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

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A B S T R A C T

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‰ ± 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.

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 ^{13}C 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 ($\delta^{13}C_{BC}$). 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 ($\delta^{13}C_{soot\ BC}$) and assess differences between $\delta^{13}C_{soot\ BC}$ and $\delta^{13}C_{OC}$. 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 km^2, or 154,110 m^2/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)	$\delta^{13}C_{SM}$ (‰)	Burned byproduct (BB)	$\delta^{13}C_{BB}$ (‰)	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 $\Delta\delta^{13}C$ values.
[g] Uncertainties reported in the literature are ±1‰.