

The nature of sequestered carbon in different Irish mineral soils

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Introduction Humic substances (HS) provide the major sinks for carbon (C) in soils. Although HS have a degree of resistance to microbial degradation, they are degraded in time. Humin, the HS component in association with the soil mineral colloids, has greatest resistance to degradation. To understand the extent to which soil can be a sink for C it is important to know the soil mineralogy, and to be aware of aspects of the structures of the humic components. Enhanced biological oxidation occurs in soils in long term cultivation. Its effects can be observed by comparing the amounts and compositions of the humic components in cultivated soils with those in the same soil types in long term grassland. Three such paired soils were included in the study as well as three grassland soils that are in new lysimeter studies at the Environmental Research Centre, Johnstown Castle. In a study of the humification process, maize (*Zea mays L.*, a C4 plant, with a $\delta^{13}\text{C}$ value of the order of -12) was incubated in calcareous organic C-free sand, and the products were studied in the same way as those from the soils

Materials and methods Soil samples were H^+ -exchanged and exhaustively extracted (until the extracts had negligible colour) with 0.1 M NaOH adjusted to pH 7, then with the NaOH solution adjusted to pH 10.6, then at pH 12.6, and finally with 6 M urea in the 0.1 M NaOH solution. Sand (20 Kg, 38% CaCO_3) was incubated with 3.6 Kg of maize. Prior to extraction (on a yearly basis) the CaCO_3 was removed (1 M HCl), and the system was then treated as for the soils. Humic acids (HAs) were precipitated at pH 1, dialysed to remove the salt, then freeze dried. Fulvic acids (FAs) were subjected to the standard XAD-8 treatment, recovered in 0.1 M NaOH, H^+ -exchanged (IR-120 resin), and freeze dried. Each sample was titrated (potentiometric), subjected to $\delta^{13}\text{C}$, neutral sugar, and amino acids analyses, and to infrared, solid state NMR, and ESR spectroscopies. X-ray diffraction was used to classify the soil clays.

Results Organic matter (OM) contents of soils in long-term cultivation were significantly less (about 50%) than those of the same soils in long-term grassland. Approximately 30% of the soil OM content comprised of HAs and FAs, and humin was invariably the most abundant component. The compositions of the HAs and FAs in the different fractions highlighted the greater extents of oxidation/humification in the cultivated soils. This was illustrated by the titration data, and by the carboxyl (160-180 ppm) and O-aromatic (140-160 ppm, includes phenols) resonances in the NMR spectra. Figure 1 is one illustration of how CP/TOSS, Dipolar Dephasing, and Chemical Shift Anisotropy (CSA) NMR spectra show differences between HAs isolated from the same soil type in cultivation and in grassland management, and the data show distinct differences between these and the HA products from plants undergoing humification. The extensive data we have for a variety of soil types clearly show distinctive differences between the humic components in the different soil types. The components can be related to the types and contents of the clays and to the drainage regimes.

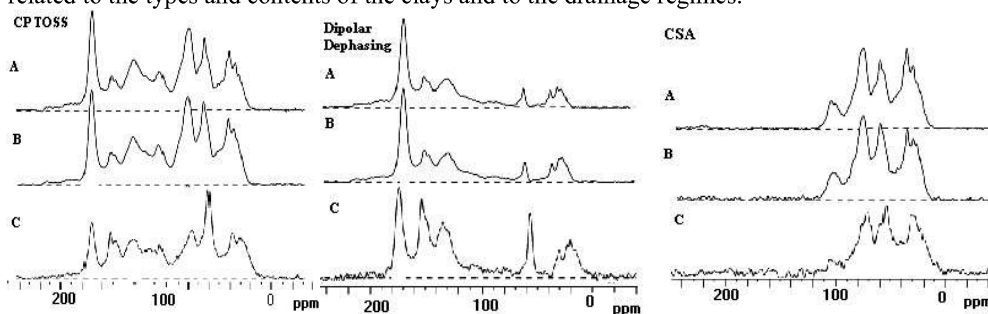


Figure 1 CP/TOSS, Dipolar Dephasing, and Chemical Shift Anisotropy (CSA), spectra of humic acids isolated at pH 12.6 from a coarse sandy loam cultivated (A) and uncultivated (B) soil, and from the sand/maize incubation system (C).

Conclusions The variety of data that will be presented, from a range of analytical and spectroscopic procedures, will show clearly that mineral grassland soils are good sinks for C. These vary, however, in their abilities to sequester C. The variations can be related to the nature of the vegetation, to the soil aeration, to the water holding capacity, and to the amounts and compositions of the inorganic as well as the organic colloids, and to the management. Research is needed to understand how humin, the major OM component, is protected.