most numerous plant species found in central AZ are small shrubs and trees (all C_3 plants) and a variety of annual plants (C_3 and C_4). Triangle-leaf bursage (*Ambrosia deltoidea*), brittlebush

Table 1
Isotopic composition of various carbon sources and combustion byproducts (modified from Bird and Ascough (2010)).

Starting material (SM)	$\delta^{13}\text{C}_{\text{SM}}$ (‰)	Burned byproduct (BB)	$\delta^{13}\text{C}_{\text{BB}}$ (‰)	Isotopic change
C_3 vegetation ^a	–25 to –26	Ash	–25 to –26 ^{f,g}	No change
C_3 vegetation ^a	–25 to –26	smoke/soot BC	–25 to –26 ^{f,g}	No change
C_4 vegetation ^a	–12 to –14	Ash	–11 to –18 ^{f,g}	Depleted
C_4 vegetation ^a	–12 to –14	Smoke/soot BC	–13 to –21 ^{f,g}	Depleted
C_4 vegetation ^b	–12 to –15	char	–12 to –18	Depleted
C_4 vegetation ^c	–12 to –14	Aerosol	–13 to –19	Depleted
Fossil fuel ^d	–26 to –29	Soot	–21 to –28	Enriched
Fossil fuel ^e	–27 to –29	Particles	–24 to –27	Enriched

^a Das et al. (2010).

^b Krull et al. (2003).

^c Cachier et al. (1985).

^d Widory (2006).

^e Lopez-Veneroni (2009).

^f Range calculated from reported $\Delta\delta^{13}\text{C}$ values.

^g Uncertainties reported in the literature are $\pm 1\%$.

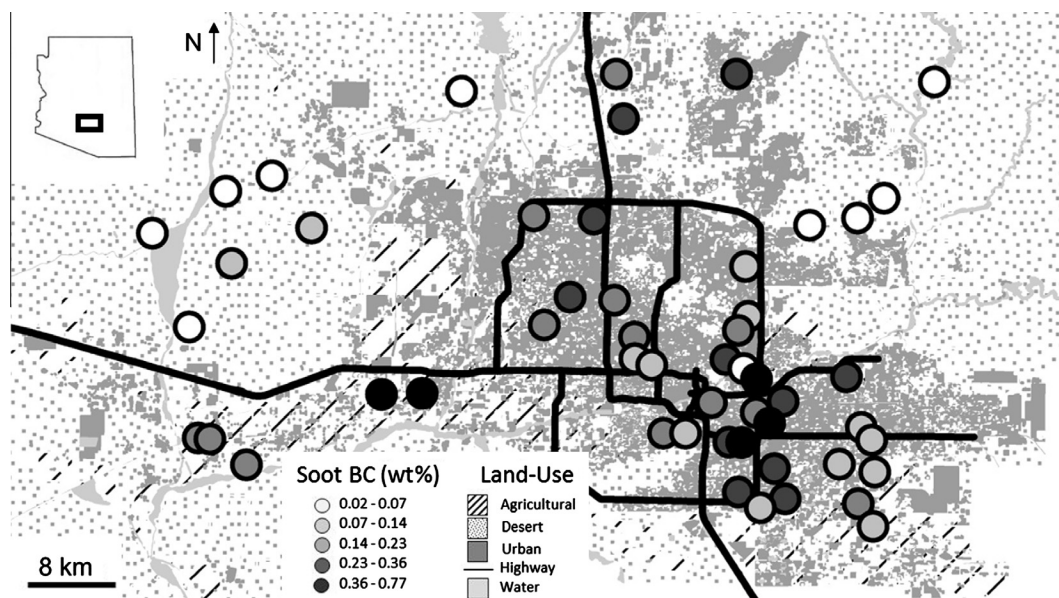


Fig. 1. Map of the Phoenix metropolitan area, with land use type (background shading), roads (solid lines), sample locations (circles) and soot BC concentrations (circle shading). The inset map shows the state of Arizona and the box indicates the location of the CAP-LTER study area.

(*Encelia farinosa*) and creosote bush (*Larrea tridentata*) are examples of the dominant shrub species; blue palo verde (*Parkinsonia florida*) is an example of a dominant tree species; and prickly lettuce (*Lactuca serriola*; C₄), Mexican lovegrass (*Eragrostis mexicana*; C₄), wild cabbage (*Brassica oleracea*; C₃), and spiny sowthistle (*Sonchus asper*; C₃) are examples of dominant annual species. While cacti (CAM plants) grow in the region, they are not the dominant plant type at any of our sites. At the agricultural samples sites, the predominant crop species are corn (*Zea mays*; C₄) and alfalfa (*Medicago sativa*; C₃); however, agricultural sites were not always in cultivation at the time of sampling. Although C₄ plants are found in central AZ the majority of plant biomass in the region is C₃ plants (see Section 3.2).

Because central AZ is densely populated, the Maricopa County Community Wildfire Protection Plan has been established to suppress wildfires in this area. Therefore, large scale brush and shrub fires in central AZ are rare. Most of the sites in this study are located in areas with very low wildfire occurrence over the period 1980–2010 (0–2 occurrences per 4 km² (1000 acres; Maricopa County Department of Emergency Management, 2010).

