Contributions of *Pinus Ponderosa* Charcoal to Soil Chemical and Physical Properties

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Abstract Charcoal results from the incomplete burning of plant material and is found in most soil surface horizons, but little is known about its effects on soil properties. The objectives of this study were (1) to determine the chemical and physical properties of ponderosa pine charcoal produced under controlled conditions, (2) to compare the properties of the laboratory-produced charcoal to those of wildfire-produced charcoal after it had resided in the soil for a number of years, and (3) to determine how charcoal additions to soil affect soil properties. We collected our samples from a pine forest in the San Bernardino Mountains of southern California. We found that laboratory-produced ponderosa pine charcoal has a cation exchange capacity on the order of 20-30 cmol kg^{-1} and field-collected samples accumulate native cations on their exchange sites. Field-collected charcoal samples from immediately below the litter layer were much less water repellent (water drop penetration time <10 s) than all other field-collected and laboratory-produced samples (water drop penetration time >2 h). The laboratory-produced charcoal C/N ratio (644) was about three times larger than the field-collected charcoal ratio (196-263). Addition of finely divided charcoal to mineral soil significantly increased the available water capacity and darkened the soil. We conclude that charcoal is not simply an inert compound in soils. It may play an important role in determining the properties and behavior of some surface soil horizons.

Introduction

Charcoal results from the incomplete burning of plant material, and is also called char or wood char. Charcoal is produced by wildfires in natural environments and is found in the surface horizons of soils across the globe. It can persist in the soil environment for thousands of years (Teixeira *et al.*, 2002). Wood charcoal has historically been used in filtration and purification, due to its large specific surface area (Bansal *et al.*, 1988), suggesting that it may impart unique physical and chemical properties to soils.

Early research on charcoal addressed its properties as an amendment to agricultural soils. Charcoal additions were found to soil increase water content (Retan, 1915) and retention (Tryon, 1948). Charcoal was also shown to increase soil cation exchange capacity (Swenson, 1939), an important aspect of soil fertility. Tryon (1948) conducted extensive experiments on other chemical and biological effects of charcoal in soils, and found that conifer charcoal increased soil pH and limited the growth of pine seedlings. Early studies showed charcoal effects at high concentrations (up to 450 g charcoal kg soil^{-1}), but it has been suggested that charcoal amendments could be beneficial at concentrations closer to those occurring naturally in soils (Glaser *et al.*, 2002), which generally do not exceed 10 g kg soil^{-1} (Skjemstad *et al.*, 1996, Schmidt *et al.*, 1999).

Research related to the preparation of charcoal for industrial purposes has shown that the temperature of charcoal formation, burn time, and gaseous environment are influential in determining charcoal properties such as pH (Chang *et al.*, 1982) and carbon to nitrogen ratio (Glaser *et al.*, 1998). Charcoal pH may vary along a gradient from acidic to basic as the temperature at its exposure to oxygen increases. Oxides form during complete combustion and are transformed to carbonates and hydroxides (Etiegni and Campbell, 1991), and these transformed oxides may raise charcoal pH. Nitrogen in plant material is easily volatilized at high temperatures (White *et al.*, 1973), and the C/N ratio of pine wood charcoal, produced at 300°C, has been found to increase with longer burn times (Glaser *et al*., 1998). It is clear, then, that charcoal properties are dependent on burn length, temperature, and oxygen availability.

Despite the ubiquity of charcoal in soil surface horizons, particularly in forest soils, few studies have addressed how charcoal might influence soil properties. Early studies that did address this topic did not report the methods of producing charcoal used in the studies (e.g., Tryon, 1948). The objectives of this study were (1) to determine the chemical and physical

properties of ponderosa pine charcoal produced under controlled conditions, (2) to compare the properties of the laboratory-produced charcoal to those of wildfire-produced charcoal. The wildfire-produced charcoal was collected from the field after it had resided in the soil for a number of years, and in this paper is referred to as field-collected charcoal. We assumed that the addition of charcoal to a soil shifts the properties of the soil toward the properties of the charcoal, proportionate to the charcoal concentration in the soil. By testing properties of pure charcoal, we allow the calculation of soil-chemical mixture properties. Due to the dark color of and difficulty in wetting the pure charcoal samples, we tested soil-charcoal mixtures to (3) determine how charcoal additions to soil material affect water-holding capacity and soil color.

