

Persistent C in soils

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There is general agreement that in many soils some C compounds persist for centuries and perhaps millenia, particularly deep in the soil profile. Various chemistries and mechanisms of stabilization of C compounds have been proposed to explain their longevity in soils. There is evidence that some part of the reason for the persistence of C in soils is related to a range of interactions with mineral surfaces and secretion within the mineral matrix, but in recent years charcoal has emerged as a major contributor to the so called 'inert pool' of C in soils.

Finely divided charcoal appears to be a major constituent of many Australian soils (Skjemstad *et al.*, 1996). It is not currently possible to measure quantitatively the charcoal present in soils but combinations of controlled high energy ultra-violet photo-oxidation with CPMAS ^{13}C NMR and scanning electron microscopy allow a good assessment of the charcoal present in soil and soil fractions. Charcoal is relatively resistant to ultra-violet photo-oxidation which essentially removes other plant and microbially derived organic materials as CO_2 . Thus the charcoal can be concentrated and often recognised by scanning electron microscopy because it has a wood-like morphology. Such samples exhibit strong NMR signals in the 130 ppm region because of the strong aromaticity. The strong aromaticity of 'humic acid' fractions also results in signals in the 130 ppm region and it is quite likely that a significant proportion of the aromatic components in humic acids originate in charcoal.

In a limited range of soils as much as one third of the organic C appears to be charcoal and a relationship between charcoal in soil and previous histories of fire are being slowly established. For example, the controlled burning of vegetation to maintain grasslands on volcanic ash soils in Japan has established a clear relationship between fires and the chemistry of the soil organic matter (Golchin *et al.*, 1997a,b). Soils subject to fire for decades were richer in aromatic components which were concen-

trated in humic acid fractions. Studies by solid state ^{13}C CPMAS Bloch decay and proton spin relaxation editing (PSRE) indicate an accumulation of charcoal after decades of burning. The Bloch decay also showed that in soils containing significant amounts of aromatic components charcoal is likely to be present and also that the amount of aromatic material present is likely to be seriously underestimated by ^{13}C CPMAS NMR.

Unfortunately, we know little about the dynamics of charcoal in soils, or about the significance of charcoal in the global C cycle. However, considerations of the global situation with respect to charcoal and related materials indicates that it is not inert although we have no good information of its longevity (Waters *et al.*, unpublished). Microbiologically condensed ring compounds are very resistant to oxidation but limited data suggest that charcoal may not be a major sink for C in the global C cycle.

A second group of C compounds which are resistant biochemically are aliphatic C chains. During ^{13}C NMR studies with metal probes we have concluded that domains of aliphatic materials occur in soils (Smernik and Oades, submitted to *Geoderma*). These domains are hydrophobic aliphatic components probably nanometers in size. Currently we do not know their origin or dynamics but they represent part of the colloidal fraction in some soils. Currently we are unable to separate these components from the alkyl-nitrogen rich materials which are concentrated in the colloidal or clay fractions of soils.

References

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