

Soot black carbon dynamics in an arid/urban ecosystem

by

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## ABSTRACT

Black carbon (BC) is the product of incomplete combustion of biomass and fossil fuels. It is found ubiquitously in nature and is relevant to studies in atmospheric science, soil science, oceanography, and anthropology. Black carbon is best described using a combustion continuum that sub-classifies BC into slightly charred biomass, char, charcoal and soot. These sub-classifications range in particle size, formation temperature, and relative reactivity. Interest in BC has increased because of its role in the long-term storage of organic matter and the biogeochemistry of urban areas. The global BC budget is unbalanced. Production of BC greatly outweighs decomposition of BC. This suggests that there are unknown or underestimated BC removal processes, and it is likely that some of these processes are occurring in soils. However, little is known about BC reactivity in soil and especially in desert soil. This work focuses on soot BC, which is formed at higher temperatures and has a lower relative reactivity than other forms of BC. Here, I assess the contribution of soot BC to central AZ soils and use the isotopic composition of soot BC to identify sources of soot BC. Soot BC is a significant (31%) fraction of the soil organic matter in central AZ and this work suggests that desert and urban soils may be a storage reservoir for soot BC. I further identify previously unknown removal processes of soot BC found naturally in soil and demonstrate that soil soot BC undergoes abiotic (photo-oxidation) and biotic reactions. Not only is soot BC degraded by these processes, but its chemical composition is altered, suggesting that soot BC contains some chemical moieties that are more reactive than others. Because soot BC demonstrates both refractory and reactive character, it is likely that the structure of

soot BC; therefore, its interactions in the environment are complex and it is not simply a recalcitrant material.

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## Chapter 1

### INTRODUCTION

What is black carbon?

Incomplete combustion of fossil fuels and biomass produces material known as black carbon (BC). It is traditionally thought to be the most refractory substance remaining after combustion (Goldberg 1985). Black carbon is best described as a continuum of combustion products (Figure 1.1) that range from slightly charred and relatively degradable biomass to highly condensed and refractory soot (Hedges et al. 2000; Masiello 2004). The continuum is primarily arranged by formation temperature. All the components of the continuum have high C:H and C:O ratios, are chemically heterogeneous, and are dominated by mostly aromatic structures (Masiello 2004). Several key characteristics of black carbon are a function of formation temperature. As combustion temperature increases, the BC produced has smaller particle sizes, lower chemical reactivity, and greater aromaticity. Soot, on the right side of the continuum (Figure 1.1), has unique characteristics that differ significantly from those of the materials on the left side of the continuum (i.e., char or charcoal). Soot is formed from a gas-phase reaction where the volatilized molecules condense to form nano-sized particles. Soot retains none of the original structure of the burned material, whereas charcoal does (Masiello 2004). The mechanistic details of soot formation are not well understood, but it is generally accepted that two-carbon molecules (i.e., ethane or acetylene) or radicals join to form polycyclic aromatic hydrocarbons (PAHs). These PAHs continue to condense into larger aromatic ring structures that form spherical particles (Kennedy 1997; Johnson and Miyanishi 2001). The non-soot material (char, charcoal), in contrast, is

generally a remnant, partially burned material. 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 (650°–900°C).

Soot BC is small. It is generally less than  $<1\ \mu\text{m}$  in size and is smaller than biochar and charcoal. These small particles can travel thousands of kilometers and can remain suspended in the atmosphere for months before deposition (Ogren and Charlson 1983). Char and charcoal, in contrast, are larger particles ( $>1\ \text{mm}$ ), that are generally deposited quickly and near the point of combustion (Clark and Patterson 1997). Thus, the larger BC particles generally reflect local biomass burning (Mensing et al. 1999), while soot BC may represent combustion that occurred at some distance from where the soot BC was deposited. This does not preclude soot BC from having local combustion sources; Hamilton and Hartnett (2013) demonstrated that soot BC can have a local source in areas with significant anthropogenic inputs.

#### Detection of black carbon

The various components of the black carbon continuum have operational definitions; that is, BC is defined according to the process by which it is detected. There is a wide range of BC detection techniques currently in use (Gustafsson et al. 1997; Masiello and Duffel 1998; Glaser et al. 2000; Skjemstad et al. 2002) and this has produced significant uncertainty in how best to quantify BC. The main issues are that different methods address different parts of the BC continuum (Elmquist et al. 2004) and each method has its own set of limitations (i.e., detection limits and occurrence of false positives). Taken together, these analytical issues have

contributed to significant uncertainty about natural variations in the amount of BC present in different environments.

In an effort to remedy this situation, a methods continuum, similar to the combustion continuum, has been established that clarifies which parts of the combustion continuum are quantified using each of the specific methods (Masiello 2004). Visual and microscope methods can identify large particles of slightly charred biomass and char, but are unable to identify small ( $< 1\text{ mm}$ ) particles. Other methods quantify the entire continuum because they identify inherent chemical information about each component (i.e., ultra-high resolution mass spectrometry,  $^{13}\text{C}$ -nuclear magnetic resonance (NMR), Fourier-transform infrared (FTIR) spectroscopy; Hockaday et al. 2006; Nguyen et al. 2009). While the inclusion of mass spectrometry as a detection method for BC might be surprising, ultrahigh-resolution instruments can predict empirical formula, that can reveal the presence of condensed aromatic ring structures (CARS) which are likely to be the soluble products of BC degradation (Hockaday et al. 2006). Both NMR and FTIR methods have proven useful for investigating BC reactivity by detecting changes in BC structural chemistry that result from chemical reactions. These broad detection techniques can identify chemical structures and can be used to estimate the degree of aromaticity. However, NMR can be costly and requires large amounts of BC material. Black carbon has been quantified in solution using a molecular marker technique that quantifies BC as the sum of benzene polycarboxylic acids (BPCA) which are measured using gas chromatography. BPCA detects nearly all components of the BC continuum, yet also is prone to positive bias from non-black organic matter (Hammes et al. 2007). Thermal techniques measure the BC remaining after heating

(thermal/optical transmittance and reflectance; Huang et al. 2006) and chemical techniques measure BC remaining after removal of inorganic carbon and non-black organic carbon (i.e., acid dichromate oxidation, and CTO375; Song et al. 2002; Gustafsson et al. 1997). These thermal/chemical techniques can distinguish the most recalcitrant BC material and are generally considered to isolate the soot BC fraction of the continuum. They are also unique in that they have very few interfering compounds (Hammes et al. 2007). For example, the thermochemical method does not detect coal or tar which optical methods have been shown to do (Hammes et al. 2007). It is important to note that comparisons of BC concentration and chemical composition using different methods might not be meaningful because different methods quantify different components of the BC continuum. Recently, the BC community has begun a conscious effort to identify specifically which class of BC is under investigation. Because operational definitions are commonly used to describe BC, care must be taken to offer a full and complete description of the material being studied. A universal lexicon is slowly being integrated into the field of BC research; notable examples include Michelsen et al. (2007) and Adachi et al. (2010) who describe soot as combustion-generated particles, composed of small (15 – 50 nm) carbon spheres held together by covalent bonds to form branched chain aggregates of various sizes. Hammes et al. (2007) published a methods inter-comparison that has also aided in the use of consistent terminology, however, more work must be done establish a systematic nomenclature.

I use a thermo-chemical oxidation method known as CTO375 to quantify soot BC. This method (CTO375) is considered to detect “soot” carbon exclusively and the product of this isolation technique is referred to, hereafter, as soot BC. The method

(CTO375) is a two step process for the isolation of soot BC in soils and sediments. First, inorganic carbon is removed from soil by acidification (chemical isolation). Second, non-black organic carbon is removed by combusting the soil at 375°C for 24 h (thermal isolation). The carbon remaining in the soil is defined as soot BC. The CTO375 technique for soot isolation has been an accepted method for over 15 years (Gustafsson et al. 1997; Gelinas et al. 2001; Hammes et al. 2007; Hamilton and Hartnett 2013) and is considered a conservative estimate of soot BC because it consistently produced the lowest BC concentrations for a variety of standard materials as compared to other BC detection techniques (Hammes et al. 2007). The CTO375 method has very few interfering compounds (i.e., coal or shale), as compared to optical or thermal-only methods (Hammes et al. 2007).

Why study black carbon?

A number of early studies showed BC to be a very refractory material (Goldberg 1985; Skjemstad et al. 2002; Kuhlbusch 1998). However, BC is ubiquitous in the environment and has the potential to play an important role in the carbon cycle. The best estimates of the global black carbon budget are actually quite uncertain (Table 1.1). Only two reservoirs (the atmosphere and marine sediments) have been well quantified with respect to BC inputs and outputs (Verardo and Ruddiman 1996; Penner et al. 1993; Middleberg et al. 1999). According to the most recent BC budget estimates, the inputs of BC greatly outweigh the outputs (Penner et al. 1993; Kuhlbusch and Crutzen 1995; Masiello and Druffel 1998). Estimates of BC production globally are between 50 and 260 Tg BC/year (1 Tg =  $10^{12}$ g) for biomass burning and between 12 to 24 Tg BC/year for fossil fuel combustion

(Kuhlbusch and Crutzen 1995). However, only about 10 Tg BC/year are deposited in ocean sediments (Masiello and Druffel 1998). This budget imbalance suggests that BC could be more reactive than the early studies concluded. The fact that sources are greater than sinks (by 10s to 100s of Tg BC/y) suggests either that some fraction of the BC produced is incorporated into an unknown reservoir, or that BC is reactive and removed from the BC pool. Black C is older than organic carbon in ocean sediments sampled at equal depth but it can be oxidized slowly in marine sediments over long time periods (10-20 kyr; Middelburg et al. 1999). The difference in age for bulk OC and BC in sediments is also an indication that black carbon may be “aged” in at least one intermediate organic carbon pool between its production on land and its deposition in ocean sediments. Likely possibilities for these intermediate pools are terrestrial soils and surface water dissolved organic carbon (DOC; Jaffé et al. 2013; Dittmar et al. 2012)

Black C contains a soil record of local fire history (Bird and Cali 1998) and can have a profound effect on the biogeochemistry of soils. Black C generally comprises ~1 to 8% of soil organic carbon (Gonzalez-Perez et al. 2004), but can be as much as 35% of soil OC in frequently burned soils (Skjemstad et al. 2002). The environmental distribution of organic pollutants can be governed by BC. Specifically, sorption of PAHs in soil can be increased by the presence of soot because soot acts similarly to activated carbon, where smaller particle sizes (and therefore, higher surface area) increase sorption (Accardi-Dey and Gschwend 2002; Gustafsson and Gschwend 1997; Gustafsson et al. 1997). Some fraction of the black carbon in soils is refractory. Evidence for the refractory nature of soot BC includes the radiocarbon age of BC in soil which is estimated to be on the order of thousands of years



(Schmidt et al. 2002). Black carbon has also been shown to be a large portion of the chemically resistant fraction of fire-prone soils based on chemical functional group identification (Skjemstad et al. 2001). However, black carbon can also play a dynamic role in soils. Several studies have shown that BC can be degraded via biological, chemical, physical mechanisms. Specifically, BC can be chemically altered by microbial degradation (Hilscher et al. 2009; Solomon et al. 2007; Steinbeiss et al. 2009), photo-chemical degradation (Stubbins et al. 2012) and by physical solubilization (Jaffé et al. 2013). Because BC has been shown to be both refractory and reactive, it is likely that BC is more complex than originally posited by Goldberg (1985).

#### Black carbon reactivity in the environment

Very few studies have specifically addressed soot BC reactivity; but a survey of results for “BC” is somewhat revealing. The imbalance in the BC budget (discussed above) offers indirect evidence for BC loss or degradation in the environment. More direct observations, including biological interactions with BC, photo-chemical alteration of BC, and solubilization of BC, strongly suggest that BC has a reactive role in some environments. Studies of microbial interactions with BC have mostly been limited to interactions between microorganisms and biochars synthesized in the laboratory. In one study, biochar and glucose were shown to undergo co-metabolism in the presence of an inoculum extracted from arable soil. The presence of biochar promoted the growth of microorganisms and the decomposition of labile carbon compounds rather than having a stabilizing effect against degradation (Hamer et al. 2004). In a more recent study, Hilscher et al. (2009) showed that

pyrogenically produced organic matter (combusted rye grass and pine wood) can be incorporated by microbes when used as a co-substrate with a non-pyrogenic organic carbon source. This implies that the role of pyrogenic organic matter as a refractory substance should be reconsidered. Steinbeiss et al. (2009) investigated residence times for various biochars and calculated a mean residence time of 4 to 29 years based on mineralization of charred yeast and charred glucose by fungi and gram negative bacteria. This is a much shorter timescale than the 1000-year timescales presented previously (Bird and Cali 1998; Schmidt et al. 2002). In a field study, Major et al. (2009) detected an increase in above-ground biomass production, which was linked to greater below-ground net primary production, following a biochar addition. They suggested that biochar can migrate down the soil column, and that the presence of biochar can enhance microbial growth. Taken together, these studies indicate that burned material can play an active role in microbial metabolism. However, these studies link the degradation of labile organic carbon to the presence of BC and, in all cases, utilize a laboratory-produced biochar as their BC source. More work that seeks to develop a specific understanding of the degradation of natural soot BC in the environment is needed.

The literature on BC also includes evidence for non-biological BC alteration. Nguyen et al. (2009) show that weathering changes the molecular properties of BC particle surfaces more rapidly than those of BC particle interiors. Specifically, the presence of carbonyl groups (C=O) increased by 133% during the first 30 years after BC deposition. Based on this result, Nguyen et al. (2009) conclude that oxidation is an important process in controlling BC functional group composition. A portion of natural dissolved organic carbon (DOC) has been identified as PAHs. Jaffé et al.

(2013) estimated that a significant amount (~10% globally) of the DOC transferred from soils to rivers was BC. The fact that BC can be solubilized suggests it could undergo further chemical and physical change. Recently it has been shown that BC from a forested watershed in the Atlantic forest in Brazil (a region with a well-documented fire history) is exported from the watershed to the ocean in significant amounts ( $2.7 \times 10^6$  kg) even 24 years after burning has ceased (Dittmar et al. 2012). Jaffé et al. (2013) and Dittmar et al. (2012) each strongly suggest a portion of the BC continuum can be transported from soil to surface water in the dissolved phase. Dissolved BC also has been shown to undergo photo-chemical oxidation; Stubbins et al. (2012) demonstrated that deep ocean BC was more susceptible to photo-oxidation than was non-black organic matter.

The structure of this dissertation

While the chemical reactivity of a portion of the BC continuum (i.e., biochars) has been investigated relatively rigorously, very little is known about loss processes for soot BC found in the natural environment. Soils have been suggested as a possible intermediate reservoir for black carbon (Schmidt et al. 2002); however, little is known about the amount and reactivity of black carbon in soils (generally) and even less is known about soot BC (putatively the least reactive form of BC), in particular.

The work I present here investigates the presence of soot BC in soil (a likely intermediate reservoir) and the reactivity of soot BC with respect to microbial degradation, photochemical oxidation, and physical solubilization. In particular, I assess the presence and reactivity of soot BC, a previously unstudied but potentially

significant portion of the soil organic carbon in central AZ. This was made possible because the region is part of the Central Arizona Phoenix Long-Term Ecosystem Research Program (CAP-LTER) which collects soils, soil property data, and land-use data as part of a large semi-decadal field survey. Central AZ is a unique study site because the region has an urban center (Phoenix, AZ) with correspondingly high soil organic carbon, including significant anthropogenic carbon sources, as well as large tracts of largely pristine desert with low soil organic carbon. The fact that soot BC may be somewhat recalcitrant suggests that soot BC may be a significant fraction of the soil organic carbon in desert areas. The work presented here is relevant to other urban areas and especially arid/urban environments. I present results that, taken together, demonstrate the prevalence and sources of soot BC in central AZ soils, and the reactivity of soot BC to photochemical and biological degradation as well as physical solubilization.

In the following, I summarize the chapters of this dissertation. In chapter two, I present the concentrations and spatial distributions of soot BC in central AZ soils and assess potential sources of soot BC. I found that soot BC is present in central AZ soils and constitutes a very large fraction of the soil organic carbon (on average 31%) in the region. Soot BC concentration in central AZ is a strong function of land-use, and concentrations of soot BC are higher in urban soils (0.25 weight percent, wt. %) and lower in desert (0.08 wt. %) and agricultural (0.14 wt. %) soils. The presence of the urban soot BC 'hotspots' suggest that soot BC could be anthropogenically produced. I present carbon isotopic composition data and mass balance calculations that suggest a large fraction of the soot BC in AZ soils must be produced by fossil

fuel combustion (presumably in the form of vehicle emissions) while a smaller fraction is likely derived from non-local biomass burning.

In chapter three, I present results from photo-oxidation experiments that indicate soot BC can be photochemically degraded in the laboratory over relatively short timescales (hours to days). When the laboratory rates are scaled to solar irradiances, the degradation rates are still on the order of years to decades. I assess changes in the chemical functional group composition of soot BC during photo-oxidation by Fourier-transform infrared (FTIR) spectroscopy. The appearance of carbonyl functional groups after laboratory photo-oxidation indicates that soot BC may also be altered photo-chemically in the environment. I surmise that these compositional changes could increase soot BC reactivity.

In the fourth chapter, I present results from soot BC solubilization studies. At least a portion of the soot BC found in soil is solubilized (or mobilized) into water on short time scales (7 days). The dissolved organic carbon content of soil extracts containing only soot BC increases with longer extraction times. Up to 9% of the soil soot BC was mobilized to the aqueous phase. The chemical composition of the water-extractable soot BC was analyzed using fluorescence spectroscopy. Fluorescence analysis identified the presence of a terrigenous carbon source and the presence of highly conjugated systems which are both consistent with the characteristics of soot BC (i.e., aromatic and produced from terrestrial biomass). This is the first report of the aqueous mobility of carbon isolated by CTO375 (soot BC) and the first attempt to characterize solubilized soot BC using fluorescence analysis.

In chapter five, I present results from laboratory microbial oxidation studies using aqueous extracts of soot BC and soil-derived microbial inocula. Carbon-limited

microbes were exposed to soot BC extracts, and biological oxidation was monitored as CO<sub>2</sub> evolution. Carbon dioxide concentrations were greater in experiments containing microbial communities than in experiments without microbial communities, strongly suggesting soot BC can undergo microbial oxidation. Fluorescence spectroscopy and parallel factor analysis (PARAFAC) conducted before and after microbial degradation revealed that microbial oxidation alters the chemical composition of soot BC. My results indicate that microbial degradation of soot BC increases the presence of oxidized quinone-like fluorophores and decreases the presence of other, as yet unknown, fluorophores. This suggests the oxidized quinone-like fluorophores present in soot BC are more resistant to microbial degradation while the unknown fluorophores present in soot BC may be more conducive to microbial degradation.

In the final chapter, chapter 6, I summarize the new contributions to the field of black carbon research made by this work, discuss a few smaller datasets not directly relevant to the previous chapters, and suggest future directions for this line of research.

## Literature Cited

- Accardi-Dey, A., and P. M. Gschwend. 2002. "Assessing the combined roles of natural organic matter and black carbon as sorbents in sediments." *Environmental Science & Technology* no. 36 (1):21-29.
- Adachi, K., and P. R. Buseck. 2008. "Internally mixed soot, sulfates, and organic matter in aerosol particles from Mexico City." *Atmospheric Chemistry & Physics* no. 8 (21):6469-6481. D15206.
- Bird, M. I., and J. A. Cali. 1998. "A million-year record of fire in sub-Saharan Africa." *Nature* no. 394 (6695):767-769.
- Clark, J. S., and W. A. I. Patterson. 1997. *Background and local charcoal in sediments: scales of fire evidence in the paleorecord, sediment records of biomass burning and global change*. Berlin: Springer-Verlag.
- Dittmar, T., C. E. de Rezende, M. Manecki, J. Niggemann, A. R. C. Ovalle, A. Stubbins, and M. C. Bernardes. 2012. "Continuous flux of dissolved black carbon from a vanished tropical forest biome." *Nature Geoscience* no. 5 (9):618-622.
- Elmquist, M., O. Gustafsson, and P. Andersson. 2004. "Quantification of sedimentary black carbon using the chemothermal oxidation method: an evaluation of ex situ pretreatments and standard additions approaches." *Limnology and Oceanography-Methods* no. 2:417-427.
- Gelinas, Y., K. M. Prentice, J. A. Baldock, and J. I. Hedges. 2001. "An improved thermal oxidation method for the quantification of soot/graphitic black carbon in sediments and soils." *Environmental Science & Technology*. no. 35 (17):3519-3525.
- Glaser, B., E. Balashov, L. Haumaier, G. Guggenberger, and W. Zech. 2000. "Black carbon in density fractions of anthropogenic soils of the Brazilian Amazon region." *Organic Geochemistry* no. 31 (7-8):669-678.
- Goldberg, E.D. 1985. "Black Carbon in the Environment." New York: *John Wiley & Sons*.
- Gonzalez-Perez, J. A., F. J. Gonzalez-Vila, G. Almendros, and H. Knicker. 2004. "The effect of fire on soil organic matter - a review." *Environment International* no. 30 (6):855-870.
- Gustafsson, O., F. Haghseta, C. Chan, J. MacFarlane, and P. M. Gschwend. 1997. "Quantification of the dilute sedimentary soot phase: Implications for PAH speciation and bioavailability." *Environmental Science & Technology* no. 31 (1):203-209.

- Gustafsson, O., and P. M. Gschwend. 1997. "Soot as a strong partition medium for polycyclic aromatic hydrocarbons in aquatic systems." *Molecular Markers in Environmental Geochemistry* no. 671:365-381.
- Hamer, U., B. Marschner, S. Brodowski, and W. Amelung. 2004. "Interactive priming of black carbon and glucose mineralisation." *Organic Geochemistry* no. 35 (7):823-830.
- Hamilton, G. A., and H. E. Hartnett. 2013. "Soot black carbon concentration and isotopic composition in soils from an arid urban ecosystem." *Organic Geochemistry* no. 59:87-94.
- Hammes, K., M. W. I. Schmidt, R. J. Smernik, L. A. Currie, W. P. Ball, T. H. Nguyen, P. Louchouart, S. Houel, O. Gustafsson, M. Elmquist, G. Cornelissen, J. O. Skjemstad, C. A. Masiello, J. Song, P. Peng, S. Mitra, J. C. Dunn, P. G. Hatcher, W. C. Hockaday, D. M. Smith, C. Hartkopf-Froeder, A. Boehmer, B. Luer, B. J. Huebert, W. Amelung, S. Brodowski, L. Huang, W. Zhang, P. M. Gschwend, D. X. Flores-Cervantes, C. Largeau, J. N. Rouzaud, C. Rumpel, G. Guggenberger, K. Kaiser, A. Rodionov, F. J. Gonzalez-Vila, J. A. Gonzalez-Perez, J. M. de la Rosa, D. A. C. Manning, E. Lopez-Capel, and L. Ding. 2007. "Comparison of quantification methods to measure fire-derived (black/elemental) carbon in soils and sediments using reference materials from soil, water, sediment and the atmosphere." *Global Biogeochemical Cycles* no. 21 (3). GB3016
- Hedges, J. I., G. Eglinton, P. G. Hatcher, D. L. Kirchman, C. Arnosti, S. Derenne, R. P. Evershed, I. Kogel-Knabner, J. W. de Leeuw, R. Littke, W. Michaelis, and J. Rullkotter. 2000. "The molecularly-uncharacterized component of nonliving organic matter in natural environments." *Organic Geochemistry* no. 31 (10):945-958.
- Hilscher, A., K. Heister, C. Siewert, and H. Knicker. 2009. "Mineralisation and structural changes during the initial phase of microbial degradation of pyrogenic plant residues in soil." *Organic Geochemistry* no. 40 (3):332-342.
- Hockaday, W. C., A. M. Grannas, S. Kim, and P. G. Hatcher. 2006. "Direct molecular evidence for the degradation and mobility of black carbon in soils from ultrahigh-resolution mass spectral analysis of dissolved organic matter from a fire-impacted forest soil." *Organic Geochemistry* no. 37 (4):501-510.
- Huang, L., J. R. Brook, W. Zhang, S. M. Li, L. Graham, D. Ernst, A. Chivulescu, and G. Lu. 2006. "Stable isotope measurements of carbon fractions (OC/EC) in airborne particulate: A new dimension for source characterization and apportionment." *Atmospheric Environment* no. 40 (15):2690-2705.
- Jaffé, R., Y. Ding, J. Niggemann, A. V. Vähätalo, A. Stubbins, R. G. M. Spencer, J. Campbell, and T. Dittmar. 2013. "Global charcoal mobilization from soils via



- dissolution and riverine transport to the oceans." *Science* no. 340 (6130):345-347.
- Johnson, E. A., and K. Miyanishi. 2001. *Forest Fires: Behavior and Ecological Effects*. San Diego: Academic Press.
- Kennedy, I. M. 1997. "Models of soot formation and oxidation." *Progress in Energy and Combustion Science* no. 23 (2):95-132.
- Kuhlbusch, T. A. J. 1998. "Black carbon and the carbon cycle." *Science* no. 280 (5371):1903-1904.
- Kuhlbusch, T. A. J., and P. J. Crutzen. 1995. "Towards a global estimate of black carbon in residues of vegetation fires representing a sink of atmospheric CO<sub>2</sub> and a source of O<sub>2</sub>." *Global Biogeochemical Cycles* no. 9 (4):491-501.
- Major, J., J. Lehmann, M. Rondon, and C. Goodale. 2009. "Fate of soil-applied black carbon: downward migration, leaching and soil respiration." *Global Change Biology* no. 16 (4):1366-1379.
- Masiello, C. A., and E. R. M. Druffel. 1998. "Black carbon in deep-sea sediments." *Science* no. 280 (5371):1911-1913.
- Masiello, C.A. 2004. "New directions in black carbon organic geochemistry." *Marine Chemistry* no. 92:201-213.
- Mensing, S. A., J. Michaelson, and R. Byrne. 1999. "A 560-year record of Santa Ana fires reconstructed from charcoal deposited in the Santa Barbara Basin, California." *Quaternary Research* no. 51 (3):295-305.
- Michelsen, H. A., A. V. Tivanski, M. K. Gilles, L. H. van Poppel, M. A. Dansson, and P. R. Buseck. 2007. "Particle formation from pulsed laser irradiation of soot aggregates studied with a scanning mobility particle sizer, a transmission electron microscope, and a scanning transmission X-ray microscope." *Applied Optics* no. 46 (6):959-977.
- Middelburg, J. J., J. Nieuwenhuize, and P. van Breugel. 1999. "Black carbon in marine sediments." *Marine Chemistry* no. 65 (3-4):245-252.
- Nguyen, B. T., J. Lehmann, J. Kinyangi, R. Smernik, S. J. Riha, and M. H. Engelhard. 2009. "Long-term black carbon dynamics in cultivated soil." *Biogeochemistry* no. 92 (1-2):163-176.
- Ogren, J. A., and R. J. Charlson. 1983. "Elemental carbon in the atmosphere - cycle and lifetime." *Tellus Series B-Chemical and Physical Meteorology* no. 35 (4):241-254.

- Penner, J. E., H. Eddleman, and T. Novakov. 1993. "Towards the development of a global inventory for black carbon emissions." *Atmospheric Environment Part a-General Topics* no. 27 (8):1277-1295.
- Schmidt, M. W. I., and A. G. Noack. 2000. "Black carbon in soils and sediments: Analysis, distribution, implications, and current challenges." *Global Biogeochemical Cycles* no. 14 (3):777-793.
- Schmidt, M. W. I., J. O. Skjemstad, and C. Jager. 2002. "Carbon isotope geochemistry and nanomorphology of soil black carbon: Black chernozemic soils in central Europe originate from ancient biomass burning." *Global Biogeochemical Cycles* no. 16 (4). GB001939
- Skjemstad, J. O., R. C. Dalal, L. J. Janik, and J. A. McGowan. 2001. "Changes in chemical nature of soil organic carbon in Vertisols under wheat in south-eastern Queensland." *Australian Journal of Soil Research* no. 39 (2):343-359.
- Skjemstad, Jan O., Donald C. Reicosky, Alan R. Wilts, and Janine A. McGowan. 2002. "Charcoal carbon in U.S. agricultural soils." *Soil Science Society of America Journal* no. 66 (4):1249-1255.
- Solomon, D., J. Lehmann, J. Thies, T. Schäfer, B. Liang, J. Kinyangi, E. Neves, J. Petersen, F. Luizão, and J. Skjemstad. 2007. "Molecular signature and sources of biochemical recalcitrance of organic C in Amazonian Dark Earths." *Geochimica et Cosmochimica Acta* no. 71 (9):2285-2298.
- Song, J. Z., P. A. Peng, and W. L. Huang. 2002. "Black carbon and kerogen in soils and sediments. 1. Quantification and characterization." *Environmental Science & Technology* no. 36 (18):3960-3967.
- Steinbeiss, S., G. Gleixner, and M. Antonietti. 2009. "Effect of biochar amendment on soil carbon balance and soil microbial activity." *Soil Biology & Biochemistry* no. 41 (6):1301-1310.
- Stubbins, A., J. Niggemann, and T. Dittmar. 2012. "Photo-lability of deep ocean dissolved black carbon." *Biogeosciences* no. 9 (5):1661-1670.
- Suman, D.O., T.A.J. Kuhlbusch, and B. Lim. 1997. *Sediment records of biomass burning and global change*. Berlin: Springer-Verlag.
- Verardo, D. J., and W. F. Ruddiman. 1996. "Late pleistocene charcoal in tropical Atlantic deep-sea sediments: Climatic and geochemical significance." *Geology* no. 24 (9):855-857.

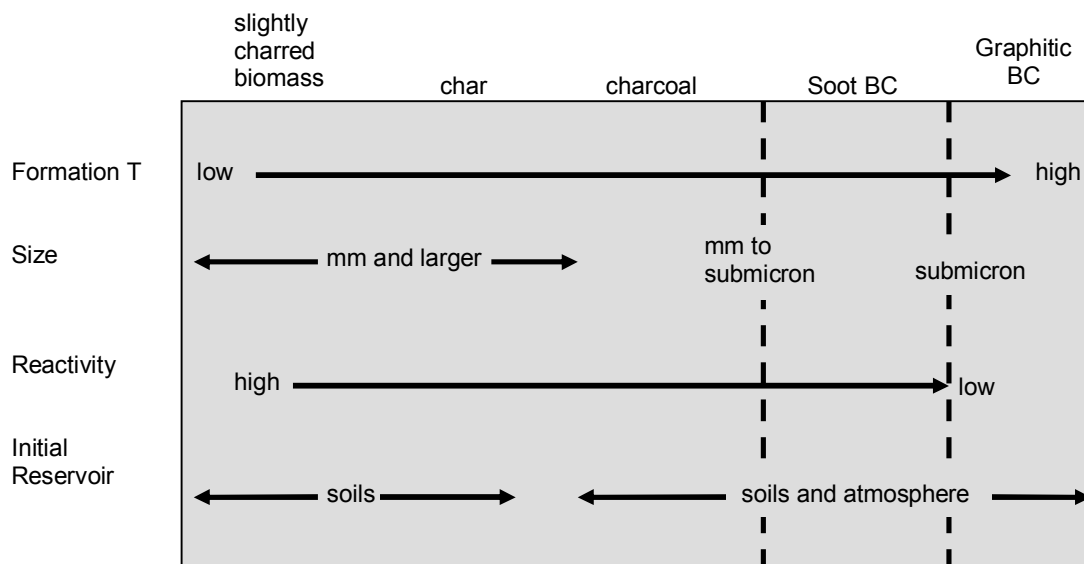


Figure 1.1. Schematic representation of the black carbon (BC) combustion continuum (Figure modified from Hedges et al. 2000). The area inside the dashed lines represents characteristics of soot BC.

Table 1.1. Estimates of known sources and sinks of BC.

<b>Sources</b>	<b><sup>a</sup>Tg of BC y<sup>-1</sup></b>	<b>Reference</b>
Biomass burning	50 – 260	Kuhlbusch and Crutzen (1995)
Fossil fuel combustion	12 – 24	Penner et al. (1993)
<b>Sinks</b>		
Deposition in ocean sediments	10	Suman et al. (1997)

<sup>a</sup>Tg = 10<sup>12</sup> g

## Chapter 2

### SOOT BLACK CARBON CONCENTRATION AND ISOTOPIC COMPOSITION IN SOILS FROM AN ARID URBAN ECOSYSTEM

#### 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 fifty-two soils (desert, agricultural, and urban) ranges from 0.02 to 0.54 weight percent, and comprises from <1 to as much as 89 percent 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  $-18\text{‰} \pm 3\text{‰}$ ; 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.

#### 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  $<1\ \mu\text{m}$  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). 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  $^{13}\text{C}$  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  $250^{\circ}\text{C}$ , 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  $800^{\circ}\text{C}$  (Johnson and Miyanishi 2001)

suggesting that forest fires are more than hot enough to generate soot BC. 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). My 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 terrestrial 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 1998; Masiello 2004). Black carbon generally comprises roughly 1 to 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 terrestrial 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; Czimeczik 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 2.1). For example, burned  $\text{C}_4$  plant material is isotopically depleted in  $^{13}\text{C}$  by  $-4\text{‰}$  to  $-6\text{‰}$  relative to the unburned  $\text{C}_4$  material (Das et al. 2010; Krull et al. 2003). In contrast, burned fossil fuel is enriched in  $^{13}\text{C}$  by  $+1\text{‰}$  to  $+8\text{‰}$  relative to the starting material (Widory 2006; Lopez-Veneroni 2009). Generally,  $\text{C}_3$  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  $\text{C}_3$  and  $\text{C}_4$  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.

## Method

### *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 (Figure 2.1). 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 ten years the Phoenix metropolitan population increased by about 30% to its current population of 4.2 million (U. S. Census 2010). Between 2000 and 2004, this rapid growth expanded the footprint of the Phoenix metropolitan area by 225 km<sup>2</sup>, or 154,110 m<sup>2</sup>/day (Maricopa Association of Governments 2010), making Phoenix one of the fastest growing areas in the U.S.

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 x 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<sub>3</sub> plants) and a variety of annual plants (C<sub>3</sub> and C<sub>4</sub>). Triangle-leaf bursage (*Ambrosia deltoidea*), brittlebush (*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*; C<sub>4</sub>), Mexican lovegrass (*Eragrostis mexicana*; C<sub>4</sub>), wild cabbage (*Brassica oleracea*; C<sub>3</sub>), and spiny sowthistle (*Sonchus asper*; C<sub>3</sub>) 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*; C<sub>4</sub>) and alfalfa (*Medicago sativa*; C<sub>3</sub>); however, we note that agricultural sites were not always in cultivation at the time of sampling. We also note that although C<sub>4</sub>

plants are found in central AZ the majority of plant biomass in the region is C<sub>3</sub> plants.

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 km<sup>2</sup> (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).

#### *Chemo-thermo oxidation method*

We quantify soot BC using chemo-thermo oxidation (CTO375; Gustafsson et al. 1997; Gustafsson et al. 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 2.2). 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<sup>™</sup> 25-well tray. Samples were wetted with deionized H<sub>2</sub>O (18.2 M $\Omega$ ·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 aluminum tray, and baked at 375°C for 24 h in a

well-ventilated furnace under ambient atmospheric conditions (20% O<sub>2</sub>) 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 (Table 2.3). Samples from these sites were acidified, but not thermally oxidized, prior to analysis.

The EA-IRMS detection limits are 1  $\mu\text{g C}$  for [C] and 4  $\mu\text{g C}$  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 weight percent, 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 ( $\delta$ ) notation relative to the V-PDB standard:  $\delta^{13}\text{C} = (\text{R}_{\text{sa}}/\text{R}_{\text{std}} - 1) \times 1000$ , where  $\text{R}_{\text{sa}}$  and  $\text{R}_{\text{std}}$  are the  $^{13}\text{C}/^{12}\text{C}$  ratio in the sample and standard, respectively. Samples were generally analyzed in duplicate or triplicate (Table 2.2).

### *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 a Mann-Whitney rank sum test (Sigma Plot 11;

Systat Software, Inc.). Values are considered significant for  $p < 0.05$ .

## Results and Discussion

### *Soot BC concentrations*

Soot BC is found in all 52 samples (Figure 2.1, Table 2.2). Soot BC concentration, i.e., soot [BC], ranges from 0.02 to 0.54 wt. % (avg: 0.23 wt. %) based on dry soil mass. The average standard deviation of our soot [BC] determination based on replicate analyses is  $\pm 0.02$  wt. % ( $n = 30$ ; Table 2.2). 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 (Figure 2.1). 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 to 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 (Figure 2.2, Table 2.4); 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):  $\pm 0.03$ ); 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:  $\pm 0.04$ ) on average, and agricultural soils have an intermediate

soot [BC] of 0.14 wt. % (95% CL:  $\pm 0.03$ ). 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 exhibit the greatest variation in soot [BC] while desert and agricultural soils are less variable (Figure 2.2). The inherent site-to-site heterogeneity of soil accounts for the variation in average soot [BC] and [OC] within land-use types (Table 2.4 and Figure 2.2); 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 (Ziolkowski et al. 2011; Maseillo 2004).

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 to 89 % (average soot BC/OC: 31%,  $n = 52$ ; Figure 2.3, Table 2.4). Because of the large range, soot BC/OC ratios for the three land use types are not statistically different from each other (Figure 2.3;  $p > 0.05$ ). 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 (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 and char to increase soil fertility (BC/OC = ~20%; Glaser et al. 2001). The soot BC/OC ratios reported here are high despite our 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 was comprised of 30 – 36% elemental carbon in the Phoenix-metro area. This percentage is similar to the average soot BC/OC value. We note that 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.

#### *Soot BC isotopic composition*

The  $\delta^{13}\text{C}_{\text{soot BC}}$  ranges from  $-26\text{‰}$  to  $-10\text{‰}$  (avg:  $-18\text{‰}$ ) and the bulk soil  $\delta^{13}\text{C}_{\text{OC}}$  ranges from  $-25\text{‰}$  to  $-18\text{‰}$  (avg:  $-23\text{‰}$ ) for all the sites analyzed (Figure 2.4A). 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 (Figure 2.4A,  $p > 0.05$ ), 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  $^{13}\text{C}$  relative to bulk soil OC by  $\sim 5.5\text{‰}$  ( $p < 0.05$ ; Figure 2.4B). The bulk soil OC isotopic composition is consistent, not surprisingly, with a predominantly  $\text{C}_3$  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 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.

