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Biotic and abiotic influences on black carbon properties in soil

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Black carbon (BC) is a product of incomplete biomass and fossil fuel combustion. It is relatively resistant to degradation and occurs ubiquitously in natural environments, including soils, sediments, seawater and the atmosphere. Very few information is available about the factors affecting BC properties in soil. This study investigates the effects of biotic and abiotic oxidation on the properties of biomass-derived BC (charcoal) and in soil-charcoal mixtures. Soil samples were collected from an anionic Acrustox in Brazil and charcoal was produced from black locust (Robinia pseudoacacia L.) by combusting it at 300°C for 16 hours in a muffle furnace. The charcoal and charcoal-soil mixtures samples were incubated at 30°C and 70°C and with and without microbial inoculation. Additional incubation experiments were setup with the addition of a nutrient solution and manure to test the effect of inorganic and organic fertilization on charcoal properties. All samples were sterilized by gamma irradiation before the experiment and samples for biotic incubation were re-inoculated. The samples were incubated at 60 % water holding capacity for 4 months period. Chemical characteristics such as pH, exchangeable acidity, effective cation exchange capacity (CEC), and potential CEC of both pure charcoal and soil-charcoal mixture samples were measured. Our investigation revealed that microbial inoculation or additions of mineral fertilizers did not change the chemical properties of charcoal, whereas temperature significantly affected the properties of samples. Samples incubated at 70°C showed significantly lower pH and higher exchangeable acidity and CEC compared with the samples incubated at 30°C and the original charcoal. For example, their pH in KCl solution dropped from 4.2 to 3.5 in soil-charcoal mixtures and from 4.1 to 2.4 in pure charcoal samples, where as the potential CEC increased from 24 mmole/kg to 87 mmole/kg in soil-charcoal mixtures and from 140 mmole/kg to 800 mmole/kg in pure charcoal samples. Boehm titration method was used to determine the surface functional groups. The distribution of functional groups of charcoal incubated at 30°C was not significantly different both in samples with and without microbial inoculation. Both had higher carbonyl functional groups (1990 mmole/kg) compared to the original charcoal (290 mmole/kg) and the carboxylic (200 mmole/kg) and phonic and lactonic (1400 mmole/kg) functional groups did not change significantly. However, the total surface functional groups were 84% higher than original charcoal. The charcoal incubated at 70°C showed much higher contents of carboxylic (860 mmole/kg) and phenolic and lactonic (1790 mmole/kg) functional groups. The total surface functional groups were also 133% higher than the original charcoal. Fourier transform infrared (FTIR) spectra confirmed that charcoal incubated at higher temperature had higher proportions of carboxylic (1705 cm-1) and ether groups (1223 cm-1). FTIR spectra from samples incubated at 30°C with or without microbial inoculation were not significantly different from the original charcoal spectra, but had higher ratios of C=O and C=C stretches (1607cm-1) to O-H stretches (3433cm-1) than the original charcoal. Our results indicated that abiotic oxidation by chemisorption of oxygen on the surface of charcoal at higher temperature could have a profound effect on chemical composition and surface properties of biomass-derived BC compared to biotic oxidation, and such changes may have significant impact on soil biogeochemistry.