We used data from CAP-LTER for site locations, land use categories and bulk soil organic carbon concentrations. Briefly, organic carbon was calculated as the difference between total carbon (TC) and inorganic carbon (IC; see <http://caplter.asu.edu/data/protocols/?id=47>); TC was measured using elemental analysis and IC was measured using calcimetry (Sherrod et al., 2002).

2.2. Chemo-thermo oxidation method

We quantify soot BC using chemo-thermo oxidation (CTO375; Gustafsson et al., 1997, 2001) followed by elemental analysis and isotope ratio mass spectrometry (EA-IRMS). Soot [BC] and $\delta^{13}\text{C}_{\text{soot BC}}$ were measured in 83 soil samples from 52 different CAP-LTER sites (Table 2). The samples were ground to a fine powder in a ball mill, weighed (~18 mg) into silver capsules (Costech Analytical Technologies, Valencia, CA, USA) and placed in a custom built, Teflon™ 25 well tray. Samples were wetted with deionized H₂O (18.2 MΩ cm; NANOpure Diamond, Barnstead, Inc. Dubuque, IA, USA) and carbonate was removed by incremental additions of 4 M hydrochloric acid (J.T. Baker, Inc., Philipsburg, NJ, USA). Samples were dried again, transferred to an aluminium tray, and baked

at 375 °C for 24 h in a well ventilated furnace under ambient atmospheric conditions (20% O₂) to remove labile (non-black) organic carbon. Oven temperatures were monitored closely using a thermocouple until temperature reached 375 °C in order to prevent temperature overshoot. Carbon detected by EA-IRMS after CTO375 was defined as soot BC; this method yields a very conservative estimate of soot [BC] based on laboratory inter-comparison studies (Hammes et al., 2007). We also independently measured bulk OC and $\delta^{13}\text{C}_{\text{OC}}$ in 62 samples from 25 of the CAP-LTER sites (see Supplementary Table S1). Samples from these sites were acidified, but not thermally oxidized, prior to analysis.

The EA-IRMS detection limits are 1 μg C for [C] and 4 μg C for $\delta^{13}\text{C}$, respectively. We determined analytical precision and accuracy for soot BC concentration using a standard reference material (an Australian vertisol, 0.18 wt%, BC from CSIRO Land & Water, Adelaide, Australia; Gustafsson et al., 1997; Hammes et al., 2007); replicate analyses of the reference soil yielded a relative standard deviation (RSD) of 6% (n = 6). A Montana soil ($\delta^{13}\text{C}_{\text{OC}} = -24.7\text{‰}$; NIST 2710) was the standard reference material for the carbon isotope ratios; replicate analyses of the Montana soil yielded an RSD of 0.9% (n = 7). Isotopic compositions for soot BC are expressed in delta (δ) notation relative to the V-PDB standard: $\delta^{13}\text{C} = (R_{\text{sa}}/R_{\text{std}} - 1) \times 1000$, where R_{sa} and R_{std} are the ¹³C/¹²C ratio in the sample and standard, respectively. Samples were generally analyzed in duplicate or triplicate (see Table 2).

2.3. Data processing

Linear regression statistics are presented for all data (SPSS 17; SPSS, Inc.). A Shapiro–Wilk test for normality was completed for all data sets. Data for each land use type were compared using Mann–Whitney rank sum test (Sigma Plot 11; Systat Software, Inc.). Values are considered significant for $p < 0.05$.

3. Results and discussion

3.1. Soot BC concentrations

Soot BC is found in all 52 samples (Fig. 1, Table 2). Soot BC concentration, i.e., soot [BC], ranges from 0.02–0.54 wt% (avg: 0.23 wt%) based on dry soil mass. The average standard deviation

Table 2
Land use type, carbon content (inorganic, organic and soot BC), BC/OC ratio and carbon isotopic composition ($\delta^{13}\text{C}_{\text{soot BC}}$, $\delta^{13}\text{C}_{\text{OC}}$) for the 52 CAP-LTER sites used in this study.