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 2.1 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  $\mu\text{m}$  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 Miyanishi 2001).

The isotopic compositions of the soot or smoke from  $\text{C}_3$  plants are generally similar to those of the unburned vegetation (i.e.,  $<1$  to  $0\text{‰}$  isotopic fractionation relative to the starting material; Table 2.1). In contrast, burned  $\text{C}_4$  plant material is generally depleted in  $^{13}\text{C}$  relative to the unburned starting material. The reported range in isotopic composition for burned  $\text{C}_3$  and  $\text{C}_4$  plant material ( $-26$  to  $-25\text{‰}$  for  $\text{C}_3$  and  $-21$  to  $-11\text{‰}$  for  $\text{C}_4$  materials, respectively; Table 2.1) is within in the range of measured  $\delta^{13}\text{C}_{\text{soot BC}}$  values presented here ( $-26$  to  $-10\text{‰}$ ), suggesting that soot BC in the Phoenix-area soils may include a contribution from  $\text{C}_3$  and  $\text{C}_4$  plants. Fossil fuel burning, on the other hand, results in combustion byproducts enriched by  $\sim 2$  to  $6\text{‰}$  relative to the unburned starting material (Widory 2006; Lopez-Veneroni 2009; Table 2.1). Our  $\delta^{13}\text{C}_{\text{soot BC}}$  values ( $-26$  to  $-10\text{‰}$ ) 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  $\text{C}_3$  and  $\text{C}_4$  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  $\text{C}_3$  and  $\text{C}_4$  plant material to the bulk OC pool, we may be able to eliminate possible sources of soot BC to central AZ soils.

#### *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  $\text{C}_3$  and  $\text{C}_4$  bulk organic material at each site. We assume the major inputs to soil organic carbon are  $\text{C}_3$  and  $\text{C}_4$  plant derived carbon and soot carbon. The mass balance for these species is

$$[\text{OC}] = [\text{C}_3] + [\text{C}_4] + \text{soot } [\text{BC}] \quad \text{eq. 2.1,}$$

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

$$\delta^{13}\text{C}_{\text{OC}} \cdot [\text{OC}] = \delta^{13}\text{C}_{\text{C}_3} \cdot [\text{C}_3] + \delta^{13}\text{C}_{\text{C}_4} \cdot [\text{C}_4] + \delta^{13}\text{C}_{\text{soot BC}} \cdot \text{soot } [\text{BC}] \quad \text{eq. 2.2.}$$

The only unknown values in equations (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  $-33\text{‰}$  to  $-24\text{‰}$ , and for  $\delta^{13}\text{C}_{\text{C}_4}$  they range from  $-16\text{‰}$  to  $-10\text{‰}$  (Oleary, 1988).

Using the median values for  $\delta^{13}\text{C}_{\text{C}_3}$  and  $\delta^{13}\text{C}_{\text{C}_4}$  ( $-28.5\text{‰}$  and  $-13\text{‰}$ , respectively; Oleary 1988), we calculated that the median wt. %  $\text{C}_4$  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  $\text{C}_4$  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 a range in wt. %  $\text{C}_4$  vegetation as a

fraction of the total OC that is at most 23%, and at least <1%. This supposition is further supported by results from Rasmussen and White (2010) who found C<sub>3</sub> 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  $-26.2\text{‰}$ . Given the range of isotopic compositions reported by O'Leary (1988) it appears C<sub>3</sub> 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<sub>4</sub> 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<sub>4</sub> plants is very likely less than our estimate of 12%.

We suggest the soot BC enrichment in  $^{13}\text{C}$  relative to bulk soil OC ( $\sim 5.5\text{‰}$ ;  $p < 0.05$ ; Figure 2.4B) 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<sub>3</sub>-derived based on our isotopic mass balance. If our soot BC is derived from local C<sub>3</sub> material it should be unfractionated and reflect the more depleted  $\delta^{13}\text{C}$  of C<sub>3</sub> plants, which it does not. This supposition is based on literature data that show no isotopic fractionation between burned C<sub>3</sub> vegetation and the starting material (Table 2.1). Our measured  $\delta^{13}\text{C}_{\text{soot BC}}$  is enriched, consistent with a predominantly C<sub>4</sub> source that was fractionated during burning; however, this C<sub>4</sub> source cannot be local based on the isotopic mass balance. The observation that soot BC is significantly enriched in  $^{13}\text{C}$  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<sub>4</sub> burned material in central AZ soil is likely derived from a non-local (i.e., distant) source.

#### *Isotope W-to-E 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 ( $p < 0.05$ ; Figure 2.5). 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<sub>4</sub> grasses (Das et al. 2010), we suggest that soot BC in this area was produced mostly from biomass burning of C<sub>4</sub> 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<sub>3</sub> 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.

*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 come from 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 ( $-16\text{‰}$ ) 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 ( $-20\text{‰}$ ) 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 ( $4\text{‰}$ ) 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  $-21\text{‰}$ ; Table 2.1) is the most likely of these scenarios.

This is, to our knowledge, the first study of soil soot BC concentration and  $\delta^{13}\text{C}_{\text{soot BC}}$  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.

## Literature Cited

- Baldock, J. A., and R. J. Smernik. 2002. "Chemical composition and bioavailability of thermally, altered *Pinus resinosa* (Red Pine) wood." *Organic Geochemistry* no. 33 (9):1093-1109.
- Bird, M. I., and D. R. Grocke. 1997. "Determination of the abundance and carbon isotope composition of elemental carbon in sediments." *Geochimica et Cosmochimica Acta* no. 61 (16):3413-3423.
- Bird, M. I., C. Moyo, E. M. Veenendaal, J. Lloyd, and P. Frost. 1999. "Stability of elemental carbon in a savanna soil." *Global Biogeochemical Cycles* no. 13 (4):923-932.
- Bird, M. I., and P. L. Ascough. 2012. "Isotopes in pyrogenic carbon: A review." *Organic Geochemistry* no. 42 (12):1529-1539.
- Bohn, H.L., McNeal, B.L., O'Connor, G.A. 2001. "Soil Chemistry." New York: *John Wiley & Sons*.
- Cachier, H., P. Buatmenard, M. Fontugne, and J. Rancher. 1985. "Source terms and source strengths of the carbonaceous aerosol in the tropics." *Journal of Atmospheric Chemistry* no. 3 (4):469-489.
- Cachier, H., C. Liousse, P. Buatmenard, and A. Gaudichet. 1995. "Particulate content of savanna fire emissions." *Journal of Atmospheric Chemistry* no. 22 (1-2):123-148.
- Czimczik, C. I., C. M. Preston, M. W. I. Schmidt, R. A. Werner, and E. D. Schulze. 2002. "Effects of charring on mass, organic carbon, and stable carbon isotope composition of wood." *Organic Geochemistry* no. 33 (11):1207-1223.
- Das, O., Y. Wang, and Y.P. Hsieh. 2010. "Chemical and carbon isotopic characteristics of ash and smoke derived from burning of C3 and C4 grasses." *Organic Geochemistry* no. 41 (3):263-269.
- Glaser, B., L. Haumaier, G. Guggenberger, and W. Zech. 2001. "The 'Terra Preta' phenomenon: a model for sustainable agriculture in the humid tropics." *Naturwissenschaften* no. 88 (1):37-41.
- Goldberg, E.D. 1985. "Black Carbon in the Environment." New York: *John Wiley & Sons*.

- Gonzalez-Perez, J. A., F. J. Gonzalez-Vila, G. Almendros, and H. Knicker. 2004. "The effect of fire on soil organic matter - a review." *Environment International* no. 30 (6):855-870.
- Gustafsson, O., T. D. Bucheli, Z. Kukulska, M. Andersson, C. Largeau, J. N. Rouzaud, C. M. Reddy, and T. I. Eglinton. 2001. "Evaluation of a protocol for the quantification of black carbon in sediments." *Global Biogeochemical Cycles* no. 15 (4):881-890.
- Gustafsson, O., F. Haghseta, C. Chan, J. MacFarlane, and P. M. Gschwend. 1997. "Quantification of the dilute sedimentary soot phase: Implications for PAH speciation and bioavailability." *Environmental Science & Technology* no. 31 (1):203-209.
- Hammes, K., M. W. I. Schmidt, R. J. Smernik, L. A. Currie, W. P. Ball, T. H. Nguyen, P. Louchouart, S. Houel, O. Gustafsson, M. Elmquist, G. Cornelissen, J. O. Skjemstad, C. A. Masiello, J. Song, P. Peng, S. Mitra, J. C. Dunn, P. G. Hatcher, W. C. Hockaday, D. M. Smith, C. Hartkopf-Froeder, A. Boehmer, B. Luer, B. J. Huebert, W. Amelung, S. Brodowski, L. Huang, W. Zhang, P. M. Gschwend, D. X. Flores-Cervantes, C. Largeau, J. N. Rouzaud, C. Rumpel, G. Guggenberger, K. Kaiser, A. Rodionov, F. J. Gonzalez-Vila, J. A. Gonzalez-Perez, J. M. de la Rosa, D. A. C. Manning, E. Lopez-Capel, and L. Ding. 2007. "Comparison of quantification methods to measure fire-derived (black/elemental) carbon in soils and sediments using reference materials from soil, water, sediment and the atmosphere." *Global Biogeochemical Cycles* no. 21 (3). GB3016.
- Han, Y. M., J. R. Marlon, J. J. Cao, Z. D. Jin, and Z. S. An. 2012. "Holocene linkages between char, soot, biomass burning and climate from Lake Daihai, China." *Global Biogeochemical Cycles* no. 26:9. GB4017.
- Hilscher, A., K. Heister, C. Siewert, and H. Knicker. 2009. "Mineralisation and structural changes during the initial phase of microbial degradation of pyrogenic plant residues in soil." *Organic Geochemistry* no. 40 (3):332-342.
- Johnson, E. A. K. Miyanishi. 2001. *Forest Fires: Behavior and Ecological Effects*. San Diego: Academic Press.
- Kawashima, H., and Y. Haneishi. 2012. "Effects of combustion emissions from the Eurasian continent in winter on seasonal delta C-13 of elemental carbon in aerosols in Japan." *Atmospheric Environment* no. 46:568-579.
- Kaye, J. P., S. E. Eckert, D. A. Gonzales, J. O. Allen, S. J. Hall, R. A. Sponseller, and N. B. Grimm. 2011. "Decomposition of urban atmospheric carbon in Sonoran Desert soils." *Urban Ecosystems* no. 14 (4):737-754.



- Krull, E. S., J. O. Skjemstad, D. Graetz, K. Grice, W. Dunning, G. Cook, and J. F. Parr. 2003. "C-13-depleted charcoal from C4 grasses and the role of occluded carbon in phytoliths." *Organic Geochemistry* no. 34 (9):1337-1352.
- Leavitt, S. W., D. J. Donahue, and A. Long. 1982. "Charcoal production from wood and cellulose - Implications to radiocarbon-dates and accelerator target production." *Radiocarbon* no. 24 (1):27-35.
- Lopez-Veneroni, D. 2009. "The stable carbon isotope composition of PM2.5 and PM10 in Mexico City metropolitan area air." *Atmospheric Environment* no. 43 (29):4491-4502.
- Mannino, A., and H. R. Harvey. 2004. "Black carbon in estuarine and coastal ocean dissolved organic matter." *Limnology and Oceanography* no. 49 (3):735-40.
- Maricopa County. Maricopa County Community Wildfire Protection Plan Maricopa County Department of Emergency Management: Logan Simpson Design, Inc. Phoenix, AZ. 2010.
- Marusenko, Y., P. Herckes, and S. J. Hall. 2011. "Distribution of Polycyclic Aromatic Hydrocarbons in Soils of an Arid Urban Ecosystem." *Water Air and Soil Pollution* no. 219 (1-4):473-487.
- Masiello, C. A., and E. R. M. Druffel. 1998. "Black carbon in deep-sea sediments." *Science* no. 280 (5371):1911-1913.
- Masiello, C.A. 2004. "New directions in black carbon organic geochemistry." *Marine Chemistry* no. 92:201-213.
- McCrackin, M. L., T. K. Harms, N. B. Grimm, S. J. Hall, and J. P. Kaye. 2008. "Responses of soil microorganisms to resource availability in urban, desert soils." *Biogeochemistry* no. 87 (2):143-155.
- Menon, S., J. Hansen, L. Nazarenko, and Y. Luo. 2002. "Climate effects of black carbon aerosols in China and India." *Science* no. 297 (5590):2250-2253.
- Ogren, J. A., and R. J. Charlson. 1983. "Elemental carbon in the atmosphere - cycle and lifetime." *Tellus Series B-Chemical and Physical Meteorology* no. 35 (4):241-254.
- Oleary, M. H. 1988. "Carbon isotopes in photosynthesis." *Bioscience* no. 38 (5):328-336.
- Penner, J. E., H. Eddleman, and T. Novakov. 1993. "Towards the devolvement of a global inventory for black carbon emissions." *Atmospheric Environment Part a-General Topics* no. 27 (8):1277-1295.

- Preston, C. M., and M. W. I. Schmidt. 2006. "Black (pyrogenic) carbon: a synthesis of current knowledge and uncertainties with special consideration of boreal regions." *Biogeosciences* no. 3 (4):397-420.
- Ramanathan, V., and G. Carmichael. 2008. "Global and regional climate changes due to black carbon." *Nature Geoscience* no. 1 (4):221-227.
- Rasmussen, C., and D. A. White. 2010. "Vegetation effects on soil organic carbon quality in an arid hyperthermic ecosystem." *Soil Science* no. 175 (9):438-446.
- Rivas, Y., F. Matus, C. Rumpel, H. Knicker, and E. Garrido. 2012. "Black carbon contribution in volcanic soils affected by wildfire or stubble burning." *Organic Geochemistry* no. 47:41-50.
- Sakurai, H., H. J. Tobias, K. Park, D. Zarling, K. S. Docherty, D. B. Kittelson, P. H. McMurry, and P. J. Ziemann. 2003. "On-line measurements of diesel nanoparticle composition and volatility." *Atmospheric Environment* no. 37 (9-10):1199-1210.
- Schmidt, M. W. I., and A. G. Noack. 2000. "Black carbon in soils and sediments: Analysis, distribution, implications, and current challenges." *Global Biogeochemical Cycles* no. 14 (3):777-793.
- Sherrod, L. A., G. Dunn, G. A. Peterson, and R. L. Kolberg. 2002. "Inorganic carbon analysis by modified pressure-calorimeter method." *Soil Science Society of America Journal* no. 66 (1):299-305.
- Skjemstad, J. O., D. C. Reicosky, A. R. Wilts, and J. A. McGowan. 2002. "Charcoal carbon in U.S. agricultural soils." *Soil Science Society of America Journal* no. 66 (4):1249-1255.
- Solomon, D., J. Lehmann, J. Thies, Thorsten Schäfer, B. Liang, J. Kinyangi, E. Neves, J. Petersen, F. Luizão, and J. Skjemstad. 2007. "Molecular signature and sources of biochemical recalcitrance of organic C in Amazonian dark earths." *Geochimica et Cosmochimica Acta* no. 71 (9):2285-2298.
- Steinbeiss, S., G. Gleixner, and M. Antonietti. 2009. "Effect of biochar amendment on soil carbon balance and soil microbial activity." *Soil Biology & Biochemistry* no. 41 (6):1301-1310.
- Widory, D. 2006. "Combustibles, fuels and their combustion products: A view through carbon isotopes." *Combustion Theory and Modelling* no. 10 (5):831-841.
- Yan, B. Z., T. A. Abrajano, R. F. Bopp, L. A. Benedict, D. A. Chaky, E. Perry, J. Song, and D. P. Keane. 2006. "Combined application of delta C-13 and molecular ratios in sediment cores for PAH source apportionment in the

- New York/New Jersey harbor complex." *Organic Geochemistry* no. 37 (6):674-687.
- Zimmerman, A. R. 2010. "Abiotic and Microbial Oxidation of Laboratory-Produced Black Carbon (Biochar)." *Environmental Science & Technology* no. 44 (4):1295-1301.
- Ziolkowski, L. A., A. R. Chamberlin, J. Greaves, and E. R. M. Druffel. 2011. "Quantification of black carbon in marine systems using the benzene polycarboxylic acid method: a mechanistic and yield study." *Limnology and Oceanography-Methods* no. 9:140-149.

Table 2.1. Isotopic composition of various carbon sources and combustion byproducts (Modified from Bird and Ascough 2010).

Starting Material (SM)	$\delta^{13}\text{C}_{\text{SM}} (\text{‰})$	Burned Byproduct (BB)	$\delta^{13}\text{C}_{\text{BB}} (\text{‰})$	Isotopic change
C <sub>3</sub> vegetation <sup>1</sup>	-25 to -26	ash	-25 to -26 <sup>ab</sup>	no change
C <sub>3</sub> vegetation <sup>1</sup>	-25 to -26	smoke/soot BC	-25 to -26 <sup>ab</sup>	no change
C <sub>4</sub> vegetation <sup>1</sup>	-12 to -14	ash	-11 to -18 <sup>ab</sup>	depleted
C <sub>4</sub> vegetation <sup>1</sup>	-12 to -14	smoke/soot BC	-13 to -21 <sup>ab</sup>	depleted
C <sub>4</sub> vegetation <sup>2</sup>	-12 to -15	char	-12 to -18	depleted
C <sub>4</sub> vegetation <sup>3</sup>	-12 to -14	aerosol	-13 to -19	depleted
fossil fuel <sup>4</sup>	-26 to -29	soot	-21 to -28	enriched
fossil fuel <sup>5</sup>	-27 to -29	particles	-24 to -27	enriched

<sup>1</sup>Das et al. 2010, <sup>2</sup>Krull et al. 2003, <sup>3</sup>Cachier et al. 1985, <sup>4</sup>Widory 2006,

<sup>5</sup>Lopez-Veneroni 2009; <sup>a</sup> Range calculated from reported  $\Delta\delta^{13}\text{C}$  values. <sup>b</sup> Uncertainties reported in literature are  $\pm 1\text{‰}$ .

**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 <sup>a</sup>	Land-Use	Inorg. C <sup>b</sup> (wt %)	Org. C <sup>b</sup> (wt %)	Soot BC <sup>c</sup> (wt %)	Soot BC (mg BC/g Soil)	BC/OC (%)	$\delta^{13}\text{C}_{\text{soot BC}}^{\text{c,d}}$ (‰)	$\delta^{13}\text{C}_{\text{OC}}^{\text{c,d}}$ (‰)
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 0.039 ±	0.003	2	-21.3	
8	2	desert	0.23	1.43	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 0.058 ±	0.018	41	-21.1	
16	3	desert	0.12	1.13	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

Table 2.2. Continued.

Site	n <sup>a</sup>	Land-Use	Inorg. C <sup>b</sup> (wt %)	Org. C <sup>b</sup> (wt %)	Soot BC <sup>c</sup> (wt %)	Soot BC (mg BC/g Soil)	BC/OC (%)	$\delta^{13}\text{C}_{\text{soot BC}^{\text{c,d}}}$ (‰)	$\delta^{13}\text{C}_{\text{OC}^{\text{c,d}}}$ (‰)
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 ± 0.07	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

Table 2.2. Continued

Site	n <sup>a</sup>	Land-Use	Inorg. C <sup>b</sup> (wt %)	Org. C <sup>b</sup> (wt %)	Soot BC <sup>c</sup> (wt %)	Soot BC (mg BC/g Soil)	BC/OC (%)	$\delta^{13}\text{C}_{\text{soot BC}^{\text{c,d}}}$ (‰)	$\delta^{13}\text{C}_{\text{OC}^{\text{c,d}}}$ (‰)
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	

<sup>a</sup> n = number of samples<sup>b</sup> data from CAP LTER<sup>c</sup> mean ± 1 S.D.<sup>d</sup> values are in permil vs. the VPDB standard

Table 2.3. Organic carbon content and organic carbon isotopic composition ( $\delta^{13}\text{C}_{\text{oc}}$ ) for the 25 CAP-LTER sites used in this study.

Site <sup>a</sup>	n <sup>b</sup>	Org. C <sup>c</sup> (wt %)	$\delta^{13}\text{C}_{\text{oc}}^{\text{c,d}}$ (‰)
A, 1	2	0.63	-22.3 $\pm$ 0.4
B, 5	2	0.49 $\pm$ 0.01	-22.62 $\pm$ 0.07
C, 6	2	0.97 $\pm$ 0.02	-24.6 $\pm$ 0.1
D, 11	2	0.12 $\pm$ 0.00	-24.8 $\pm$ 0.4
E	2	0.24 $\pm$ 0.01	-24.4 $\pm$ 0.0
F	1	0.08	-24.7
G, 19	1	0.62	-22.3
H, 20	2	0.85 $\pm$ 0.01	-24.66 $\pm$ 0.03
I, 33	1	0.36	-23.4
J, 34	2	0.62 $\pm$ 0.01	-19.0 $\pm$ 0.5
K, 39	2	0.28 $\pm$ 0.02	-22.3 $\pm$ 0.2
L, 40	2	0.33 $\pm$ 0.01	-23.35 $\pm$ 0.04
M, 41	2	0.14 $\pm$ 0.01	-23.77 $\pm$ 0.01
N, 50	2	0.57 $\pm$ 0.00	-21.60 $\pm$ 0.01
O, 51	2	0.79 $\pm$ 0.01	-23.05 $\pm$ 0.03
P	1	0.71	-24.2
Q	4	0.52 $\pm$ 0.02	-24.6 $\pm$ 0.1
R	2	1.27 $\pm$ 0.02	-18.1 $\pm$ 0.3
S	2	0.25 $\pm$ 0.07	-23.7 $\pm$ 0.6
T	4	0.27 $\pm$ 0.03	-24.4 $\pm$ 0.1
U	3	0.52 $\pm$ 0.07	-22.4 $\pm$ 0.3
V	4	0.30 $\pm$ 0.04	-23.1 $\pm$ 0.6
W	2	0.25 $\pm$ 0.00	-22.6 $\pm$ 0.1
X	10	0.71 $\pm$ 0.06	-21.8 $\pm$ 0.6
Y	4	1.47 $\pm$ 0.1	-24 $\pm$ 1

<sup>a</sup> sites with number codes correspond to sites that also have soot BC measurements (see Table 2.2)

<sup>b</sup> n = number of samples

<sup>c</sup> mean  $\pm$  1 S.D.

<sup>d</sup> values are in permil vs. the VPDB standard



Table 2.4. 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. %) <sup>a</sup>	Soot BC/OC <sup>b</sup>
Desert (n=14)	$0.08 \pm 0.02$	$0.9 \pm 0.2$	$0.29 \pm 0.09$
Urban (n=32)	$0.25 \pm 0.02$	$1.4 \pm 0.1$	$0.27 \pm 0.03$
Agricultural (n=6)	$0.14 \pm 0.01$	$0.9 \pm 0.1$	$0.20 \pm 0.04$

<sup>a</sup> OC data from LTER database.

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

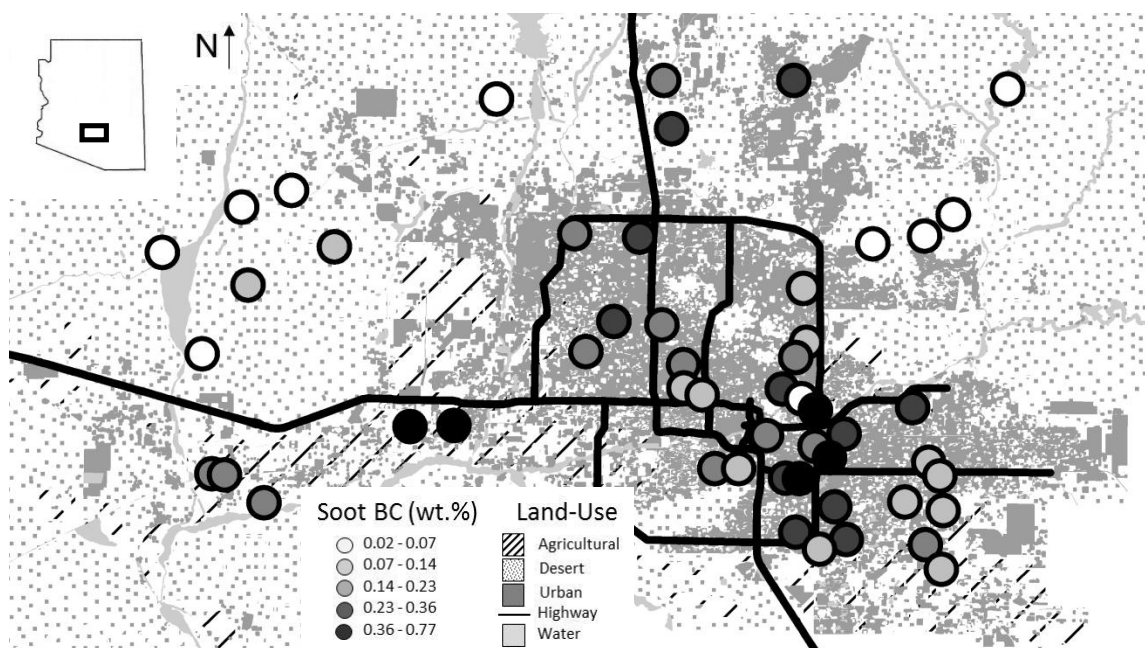


Figure 2.1. Map of the Phoenix metropolitan area, with land-use type (background shading), roads (solid lines), sample locations (circles), and soot BC concentrations (circle shading). The inset map shows the state of Arizona and the box indicates the location of the CAP-LTER study area.

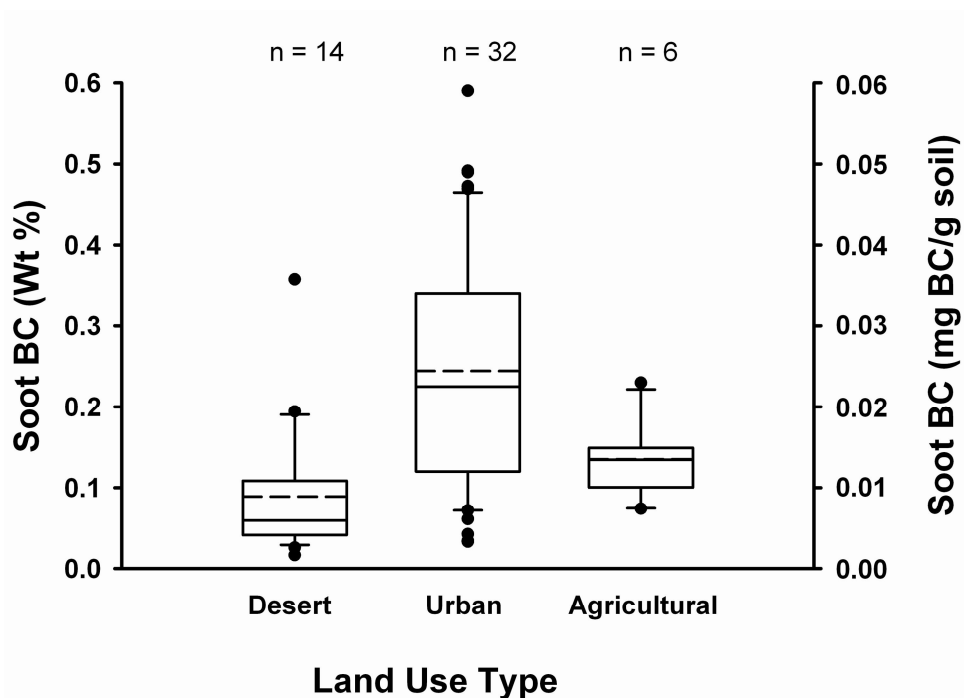


Figure 2.2. Concentration of soot BC (wt. %) for individual land-use categories. Solid and dashed horizontal lines within the boxes indicate median and mean values, respectively. The upper and lower box boundaries denote the 25<sup>th</sup> and 75<sup>th</sup> percentiles, respectively; the upper and lower whiskers denote the 90<sup>th</sup> and 10<sup>th</sup> percentiles, respectively; the symbols are outlying points. Note, the agricultural mean and median lines overlap. The observed range of desert soot [BC] in Figure 2.2 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 ( $p < 0.05$ )

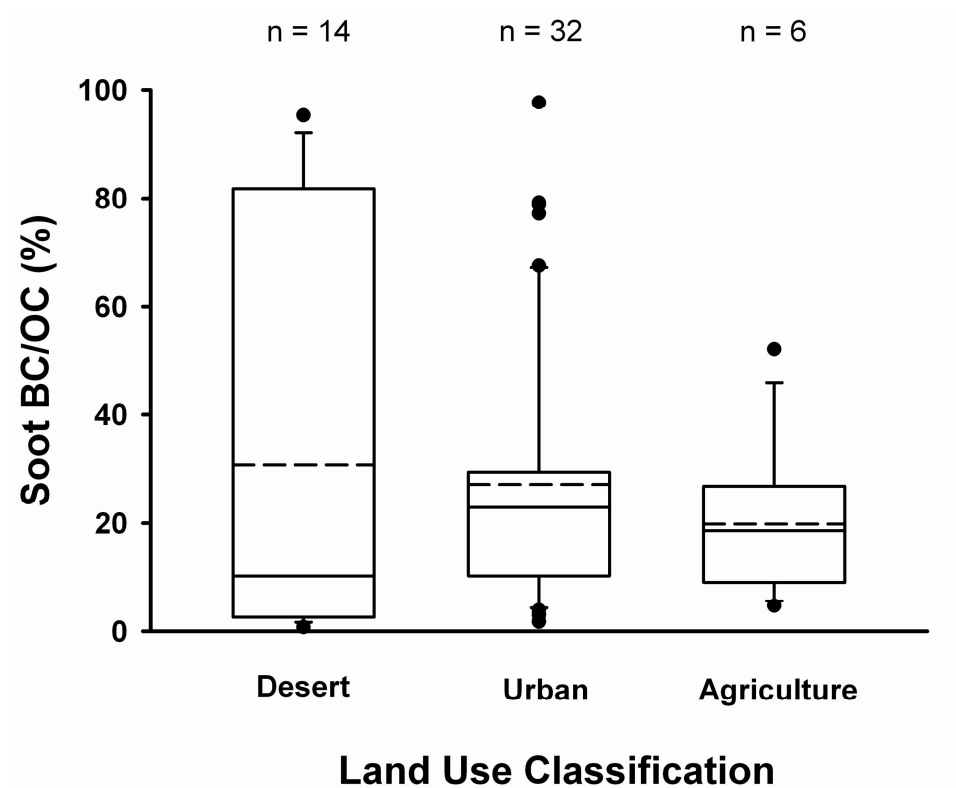


Figure 2.3. Soot BC/OC (%) for individual land-use categories. Solid and dashed horizontal lines within the boxes indicate median and mean values, respectively; upper and lower box boundaries denote the 25<sup>th</sup> and 75<sup>th</sup> percentiles, respectively; upper and lower whiskers denote the 90<sup>th</sup> and 10<sup>th</sup> percentiles, respectively; symbols are outlying points. There is no statistical difference among the median values for the three land-use types ( $p > 0.05$ )

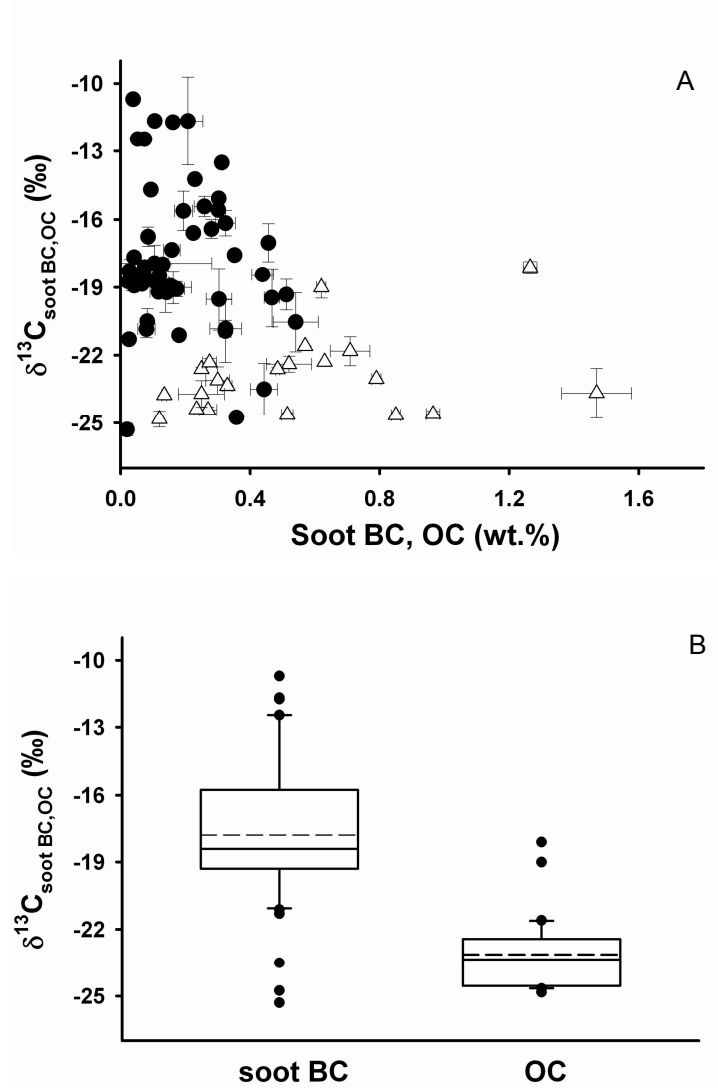


Figure 2.4. Isotopic composition of OC and soot BC in central AZ. (A)  $\delta^{13}\text{C}_{\text{soot BC}}$  (●) and  $\delta^{13}\text{C}_{\text{OC}}$  (Δ) as a function of soot BC or soil OC content, respectively. Error bars are  $\pm 1$  SD based on three independent analyses; where error bars are 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 25<sup>th</sup> and 75<sup>th</sup> percentiles, respectively; upper and lower whiskers denote the 90<sup>th</sup> and 10<sup>th</sup> 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 ( $p < 0.05$ ).

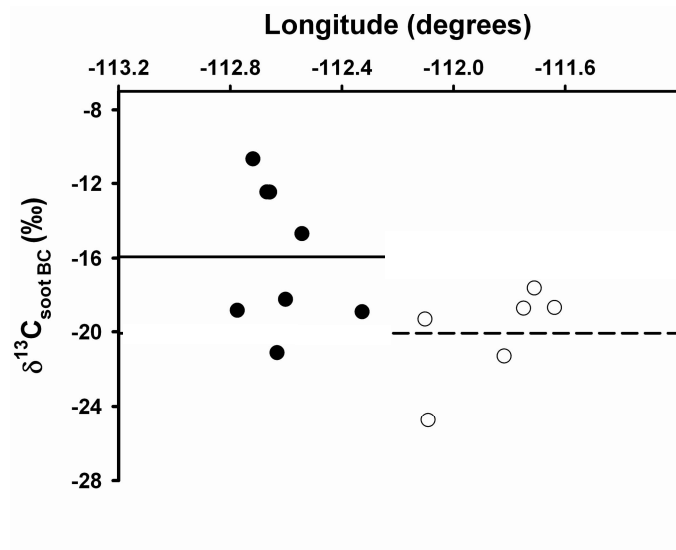


Figure 2.5. Isotopic composition of soot BC at desert sites as a function of longitude (position W and E of the city). Desert sites west of the city are solid circles (●) and desert sites east of the city are open circles (○). The solid and dashed lines represent the mean isotopic composition for desert soils west and east of the city, respectively ( $p < 0.05$ ).

## Chapter 3

### PHOTO-OXIDATION AND HISTORICAL LAND-USE CHANGE OBSERVATIONS OF SOOT BLACK CARBON: AN ASSESSMENT OF DEGRADATION RATES

#### Abstract

Soot black carbon (BC) is produced from the incomplete combustion of biomass and fossil fuel, and it is a significant fraction of the soil organic carbon in central Arizona (AZ). Soot BC concentrations in non-urban areas are low compared to those in urban areas, suggesting soot BC concentration is related to land-use. I present results from photo-oxidation studies demonstrating that a portion of soot BC from central AZ can be significantly degraded on short time scales, with an average oxidation rate of  $\sim 0.55$  g soot BC/kg soil·y. The functional group chemistry of soot BC also changes during photo-oxidation; aliphatic and aromatic hydrocarbon structures are photochemically oxidized to carbonyl containing structures such as aldehydes and ketones. The historical pattern of land-use change in central AZ provides further evidence that a significant source of soot BC is the process of urbanization (land conversion from desert to urban land use). Based on this land-use change history, I estimate an effective environmental degradation rates for soot BC of  $\sim 0.03$  g soot BC/kg soil·y. These results suggest that soot BC in central AZ soils is relatively photo-reactive and, that in the future, work assessing the fate of soot BC in the environment should consider a photo-degradative sink.

#### Introduction

Incompletely combusted material known as black carbon (BC) is generally considered to be less reactive than the unburned starting materials (biomass and

fossil fuel; Goldberg 1985). Black C is traditionally thought to be unreactive because it is comprised of mostly hydrocarbons oriented in aliphatic and aromatic structures. Generally, BC has been shown to be refractory (Kuhlbusch 1998; Skjemstad et al. 2002) and residence times on the order of thousands of years have been calculated based on radiocarbon ( $^{14}\text{C}$ ) dating of char in soil (Saldarriaga and West 1986). However, recently, there is evidence that BC is more reactive in environmental systems both as a potential carbon source for microbial metabolism and as a portion of the riverine dissolved organic carbon flux (Hilscher et al. 2009; Zimmerman 2010; Jaffé et al. 2013).

There is interest in BC because BC is relevant to a number of topics including pollution chemistry, climate change, and air quality (Gustafsson 1997; Gustafsson and Gschwend 1997; Accardi-Dey and Gschwend 2002; Adachi et al. 2010; Gerde et al. 2001). Because BC is fairly refractory, it plays a role in long-term organic matter storage (Czimczik and Masiello 2007). Investigations into the source and decomposition of organic carbon must consider the presence of BC (Alexis et al. 2010; Hamilton and Hartnett 2013) because the carbon cycle in terrestrial ecosystems can be altered by carbon input from combustion. Understanding degradation pathways for BC is important to assessing how ecosystems respond to inputs of fire-derived carbon.

