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Soil Biology & Biochemistry 39 (2007) 993–1006

Soil Biology & Biochemistry

www.elsevier.com/locate/soilbio

^{13}C-NMR analysis of decomposing litter and fine roots in the semi-arid Mulga Lands of southern Queensland

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Received 7 March 2006; received in revised form 24 October 2006; accepted 9 November 2006
Available online 11 December 2006

Abstract

Plant litter and fine roots are important carbon (C) inputs to soil and a direct source of CO_2 to the atmosphere. Solid-state carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectroscopy was used to investigate the nature of C changes during decomposition of plant litter and fine roots of mulga (*Acacia aneura* F. Muell. Ex. Benth.), wheat (*Triticum aestivum* L.), lucerne (*Medicago sativa*) and buffel grass (*Cenchrus ciliaris*) over an 18-month period. Alkyl C was closely associated with total N concentrations in all litter materials during decay and as alkyl C increased so did total N, indicating an increase in refractory biomacromolecules. Mulga phyllodes had the greatest alkyl C concentration of all litter and fine root materials, and also exhibited the NMR peaks assigned to tannins that may slow or hinder decomposition rates and nitrification. Mulga litter and fine roots decomposed slower than all other litter materials and the soil under mulga had the highest soil C concentration, indicating slower CO_2 release. The alkyl C-to-*O*-alkyl C ratio is generally used as an index of the extent of decomposition, but is not useful for the decay of woody components. Of all the NMR ratios studied that may indicate the extent of decomposition, the carbohydrate C-to-methoxyl C ratio proved to have the strongest and most consistent relationship with decay time, fraction of mass remaining and total C, even though increases in alkyl C were observed with decreases in carbohydrate C.

Keywords: Litter decomposition; Fine roots; ^{13}C-NMR spectroscopy; Mulga; Buffel grass; Semi-arid; C sequestration; Land-use change

1. Introduction

The amount of carbon (C) contained in terrestrial soil organic matter (SOM) is about twice the C amount in the atmosphere and three times that of the land biomass (Batjes and Sombroek, 1997). The size of this organic C reservoir in soil depends on both plant production and the mineralisation of plant and organic residues, and has recently estimated to be between 1200 and 2000 Pg (Pg = 10^{15} g) in the top 1 m of soil (Batjes and Sombroek, 1997), although Swift (2001) indicates there is a consensus estimate of ~1500 Pg globally. The annual global carbon dioxide (CO_2) flux from soils is estimated to average 68 Pg C y^{-1} (Raich and Schlesinger, 1992) and mineralisation of the annual litterfall contributes to approximately half of this output, demonstrating the importance of litter decomposition as a direct source of CO_2 to the atmosphere (Coûteaux et al., 1995).

Solid-state carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectroscopy has been used successfully to understand the C transfer pathways and effects of litter quality on decomposition (Huang et al., 1998; Almendros et al., 2000; Preston et al., 1997; Preston and Trofymow, 2000; Quideau et al., 2000; Kögel-Knabner, 2002; Lorenz et al., 2004; Wang et al., 2004; Baldock et al., 1997, 2004). Determination of C fractions by ^{13}C-NMR in litter has proven useful in characterising litters with respect to their

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0038-0717/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.soilbio.2006.11.009

potential to decompose and release nutrients. Blumfield et al. (2004) suggested that the carbohydrate C-to-methoxyl C ratio (CC/MC) might be a useful indicator of decomposition, despite both regions belonging to the *O*-alkyl C region, because their relationship with the other variables studied (mass loss, total N, ^{15}N enrichment) moved in opposite directions. It is well known that the alkyl C to *O*-alkyl C (A/O-A) ratio is not suitable to distinguish stages of decomposition in wood or woody residues (Baldock et al., 1997). Other ratios have been proposed (Blumfield et al., 2004; Quideau et al., 2000; Wang et al., 2004), but further research would be required to examine whether these alternative ratios could be useful in distinguishing the extent of decomposition in other litter types and woody debris. As no direct measure of the molecular composition of decomposing organic residues can be obtained from ^{13}C-NMR, Baldock et al. (2004) have developed an extended molecular mixing model (MMM) using solid-state ^{13}C-NMR, based on earlier models (Hedges et al., 2002; Nelson and Baldock, 2005), to estimate the biomolecular and elemental composition of decomposing terrestrial and aquatic organic matter. Decomposition-induced changes obtained from the MMM may be more useful in determining the extent of decomposition than the decomposition indices obtainable from the NMR data.