Site	n^a	Land use	Inorg. C ^b (wt%)	Org. C ^b (wt%)	Soot BC ^c (wt%)	Soot BC (mgBC/gSoil)	BC/OC (%)	$\delta^{13}\text{C}_{\text{soot BC}}^{c,d}$ (‰)	$\delta^{13}\text{C}_{\text{OC}}^{c,d}$ (‰)
1	3	Agriculture	0.21	0.68	0.14 ± 0.01	0.014 ± 0.001	21	-19.23 ± 0.06	-22.3 ± 0.4
2	2	Agriculture	0.33	1.70	0.11 ± 0.04	0.011 ± 0.004	6	-18.74 ± 0.04	
3	1	Agriculture	0.23	0.97	0.07	0.007	8	-18.1	
4	1	Agriculture	1.00	0.81	0.23	0.023	29	-14.2	
5	2	Agriculture	0.30	0.39	0.16 ± 0.06	0.016 ± 0.006	42	-19.0 ± 0.7	-22.62 ± 0.07
6	3	Agriculture	0.17	0.84	0.12 ± 0.03	0.012 ± 0.003	14	-19.2 ± 0.1	-24.6 ± 0.1
7	1	Desert	0.04	1.50	0.03	0.003	2	-21.3	
8	2	Desert	0.23	1.43	0.039 ± 0.003	0.0039 ± 0.0003	3	-18.74 ± 0.06	
9	1	Desert	0.72	0.78	0.04	0.004	5	-17.7	
10	2	Desert	0.09	2.88	0.04 ± 0.03	0.004 ± 0.003	1	-18.7 ± 0.5	
11	3	Desert	0.11	0.07	0.07 ± 0.01	0.007 ± 0.001	89	-18.85 ± 0.07	-24.8 ± 0.4
12	1	Desert	0.14	0.23	0.04	0.004	17	-10.7	
13	1	Desert	0.13	0.39	0.05	0.005	14	-12.5	
14	1	Desert	0.56	0.40	0.07	0.007	19	-12.5	
15	1	Desert	0.83	0.44	0.18	0.018	41	-21.1	
16	3	Desert	0.12	1.13	0.058 ± 0.001	0.0058 ± 0.0001	5	-18.3 ± 0.5	
17	1	Desert	0.12	1.39	0.09	0.009	7	-14.7	
18	1	Desert	0.26	1.00	0.04	0.004	4	-18.9	
19	3	Desert	0.87	0.61	0.18 ± 0.02	0.018 ± 0.002	29	-19.3 ± 0.7	-22.3
20	1	Desert	0.04	0.43	0.36	0.036	83	-24.8	-24.66 ± 0.03
21	2	Urban	0.40	1.73	0.09 ± 0.01	0.009 ± 0.001	5	-16.8 ± 0.4	
22	2	Urban	0.33	3.38	0.08 ± 0.03	0.008 ± 0.003	2	-20.9 ± 0.4	
23	2	Urban	1.16	1.15	0.04	0.004	3	-25.3 ± 0.3	
24	1	Urban	0.82	3.21	0.15	0.015	5	-18.9	
25	1	Urban	1.09	0.28	0.22	0.022	79	-16.6	
26	2	Urban	0.23	2.11	0.19 ± 0.03	0.019 ± 0.003	9	-15.6 ± 0.9	
27	3	Urban	0.40	1.77	0.21 ± 0.05	0.021 ± 0.005	12	-11 ± 2	
28	1	Urban	1.82	0.55	0.35	0.035	65	-17.6	
29	2	Urban	1.35	0.82	0.17 ± 0.02	0.017 ± 0.002	21	-19.1 ± 0.3	
30	1	Urban	1.03	1.32	0.30	0.03	23	-15.6	
31	1	Urban	0.19	3.42	0.11	0.011	3	-11.7	
32	2	Urban	1.46	0.95	0.54 ± 0.07	0.054 ± 0.007	57	-21 ± 1	
33	2	Urban	0.23	0.33	0.130 ± 0.003	0.0130 ± 0.003	40	-18.0 ± 0.3	-23.4
34	1	Urban	0.12	0.51	0.07	0.007	14	-18.4	-19.0 ± 0.5
35	2	Urban	0.88	1.59	0.46 ± 0.01	0.046 ± 0.001	29	-17.0 ± 0.8	
36	1	Urban	1.46	0.59	0.16	0.016	28	-11.7	
37	2	Urban	0.38	1.87	0.08 ± 0.02	0.008 ± 0.002	4	-20.5 ± 0.6	
38	2	Urban	0.79	1.37	0.26 ± 0.03	0.026 ± 0.003	19	-15.4 ± 0.5	
39	2	Urban	0.38	0.26	0.16 ± 0.03	0.016 ± 0.003	60	-17.3 ± 0.1	-22.3 ± 0.2
40	2	Urban	0.14	0.37	0.11 ± 0.01	0.011 ± 0.001	28	-17.9 ± 0.8	-23.35 ± 0.04
41	2	Urban	0.66	0.37	0.32 ± 0.05	0.032 ± 0.005	88	-20.8 ± 0.4	-23.77 ± 0.01
42	1	Urban	0.71	0.62	0.12	0.012	19	-18.5	
43	1	Urban	0.96	1.16	0.31	0.031	27	-13.5	
44	1	Urban	1.19	1.64	0.30	0.03	19	-15.1	
45	2	Urban	0.77	2.05	0.14 ± 0.03	0.014 ± 0.003	7	-19 ± 1	
46	2	Urban	1.24	1.72	0.44 ± 0.03	0.044 ± 0.003	26	-18.43 ± 0.09	
47	2	Urban	0.28	2.58	0.32 ± 0.03	0.032 ± 0.003	13	-16.2 ± 0.6	
48	3	Urban	1.52	2.57	0.47 ± 0.02	0.047 ± 0.002	18	-19 ± 1	
49	2	Urban	0.99	1.13	0.281 ± 0.001	0.0281 ± 0.0001	25	-16.4 ± 0.4	
50	2	Urban	1.17	0.61	0.44 ± 0.04	0.044 ± 0.004	72	-24 ± 1	-21.60 ± 0.01
51	2	Urban	0.64	1.21	0.32 ± 0.02	0.032 ± 0.002	27	-21 ± 1	-23.05 ± 0.03
52	2	Urban	0.50	1.02	0.30 ± 0.04	0.030 ± 0.004	30	-20 ± 1	

^a n = number of samples.

