Geoderma 151 (2009) 351–356

Contents lists available at ScienceDirect

Geoderma

journal homepage: www.elsevier.com/locate/geoderma

Organic carbon accumulation processes on a forest floor during an early humification stage in a temperate deciduous forest in Japan: Evaluations of chemical compositional changes by ^{13}C NMR and their decomposition rates from litterbag experiment

Kenji Ono [a,*], Keizo Hirai [a], Sayaka Morita [b], Kenji Ohse [b], Syuntaro Hiradate [b]

[a] *Tohoku Research Center, Forestry and Forest Products Research Institute, 92-25, Shimokuriyagawa, Morioka, Iwate 020-0123, Japan*
[b] *National Institute for Agro-Environmental Sciences, 3-1-3 Kan-nondai, Tsukuba, Ibaraki 305-8604, Japan*

ARTICLE INFO

Article history:
Received 17 June 2008
Received in revised form 15 April 2009
Accepted 2 May 2009
Available online 22 May 2009

Keywords:
Solid-state ^{13}C CPMAS NMR
Litterbag experiment
Humification
Carbon component of humified litter
Forest floor

ABSTRACT

To quantitatively clarify the organic carbon accumulation processes on the forest floor during an early stage of humification (3 years), solid-state ^{13}C cross polarization magic angle spinning nuclear magnetic resonance (CPMAS NMR) signals were monitored for phased–humified beech and oak litters and soil surface horizons in the northern Kanto District, Japan. The mass loss rate of the carbon components during the humification for both litters was in the following order: *O*-alkyl > aromatic > aliphatic > carbonyl carbons. This result indicates that the labile *O*-alkyl carbons, probably dominated by holocellulose were selectively degraded compared to the other components. 44% of *O*-alkyl carbon mass for beech and 38% for oak lost throughout 3 years of incubation. Inversely, the mass of aliphatic carbons, which is mainly composed of saturated hydrocarbons, decreased quite slowly from 20 to 10% with humification, probably because a large proportion of the aliphatic carbons are secondary products of microorganisms. The aromatic carbon mass, which would be derived from lignin/tannin and their metabolites, also decreased gradually from 17 to 6% over 3 years. While, the carbonyl carbon mass was quite stable at around 2% throughout the incubation period, probably because the hydrolysis reactions of organic carbon would contribute to the formation of the carbonyl carbons. According to an exponential model, the total carbon stocks on the forest floor converged at 4.2 Mg C ha^{-1} for the first few years at the studying site. The carbon compositions converged to intermediate levels between those of the *F* and A_1 horizons. The simulation in the present study is able to represent the carbon accumulation process on the forest floor including a part of the mineral.

1. Introduction

The understanding of soil organic matter (SOM) dynamics in terrestrial ecosystems are of great importance because soils are the largest pool of terrestrial organic carbons so any future climatic disturbances have a possibility of greatly affecting them. Various compartment models have been proposed to evaluate the behavior of SOM stocks in terrestrial ecosystems (e.g., Parton et al., 1987; Liski et al., 2005; Coleman and Jenkinson, 2008). Most models have several 'conceptual' compartments that take into account the differences of decomposability. The simulation results using these SOM models often show a satisfactory match between predicted and measured data of the total carbon stocks (e.g., Roth C model; Jenkinson and Rayner, 2006). In addition, the use of models enables us to predict the response of labile and recalcitrant organic carbon pools in soils according to climate changes (Davidson and Janssens, 2006). Thus, the SOM model is considered to be useful for predicting the SOM dynamics in soils. Despite the advancement of modeling studies, the actual chemical forms of these 'conceptual' compartments remain ambiguous. Therefore, there are substantial gaps between the organic carbons constituting SOM in the modeling studies and laboratory experiments. It is necessary to develop and introduce new methods and technologies for a deeper understanding of the humification process.

One solution is the use of solid-state ^{13}C nuclear magnetic resonance (NMR). Solid-state ^{13}C NMR is a powerful tool for studying humification processes from litter materials to SOM in soil (Fründ and Lüdeman, 1991; Kögel-Knabner, 1997). It can easily compare quantitatively the composition of organic carbons among samples. Therefore, the changes in the chemical composition of humified forest organic materials (woody debris, forest litter, soil, peat, etc.) have been characterized by using solid-state ^{13}C NMR in numerous studies (Kögel-Knabner et al., 1988; Baldock and Preston, 1995;

---

[*] Corresponding author. Tel.: +81 19 641 2150x3944; fax: +81 19 641 6747.
E-mail address: don@ffpri.affrc.go.jp (K. Ono).

0016-7061/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.geoderma.2009.05.001

Baldock et al., 1997; Osono et al., 2008). They provide a valuable index for the humification degree of organic materials (i.e., the ratio of aliphatic to *O*-alkyl carbon contents: Baldock et al., 1997). However, these studies did not focus on the time of humification of the organic carbons. In addition, the results provided by previous ^{13}C NMR studies have not let us estimate the decomposition rates of the organic carbon components, because most previous studies did not consider how their mass changed, although they focused on the qualitative changes in forest organic materials during the humification. To predict the carbon dynamics in the terrestrial ecosystem in detail, it is indispensable to understand the dynamics of each organic carbon component during the litter humification.

In the present study, we conducted a litterbag experiment at Ogawa Forest Reserve (OFR), a typical temperate deciduous forest in Japan, dominated by beech (*Fagus crenata*) and oak (*Quercus crispila*). We determined the compositional changes (i.e., carbonyl, aromatic, *O*-alkyl, and aliphatic carbons) of humified litters by using solid-state ^{13}C NMR and quantified the mass changes of these carbon components on the forest floor during a 3 year period. We also estimated a specific decomposition constant, '*k* value' of an exponential equation proposed by Olson (1963), for each carbon component to evaluate its decomposability. By using the estimated *k* values, we predicted the accumulation process of the organic carbons on the forest floor. This approach allowed us to: 1) clarify the chemical compositional changes in litter materials during the early humification process on the forest floor, 2) assess the decomposability of carbon components quantitatively based on the time, and 3) simulate the formation of the forest floor during the early humification process quantitatively.