Jalota et al. (2006) reported on the decomposition of litter and fine root materials from mulga woodlands (*Acacia aneura* F. Muell. Ex. Benth.), buffel grass pasture (*Cenchrus ciliaris*), lucerne (*Medicago sativa*) and wheat (*Triticum aestivum* L.) cropping in semi-arid southern Queensland. Fine roots of mulga and buffel grass turned over more slowly than the mulga phyllodes and buffel grass litter, whilst wheat and lucerne fine roots turned over more quickly than the aboveground litter components of these species (Jalota et al., 2006). The slower decomposition rates of mulga litter and fine roots supports the findings of Dalal et al. (2005a) who found C losses of 31% and 35% in the top 5 cm depth under buffel grass pasture and cropping, respectively, more than 20 years after clearance of the native mulga woodland.

The objective of the current study was to extend the information obtained by Jalota et al. (2006) and Dalal et al. (2005a, b) by examining the C changes (observed as C functional groups using ^{13}C-NMR) during decomposition of mulga, lucerne, buffel grass and wheat litter and fine roots in the Mulga Lands soil of southern Queensland.

2. Materials and methods

2.1. Study site

The study site 'Mulga View' has been described in detail previously (Dalal et al., 2005a, b). It is located near the township of St. George (27°59′S, 148°33′E) in southwest Queensland, Australia. Briefly, the soil type is a red Kandosol (Isbell, 2002), Rhodic Paleustalf (Soil Survey Staff, 2003) or Profondic Lixisol (FAO, 1998), with a clay concentration of 12% and soil pH of 6.0 in the 0–10 cm layer, increasing with depth to 22% clay and pH 6.2 in the 60–100 cm soil layer (Dalal et al., 2005a). Mean annual temperature at St. George is 21 °C and mean annual rainfall and pan evaporation are 516 and 1954 mm, respectively.

2.2. Litter and fine root decomposition experiments

Jalota et al. (2006) have previously described the litterbag decomposition experiments in detail. The litter (aboveground plant material) and fine roots (<2 mm in diameter) of wheat, lucerne and buffel grass were collected from the field sites at the time of wheat harvest. At the same time, mulga phyllodes (leaves), twigs (<2 mm in diameter) and fine roots from the 0–30 cm depth were collected from the mulga site. For mulga, lucerne and buffel grass roots, 1.7 g of air-dried root material was placed in each litterbag, however only 0.9 g of material was used for the wheat roots due to the limited availability of material. Ten grams of aboveground litter material was placed in each bag for all plant litter materials, including mulga twigs. Litterbags were constructed from 0.15 μm × 0.35 μm polypropylene mesh and were 15 cm^2 in area for litter material and 10 cm^2 for fine root material.

Litterbags containing fine root materials were buried at 10 and 30 cm depths, while those containing litter materials were placed on the soil surface. All litterbags placed in the field were replicated three times. Another set of litterbags for each type of plant material was constructed exactly as described above to calculate the average weight of material lost from these bags during transport to and from the field. This value was then subtracted from any weight loss recorded during each collection period. The litterbags were removed from the field after 0, 15, 45, 90, 180, 360 and 562 days (18 months), adhered soil was gently removed and the residual litter and root materials were dried, weighed and finely ground. Ash concentration of all the litter and root materials was determined by ignition at 550 °C for 1 h and weights of decomposing materials were expressed on an ash-free basis (Jalota et al., 2006). The decomposition rate for each of the materials was calculated using a non-linear curve fit of the remaining biomass with an exponential decay function:

$$A_t = A_0 e^{-kt},$$

where A_t is the weight of plant material remaining at time t, A_0 the initial weight of plant material, and k the decomposition rate constant.

Litter and fine roots in those litterbags that had been *in situ* for 0, 180, 360 and 562 days were analysed by ^{13}C-NMR spectroscopy to follow C functional group changes induced by decomposition. Total C and N concentrations in the plant litter and fine root materials were determined on a LECO CNS-2000 analyser (LECO Corp., St Joseph, MI, USA).