^b Data from CAP-LTER.

^c Mean ± 1 S.D.

^d Values are in permil vs. the VPDB standard.

of our soot [BC] determination based on replicate analyses is ± 0.02 wt% ($n = 30$; Table 2). The sample sites from this study are diverse with respect to land use, proximity to city center and other infrastructure (i.e., roads). Notably, soil soot BC is not evenly distributed across the CAP-LTER region, but appears to be concentrated near roads, and near the urban core (Fig. 1). In fact, soot [BC] and distance from city center are negatively correlated ($p < 0.05$, data not shown). Bulk soil OC concentrations, i.e., [OC], range from 0.07–3.7 wt% (avg: 1.2 wt%; McCrackin et al., 2008). There is no correlation between soot [BC] and [OC] in central AZ soils ($p > 0.05$, data not shown). This suggests either that soot BC and OC have different sources (i.e., burning events for soot BC and plant litter for OC) or that soot BC and OC have different reactivity in soil (i.e., bioavailability or photo-reactivity).

The amount of soot BC in central AZ soil varies with land use type (Fig. 2, Table 3); desert soils in general have lower soot [BC] than both urban and agricultural soils. Desert soils have an average soot [BC] of 0.1 wt% (95% confidence limit (CL): ± 0.03); significantly lower than both urban soot [BC] ($p < 0.001$) and agricultural soot [BC] ($p < 0.05$). Urban soils have the highest soot [BC], 0.3 wt% (95% CL: ± 0.04) on average and agricultural soils have an intermediate soot [BC] of 0.14 wt% (95% CL: ± 0.03). The amount of soot BC is statistically different for each land use type, suggesting that land use has an influence on the amount of soot BC added to or removed from the soil. This land use dependence should be considered in future assessments of regional or global BC budgets. Neither soot BC nor bulk organic carbon concentration was correlated with any soil size fraction (i.e., percent sand, silt, clay; $p > 0.05$). Urban soils

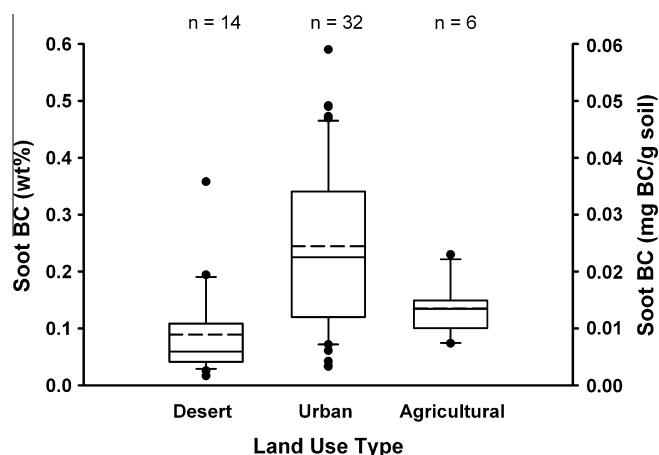


Fig. 2. Concentration of soot BC (wt%) for individual land use categories. Solid and dashed horizontal lines within the boxes indicate median and mean values, respectively. The upper and lower box boundaries denote the 25th and 75th percentiles, respectively; the upper and lower whiskers denote the 90th and 10th percentiles, respectively; the symbols are outlying points. Note, the agricultural mean and median lines overlap. The observed range of desert soot [BC] in Fig. 2 is skewed by two desert sites with very high soot [BC] (0.36 and 0.18 wt%). The median values for all three land use types are statistically different from each other ($p < 0.05$).

exhibit the greatest variation in soot [BC] while desert and agricultural soils are less variable (Fig. 2). The inherent site to site heterogeneity of soil accounts for the variation in average soot [BC] and [OC] within land use types (Table 3 and Fig. 2); nonetheless, the differences in soot [BC] among the three land use classifications are statistically significant. High soot [BC] in urban soils relative to desert and agricultural soils suggests that soot BC in central AZ may be anthropogenic. We suspect a major fraction of soot BC found in urban soils is derived from fossil fuel combustion, presumably from vehicle emissions (Sakurai et al., 2003). This conclusion is further supported by the accumulation of polycyclic aromatic hydrocarbons (PAHs) in urban Phoenix soils near roads (Marusenko et al., 2011). PAHs are individual molecules that have been classified as BC precursor molecules (Johnson and Miyanishi, 2001) and some methods (i.e., BPCA) can be used to identify both PAHs and soot BC (Masiello, 2004; Ziolkowski et al., 2011).

In central AZ soils, soot BC is a small fraction of the soil on a mass basis, but it can comprise a very large fraction of bulk soil organic carbon. Soot BC/OC ratios range from 1–89% (average soot BC/OC: 31%, $n = 52$; Fig. 3, Table 3). Because of the large range, soot BC/OC ratios for the three land use types are not statistically different from each other (Fig. 3; $p > 0.05$). The average BC/OC value of 31% is as high as some of the highest reported values from other places. For example, in the Australian vertisol (our SRM) and in a German chernozem, soot [BC] has been shown to comprise 1.2% and 8.7% of soil OC (respectively) based on analyses using the same CTO375 method we employ here (Hammes et al., 2007). The central AZ soot BC/OC values are higher even than those found in Amazonian *Terra Preta* soils, where pre-Columbian farmers added ash

Table 3

Average soot BC and soil OC concentrations, and soot BC/OC ratios for three land use types. Errors are \pm the standard error of the mean.