The term black carbon refers to a continuum of combustion products ranging from slightly charred, degradable biomass to highly condensed, refractory soot (Hedges et al. 2000). Soot BC, specifically, is formed when small molecules condense from the gas-phase to form nano-sized particles (Kennedy 1997). Soot BC is different from charred material (i.e, biochar or charcoal), in that it does not retain the



physical or chemical characteristics of the starting material. The work presented in this paper focuses specifically on the soot BC fraction of the soil organic carbon (OC) in the Phoenix, Arizona, USA metropolitan area. Soot BC is a significant contributor to the bulk soil organic carbon in central AZ (31% on average) and soils in this region generally have among the highest BC/OC ratios reported in the literature (Hamilton and Hartnett, 2013). These high ratios are attributed to both below average bulk soil organic carbon content, which is typical in an arid desert environment (Bohn et al. 2001), and above average soot BC content which is typical of an urban environment (Adachi and Buseck 2008). Soot BC and bulk OC have different sources and likely react differently in AZ soils; therefore, the high BC/OC ratios suggest that soot BC is relevant to carbon cycling in the region (Hamilton and Hartnett 2013). I focus on soot BC because its isolation technique is well established (Gustafsson et al. 1997) and the method detects very few non-soot compounds or materials (Gustafsson et al. 2001; Elmquist et al. 2004; Hammes et al. 2007). Although great strides have been made toward understanding the environmental reactivity of biochar and charcoal (i.e., remnant materials; Hilscher and Knicker 2011; Zimmerman 2010; Hilscher et al. 2009; Hamer et al. 2004) comparatively little is known about the reactivity of soot BC. In Arizona, soot BC can constitute a large fraction of bulk OC; thus, understanding soot BC reaction characteristics gives insight into soil carbon cycling in central AZ.

Photochemistry is a major driver of carbon cycling, especially in a desert ecosystem where direct sunlight exposure is prevalent as a result of the nearly constant cloudless skies (Quinn et al. 2007). Ultraviolet and visible light can excite electrons from bonding or non-bonding molecular orbitals to molecular antibonding

orbitals. When this occurs a molecule is said to be in an excited state and becomes a more reactive species (Schwarzenbach et al. 1993). The effect of photo-oxidation on bulk organic matter and the less refractory types of black carbon material (biochar and charcoal) has been demonstrated for both solid and dissolved phases. For example, solar radiation has been shown to convert synthetic lignin (an aromatic species) to CO<sub>2</sub> and soluble organic photo-products (Vahatalo et al. 1999). Similarly, photo-degradation of dissolved BC has been shown using condensed aromatics isolated from seawater. Photo-degradation of dissolved BC was found to be more rapid and more extensive than photodegradation of bulk dissolved OC and the more limited pool of colored dissolved organic matter (Stubbins et al. 2012). Photo-oxidation experiments using soil organic matter from plant litter have demonstrated an increase in aliphatic products as well as an increase in soil organic matter solubility as a result of UV-light exposure (Feng et al. 2011). These studies describe results for individual components of the organic matter pool. There are very few reports of photochemical transformation of laboratory-produced soot BC and fewer still for soot BC isolated from natural systems.

Urbanization in central AZ over the last 80 to 90 years has had a direct impact on almost every aspect of biogeochemistry in the city including: the hydrology, temperature, chemistry, and phenology (plant and animal life-cycles) of the region. Urbanization has also been linked to the presence of combustion by-products in central AZ and other locations. Land-use and land-cover change information have been used to help determine the sources of both elemental carbon in atmospheric particulate matter (Kaye et al. 2011) and soot BC in central AZ soils (Hamilton and Hartnett 2013). Notably, urban areas have significantly higher soil soot BC content

than surrounding desert soils (Hamilton and Hartnett 2013). The PAHs, a known combustion by-product, in central AZ soil are predominantly derived from fossil fuel combustion (Marusenko et al. 2011). Furthermore, the relationship between urbanization and high soil BC content is not unique to the Phoenix area; He and Zhang (2009) demonstrated that black carbon concentrations in urban soils from Nanjing, China were higher in industrial and commercial area than in residential areas. Their study also indicated that BC found in surface soil could be attributed to a fossil fuel source and BC found at depth could be attributed to a coal burning source (He and Zhang 2009). Together, these studies indicate that activities typically related to urbanization contribute to the presence of BC in affected regions.

Here, I present laboratory measurements of soot BC photo-oxidation rates and chemical functional group changes occurring as a result of photochemical oxidation as well as field observations of soot BC from a variety of locations and land-use types in Phoenix, AZ. I monitored photo-oxidative changes in soot BC chemical functional groups using Fourier transform infrared (FTIR) spectroscopy. FTIR spectroscopy has been used as a tool to help identify functional group chemistry of solid-state black carbon in laboratory produced soot (Smith and Chughtai 1995) and soils (Solomon et al. 2007; Sun et al. 2007; Cheng et al. 2008; Nguyen et al. 2009). My field observations correlate soot BC at urban sites with historical land-use information for each location. Correlation analysis indicates recently urbanized areas have higher soot BC concentrations than areas where urbanization occurred in the more distant past. This correlation allows an estimate of the effective environmental soot BC degradation rate. Although less constrained than a laboratory-derived photo-oxidation rate, the effective environmental degradation

rate places a lower bound on the natural rate of soot BC degradation. Based on the broad agreement between the lab-derived and field-based rate estimates, I hypothesize that at least a portion of soot BC in central AZ is photochemically degraded on monthly to decadal timescales and is part of a relatively labile pool of soil black carbon.

## Methods

### *Sampling region*

The Central Arizona–Phoenix Long-Term Ecological Research (CAP-LTER) program examines the ecosystem of metropolitan Phoenix and the surrounding Sonoran desert. Central AZ is semi-arid with annual rainfall of <18 cm; the area consists of an urban core, rapidly developing suburbs, agricultural areas of various ages, and undeveloped native desert. The Phoenix metropolitan population increased by about 30% from 2000 to 2010 and its current population is 4.2 million (U. S. Census 2010). From 2000 to 2004, this population increase expanded the urban area of metropolitan Phoenix by 225 km<sup>2</sup>, or 154,110 m<sup>2</sup>/day (Maricopa Association of Governments 2010), making it one of the fastest growing areas in the U.S.

Central AZ receives an erythemal UV irradiance (direct plus diffuse) of 240–360 mW/m<sup>2</sup> in the summer months (June, July, and August) and 60–120 mW/m<sup>2</sup> in the winter months (December, January, and February; NASA Center for Ozone and Air Quality 2005). The region receives direct sunlight during ~86% of daylight hours (on average), ranging from a minimum monthly average of 78% in winter months to a maximum of 94% in summer months (Central Arizona-Phoenix Long-term

Ecological Research 2010).

### *Sample collection*

I analyzed soil samples collected in 2005 during CAP-LTER's semi-decadal field survey of urban, agricultural, and open desert (i.e., rural) sites (CAP Central Arizona-Phoenix Long-term Ecological Research 2010). CAP-LTER data was used for site location and for land-use categorization at each site. The agricultural and open desert sites will be, henceforth, referred to as non-urban sites because they sit in relatively close proximity to urban areas, but do not contain urban infrastructure. At each site (30 x 30 m plots) samples were collected from four 30-cm soil cores collected at the cardinal points (NSEW). The cores were homogenized, dried, and stored in the dark at 20°C. Each location has a land-use description from the years 1917 to 2005, at increments of 5, 10, 20, 25, 30, 45, 66, and 88 years before 2005, respectively.

### *Chemical Analyses*

Soot BC concentration, soot [BC], is quantified using chemo-thermal oxidation (CTO375; Gustafsson et al. 2001; Gustafsson et al. 1997) followed by elemental analysis and isotope ratio mass spectrometry (EA-IRMS). Carbon detected by EA-IRMS after CTO375 is defined as soot BC. The EA-IRMS detection limits are 1 µg C for [C]. I determined analytical precision and accuracy for soot BC concentration using a standard reference material (an Australian vertisol, 0.18 weight percent, 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). Briefly, a ball mill was used to grind soil samples to a fine powder. Soil samples were weighed (~18 mg) into silver capsules

(Costech Analytical Technologies, Valencia, CA, USA) and placed in a custom-built, Teflon™ 25-well tray. Deionized H<sub>2</sub>O (18.2 MΩ·cm; NANOpure Diamond, Barnstead, Inc. Dubuque, IA, USA) was used to wet samples and incremental additions of 4 M hydrochloric acid (J.T. Baker, Philipsburg, NJ, USA) were used to remove carbonate. After drying, samples were placed in an aluminum tray, and baked at 375°C (thermal oxidation) for 24 h under ambient atmospheric conditions to remove labile (non-black) organic carbon. In order to prevent temperature overshoot, the oven temperature was monitored closely using a thermocouple until temperature reached 375°C. According to a recent laboratory inter-comparison study, this method yields a conservative estimate of soot [BC] (Hammes et al. 2007). Carbon concentration was quantified in samples using EA-IRMS (Hamilton and Hartnett 2013). Organic carbon concentration, [OC], is quantified using the above technique without the thermal oxidation step.

#### *Photo-oxidation*

Photo-oxidation was performed on homogeneous sub-samples of soils from an urban and a non-urban site. Samples were taken from the bottom portion of the soil cores (16 – 30 cm depth). Sub-surface cores (16 – 30 cm) were used for photo-oxidation simply because they had not been exposed to direct sunlight in the recent past.

Soot BC and organic carbon (OC) were isolated separately from each site yielding a total of four samples (urban OC, urban soot BC, non-urban OC, and non-urban soot BC). After the two organic fractions (soot BC and OC) were isolated, each was photo-oxidized individually. Each sample was placed into a custom-built, relatively flat, quartz cuvette (1.0 x 0.4 x 2.6 cm; l x w x h). The cuvettes were placed

in front of an HBO Mercury short-arc 200 W/2 lamp (OSRAM; Munich, Germany) for a total of 24 hrs (Figure 3.1). The lamp emits radiation from <250 to 700 nm; a quartz cylinder filled with deionized water is placed in-line before the sample to absorb infrared radiation which prevents heating of the sample during irradiation. Spectral irradiance from the lamp attributed to the UV wavelengths (<250 nm to 400 nm) is 18 W/m<sup>2</sup> at a distance of 0.5 m, which is about 50 times the maximum summertime solar UV irradiance in central AZ (360 mW/m<sup>2</sup>) and about 300 times the minimum wintertime solar UV irradiance (240 mW/m<sup>2</sup>). Soil in each cuvette was mixed every hour to ensure maximum UV radiation exposure to all particles. Soils were sub-sampled (~18 mg) at time = 0, 6, 12, 18, and 24 hours to quantify soot BC and OC concentrations (soot [BC] and [OC], respectively). The number of hours of lamp exposure was converted to solar equivalent hours by multiplying the number of hours of lamp exposure by 50 to estimate the maximum rate of oxidation. Carbon concentrations in each sample were measured by EA-IRMS after UV exposure.

#### *FTIR Analysis*

Fourier-transform infrared (FTIR) spectroscopy was performed on OC and soot BC from urban and non-urban soils before and after photo-oxidation. Samples were homogenized with potassium bromide (KBr) at a ratio of 1:50 using a mortar and pestle (similarly to Nguyen et al. 2009). Pellets were placed in a Bruker IFS 66V/S FTIR spectrometer (Bruker Corporation, Billerica, MA, USA) and spectral data were collected from 400 to 4800 cm<sup>-1</sup> with a resolution of 2 cm<sup>-1</sup> using the OPUS 2.0 software provided by Bruker. The interpreted spectra are averages of 64 scans and all spectra were background subtracted using a blank pellet (i.e., KBr without sample).

### *Data Processing*

A Shapiro-Wilk test for normality was completed for all data sets. Linear regression statistics are presented for all data. Linear regression with interaction was performed to assess differences in photo-oxidation rates for urban and non-urban sites (SPSS 17; SPSS, Inc.). Data for each land use type are compared using a Mann-Whitney rank sum test (Sigma Plot 11; Systat Software, Inc.). Values are considered significant for  $p < 0.1$  and highly significant for  $p < 0.05$ .

## Results

### *Photo-oxidation rates*

Organic and soot BC concentrations decreased over the course of 24 h of UV light exposure or 1200 solar-equivalent hours (Table 3.1). Average values for carbon concentration (g C/kg soil) are higher for OC samples than for soot BC samples throughout the entire experiment (Figure 3.2A and 3.2B). Initial concentrations of OC in urban and non-urban soils were  $9.3 \pm 0.9$  and  $5.6 \pm 0.6$ , respectively. Final concentrations(after photo-oxidation) of OC in urban and non-urban soils were  $8.6 \pm 0.4$  and  $4.0 \pm 0.1$ , respectively. Initial concentrations of soot BC in urban and non-urban soils were  $0.81 \pm 0.04$  and  $0.6 \pm 0.2$ , respectively. Final concentrations of soot BC in urban and non-urban soils were  $0.7 \pm 0.1$  and  $0.45 \pm 0.03$ , respectively. Percent decreases in carbon concentration were calculated for each sample from  $t = 0$  h to  $t = 1200$  solar equivalent hours. The percent decrease for urban and non-urban OC samples was 8 and 28%, respectively, and the percent decrease for the urban and non-urban soot BC samples was 18 and 21%, respectively. Oxidation rates were calculated using regression lines fit to plots of carbon concentration vs.



time using the method of least squares. Photo-oxidation rates were  $4 \pm 4$  and  $5.7 \pm 0.4$  g C/kg soil·y for urban OC and non-urban OC, respectively, and  $0.6 \pm 0.1$  and  $0.5 \pm 0.3$  g C/kg soil·y for urban soot BC and non-urban soot BC, respectively (Table 3.1). The photo-oxidation rates in g C/kg soil·y were calculated assuming an average of 12 hours of sunlight per day. The negative slopes (Figure 3.2) are statistically different from zero in all samples, except for the urban OC sample.

Fourier transform infrared (FTIR) spectroscopy of urban and non-urban soot BC reveals the chemical functional groups present before and after photo-oxidation (Figure 3.3). Spectra of soot BC in both the urban and non-urban soils from before photo-oxidation exhibit hydroxyl groups detected as a broad peak from  $2930 - 3800$   $\text{cm}^{-1}$ , carbon-carbon single and double bonds detected by a peak at  $1040$   $\text{cm}^{-1}$ , and aromatic carbon bonds detected by peaks at  $790$ ,  $1425$  (urban only), and  $1630$   $\text{cm}^{-1}$  (Figure 3.3A and 3.3C). FTIR spectra of soot BC in both urban and non-urban soils after photo-oxidation indicate the presence of additional oxygenated functional groups that were not detected prior to UV exposure. Specifically, I note the appearance of aldehydes and ketones which contain carbonyl groups detected by broad peaks from  $2867 - 3000$   $\text{cm}^{-1}$  and  $1640 - 1800$   $\text{cm}^{-1}$  (Figure 3.3B and 3.3D). Note, the aromatic and aliphatic hydrocarbon peaks are still present after UV exposure.

#### *Historical land-use trends from 1917 to 2005*

Soot [BC] is higher in urban soils ( $n = 31$ ) than in non-urban soils ( $n = 21$ ;  $p < 0.05$ ; [BC] data from Hamilton and Hartnett 2013). There is a negative correlation between soot BC concentration and distance from city center (Figure 3.4A;  $p < 0.05$ ). A similar plot for just the urban soils reveals a slightly weaker, but notably positive,

correlation between urban soot BC concentration and distance from city center (Figure 3.4B;  $p < 0.1$ ). The x-axis in Figure 3.4C and 3.4D is time with units of 'years since land-use change'. This always reflects a change from non-urban to urban land use. The time is calculated from the year 2005; the last year for which land-use change data was collected. To clarify, 'years since land-use change' is the number of years a site has been under a specific land-use. For example, if a site was converted from non-urban to urban land-use in 1950, then the years since land-use change would be 55 years ( $2005 - 1950 = 55$ ). There is a significant negative correlation between distance from city center and years since land-use change (Figure 3.4C;  $p < 0.05$ ) and a significant negative correlation between soot [BC] and years since land-use change (Figure 3.4D;  $p < 0.05$ ).

## Discussion

### *Photo-oxidation*

Photochemical oxidation of environmental organic materials has been demonstrated many times; however, there are few reports on the photo-oxidation of soot BC. I present a summary of published photo-oxidation rates for a few representative forms of solid and dissolved organic matter including soot BC in Table 3.2. Soot black carbon is found throughout the soil cores I collected and there was no statistically significant difference in soot BC concentration between the surface (0-10 cm) and sub-surface (16-30 cm) samples (data not shown). This is not surprising as other forms of black carbon have been shown to migrate rapidly to depths of up to 15 – 30 cm in soils after being applied to the soil surface (Major et al. 2009).

Ultraviolet light exposure studies using urban and non-urban central AZ soils demonstrate that both bulk organic carbon and soot BC can be removed from soil by photo-oxidation, presumably by oxidation to CO<sub>2</sub>. The 24-hour laboratory study corresponds to 1200 solar-equivalent hours or ~100 days of sun exposure, (assuming 12 h of sunlight per day). I use solar-equivalent hours to calculate degradation rates and not lamp-hours in order to simplify comparisons with natural environmental processes. I related the lamp output to the maximum summertime solar irradiance (360 mW/m<sup>2</sup>) in calculating oxidation rates because the majority of the photo-oxidation is likely to occur when UV irradiance is greatest (i.e., in the summer months). Not surprisingly, oxidation rates are faster for OC samples (4 – 5.7 g C/kg soil·y) than for soot BC samples (0.5 – 0.6 g C/kg soil·y) by about an order of magnitude (Table 3.1) because the bulk OC portion of the soil contains more labile carbon (e.g., residues from plant roots and living organisms; Bohn et al. 2001). Organic carbon in urban soil degraded more slowly under UV light than organic carbon in non-urban soil by ~2 g C/kg soil·y (Table 3.1;  $p < 0.05$ ). This could be because non-urban soils (agricultural or desert) have more fresh vegetation input, or because urban soils contain more soot BC and, potentially, other recalcitrant forms of carbon (slightly charred biomass, char, charcoal) than the non-urban sites (Hamilton and Hartnett 2013). Soot BC degradation rates for the urban and non-urban soils were not statistically different from each other ( $p > 0.1$ ; Figure 3.2). The statistically similar BC degradation rates for urban and non-urban sites suggest the soot BC found in both locations has similar chemical composition (i.e., functional groups) and thus responds similarly to UV irradiation. If I assume all soil carbon is photo-oxidized at the same rate (a poor assumption at best), based on my laboratory

results, OC and soot BC could be completely removed from the samples in less than 4 solar-equivalent years. In other words, the x-intercepts (i.e., where  $[C] = 0$ ) for all lines in Figure 3.2 are  $< 4$  years. While this is an end-member approximation for carbon turnover time, it is unlikely that all soil carbon is removed at the same rate; moreover, soil carbon is slowly buried as soil is deposited which will further increase its residence time with respect to photo-degradation. None-the-less, I clearly demonstrate that at least a portion of the soot BC in central AZ soil can be photo-oxidized over a relatively short ( $\sim 100$  days) timescale.

My FTIR analysis of soot BC from central AZ is consistent with other reports of black carbon functional group composition (Smith and Chughtai. 1995; Solomon et al. 2007; Sun et al. 2007; Cheng et al. 2008; Nguyen et al. 2009). The presence of aromatic and aliphatic carbon in the soot BC before photo-oxidation (Figure 3.3) is to be expected, as carbon-carbon bonds in straight chains and ring structures are commonly present in soot BC (Masiello 2004). Cheng et al. (2008) examined aged BC samples collected from the field and showed that O/C ratios were increased in aged BC samples. The increase in the O/C was attributed to an increase in both hydroxyl and carbonyl functional groups. I attribute the hydroxyl groups detected here to a similar process. My FTIR analysis did not reveal any obvious functional group differences in soot BC from urban and non-urban soils prior to UV oxidation. The FTIR analysis after laboratory photo-oxidation indicates the presence of aldehydes and ketones, which contain carboxyl functional groups. In these groups, oxygen is covalently bonded to carbon and not merely adsorbed to the surface of soot BC particles. The changes in the FTIR spectra after photo-oxidation clearly indicate that over UV exposure timescales of  $\sim 100$  days, soot BC can be chemically oxidized

in soils. Similar functional group changes resulting from UV oxidation have also been demonstrated in natural lignin where photochemical reactions increased the number of hydroxyl, carboxyl, and ketone groups in lignin (Argyropoulos and Sun 1996). The data presented in this study demonstrate that soot BC is not chemically inert to photo-oxidation but rather, can be functionalized over time. This functionalization may allow the soot BC to become available to microbial degradation and thus, enhance the role played by soot BC in pedologic chemistry.

#### *Historical land-use trends from 1917 to 2005*

A better understanding of soot BC distribution patterns and the effects of degradation in central AZ soils can be gained by examining historical land-use data for the city of Phoenix. Soot BC is not evenly distributed throughout central AZ; the highest soot BC concentrations are found in urban areas, while desert sites furthest from the city center have the lowest soot BC concentrations (Hamilton and Hartnett 2013). Overall, soot BC concentrations (inclusive of all land-use types) are negatively correlated with distance from city center (Figure 3.4A). The urban soot BC concentrations are, however, positively correlated with distance from city center (Figure 3.4B). Distance from city center is, of course, related to the development of the city and is negatively correlated with years since land-use change (Figure 3.4C). The highest soot [BC] contents are associated with sites that have been converted from non-urban to urban land use most recently (in the last 25-30 years; Figure 3.4D). The presence of these soot BC “hotspots” suggests much of the soot BC in central AZ originates from the urban area. Phoenix, like other cities, has grown radially from a central point (now near city center). This outermost ring of urbanization or ‘urban fringe’ has become more distant from the center of the city

over time. Metropolitan Phoenix is young compared to almost all other metropolitan areas in the United States; Phoenix's population has more than tripled since 1980 with a corresponding 43% increase in urban land area from 2000 to 2010 (Maricopa Association of Governments 2010). Though it is important to note, open desert land has been converted to urban land over the entire history of development in metropolitan Phoenix, AZ (100 years).

The positive correlation between soot [BC] and distance from city center (Figure 3.4B) specifically for the urban sites reveals that sites at considerable distances from the city center (~33 km) have higher soot [BC] than sites closer to city center. In fact, sites nearest to city center have soot [BC] that are as low as those in open desert areas (note, the gray symbols in Figure 3.4B are non-urban desert sites). To be absolutely clear, this pattern is opposite from what one sees using all the Phoenix area sites (Figure 3.4A) and suggests soot [BC] increases as urban sites get further from city center. I evaluate two possible explanations for the presence of higher soot [BC] in the outermost urban areas. (1) The presence of beltways or looped highways 'funnel' a large percentage of vehicle traffic, and thus soot BC, to the outermost urban areas (Figure 3.5). (2) Urbanization or the conversion of land-use from non-urban to urban can deposit soot BC to soils. Each of these explanations will be discussed in turn.

It is well known that soot BC and its precursor molecules have an anthropogenic source via fossil fuel combustion (Penner et al. 1993; Marusenko et al. 2011). The highway system in central AZ consists of several looped beltways and highways that move large volumes of traffic (up to 300k vehicles per weekday) around the urban fringe (Figure 3.5). The sample sites located closest to the vicinity

where two major highways intersect (marked “H” on Figure 3.5) have some of the highest soot [BC] in the region (0.3 to 0.5 weight percent). This area is located at an intermediate distance ( $17 \pm 3$  km) from city center. However, other sites near city center are also proximate to major highway interchanges and yet, do not have high soil soot [BC] suggesting highway proximity alone is not causing high soot BC concentrations. In fact, the average weekday traffic volume on highways within 5 km of city center is greater (by as much as 124,000 vehicles/day) than traffic volumes on the looped roadways at distances of up to 25 km from city center (Maricopa Association of Governments 2010). Therefore, traffic volume in central AZ could be responsible for some of the higher soot [BC] at intermediate distances from city center but is likely not responsible for soot [BC] at all sites. The idea that BC may be highest at some distance away from highways is not without precedent. A study in Rochester, NY (albeit a smaller city with much lower growth) demonstrated that the highest atmospheric [BC] was found at a site furthest from the major regional highway (Wang et al. 2011) which suggests that [BC] is not necessarily a function of distance from roadways in urban areas.

Urbanization of open space is another likely source of soot BC because the process of converting land-use typically involves heavy machinery that burns diesel fuel. Reports from southwest China indicate that soil [OC] at construction sites were comparable to soil [OC] in heavily forested (high carbon) sites though, I presume, the composition of that carbon is different (Descoux et al. 2011). Sites closer to Phoenix city center were converted from desert to urban land-use in the more distant past than urban sites further from the city center (Figure 3.4C). Some sites on the ‘urban fringe’ have undergone land-use changes as recently as 5 to 10 years

ago. In contrast, sites near city center have not undergone a land-use change in nearly 100 years. The negative correlation between soot [BC] and years since last land-use change implies either that the process of urbanization deposits soot BC in soils that can then be degraded over time, or that urbanization in the recent past deposits more soot BC to soils than urbanization in the more distant past. Sites that were urbanized 25 and 30 years ago are somewhat above the trend line in Figure 3.4D. Many of the sites that comprise these two data points are also located near the intersections of the major looped highways discussed earlier (Figure 3.5) and thus may also exhibit some increase in soot BC due to vehicle emissions.

#### *Rate Comparison*

Land use history in the Phoenix area is well documented over the last 90 years, and the amount of soot BC in urban soils appears to be lower in sites with a longer urban history (Figure 3.4D). By assuming soot BC inputs after the primary land-use change (i.e., urbanization from non-urban to urban land-use) are uniform throughout the urban region I can gain some insight into environmental soot BC degradation rates. An effective environmental degradation rate can be estimated using the decrease in soot [BC] and the time scale derived from the land-use change information (Figure 3.4D). Soot BC concentrations decrease by about 2.5 g soot BC/kg soil over 88 years, which corresponds to an effective environmental degradation rate of  $\sim 0.03$  g soot BC/kg soil $\cdot$ y. This value suggests that soot BC is degraded over decadal time scales in AZ soils. I present the effective environmental degradation rate only as a point of comparison with the laboratory-based soot BC photo-oxidation rates. I do not assume the environmental rate is due entirely to photo-oxidation; in actuality, it is probably due to both photochemical and biological



oxidation. It is important to note that this environmental estimate is not particularly well constrained; however, the effective environmental soot BC degradation rate calculated using the historical land-use trend suggests soot BC does not accumulate in soil and, in fact, is not in steady state with soot BC deposition. Taken together, the increasing trend in soot BC as a function of distance from city center (Figure 3.4B) and the decreasing trend in soot BC as a function of years since land use change (Figure 3.4D) suggest soot [BC] in urban soil is controlled by recent urbanization.

The laboratory photo-oxidation rate for urban soot BC ( $0.6 \pm 0.1$  g soot BC/kg soil·y) is greater than the rate calculated from the change in the amount of BC as a function of the timing of land-use change ( $0.03 \pm 0.01$  g soot BC/kg soil·y). I note that photo-oxidation studies are under highly controlled conditions (constant temperature, i.e., 20°C) in a closed system, where additional inputs are eliminated. The rate I present is a maximum estimate of the rate assuming the highest summertime UV irradiance values. If I assume the lowest winter irradiance values the rate is  $0.09 \pm 0.02$  g soot BC/kg soil·y. Soils in central AZ are very likely continuously recharged with both labile and recalcitrant organic carbon from natural and anthropogenic sources. In addition, they are exposed to wet and dry deposition and they experience a wide range in temperature (both seasonally and daily) which may affect photochemical oxidation rates, and which certainly affect biological degradation rates. When these variables are considered, it is not surprising that the effective environmental degradation rates are slower than laboratory photo-oxidation rates. The laboratory photo-oxidation rates and the effective environmental degradation rates for soot BC presented here are both

comparable to published degradation rates for similarly recalcitrant materials (e.g., charcoal, biochar, aerosols; Table 3.3). What is clear from these estimates is that soot black carbon is reactive in the environment and that photo-oxidation can contribute to soot BC degradation.

I have demonstrated via laboratory photo-oxidation studies that at least a portion of soot BC can be photo-degraded on monthly timescales. Not only does soot [BC] decrease significantly over time, the soot BC chemical composition is altered by photo-oxidation as indicated by the addition of oxygenated functional groups. Soot BC photo-oxidation rates suggest that photo-oxidation by sunlight may be an important loss process for soot BC in areas with high solar irradiance. Land-use and soot [BC] data suggest that anthropogenic sources such as vehicle emission and urbanization deposit soot BC to soil. I do not speculate about what specific processes associated with urbanization are the source of soot BC, but I lay the groundwork for further investigation of this soot BC source. I infer from patterns in soil BC content and land-use change data that soot BC is degraded in the Phoenix area on something less than 100-y timescales. The effective environmental soot BC degradation rates estimated from the land-use change data are slower than rates of soot BC loss from laboratory photo-oxidation studies. Taken together, these studies indicate that soot BC in soils may be more reactive than originally thought by Goldberg (1985) and others and can be degraded in soil over monthly and decadal time-scales, rather than over millennial timescales.

## Literature Cited

- Accardi-Dey, A., and P. M. Gschwend. 2002. "Assessing the combined roles of natural organic matter and black carbon as sorbents in sediments." *Environmental Science & Technology* no. 36 (1):21-29.
- Adachi, K., and P. R. Buseck. 2008. "Internally mixed soot, sulfates, and organic matter in aerosol particles from Mexico City." *Atmospheric Chemistry & Physics* no. 8 (21):6469-6481.
- Adachi, K., S. H. Chung, and P. R. Buseck. 2010. "Shapes of soot aerosol particles and implications for their effects on climate." *Journal of Geophysical Research-Atmospheres* no. 115. D15206.
- Alexis, M. A., C. Rumpel, H. Knicker, J. Leifeld, D. Rasse, N. Pechot, G. Bardoux, and A. Mariotti. 2010. "Thermal alteration of organic matter during a shrubland fire: A field study." *Organic Geochemistry* no. 41 (7):690-697.
- Argyropoulos, D. S., and Y. J. Sun. 1996. "Photochemically induced solid-state degradation, condensation, and rearrangement reactions in lignin model compounds and milled wood lignin." *Photochemistry and Photobiology* no. 64 (3):510-517.
- Bohn, H.L., B.L. McNeal, and G.A. O'Connor. 2001. "Soil Chemistry." New York: *John Wiley & Sons*.
- Cheng, C. H., J. Lehmann, and M. H. Engelhard. 2008. "Natural oxidation of black carbon in soils: Changes in molecular form and surface charge along a climosequence." *Geochimica et Cosmochimica Acta* no. 72 (6):1598-1610.
- Central Arizona-Phoenix Long-term Ecological Research. 2010. "Site Description." Accessed March 15, 2007. <http://caplter.asu.edu/about/site-description/>
- Czimczik, C. I., and C. A. Masiello. 2007. "Controls on black carbon storage in soils." *Global Biogeochemical Cycles* no. 21. GB3005
- Descloux, S., V. Chanudet, H. Poilve, and A. Gregoire. 2011. "Co-assessment of biomass and soil organic carbon stocks in a future reservoir area located in Southeast Asia." *Environmental Monitoring and Assessment* no. 173 (1-4):723-741.
- Elmquist, M., O. Gustafsson, and P. Andersson. 2004. "Quantification of sedimentary black carbon using the chemothermal oxidation method: an evaluation of ex situ pretreatments and standard additions approaches." *Limnology and Oceanography-Methods* no. 2:417-427.

- Feng, X. J., K. M. Hills, A. J. Simpson, J. K. Whalen, and M. J. Simpson. 2011. "The role of biodegradation and photo-oxidation in the transformation of terrigenous organic matter." *Organic Geochemistry* no. 42 (3):262-274.
- Gerde, P., B. A. Muggenburg, M. Lundborg, and A. R. Dahl. 2001. "The rapid alveolar absorption of diesel soot-adsorbed benzo a pyrene: bioavailability, metabolism and dosimetry of an inhaled particle-borne carcinogen." *Carcinogenesis* no. 22 (5):741-749.
- Goldberg, E.D. 1985. "Black Carbon in the Environment." New York: *John Wiley & Sons*.
- Gustafsson, O., T. D. Bucheli, Z. Kukulska, M. Andersson, C. Largeau, J. N. Rouzaud, C. M. Reddy, and T. I. Eglinton. 2001. "Evaluation of a protocol for the quantification of black carbon in sediments." *Global Biogeochemical Cycles* no. 15 (4):881-890.
- Gustafsson, O., and P. M. Gschwend. 1997. "Soot as a strong partition medium for polycyclic aromatic hydrocarbons in aquatic systems." *Molecular Markers in Environmental Geochemistry* no. 671:365-381.
- Gustafsson, O., F. H., C. Chan, J. MacFarlane, and P. M. Gschwend. 1997. "Quantification of the dilute sedimentary soot phase: Implications for PAH speciation and bioavailability." *Environmental Science & Technology* no. 31 (1):203-209.
- Hamer, U., B. Marschner, S. Brodowski, and W. Amelung. 2004. "Interactive priming of black carbon and glucose mineralisation." *Organic Geochemistry* no. 35 (7):823-830.
- Hamilton, G. A., and H. E. Hartnett. 2013. "Soot black carbon concentration and isotopic composition in soils from an arid urban ecosystem." *Organic Geochemistry* no. 59:87-94.
- Hammes, K., M. W. I. Schmidt, R. J. Smernik, L. A. Currie, W. P. Ball, T. H. Nguyen, P. Louchouart, S. Houel, O. Gustafsson, M. Elmquist, G. Cornelissen, J. O. Skjemstad, C. A. Masiello, J. Song, P. Peng, S. Mitra, J. C. Dunn, P. G. Hatcher, W. C. Hockaday, D. M. Smith, C. Hartkopf-Froeder, A. Boehmer, B. Luer, B. J. Huebert, W. Amelung, S. Brodowski, L. Huang, W. Zhang, P. M. Gschwend, D. X. Flores-Cervantes, C. Largeau, J. N. Rouzaud, C. Rumpel, G. Guggenberger, K. Kaiser, A. Rodionov, F. J. Gonzalez-Vila, J. A. Gonzalez-Perez, J. M. de la Rosa, D. A. C. Manning, E. Lopez-Capel, and L. Ding. 2007. "Comparison of quantification methods to measure fire-derived (black/elemental) carbon in soils and sediments using reference materials from soil, water, sediment and the atmosphere." *Global Biogeochemical Cycles* no. 21 (3). GB3016.

- He, Y., and G. L. Zhang. 2009. "Historical record of black carbon in urban soils and its environmental implications." *Environmental Pollution* no. 157 (10):2684-2688.
- Hedges, J. I., G. Eglinton, P. G. Hatcher, D. L. Kirchman, C. Arnosti, S. Derenne, R. P. Evershed, I. Kogel-Knabner, J. W. de Leeuw, R. Littke, W. Michaelis, and J. Rullkotter. 2000. "The molecularly-uncharacterized component of nonliving organic matter in natural environments." *Organic Geochemistry* no. 31 (10):945-958.
- Hilscher, A., and H. Knicker. 2011. "Carbon and nitrogen degradation on molecular scale of grass-derived pyrogenic organic material during 28 months of incubation in soil." *Soil Biology & Biochemistry* no. 43 (2):261-270.
- Hilscher, A., K. Heister, C. Siewert, and H. Knicker. 2009. "Mineralisation and structural changes during the initial phase of microbial degradation of pyrogenic plant residues in soil." *Organic Geochemistry* no. 40 (3):332-342.
- Jaffé, R., Y. Ding, J. Niggemann, A. V. Vähätalo, A. Stubbins, R. G. M. Spencer, J. Campbell, and T. Dittmar. 2013. "Global Charcoal Mobilization from Soils via Dissolution and Riverine Transport to the Oceans." *Science* no. 340 (6130):345-347.
- Kaye, J. P., S. E. Eckert, D. A. Gonzales, J. O. Allen, S. J. Hall, R. A. Sponseller, and N. B. Grimm. 2011. "Decomposition of urban atmospheric carbon in Sonoran Desert soils." *Urban Ecosystems* no. 14 (4):737-754.
- Kennedy, I. M. 1997. "Models of soot formation and oxidation." *Progress in Energy and Combustion Science* no. 23 (2):95-132.
- Kuhlbusch, T. A. J. 1998. "Black carbon and the carbon cycle." *Science* no. 280 (5371):1903-1904.
- Major, J., J. Lehmann, M. Rondon, and C. Goodale. 2009 "Fate of soil-applied black carbon: downward migration, leaching and soil respiration." *Global Change Biology* no. 16 (4):1366-1379.
- Maricopa Association of Governments. Regional Transportation Plan. 2010. Phoenix, AZ. Maricopa Association of Governments.
- Marusenko, Y., P. Herckes, and S. J. Hall. 2011. "Distribution of Polycyclic Aromatic Hydrocarbons in Soils of an Arid Urban Ecosystem." *Water Air and Soil Pollution* no. 219 (1-4):473-487.
- Masiello, C.A. 2004. "New directions in black carbon organic geochemistry." *Marine Chemistry* no. 92:201-213.
- NASA Center for Ozone and Air Quality. Earth Probe Erythemal. Last modified December 31, 2005. <http://ozoneaq.gsfc.nasa.gov/EPY2005Erythemal.md>.

