



Monitoring changes in OM in afforested soils by calorespirometry, thermal analysis and NMR

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Calorimetry and thermal analysis can be applied to studies of the stabilization of soil organic matter (SOM) under different environment situations and types of management. In this study, differential scanning calorimetry (DSC) and isothermal calorimetry were applied, along with ^{13}C CPMAS NMR, to assess the changes in SOM quality in afforested lands in a humid temperate region. The techniques were applied to soils in chronosequences of pines and eucalypts (*Pinus radiata* and *Eucalyptus globulus*) established on former grasslands subjected to a low intensity of management throughout several years. The plantations differed greatly in litter accumulation and underground vegetation, which may lead to different SOM stabilization patterns throughout stand development. The heat and CO_2 production rates during soil basal metabolism can be measured continuously and simultaneously by calorespirometry. These rates can be used to calculate a novel parameter known as the calorespirometric ratio, which provides a measure of microbial metabolism. The ratio relates the degradability and the nature of SOM. The composition and structure of the SOM were also studied by DSC and NMR to aid interpretation of the calorespirometric ratios.

An initial period of strong SOM loss was observed in both types of chronosequences. In the eucalyptus stands, up to 50 % of the SOM was lost over 10 years. In the pine stands, the loss was up to 65 %, over a period of 25 years. The soils partially recovered the initial SOM contents (70-80 %) after the period of loss, by the end of the rotation. The carbon contents were highest in the most recently afforested stands and the SOM contained highly diverse mixture of aliphatic fractions, carbohydrates, cellulose, aromatic C and carboxyl groups. The heat of combustion was also highest in these samples, and the calorespirometric ratios were higher than for carbohydrates (for which the range is -250 to -455 $\text{kJ mol}^{-1} \text{CO}_2$), indicating that the degraded SOM is more reduced than carbohydrates. This is compatible with the existence of aliphatic and aromatic C compounds in those samples as detected by NMR.

The loss of SOM affected the aliphatic fraction and carbonyl groups, which could not be identified in the NMR spectrum or in the DSC curves of those samples. Carbohydrates and aromatic C persisted, but at lower quantities than in the youngest stands, indicating that these fractions were also degraded. The calorespirometric ratios varied from higher values than for carbohydrates in the youngest stands (-570 $\text{kJ mol}^{-1} \text{CO}_2$) to similar values for carbohydrate respiration, demonstrating changes in the nature of the SOM being degraded.

Samples from the oldest forest stands (18 years for eucalyptus and 40 years for pines) showed C gains that predominantly affected the aliphatic and aromatic fractions in the pine stands and the aliphatic and carbohydrate fractions in the eucalyptus stands. This gain was accompanied by slight increases in the calorespirometric ratios. The results showed changes in the pattern of soil microbial metabolism throughout the period following afforestation, as a consequence of the variation in the nature of the SOM. The calorimetric data revealed changes in the SOM being degraded, from more reduced than carbohydrates in the youngest stands to more oxidized than carbohydrates in the oldest stands. The data also revealed changes in the dynamics and nature of the SOM attributable to the tree species used for reforestation; the SOM was more aromatic in the pine stands than in the eucalyptus stands, possibly due to the type of organic compounds generating SOM.