2. Materials and methods

2.1. Study area

The study was carried out at Ogawa Forest Reserve, a temperate deciduous forest dominated by beech (*Fagus crenata*) and oak (*Quercus crispula*) in Ibaraki prefecture in the northern Kanto District, Japan. The study site is located on an undulating plateau at the southern edge of the Abukuma mountainous region (36°56′N, 140°35′E, 670 masl). Mean annual air temperature from 1986 to 1995 was about 10.7 °C and the mean monthly temperature ranged from −0.9 °C in January to 22.6 °C in August (Mizoguchi et al., 2002). The mean annual precipitation was 1910 mm (Mizoguchi et al., 2002). The soils in the studying site are heterogeneously and mosaically distributed between Cambisols and Andosols (Yoshinaga et al., 2002). The parent material is metamorphic rock and Late Quaternary volcanic ash (Yoshinaga et al., 2002). A 10 m × 10 m plot was settled on the upper part of a slope to conduct a litterbag experiment.

2.2. Sampling and preparation of humified litters and samples in L, F, and A_1 horizons

The litterbag method (Crossly and Hoglund, 1962) was applied to obtain humified litter samples (litterbag size: 1 mm-mesh polyethylene bag, and150 mm × 200 mm). Fresh litterfalls of beech and oak collected at the forest floor in November 2002 were dried in an oven at 40 °C overnight for the use of the litterbag experiment. In April 2003, 10 g of each species' litter was put into a separate litterbag and placed on the forest floors dominated by each species litter. The litterbags were collected four times thereafter: 4 months later in August 2003, 1 year in April 2004, 2 years in April 2005, and 3 years in April 2006. Humified litter fragments in the litterbags were picked out with tweezers to remove contaminated soil particulars as carefully as possible and dried in an oven at 40 °C for 48 h before weighing. The remnant mass of the humified litter was used to calculate the remnant carbon masses.

A soil survey was carried out near the studying plot. Soil samples were taken from the forest floor (*L* and *F* horizons) and the top mineral horizon (A_1 horizon). The color and texture of these samples were examined following the guidelines for soil description (FAO, 2006). The bulk density of the A_1 horizon was measured using 100-ml soil core cylinders.

2.3. Sample preparation

The samples of humified litters, *L*, *F*, and A_1 horizons were air-dried and then sufficiently ground to pass through a 200-mesh (75-µm mesh) sieve using a high-speed vibrating sample mill (TI-200; CMT Co. Ltd., Tokyo, Japan). The powdered samples were supplied for the analyses of carbon content and solid-state ^{13}C NMR spectroscopy.

For the solid-state ^{13}C NMR measurement, all the samples were treated with hydrofluoric acid (HF) to remove inorganic minerals as follows. A 0.5 to 1.0 g portion of the samples was weighed into a 50-ml polyethylene bottle. After adding 10 ml of 46% HF, the bottles were tightly capped and horizontally shaken. Then, 40 ml of deionized water was added to the bottles, and the bottles were centrifuged for 10 min at 3000 rpm. The supernatant was removed and discarded. The residue was further washed 3 times with 50 ml of deionized water to remove HF completely, and then was dried at 60 °C in an oven. These HF-treated samples were used for the solid-state ^{13}C NMR analysis.

2.4. Determination of carbon content in the litters, L, F, and A_1 horizons

Carbon contents in the litters, *L*, *F*, and A_1 horizons were determined by a dry combustion method (CHN analyzer 2400 II, Perkin-Elmer, Massachusetts, USA). A carbon stock from *L* to A_1 horizons was estimated as follows:

$$\begin{aligned}\text{a carbon stock} = {} & \sum\{\text{carbon content of each horizon}\\ & \times \text{bulk density of each horizon}\\ & \times \text{depth of each horizon}\} \times \text{area}\end{aligned}$$

2.5. Measurement of solid-state ^{13}C NMR spectra

Solid-state ^{13}C NMR spectra of HF-treated powder samples were recorded with an FT NMR system (Alpha 300, JEOL, Tokyo, Japan) employing the cross polarization magic angle spinning (CPMAS) technique. The analytical condition in the present study was the same as described in Hiradate et al. (2006). A powder sample was transferred into a KEL-F spinning tube (6 mm ϕ, JEOL, Tokyo, Japan), and signals of ^{13}C were recorded at 75.45 MHz with magic angle spinning of 6 kHz, a contact time of 1 ms, and a pulse interval of 3 s. A broadening factor of 100 Hz was employed in the Fourier transform procedure. Chemical shifts were quoted with respect to tetramethylsilane but were determined by referring to an external sample of adamantane (29.50 ppm). According to Skene et al. (1996, 1997), the NMR spectrum was divided into four chemical shift regions representative of the major types of carbons present in these samples: 0–45 ppm (aliphatic carbons), 45–110 ppm (*O*-alkyl carbons), 110–160 ppm (aromatic carbons), and 160–190 ppm (carbonyl carbons). The proportion of each type of carbon was determined based on the integration of the spectral regions.

2.6. Simulation of the accumulation process of carbon components on the forest floor

Accumulation processes of carbon components on the forest floor were simulated using the annual decomposition rates of the litters estimated from the annual litterfall input and its specific decomposition constants (*k* values; Olson, 1963) of the individual carbon