- Nguyen, B. T., J. Lehmann, J. Kinyangi, R. Smernik, S. J. Riha, and M. H. Engelhard. 2009. "Long-term black carbon dynamics in cultivated soil." *Biogeochemistry* no. 92 (1-2):163-176.
- Penner, J. E., H. Eddleman, and T. Novakov. 1993. "Toward the development of a global inventory for black carbon emissions." *Atmospheric Environment Part a-General Topics* no. 27 (8):1277-1295.
- Quinn, R. C., P. Ehrenfreund, F. J. Grunthaner, C. L. Taylor, and A. P. Zent. 2007. "Decomposition of aqueous organic compounds in the Atacama Desert and in Martian soils." *Journal of Geophysical Research-Biogeosciences* no. 112 (G4):9. G04S18.
- Saldarriaga, J. G., and D. C. West. 1986. "Holocene fires in the northern Amazon basin." *Quaternary Research* no. 26 (3):358-366.
- Schwarzenbach, R. P., P. M. Gschwend, and D. M. Imboden. 1993. Environmental Organic Chemistry. New York: *John Wiley & Sons*.
- Skjemstad, J. O., D. C. Reicosky, A. R. Wilts, and J. A. McGowan. 2002. "Charcoal carbon in U.S. agricultural soils." *Soil Science Society of America Journal* no. 66 (4):1249-1255.
- Smith, D. M., and A. R. Chughtai. 1995. "The surface structure and reactivity of black carbon." *Colloids and Surfaces A: Physicochemical and Engineering Aspects* no. 105 (1):47-77.
- Solomon, D., J. Lehmann, J. Thies, T. Schäfer, B. Liang, J. Kinyangi, E. Neves, J. Petersen, F. Luiz, and J. Skjemstad. 2007. "Molecular signature and sources of biochemical recalcitrance of organic C in Amazonian Dark Earths." *Geochimica et Cosmochimica Acta* no. 71 (9):2285-2298.
- Spencer, R. G. M., A. Stubbins, P. J. Hernes, A. Baker, K. Mopper, A. K. Aufdenkampe, R. Y. Dyda, V. L. Mwamba, A. M. Mangangu, J. N. Wabakanghanzi, and J. Six. 2009. "Photochemical degradation of dissolved organic matter and dissolved lignin phenols from the Congo River." *Journal of Geophysical Research-Biogeosciences* no. 114. G03010
- Stubbins, A., J. Niggemann, and T. Dittmar. 2012. "Photo-lability of deep ocean dissolved black carbon." *Biogeosciences* no. 9 (5):1661-1670.
- Sun, K., Y. Ran, Y. Yang, Y. P. Zeng, and B. S. Xing. 2007. "Characterization of condensed organic matter in soils and sediments." *Chinese Journal of Analytical Chemistry* no. 35 (8):1164-1167.
- U.S. Department of Commerce. United States Census. Washington D.C.: United States Government Printing Office, 2010.

- Vahatalo, A. V., K. Salonen, M. Salkinoja-Salonen, and A. Hatakka. 1999. "Photochemical mineralization of synthetic lignin in lake water indicates enhanced turnover of aromatic organic matter under solar radiation." *Biodegradation* no. 10 (6):415-420.
- Wang, Y., P. K. Hopke, and M. J. Utell. 2011. "Urban-scale spatial-temporal variability of black carbon and winter residential wood combustion Particles." *Aerosol and Air Quality Research* no. 11 (5):473-481.
- Zimmerman, A. R. 2010. "Abiotic and Microbial Oxidation of Laboratory-Produced Black Carbon (Biochar)." *Environmental Science & Technology* no. 44 (4):1295-1301.
- Zimmermann, M., M. I. Bird, C. Wurster, G. Saiz, I. Goodrick, J. Barta, P. Capek, H. Santruckova, and R. Smernik. 2012. "Rapid degradation of pyrogenic carbon." *Global Change Biology* no. 18 (11):3306-3316.

Table 3.1. Initial and final carbon concentrations, percent decreases in OC and soot BC, and corresponding photo-oxidation rate for soil OC and BC from urban and non-urban locations.

Sample type	Initial Concentration (g C/kg soil)	Final Concentration (g C/kg soil)	Concentration Decrease (%)	Photo-oxidation rate (g C/kg soil·y) <sup>a</sup>	<i>P</i> -value <sup>b</sup>
Urban OC	9.3 ± 0.9	8.6 ± 0.4	8	4 ± 4	> 0.1
Non-urban OC	5.6 ± 0.6	4.0 ± 0.1	28	5.7 ± 0.4	<b>&lt; 0.001</b>
Urban soot BC	0.81 ± 0.04	0.7 ± 0.1	18	0.6 ± 0.1	<b>&lt; 0.001</b>
Non-urban soot BC	0.6 ± 0.2	0.45 ± 0.03	21	0.5 ± 0.3	<b>&lt; 0.1</b>

<sup>a</sup> Photo-oxidation rate was calculated by converting the slope of a line-of-best-fit in g C/kg soil·h (Figure 3.1) for each site and sample type to g C/kg soil·y by assuming 12 h of sunlight per day.

<sup>b</sup> Bold *p*-values indicate a photo-oxidation rate significantly different from zero.



Table 3.2. Summary of recent photo-oxidation rates for various forms of natural organic matter.

Sample type	Oxidation Rate	Mechanism	Reference
<i>Particulate carbon</i>			
Bulk soil OC	4 g C/kg soil·y	Photo-oxidation	Feng et al., 2011
Corn leaf litter OC	129 g C/kg soil·y	Photo-oxidation	Feng et al., 2011
Pine needle litter OC	97 g C/kg soil·y	Photo-oxidation	Feng et al., 2011
<i>Dissolved carbon</i>			
Riverine DOC	0.03 g C/L·y	Photo-oxidation	Spencer et al., 2009
Dissolved lignin phenols	4.8x10 <sup>-4</sup> g C/L·y	Photo-oxidation	Spencer et al., 2009
Deep-ocean black carbon	0.1 g C/L·y	Photo-oxidation	Stubbins et al. 2012
<i>Soil Black Carbon</i>			
Soil soot BC	0.09-0.55 g C/kg soil·y	Photo-oxidation	this study
Soil soot BC	0.03 g C/kg soil·y	Soot BC/time since land-use change	this study

Table 3.3. Degradation rates for various recalcitrant forms of OM including soot BC.

<b>Sample type</b>	<b>Degradation rate (g C/kg soil·y)</b>	<b>Mechanism</b>	<b>Source</b>
Pyrogenic carbon (charcoal)	3.5	Repeated incubation up to 60°C	Zimmermann et al. 2012
Atmospheric particulate matter	0.9	Microbial degradation	Kaye et al. 2011
Soil soot BC	0.09-0.55	Photo-oxidation	this study
Deep-ocean black carbon	0.1	Photo-oxidation	Stubbins et al. 2012
Soil soot BC	0.03	Historic land-use calculation	this study

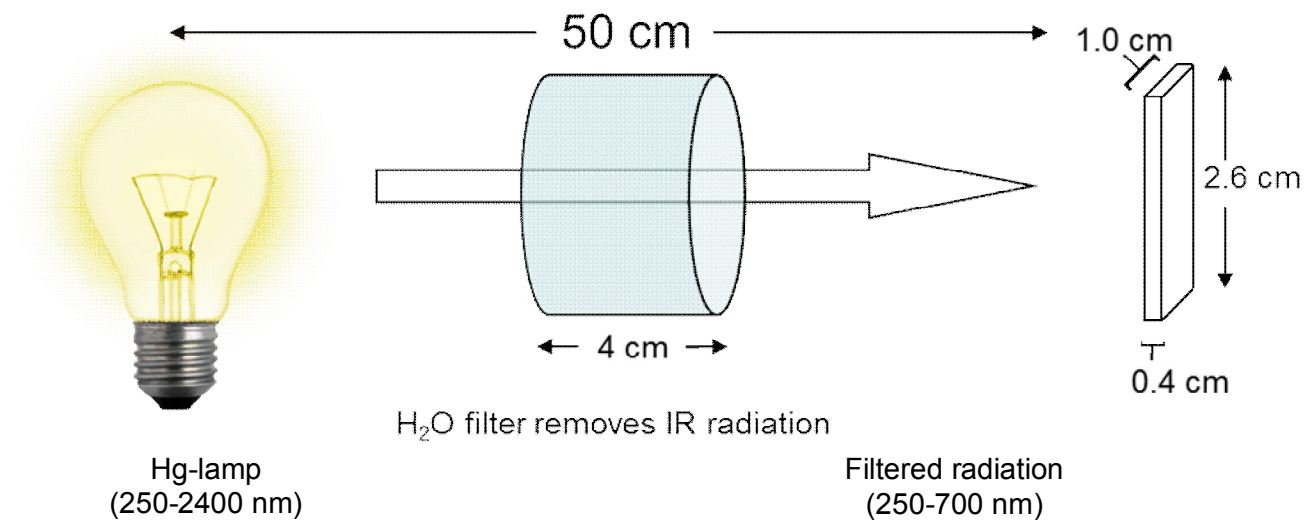


Figure 3.1. Schematic of laboratory photo-oxidation setup. Figure not to scale.

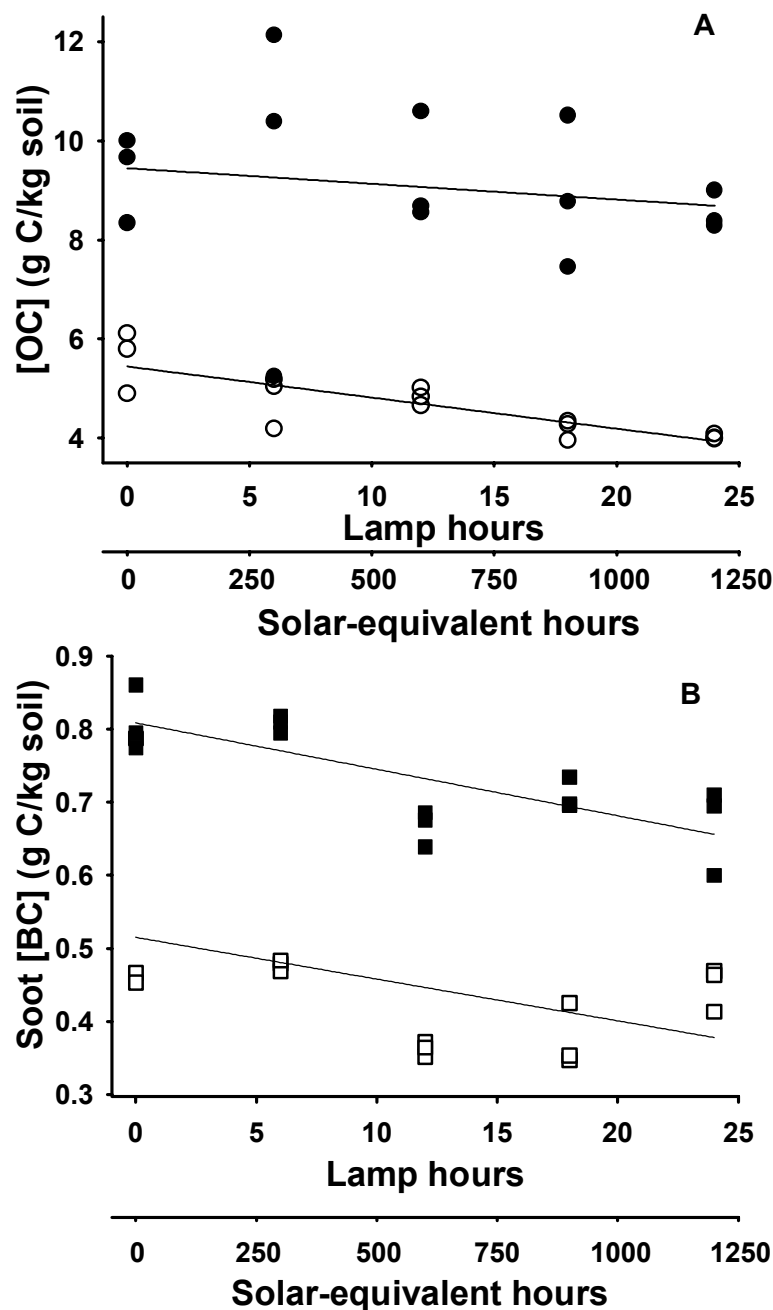


Figure 3.2. Organic carbon (A; circles) and soot Black Carbon (B; squares) concentrations in g C/kg soil as a function of time in lamp hours and solar-equivalent hours. Closed symbols are urban sites and open symbols are non-urban sites. The slopes for the lines-of-best-fit are significantly different from zero for all samples ( $p < 0.05$ ), except the urban OC (i.e., filled circles;  $p > 0.1$ ). The slopes for the OC samples are significantly different from each other ( $p < 0.1$ ); slopes for the soot BC samples are not significantly different from each other ( $p > 0.1$ ).

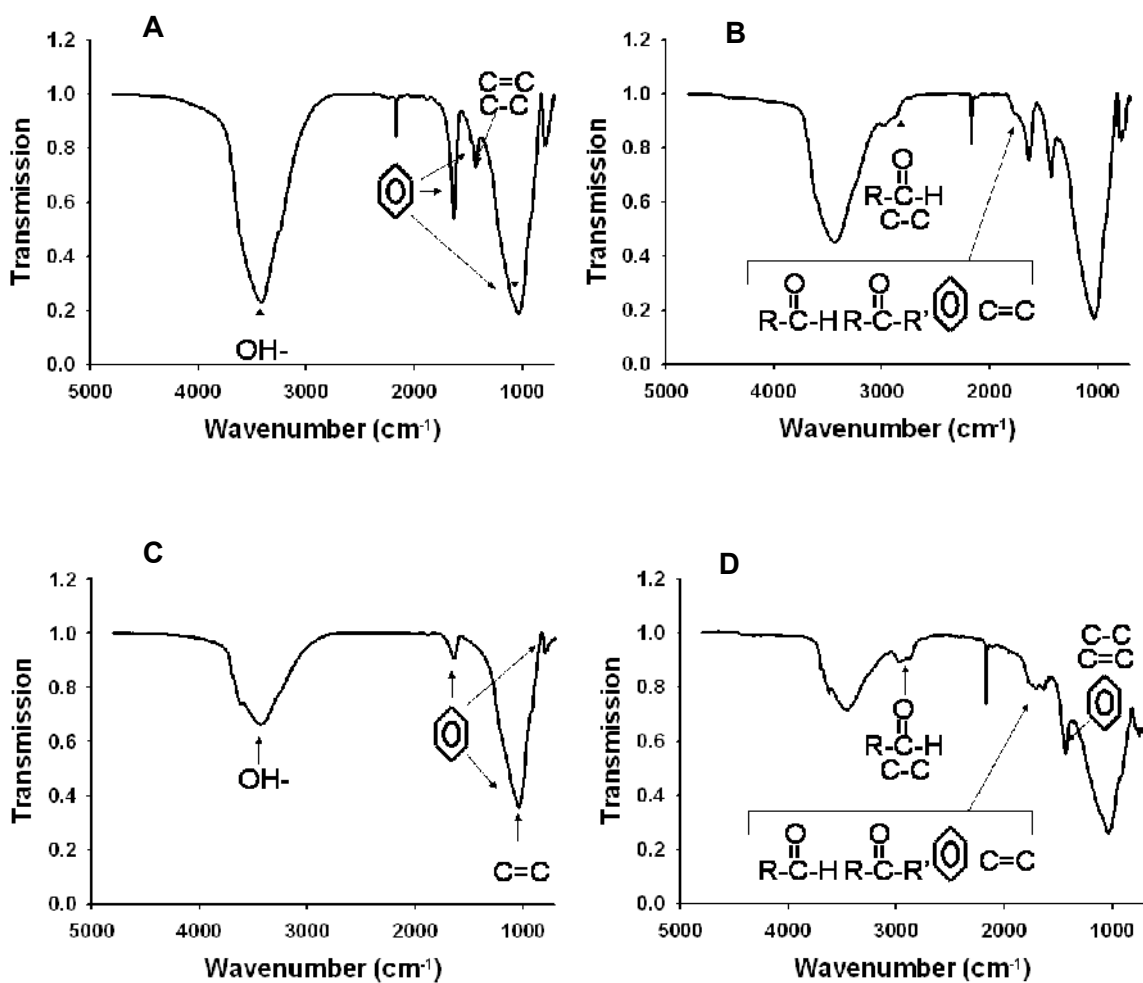


Figure 3.3. Fourier-transform infrared (FTIR) spectra of non-urban soils (upper panels; A, B) and urban soils (lower panels; C, D) collected before photo-oxidation (left panels; A, C) and after photo-oxidation (right panels; B, D). Transmission minima correspond to the functional groups noted on the figure.

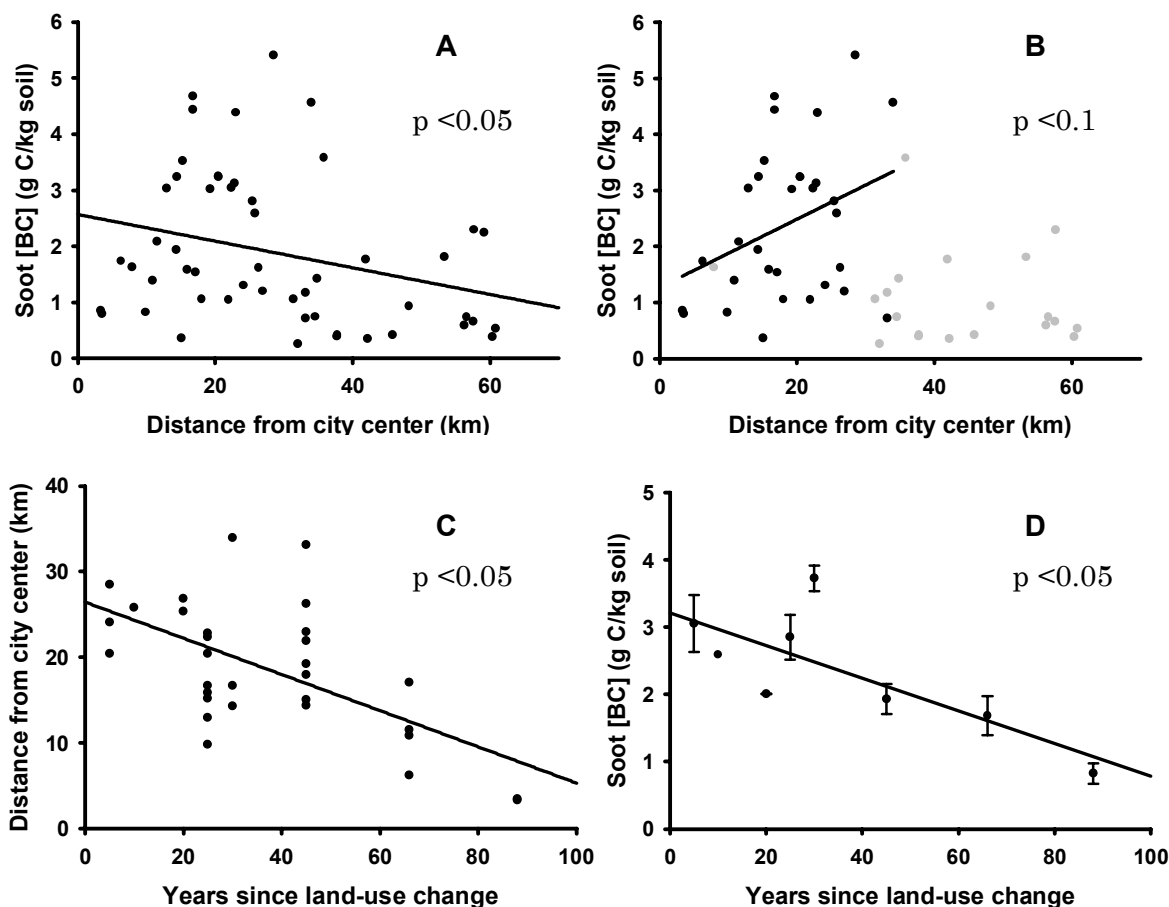


Figure 3.4. Soot BC concentration as a function of sample location and land-use history. In all cases, the lines are least-squares fits to the data and the slopes are significantly different from zero. (A) Soot BC concentration (g C/kg soil) versus distance from city center. (B) The same data points as in (A) with the urban sites highlighted in black and the non-urban sites in gray. The positive slope is a fit to the urban sites only. (C) Distance from city center versus years since land-use change; the data points are the same black urban sites from panel B. (D) Soot BC concentration (g C/kg soil) versus years since land-use change. The data points are the average soot [BC] for sites with 5, 10, 20, 25, 30, 45, 66, and 88 years since land-use change, respectively.

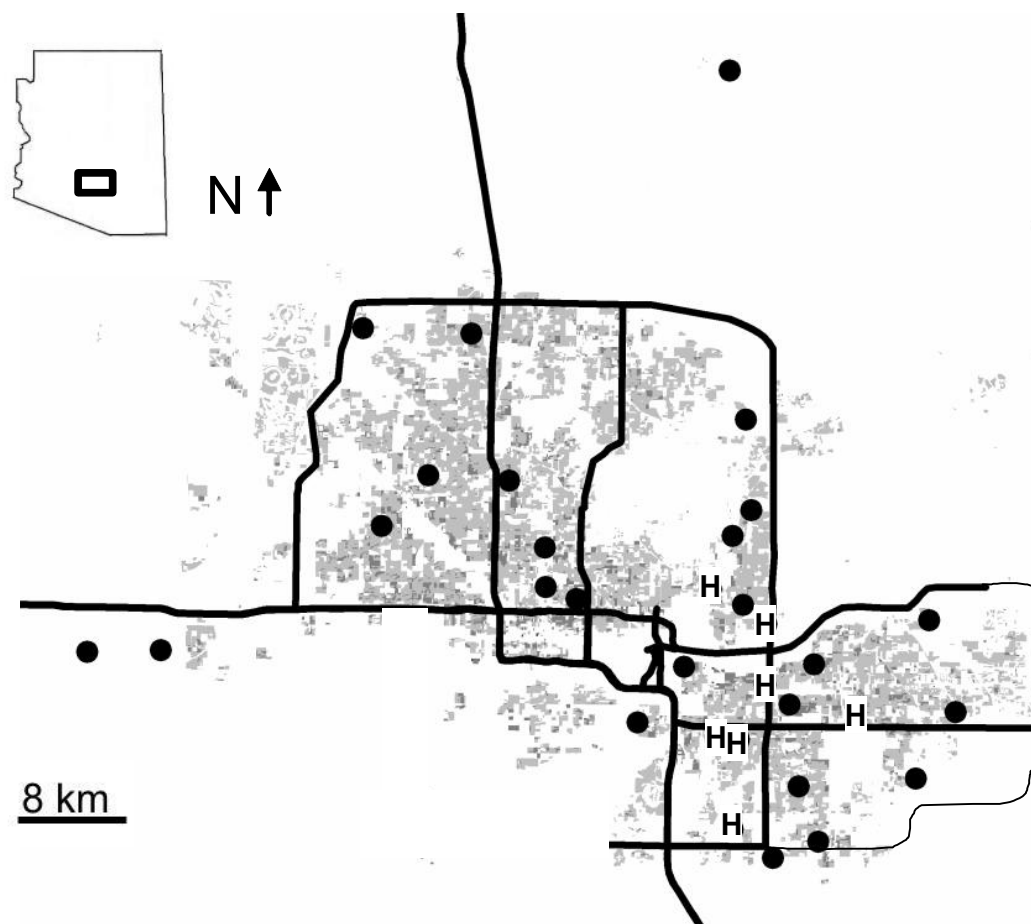


Figure 3.5. Map of the Phoenix, AZ metropolitan area. Black lines indicate major highways and solid symbols are the locations of the urban sample sites. The “H” symbols are sample sites with high soot [BC] (i.e.,  $>3$  g soot BC/kg soil) and where urbanization occurred between 25 and 30 years ago. The map shading is population density from white ( $<800$  people per  $\text{km}^2$ ) to dark gray ( $>5200$  people per  $\text{km}^2$ ). The inset map shows the state of Arizona and the box indicates the location of the CAP-LTER study area. Figure is modified from Hamilton and Hartnett (2013).

## Chapter 4

### THE SOLUBILITY OF CENTRAL ARIZONA SOOT BLACK CARBON

#### Abstract

Incomplete combustion of both biomass and fossil fuel produces black carbon. In this study, I investigate aqueous solubilization of soil soot BC isolated from soil and extracted using a water agitation technique. Dissolved organic carbon (DOC) concentrations in the extracts ranged from  $2.7 \pm 0.7$  to  $5.1 \pm 0.9$  mg/L/g soot BC. Soil-water partition coefficients (a measure of the proportion of solid soot BC transferred to the aqueous-phase) ranged from 0.04 to 0.09. Solubilized soot BC concentration increased over time; and about 9% of the soot BC in soil was mobilized to the aqueous-phase by day 7 of the extraction. Fluorescence analysis revealed that solubilized soot BC contained a greater fraction of oxidized quinone-like fluorophores than were present in similar extracts of bulk soil. The presence of soot BC in an aqueous-phase suggests that solubilized soot BC could be more functionalized than its solid-phase counterpart and therefore, has the potential for further degradation via biotic or abiotic processes.

#### Introduction

The term black carbon (BC) describes organic material produced from the incomplete combustion of biomass and fossil fuel (Goldberg 1985). The general term 'black carbon' includes partially burned plant material, char, charcoal, soot, and graphitic BC. These sub-classes have a range of combustion temperatures and particle sizes; they also exhibit different degrees of reactivity in the environment



(Masiello 2004). Black C is ubiquitous in the environment and some portion of it has been shown to be preserved for thousands of years (Middleburg et al. 1999; Schmidt and Noack 2000; Skjemstad et al. 2002). Nonetheless, there is mounting evidence to suggest that some BC can be degraded on much shorter timescales (e.g., months to years; Stubbins 2012; Zimmerman 2010). Interest in understanding the reactivity and transport of BC has increased because BC plays a role in long-term organic matter storage in sediments, and presumably in soils. It has even been suggested that because BC is fairly recalcitrant, it could be an effective material in which to sequester anthropogenic CO<sub>2</sub> (Lehmann 2007); however, any sequestration potential is contingent on whether BC can be stored in soils and sediments over long time-scales (Czimczik and Masiello 2007).

The black C global budget currently has production rates that are significantly greater than removal rates. At present, the best quantified removal term is deposition in ocean sediments (Masiello and Druffel 1998; Masiello 2004). There must be an as yet uncharacterized reservoir and/or loss term for black carbon; otherwise, all the organic carbon in terrestrial soils would have to be black carbon, which is clearly not the case (Masiello 2004; Schmidt 2004). In addition, current flux estimates for BC deposition to marine systems are relatively small, suggesting there are additional underestimated or unknown BC sinks. If soils are a significant reservoir for BC, then there must be a large amount of BC transported from the landscape to the oceans via rivers. And yet, relatively little is known about the solubilization of black carbon, an important first step in transferring BC from soil to water.

Black carbon is best described using a combustion continuum where BC is sub-classified as slightly charred biomass, char, charcoal, and soot BC (Masiello 2004). These sub-classifications range in formation temperature, relative reactivity, and particle size. Soot BC, the focus of this work, is formed at a relatively high temperature, is less reactive and has a smaller particle size than other forms of BC. Soot BC is formed from a gas-phase, where small organic molecules condense to form nanometer-scale particles and is not simply a residual material like other forms of BC (i.e., char and charcoal).

Only a few studies have directly shown that BC can be mobilized from soils into solution phase as dissolved BC (Jaffé et al. 2013; Dittmar et al. 2012; Mannino and Harvey 2004). They estimate that dissolved black carbon constitutes ~10% of the dissolved organic carbon flux from rivers. Their conclusions are based on total polycyclic aromatic hydrocarbon content of river water samples from a variety of locations and from rivers of various sizes. In a separate study, Dittmar et al. (2012) used historic land-use records and satellite data to estimate the amount of black carbon produced from biomass burning in the Atlantic forest in Brazil (~200 km northwest of Rio de Janeiro); they determined that BC (estimated as benzenepolycarboxylic acids) has been continuously mobilized from this watershed even though burning ceased nearly 25 years before they began their study. Their study also suggests that BC production on land increases the pool of refractory dissolved organic carbon in the deep ocean. Mannino and Harvey (2004) is the only study to examine the soot BC fraction of dissolved organic matter. Soot BC is produced from the condensation of small gas-phase organic molecules and is relatively more aromatic and non-reactive than other BC components. Mannino and

Harvey (2004) looked at the <30kDa fraction of ultra-filtered high-molecular weight DOM collected from riverine, estuarine and coastal waters and isolated BC using the chemo-thermal oxidation method described by Gustafsson et al. (1997). They estimated that soot BC comprised 4 to 7% of the dissolved organic carbon and showed that soot BC concentrations were higher in estuarine waters near highly urbanized areas as compared with river water near rural areas and coastal seawater (Manino and Harvey 2004).

In order to assess the extent to which soil black carbon can be mobilized to an aqueous phase and, thus, the potential importance of BC transport by rivers, it is necessary to determine the extent to which the most aromatic and recalcitrant portions of the black carbon continuum can be solubilized. I specifically examine soot BC which has a smaller particle size (<1  $\mu\text{m}$ ) and is more aromatic than other forms of black carbon (i.e., biochar and charcoal). The research questions driving this investigation are:

- (1) *How much soil soot BC can be mobilized in (or solubilized to) water?*
- (2) *Can solubilized soot BC be characterized in the aqueous phase?*

It is important to note that the term “dissolved” is not used here to describe the soot BC in water. Dissolved is an operational definition which is accepted to be any material that will pass through a 0.45  $\mu\text{m}$  filter. While soot BC has a particle size < 1  $\mu\text{m}$  (Cachier et al. 1995) and would certainly qualify as dissolved under this definition, I use the terms *mobilized* or *solubilized* soot BC because solubilization refers to a colloidal solution rather than charged particles or ions in solution (IUPAC 1997). Soot BC consists of mostly carbon and hydrogen (i.e., non-polar bonds) and I consider the terms *mobilized* or *solubilized* to be a more accurate description of the

material under investigation. Soot BC is generally thought to be made up of small nanometer-scale particles that will simply pass through the 0.45  $\mu\text{m}$  filter. Here, I demonstrate that this relatively recalcitrant form of black carbon (soot BC) can be solubilized to an aqueous phase and that the fraction of soot BC that can be solubilized is comparable to the fraction of bulk organic carbon (OC) that can be solubilized. I also show that the solubilized soot BC can be distinguished from solubilized bulk organic carbon as well as from typical dissolved organic carbon using 3D fluorescence analysis. This is the first description of the water extractable fraction of soot BC found in AZ soils and the results suggest that soil soot BC may be easily lost from soils due to aqueous mobilization.

## Method

### *Sample site and collection method*

Soil was collected in 2010, during the long-term land-use and land-cover survey of the Central Arizona-Phoenix Long-Term Ecological Research (CAP-LTER) project. Central AZ is semi-arid and consists of a high-density urban core, the surrounding sub-urban and agricultural areas, as well as open Sonoran desert. Average annual rainfall for central AZ, including the surrounding desert, is <18 cm/y. There are two rainy seasons in central AZ. Summer monsoon rains occur from early July until mid-September and can cause heavy, localized precipitation. Winter rains generally occur from December to March; typically, March is the wettest month with an average monthly rainfall of 2.9 cm (CAP-LTER 2010).

Soil samples were collected from a site classified as “open desert” by the CAP-LTER survey and by the Maricopa Association of Governments (MAG 2010). At the

site (a 30 x 30 m plot), four 30-cm soil cores were collected at 12 m from site center (NSEW) using a slide hammer. After collection, the soil cores were separated into top (0-15 cm) and bottom (16-30 cm) portions and allowed to dry in the dark at 25°C. Soil cores were then milled to <1 mm and the four cardinal directional samples were combined and homogenized. The bottom sample was used here because it contained less fresh plant material and had lower rock and pebble content.

#### *Solid-phase analysis*

Soot black carbon content (weight percent; wt. %) was quantified in soil samples by chemo-thermal oxidation at 375°C (CTO375; Gustafsson et al. 1997). Briefly, triplicate soil samples (~18 mg) were placed in silver (Ag) capsules (Costech Analytical Technologies, Valencia, CA, USA) and were acidified with 1 mL of 4 M hydrochloric acid, HCl (J. T. Baker, Inc., Philipsburg, NJ, USA) to remove carbonate. The acidification step was followed by thermal oxidation (under ambient oxygen conditions) at 375°C for 24 h in a muffle furnace. The thermal oxidation removes labile organic carbon. The carbon remaining in the samples after chemo-thermal oxidation is classified as soot BC (Gustafsson et al. 1997; Hammes et al. 2007) and is quantified by an elemental analyzer coupled to an isotope ratio mass spectrometer (EA-IRMS). The EA-IRMS detection limits are 1 µg C for [C]. Analytical precision and accuracy for soot BC concentration was determined using a standard reference material (Australian vertisol, 0.18 weight percent, wt. %, BC from CSIRO Land & Water, Adelaide, Australia; Gustafsson et al. 1997; Hammes et al. 2007); replicate analyses of reference soil yielded a relative standard deviation (RSD) of 6% (n = 6).

#### *Soil carbon solubilization*

Samples containing either unaltered bulk soil or soot BC (isolated by CTO375) were extracted using an aqueous agitation technique. Triplicate extractions were conducted for each soil type at each time point over the course of 7 days (7 time points x 3 replications x 2 sample types = 42 total samples). One gram of unaltered soil or soil soot BC was placed in individual 15 mL polypropylene centrifuge tubes. Deionized H<sub>2</sub>O (5 mL; 18.2 MΩ·cm; NANOpure Diamond, Barnstead, Inc. Dubuque, IA, USA) was placed in the centrifuge tube to create a soil slurry. Tubes were placed on an orbital shaker table, and agitated at medium speed (80 rpm); each tube was sampled once at discrete time points (i.e., 0, 0.5, 1, 2, 4, 5, and 7 days). Prior to sampling, each slurry was allowed to settle for ~10 minutes and the supernatant was removed from the soil slurry by decanting it into a 15 mL syringe. The supernatant was filtered through a 0.2 µm filter (Arcodisc, Supor<sup>tm</sup>, Pall Corporation, Ann Arbor, MI, USA) to remove particulate matter including any microbial biomass (Fellman et al. 2008). The aqueous extracts were stored at -20°C in a freezer until analysis for dissolved organic carbon. Soot BC extractions were completed twice over different seven-day periods using soil from the same location in order to assess reproducibility.

#### *Dissolved organic carbon analysis*

Dissolved organic carbon (DOC) analysis was completed on the aqueous extracts of unaltered soil and soil soot BC. Prior to DOC analysis all samples were acidified with HCl (J. T. Baker, Inc., Philipsburg, NJ, USA) to a pH of 2.0 in order to remove any inorganic carbon. The extracts were diluted 1:15 (v:v) with deionized carbon-free H<sub>2</sub>O. Dissolved organic carbon concentration was determined using a Shimadzu TOC-V (Shimadzu, Inc., Kyoto, Japan) analyzer where samples are

combusted at 680°C in an oxygen-rich environment with a platinized-alumina catalyst to convert all carbon in the sample to CO<sub>2</sub>(g) and detected by a non-dispersive infra-red gas analyzer (Hedges et al. 1993; Sharp et al. 1993; Sharp 1993; Sharp 1997).

#### *Fluorescence spectroscopy*

Fluorescence analysis was used to characterize solubilized organic matter in the bulk soil extracts and the soot BC extracts. Fluorescence excitation-emission matrices (EEMs) were obtained using a Fluormax-4 fluorescence spectrometer (HORIBA Jobin–Yvon, Edison, NJ, USA). Spectra were collected over an excitation range of 240 to 450 nm in 10 nm increments and fluorescence intensity monitored over an emission range of 300 to 550 nm in 2 nm increments. Samples were screened using UV absorbance at 254 nm ( $A_{254}$ ) and inner filter corrections were applied to all samples with  $A_{254} > 0.3$  (Ohno 2002). The raw spectra were blank corrected each day using a water blank spectrum and normalized to the water Raman peak intensity. Rayleigh scattering was automatically masked by the HORIBA software (FluorEssence 1.0).

Corrected EEMs were modeled using parallel factor (PARAFAC) analysis. This technique decomposes a spectrum into a set of independent components. I applied a 13 component model established by Cory and McKnight (2005) that is based on 379 surface water samples from a range of aquatic systems. The 13 components include 9 components attributed to known fluorophores (a variety of quinone-like structures, as well as tryptophan and tyrosine) and 4 unidentified fluorophores (Cory and McKnight 2005). Absolute fluorescence intensity for each component is proportional to the component's fractional contribution to the total fluorescence intensity

(Stedmon et al. 2003; Cory and McKnight 2005). I binned the relative contribution of the thirteen fluorescent components into four groups with similar chemical structures. Components 2, 11, and 12 represent oxidized quinones, components 4, 5, 7, and 9 represent reduced quinones, components 8 and 13 are tryptophan and tyrosine, respectively (protein-like), and components 1, 3, 6, and 10 are described as unknown structures (Cory and McKnight 2005).

Regression analysis was conducted using Sigma Plot 11.0 (Systat Software Inc. San Jose, CA, USA) on solubilized soot BC concentration and partition coefficient over time (Figure 4.1 and 4.2). Slopes of the regression lines from each analysis were deemed significant for  $p < 0.05$ .

## Results

### *Carbon concentration*

Solid-phase carbon concentrations are reported in weight percent (wt. %) for both organic carbon and soot BC. Bulk organic carbon and soil soot BC concentrations were  $0.25 \pm 0.04$  wt. % and  $0.03 \pm 0.002$  wt. % respectively.

Dissolved organic carbon was measurable in all samples at all time points. The blank corrected and soil weight-normalized DOC concentrations in bulk soil organic carbon extracts ranged from  $11.1 \pm 0.7$  mg C/L•g soil to  $18.1 \pm 0.6$  mg C/L•g soil (data not shown). In the soil soot BC extracts (blank corrected and soil weight-normalized), DOC concentrations ranged from  $2.7 \pm 0.7$  mg C/L•g soil on day zero to a maximum of  $5.1 \pm 0.9$  mg C/L•g soil on day 7 (Figure 4.1). Organic carbon concentrations were not correlated with time ( $p > 0.05$ ). Soot BC concentrations were positively correlated with time ( $p < 0.05$ ).



Partition coefficients ( $K$ ) for soot BC were calculated at each time point using the following equation:

$$K_{\text{soot BC}} = [C_{\text{soln}}]/[C_{\text{solid}}] \quad \text{eq 4.1}$$

where  $[C_{\text{soln}}]$  is the DOC in solution (mg C/kg water) and  $[C_{\text{solid}}]$  is the concentration of carbon in the solid-phase (mg C/kg soil). I assume the density of pure water is 1.0 g/cm<sup>3</sup>. To calculate the percentage of solid soot BC solubilized in the aqueous-phase, eq. 4.1 is multiplied by 100. The soot BC partition coefficients ( $K_{\text{soot BC}}$ ) ranged from  $0.04 \pm 0.01$  to  $0.09 \pm 0.02$  and were positively correlated with time ( $p < 0.05$ ; Figure 4.2). The partition coefficients for OC ( $K_{\text{oc}}$ ) extract ranged from  $0.023 \pm 0.004$  to  $0.043 \pm 0.007$  (data not shown) and were not correlated with time ( $p > 0.05$ ).

