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ScienceDirect

Geoderma 136 (2006) 331 – 341

GEODERMA

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Effect of land use on the composition of soil organic matter in density and aggregate fractions as revealed by solid-state ^{13}C NMR spectroscopy

Mirjam Helfrich [a,b,*], B. Ludwig [b], P. Buurman [c], H. Flessa [a]

[a] *Institute of Soil Science and Forest Nutrition, University of Göttingen, Büsgenweg 2, 37077 Göttingen, Germany*
[b] *Department of Environmental Chemistry, University of Kassel, Nordbahnhofstr. 1a, 37213 Witzenhausen, Germany*
[c] *Laboratory of Soil Science and Geology, Department of Environmental Sciences, Wageningen University, P.O. Box 37, 6700 AA Wageningen, The Netherlands*

Received 7 December 2004; received in revised form 26 January 2006; accepted 31 March 2006

Abstract

Changes in soil organic carbon (SOC) contents with soil cultivation have been investigated extensively, but information on the influence of land use changes on the chemistry of soil organic matter (SOM) and SOM fractions is scarce. To make a contribution in this context, we sampled silty soils under different land use (spruce forest (A_h horizon, 0–7 cm), continuous maize cropping (A_p horizon, 0–30 cm), and grassland (A_h horizon, 0–10 cm)) as well as the organic layer (L, O_f, and O_h) of the forest floor and collected plant materials from the three sites. Separation of SOM density fractions (free particulate organic matter, occluded particulate organic matter, and mineral-associated organic matter) and water-stable aggregate size fractions of the surface soils was performed in order to follow changes in the chemical composition of SOM in physical soil fractions using CPMAS ^{13}C NMR spectroscopy and to determine land use effects on the chemistry of SOM fractions.

The CPMAS ^{13}C NMR spectra showed that maize litter had the highest content of O-alkyl-C and the lowest content of alkyl-C, aryl-C and carbonyl-C compared with the plant material from the spruce stand and the grassland. The forest litter had the largest content of aromatic and alkyl-C. Decomposition of spruce litter in the humus layer resulted in a decreasing O-alkyl-C content and an increasing alkyl-C content. The SOM of the acid forest soil consisted mainly of particulate organic matter (POM) with a high content of spruce litter-derived alkyl-C. The SOC stocks in the grassland and maize soil were dominated by mineral-associated SOM which contained relatively larger proportions of aryl and carbonyl-C. The decrease of the SOC concentration induced by cultivation resulted in a relative accumulation of aromatic C structures in the mineral-bound SOM. In all soils, the free POM had a smaller proportion of alkyl-C and a larger proportion of O-alkyl-C than the POM occluded in aggregates. The mean age of the SOM in the density fractions of the maize soil increased with increasing aromaticity in the order free POM < occluded POM < mineral-associated organic matter.

Keywords: CPMAS ^{13}C NMR spectroscopy; Density fractionation; Particulate organic matter; Water-stable aggregates

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1. Introduction

Soil organic matter (SOM) is composed of many organic substances in various stages of decomposition. A

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* Corresponding author. Institute of Soil Science and Forest Nutrition, University of Göttingen, Büsgenweg 2, 37077 Göttingen, Germany. Tel.: +49 551 393517; fax: +49 551 393310.
E-mail address: mhelfri@gwdg.de (M. Helfrich).

doi:10.1016/j.geoderma.2006.03.048

range of physical and chemical fractionation procedures have been developed to identify SOM pools with different chemistries and stabilities. Since the conventional SOM fractionation in humic acids, fulvic acids, and humin produce SOM pools that hardly differ with respect to turnover rates (Balesdent, 1996) and contents of functional groups (Krosshavn et al., 1992), physical fractionation methods such as particle size and density fractionation have been proposed to analyze the processes of organic matter stabilization in soils (Christensen, 1992; Golchin et al., 1997). For instance, the light (<1.6 g cm^{-3}) free particulate organic matter (fPOM$_{<1.6}$) and the macroorganic matter (50 to 2000 μm) obtained by sieving were found to represent SOM pools with a short turnover time and these SOM fractions were found to be sensitive to soil management (Gregorich and Janzen, 1996; Six et al., 1998; Chan, 2001). In contrast, mineral-associated organic matter and organic matter entrapped at sites inaccessible to microbial attack or physically protected within soil aggregates belong to more stable organic matter pools with a turnover time of decades to centuries (Christensen, 1992; Piccolo, 1996; Golchin et al., 1997).

