Geophysical Research Abstracts
Vol. 14, EGU2012-3778, 2012
EGU General Assembly 2012

Chemical changes in soil charcoal of differing ages inferred from DRIFT spectra

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Visible charcoal fragments were manually isolated from a sandy soil from the Southern Highlands of NSW, Australia, at depths of 0 – 30 cm and 30 – 60 cm. In the topsoil, the charcoal had a radiocarbon age of 85 $\pm$ 35 years BP, whereas the charcoal from the 30 – 60 cm layer was radiocarbon dated at 2540 $\pm$ 35 years BP. Diffuse reflectance FTIR (DRIFT) spectra of the charcoal reveal differences in both the number of peaks detected and their magnitudes. In the IR region 750 – 3800 cm^{-1}, the charcoal from the lower depth had less peaks (140) than that of the topsoil (217). In the 1400 – 1600 cm^{-1} region, generally attributed to aromatics, the peaks were larger and more numerous (22 peaks) in the 0 – 30 cm sample than those of the 30 – 60 cm depth (14 peaks). The C-H stretch of alkenes and aromatics (3000 – 3100 cm^{-1}) was similar at both depths, but the peak generally associated with the C-H stretch of alkanes (methyl and methylene groups) at 2850 – 3000 cm^{-1} was smaller in 30 – 60 cm depth than in the topsoil. In contrast to the reduction in aromatic and alkane signatures, oxidised forms were more pronounced in the older, deeper charcoal. Peaks associated with the free hydroxyl O-H stretch (alcohols and phenols) at 3640 – 3610 cm^{-1}, carboxylic acids (910 – 950 cm^{-1}), aliphatic O-H (alcohols) (1050 - 1150 cm^{-1}) and cellulose-like structures (1020 cm^{-1}), which contain a large number of uncondensed, oxidised rings, were larger in the charcoal from 30 – 60 cm than in that from the topsoil. Our results confirm that charcoal is highly persistent in soils, being retained for millennia. Aromatic structures are present in both younger and older charcoal, but decay leads to a reduction in the number and area of peaks detected at 1400 – 1600 cm^{-1}, indicating less aromaticity. Alkane C-H also decreases with aging, probably attributable to its preferential degradation by soil microbes compared with condensed aromatic structures. Concurrent with diminished aromatic and alkane structures, aging of charcoal leads to an increase in oxidised organic matter detectable as carboxylic acids, alcohols and cellulose-like structures.