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SPATIAL DISTRIBUTION, CHEMISTRY AND TURNOVER OF ORGANIC MATTER IN SOILS

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by

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SUMMARY

The concept of organic matter turnover is described and various methods used to measure the decay rates of organic materials in soil are reviewed. Factors affecting the dynamics of organic carbon in soils are also reviewed. From an examination of the literature, the soil mineral matrix was identified as one of the most important controls over decomposition processes in terrestrial ecosystems. Information provided in the literature indicates that the rates of decay of organic materials in the presence of soil are slower than the rates of decay in the absence of soil. One of the major hypotheses found in the literature to account for the retention of organic matter in soil is that the soil mineral matrix protects soil organic matter against microbial decomposition, either through adsorption of substrates to mineral surfaces or by sequestration in soil aggregates at sites inaccessible to soil organisms. To examine this hypothesis and to seek further evidence for the role of soil structure in carbon cycling, a series of interrelated experiments were carried out.

A densimetric method for separation of SOM from different locations within the soil matrix was developed and applied to several soils. The free particulate organic matter (POM), located between or outside the soil aggregates, was isolated by suspending the soil in sodium polytungstate solution ($d = 1.6 \text{ Mg m}^{-3}$) and decanting the light material. The remaining soil was disaggregated by sonification to separate occluded POM from the rest of SOM associated with mineral materials. The chemical structures of free POM, occluded POM and clay-associated OM were determined by solid-state ^{13}C NMR spectroscopy. The compositional differences noted among these three components of SOM were used to describe the changes that OM undergoes during decomposition when it enters the soil, is enveloped in aggregates and eventually incorporated into microbial biomass and metabolites and becomes associated with clay minerals.

The occluded organic materials, released as a result of aggregate disruption, were in various stages of decomposition and had different degrees of association with mineral particles. Changes in the degree of association of occluded organic materials and mineral particles with decomposition were outlined and formed the basis of a model which illustrates the simultaneous dynamics of microaggregates and their organic cores. This model links structural stability of microaggregates with the chemistry of their organic cores and indicates a major role for carbohydrate-rich plant debris in formation and stabilisation of microaggregates.

Turnover studies of SOM and its fractions were carried out by examining the changes in the content and isotopic composition of organic carbon as a result of deforestation and pasture establishment in three neighbouring areas on an Oxisol from Australia. The $\delta^{13}\text{C}$ natural abundance combined with solid-state ^{13}C NMR spectroscopy and pyrolysis mass spectrometry indicated that free POM, occluded POM and clay associated OM have different structural and dynamic properties. The ^{13}C natural abundance showed that the free particulate organic matter decomposed most quickly and formed a significant pool for soil organic matter turnover when forest was replaced by pasture. Compared to free POM, the organic materials occluded within aggregates had slower turnover times. The most persistent OM was associated with clay minerals. The occluded organic materials were in different stages of decomposition and had different chemical stabilities. Comparison of the chemistry and isotopic composition of occluded organic materials indicated that the O-alkyl C content of the occluded organic materials was inversely related to their stabilities whereas their aromatic C content was directly related to their stabilities.

The results obtained from the $\delta^{13}\text{C}$ study confirmed the original hypothesis and validated the model proposed for formation, stabilisation and degradation of aggregates. This study revealed two modes of stabilisation, physical and chemical, for POM in soil.

The effect of cultivation and management systems on the quantity and composition of SOM and its fractions were evaluated by comparing paired sites of virgin soils with adjacent cultivated soils. Changes in the nature of organic carbon with cultivation were different in different soils and resulted from variations in the chemistry of carbon inputs to the soils and a greater extent of decomposition of organic materials in cultivated soils. Differences in the chemical composition of organic carbon between cultivated and uncultivated soils resided mostly in organic materials occluded within aggregates whereas the chemistry of organic matter associated with clay particles showed only small changes. The results indicated a faster decomposition of O-alkyl C in the cultivated soils.

Wet aggregate stability, mechanically dispersible clay and modulus of rupture tests were used to assess the effects of cultivation on structural stability of soils. Generally, the virgin sites and sites which had been under long-term pasture had a greater aggregate stability and a lower modulus of rupture than the cultivated sites. Neither total organic matter nor total O-alkyl C content was closely correlated with aggregate stability, suggesting that only a part of soil carbon or carbohydrate was involved in aggregate stability. The fractions of carbon and O-alkyl C present in the form of particulate organic matter occluded within aggregates were better correlated with aggregate stability ($r = 0.86^{**}$ and 0.88^{**} respectively).

Homoionic Na-, Ca-, and Al-clays were prepared from the $< 2 \mu\text{m}$ fractions of Georgia kaolinite or Wyoming bentonite and mixed with sand to give artificial soils with 5, and 25% clay. The artificial soils were inoculated with microbes from a natural soil before incubation. Unlabelled and uniformly ^{13}C -labelled (99.9 % atom) glucose were incorporated into the artificial soils to study the effects of clay types, exchangeable cations and clay contents on the mineralisation of glucose-carbon and glucose-derived organic materials. Chemical

transformation of glucose-carbon upon incorporation into microbial products and metabolites, was followed using solid-state ^{13}C CP/MAS NMR spectroscopy.

There was a significant influence of exchangeable cations on the mineralisation of glucose-carbon over a period of 33 days. At 25% clay content, mineralisation of glucose-carbon was highest in Ca-soils and lowest in Al-soils. The influence of exchangeable cations on mineralisation of glucose-carbon was more pronounced in soils with bentonite clay than those with kaolinite clay. Due to the increased osmotic tension induced by the added glucose, mineralisation of glucose-carbon was slower in soils with 5% clay than soils with 25% clay.

Despite the differences in the chemical and physical characteristics of soils with Ca-, Na- and Al-clays, the chemical composition of organic materials synthesised in these soils were similar in nature. Assuming CP/MAS was quantitative, incorporation of uniformly ^{13}C -labelled glucose (99.9% atom) in these soils resulted in distribution of carbon in alkyl (24-25%), O-alkyl (56-63%), carbonyl (11-15%) and small amounts of aromatic and olefinic carbon (2-4%). However, as decomposition proceeded, the chemistry of synthesised material showed some changes with time. In the Ca- and Na-soils, the proportions of alkyl and carbonyl carbon decreased and that of O-alkyl carbon increased with time of incubation. The opposite trend, however, was found for the Al-soil.

Proton-spin relaxation editing (PSRE) subspectra clearly showed heterogeneity within the microbial products. Subspectra of the slowly-relaxing (long $T_1(\text{H})$) domains were dominated by alkyl carbon in long and short chain structures. The signals due to N-alkyl (55 ppm) and carbonyl carbon were also strong in these subspectra. These subspectra were very similar to spectra obtained for microbial and fungal materials and were probably microbial tissues attached to clay surfaces by polysaccharide extracellular mucilage. Subspectra of fast-relaxing (short $T_1(\text{H})$) domains comprised mostly O-alkyl and carbonyl carbon and were probably microbial metabolites released as neutral and acidic sugars into the extracellular environment, and strongly sorbed by clay surfaces.

The contribution of charcoal to aromatic carbon contents of soils and methods for its separation from SOM was discussed in another experiment. Development of methods for separation of charcoal from soil was found to be a prerequisite for understanding its distribution and biological and physico-chemical properties in soils.