Methods

In this study we focused on charcoal from ponderosa pine (*Pinus ponderosa*) because it is a dominant conifer species in many of forests of the western United States, where fires are common. We collected freshly cut ponderosa pine wood at the Skyforest Ranger Station in the San Bernardino Mountains of southern California. We also collected charcoal samples from ponderosa pine logs near Jenks Lake in the San Bernardino Mountains. These logs had burned in a prescribed fire ~ 7 years prior to sample collection. We took charcoal only from logs we could identify as ponderosa pine to ensure uniformity of wood species between laboratory and field samples. Some charcoal was collected from the surface of the litter, some below the litter layer and above the soil, and some within the top 10 cm of mineral soil. The pieces of charcoal were 0.5 to 15 cm^3 in size. Some soil material adhered to the charcoal, so we used a small dry brush to clean each piece.

The soil material used in the laboratory part of this study was a sandy loam (coarse-loamy, mixed, superactive, mesic Typic Dystroxerept) derived from granitic rock, similar to soils of many ponderosa pine habitats (Burns and Honkala, 1990). It is from the C horizon of a soil in the Sequoia National Forest, California, and it is more fully characterized by Hubbert *et al.* (2001). We chose to use the C horizon instead of samples closer to the surface because, coming from the 53 to 80 cm depth, it was unlikely to contain charcoal. The C horizon sample contained 0.48% organic carbon, while the soil's A horizon contained 2.68% organic carbon (Hubbert *et al.*, 2001), some of which could be charcoal and could confound studies relating charcoal additions to soil properties.

The unburned wood samples were cut into 2-by-2 by-3-cm pieces in preparation for controlled burning. Small chunk size encouraged even and complete burning, and produced charcoal pieces that were comparable in volume to our field samples. After placing the wood pieces in covered ceramic crucibles, we burned them in a preheated muffle furnace for 30 minutes at 450°C (Zackrisson *et al.*, 1996). This temperature best reflects ground temperatures of natural wildfires (Chandler *et al.*, 1983). We burned the wood for 30 minutes because this was the minimum time required to expel all vaporizable organic materials. We judged that all volatiles were vaporized when smoke was no longer visible in the furnace exhaust (FAO, 1983). The samples cooled inside the closed furnace for 15 minutes after the burn to prevent the samples from bursting into flame when we opened the furnace. This procedure was adapted from the method employed by Glaser *et al.* (1998), in which the covered crucibles limit the oxygen available to the samples. In trial runs, too much oxygen led to the production of some completely oxidized ash instead of pure charcoal.

We powdered both the laboratory- and field-produced charcoals with mortar and pestle to pass through a 150-μm-mesh sieve. This particle size was small enough to prevent the powdered charcoal from floating on the surface of water and ethanol in centrifuge tubes. Floating was problematic during determinations of CEC and exchangeable cations because the centrifuge supernatants are meant to be free of sample material.

We measured the cation exchange capacity (CEC) of the pure charcoal samples by saturating exchange sites with Na (sodium acetate), washing out excess Na with ethanol, and extracting Na from exchange sites using 1 M ammonium acetate, all at pH 7 (Bower and Hatcher, 1966). Exchangeable cations were displaced using ammonium acetate (method 5B1 in USDA-NRCS, 1996). All displaced cations were measured by atomic absorption spectroscopy, using a Perkin Elmer AAnalyst 800 Atomic Absorption Spectrometer with a Flow Injection Mercury System (FIMS) 400 (Perkin Elmer, Inc., Wellesley, MA, U.S.A.). We measured the pH of the charcoal samples using both water and 0.01 M calcium chloride solution dilutions (method 8C1f in USDA-NRCS, 1996). This method was slightly modified (1:3 water dilutions and 1:6 calcium chloride dilutions) to overcome the difficulty of wetting the charcoal samples.