Land use type	Soot BC (wt%)	OC (wt%) ^a	Soot BC/OC ^b
Desert ($n = 14$)	0.08 ± 0.02	0.9 ± 0.2	0.29 ± 0.09
Urban ($n = 32$)	0.25 ± 0.02	1.4 ± 0.1	0.27 ± 0.03
Agricultural ($n = 6$)	0.14 ± 0.01	0.9 ± 0.1	0.20 ± 0.04

^a OC data from LTER database.

^b Ratio of soot BC to bulk OC (BC/OC) is calculated for individual sites within each land use type.

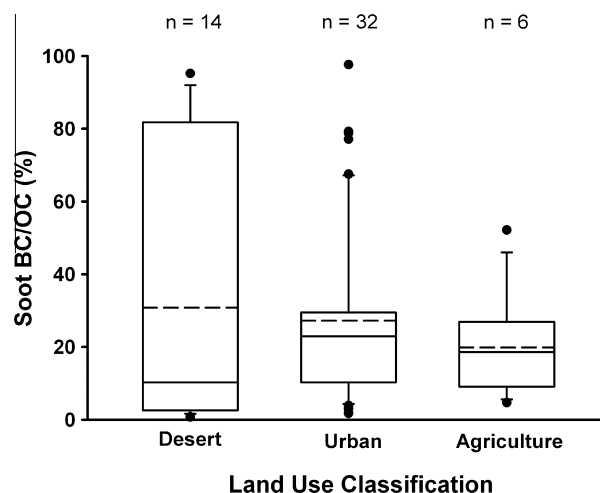


Fig. 3. Soot BC/OC (%) for individual land use categories. Solid and dashed horizontal lines within the boxes indicate median and mean values, respectively; upper and lower box boundaries denote the 25th and 75th percentiles, respectively; upper and lower whiskers denote the 90th and 10th percentiles, respectively; symbols are outlying points. There is no statistical difference among the median values for the three land use types ($p > 0.05$).

and char to increase soil fertility (BC/OC = ~20%; Glaser et al., 2001). The soot BC/OC ratios reported here are high despite the use of a rather conservative soot [BC] estimate (i.e., CTO375; Hammes et al., 2007).

We know of no published evidence suggesting soot BC inputs are anomalously high in central AZ. However, Kaye et al. (2011) found that aerosol carbon deposited from the atmosphere comprised 30–36% elemental carbon in the Phoenix-metro area. This percentage is similar to our average soot BC/OC value. Elemental carbon and the soot BC reported here are not exactly analogous, but the two materials are generally thought to have similar characteristics (Masiello, 2004). The high soot BC/OC ratios in the Phoenix area soils could be a result of very high soot BC inputs to central AZ soils (relative to other locations) or they may be the result of low soil OC contents. Previous work has shown that soil OC is quite low in this region (Bohn et al., 2001). If the high soot BC/OC ratio is due to low OC, we suggest that biogeochemical processes may remove soot BC less effectively than OC in arid land soils.

3.2. Soot BC isotopic composition

The $\delta^{13}\text{C}_{\text{soot BC}}$ ranges from -26‰ to -10‰ (avg: -18‰) and the bulk soil $\delta^{13}\text{C}_{\text{OC}}$ ranges from -25‰ to -18‰ (avg: -23‰) for all the sites analyzed (Fig. 4A). The average soot BC isotopic composition reported here compares well with other measurements of soil BC isotopic composition ($-18.8\text{‰} \pm 3.4\text{‰}$; Kawashima and Haneishi, 2012). The $\delta^{13}\text{C}_{\text{soot BC}}$ does not appear to be a function of black or organic carbon content (Fig. 4A, $p > 0.05$), nor is there any relation between $\delta^{13}\text{C}_{\text{soot BC}}$ and land use type (data not shown, $p > 0.05$). On average, soot BC in central AZ soils is enriched in ^{13}C relative to bulk soil OC by $\sim 5.5\text{‰}$ ($p < 0.05$; Fig. 4B). The bulk soil OC isotopic composition is consistent, not surprisingly, with a predominantly C_3 vegetation source, although, the $\delta^{13}\text{C}_{\text{soot BC}}$ is not. The difference in bulk OC and soot BC isotopic composition can either be attributed to different sources of soot BC and OC, to isotopic fractionation during the formation of soot BC from local plant life, or to different fractionation processes occurring post-deposition for OC and soot BC. While there is no clear relationship with soil carbon content, there is, however, a significant difference in the $\delta^{13}\text{C}_{\text{soot BC}}$ of the desert sites west and east of Phoenix. The average $\delta^{13}\text{C}_{\text{soot BC}}$ of desert sites to the west of the urban area

