



Characterization of black carbon in wood ash from different feedstocks and types of furnaces

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Due to the increase use of biomass as fuel, wood ash, generated in biomass power plants, can be an important source of biochar to be used in agriculture. Two different types of wood ash are generated in biomass power plants: fly ash (obtained in cyclone separators) and mixed wood ash, also known as bottom ash (from wood fire furnaces), which is a mixture of fly ash and charcoal. Both types of wood ash contain moderate amounts of carbon residues, classified as chars or black carbon, as a result of the incomplete combustion of biomass. In spite that wood ash is produced in huge amounts, the characteristics of the black carbon has not been characterized yet. The properties of both wood ash and biochar are influenced by the feedstock and the pyrolysis temperature.

In this study we compare the influence of three feedstocks (sugarcane bagasse, woodchip of pine and woodchip of eucalypt) on the properties of the black carbon contained in both wood ash generated in 7 different power plants. Three size-particles were selected < 2cm, 2-5 cm and > 5cm.

Elemental composition (C, H, N, O), Solid state ^{13}C CPMAS NMR spectrometry, differential scanning calorimetry (DSC) and Fourier-transformed infrared spectroscopy (FTIR) were used to obtain information on black carbon's molecular characteristics. Total polycyclic aromatic hydrocarbon (PAH) content and PAH composition were determined using organic solvent extraction and/or SPE techniques and analyzed by an optimized RP-HPLC-FLD method. Polychlorinated dibenzodioxins and dibenzofurans were analyzed by extraction/gas chromatography HRGC-HRMS. The toxicity equivalent quotient (TEQ) was calculated by multiplying the concentration of each dioxin or furan present by its international toxicity equivalency factor (I-TEF).

The type of combustion (cyclone or wood fire furnace), feedstock and size-particle determined the amount of black carbon and the degree of aromatization.

Mixed wood ash shows higher amounts of black carbon than fly ash. The ^{13}C CPMAS NMR, DSC and FTIR analysis showed the loss of carbohydrates and aliphatic constituents and revealed the formation of aromatic compounds. The atomic H/C ratios, NMR spectra, DSC and FTIR confirmed the presence of condensed structures, specially in the coarse particles. However, the different wood ash showed an important range of properties revealing the presence from charred material (H/C ratios higher than 0.7; aromaticity lower than 60 % and T50-DSC lower than 450 °C) to charcoal containing condensed structures (H/C ratios lower than 0.6; aromaticity higher than 80 % and T50-DSC higher than 500 °C). Feedstock determined important differences in molecular composition. High concentration of recalcitrant compounds were found in the pine sawdust-derived wood ash; whereas eucalypt and sugarcane straw showed significant contents of labile compounds.

PAH and dioxins linked to the combustion of wood, show slight differences between bottom ash and fly ash. The first one, with lower combustion temperatures, showed higher PAH values. Fly ash, on the contrary, showed greater dioxins' concentrations.

The results demonstrate the important differences in the properties of wood ash determined by the feedstock, size-particle and the combustion temperature, which surely greatly affect the properties of soils and the response of crop in wood ash-amended soils.