We measured the water retention of soil-charcoal mixtures at -10 and -1500 kPa with pressure chambers and pressure plate extraction methods (4B1a and 4B2a in USDA-NRCS, 1996). The difference between the water holding capacities at -10 and -1500 kPa is considered

an approximation of plant-available water capacity (Brady and Weil, 1999). We mixed the powdered charcoal with the sandy loam in concentrations of 5, 10, and 50 g kg^{-1}. The concentrations of 5 and 10 g kg^{-1} reflect the levels of charcoal found in soils (Sanford *et al.*, 1985; Skjemstad *et al.*, 1996; Zackrisson *et al.*, 1996; Schmidt *et al.*, 1999; Glaser *et al.*, 2000).

The inorganic content of the charcoal samples was measured by loss on ignition at 400°C (method 8F1 in USDA-NRCS, 1996) to assess the level of contamination with mineral grains in the samples collected from the field. When preparing samples for water retention testing, we noticed that mixing charcoal with soil darkened the soil appreciably. We measured the Munsell and CIE color of the air-dry soil and charcoal mixtures using a Minolta Chroma Meter CR-200 (Konica Minolta Photo Imaging U.S.A., Mahwah, NJ, U.S.A.), to determine if the darkening was significant with only 5 to 10 g kg^{-1} of charcoal in the soil. We measured water repellency on pure charcoal samples using the field technique of Water Drop Penetration Time (WDPT) (King, 1981). We measured the C/N ratios of our charcoal samples with a FlashEA 1112 NC Soil Analyzer (Thermo Electron Corp., CE Elantech, Inc., Waltham, MA, U.S.A.).

Our statistical analyses were performed with JMP software (SAS Institute, Inc., Cary, NC, U.S.A.). Analyses of variance (ANOVA) and Tukey's Honestly Significant Difference (HSD) tests established differences among samples regarding inorganic content, CEC, extractable cations, pH, and C/N ratio. We used simple linear regression to fit lines to our water-holding capacity and soil color data.

Results and Discussion

Upon removal from the furnace, the charcoal pieces were shiny black and produced a sharp, glass-like sound when they rubbed together. In comparison, the field charcoal pieces were flat black and several had fine roots or a mesh of fungal hyphae on their surfaces or partially penetrating their layers. At 50X magnification we saw some mineral particles lodged in the pores of the field charcoal, even after brushing the pieces by hand. All samples were a deep, shiny black after grinding.

The inorganic content of the field charcoal samples (3-16%) was higher than that of the laboratory-produced charcoal (1%) (Table 1). Variation in inorganic content is likely due to contamination of field charcoal by mineral grains from the soil, since the charcoal produced in the laboratory was never exposed to soil. Even charcoal collected from the soil surface probably

had soil particles splashed onto them by raindrop impact or blown on by wind. Brodowski *et al.* (2004) suggest that contamination by mineral grains is a natural outcome of charcoal oxidation, and note that the close association of charcoal and mineral grains could protect the charcoal from further oxidation.

The charcoal CEC and exchangeable cation values were several times greater than the sandy loam values (Table 1). Additionally, the field charcoal samples contained two to four times as much Ca and less than a tenth of the Na as the laboratory sample. The CEC was within the same range for both field and laboratory charcoal samples. Because field charcoal samples contained soil particles, they might be expected to have lower CEC values relative to the laboratory charcoal, but this was not the case. Previous work shows that pine charcoal has a CEC low enough to decrease the CEC of a brown podsolic Maltby sandy loam (Tryon, 1948). Our results indicate that CEC may be enhanced by charcoal additions to soil, and while our results contrast with the findings of Tryon (1948), they complement more recent studies that demonstrate soil CEC magnification by charcoal. For example, the presence of pyrogenic carbon in Amazonian dark earths is strongly correlated with effective CEC (Glaser *et al.*, 2004), and charcoal additions to an Amazonian Xanthic Ferralsol also increased CEC (Lehmann *et al.*, 2003). Glaser *et al.* (2002, 2004) suggest that carboxylic groups on the charcoal aromatic backbone (Glaser *et al.*, 2000, 2001) are responsible for augmenting soil CEC.