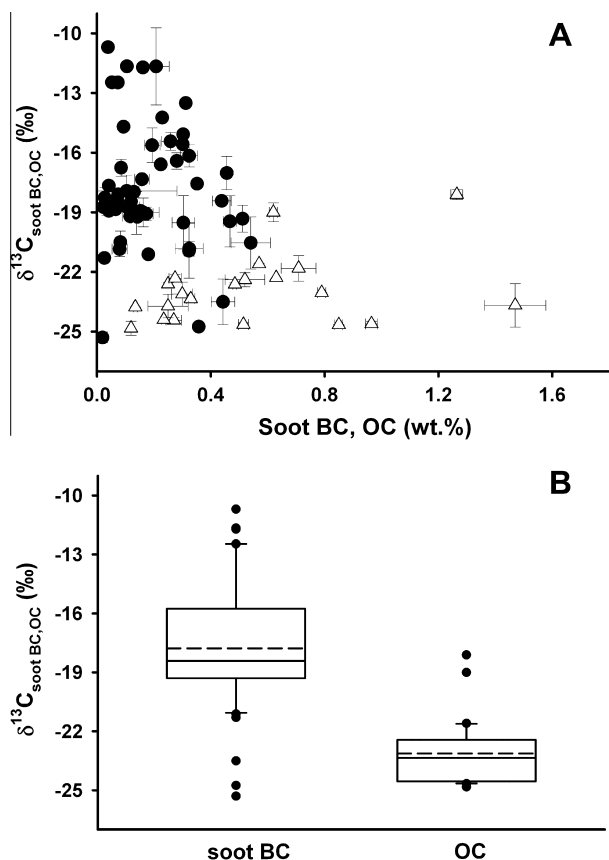


Fig. 4. Isotopic composition of OC and soot BC in central AZ. (A) $\delta^{13}\text{C}_{\text{soot BC}}$ (●) and $\delta^{13}\text{C}_{\text{OC}}$ (△) as a function of soot BC or soil OC content, respectively. Error bars are ± 1 SD based on three independent analyses; where error bars are not visible they smaller than the symbols. The analytical uncertainty is $\pm 0.03\text{‰}$ (not shown) and the relationship between $\delta^{13}\text{C}$ and concentration for either soot BC or OC is not significant ($p > 0.05$). (B) Summary of the range and variability in $\delta^{13}\text{C}_{\text{soot BC}}$ and $\delta^{13}\text{C}_{\text{OC}}$. Solid and dashed horizontal lines within the boxes indicate median and mean values, respectively; upper and lower box boundaries denote the 25th and 75th percentiles, respectively; upper and lower whiskers denote the 90th and 10th percentiles, respectively; symbols are outlying points. The median values for $\delta^{13}\text{C}_{\text{soot BC}}$ and $\delta^{13}\text{C}_{\text{OC}}$ are statistically different from each other ($p < 0.05$).

are $-16\text{‰} \pm 4\text{‰}$ while the desert sites east of the city have an isotopic composition of $-20\text{‰} \pm 3\text{‰}$. This difference strongly suggests the city is a source of soot BC to the downwind desert sites (see Section 3.4).

Examining the isotopic composition of parent and burned materials for plants and fossil fuels reveals information about the source of soot BC in soil. A recent review (Bird and Ascough, 2010) of the $\delta^{13}\text{C}$ of combusted material relative to that of starting materials provides context for interpreting these results. Table 1 is a summary of $\delta^{13}\text{C}$ values from the literature for various source materials and their corresponding combustion byproducts. It should be noted that the vegetation-derived combustion byproducts reported in these studies are char, ash and smoke. Char and ash are residual materials that are inherently different from soot (a byproduct formed in the gas phase). Smoke is generally classified as a large cluster of soot particles (100 μm or larger) and is usually big enough to be visible to the human eye; however, no clear cut distinction is made between smoke and soot (Johnson and Miyani-shi, 2001).

The isotopic compositions of the soot or smoke from C_3 plants are generally similar to those of the unburned vegetation (i.e., $<1\text{‰}$ isotopic fractionation relative to the starting material; Table 1). In contrast, burned C_4 plant material is generally depleted in ^{13}C relative to the unburned starting material. The reported

range in isotopic composition for burned C_3 and C_4 plant material (-26‰ to -25‰ for C_3 and -21‰ to -11‰ for C_4 materials, respectively; Table 1) is within in the range of measured $\delta^{13}\text{C}_{\text{soot BC}}$ values presented here (-26‰ to -10‰), suggesting that soot BC in the Phoenix area soils may include a contribution from C_3 and C_4 plants. Fossil fuel burning, on the other hand, results in combustion byproducts enriched by $\sim 2\text{--}6\text{‰}$ relative to the unburned starting material (Widory, 2006; Lopez-Veneroni, 2009; Table 1). Our $\delta^{13}\text{C}_{\text{soot BC}}$ values (-26‰ to -10‰) also correspond with the expected range for burned fossil fuels, suggesting a contribution of soot BC from this source to Phoenix area soils as well. The isotopic composition of soot BC presented here suggests all three potential sources (both C_3 and C_4 biomass, and fossil fuel) could contribute to soot BC in central AZ soil. Thus, we cannot eliminate any sources of soot BC based on isotopic composition alone. However, by determining the contribution of C_3 and C_4 plant material to the bulk OC pool, we may be able to eliminate possible sources of soot BC to central AZ soils.