Solid-state CPMAS ^{13}C NMR spectroscopy has been successfully applied in studies on changes of SOM structure during organic matter decomposition (Golchin et al., 1994a; Baldock et al., 1997; Conte et al., 1997; Kögel-Knabner, 1997; Skjemstad et al., 1997; Kölbl and Kögel-Knabner, 2004). These studies have shown that polysaccharides are first affected by decomposition, leading to a decrease in O-alkyl-C. Additionally, in many studies a concomitant increase in the alkyl-C content has been observed and explained by selective preservation and in situ synthesis (Golchin et al., 1994b; Baldock et al., 1997; Kölbl and Kögel-Knabner, 2004). Thus, the alkyl-C/O-alkyl-C ratio usually increases markedly with an increasing extent of degradation of the organic material and hence is considered to be a sensitive indicator of the degree of decomposition (Baldock et al., 1997). Additionally, the aryl-C/O-alkyl-C ratio was proposed as an indicator of the stage of decomposition of particulate organic matter (POM) in soils of differing textures (Kölbl and Kögel-Knabner, 2004). However, the changes in aryl-C contents during decomposition were highly variable in several studies (Golchin et al., 1994b; Baldock et al., 1997); thus, it remains unclear if the aryl-C/O-alkyl-C ratio is capable of serving as a general indicator of decomposition.

Cultivation of virgin soils results in a decrease in soil organic carbon (SOC) and total nitrogen (N_t) contents. Maximum losses of SOC after cultivation affect the POM fraction, because tillage breaks up large macroaggregates and exposes some of the labile organic matter to microbial attack (Cambardella and Elliott, 1992; Besnard et al., 1996). The type of land use not only controls the magnitude of SOC stocks, but also influences the composition and quality of organic matter in soils. However, only few studies address the effect of land use on the composition of different SOM fractions (Preston et al., 1994; Guggenberger et al., 1994, 1995; Golchin et al., 1995; Gregorich et al., 1996). Guggenberger et al. (1994) investigated effects of land use on SOM composition in particle-size fractions of four silty loams under different land use regimes. Using alkaline CuO oxidation, they found that after 49 years of cultivation, the acid-to-aldehyde ratios of the vanillyl units [(ac/al)v] tended to be higher under forest than under the arable soil, indicating advanced lignin degradation under forest. The mineral soil of the forest site was depleted in carbohydrates (139 g kg^{-1}) compared to the arable soil (168 g kg^{-1}), probably mainly because of storage of considerable amounts of plant residues in the humus layer. Application of solid- and liquid-state ^{13}C NMR to these four sites, however, showed only minor differences in the chemical composition of SOM between differently used soils (Guggenberger et al., 1995). Significant chemical changes of SOM induced by land use may occur primarily in labile SOM fractions such as the 'light' SOM pool (Golchin et al., 1995) or the SOM in the sand fraction (Guggenberger et al., 1994). Summarizing the findings above, there is still insufficient information on the effect of land use on the chemical composition of SOC in aggregate and density fractions of soils.

In a previous paper (John et al., 2005) we reported results of the effect of land use (spruce, grassland, wheat, and maize) on SOC and total nitrogen storage in different soil aggregate and density fractions. We found that the type of land use resulted in a different distribution of litter carbon over functionally different SOM pools. At the grassland, maize, and wheat sites the majority of the SOC (86–91%) was found in the heavy (>2 g cm^{-3}) mineral-associated SOM fraction, whereas in the A horizon under spruce the free and occluded POM (<2 g cm^{-3}) accounted for 52% of the total SOC content. Additionally, we found that the turnover time of organic carbon in the water-stable aggregates in the A$_p$ horizon of the maize site increased with decreasing aggregate size from 35 yr (>1000 μm) to 86 yr (<53 μm). The mean age of SOC in density fractions was between 22 yr (fPOM$_{<1.6}$) and 83 yr (occluded POM with a density <1.6 g cm^{-3}, oPOM$_{<1.6}$).

In this study, CPMAS ^{13}C NMR spectroscopy is used to analyze the chemical structure of SOM in the different