### *Fluorescence*

Excitation-emission matrices (EEMs) for extracts of bulk OC and soot BC are presented in Figures 4.3 and 4.4, respectively. A region of high fluorescence intensity is observed in the solubilized bulk OC between excitation wavelengths from 250 nm to 275 nm and emission wavelengths from 400 nm to 500 nm (Figure 4.3A). The solubilized soot BC spectrum exhibits two regions of high fluorescence intensity; one between excitation wavelengths from 250 nm to 270 nm at emission wavelengths from 380 nm and 475 nm, and another between excitation wavelengths from 290 nm to 325 nm at emission wavelengths from 390 nm and 450 nm (Figure 4.4A).

## Discussion

### *Soot BC solubility*

The first goal of this study was to demonstrate that soot BC in central AZ soils can be solubilized in water. Evidence for solubilization consists of DOC detectable above background levels in the supernatant of soot BC-water slurries. Solubilized soot BC was detected at all time points. The concentration of solubilized soot BC generally increased over time ( $p < 0.05$ ; Figure 4.1). The range of dissolved concentrations obtained for solubilized soot BC (i.e.,  $2.7 \pm 0.7$  mg C/L  $\cdot$  g soil to  $5.1 \pm 0.9$  mg C/L  $\cdot$  g soil) is comparable to what would be predicted based on the solubility of some of the more soluble PAH molecules, assuming that the soot BC solubility estimated here is approaching equilibrium. For example, acenaphthalene ( $C_{12}H_{10}$ ) has a solubility of 3.93 mg/L which equates to a carbon solubility of 3.1 mg C/L (Mackay and Shui 1977). Similarities between the solubility of soot BC and the solubilities of PAHs are to be expected because PAHs are considered soot precursor molecules (Masiello 2004 and others). Note, although the units for solubilized soot BC are mg C  $\cdot$  L<sup>-1</sup>/g soil, about one gram of soil was used for all extractions and the soil weight-normalization correction is small ( $<0.1$  mg C/L  $\cdot$  g soil). The concentrations of solubilized soot BC are considerably lower than the concentrations of solubilized bulk OC (11.1 to 18.1 mg C/L  $\cdot$  g soil). Notably, the AZ soils have very low OC contents (Bohn et al. 2001). There are few studies that investigate the solubility of complex mixtures of molecules such as bulk soil organic carbon. However, I make the assumption that DOC in pore water is likely near equilibrium with solid-phase soil carbon and, further, that it is reasonable to compare pore water DOC

concentrations with values presented here. Published DOC concentrations from grassland soil (21 mg C/L; Xu et al. 2013) and forested soil (92 mg C/L; Wickland et al. 2007) are much higher than the concentrations for solubilized soot BC reported here ( $2.7 \pm 0.7$  mg C/L • g soil to  $5.1 \pm 0.9$  mg C/L • g soil). This is likely due to higher bulk soil organic carbon concentrations in grassland and forested soils.

The soot BC–water partition coefficient ( $K_{\text{soot BC}}$ ) is presented as the ratio of the concentration of soot BC in solution to the concentration of soot BC in soil (eq. 4.1). The range in  $K_{\text{soot BC}}$  over time is 0.04 to 0.09. Partition coefficients for bulk OC ( $K_{\text{OC}}$ ) were calculated for comparison and ranged from 0.023 to 0.043, somewhat lower than those for soot BC. The  $K_{\text{soot BC}}$  values as a function of time demonstrate a temporal-trend similar to that of the solubilized soot BC concentration (Figure 4.2). Partition coefficients for soot BC increase with longer slurry times ( $p < 0.05$ ). This is due to the increase in solubilized soot BC concentration (Figure 4.1) and a finite concentration of soil soot BC (soil soot [BC]:  $0.03 \pm 0.002$  wt. %). The fact that this experiment yielded similar partition coefficients for bulk OC and for soil soot BC is not without precedent. Solubilities for n-hexane soot (a soot BC analog) and bulk organic matter derived from soft and hardwood lignin were also shown to be of similar magnitude (Zhang and LeBoeuf 2009).

To my knowledge this is the first study to quantify the water extractable fraction of organic carbon from soil soot BC. There are reports of water extractable organic carbon from biochars (a remnant burned material), but chars are fundamentally different from soot BC (a gas-phase derived combustion product). Lin et al. (2012) used size exclusion chromatography to identify the chemical fractions of a biochar extract (i.e., biopolymers, humics, oxidation products of humics, low

molecular-weight acids and neutrals, as well as hydrophobic organic carbon); they determined total water-extractable organic carbon as the sum of the individual fractions and estimated that <1 % of the biochar was water extractable. While the solubility of biochar from Lin et al. (2012) is less than the solubility of soot BC calculated here (4 to 9%; calculated by converting partition coefficient to a percentage;  $K_{soot\ BC} \times 100$ ), it is likely that the Lin et al. (2012) chromatography method identifies a different portion of the BC continuum than the chemo-thermal oxidation method I used to isolate soot BC. The biochar solubility presented in Lin et al. (2012) is more comparable to bulk OC solubility reported here (2.3 to 4.3%; calculated as  $K_{OC} \times 100$ ) suggesting that the composition of bulk OC is more similar to the composition of biochar than it is to soot BC. This makes intuitive sense, since the biochar is remnant material, more similar to the starting biomass, which should be qualitatively similar to the bulk soil organic carbon. Furthermore, it's worth noting that comparing black carbon data sets that utilize different detection methods is dubious, at best (Masiello 2004; Hammes et al. 2007).

### *Fluorescence Analysis*

I assessed the chemical composition of solubilized soot BC via fluorescence spectroscopy. Natural organic matter, including soot BC is a complex mixture of compounds that is almost impossible to separate into individual components (Hedges et al. 2000). Fluorescence spectroscopy is sensitive to a wide range of fluorophores and can be used to screen aqueous samples quickly with little or no sample manipulation. Fluorescence analysis has been widely used to identify chemical characteristics of dissolved organic matter from a wide range of environments (Fellman et al. 2010; Wickland et al. 2007; Xu et al. 2013; Cory and

McKnight 2005). Three-dimensional fluorescence analysis generates information about fluorescence intensity as a function of both excitation wavelength and emission wavelength. The plots are referred to as excitation-emission matrices, EEM's. . Fluorescence intensity in specific regions of the EEM corresponds to specific chemical moieties such as humic-like and protein-like fluorophores (Coble et al. 1990; Coble 1996).

Solubilized soot BC has a distinctive 3D fluorescence spectrum. Extractable soot BC has some characteristics in common with those of the fluorescence spectrum for a bulk soil OC extract (Figure 4.3A and figure 4.4A). A peak (excitation wavelengths from 250 nm to 275 nm and emission wavelengths from 400 nm to 500 nm) is present in both bulk OC and soot BC extracts that is coincident with a peak suggested to correspond with humic-like material, derived from vascular plants, that is aromatic or highly conjugated. This peak often corresponds with the high-molecular weight fraction of the dissolved organic matter pool (Coble et al. 1990; Parlanti et al. 2000; Fellman et al. 2010). A unique peak is present in the spectrum of solubilized soot BC between excitation wavelengths from 290 nm to 325 nm and emission wavelengths from 390 nm and 450 nm; this region is generally thought to be representative of a more aromatic humic-like material (Wickland et al. 2007; Fellman et al. 2010). However, the peak in the solubilized soot BC spectrum (excitation: 290 to 325 nm; emission: 390 to 450 nm) is shifted slightly towards shorter emission wavelengths (often referred to as “blue shifted”) compared to the peaks found in Wickland et al. (2007) and Fellman et al. (2010). The blue shift could represent fluorophores present in soot BC that are distinctly different than fluorophores from bulk OC.

Parallel factor (PARAFAC) analysis was used to model the fluorescence EEMs for solubilized bulk OC and soot BC (Figure 4.3B and 4.4B). The PARAFAC analysis generates a model EEM, compares it to the actual fluorescence spectrum, and calculates a map in excitation-emission space for both the absolute and relative residual intensities (Figure 4.3C and D and Figure 4.4C and D, respectively). PARAFAC analysis provides an estimate of the relative contribution of each component to the total fluorescence (Fellman et al. 2010; Cory and McKnight 2005). Residual values near zero correspond to regions where the modeled EEM and the actual fluorescence spectrum are in good agreement. Residual values far from zero represent regions where the 13 fluorophores in the model cannot account for the fluorescence in the actual sample. Similar regions with higher residual intensities are found for both the bulk OC and soot BC extracts (Figure 4.3C and D; Figure 4.4C and D). Fluorescence intensity in regions with low excitation and emission wavelengths (bottom-left side of the contour plots) typically represents protein-like fluorophores (Coble et al. 1998; Parlanti et al. 2000; Fellman et al. 2010). In my study, these are regions with high residual intensities. Since the PARAFAC analysis accounts for protein-like fluorophores, it is likely that fluorescence in this region is not due to protein-like fluorophores and could represent a fluorescent signature unique to samples with high soot BC. However, high residual intensities at the outer boundaries of the EEM are common and may be “edge effects” in the matrix calculation (Cory and McKnight 2005). The region of high residual intensity between excitation wavelength 290 to 325 nm and emission wavelength 390 to 450 nm in the soot BC extract, which appears in the middle of excitation-emission space, is likely to be diagnostic for fluorophores unique to soot BC.

The contributions of the 13 PARAFAC components (Cory and McKnight 2005) were binned into 4 separate groups based on their general chemical composition (oxidized quinone-like components, reduced quinone-like components, protein-like components, and unknown components). The contribution of each group to total fluorescence is presented in Table 4.1. Bulk OC and soot BC differ greatly in the percent contribution from reduced and oxidized quinone-like components. In bulk OC, reduced and oxidized quinones each contribute 37% to the total fluorescence. In soot BC, reduced quinones contribute to 16% of the total fluorescence and oxidized quinones contribute to 47% of the total fluorescence. The Redox Index (RI; Miller et al. 2006) parameterizes the relative contribution of oxidized and reduced quinones:

$$RI = (\Sigma \text{ reduced quinones}) / (\Sigma \text{ reduced quinones} + \Sigma \text{ oxidized quinones}) \quad \text{eq. 4.2.}$$

Larger values of RI indicate more reduced quinone-like moieties; the solubilized bulk OC had a larger RI than the solubilized soil soot BC. The solubilized soot BC has greater contribution from oxidized quinone-like components, and a correspondingly lower RI. The presence of an oxidized component is consistent with chemical changes to soot BC that occur during photo-oxidation and during “aging” in soils (Stubbins 2012; Chang et al. 2008). Humification index (HIX; Table 4.1) is an indicator of humic content and is based on the idea that emission spectra will shift towards longer wavelengths due to lower H:C ratios as humification proceeds (Fellman et al. 2010). Here, HIX is used as an indicator of aromaticity. Solubilized soot BC has a larger HIX than solubilized OC which is expected considering soot BC is likely more

aromatic than bulk OC. Soot BC fluorescence exhibited a larger contribution from protein-like components, and from the unknown components as compared to solubilized bulk OC (Table 4.1). It seems clear that a contribution from “protein-like” material does not actually represent tyrosine and tryptophan (i.e., components 13 and 8, respectively) because these molecules would not survive the chemo-thermal oxidation treatment used to isolate soot BC. Rather the peaks in the region of protein-like fluorescence are likely representative of something unique to soot BC. The contribution from unknown fluorophores found here is relatively high compared to other pore water samples (32% reported here versus 4-10% in Wickland et al. (2007)). The high contribution from the unknown fluorophores in the solubilized soot BC sample suggests the unknown fluorophores and the solubilized soot BC fluorophores share some inherent chemical characteristics. Given the relatively high solubility of soot BC in water, it’s not unreasonable to suggest that solubilized soot BC could be a significant contribution to the DOC in surface waters. The intensity in the region between excitation wavelengths 290 nm to 325 nm and emission wavelengths 390 nm and 450 nm (Figure 4.4A) does not agree well with the modeled EEM as reflected by the high residuals in that region (Figure 4.4C and D) and could represent fluorophores unique to soot BC.

The goal of this study was to demonstrate that a portion of the soot BC in central AZ soil could be solubilized (or mobilized) to an aqueous phase. Solubilization of soot BC strongly implies that soot BC can be easily transported and further suggests that degradation of soot BC might be possible. Soil soot BC was found to leach organic carbon during 7 days of water agitation. The concentration of solubilized soot BC increased with increasing water agitation time. Partition



coefficients indicated that soil soot BC showed slightly greater tendency toward solubilization than bulk OC from the same soils. The presence of a mobile fraction of the soil soot BC in central AZ suggests that solubilization could represent an as yet under-reported removal process. This mobile portion of soot BC must be accounted for when considering soil BC removal processes in the global BC budget. Solubilized soot BC contained detectable fluorophores and the EEMs were broadly similar to EEMs from other dissolved organic carbon sources. In solubilized soot BC, oxidized quinone-like fluorophores and unknown fluorophores contributed 79% to the total fluorescence intensity. This indicates that the “aged” soot BC in soils has some oxidized character. The unknown fluorophores in the Cory and McKnight (2005) model may be characteristic of solubilized soot BC. This work also demonstrates that fluorescence analysis may be useful for assessing changes in DOM composition due to contributions from solubilized soot BC in the environment. The potential for a significant component of solubilized soot BC in surface waters implies that streams and rivers may be important transporters of soot BC.

## Literature Cited

- Bohn, H. L., B. L. McNeal, and G. A. O'Connor. 2001. "Soil Chemistry." New York: *John Wiley & Sons*.
- Cachier, H., C. Lioussé, P. Buatmenard, and A. Gaudichet. 1995. "Particulate content of savanna fire emissions." *Journal of Atmospheric Chemistry* no. 22 (1-2):123-148.
- Central Arizona-Phoenix Long-term Ecological Research. 2010. "Site Description." Accessed March 15. <http://caplter.asu.edu/about/site-description/>
- Cheng, C. H., J. Lehmann, and M. H. Engelhard. 2008. "Natural oxidation of black carbon in soils: Changes in molecular form and surface charge along a climosequence." *Geochimica et Cosmochimica Acta* no. 72 (6):1598-1610.
- Coble, P.G., S.A. Green, N.V. Blough, and R.B. Gagosian. 1990. "Characterization of dissolved organic-matter in the Black sea by fluorescence spectroscopy." *Nature* no. 348 (6300):432-435.
- Coble, P.G. 1996. "Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy." *Marine Chemistry* no. 51 (4):325-346.
- Cory, R. M., and D. M. McKnight. 2005. "Fluorescence spectroscopy reveals ubiquitous presence of oxidized and reduced quinones in dissolved organic matter." *Environmental Science & Technology* no. 39 (21):8142-8149.
- Czimczik, C. I., and C.A. Masiello. 2007. "Controls on black carbon storage in soils." *Global Biogeochemical Cycles* no. 21. GB3005
- Dittmar, T., C. E. de Rezende, M. Manecki, J. Niggemann, A. R. C. Ovalle, A. Stubbins, and M. C. Bernardes. 2012. "Continuous flux of dissolved black carbon from a vanished tropical forest biome." *Nature Geoscience* no. 5 (9):618-622.
- Fellman, J. B., E. Hood, and R. G. M. Spencer. 2010. "Fluorescence spectroscopy opens new windows into dissolved organic matter dynamics in freshwater ecosystems: A review." *Limnology and Oceanography* no. 55 (6):2452-2462.
- Fellman, J. B., D.V. D'Amore, E. Hood, and R.D. Boone. 2008. "Fluorescence characteristics and biodegradability of dissolved organic matter in forest and wetland soils from coastal temperate watersheds in southeast Alaska." *Biogeochemistry* no. 88 (2):169-184.
- Goldberg, E.D. 1985. "Black Carbon in the Environment." New York: *John Wiley & Sons*.

- Gustafsson, O. F. Haghseta, C. Chan, J. MacFarlane, and P.M. Gschwend. 1997. "Quantification of the dilute sedimentary soot phase: Implications for PAH speciation and bioavailability." *Environmental Science & Technology* no. 31 (1):203-209.
- Hammes, K., M. W. I. Schmidt, R. J. Smernik, L. A. Currie, W. P. Ball, T. H. Nguyen, P. Louchouart, S. Houel, O. Gustafsson, M. Elmquist, G. Cornelissen, J. O. Skjemstad, C. A. Masiello, J. Song, P. Peng, S. Mitra, J. C. Dunn, P. G. Hatcher, W. C. Hockaday, D. M. Smith, C. Hartkopf-Froeder, A. Boehmer, B. Luer, B. J. Huebert, W. Amelung, S. Brodowski, L. Huang, W. Zhang, P. M. Gschwend, D. X. Flores-Cervantes, C. Largeau, J. N. Rouzaud, C. Rumpel, G. Guggenberger, K. Kaiser, A. Rodionov, F. J. Gonzalez-Vila, J. A. Gonzalez-Perez, J. M. de la Rosa, D. A. C. Manning, E. Lopez-Capel, and L. Ding. 2007. "Comparison of quantification methods to measure fire-derived (black/elemental) carbon in soils and sediments using reference materials from soil, water, sediment and the atmosphere." *Global Biogeochemical Cycles* no. 21 (3). GB3016
- Hedges, J. I., B. A. Bergamaschi, and R. Benner. 1993. "Comparative analysis of DOC and DON in natural waters." *Marine Chemistry* no. 41 (1-3):121-134.
- Hedges, J. I., G. Eglinton, P. G. Hatcher, D. L. Kirchman, C. Arnosti, S. Derenne, R. P. Evershed, I. Kogel-Knabner, J. W. de Leeuw, R. Littke, W. Michaelis, and J. Rullkotter. 2000. "The molecularly-uncharacterized component of nonliving organic matter in natural environments." *Organic Geochemistry* no. 31 (10):945-958.
- International Union of Pure and Applied Chemistry (IUPAC). 1997. "Compendium of chemical terminology." Oxford: *Blackwell Scientific Publications*.
- Jaffé, R., Y. Ding, J. Niggemann, A.V. Vähätalo, A. Stubbins, R.G. M. Spencer, J. Campbell, and T. Dittmar. 2013. "Global charcoal mobilization from soils via dissolution and riverine transport to the oceans." *Science* no. 340 (6130):345-347.
- Lehmann, J. 2007. "A handful of carbon." *Nature* no. 447 (7141):143-144.
- Lin, Y., P. Munroe, S. Joseph, R. Henderson, and A. Ziolkowski. 2012. "Water extractable organic carbon in untreated and chemical treated biochars." *Chemosphere* no. 87 (2):151-157.
- Mackay, D., and W. Y. Shiu. 1977. "Aquatic solubility of polynuclear aromatic-hydrocarbons." *Journal of Chemical and Engineering Data* no. 22 (4):399-402.
- Maricopa Association of Governments. Regional Transportation Plan. Phoenix, AZ. Maricopa Association of Governments. 2010.

- Mannino, A., and H.R. Harvey. 2004. "Black carbon in estuarine and coastal ocean dissolved organic matter." *Limnology and Oceanography* no. 49 (3):735-740.
- Masiello, C. A., and E. R. M. Druffel. 1998. "Black carbon in deep-sea sediments." *Science* no. 280 (5371):1911-1913.
- Masiello, C.A. 2004. "New directions in black carbon organic geochemistry." *Marine Chemistry* no. 92:201-213.
- Middleburg, J. J., J. Nieuwenhuize, and P. van Breugel. 1999. "Black carbon in marine sediments." *Marine Chemistry* no. 65 (3-4):245-252.
- Miller, M. P., D. M. McKnight, R. M. Cory, M. W. Williams, and R. L. Runkel. 2006. "Hyporheic exchange and fulvic acid redox reactions in an alpine stream/wetland ecosystem, Colorado front range." *Environmental Science & Technology* no. 40 (19):5943-5949.
- Ohno, T. 2002. "Fluorescence inner-filtering correction for determining the humification index of dissolved organic matter." *Environmental Science & Technology* no. 36 (4):742-746.
- Parlanti, E., K. Worz, L. Geoffroy, and M. Lamotte. 2000. "Dissolved organic matter fluorescence spectroscopy as a tool to estimate biological activity in a coastal zone submitted to anthropogenic inputs." *Organic Geochemistry* no. 31 (12):1765-1781.
- Schmidt, M. W. I. 2004. "Biogeochemistry - Carbon budget in the black." *Nature* no. 427 (6972):305-307.
- Schmidt, M. W. I., and A. G. Noack. 2000. "Black carbon in soils and sediments: Analysis, distribution, implications, and current challenges." *Global Biogeochemical Cycles* no. 14 (3):777-793.
- Skjemstad, J. O., D. C. Reicosky, A. R. Wilts, and J. A. McGowan. 2002. "Charcoal carbon in U.S. agricultural soils." *Soil Science Society of America Journal* no. 66 (4):1249-1255.
- Sharp, J. H. 1997. "Marine dissolved organic carbon: Are the older values correct?" *Marine Chemistry* no. 56 (3-4):265-277.
- Sharp, J. H., R. Benner, L. Bennett, C. A. Carlson, R. Dow, and S. E. Fitzwater. 1993. "Reevaluation of the high-temperature combustion and chemical oxidation measurements of dissolved organic-carbon in seawater." *Limnology and Oceanography* no. 38 (8):1774-1782.
- Sharp, J.H. 1993. "The dissolved organic carbon controversy: an update." *Oceanography* no.6: 45-50.

- Stedmon, C. A., S. Markager, and R. Bro. 2003. "Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy." *Marine Chemistry* no. 82 (3-4):239-254.
- Stubbins, A., J. Niggemann, and T. Dittmar. 2012. "Photo-lability of deep ocean dissolved black carbon." *Biogeosciences* no. 9 (5):1661-1670.
- Wickland, K. P., J. C. Neff, and G. R. Aiken. 2007. "Dissolved organic carbon in Alaskan boreal forest: Sources, chemical characteristics, and biodegradability." *Ecosystems* no. 10 (8):1323-1340.
- Xu, N., H. F. Wilson, J. E. Saiers, and M. Entz. 2013. "Effects of crop rotation and management system on water-extractable organic matter concentration, structure, and bioavailability in a chernozemic agricultural soil." *Journal of Environmental Quality* no. 42 (1):179-190.
- Zhang, L., and E. J. LeBoeuf. 2009. "A molecular dynamics study of natural organic matter: 1. Lignin, kerogen and soot." *Organic Geochemistry* no. 40 (11):1132-1142.
- Zimmerman, A. R. 2010. "Abiotic and microbial oxidation of laboratory-produced black carbon (biochar)." *Environmental Science & Technology* no. 44 (4):1295-1301.

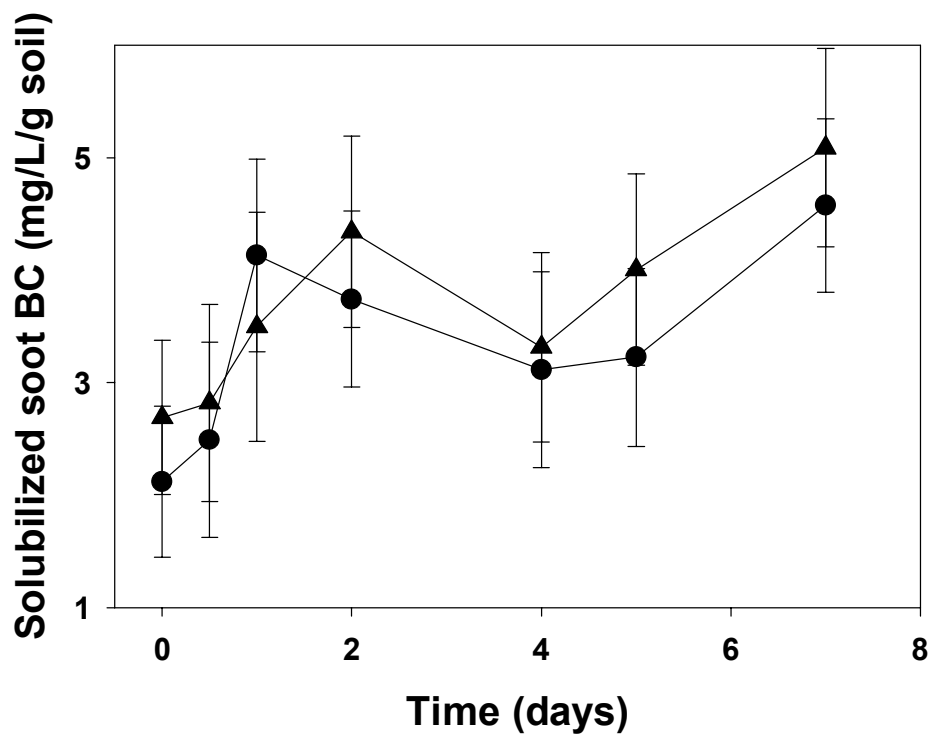


Figure 4.1. Solubilized soot BC concentrations versus time. Different symbols represent two different trials (●, ▲). Concentrations are normalized to weight of soil in each trial and are blank corrected. Error bars are  $\pm 1$  standard deviation ( $n = 3$ ).

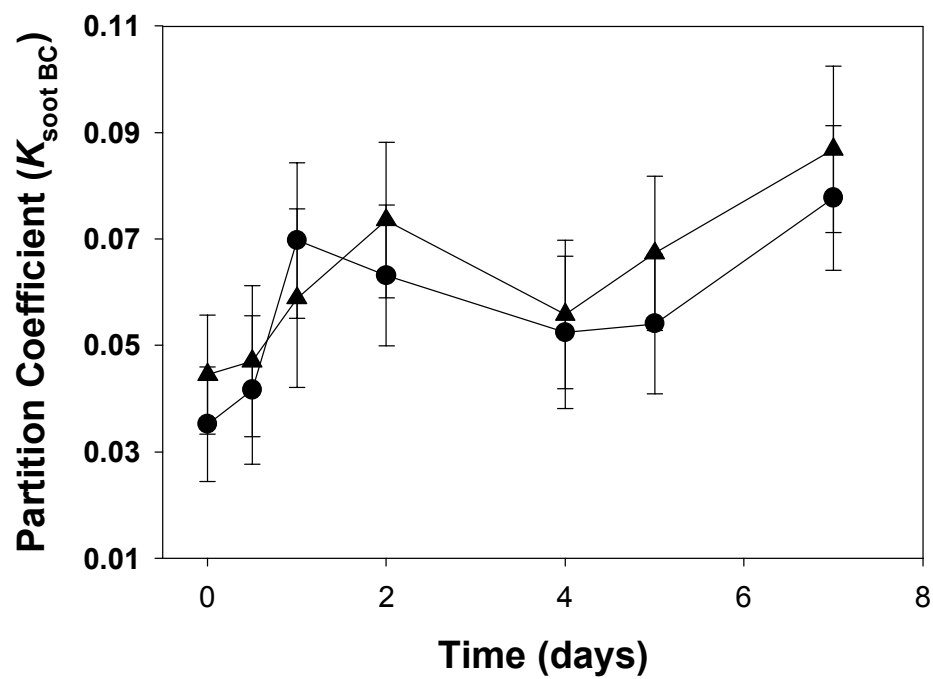


Figure 4.2. Soot BC partition coefficients as a function of time. Different symbols represent two different trials ( $\bullet$ ,  $\blacktriangle$ ). Error bars are  $\pm 1$  standard deviation ( $n = 3$ ).

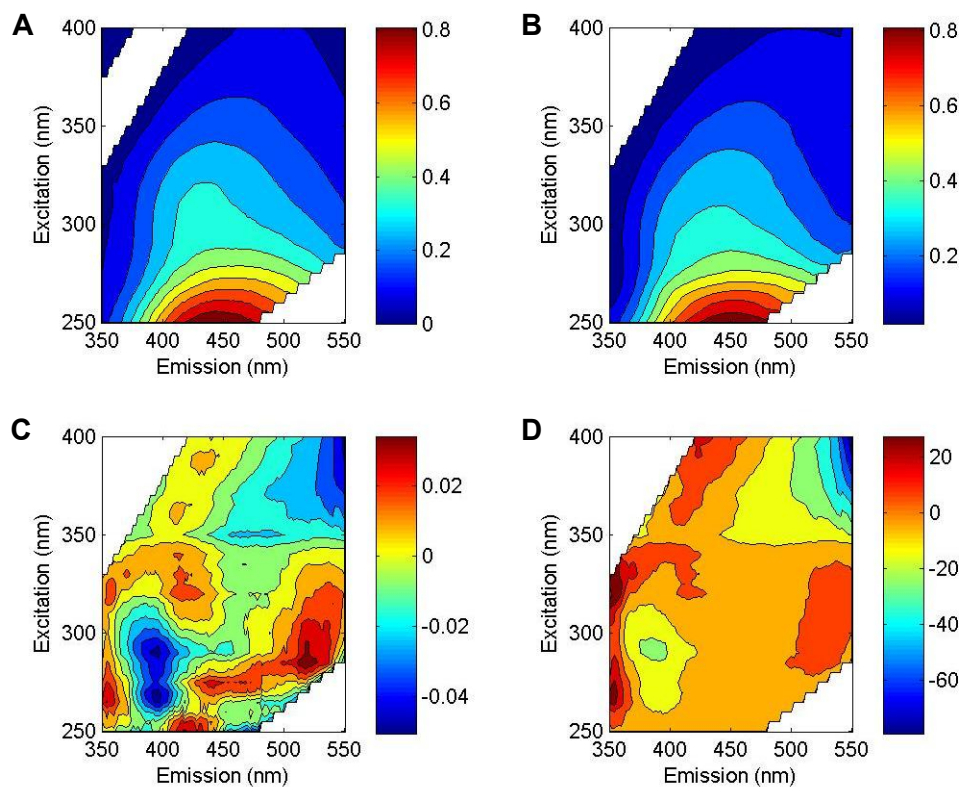


Figure 4.3. Contour plots of fluorescence intensity (Raman units) from an extract of desert soil organic carbon. (A) The corrected EEM, (B) modeled EEM from PARAFAC analysis, (C) the plot of the absolute residual (Raman units), and (D) a plot of relative residuals (in %).



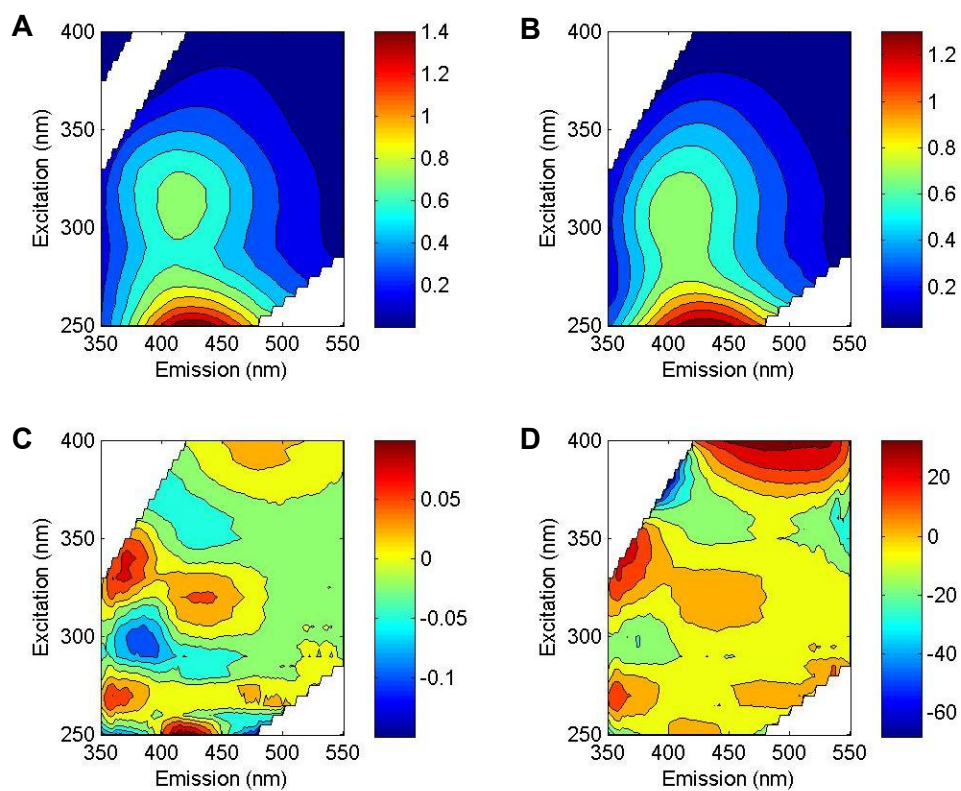


Figure 4.4. Contour plots of fluorescence intensity (Raman units) in an extract of soil soot BC. (A) The corrected EEM, (B) modeled EEM from PARAFAC analysis, (C) the plot of the absolute residuals (Raman units), and (D) the plot of relative residuals (in %).

Table 4.1. Percent contribution of grouped PARAFAC components, Redox Index, and Humification Index, in bulk OC and soot BC extracts.

	Bulk OC	Soot BC
$\Sigma$ oxidized quinone (%)	37	47
$\Sigma$ reduced quinone (%)	37	16
$\Sigma$ protein (%)	2	5
$\Sigma$ unknown (%)	24	32
Redox Index	0.5	0.25
HIX	12	16

<sup>a</sup> Redox Index = ( $\Sigma$  reduced quinone)/( $\Sigma$  reduced +  $\Sigma$  oxidized quinone) (Miller et al. 2006)

<sup>b</sup> Humification index (HIX) = ( $\Sigma$  emission  $I_{435 \rightarrow 480}$  /  $\Sigma$  emission  $I_{300 \rightarrow 345}$ ) at excitation wavelength 254 nm ( $I_{x \rightarrow y}$  is fluorescence intensity from x nm to y nm; Ohno et al. 2002).

## Chapter 5

### BIODEGRADATION AND SPECTROFLUOROMETIC ANALYSIS OF DISSOLVED SOOT BLACK CARBON FROM CENTRAL AZ SOIL

#### Abstract

Soot black carbon (BC) can be a large fraction of the soil organic carbon. I investigated the biodegradation of soot BC in soils from desert and urban land-use areas in Phoenix, Arizona. Biological carbon dioxide production from soot BC extracts was measured in time-series laboratory incubations. Greater CO<sub>2</sub> production was observed when both the microbes and the soot BC were derived from the same soils compared to when microbes and soot BC were derived from different soils. Fluorescence spectroscopy and parallel factor analysis modeling indicated that microbial oxidation altered the relative contribution of oxidized and reduced fluorophores in soil soot BC extracts. These results suggest that soil microbes degrade soot BC in the environment.

#### Introduction

Black carbon (BC), material formed from the incomplete combustion of both biomass and fossil fuel, is best described as a combustion continuum of organic materials described as slightly charred biomass, char, charcoal and soot (Hedges et al. 2000; Masiello 2004; Poot et al. 2009). In the continuum, BC is described as a series of pyrogenic materials with a range in reactivity, source, particle size, and formation temperature. Interest in the biogeochemical properties of BC has been growing because BC plays a role in the long-term storage of organic matter (Masiello 2004; Czimczik and Masiello 2007), it contributes to the formation of soil organic

carbon (especially in frequently burned soils; Glaser 2001; Han 2012), it is a major source of anthropogenically produced sedimentary organic matter (Bird and Grocke 1997), and it is an important component of Earth's radiative budget (IPCC 2007). Black C also modifies concentrations of organic pollutants in soil by acting as a sorbant for polycyclic aromatic hydrocarbons (Gustafsson et al. 1997; Gustafsson and Gershwin 1997; Accardi-Dey and Gschwend 2002). In addition, BC has been shown to increase cation exchange capacity in soil (Mao et al. 2012; Preston and Schmidt 2006).

Black carbon was once thought to be recalcitrant because it consists almost entirely of straight chain and cyclic hydrocarbon structures, and because it is present in ancient soils and sediments (Schmidt and Noack 2000; Skjemstad et al. 2002; Middleberg et al. 1999). However, a number of recent studies demonstrate direct evidence that BC is reactive to both abiotic and biotic processes (Stubbins et al. 2012; Cheng and Lehmann. 2009; Jaffé et al. 2013; Hockaday et al. 2007). Black carbon reactivity is also implied, indirectly, by the BC global budget. The BC global budget is imbalanced and suggests that significant unknown terrestrial and/or marine BC sinks must exist to balance the relatively well-constrained and large natural and anthropogenic sources (Masiello 2004). Potential terrestrial sinks include both non-biological (photo-oxidation or solubilization and subsequent runoff) and biological (microbial decomposition) processes.

The biological degradation of some of the non-soot components of the BC continuum (i.e., char, charcoal) have been investigated, but there are few, if any, studies of the biological degradation of soot BC. Early studies of biochar biodegradation showed that biochar can act as a primer for the oxidation of simple

carbohydrates such as glucose, and that it may also undergo direct microbial degradation (Hilscher et al. 2009; Hamer et al. 2004). Biological turnover rates using a laboratory-derived biochar (a burned residual solid) have been reported to be between 4 and 29 years (Steinbeiss et al. 2009). A more recent study predicted that up to ~25% of biochar could be biomineralized over ~100 years (Zimmerman 2010). Hilscher and Knicker (2011) demonstrated that microbial degradation alters the relative abundance of chemical functional groups in pyrogenic material; specifically, they found the proportion of oxygen-containing functional groups increased and the proportion of aryl carbon decreased over the course of a 20-month incubation. None of the studies summarized here consider the biodegradation of the highly-aromatic and more recalcitrant material defined as soot BC.

Soot BC is an easily distinguishable component of the BC combustion continuum. Soot BC (unlike char and charcoal) is produced by condensation of gas-phase molecules to form nanosized soot particles. In contrast, char or biochar is a remnant material that remains in the solid-phase during combustion, and typically has particle sizes  $>1\ \mu\text{m}$  (Masiello 2004). The established methods that quantify soot BC have very few interfering compounds and yield a conservative estimate of soot BC concentration; therefore, soot BC is a well-defined component of the BC continuum (Hammes et al. 2007). This work focuses on microbial degradation of soot BC in desert and urban soils from central Arizona (AZ). The region is home to a major metropolitan area (Phoenix, AZ) and the city is a source of at least some of the soot BC found in soil (Hamilton and Hartnett 2013). Soot BC constitutes a large fraction of the soil organic matter in central AZ (on average 31%) and there are

differences in the soot BC content of urban and non-urban soils (Hamilton and Hartnett 2013).