3.3. Isotope mass balance

We were able to determine soot BC and OC concentration as well as soot BC and OC isotopic composition ($\delta^{13}\text{C}$) for the exact same soil samples at 13 of the CAP-LTER sites. This allowed us to make mass balance estimates of the percentage of C_3 and C_4 bulk organic material at each site. We assume the major inputs to soil organic carbon are C_3 and C_4 plant derived carbon and soot carbon. The mass balance for these species is

$$[\text{OC}] = [\text{C}_3] + [\text{C}_4] + \text{soot}[\text{BC}], \quad (1)$$

where $[\text{OC}]$, $[\text{C}_3]$, $[\text{C}_4]$, and soot $[\text{BC}]$ are the concentrations of each species. The corresponding isotopic mass balance for these components is

$$\delta^{13}\text{C}_{\text{OC}} \cdot [\text{OC}] = \delta^{13}\text{C}_{\text{C}_3} \cdot [\text{C}_3] + \delta^{13}\text{C}_{\text{C}_4} \cdot [\text{C}_4] + \delta^{13}\text{C}_{\text{soot BC}} \cdot \text{soot}[\text{BC}]. \quad (2)$$

The only unknown values in Eqs. (1) and (2) are $[\text{C}_3]$ and $[\text{C}_4]$. We measure $[\text{OC}]$, soot $[\text{BC}]$, $\delta^{13}\text{C}_{\text{OC}}$, $\delta^{13}\text{C}_{\text{soot BC}}$ directly, and we assume typical literature values for $\delta^{13}\text{C}_{\text{C}_3}$ and $\delta^{13}\text{C}_{\text{C}_4}$. The literature values for $\delta^{13}\text{C}_{\text{C}_3}$ range from -33‰ to -24‰ , and for $\delta^{13}\text{C}_{\text{C}_4}$ they range from -16‰ to -10‰ (Oleary, 1988).

Using the median values for $\delta^{13}\text{C}_{\text{C}_3}$ and $\delta^{13}\text{C}_{\text{C}_4}$ (-28.5‰ and -13‰ , respectively; Oleary, 1988), we calculated that the median wt% C_4 vegetation as a fraction of the total OC is $12 \pm 6\%$. This relatively low percentage is in agreement with our assumption (based on vegetation abundances) that carbon from C_4 plants constitutes a small amount of the total organic carbon in central AZ soils. By using the end member values for $\delta^{13}\text{C}_{\text{C}_3}$ and $\delta^{13}\text{C}_{\text{C}_4}$, we calculate C_4 vegetation as a fraction of the total OC is at most 23 wt% and as little as $<1\%$. This supposition is further supported by results from Rasmussen and White (2010) who found C_3 plant material was the dominant input to soil organic carbon in samples collected southeast of Phoenix, AZ in the same Sonoran desert region. Rasmussen and White (2010) did not report any plant litter more depleted in $\delta^{13}\text{C}$ than -26.2‰ . Given the range of isotopic compositions reported by Oleary (1988) it appears C_3 material in central AZ is somewhat more enriched than is typical on a global scale. In our model, the fraction of bulk OC that can be attributed to C_4 plants becomes smaller as the value for $\delta^{13}\text{C}_{\text{C}_3}$ becomes more positive (enriched), which suggests the actual contribution from C_4 plants is very likely less than our estimate of 12%.

In Section 3.2, we suggested the soot BC enrichment in ^{13}C relative to bulk soil OC ($\sim 5.5\text{‰}$; $p < 0.05$; Fig. 4B) can be interpreted multiple ways. One interpretation is that soot BC is derived from

the local soil OC and has undergone a fractionating process either during or after burning. An alternate interpretation is that the soot BC and the bulk soil OC are not derived from the same material. We address each of these in turn. The local soil OC is predominantly C_3 derived based on our isotopic mass balance. If our soot BC is derived from local C_3 material it should be unfractionated and reflect the more depleted $\delta^{13}C$ of C_3 plants, which it does not. This supposition is based on literature data that show no isotopic fractionation between burned C_3 vegetation and the starting material (Table 1). Our measured $\delta^{13}C_{\text{soot BC}}$ is enriched, consistent with a predominantly C_4 source that was fractionated during burning; however, this C_4 source cannot be local, based on the isotopic mass balance. The observation that soot BC is significantly enriched in ^{13}C relative to the bulk OC, supports the interpretation that soot BC and bulk OC have different sources. To further build on the argument that soot BC is not predominantly derived from local OC, large scale fires hot enough to produce soot BC are rare in central AZ. We suggest that deposition of C_4 burned material in central AZ soil is likely derived from a non-local (i.e., distant) source.