Higher exchangeable Ca and Mg in field-collected compared to laboratory charcoal imply that charcoal retains and accumulates these cations. On the other hand, extractable Na is lost in the field where it is readily leached. Our finding that exchangeable cations were more plentiful in laboratory-produced charcoal than in our sandy loam is consistent with the findings of Tryon (1948), which show that the addition of field-produced conifer charcoal to loam and sand increases amounts of available K, Ca, and Mg.

The laboratory charcoal pH was more than a full pH value higher than the field charcoal pH values. Charcoal pH is influenced by burn temperature and gases present during combustion (Chang *et al.* 1982), and these factors may be responsible for the observed pH difference between laboratory and field charcoal. Plant material contains Ca, K, and Mg that are released by thorough combustion to form oxides, which transform to carbonates and hydroxides upon exposure to ambient environmental conditions (Etiegni and Campbell, 1991). These cations are leached into the soil where they can increase soil pH (Chandler *et al.* 1991). All of these

compounds produce an alkaline pH in water.   High burn temperatures and large amounts of available oxygen lead to more complete combustion and a greater increase in pH.   Since the laboratory charcoal may have burned at a higher temperature than the field charcoal, more cations may have been released, causing the high pH.   An alternative explanation is that alkaline earth oxides were leached from the field charcoal during the seven years since it formed.   The laboratory charcoal was never wetted, so thermally produced alkaline compounds would still be present.   All charcoal samples were highly water repellent except samples taken from below the litter layer (Table 1).   The weak repellency of the charcoal collected below the litter layer contrasts with the very strong water repellency of the other charcoal samples.   The weakly repellent charcoal may have lost its hydrophobic qualities after leaching by organic acids from the surrounding litter layer.

The charcoal C/N ratios were very high, and the laboratory sample ratio (644) was about three times the field sample ratios (196-263) (Table 1).   The large C/N ratio of the laboratory charcoal suggests that it had a longer burning time and/or a higher burning temperature than the field charcoal (White *et al.*, 1973; Glaser *et al.*, 1998).   The C/N ratios of an Amazonian Xanithic Ferralsol (Lehmann *et al.*, 2003) and Netherlands sandy soils (Hassink, 1994) increase with charcoal content, as could be expected of our sandy loam with ponderosa pine charcoal amendments.

Available water holding capacity increased linearly upon charcoal additions (Table 2), and the magnitude of increase was larger than the changes observed by Tryon (1948), who used charcoal concentrations in soil approximately twice those used in this study.   Wood charcoal surface area can be on the order of 10^3 m^2 g^{-1} (Cheremisinoff and Ellerbusch, 1978), and this property may contribute to water-holding capacity in charcoal-rich soils (Glaser *et al.*, 2002).

Charcoal is an effective darkening agent (Table 2).   We found excellent agreement between the Munsell and CIE color measurement systems in terms of soil darkness.   The degree of darkening is probably related to charcoal particle size, since finely divided charcoal has more exposed surface area and is most likely to become incorporated and blended into soil.   In the U.S. soil taxonomy system, dark colors are part of the criteria for diagnostic surface horizons, the anthropic, melanic, mollic, and umbric epipedons (Soil Survey Division Staff, 2003). The mollic, umbric, and anthropic epipedons must have Munsell values and chromas ≤3 when moist and values ≤5 when dry.   Melanic epipedons must have a Munsell color value and chroma ≤2 when

moist. Their dark color of these horizons is usually attributed to humic matter, but our measurements suggest that finely divided could contribute substantially to this darkening. Charcoal concentrations of 10 g kg^{-1} can darken light soils sufficiently to meet the color requirements for the mollic epipedon (Table 2) even when humic matter is negligible in the soil. Of ecological importance is the effect of soil darkening on increased sunlight absorption, increased soil temperature, and increased evaporation rates.