Urbanization (which includes the input of anthropogenically produced carbon to soil) has been shown to alter microbial functioning in central AZ soils (Hall et al. 2009) through changes in land-use and land-cover, and by exposure to the urban environment. For example, in the dry soils of arid ecosystems, soil organic matter degradation is regulated by oxidative enzyme activity; these enzymes are optimized at high pH and stabilized by accumulation on carbonate mineral surfaces (Sinsabaugh et al. 2008; Stursova and Sinsabaugh 2008). Hall et al. (2009) reported lower activities of organic matter-standardized peroxidase in soils from urban remnant-desert sites as compared to activities in soils from outlying desert sites; they suggest that desert-remnant ecosystems are being ‘domesticated’ by exposure to the urban environment because desert preserves within the city functionally resemble managed xeriscapes and lawns. The input of anthropogenically produced soot BC could contribute to urbanization.

The goal of this work is to evaluate the microbial oxidation of soot BC from locations with different land-use types and to evaluate the resulting compositional changes in soot BC. Chemical compositional changes to the solubilized soot BC were evaluated using fluorescence analysis. Fluorescence analysis is a powerful tool for characterizing dissolved and extractable organic matter from a variety of marine, aquatic, and terrestrial environments (Cory and McKnight 2005; Burdige et al. 2004; Coble 1996). While not all molecules fluoresce, a few key chemical fluorophores have been identified in dissolved organic carbon from both fresh waters and seawater (Fellman et al. 2010; Osburn et al. 2012). The fluorescent chemical

moieties can be used to assess the source, redox-state, and aromaticity of dissolved organic matter (Fellman et al. 2010). Fluorescence analysis has been implemented to monitor the biodegradation of dissolved organic matter (DOM) and of water-extractable organic matter in sediment and soil (Xu et al. 2013; Wickland et al. 2007; Fellman et al. 2008). It has even been suggested that black carbon concentrations in particulate organic matter (POM) can be quantified by the decrease in fluorescence intensity after pyrene additions to POM suspensions (Flores-Cervantes et al. 2009); the authors state that pyrene-fluorescence loss (PFL) coupled with CTO375 (i.e., Gustafsson et al. 1997) can identify nearly all the components in the combustion continuum from relatively labile char to more recalcitrant soot.

The research questions that guide this study are: 1) *can soil microbial communities use soot BC as a carbon source?* and 2) *is there a quantifiable change in the chemical composition of soot BC due to microbial degradation?* This study investigates soot BC from an urban/desert ecosystem and determines how microbial degradation affects soot BC concentration and composition.

## Methods

### *Sample sites and sample collection*

This work was completed in conjunction with the Central Arizona–Phoenix Long-Term Ecological Research (CAP-LTER) project that investigates biogeochemical processes in the urban ecosystem of metropolitan Phoenix, AZ, USA and the surrounding Sonoran desert. The central AZ climate is semi-arid (<18 cm precipitation, annually) and the area includes an urban core, quickly expanding suburbs, agricultural lands, and undeveloped native desert. Phoenix has one of the

fastest growing populations in the U.S. Within the last ten years the metropolitan Phoenix population increased by about 30% to its current population of 4.2 million (2010 U. S. Census). Rapid urban and suburban growth has expanded the footprint of the Phoenix urban area (generally at the expense of desert areas) by 225 km<sup>2</sup>, or 154,110 m<sup>2</sup>/day (Maricopa Association of Governments).

Central AZ is diverse with respect to land-use and land-cover. The region consists predominantly of open Sonoran Desert (36%), followed by managed mesic landscapes (11%; primarily allocated in residential lots, municipal/industrial areas, and golf courses), managed xeric landscapes (13%; in residential lots, municipal/industrial areas, and transportation corridors), agriculture (8%), bare ground (9%; as vacant lots and dirt roads), and water (1%; in canals, streams), as well as a large fraction of impervious surface (22%; Hall et al. 2009).

I used soil samples from an urban and a desert location that were collected in 2010 during CAP-LTER's semi-decadal field survey. Samples were collected from 30 x 30 m plots; in each plot, four 30-cm soil cores were collected at the cardinal points (NSEW). The bottom half (16 – 30 cm) of each core was homogenized and dried. The four cores collected at each plot were then combined to make one composite soil sample for each site. Combined core samples were stored in the dark at 20°C until the experiments were conducted. I used CAP-LTER data for land-use categories, and site locations.

#### *Soot BC isolation by chemo-thermal oxidation*

Soot BC was isolated in soil samples using chemo-thermal oxidation (CTO375; Gustafsson et al. 1997). Briefly, soil samples were weighed (1 g) into small glass beakers and carbonate was removed by acidification with 1 mL of 4 M HCl. In



samples with high carbonate content, additional acid was added until effervescence ceased. Soil was allowed to dry overnight in a warm oven (40°C). Dry soil was removed from the beakers and ground to a powder with an agate mortar and pestle. Soil was placed back in the beakers and into a muffle furnace for 24 hours at 375°C under ambient atmospheric conditions to remove labile (non-black) organic carbon (Gustafsson et al. 1997; Gustafsson et al. 2001; Hammes et al. 2007). I quantify soot BC concentration in soil using chemo-thermo oxidation of soil followed by elemental analysis (EA) using a Costech Elemental Analyzer (Costech Analytical Technologies, Valencia, CA, USA) coupled to an isotope ratio mass spectrometer (EA-IRMS) similar to the procedure presented in Hamilton and Hartnett (2013). Carbon detected by EA-IRMS after CTO375 was defined as soot BC.

*Preparation of Soot BC extracts, microbial inocula, and nutrient solutions*

Soot BC extracts were made from soil slurries by placing 1 g of CTO375-treated soil and 5 mL of deionized H<sub>2</sub>O (18.2 MΩ·cm; NANOpure Diamond, Barnstead, Inc. Dubuque, IA, USA) in a 15 mL centrifuge tube. Tubes were placed on a rotary table and agitated at medium speed (80 rpm) for 3 days. Slurries were then syringe filtered (0.2 µm; Acrodisc PES, polyethersulfone Supor<sup>tm</sup> membrane filter; Pall Corporation, Ann Arbor, MI, USA) to remove particles and bacteria (Fellman et al. 2008). The resulting filtrate is the soil soot BC extract. Soil microbe inocula were made using a slight modification of the procedure described above. Microbial inocula were prepared from a 3-day slurry of unaltered (raw) soil and filtered through a 1.2 µm syringe filter (Acrodisc PES, polyethersulfone Supor<sup>tm</sup> membrane filter; Pall Corporation, Ann Arbor, MI, USA) in order to remove particles but retain cells. A nutrient solution (nitrogen and phosphorus only) was prepared

using 0.45 M  $\text{NH}_4\text{NO}_3$  and 0.03 M  $\text{K}_2\text{HPO}_4$  (98+%, Sigma Aldrich, St. Louis, MO, USA) according to the method presented in Zimmerman (2010).

### *Cell visualization*

The presence (in inocula) or absence (in soot BC extracts) of microbial cells was determined by direct visualization (cell counting) using a protocol modified from O'Connor (2009). Briefly, the microbial inoculum or soot BC extract was fixed with formaldehyde (5% by volume) and a 10  $\mu\text{L}$  sample was pipetted directly onto a microscope slide and allowed to dry. After the slide was completely dry, 10  $\mu\text{L}$  of 4', 6-diamidino-2-phenylindole (DAPI; 3.6 mM) was placed directly onto the slide on top of the sample and the slide was allowed to dry again in the dark. A small amount of Citifluor mounting oil (Electron Microscopy Sciences, Hatfield, PA, USA) was placed on the slide followed by a cover slip; type-F immersion oil (Cargille Laboratories, Inc., Cedar Grove, NJ, USA) was applied on top of the cover slip. The slides were viewed using a Nikon Alphaphot-2 YS2 microscope under epifluorescent light and imaged with an integrated camera attachment. Ten fields (0.1 mm x 0.1 mm) were randomly selected. The cells in each field were counted and an average count/field was calculated. The number of fields in the deposition area was calculated by dividing the wetted deposition area by the field area. The total cell count is calculated by multiplying the average cell count per field by the number of fields in the deposition area. Total cell density is calculated by dividing the total number of cells by the volume of sample. The cell counting method has a reproducibility of 9% (RSD; O'Connor 2009).

### *Design of experimental incubations*

The experimental design presented here is modified from Zimmerman (2010)

and Kaye et al. (2011). The incubations used microbes derived from either desert or urban soils with soot BC extracts from either desert or urban soils. Thus, a total of four separate degradation experiments were completed (in triplicate) using the two microbial inocula (i.e., desert and urban) and the two soot BC extracts (i.e., desert and urban). The first pair of experiments used desert inocula with a desert soot BC extract ( $D_i$ - $D_e$ ) and urban inocula with an urban soot BC extract ( $U_i$ - $U_e$ ). Two additional experiments were conducted; one with desert inocula and urban soot BC extract ( $D_i$ - $U_e$ ) and one with urban inocula and desert soot BC extract ( $U_i$ - $D_e$ ). I refer to experiments where the inoculum and the soot BC extract are from different locations, as reciprocal experiments (i.e.,  $D_i$ - $U_e$  and  $U_i$ - $D_e$ ). All experiments are named as the land-use type for the inoculum source followed by the land-use type for the soil soot BC extract. All incubations contained 1 mL of the nutrient solution in order to prevent N and P limitation. Abiotic incubations of the desert and urban soil soot BC extract were set up in parallel using the same procedure as the biotic incubations except that 1 mL of deionized  $H_2O$  was used in place of the microbial inoculum.

#### *CO<sub>2</sub> Production Measurements*

Pre-incubations consisting of 1 mL of the nutrient solution and 1 mL of the microbial inoculum in a 30 mL glass vial (Wheaton Industries, Millville, NJ, USA) were conducted to evaluate the C and N limitation status of the inoculum. Vials were sealed with a rubber septum and an aluminum crimp-top fitting, and placed in the dark at room temperature. After 24 hours, 5 mL of the headspace gas in each vial was sampled using a gas-tight syringe and a 0.80 mm x 38 mm needle (SGE Analytical Science, Ringwood, Victoria, Australia). The headspace sample was

injected into a CO<sub>2</sub> analyzer (PP Systems, Inc., Amesbury, MA, USA) to quantify of CO<sub>2</sub> concentration. The CO<sub>2</sub> analyzer was pre-calibrated by the manufacturer and was operated in static sampling mode. After a sample was injected into the instrument inlet, the CO<sub>2</sub> concentration (ppm) was recorded directly from the instrument read-out screen. Background CO<sub>2</sub> was determined by sampling a capped vial filled with laboratory air. All reported CO<sub>2</sub> measurements are the average of single injections from three separate vials. I did not make multiple injections from each vial because the amount of CO<sub>2</sub> in the vial decreased after every injection. After the headspace was sampled, the vials were uncapped and flushed with laboratory compressed air (the lab air was filtered to prevent contamination by particles or organic lubricants) to dilute CO<sub>2</sub> in the headspace. Vials were closed again and placed in the dark at room temperature for 24 hours, after which time, the headspace CO<sub>2</sub> was sampled again. Pre-incubations continued until no CO<sub>2</sub> production was detected (approximately 4 days). Soot BC extract (1 mL) was added to the vials and experimental incubations were begun only after the pre-incubations stopped producing detectable amounts of CO<sub>2</sub>. The day that soot BC extract was added to the incubation vial was designated day zero. Soot BC extract was added to biotic and abiotic vials at the same time and headspace CO<sub>2</sub> was sampled in abiotic vials on the same schedule used for the biotic vials.

Prior to conducting the experiments and the pre-incubations, separate trials to determine whether the microbial inocula were carbon or nutrient limited were conducted by adding 1 mL of either glucose (30 mg C/L) or nutrient solution (nitrogen plus phosphorus) to incubations instead of soot BC extract and monitoring CO<sub>2</sub> production. Negative controls were also conducted using vials containing only

nutrient solution, soot BC extract, or microbial inoculum. Based on these trials, I determined that incubations required both a nutrient and a carbon source to produce CO<sub>2</sub> and that microbial inocula were carbon-limited.

#### *Dissolved organic carbon analysis*

Non-purgable organic carbon, i.e., dissolved organic carbon (DOC), was quantified using a Shimadzu TOC-V carbon analyzer. Briefly, samples were acidified to a pH of 2 and then combusted at 680°C in an oxygen-rich environment over a platinized-alumina catalyst to convert all dissolved carbon in the sample to CO<sub>2</sub>(g) (Hedges et al. 1993; Sharp et al. 1993; Sharp 1993; Sharp 1997). The CO<sub>2</sub>(g) is detected with a non-dispersive infrared detector. The non-purgable organic carbon analysis in this case is roughly equivalent to dissolved black carbon because the soot BC extract has no inorganic carbon and little or no non-black organic material.

#### *Fluorescence Analysis*

Soot BC chemical composition was assessed using fluorescence spectroscopy for all incubation types on day 1 (the initial day that CO<sub>2</sub> was sampled) and on day 7 (the final day that CO<sub>2</sub> was sampled). Fluorescence excitation-emission matrices (EEMs) were obtained using a Fluoromax 4 fluorescence spectrometer (Jobin–Horiba, Inc., Edison, NJ, USA); spectra were collected over an excitation range from 240 to 450 nm in 10 nm increments and emission was monitored from 300 to 550 nm in 2 nm increments. Pure water blanks and cuvette checks were run each day prior to sample analysis. Raw fluorescence spectra were blank corrected and peak intensity was normalized to the water Raman spectrum (excitation = 350 nm) each day. Inner-filter corrections were performed for any sample when the UV absorbance at 240 nm was >0.3 absorbance units (Ohno et al. 2012). The corrected excitation-emission

matrices were then modeled using parallel factor (PARAFAC) analysis, a three-way deconvolution method. This technique deconvolves the spectra from each sample into thirteen independent components, where the components represent known and unknown fluorophores. The thirteen components are those developed the Cory and McKnight (2005) PARAFAC model based on 379 different aquatic samples. Absolute fluorescence intensity for each component is proportional to the component's contribution to the total fluorescence intensity (Stedmon et al. 2003; Cory and McKnight 2005). I binned the relative contributions of the thirteen fluorescent components into four groups based on their chemical structures; specifically, oxidized quinones (3 components), reduced quinones (4 components), two amino-acid like components (tryptophan and tyrosine), and unknown humic-like structures (4 components).

### *Statistical Analysis*

Regression analysis was conducted using Sigma Plot 11.0 (Systat Software Inc. San Jose, CA, USA) on cumulative total CO<sub>2</sub> production over time (Figure 5.1 and 5.2). Regression analysis was completed for data from day 1 to day 3, for day 3 to day 7, and for day 1 to day 7. Regression analysis was also completed for cumulative biologically produced CO<sub>2</sub> over time (Figure 5.4). The slopes of the regression lines from each analysis were deemed significant for  $p < 0.05$ .

## Results

### *Dissolved black carbon analysis of soot BC extracts and cell counts from the microbial inocula*

The amounts of soot BC in the soil samples used to generate the soot BC

extract were  $0.048 \pm 0.005$  and  $0.14 \pm 0.01$  wt. % soot BC for the desert and urban site, respectively. Carbon concentrations in desert and urban soot BC extracts were  $12 \pm 1$  and  $10.6 \pm 0.9$  mg C/L, respectively. The microbial inoculum had an average of  $3.4 \times 10^8$  ( $\pm 20\%$  RSD) cells/mL at the start of the experiments. There were not enough cells present in the soot BC extracts to obtain accurate cell counts.

### *CO<sub>2</sub> Production*

All headspace CO<sub>2</sub> concentrations were background corrected using measurements from vials containing only the ambient laboratory air. Background CO<sub>2</sub> concentrations in the laboratory air were  $\sim 410$  ppm. Negative values for corrected CO<sub>2</sub> concentration occurred when the headspace CO<sub>2</sub> concentration in a sample vial was lower than the ambient laboratory CO<sub>2</sub> concentration.

Control incubations consisting of just the inoculum, the soot BC extract, or the nutrient solution yielded no measurable CO<sub>2</sub> production. Similarly, incubations consisting of the inoculum and soot BC extract (without the nutrient solution) never produced measurable CO<sub>2</sub>. The abiotic incubations, consisting of soot BC extract and the nutrient solution, produced CO<sub>2</sub> from day 1 to day 2 (Figure 5.1, top panel). Starting on day 3, the daily CO<sub>2</sub> production in the abiotic incubation was below zero (i.e., CO<sub>2</sub> concentrations in the vials were less than the background CO<sub>2</sub> concentration; Figure 5.1, top panel). The cumulative production of CO<sub>2</sub> in the abiotic incubations increased over the first two days to  $300 \pm 20$  ppm in desert soot BC incubations and to  $200 \pm 20$  ppm in urban soot BC incubations (Figure 5.1, bottom panel). Cumulative CO<sub>2</sub> production in both incubations decreased after day 2 due to negative daily CO<sub>2</sub> production (Figure 5.1, bottom panel). In general, the incubations using desert soil soot BC extracts produced more CO<sub>2</sub>, cumulatively,

than incubations using urban soil soot BC ( $p < 0.05$ ; Figure 5.1, bottom panel).

The four biotic experiments each produced CO<sub>2</sub> over the course of the incubation period. In all cases, the experiments produced significant amounts of CO<sub>2</sub> on day 1; the CO<sub>2</sub> concentrations measured on subsequent days decreased over the course of the incubation period, but remained at or above zero (Figure 5.2, top panel) over the full seven days. In D<sub>i</sub>-D<sub>e</sub> and U<sub>i</sub>-U<sub>e</sub> experiments, the daily CO<sub>2</sub> concentration range was  $310 \pm 20$  ppm on day 1, and dropped to zero (or near zero) ppm on days 5, 6, and 7 (Figure 5.2; top panel). The cumulative increase in concentration over the 7 days was  $400 \pm 20$  ppm for the D<sub>i</sub>-D<sub>e</sub> incubation and  $360 \pm 20$  ppm for the U<sub>i</sub>-U<sub>e</sub> incubation (Figure 5.2; bottom panel). In the U<sub>i</sub>-D<sub>e</sub> incubations, absolute CO<sub>2</sub> concentration was  $280 \pm 20$  ppm on day 1 and dropped to zero ppm on days 3, 5, 6, and 7 (Figure 5.2; top panel) and the cumulative increase in concentration over the 7 days was  $320 \pm 20$  ppm (Figure 5.2; bottom panel). Finally, the D<sub>i</sub>-U<sub>e</sub> incubations only produced CO<sub>2</sub> on day 1 ( $250 \pm 20$  ppm; Figure 5.2 top panel); consequently, the cumulative production was  $250 \pm 20$  ppm (Figure 5.2; bottom panel). Cumulative CO<sub>2</sub> concentrations increased over the first 3 days for all experiments ( $p < 0.05$ ) except in the D<sub>i</sub>-U<sub>e</sub> incubation where concentrations remained essentially constant ( $p > 0.05$ ). After day 3, cumulative CO<sub>2</sub> concentrations remained essentially constant (i.e., the slopes were not statistically different from zero,  $p > 0.05$ ) for all experiments. Only the U<sub>i</sub>-U<sub>e</sub> incubation exhibited a significant increase over the course of the entire experiment (i.e., day 1 to day 7;  $p < 0.05$ ; Figure 5.2, bottom panel).

Experiments with a microbial inoculum and a soil soot BC extract from the same land-use type (i.e., D<sub>i</sub>-D<sub>e</sub> and U<sub>i</sub>-U<sub>e</sub>) produced more CO<sub>2</sub> (cumulatively) than



did the reciprocal (i.e.,  $U_i\text{-}D_e$  and  $D_i\text{-}U_e$ ) experiments (Figure 5.2, bottom panel). In addition, for both experiment types (direct and reciprocal), experiments using the desert soot BC extract produced more  $\text{CO}_2$  than did experiments using the urban soot BC extract (Figure 5.2, bottom panel).

### *Fluorescence results*

Fluorescence analysis was conducted on aliquots from all experiments on day 1, immediately after the soil soot BC extract was added to the vial (initial), and on day 7 of the experiment (final). Corrected EEMs from incubations containing soot BC extract exhibited two distinct regions of relatively high fluorescence intensity (Figure 5.3A and B). The first region is located between excitation wavelengths from 280 nm to 340 nm and emission wavelengths from 400 nm to 450 nm. The second, more intense, region is located between excitation wavelengths from 250 nm to 270 nm and emission wavelengths from 400 nm to 475 nm. These same fluorescent regions appear in both the initial and final samples. The basic fluorescence patterns and the absolute fluorescence intensities of these two regions did not change significantly over the course of the experiment.

## Discussion

### *Biological production of $\text{CO}_2$*

Carbon dioxide was only produced in the abiotic and biotic experiments when both the nutrient solution and the soot BC extract were present (Figure 5.1 and 5.2, respectively). The abiotic production of  $\text{CO}_2$  was somewhat expected because similar experiments using biochar as the solitary carbon source also exhibited abiotic  $\text{CO}_2$  production (Zimmerman 2010). Generally, the abiotic production of  $\text{CO}_2$  has been

attributed to ring-cleavage and decarboxylation reactions of phenols and organic acids in soil in the presence of a metal oxide (Majcher et al. 2000; Wang and Huang 2000). Zimmerman (2010) suggests that the acidic surface of biochar may have catalytic properties to carry out the oxidation of phenols and organic acids. Activated carbon, a material similar to soot BC (Gustafsson et al. 1997), also has acidic surface characteristics (Goyal et al. 2008) and could act as a catalyst for the ring-cleavage and decarboxylation reactions described above. While phenol moieties are not typically present in freshly produced black carbon, “aged” black carbon found in soils has been shown to display relatively higher H:C and O:C values over time (Cheng et al. 2008). Fourier-transform infrared (FTIR) analysis has been used to demonstrate that hydroxyl functional groups (indicative of phenols) appear in older soil black carbon (Cheng et al. 2008) and in photo-oxidized soot BC in soil (Hamilton unpublished data). The soot BC used in this experiment was not freshly synthesized; it was isolated from environmental soil samples and has likely undergone a similar aging processes. Another potential mechanism for the abiotic production of CO<sub>2</sub> is the oxidation of PAHs by nitrate (Ringuet et al. 2012), which is present in the nutrient solution.

The higher CO<sub>2</sub> production in abiotic incubations with desert soot BC than in abiotic incubations with urban soot BC (Figure 5.1, bottom panel) could be related compositional differences in desert and urban soot BC. My previous work showed that the urban environment produces <sup>13</sup>C-depleted soot BC that is consistent with a fossil fuel source (Hamilton and Hartnett 2013). Thus, it is possible the soot BC from urban sites has been produced more recently, because it is sourced from vehicle emissions, and has not had much time to be “aged” or degraded.

Carbon dioxide concentrations below zero (Figure 5.1; top panel) and subsequent decreases in cumulative CO<sub>2</sub> concentration (Figure 5.1; bottom panel) in the abiotic experiment were due to headspace CO<sub>2</sub> concentration values below the background CO<sub>2</sub> concentration. Negative CO<sub>2</sub> concentrations indicate that some CO<sub>2</sub> (~40 ppm) is dissolved into the vial solution. The amount of CO<sub>2</sub> dissolved is consistent with the measured pH of the solution (6.0) in the vials. The daily output of CO<sub>2</sub> in biotic experiments remains above the ambient CO<sub>2</sub> levels throughout the experiment (Figure 5.2, top panel).

Slurries of microbial inocula and nutrient solution produced some CO<sub>2</sub> prior to the addition of soot BC extract. I inferred that the inocula contained some initial amount of bioavailable carbon. Once CO<sub>2</sub> production ceased, I concluded that the inocula were “starved” for either a carbon or nutrient source. In separate experimental trials, the microbial inocula were confirmed to be carbon-limited by providing incubations with a carbon source (glucose) and nutrient source (nutrient solution). Headspace CO<sub>2</sub> production increased when “starved” microbial inocula were given glucose and did not increase when given additional nutrient solution. By “starving” microbial inocula, I confirm that the CO<sub>2</sub> produced in the incubations containing microbial inocula and soot BC extract is from the extract addition and not from the inoculum itself. To my knowledge, this is the only experiment to use a carbon-limited microbial inoculum in a black carbon degradation study.

Carbon dioxide was produced in incubations both with and without microbial inocula. I calculated the biological CO<sub>2</sub> production as the difference between the amount of CO<sub>2</sub> generated in the abiotic and biotic experiments over time. It is difficult to see the differences between the abiotic and biotic experiments in Figures

5.1 and 5.2 because the amounts of CO<sub>2</sub> produced each day are small. To illustrate differences between the abiotic and biotic experiments, the daily difference in CO<sub>2</sub> production between the two experiments was calculated and plotted as the cumulative CO<sub>2</sub> concentration over time (Figure 5.4; all plots). Values above zero occur when cumulative CO<sub>2</sub> production in the biotic experiment is greater than the cumulative CO<sub>2</sub> production in the abiotic experiment. Values below zero occur when cumulative CO<sub>2</sub> production in the biotic experiment is less than the cumulative production of CO<sub>2</sub> in the abiotic experiment. In all cases, cumulative biological CO<sub>2</sub> production is positive after day 1 (Figure 5.4; all plots). Notably, biological CO<sub>2</sub> production is greater than abiotic production even though the only carbon source is the soot BC extract. The soot BC extract is clearly not completely recalcitrant; and these results suggest the soil microbial communities can oxidize at least some portion of the solubilized soot BC. Thus, Soot BC is likely biologically reactive in the environment.. Nearly all components of the BC continuum (charred biomass, char, charcoal and soot BC) have now been demonstrated to undergo microbial degradation. The addition of a microbially mediated loss term for soot BC in soil must be considered in future assessments of the global BC budget.

More CO<sub>2</sub> is produced when the microbial inoculum and the soot BC extract are derived from the same location (i.e., D<sub>i</sub>-D<sub>e</sub>, U<sub>i</sub>-U<sub>e</sub>; Figure 5.4A and B) than when they are derived from reciprocal locations (i.e., D<sub>i</sub>-U<sub>e</sub>, U<sub>i</sub>-D<sub>e</sub>; Figure 5.4C and D). This is presumably because microbes are better equipped to metabolize soot BC from their own soils than soot BC from a different location. Hall et al. (2009) refer to the ‘domestication’ of desert remnant ecosystems as a result urbanization which could imply a shift in the microbial species present in urban areas. The differences in

biodegradation for reciprocal experiments using desert and urban soot BC extracts could be due to differences in the microbial consortia present in the urban and desert soils; but, a detailed assessment of species composition would be necessary to confirm this supposition. It is also entirely likely that soot BC extracts from different land-use types are degraded differently because there are compositional differences in soot BC from different locations (i.e., urban vs. desert land-use sites). As stated earlier, “aging” of soot BC can impart chemical compositional changes (i.e., increased O:C and H:C; Cheng et al. 2008; Cheng et al. 2009), and it is likely that soot BC from urban and desert areas have undergone different extents of aging, presumably because they have different sources. There is evidence for differences in the sources of soot BC to urban and non-urban soils based on their  $^{13}\text{C}$  composition (Hamilton and Hartnett 2013). The difference in chemical and carbon isotopic composition could affect how soot BC is degraded in different land-use areas.

#### *PARAFAC modeling of fluorophores*

Excitation-emission contour plots for soot BC extracts are distinct from those of bulk OC extracts (Chapter 4; Figure 4.3 and 4.4). Contour plots for soot BC show two distinct peaks that represent terrestrially-derived aromatic moieties (Figure 5.3), whereas contour plots of bulk OC exhibit less distinct contours (Chapter 4; Figure 4.3). Fluorescence analysis was conducted on soot BC samples from the abiotic and biotic incubations on day 1 (initial) and day 7 (final). Representative contour plots of corrected EEMs (i.e., intensity as a function of excitation-emission wavelengths) are presented for desert and urban soot BC extracts (Figure 5.3A and B, respectively). Typically, these plots are interpreted in terms of regions where known components of dissolved organic matter have been shown to fluoresce (i.e., protein, terrestrial

humic material, aromatic terrestrial material; see labels on Figure 5.3A). The EEMs for both desert and urban soil soot BC extracts exhibit patterns of fluorescence consistent with those associated with “humic-like” organic matter (Fellman 2010). “Humic-like” generally refers to complex and often conjugated aromatic molecules that have a terrestrial source. Peaks in the region located between excitation wavelengths 280 nm and 340 nm and emission wavelengths 400 nm to 450 nm and between excitation wavelengths 250 nm and 270 nm and emission wavelengths 400 nm to 475 nm are at longer emission wavelengths and are considered “red shifted” compared to peaks that typically represent protein-like fluorophores (Fellman 2010). The two peaks in soot BC fluorescence are also consistent with those of other highly-conjugated fluorescent molecules present in the high-molecular weight fraction of dissolved organic matter (Fellman et al. 2010). Many of these molecules are thought to be derived primarily from vascular plants and are highly aromatic (Coble et al. 1998). The chemical characteristics of molecules known to fluoresce in these regions are quite similar to the characteristics of soot BC; i.e., a portion of the soot BC in central AZ is known to have a biomass source (Hamilton and Hartnett 2013) and there are numerous reports of soot BC having a highly-condensed aromatic structure (Gustafsson 1997; Baldock and Smernik 2002).

Total fluorescence intensity remained quite constant over the course of all the incubations. The regions of high fluorescence intensity shown here did not typically exhibit changes due to biodegradation. For example, in incubations of moss leachate, Wickland et al (2007) showed that the most significant decreases in fluorescence occurred for “protein-like” moieties that fluoresce at low excitation/emission wavelength regions which they described as “blue shifted.” Peaks that typically

represent protein-like molecules appear at excitation wavelengths of 260 to 280 nm and at emission wavelengths of 325 to 375 nm (see “P” in Figure 5.3A; Wickland et al. 2007; Fellman 2010). The fluorescence intensity in the protein region is relatively low in my samples, compared to intensities in other regions (Figure 5.3).

I analyzed the corrected EEMs for all four experiments (initial and final) using the Cory and McKnight (2005) parallel factor analysis (PARAFAC) model. This technique produced best-fit models based on contributions from 13 components. Loading vectors represent the relative abundance of each component. The 13 components are representative of both known and unknown fluorophores. I determined the contribution of each component to the total fluorescence in the initial and final samples and calculated the changes in the contribution of each fluorophore for each experiment. The 13 components are then grouped together based on similarities in their chemical structure (i.e., oxidized quinones, reduced quinones, amino acids, and unidentified fluorophores). The percent contribution (initial and final) as well as the changes in contribution to total fluorescence over the course of the experiment are presented in Table 5.1. The initial contribution to total fluorescence from amino acids (analogous to “protein-like”) fluorophores is relatively low (average: 3.3%). This is to be expected since the process that isolates soil soot BC should destroy protein present in the soil. The reduced quinones are the next largest contribution (20.6%) followed by the unknown fluorophores (34.7%). The oxidized quinones have the highest contribution to the total fluorescence (41.4%). A significant contribution from oxygen containing moieties is not entirely surprising considering that oxygenated functional groups such as ketones, and hydroxyl groups have been shown to be present in soil BC (Cheng et al. 2008; Cheng et al. 2009) and

the extracts used here are derived from natural soils.

While overall fluorescence intensities did not change over the course of the incubation, the relative contributions of the four types of chemical components identified by the PARAFAC model did change. The component group that displayed the greatest change was the unknown components. The unknown components decreased in all incubations, by as much as 9% (i.e., the D<sub>i</sub>-U<sub>e</sub> incubation; Table 5.1). In contrast, the oxidized quinone components increased in all incubations; increases in oxidized quinones ranged from 1.0% in the D<sub>i</sub>-D<sub>e</sub> experiment to 5.1% in the D<sub>i</sub>-U<sub>e</sub> experiment. This relative increase in the oxidized quinone component is likely due not to an actual increase in quinone content, but rather to a decrease in other contributions due to microbial degradation. Components demonstrating a positive percent changes indicated that the component's contribution to total fluorescence increased due to microbial degradation and components demonstrating a negative percent change indicated that the component's contribution to total fluorescence decreased due to microbial degradation. Increases in percent contribution suggest that fluorophores represented by those components are recalcitrant to microbial degradation and decreases in percent contribution suggest fluorophores represented by those components are conducive to microbial degradation. These patterns are somewhat similar to the patterns observed by Wickland et al. (2007), wherein oxidized quinone components increased during biodegradation of moss leachates. In Wickland et al. (2007), most of the decrease in fluorescence intensity was attributed to loss of the amino acid components. In this study, however, loss of amino acid like fluorescence is observed, but the loss is not consistent across all incubations (Table 5.1). This is likely due to the fact that amino-acid like fluorescence is extremely low



in these samples. The clear decrease in the contribution from unknown components at the end of the experiments suggest not only that some of the unknown components are present in soot BC, but also that these components are biodegradable. The significant contribution from the unknown components in my samples further suggests there could be a soot BC contribution to much of the DOC present in surface waters.

Residual analysis plots can indicate how well (or poorly) the PARAFAC model predicts the fluorescence intensity of the corrected EEM. A representative plot of residual intensities from the D<sub>i</sub>-D<sub>e</sub> experiment is shown in Figure 5.5. The residual plots for other experiments displayed a very similar pattern. Residual values near zero indicate regions where the PARAFAC model intensities agree well with the actual fluorescence data; Residual values further from zero indicate the regions where the PARAFAC model intensities are higher or lower than the actual fluorescence data. In general, the Cory and McKnight (2005) model generated residual values near zero, suggesting the model works reasonably well for soot BC extracts even though the model was designed for surface water DOC fluorescence. There are, however, regions with relatively high residual intensities. The high intensity region with excitation from 320 to 340 nm and emission from 375 to 450 nm in the residual plot (Figure 5.5) corresponds closely to a region of high fluorescence intensity in the soot BC extract data (i.e., excitation wavelengths from 280 to 340 nm and emission wavelengths from 400 to 450 nm; Figure 5.3A and B). The fluorescence in this region is not well explained by any of the 13 fluorophores in the PARAFAC model; thus, I conclude the fluorescence in this region is due to some compound (or compounds) that are unique to soot BC.

This work has demonstrated that soot BC (considered a relatively recalcitrant form of black carbon), can be degraded by soil microbes on relatively short laboratory time scales. This study also suggests that soil microbial communities are better able to degrade soot BC derived from local soils with the same land-use classification rather than soot BC from soils with a different land-use classification. Finally, biodegradation alters the composition of soot BC and changes the contribution of specific chemical moieties (the unknown components and oxidized quinone components in the Cory and McKnight (2005) model) to the overall fluorescence intensity of solubilized soot BC. I have identified biological removal of soot BC as a loss term for recalcitrant soil carbon in central AZ and suggest that soot BC may be more dynamic in the environment than previously considered.