3.4. Isotope west to east gradient

While there is no W to E pattern in the concentration of soot BC, the isotopic composition of soot BC in desert soils exhibits a statistically significant W to E gradient ($p < 0.05$; Fig. 5). The W to E gradient correlates with the dominant long term wind direction (SW to NE) for this region (Kaye et al., 2011). Kaye et al. (2011) showed that carbon deposition across the W to E gradient varies seasonally; in May, there was no clear deposition pattern among upwind, downwind and urban core sites. However, in September, urban core and downwind sites had higher rates of carbon deposition than the upwind site. The authors attribute this pattern to the advection of urban particulate matter (Kaye et al., 2011). Since the average isotopic composition of soot BC in western desert sites upwind of Phoenix, AZ (-16‰) falls near the expected range for burned C_4 grasses (Das et al., 2010), we suggest that soot BC in this area was produced mostly from biomass burning of C_4 grasses, presumably from southern California. The average isotopic composition of soot BC in the eastern desert sites downwind of Phoenix, AZ is significantly more depleted (-20‰). This pattern suggests either that urban particulate material is composed entirely of C_3 plant material (not very likely) or that urban particulate material is dominated by fossil fuel derived soot BC. The significant difference between the western and eastern desert sites ($p < 0.05$)

suggests the Phoenix metro area is a significant contributor of soot BC to the local desert ecosystem and furthermore, that urban development (and its accompanying fossil fuel derived soot BC) may influence soil chemistry on a regional scale.

3.5. Patterns in soot BC and $\delta^{13}C_{\text{soot BC}}$

While we cannot absolutely distinguish soot BC sources using only soot [BC] or $\delta^{13}C_{\text{soot BC}}$, we can draw general conclusions as to where the BC in central AZ soils may have originated by examining both data sets together. Soot particles can travel 1000s of km in the atmosphere; thus, soot BC does not necessarily represent local carbon (Ogren and Charlson, 1983). However, the uneven distribution of soot BC in central AZ soils (the presence of soot BC “hotspots”) and the relationship between soot [BC] and land use suggests a large portion of the soot BC is produced locally and is anthropogenic. Our results indicate soot BC is a large fraction of the organic carbon pool in central AZ soils and that soot BC does not correlate with soil OC suggesting soot BC has a unique source and/or is processed differently from OC. The range in isotopic composition values for soot BC presented here suggests soot BC is produced from both biomass (C_3 and C_4 plant material) and fossil fuel combustion. The measured $\delta^{13}C_{\text{soot BC}}$ is not consistent with an unfractionated C_3 derived source, and isotopic mass balance calculations suggest the majority of local soil OC (and therefore local biomass) is C_3 material, so we can rule out a significant contribution from locally burned biomass. If locally burned biomass was a significant source of soot BC the isotopic composition of soot BC would be similar to the isotopic composition of C_3 plant material. However, the isotopic composition of soot BC is enriched by $\sim 5.5\text{‰}$ relative to the isotopic composition of soil OC. Therefore, the source of isotopically enriched soot carbon must be from a non-local source. The isotopic west to east gradient also provides evidence in support of both a non-local biomass burning source and a local fossil fuel source. The isotopic composition of soot BC found in desert sites west of the city (-16‰) suggests soot BC from this area was derived from C_4 plant material. However, the isotopic composition of soot BC in the eastern desert sites (-20‰) suggests the soot BC in this area is a mixture of enriched and depleted sources. The difference between the average isotopic composition of soot BC west and east of Phoenix, AZ (4‰) suggests that fractionation processes west to east across the city either removes isotopically enriched carbon or adds isotopically depleted carbon. The addition of isotopically depleted carbon from fossil fuel burning (-28‰ to -21‰ ; Table 1) is the most likely of these scenarios.

4. Conclusions

This is, to our knowledge, the first study of soil soot BC concentration and $\delta^{13}C_{\text{soot BC}}$ for an urban/desert ecosystem. By combining soot BC concentration and isotopic composition data with an estimate of bulk soil carbon composition and basic atmospheric deposition patterns, we can say quite clearly that the soot BC in the Phoenix area soils must include an isotopically enriched non-local biomass derived component as well as an isotopically depleted local fossil fuel component. The differences in source and composition of soot BC in the Phoenix area soils very likely imparts differences in the geochemical and biogeochemical reactivity of this material and may have implications for the loss terms in the black carbon budget.

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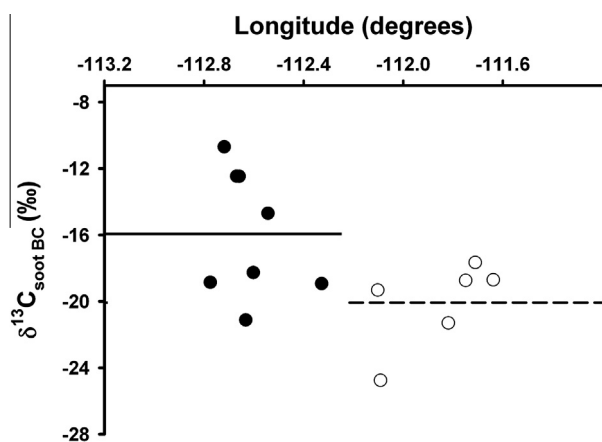


Fig. 5. Isotopic composition of soot BC at desert sites as a function of longitude (position W and E of the city). Desert sites west of the city are solid circles (●) and desert sites east of the city are open circles (○). The solid and dashed lines represent the mean isotopic composition for desert soils west and east of the city, respectively ($p < 0.05$).

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.orggeochem.2013.04.003>.

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