



Chemical characteristics, age, weathering and transport of different pools of charcoal

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Charcoal is considered one of the most stable carbon pools due to its unique chemical characteristics and the associated resistance to biological decomposition. However, estimates of the mean residence time of charcoal vary from a few hundred to several 1000s of years. These differences in estimates are mainly due to 1) the different ways that are commonly employed to measure the charcoal fraction and 2) the differences in environments that produce and accumulate charcoal (e.g. soils at different depths in different climates, aquatic sediments, etc.). It is of importance with regard to future predictions of carbon stocks, sinks and sources to develop reliable techniques to determine charcoal dynamics and mean residence time of different charcoal fractions.

The objective of our study was to investigate the chemical nature ($^{13}\text{C-NMR}$), mean residence time ($^{14}\text{C-AMS}$) and degree of weathering (SEM and EDX) of specific charcoal fractions from different soil types (all sampled prior to nuclear weapons testing of the 1950s) at various depths and geomorphological settings. The charcoal fractions were attained by different chemical procedures which had been evaluated for their effectiveness to extract charcoal in a previous study. We found that charcoal was consistently older than the bulk soil organic matter and that the ^{14}C -age of charcoal was seminal in determining the mean residence time of bulk soil organic matter and as such, its carbon storage potential. Charcoal in the subsurface soil had consistently a higher ^{14}C -age compared to the surface soil; however, even in the surface soils, ^{14}C -ages were 500 to up to 1000 years. ^{14}C -ages of both bulk soil organic matter and charcoal from a black cracking clay soil from a lowland setting were much older compared to those of a red podzolic soil from an upland setting. $^{13}\text{C-NMR}$, SEM and microprobe investigation suggested distinct chemical and morphological changes of

charcoal with increasing age and depth with increased proportion of carboxylic groups associated with aromatic charcoal carbon, increased O/C ratios and increased surface weathering.

The results of our study highlight:

1. The importance of choice of methods for extracting and determining the proportion of charcoal from soils or sediment.
2. The importance of charcoal in determining the age and turnover time of soil organic carbon.
3. The accumulation of older charcoal in lowland settings where it could act as a long-term carbon sink.
4. Chemical and physical weathering of charcoal in the soil environment and a greater susceptibility to oxidation over long periods.