## Literature Cited

- Accardi-Dey, A., and P. M. Gschwend. 2002. "Assessing the combined roles of natural organic matter and black carbon as sorbents in sediments." *Environmental Science & Technology* no. 36 (1):21-29.
- Baldock, J. A., and R. J. Smernik. 2002. "Chemical composition and bioavailability of thermally, altered *Pinus resinosa* (Red Pine) wood." *Organic Geochemistry* no. 33 (9):1093-1109.
- Bird, M. I., and D. R. Grocke. 1997. "Determination of the abundance and carbon isotope composition of elemental carbon in sediments." *Geochimica et Cosmochimica Acta* no. 61 (16):3413-3423.
- Burdige, D. J., S. W. Kline, and W. H. Chen. 2004. "Fluorescent dissolved organic matter in marine sediment pore waters." *Marine Chemistry* no. 89 (1-4):289-311.
- Cheng, C. H., and J. Lehmann. 2009. "Ageing of black carbon along a temperature gradient." *Chemosphere* no. 75 (8):1021-1027.
- Cheng, C. H., J. Lehmann, and M. H. Engelhard. 2008. "Natural oxidation of black carbon in soils: Changes in molecular form and surface charge along a climosequence." *Geochimica et Cosmochimica Acta* no. 72 (6):1598-1610.
- Czimczik, C.I., C.A. Masiello. 2007. "Controls on black carbon storage in soils." *Global Biogeochemical Cycles* no. 21. GB3005.
- Coble, P.G., C. E. Del Castillo, and B. Avril. 1998. "Distribution and optical properties of CDOM in the Arabian Sea during the 1995 Southwest Monsoon." *Deep-Sea Research -Topical Studies in Oceanography* no. 45 (10-11):2195-2223.
- Coble, P.G. 1996. "Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy." *Marine Chemistry* no. 51 (4):325-346.
- Cory, R. M., and D. M. McKnight. 2005. "Fluorescence spectroscopy reveals ubiquitous presence of oxidized and reduced quinones in dissolved organic matter." *Environmental Science & Technology* no. 39 (21):8142-8149.
- Fellman, J. B., E. Hood, and R. G. M. Spencer. 2010. "Fluorescence spectroscopy opens new windows into dissolved organic matter dynamics in freshwater ecosystems: A review." *Limnology and Oceanography* no. 55 (6):2452-2462.
- Fellman, J.B., D.V. D'Amore, E. Hood, and R.D. Boone. 2008. "Fluorescence characteristics and biodegradability of dissolved organic matter in forest and

- wetland soils from coastal temperate watersheds in southeast Alaska." *Biogeochemistry* no. 88 (2):169-184.
- Flores-Cervantes, D. X., C. M. Reddy, and P. M. Gschwend. 2009. "Inferring black carbon concentrations in particulate organic matter by observing pyrene fluorescence losses." *Environmental Science & Technology* no. 43 (13):4864-4870.
- Glaser, B., L. Haumaier, G. Guggenberger, and W. Zech. 2001. "The 'Terra Preta' phenomenon: a model for sustainable agriculture in the humid tropics." *Naturwissenschaften* no. 88 (1):37-41.
- Goyal, M., R. Dhawan, and M. Bhagat. 2008. "Adsorption of dimethyl sulfide vapors by activated carbons." *Colloids and Surfaces a-Physicochemical and Engineering Aspects* no. 322 (1-3):164-169.
- Gustafsson, O., T. D. Bucheli, Z. Kukulska, M. Andersson, C. Largeau, J. N. Rouzaud, C. M. Reddy, and T. I. Eglinton. 2001. "Evaluation of a protocol for the quantification of black carbon in sediments." *Global Biogeochemical Cycles* no. 15 (4):881-890.
- Gustafsson, O., and P. M. Gschwend. 1997. "Soot as a strong partition medium for polycyclic aromatic hydrocarbons in aquatic systems." *Molecular Markers in Environmental Geochemistry* no. 671:365-381.
- Gustafsson, O., F. Haghseta, C. Chan, J. MacFarlane, and P.M. Gschwend. 1997. "Quantification of the dilute sedimentary soot phase: Implications for PAH speciation and bioavailability." *Environmental Science & Technology* no. 31 (1):203-209.
- Hall, S. J., B. Ahmed, P. Ortiz, R. Davies, R. A. Sponseller, and N. B. Grimm. 2009. "Urbanization alters soil microbial functioning in the Sonoran desert." *Ecosystems* no. 12 (4):654-671.
- Hamer, U., B. Marschner, S. Brodowski, and W. Amelung. 2004. "Interactive priming of black carbon and glucose mineralisation." *Organic Geochemistry* no. 35 (7):823-830.
- Hamilton, G.A., and H.E. Hartnett. 2013. "Soot black carbon concentration and isotopic composition in soils from an arid urban ecosystem." *Organic Geochemistry* no. 59:87-94.
- Hammes, K., M. W. I. Schmidt, R. J. Smernik, L. A. Currie, W. P. Ball, T. H. Nguyen, P. Louchouart, S. Houel, O. Gustafsson, M. Elmquist, G. Cornelissen, J. O. Skjemstad, C. A. Masiello, J. Song, P. Peng, S. Mitra, J. C. Dunn, P. G. Hatcher, W. C. Hockaday, D. M. Smith, C. Hartkopf-Froeder, A. Boehmer, B. Luer, B. J. Huebert, W. Amelung, S. Brodowski, L. Huang, W. Zhang, P. M. Gschwend, D. X. Flores-Cervantes, C. Largeau, J. N. Rouzaud,

- C. Rumpel, G. Guggenberger, K. Kaiser, A. Rodionov, F. J. Gonzalez-Vila, J. A. Gonzalez-Perez, J. M. de la Rosa, D. A. C. Manning, E. Lopez-Capel, and L. Ding. 2007. "Comparison of quantification methods to measure fire-derived (black/elemental) carbon in soils and sediments using reference materials from soil, water, sediment and the atmosphere." *Global Biogeochemical Cycles* no. 21 (3). GB3016.
- Han, Y. M., J. R. Marlon, J. J. Cao, Z. D. Jin, and Z. S. An. 2012. "Holocene linkages between char, soot, biomass burning and climate from Lake Daihai, China." *Global Biogeochemical Cycles* no. 26 (9). GB4017
- Hedges, J. I., B. A. Bergamaschi, and R. Benner. 1993. "Comparative analysis of DOC and DON in natural-waters." *Marine Chemistry* no. 41 (1-3):121-134.
- Hedges, J. I., G. Eglinton, P. G. Hatcher, D. L. Kirchman, C. Arnosti, S. Derenne, R. P. Evershed, I. Kogel-Knabner, J. W. de Leeuw, R. Littke, W. Michaelis, and J. Rullkotter. 2000. "The molecularly-uncharacterized component of nonliving organic matter in natural environments." *Organic Geochemistry* no. 31 (10):945-958.
- Hilscher, A., and H. Knicker. 2011. "Carbon and nitrogen degradation on molecular scale of grass-derived pyrogenic organic material during 28 months of incubation in soil." *Soil Biology & Biochemistry* no. 43 (2):261-270.
- Hilscher, A., K. Heister, C. Siewert, and H. Knicker. 2009. "Mineralisation and structural changes during the initial phase of microbial degradation of pyrogenic plant residues in soil." *Organic Geochemistry* no. 40 (3):332-342.
- Hockaday, W. C., A. M. Grannas, S. Kim, and P. G. Hatcher. 2007. "The transformation and mobility of charcoal in a fire-impacted watershed." *Geochimica et Cosmochimica Acta* no. 71 (14):3432-3445.
- IPCC. 2007. "Climate Change 2007: Synthesis Report. Contribution of Working Groups I, II and III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change" IPCC, Geneva, Switzerland.
- Jaffé, R., Y. Ding, J. Niggemann, A.V. Vähätalo, A. Stubbins, R.G.M. Spencer, J. Campbell, and T. Dittmar. 2013. "Global Charcoal Mobilization from Soils via Dissolution and Riverine Transport to the Oceans." *Science* no. 340 (6130):345-347.
- Kaye, J. P., S. E. Eckert, D. A. Gonzales, J. O. Allen, S. J. Hall, R. A. Sponseller, and N. B. Grimm. 2011. "Decomposition of urban atmospheric carbon in Sonoran Desert soils." *Urban Ecosystems* no. 14 (4):737-754.
- Majcher, E. H., J. Chorover, J. M. Bollag, and P. M. Huang. 2000. "Evolution of CO<sub>2</sub> during birnessite-induced oxidation of C-14-labeled catechol." *Soil Science Society of America Journal* no. 64 (1):157-163.

- Mao, J. D., R. L. Johnson, J. Lehmann, D. C. Olk, E. G. Neves, M. L. Thompson, and K. Schmidt-Rohr. 2012. "Abundant and stable char residues in soils: implications for soil fertility and carbon sequestration." *Environmental Science & Technology* no. 46 (17):9571-9576.
- Maricopa Association of Governments. 2010. Regional Transportation Plan. Phoenix, AZ. Maricopa Association of Governments.
- Masiello, C.A. 2004. "New directions in black carbon organic geochemistry." *Marine Chemistry* no. 92:201-213.
- Middelburg, J. J., J. Nieuwenhuize, and P. van Breugel. 1999. "Black carbon in marine sediments." *Marine Chemistry* no. 65 (3-4):245-252
- O'Connor, J. T., T. O'Connor, and R. Twait. 2009. *Water Treatment Plan Evaluations and Operations*. New York: John Wiley & Sons.
- Osburn, C. L., L. T. Handsel, M. P. Mikan, H. W. Paerl, and M. T. Montgomery. 2012. "Fluorescence tracking of dissolved and particulate organic matter quality in a river-dominated estuary." *Environmental Science & Technology* no. 46 (16):8628-8636.
- Parton, W. J., D. S. Schimel, C. V. Cole, and D. S. Ojima. 1987. "Analysis of factors controlling soil organic-matter levels in great-plains grasslands." *Soil Science Society of America Journal* no. 51 (5):1173-1179.
- Poot, A., J. T. K. Q., H. Veld, and A.A. Koelmans. 2009. "Quantification methods of Black Carbon: Comparison of Rock-Eval analysis with traditional methods." *Journal of Chromatography A* no. 1216 (3):613-622.
- Preston, C. M., and M. W. I. Schmidt. 2006. "Black (pyrogenic) carbon: a synthesis of current knowledge and uncertainties with special consideration of boreal regions." *Biogeosciences* no. 3 (4):397-420.
- Ringuet, J., A. Albinet, E. Leoz-Garziandia, H. Budzinski, and E. Villenave. 2012. "Reactivity of polycyclic aromatic compounds (PAHs, NPAHs and OPAHs) adsorbed on natural aerosol particles exposed to atmospheric oxidants." *Atmospheric Environment* no. 61:15-22.
- Schmidt, M. W. I., and A. G. Noack. 2000. "Black carbon in soils and sediments: Analysis, distribution, implications, and current challenges." *Global Biogeochemical Cycles* no. 14 (3):777-793.
- Sharp, J. H. 1997. "Marine dissolved organic carbon: Are the older values correct?" *Marine Chemistry* no. 56 (3-4):265-277.

- Sharp, J. H., R. Benner, L. Bennett, C. A. Carlson, R. Dow, and S. E. Fitzwater. 1993. "Reevaluation of the high-temperature combustion and chemical oxidation measurements of dissolved organic-carbon in seawater." *Limnology and Oceanography* no. 38 (8):1774-1782.
- Sharp, J.H. 1993. "The dissolved organic carbon controversy: an update." *Oceanography* no.6: 45-50.
- Sinsabaugh, R. L., C. L. Lauber, M. N. Weintraub, B. Ahmed, S. D. Allison, C. Crenshaw, A. R. Contosta, D. Cusack, S. Frey, M. E. Gallo, T. B. Gartner, S. E. Hobbie, K. Holland, B. L. Keeler, J. S. Powers, M. Stursova, C. Takacs-Vesbach, M. P. Waldrop, M. D. Wallenstein, D. R. Zak, and L. H. Zeglin. 2008. "Stoichiometry of soil enzyme activity at global scale." *Ecology Letters* no. 11 (11):1252-1264.
- Skjemstad, J. O., D. C. Reicosky, A. R. Wilts, and J. A. McGowan. 2002. "Charcoal carbon in U.S. agricultural soils." *Soil Science Society of America Journal* no. 66 (4):1249-1255.
- Stedmon, C. A., S. Markager, and R. Bro. 2003. "Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy." *Marine Chemistry* no. 82 (3-4):239-254.
- Steinbeiss, S., G. Gleixner, and M. Antonietti. 2009. "Effect of biochar amendment on soil carbon balance and soil microbial activity." *Soil Biology & Biochemistry* no. 41 (6):1301-1310.
- Stubbins, A., J. Niggemann, and T. Dittmar. 2012. "Photo-lability of deep ocean dissolved black carbon." *Biogeosciences* no. 9 (5):1661-1670.
- Stursova, M., and R. L. Sinsabaugh. 2008. "Stabilization of oxidative enzymes in desert soil may limit organic matter accumulation." *Soil Biology & Biochemistry* no. 40 (2):550-553.
- U.S. Department of Commerce. United States Census. Washington D.C.: United States Government Printing Office, 2010.
- Wickland, K. P., J. C. Neff, and G. R. Aiken. 2007. "Dissolved organic carbon in Alaskan boreal forest: Sources, chemical characteristics, and biodegradability." *Ecosystems* no. 10 (8):1323-1340.
- Xu, N., H. F. Wilson, J. E. Saiers, and M. Entz. 2013. "Effects of crop rotation and management system on water-extractable organic matter concentration, structure, and bioavailability in a chernozemic Agricultural Soil." *Journal of Environmental Quality* no. 42 (1):179-190.

Zimmerman, A. R. 2010. "Abiotic and microbial oxidation of laboratory-produced black carbon (biochar)." *Environmental Science & Technology* no. 44 (4):1295-1301.



Table 5.1. PARAFAC-derived chemical composition (percent, %), of soot BC extracts before and after biological degradation.

Inoculum Source	Soot BC Source	PARAFAC Components*											
		Oxidized Quinones (% contribution)			Reduced Quinones (% contribution)			Amino Acid-like components (% contribution)			Unknown components (% contribution)		
		Initial	Final	% change <sup>a</sup>	Initial	Final	% change <sup>a</sup>	Initial	Final	% change <sup>a</sup>	Initial	Final	% change <sup>a</sup>
Desert	Desert	41.6	42.0	1.0	22.2	22.2	NC <sup>^</sup>	2.8	2.6	-7.1	33.5	33.3	-0.6
Urban	Urban	41.6	42.5	2.2	20.6	20.5	-0.5	3.6	3.4	-5.5	34.1	33.5	-1.7
Desert	Urban	40.8	42.9	5.1	17.0	18.2	7.1	3.7	3.9	5.4	38.5	35.0	-9.1
Urban	Desert	41.7	42.5	1.9	23.7	23.7	NC <sup>^</sup>	3.0	3.0	NC <sup>^</sup>	32.6	31.8	-2.5

\*the PARAFAC components are those from the Cory & McKnight (2005) model.

<sup>^</sup>NC = No Change

<sup>a</sup>% change = (Final contribution – Initial contribution / Initial contribution) • 100

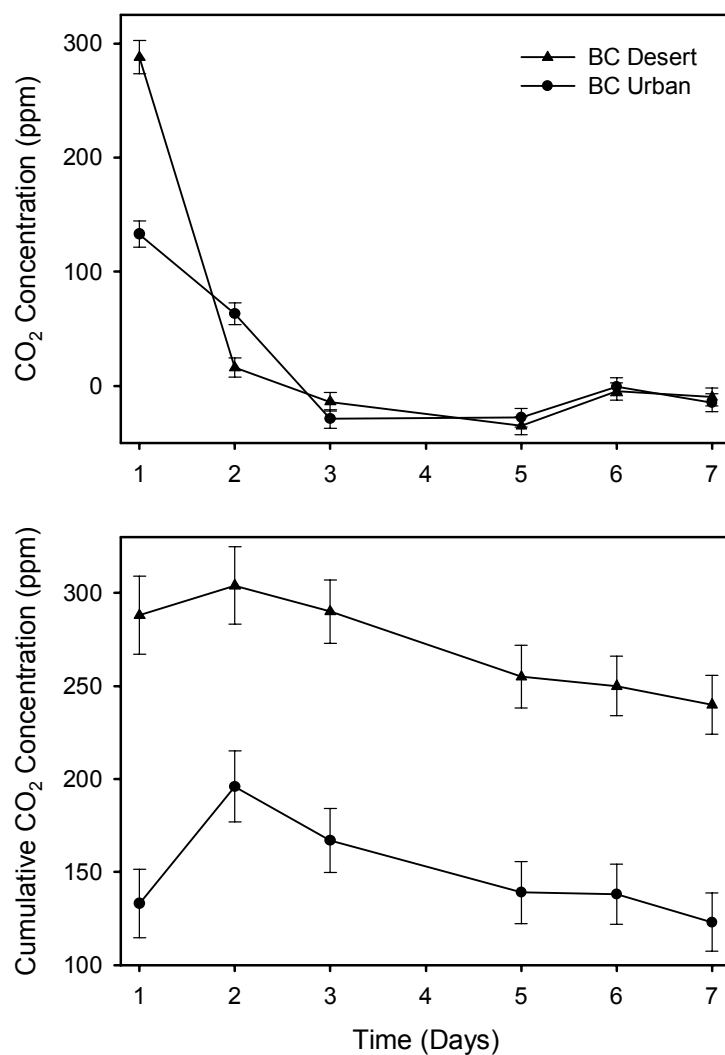


Figure 5.1. Daily (top) and cumulative (bottom) CO<sub>2</sub> concentrations in abiotic experiments with soot BC extracts and no microbial inoculum. Daily (top) CO<sub>2</sub> concentrations have been background corrected; negative values indicate vial headspace CO<sub>2</sub> concentration less than the ambient laboratory CO<sub>2</sub> concentration. Cumulative CO<sub>2</sub> production is calculated by summing the daily CO<sub>2</sub> values up to each time point. Triangles (▲) are data from desert soil soot BC extracts and circles (●) are from urban soil soot BC extracts. Error bars are  $\pm 1$  standard deviation of the mean of triplicate measurements.

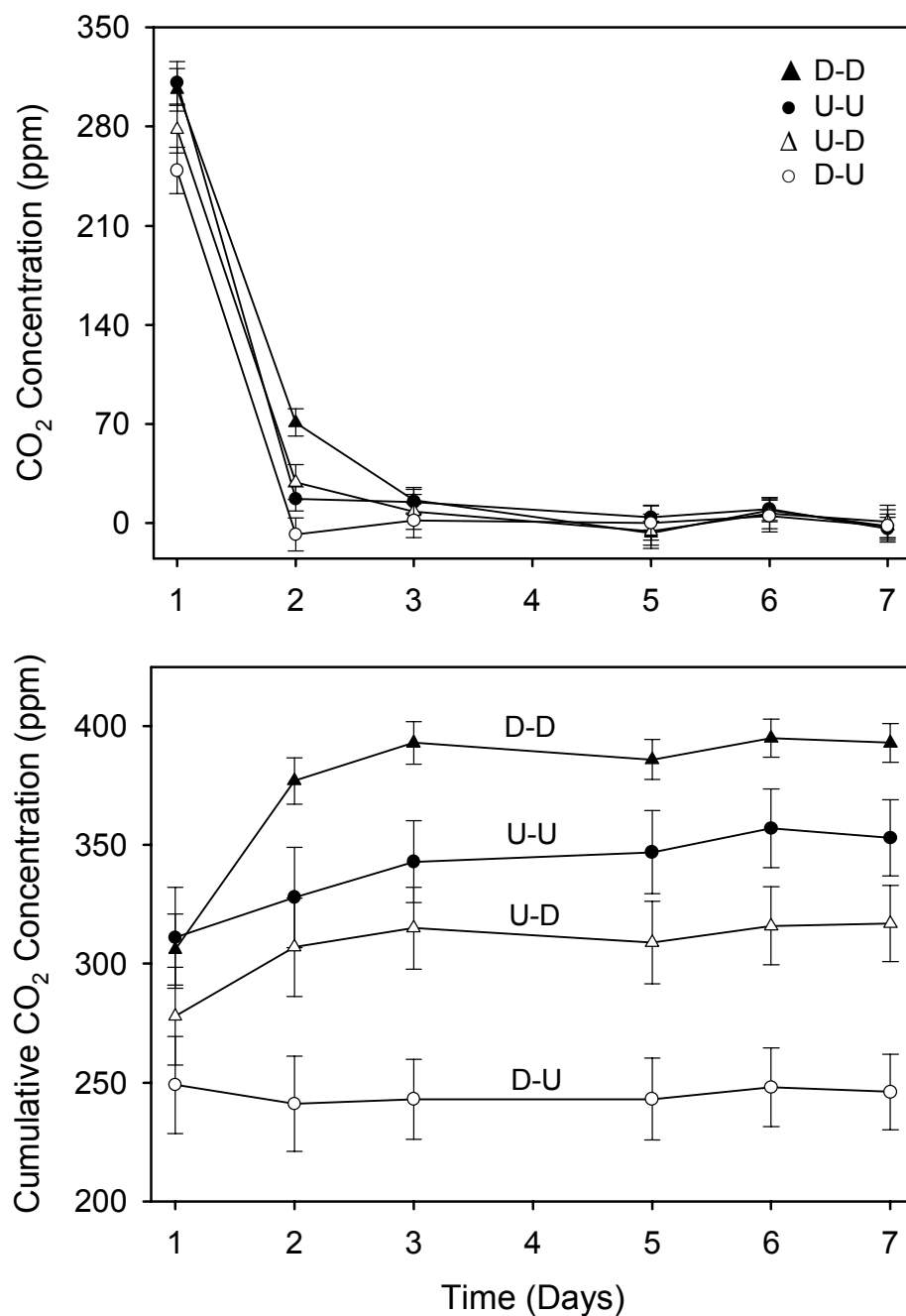


Figure 5.2. Daily (top) and cumulative (bottom) CO<sub>2</sub> concentrations in incubations using a microbial inoculum and soil soot BC extract. Triangles are data from incubations using desert soot BC extracts (▲, △: desert) and circles are data from incubations using urban soot BC extracts (●, ○: urban). Closed symbols (▲, ●) are data from incubations where the soot BC extracts and the inocula are from the same land-use type. Open symbols (△, ○) are data from incubations where the soot BC extracts and the microbial inocula from different (or reciprocal) land-use types. Error bars are ±1 standard deviation of the mean of triplicate measurements.

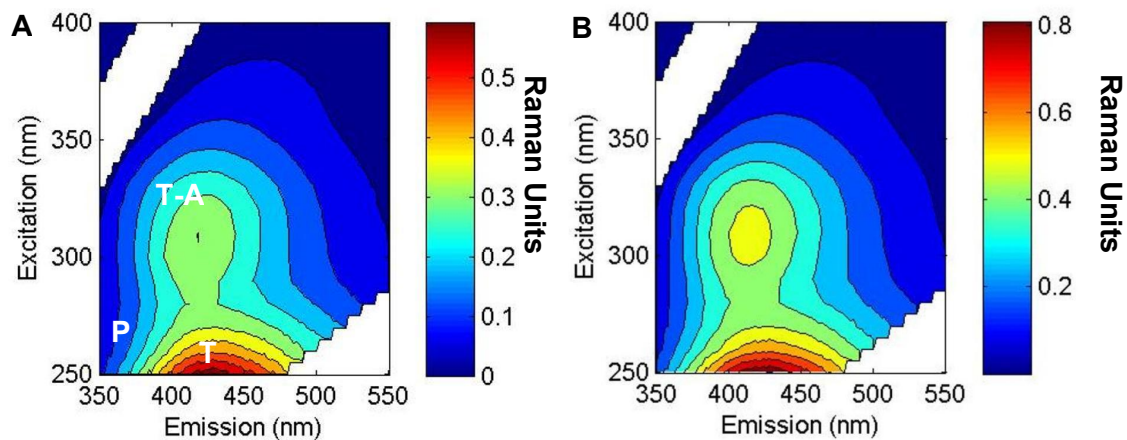


Figure 5.3. Contour plots of fluorescence intensity (Raman units) in initial biotic samples from the D<sub>i</sub>-D<sub>e</sub> experiment (A) and the U<sub>i</sub>-U<sub>e</sub> experiment (B). Diagnostic areas in excitation-emission space are labeled in panel A and represent protein (P), high molecular weight terrestrial (T), and high molecular weight terrestrial and aromatic (T-A) sources, respectively. Note the differences in the color scales for fluorescence intensity.

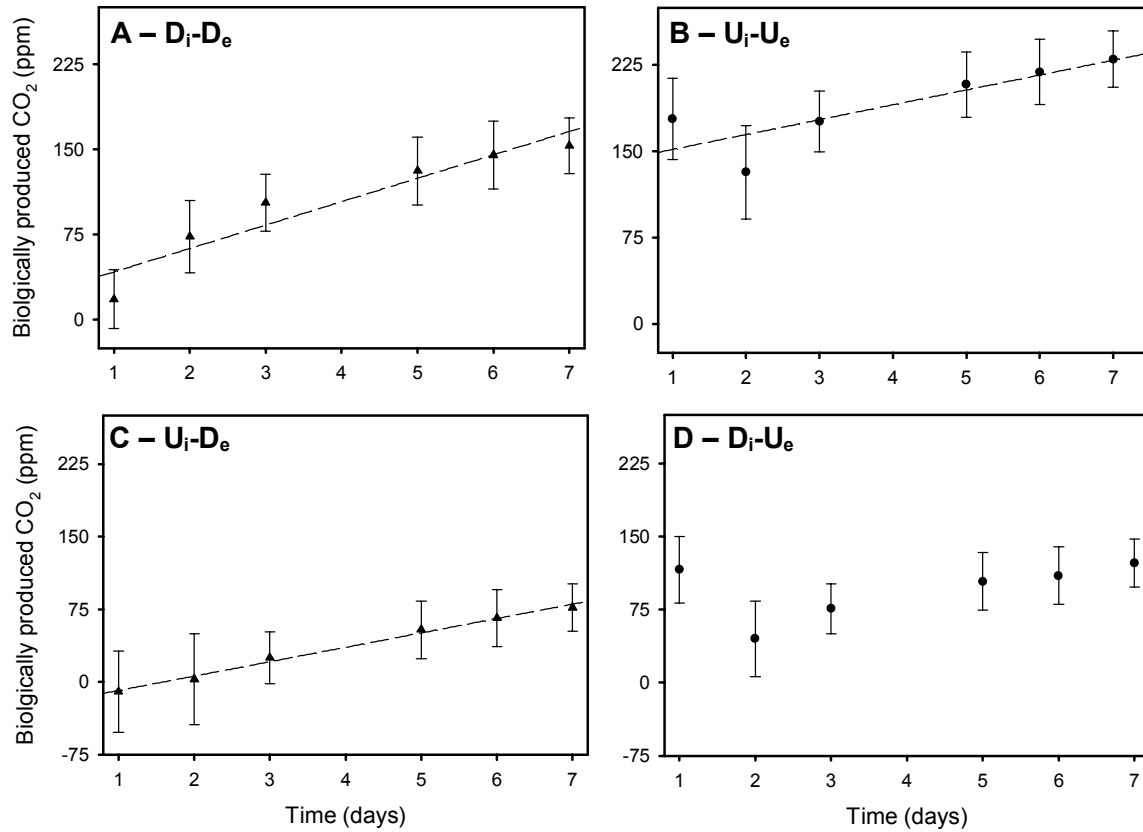


Figure 5.4. Biologically produced CO<sub>2</sub> in incubations with desert soot BC extracts (▲: A and C) and urban soot BC extracts (●: B and D) calculated as the difference between cumulative CO<sub>2</sub> production in the biotic and abiotic incubations. A and B are incubations where the microbial inoculum and the soil soot BC extract were from the same soils; C and D are incubations where the microbial inoculum and the soil soot BC extract are from soils with different land-use types (i.e., reciprocal experiments). Dashed lines are least-squares fits and all slopes are statistically significant ( $p < 0.05$ ) except for in D ( $p > 0.05$ ). Error bars are fully propagated errors ( $\pm 1$  standard deviation).

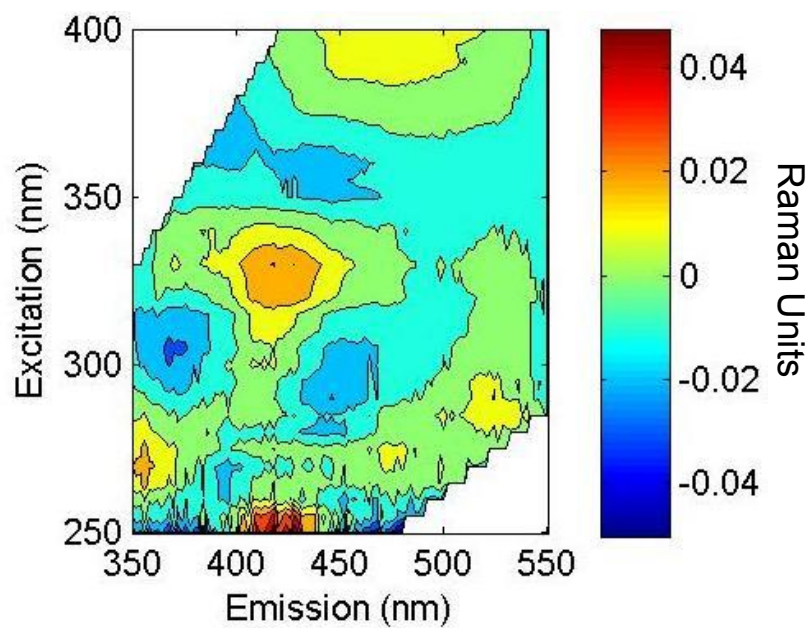


Figure 5.5. Residual EEM from the D<sub>i</sub>-D<sub>e</sub> experiment (day 1). The residual is the difference between the actual and modeled EEM. Units on the color scale are Raman units.

## Chapter 6

### CONCLUSION

#### Conclusion

The work presented in this dissertation was inspired by a fairly simple, yet puzzling concept: globally, the known sources of black carbon heavily outweigh the known sinks of black carbon. If this were true, BC would be building up in the environment, and there would be more BC than OC in some reservoirs (i.e., soils). This is not the case, which suggests there are unknown or underestimated BC sinks. At the onset of this project, the best constrained black carbon sink was deposition in ocean sediments; and yet, the flux of BC to ocean sediments cannot account for the amount of BC produced. My goal was to quantify soot BC and investigate possible soot BC degradation processes in soil because soil has been suggested as a possible temporary reservoir that is not well quantified by the black carbon budget. My goal was not to remedy the budget imbalance; rather, I focused on quantifying soot BC in soil. The first phase of my project investigated soot BC in central AZ (Phoenix) because little was known about soot BC in urban soil and I had access to a unique, spatially-explicit set of soil samples from the CAP-LTER. These soil samples included a range of different land-use types, which proved to be an important factor in understanding how soot BC is distributed throughout the central AZ region. The second phase was an investigation of the degradation of soot BC by a variety of, to date, understudied yet environmentally relevant mechanisms. I focused on photo-oxidation, aqueous solubilization, and microbial oxidation because they are known to degrade soil organic carbon, but very little is known about how these processes affect soot BC in soils.

Black carbon is a heterogeneous mixture of materials and, therefore, it can only be described by general physical and chemical characteristics. I focused on a well-constrained sub-classification that I call soot BC; however, soot BC is still a classification of heterogeneous substances, albeit less diverse than the general term “black carbon.” It is important to note that my results are specific for soot BC and not for all the forms of BC found in central AZ soils. It is also likely that not all soot BC is degraded by the same processes or at the same rate. None-the-less, my work has made significant advances toward an understanding of how soot BC reacts and is degraded in the desert environment. This work provides a specific description of the characteristics of soot BC and distinguishes it from other combustion byproducts. Soot BC is reactive on short timescales and has reactivity that is more similar to non-soot BC material (i.e., biochar, charcoal) than previously thought. In regions with low soil organic carbon and/or anthropogenic activity, soot BC can be a large fraction of the total soil organic matter. Because soot BC is reactive and can make up a large portion of the soil organic carbon in central AZ, soot BC is a key feature in soil biogeochemical process in this desert region. This also implies that soot BC may be an important component of soil carbon and thus soil biodegradation in desert soils, generally. Not only does degradation of soot BC suggest that it is reactive, but inherent chemical alteration also occurs when soot BC is degraded. This implies that detailed chemical characterization is integral to assessing soot BC reactivity.

As with any project, my dissertation work comprised more analyses and more data than could be presented within the narrative structure of the chapters. These data could reveal a promising direction for future work, so I include them here.



## Chemical characterization of soil soot BC

### *NMR*

I conducted preliminary characterization of soil soot BC using solid and liquid nuclear magnetic resonance (NMR;  $^1\text{H}$  and  $^{13}\text{C}$ ). In preparation for solid state  $^{13}\text{C}$ -NMR, I demineralized chemo-thermo oxidation-treated soil with hydrofluoric acid, thus increasing the soot BC concentration in the solid sample. Cross polarization and magic angle spinning were implemented to reduce slow spin-lattice relaxation times and line broadening. Liquid-state  $^1\text{H}$ -NMR was completed by performing an aqueous extraction of CTO375-treated soil with deuterated water ( $\text{D}_2\text{O}$ ). Since  $\text{D}_2\text{O}$  is hydroscopic, these extractions were carried out in a glove box under  $\text{N}_2$  atmosphere. Solid-state  $^{13}\text{C}$ -NMR indicated the presence of aromatic and aliphatic hydrocarbons with low contribution from additional functional groups (Figure 6.1). However, acceptable peak resolution was difficult to attain because of low carbon content in soils even after demineralization in hydrofluoric acid. Also the heterogeneous nature of soot BC lends itself to peak overlap which makes distinguishing specific functional groups difficult. Liquid-state  $^1\text{H}$ -NMR of  $\text{D}_2\text{O}$  extracted soot BC and bulk OC demonstrated a variety of peaks that indicate the presence of hydrogen atoms bound to alkane, alkene, and alkyne functional groups (Figure 6.2). There are additional peaks that represent hydrogen atoms bound to aromatic and carbonyl carbon. Peaks that appear in bulk OC samples also appear in soot BC samples at lower intensities. Water ( $\text{H}_2\text{O}$ ) was difficult to keep out of the extract indicated by the relatively broad peak at a chemical shift of  $\sim 5$  ppm (Figure 6.2). Both solid-state  $^{13}\text{C}$ - and liquid-state  $^1\text{H}$ -NMR used here indicated the presence of functional groups that are expected in soot BC. I ultimately chose to assess the

chemical functional group composition of my samples using FTIR and fluorescence analysis rather than NMR because of FTIR and fluorescence have shorter sample preparation times ( $\leq 1$  h for FTIR and fluorescence versus  $\geq 1$  day for NMR), instrument run time ( $\leq 1$ h for FTIR and fluorescence versus  $\geq 1$  day for NMR), and lower cost, without sacrificing the chemical specificity necessary for characterization work.

### *TEM*

Transmission electron microscopy (TEM) has been utilized to investigate the physical characteristics of soot aerosol particles (Michelsen et al. 2007 and others). I used TEM to image the material obtained from aqueous extracts of soil soot BC. Aqueous extractions of soot BC were dried on a Cu grid. While nano-sized particles were observed, the particle shapes did not resemble those of typical soot aerosol (Michelsen et al. 2007; Figure 6.3). It is not clear that typical soot aerosol particles would be expected in aqueous extracts of soil soot BC. Soils are clearly not reservoirs of freshly produced soot BC. If the soot BC is ‘aged’ in a soil reservoir, it is possible that there will be morphological as well as chemical changes that would alter the appearance of soot BC under TEM. If TEM is going to be considered a useful tool for investigating the physical characteristics of soot BC in soil or aqueous phase, further standardization is needed.

### Soot BC variations among urban residential landscape types

As part of my thesis work, I had the opportunity to direct the research project for undergraduate honors thesis completed by Marie Nahlik that assessed the distribution of soot BC in urban residential soils (Nahlik 2012). Ms. Nahlik’s

research focused on soot BC concentrations in urban residential (both xeric and mesic landscapes) and urban non-residential soils. She evaluated the relationship between soil soot BC concentrations and nearby residential home values. The hypotheses guiding this work were 1) that soot BC concentration is higher in non-residential soils than in residential soils and 2) that soot BC concentration is negatively correlated with nearby residential home value. Soot BC concentrations in soil were found to be statistically higher in non-residential soil than in residential soil (both for mesic and xeric landscapes;  $p < 0.05$ ). This is likely due to non-residential soils being located relatively closer to major roads or industrial areas. There was no correlation found between soot BC concentration and residential home value ( $p > 0.05$ ) when including all sample sites. However, removing statistically outlying data points reveal a slightly negative correlation between soot BC concentration and residential home value ( $p < 0.1$ ). The pattern suggests that people who live in areas with lower home values may be exposed to higher concentrations of soot BC. The type of landscaping present in the urban residential areas studied (i.e., xeric and mesic landscapes) did not correspond to any difference in soot BC concentration ( $p > 0.05$ ). The opportunity to serve as a mentor to Ms. Nahlik aided my own research by providing additional soot BC concentration and isotopic composition data as well as an opportunity to discuss my research with a capable undergraduate student.

## Future Work

While I learned a great deal about soot BC dynamics in central AZ, as with any research project many additional questions have arisen from my work. These

questions will hopefully drive future research projects. Specifically, a future direction that interests me is the detection of soot BC in urban and rural surface waters. I demonstrated that soot BC can be solubilized in water and can subsequently undergo microbial degradation in the aqueous phase. I demonstrate that the amount of CO<sub>2</sub> produced by soot BC microbial degradation is land-use dependant (more CO<sub>2</sub> produced from incubations containing urban soil microbial communities and urban soot BC than desert soil microbial communities and desert soot BC); therefore, soot BC residence times in surface water may be affected by land-use. Coupling concentration and rate of removal data for soot BC from surface water would allow a residence time estimation. The imbalance in the global BC budget indicates that, along with soils, wetlands and rivers could also contain a significant amount of BC as a portion of the dissolved organic carbon. These surface waters could act as storage reservoirs for soot BC especially in urban areas, but little is known about how much or how long soot BC is stored in these reservoirs. Some studies have started to investigate dissolved BC (DBC; Jaffé et al. 2013; Dittmar et al. 2012). However, methodological and definitional problems, similar to those that plague studies of solid-phase black carbon, have and will continue to arise and must be addressed. Quantification of soot BC in surface waters in major urban areas could demonstrate the importance of surface water reservoirs to the BC budget. Fluorescence analysis and parallel factor analysis (PARAFAC), tools used in my work, would be useful in determining the chemical composition, and predict chemical reactivity, of solubilized soot BC in surface waters.

The research question that could drive this work are:

- (1) *Do concentrations of solubilized soot BC differ in urban and rural surface waters?*
- (2) *Are the residence times for solubilized soot BC affected by adjacent land-use type?*

To answer these questions, the amount of solubilized soot BC and the rate of input or output must be determined for a given surface water body. Flores-Cervantes et al. (2007) described a method that detects soot in aqueous suspended particulate organic matter by observing fluorescence loss in pyrene spiked samples and that could be implemented in central AZ. Additionally, more data on rates of degradation of solubilized soot BC could be collected from microbial or photochemical degradation experiments, similar to the ones described in this dissertation.

#### Final thoughts

My work has demonstrated that soils are reservoirs for the soot BC fraction of black carbon. Moreover, in urban environments and desert environments, soils can store quite large amounts of soot BC. The process studies I have conducted demonstrate that soils not only store soot BC, but also provide locations for the chemical and biological degradation of soot BC. My results indicate that soot BC, once thought to be among the most recalcitrant types of BC, can be degraded by a range of processes on relatively short (laboratory) time scales. This work opens the door for further investigation of soot BC's effect on carbon cycling and ecological processes in other desert and urban ecosystems.

## Literature Cited

- Dittmar, T., C. E. de Rezende, M. Manecki, J. Niggemann, A. R. C. Ovalle, A. Stubbins, and M. C. Bernardes. 2012. "Continuous flux of dissolved black carbon from a vanished tropical forest biome." *Nature Geoscience* no. 5 (9):618-622.
- Flores-Cervantes, D. X., C. M. Reddy, and P. M. Gschwend. 2009. "Inferring Black Carbon Concentrations in Particulate Organic Matter by Observing Pyrene Fluorescence Losses." *Environmental Science & Technology* no. 43 (13):4864-4870.
- Jaffé, R., Y. Ding, J. Niggemann, A. V. Vähätalo, A. Stubbins, R. G. M. Spencer, J. Campbell, and T. Dittmar. 2013. "Global Charcoal Mobilization from Soils via Dissolution and Riverine Transport to the Oceans." *Science* no. 340 (6130):345-347.
- Michelsen, H. A., A. V. Tivanski, M. K. Gilles, L. H. van Poppel, M. A. Dansson, and P. R. Buseck. 2007. "Particle formation from pulsed laser irradiation of soot aggregates studied with a scanning mobility particle sizer, a transmission electron microscope, and a scanning transmission X-ray microscope." *Applied Optics* no. 46 (6):959-977.
- Nahlik, M. 2012. "Quantifying black carbon in urban soils in Phoenix." Undergraduate Honor's thesis, Arizona State University.