Table 1. Ponderosa pine charcoal samples listed by source and their characteristics, presented with sandy loam characteristics. Sandy loam data are from Hubbert *et al.* (2001). Different letters after numbers mean that values are different according to Tukey's Honestly Significant Difference (HSD) test. All sample errors were less than 3%. *1:1 H_2O pH, nd = not determined

Sample	Inorganic Content (%)	CEC (cmol kg^{-1})	Extractable Cations (cmol kg^{-1})				Base Saturation (%)	1:3 H_2O pH	1:6 $CaCl_2$ pH	Water Drop Penetration Time	C/N ratio
			Ca	Mg	K	Na					
Laboratory	1.15a	21.2a	2.85a	0.86a	1.80a	2.80a	39	6.86a	6.69a	> 2 hr	644a
Field: above soil	12.92b	19.2b	6.36b	0.88a	1.18b	0.13b	44	5.41b	4.94b	> 2 hr	263b
Field: below litter	3.30c	29.4c	12.05c	1.93b	3.12c	0.19b	59	5.73c	5.41c	< 10 sec	196c
Field: in soil	16.48d	23.5d	8.44d	1.02c	1.63d	0.15b	48	5.81c	5.30d	> 2 hr	215c
Sandy loam	nd	6.6e	0.90e	0.14d	0.29e	0.03c	21	5.31d*	nd	< 1 sec	21.8d

Table 2. Water holding capacity and darkness of laboratory-produced ponderosa pine charcoal mixed with sandy loam in four concentrations. All standard errors were less than 1% unless noted. [a] 0 = pure black, and 10 = pure white [b] 0 = pure black, and 100 = pure white

Charcoal Concentration (g kg^{-1})	Available Water Holding Capacity (% mass water)	Dry Munsell Color Value [a]	Dry CIE L Value [b]
0	11.9±0.3	5.5	56.4
5	12.4±0.3	5.2	53.3
10	13.0±0.2	4.9	50.0
50	18.8±0.5	3.6	37.5

Conclusions

We found that ponderosa pine charcoal has a CEC that is greater than that of a sandy loam soil material used for comparison. It appears to accumulate native cations on its exchange sites when it is in the soil. Fresh charcoal had a pH slightly less than neutral, while the pH of charcoal in a moderately to strongly acid soil for several years equilibrated with the soil pH. Samples of fresh charcoal and aged charcoal from the soil surface and within the mineral soil were extremely water repellent, but those immediately below the litter were much less so, raising the possibility of leaching by organic acids as a factor in reducing water repellency. This suggests that soil water repellency due to charcoal is highest immediately after a wildfire but decreases over time. Water-repellent soils are an important factor in increased post-fire erosion rates (Certini, 2005), and fires have been shown to alter flood frequency curves (Candela *et al*., 2005). Addition of finely divided charcoal to mineral soil significantly increases the available water capacity and darkens the soil. Soil water holding capacity is a determinant of plant success, especially in arid climates (Austin *et al*., 2004). A decrease in charcoal inputs to a soil may reduce the amount of plant-available water, stressing plants and increasing their susceptibility to disease. Charcoal inputs result from fires, and can be substantially reduced by fire suppression practices. Changes in fire properties such as temperature and duration may affect the qualities of the produced charcoal, and therefore affect soil qualities. Increases in the frequencies of large crown fires and prescribed burns may alter ecosystem structure over the long term because these types of fires are different from natural wildfires. Our results suggest that charcoal is not simply an inert compound sequestering carbon in soils, rather it may play an important role in determining the properties and behavior of entire ecosystems.

Acknowledgements

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