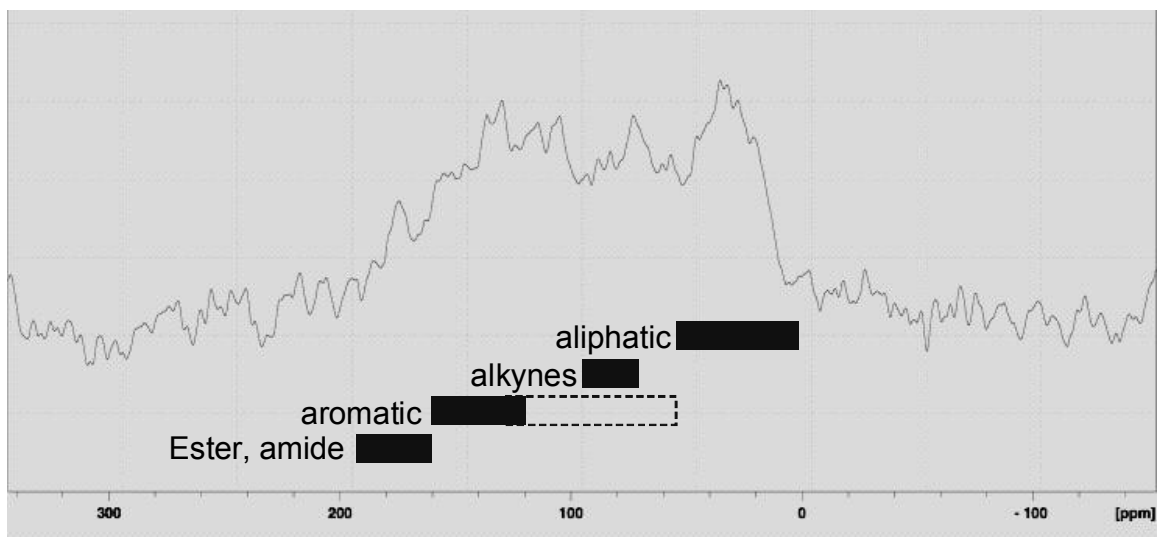


Figure 6.1. Solid-state  $^{13}\text{C}$ -NMR of soot BC from a desert soil demonstrates chemical shifts that indicate the presence of various  $^{13}\text{C}$  functional groups.

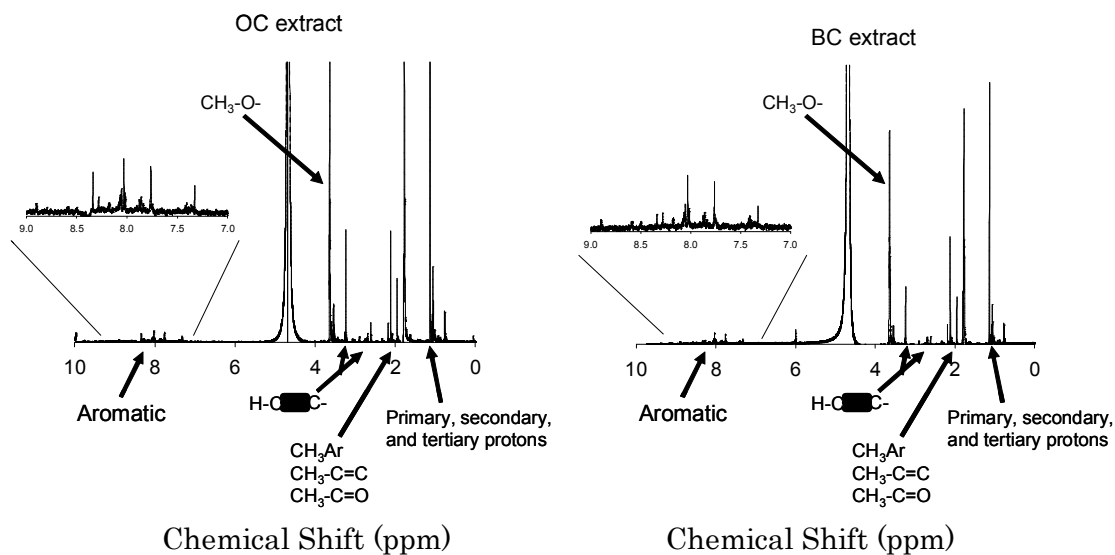


Figure 6.2. Liquid-state  $^1\text{H}$ -NMR of bulk OC and soot BC. Samples were extracted in  $\text{D}_2\text{O}$  and indicate multiple hydrogen atom molecular environments. Peak labels indicate the functional groups represented by the respective chemical shifts.



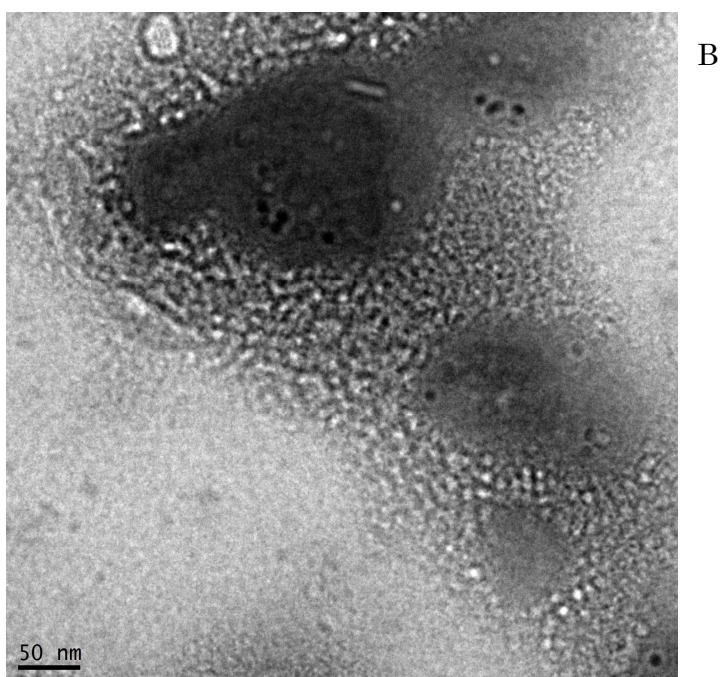
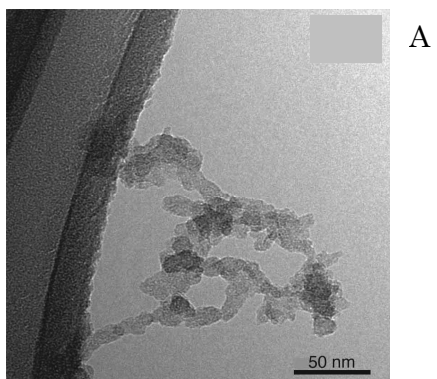


Figure 6.3. Transmission electron microscopy (TEM) images of atmospheric soot particles from Michelsen et al. 2007 (A) and from soil soot BC (B).

Table 6.1. Soot BC concentration in residential xeric, residential mesic, and in non-residential institutional soil.

Land use type	Soot BC (wt. %)
Urban; Residential; Single family; Xeric (n=6)	$0.18 \pm 0.11$ ,a
Urban; Residential; Single family; Mesic (n=6)	$0.19 \pm 0.14$ ,a
Urban; Non- Residential; Institutional (n=4)	$0.46 \pm 0.47$ ,b

a,b – indicator of statistically similar (same letter) or statistically different (different letter) averages.

## REFERENCES

- Accardi-Dey, A., and P. M. Gschwend. 2002. "Assessing the combined roles of natural organic matter and black carbon as sorbents in sediments." *Environmental Science & Technology* no. 36 (1):21-29.
- Adachi, K., and P. R. Buseck. 2008. "Internally mixed soot, sulfates, and organic matter in aerosol particles from Mexico City." *Atmospheric Chemistry & Physics* no. 8 (21):6469-6481.
- Adachi, K., S. H. Chung, and P. R. Buseck. 2010. "Shapes of soot aerosol particles and implications for their effects on climate." *Journal of Geophysical Research-Atmospheres* no. 115. D15206.
- Alexis, M. A., C. Rumpel, H. Knicker, J. Leifeld, D. Rasse, N. Pechot, G. Bardoux, and A. Mariotti. 2010. "Thermal alteration of organic matter during a shrubland fire: A field study." *Organic Geochemistry* no. 41 (7):690-697.
- Argyropoulos, D. S., and Y. J. Sun. 1996. "Photochemically induced solid-state degradation, condensation, and rearrangement reactions in lignin model compounds and milled wood lignin." *Photochemistry and Photobiology* no. 64 (3):510-517.
- Baldock, J. A., and R. J. Smernik. 2002. "Chemical composition and bioavailability of thermally, altered *Pinus resinosa* (Red Pine) wood." *Organic Geochemistry* no. 33 (9):1093-1109.
- Bird, M. I., and D. R. Grocke. 1997. "Determination of the abundance and carbon isotope composition of elemental carbon in sediments." *Geochimica et Cosmochimica Acta* no. 61 (16):3413-3423.
- Bird, M. I., and J. A. Cali. 1998. "A million-year record of fire in sub-Saharan Africa." *Nature* no. 394 (6695):767-769.
- Bird, M. I., and P. L. Ascough. 2012. "Isotopes in pyrogenic carbon: A review." *Organic Geochemistry* no. 42 (12):1529-1539.
- Bird, M. I., C. Moyo, E. M. Veenendaal, J. Lloyd, and P. Frost. 1999. "Stability of elemental carbon in a savanna soil." *Global Biogeochemical Cycles* no. 13 (4):923-932.
- Bohn, H. L., B. L. McNeal, and G. A. O'Connor. 2001. "Soil Chemistry." New York: *John Wiley & Sons*.
- Burdige, D. J., S. W. Kline, and W. H. Chen. 2004. "Fluorescent dissolved organic matter in marine sediment pore waters." *Marine Chemistry* no. 89 (1-4):289-311.

- Cachier, H., C. Liousse, P. Buatmenard, and A. Gaudichet. 1995. "Particulate content of savanna fire emissions." *Journal of Atmospheric Chemistry* no. 22 (1-2):123-148.
- Cachier, H., P. Buatmenard, M. Fontugne, and J. Rancher. 1985. "Source terms and source strengths of the carbonaceous aerosol in the tropics." *Journal of Atmospheric Chemistry* no. 3 (4):469-489.
- Central Arizona-Phoenix Long-term Ecological Research. 2010. "Site Description." Accessed March 15. <http://caplter.asu.edu/about/site-description/>
- Cheng, C. H., and J. Lehmann. 2009. "Ageing of black carbon along a temperature gradient." *Chemosphere* no. 75 (8):1021-1027.
- Cheng, C. H., J. Lehmann, and M. H. Engelhard. 2008. "Natural oxidation of black carbon in soils: Changes in molecular form and surface charge along a climosequence." *Geochimica et Cosmochimica Acta* no. 72 (6):1598-1610.
- Clark, J. S., and W. A. I. Patterson. 1997. Background and Local Charcoal in Sediments: Scales of Fire Evidence in the Paleorecord, Sediment Records of biomass burning and global change Berlin: *Springer-Verlag*.
- Coble, P. G. 1996. "Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy." *Marine Chemistry* no. 51 (4):325-346.
- Coble, P. G., C. E. Del Castillo, and B. Avril. 1998. "Distribution and optical properties of CDOM in the Arabian Sea during the 1995 Southwest Monsoon." *Deep-Sea Research Part II i-Topical Studies in Oceanography* no. 45 (10-11):2195-2223.
- Coble, P.G., S.A. Green, N.V. Blough, and R.B. Gagosian. 1990. "Characterization of dissolved organic-matter in the Black sea by fluorescence spectroscopy." *Nature* no. 348 (6300):432-435.
- Cory, R. M., and D. M. McKnight. 2005. "Fluorescence spectroscopy reveals ubiquitous presence of oxidized and reduced quinones in dissolved organic matter." *Environmental Science & Technology* no. 39 (21):8142-8149.
- Czimczik, C. I., and C. A. Masiello. 2007. "Controls on black carbon storage in soils." *Global Biogeochemical Cycles* no. 21. GB3005
- Czimczik, C. I., C. M. Preston, M. W. I. Schmidt, R. A. Werner, and E. D. Schulze. 2002. "Effects of charring on mass, organic carbon, and stable carbon isotope composition of wood." *Organic Geochemistry* no. 33 (11):1207-1223.

- Das, O., Y. Wang, and Y.P. Hsieh. 2010. "Chemical and carbon isotopic characteristics of ash and smoke derived from burning of C3 and C4 grasses." *Organic Geochemistry* no. 41 (3):263-269.
- Descoux, S., V. Chanudet, H. Poilve, and A. Gregoire. 2011. "Co-assessment of biomass and soil organic carbon stocks in a future reservoir area located in Southeast Asia." *Environmental Monitoring and Assessment* no. 173 (1-4):723-741.
- Dittmar, T., C. E. de Rezende, M. Manecki, J. Niggemann, A. R. C. Ovalle, A. Stubbins, and M. C. Bernardes. 2012. "Continuous flux of dissolved black carbon from a vanished tropical forest biome." *Nature Geoscience* no. 5 (9):618-622.
- Elmquist, M., O. Gustafsson, and P. Andersson. 2004. "Quantification of sedimentary black carbon using the chemothermal oxidation method: an evaluation of ex situ pretreatments and standard additions approaches." *Limnology and Oceanography-Methods* no. 2:417-427.
- Fellman, J. B., D. V. D'Amore, E. Hood, and R. D. Boone. 2008. "Fluorescence characteristics and biodegradability of dissolved organic matter in forest and wetland soils from coastal temperate watersheds in southeast Alaska." *Biogeochemistry* no. 88 (2):169-184.
- Fellman, J. B., E. Hood, and R. G. M. Spencer. 2010. "Fluorescence spectroscopy opens new windows into dissolved organic matter dynamics in freshwater ecosystems: A review." *Limnology and Oceanography* no. 55 (6):2452-2462.
- Feng, X. J., K. M. Hills, A. J. Simpson, J. K. Whalen, and M. J. Simpson. 2011. "The role of biodegradation and photo-oxidation in the transformation of terrigenous organic matter." *Organic Geochemistry* no. 42 (3):262-274.
- Flores-Cervantes, D. X., C. M. Reddy, and P. M. Gschwend. 2009. "Inferring black carbon concentrations in particulate organic matter by observing pyrene fluorescence losses." *Environmental Science & Technology* no. 43 (13):4864-4870.
- Gelinas, Y., K. M. Prentice, J. A. Baldock, and J. I. Hedges. 2001. "An improved thermal oxidation method for the quantification of soot/graphitic black carbon in sediments and soils." *Environmental Science & Technology*. no. 35 (17):3519-3525.
- Gerde, P., B. A. Muggenburg, M. Lundborg, and A. R. Dahl. 2001. "The rapid alveolar absorption of diesel soot-adsorbed benzo a pyrene: bioavailability, metabolism and dosimetry of an inhaled particle-borne carcinogen." *Carcinogenesis* no. 22 (5):741-749.

- Glaser, B., E. Balashov, L. Haumaier, G. Guggenberger, and W. Zech. 2000. "Black carbon in density fractions of anthropogenic soils of the Brazilian Amazon region." *Organic Geochemistry* no. 31 (7-8):669-678.
- Glaser, B., L. Haumaier, G. Guggenberger, and W. Zech. 2001. "The 'Terra Preta' phenomenon: a model for sustainable agriculture in the humid tropics." *Naturwissenschaften* no. 88 (1):37-41.
- Goldberg, E.D. 1985. "Black Carbon in the Environment." New York: *John Wiley & Sons*.
- Gonzalez-Perez, J. A., F. J. Gonzalez-Vila, G. Almendros, and H. Knicker. 2004. "The effect of fire on soil organic matter - a review." *Environment International* no. 30 (6):855-870.
- Goyal, M., R. Dhawan, and M. Bhagat. 2008. "Adsorption of dimethyl sulfide vapors by activated carbons." *Colloids and Surfaces a-Physicochemical and Engineering Aspects* no. 322 (1-3):164-169.
- Gustafsson, O. F. Haghseta, C. Chan, J. MacFarlane, and P. M. Gschwend. 1997. "Quantification of the dilute sedimentary soot phase: Implications for PAH speciation and bioavailability." *Environmental Science & Technology* no. 31 (1):203-209.
- Gustafsson, O., and P. M. Gschwend. 1997. "Soot as a strong partition medium for polycyclic aromatic hydrocarbons in aquatic systems." *Molecular Markers in Environmental Geochemistry* no. 671:365-381.
- Gustafsson, O., T. D. Bucheli, Z. Kukulska, M. Andersson, C. Largeau, J. N. Rouzaud, C. M. Reddy, and T. I. Eglinton. 2001. "Evaluation of a protocol for the quantification of black carbon in sediments." *Global Biogeochemical Cycles* no. 15 (4):881-890.
- Hall, S. J., B. Ahmed, P. Ortiz, R. Davies, R. A. Sponseller, and N. B. Grimm. 2009. "Urbanization alters soil microbial functioning in the Sonoran desert." *Ecosystems* no. 12 (4):654-671.
- Hamer, U., B. Marschner, S. Brodowski, and W. Amelung. 2004. "Interactive priming of black carbon and glucose mineralisation." *Organic Geochemistry* no. 35 (7):823-830.
- Hamilton, G. A., and H. E. Hartnett. 2013. "Soot black carbon concentration and isotopic composition in soils from an arid urban ecosystem." *Organic Geochemistry* no. 59:87-94.
- Hammes, K., M. W. I. Schmidt, R. J. Smernik, L. A. Currie, W. P. Ball, T. H. Nguyen, P. Louchouart, S. Houel, O. Gustafsson, M. Elmquist, G. Cornelissen, J. O. Skjemstad, C. A. Masiello, J. Song, P. Peng, S. Mitra, J. C. Dunn, P. G.

- Hatcher, W. C. Hockaday, D. M. Smith, C. Hartkopf-Froeder, A. Boehmer, B. Luer, B. J. Huebert, W. Amelung, S. Brodowski, L. Huang, W. Zhang, P. M. Gschwend, D. X. Flores-Cervantes, C. Largeau, J. N. Rouzaud, C. Rumpel, G. Guggenberger, K. Kaiser, A. Rodionov, F. J. Gonzalez-Vila, J. A. Gonzalez-Perez, J. M. de la Rosa, D. A. C. Manning, E. Lopez-Capel, and L. Ding. 2007. "Comparison of quantification methods to measure fire-derived (black/elemental) carbon in soils and sediments using reference materials from soil, water, sediment and the atmosphere." *Global Biogeochemical Cycles* no. 21 (3). GB3016.
- Han, Y. M., J. R. Marlon, J. J. Cao, Z. D. Jin, and Z. S. An. 2012. "Holocene linkages between char, soot, biomass burning and climate from Lake Daihai, China." *Global Biogeochemical Cycles* no. 26 (9). GB4017.
- He, Y., and G. L. Zhang. 2009. "Historical record of black carbon in urban soils and its environmental implications." *Environmental Pollution* no. 157 (10):2684-2688.
- Hedges, J. I., B. A. Bergamaschi, and R. Benner. 1993. "Comparative analysis of DOC and DON in natural-waters." *Marine Chemistry* no. 41 (1-3):121-134.
- Hedges, J. I., G. Eglinton, P. G. Hatcher, D. L. Kirchman, C. Arnosti, S. Derenne, R. P. Evershed, I. Kogel-Knabner, J. W. de Leeuw, R. Littke, W. Michaelis, and J. Rullkotter. 2000. "The molecularly-uncharacterized component of nonliving organic matter in natural environments." *Organic Geochemistry* no. 31 (10):945-958.
- Hilscher, A., and H. Knicker. 2011. "Carbon and nitrogen degradation on molecular scale of grass-derived pyrogenic organic material during 28 months of incubation in soil." *Soil Biology & Biochemistry* no. 43 (2):261-270.
- Hilscher, A., K. Heister, C. Siewert, and H. Knicker. 2009. "Mineralisation and structural changes during the initial phase of microbial degradation of pyrogenic plant residues in soil." *Organic Geochemistry* no. 40 (3):332-342.
- Hockaday, W. C., A. M. Grannas, S. Kim, and P. G. Hatcher. 2006. "Direct molecular evidence for the degradation and mobility of black carbon in soils from ultrahigh-resolution mass spectral analysis of dissolved organic matter from a fire-impacted forest soil." *Organic Geochemistry* no. 37 (4):501-510.
- Hockaday, W. C., A. M. Grannas, S. Kim, and P. G. Hatcher. 2007. "The transformation and mobility of charcoal in a fire-impacted watershed." *Geochimica et Cosmochimica Acta* no. 71 (14):3432-3445.
- Huang, L., J. R. Brook, W. Zhang, S. M. Li, L. Graham, D. Ernst, A. Chivulescu, and G. Lu. 2006. "Stable isotope measurements of carbon fractions (OC/EC) in airborne particulate: A new dimension for source characterization and apportionment." *Atmospheric Environment* no. 40 (15):2690-2705.

- International Union of Pure and Applied Chemistry (IUPAC). 1997. "Compendium of chemical terminology." Oxford: *Blackwell Scientific Publications*.
- IPCC. 2007. "Climate Change 2007: Synthesis Report. Contribution of Working Groups I, II and III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change" IPCC, Geneva, Switzerland, 104 pp.
- Jaffé, R., Y. Ding, J. Niggemann, A. V. Vähätalo, A. Stubbins, R. G. M. Spencer, J. Campbell, and T. Dittmar. 2013. "Global Charcoal Mobilization from Soils via Dissolution and Riverine Transport to the Oceans." *Science* no. 340 (6130):345-347.
- Johnson, E. A. K. Miyanishi 2001. Forest Fires: Behavior and Ecological Effects: San Diego: *Academic Press*.
- Kawashima, H., and Y. Haneishi. 2012. "Effects of combustion emissions from the Eurasian continent in winter on seasonal delta C-13 of elemental carbon in aerosols in Japan." *Atmospheric Environment* no. 46:568-579.
- Kaye, J. P., S. E. Eckert, D. A. Gonzales, J. O. Allen, S. J. Hall, R. A. Sponseller, and N. B. Grimm. 2011. "Decomposition of urban atmospheric carbon in Sonoran Desert soils." *Urban Ecosystems* no. 14 (4):737-754.
- Kennedy, I. M. 1997. "Models of soot formation and oxidation." *Progress in Energy and Combustion Science* no. 23 (2):95-132.
- Krull, E. S., J. O. Skjemstad, D. Graetz, K. Grice, W. Dunning, G. Cook, and J. F. Parr. 2003. "C-13-depleted charcoal from C4 grasses and the role of occluded carbon in phytoliths." *Organic Geochemistry* no. 34 (9):1337-1352.
- Kuhlbusch, T. A. J. 1998. "Black carbon and the carbon cycle." *Science* no. 280 (5371):1903-1904.
- Kuhlbusch, T. A. J., and P. J. Crutzen. 1995. "Towards a global estimate of black carbon in residues of vegetation fires representing a sink of atmospheric CO<sub>2</sub> and a source of O<sub>2</sub>." *Global Biogeochemical Cycles* no. 9 (4):491-501.
- Leavitt, S. W., D. J. Donahue, and A. Long. 1982. "Charcoal production from wood and cellulose - Implications to radiocarbon-dates and accelerator target production." *Radiocarbon* no. 24 (1):27-35.
- Lehmann, J. 2007. "A handful of carbon." *Nature* no. 447 (7141):143-144.
- Lin, Y., P. Munroe, S. Joseph, R. Henderson, and A. Ziolkowski. 2012. "Water extractable organic carbon in untreated and chemical treated biochars." *Chemosphere* no. 87 (2):151-157.



- Lopez-Veneroni, D. 2009. "The stable carbon isotope composition of PM2.5 and PM10 in Mexico City Metropolitan Area air." *Atmospheric Environment* no. 43 (29):4491-4502.
- Mackay, D., and W. Y. Shiu. 1977. "Aquatic solubility of polynuclear aromatic-hyrdocarbons." *Journal of Chemical and Engineering Data* no. 22 (4):399-402.
- Majcher, E. H., J. Chorover, J. M. Bollag, and P. M. Huang. 2000. "Evolution of CO2 during birnessite-induced oxidation of C-14-labeled catechol." *Soil Science Society of America Journal* no. 64 (1):157-163.
- Major, J., J. Lehmann, M. Rondon, and C. Goodale. "Fate of soil-applied black carbon: downward migration, leaching and soil respiration." *Global Change Biology* no. 16 (4):1366-1379.
- Mannino, A., and H. R. Harvey. 2004. "Black carbon in estuarine and coastal ocean dissolved organic matter." *Limnology and Oceanography* no. 49 (3):735-40.
- Mao, J. D., R. L. Johnson, J. Lehmann, D. C. Olk, E. G. Neves, M. L. Thompson, and K. Schmidt-Rohr. 2012. "Abundant and stable char residues in soils: implications for soil fertility and carbon sequestration." *Environmental Science & Technology* no. 46 (17):9571-9576.
- Maricopa Association of Governments. 2010. Regional Transportation Plan. Phoenix, AZ. Maricopa Association of Governments.
- Maricopa County. Maricopa County Community Wildfire Protection Plan Maricopa County Department of Emergency Management: Logan Simpson Design, Inc. Phoenix, AZ. 2010.
- Marusenko, Y., P. Herckes, and S. J. Hall. 2011. "Distribution of polycyclic aromatic hydrocarbons in soils of an arid urban ecosystem." *Water Air and Soil Pollution* no. 219 (1-4):473-487.
- Masiello, C. A., and E. R. M. Druffel. 1998. "Black carbon in deep-sea sediments." *Science* no. 280 (5371):1911-1913.
- Masiello, C.A. 2004. "New directions in black carbon organic geochemistry." *Marine Chemistry* no. 92:201-213.
- McCrackin, M. L., T. K. Harms, N. B. Grimm, S. J. Hall, and J. P. Kaye. 2008. "Responses of soil microorganisms to resource availability in urban, desert soils." *Biogeochemistry* no. 87 (2):143-155.
- Menon, S., J. Hansen, L. Nazarenko, and Y. Luo. 2002. "Climate effects of black carbon aerosols in China and India." *Science* no. 297 (5590):2250-2253.

- Mensing, S. A., J. Michaelsen, and R. Byrne. 1999. "A 560-year record of Santa Ana fires reconstructed from charcoal deposited in the Santa Barbara Basin, California." *Quaternary Research* no. 51 (3):295-305.
- Michelsen, H. A., A. V. Tivanski, M. K. Gilles, L. H. van Poppel, M. A. Dansson, and P. R. Buseck. 2007. "Particle formation from pulsed laser irradiation of soot aggregates studied with a scanning mobility particle sizer, a transmission electron microscope, and a scanning transmission X-ray microscope." *Applied Optics* no. 46 (6):959-977.
- Middelburg, J. J., J. Nieuwenhuize, and P. van Breugel. 1999. "Black carbon in marine sediments." *Marine Chemistry* no. 65 (3-4):245-252.
- Miller, M. P., D. M. McKnight, R. M. Cory, M. W. Williams, and R. L. Runkel. 2006. "Hyporheic exchange and fulvic acid redox reactions in an alpine stream/wetland ecosystem, Colorado front range." *Environmental Science & Technology* no. 40 (19):5943-5949.
- Nahlik, M. 2012. "Quantifying black carbon in urban soils in Phoenix." Undergraduate Honor's thesis, Arizona State University.
- NASA Center for Ozone and Air Quality. Earth Probe Erythemal. Last modified December 31, 2005. <http://ozoneaq.gsfc.nasa.gov/EPY2005Erythemal.md>.
- Nguyen, B. T., J. Lehmann, J. Kinyangi, R. Smernik, S. J. Riha, and M. H. Engelhard. 2009. "Long-term black carbon dynamics in cultivated soil." *Biogeochemistry* no. 92 (1-2):163-176.
- O'Connor, J. T., T. O'Connor, and R. Twait. 2009. Water Treatment Plan Evaluations and Operations. New York: *John Wiley & Sons*.
- Ogren, J. A., and R. J. Charlson. 1983. "Elemental carbon in the atmosphere - cycle and lifetime." *Tellus Series B-Chemical and Physical Meteorology* no. 35 (4):241-254.
- Ohno, T. 2002. "Fluorescence inner-filtering correction for determining the humification index of dissolved organic matter." *Environmental Science & Technology* no. 36 (4):742-746.
- Oleary, M. H. 1988. "Carbon isotopes in photosynthesis." *Bioscience* no. 38 (5):328-336.
- Osburn, C. L., L. T. Handsel, M. P. Mikan, H. W. Paerl, and M. T. Montgomery. 2012. "Fluorescence tracking of dissolved and particulate organic matter quality in a river-dominated estuary." *Environmental Science & Technology* no. 46 (16):8628-8636.

- Parlanti, E., K. Worz, L. Geoffroy, and M. Lamotte. 2000. "Dissolved organic matter fluorescence spectroscopy as a tool to estimate biological activity in a coastal zone submitted to anthropogenic inputs." *Organic Geochemistry* no. 31 (12):1765-1781.
- Penner, J. E., H. Eddleman, and T. Novakov. 1993. "Toward the development of a global inventory for black carbon emissions." *Atmospheric Environment Part a-General Topics* no. 27 (8):1277-1295.
- Poot, A., Quik, J. T. K., H. Veld, and A.A. Koelmans. 2009. "Quantification methods of Black Carbon: Comparison of Rock-Eval analysis with traditional methods." *Journal of Chromatography A* no. 1216 (3):613-622.
- Preston, C. M., and M. W. I. Schmidt. 2006. "Black (pyrogenic) carbon: a synthesis of current knowledge and uncertainties with special consideration of boreal regions." *Biogeosciences* no. 3 (4):397-420.
- Quinn, R. C., P. Ehrenfreund, F. J. Grunthaner, C. L. Taylor, and A. P. Zent. 2007. "Decomposition of aqueous organic compounds in the Atacama Desert and in Martian soils." *Journal of Geophysical Research-Biogeosciences* no. 112 (G4):9. G04S18.
- Ramanathan, V., and G. Carmichael. 2008. "Global and regional climate changes due to black carbon." *Nature Geoscience* no. 1 (4):221-227.
- Rasmussen, C., and D. A. White. 2010. "Vegetation effects on soil organic carbon quality in an arid hyperthermic ecosystem." *Soil Science* no. 175 (9):438-446.
- Ringuet, J., A. Albinet, E. Leoz-Garziandia, H. Budzinski, and E. Villenave. 2012. "Reactivity of polycyclic aromatic compounds (PAHs, NPAHs and OPAHs) adsorbed on natural aerosol particles exposed to atmospheric oxidants." *Atmospheric Environment* no. 61:15-22.
- Rivas, Y., F. Matus, C. Rumpel, H. Knicker, and E. Garrido. 2012. "Black carbon contribution in volcanic soils affected by wildfire or stubble burning." *Organic Geochemistry* no. 47:41-50.
- Sakurai, H., H. J. Tobias, K. Park, D. Zarling, K. S. Docherty, D. B. Kittelson, P. H. McMurry, and P. J. Ziemann. 2003. "On-line measurements of diesel nanoparticle composition and volatility." *Atmospheric Environment* no. 37 (9-10):1199-1210.
- Saldarriaga, J. G., and D. C. West. 1986. "Holocene fires in the northern Amazon basin." *Quaternary Research* no. 26 (3):358-366.
- Schmidt, M. W. I. 2004. "Biogeochemistry - Carbon budget in the black." *Nature* no. 427 (6972):305-307.

- Schmidt, M. W. I., and A. G. Noack. 2000. "Black carbon in soils and sediments: Analysis, distribution, implications, and current challenges." *Global Biogeochemical Cycles* no. 14 (3):777-793.
- Schmidt, M. W. I., J. O. Skjemstad, and C. Jager. 2002. "Carbon isotope geochemistry and nanomorphology of soil black carbon: Black chernozemic soils in central Europe originate from ancient biomass burning." *Global Biogeochemical Cycles* no. 16 (4). GB001939.
- Schwarzenbach, R. P., P. M. Gschwend, and D. M. Imboden. 1993. Environmental Organic Chemistry. New York: *John Wiley & Sons*.
- Sharp, J. H. 1997. "Marine dissolved organic carbon: Are the older values correct?" *Marine Chemistry* no. 56 (3-4):265-277.
- Sharp, J. H., R. Benner, L. Bennett, C. A. Carlson, R. Dow, and S. E. Fitzwater. 1993. "Reevaluation of the high-temperature combustion and chemical oxidation measurements of dissolved organic carbon in seawater." *Limnology and Oceanography* no. 38 (8):1774-1782.
- Sharp, J. H. 1993. "The dissolved organic carbon controversy: an update." *Oceanography* no.6: 45-50.
- Sherrod, L. A., G. Dunn, G. A. Peterson, and R. L. Kolberg. 2002. "Inorganic carbon analysis by modified pressure-calorimeter method." *Soil Science Society of America Journal* no. 66 (1):299-305.
- Sinsabaugh, R. L., C. L. Lauber, M. N. Weintraub, B. Ahmed, S. D. Allison, C. Crenshaw, A. R. Contosta, D. Cusack, S. Frey, M. E. Gallo, T. B. Gartner, S. E. Hobbie, K. Holland, B. L. Keeler, J. S. Powers, M. Stursova, C. Takacs-Vesbach, M. P. Waldrop, M. D. Wallenstein, D. R. Zak, and L. H. Zeglin. 2008. "Stoichiometry of soil enzyme activity at global scale." *Ecology Letters* no. 11 (11):1252-1264.
- Skjemstad, J. O., D. C. Reicosky, A. R. Wilts, and J. A. McGowan. 2002. "Charcoal carbon in U.S. agricultural soils." *Soil Science Society of America Journal* no. 66 (4):1249-1255.
- Skjemstad, J. O., R. C. Dalal, L. J. Janik, and J. A. McGowan. 2001. "Changes in chemical nature of soil organic carbon in Vertisols under wheat in south-eastern Queensland." *Australian Journal of Soil Research* no. 39 (2):343-359.
- Smith, D. M., and A. R. Chughtai. 1995. "The surface structure and reactivity of black carbon." *Colloids and Surfaces A: Physicochemical and Engineering Aspects* no. 105 (1):47-77.
- Solomon, D., J. Lehmann, J. Thies, T. Schäfer, B. Liang, J. Kinyangi, E. Neves, J. Petersen, F. Luizão, and J. Skjemstad. 2007. "Molecular signature and

- sources of biochemical recalcitrance of organic C in Amazonian dark earths." *Geochimica et Cosmochimica Acta* no. 71 (9):2285-2298.
- Song, J. Z., P. A. Peng, and W. L. Huang. 2002. "Black carbon and kerogen in soils and sediments. 1. Quantification and characterization." *Environmental Science & Technology* no. 36 (18):3960-3967.
- Spencer, R. G. M., A. Stubbins, P. J. Hernes, A. Baker, K. Mopper, A. K. Aufdenkampe, R. Y. Dyda, V. L. Mwamba, A. M. Mangangu, J. N. Wabakanghanzi, and J. Six. 2009. "Photochemical degradation of dissolved organic matter and dissolved lignin phenols from the Congo River." *Journal of Geophysical Research-Biogeosciences* no. 114. G03010.
- Stedmon, C. A., S. Markager, and R. Bro. 2003. "Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy." *Marine Chemistry* no. 82 (3-4):239-254.
- Steinbeiss, S., G. Gleixner, and M. Antonietti. 2009. "Effect of biochar amendment on soil carbon balance and soil microbial activity." *Soil Biology & Biochemistry* no. 41 (6):1301-1310.
- Stubbins, A., J. Niggemann, and T. Dittmar. 2012. "Photo-lability of deep ocean dissolved black carbon." *Biogeosciences* no. 9 (5):1661-1670.
- Stursova, M., and R. L. Sinsabaugh. 2008. "Stabilization of oxidative enzymes in desert soil may limit organic matter accumulation." *Soil Biology & Biochemistry* no. 40 (2):550-553.
- Suman, D. O., T. A. J. Kuhlbusch, and B. Lim. 1997. Sediment records of biomass burning and global change. Berlin: *Springer-Verlag*.
- Sun, K., Y. Ran, Y. Yang, Y. P. Zeng, and B. S. Xing. 2007. "Characterization of condensed organic matter in soils and sediments." *Chinese Journal of Analytical Chemistry* no. 35 (8):1164-1167.
- U.S. Department of Commerce. United States Census. Washington D.C.: *United States Government Printing Office*, 2010.
- Vahatalo, A. V., K. Salonen, M. Salkinoja-Salonen, and A. Hatakka. 1999. "Photochemical mineralization of synthetic lignin in lake water indicates enhanced turnover of aromatic organic matter under solar radiation." *Biodegradation* no. 10 (6):415-420.
- Verardo, D. J., and W. F. Ruddiman. 1996. "Late pleistocene charcoal in tropical Atlantic deep-sea sediments: Climatic and geochemical significance." *Geology* no. 24 (9):855-857.

- Wang, M. C., and P. M. Huang. 2000. "Ring cleavage and oxidative transformation of pyrogallol catalyzed by Mn, Fe, Al, and Si oxides." *Soil Science* no. 165 (12):934-942.
- Wang, Y., P. K. Hopke, and M. J. Utell. 2011. "Urban-scale spatial-temporal variability of black carbon and winter residential wood combustion particles." *Aerosol and Air Quality Research* no. 11 (5):473-481.
- Wickland, K. P., J. C. Neff, and G. R. Aiken. 2007. "Dissolved organic carbon in Alaskan boreal forest: Sources, chemical characteristics, and biodegradability." *Ecosystems* no. 10 (8):1323-1340.
- Widory, D. 2006. "Combustibles, fuels and their combustion products: A view through carbon isotopes." *Combustion Theory and Modeling* no. 10 (5):831-841.
- Xu, N., H. F. Wilson, J. E. Saiers, and M. Entz. 2013. "Effects of crop rotation and management system on water-extractable organic matter concentration, structure, and bioavailability in a chernozemic agricultural soil." *Journal of Environmental Quality* no. 42 (1):179-190.
- Yan, B. Z., T. A. Abrajano, R. F. Bopp, L. A. Benedict, D. A. Chaky, E. Perry, J. Song, and D. P. Keane. 2006. "Combined application of delta C-13 and molecular ratios in sediment cores for PAH source apportionment in the New York/New Jersey harbor complex." *Organic Geochemistry* no. 37 (6):674-687.
- Zhang, L., and E. J. LeBoeuf. 2009. "A molecular dynamics study of natural organic matter: 1. Lignin, kerogen and soot." *Organic Geochemistry* no. 40 (11):1132-1142.
- Zimmerman, A. R. 2010. "Abiotic and Microbial Oxidation of Laboratory-Produced Black Carbon (Biochar)." *Environmental Science & Technology* no. 44 (4):1295-1301.
- Zimmermann, M., M. I. Bird, C. Wurster, G. Saiz, I. Goodrick, J. Barta, P. Capek, H. Santruckova, and R. Smernik. 2012. "Rapid degradation of pyrogenic carbon." *Global Change Biology* no. 18 (11):3306-3316.
- Ziolkowski, L. A., A. R. Chamberlin, J. Greaves, and E. R. M. Druffel. 2011. "Quantification of black carbon in marine systems using the benzene polycarboxylic acid method: a mechanistic and yield study." *Limnology and Oceanography-Methods* no. 9:140-149.

APPENDIX A  
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