DIVISION S-2—SOIL CHEMISTRY

Soil Organic Matter Composition in the Subhumid Ethiopian Highlands as Influenced by Deforestation and Agricultural Management

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ABSTRACT

Physical fractionation, degradative wet-chemical analysis and liquid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy were used to assess the impact of land use changes on the amount and structural composition of soil organic matter (SOM) in bulk soils and size separates in the subhumid highlands of southern Ethiopia. Soil samples (0–10 cm) were collected from natural forest, tea plantations, 25-yr cultivated fields at Wushwush (Paleudalf), *Podocarpus*-dominated natural forest, *Cupressus* plantations, and 30-yr cultivated fields at Munesa (Palehumults) sites. Forest clearing and continuous cultivation led to significant depletion ($P < 0.05$) of total soil organic C (SOC) (55% and 63%) and N (52% and 60%) in the surface soils, respectively. Compared with the cultivated fields, lower proportions of SOC (51 and 27%) and N (49 and 13%) were lost from the tea and *Cupressus* plantations, respectively. The largest depletion occurred from the labile SOM associated with the sand separates concurrent with higher oxidation states of lignin. However, substantial amounts of these organic substrates were also lost from the stable SOM fraction. Particularly, SOM, associated with the silt-size separates, decreased suggesting that the SOM in silt was quite susceptible to land use changes and represents a moderately labile SOM pool in the soils under study. Solution ^{13}C NMR spectra revealed larger proportions of protonated and C- and O-substituted aryl-C in the silt than in clay-size separates. In contrast, O-alkyl-C structures were more prominent in the clay than in silt-size separates, coinciding with the lignin distribution obtained by wet-chemical analysis. Deforestation and subsequent agricultural management not only resulted in SOM depletion but also markedly altered the chemical composition of SOM in the subhumid highland ecosystems.

SOIL ORGANIC MATTER is a physically and chemically heterogeneous mixture of organic compounds of plant, animal, and microbial origin, and has components at different stages of decomposition. The total mass of organic C stored in soils has been estimated at 1576×10^{15} g C, of which about one third is found in the tropics (Mahieu et al., 1999). Thus, the SOM in tropical soils represents an important pool of the terrestrial C reserves and its transformation is an important element in the global C cycle.

Soil organic matter plays a major role in soil fertility by affecting physical and chemical properties, and also controls soil microbial activity by serving as a source of mineralizable C and N. In mature and undisturbed tropical ecosystems, a balance exists between the organic C input and output of the soil because of mineralization and leaching of dissolved organic matter (Zech et al., 1997a). Changes in land use and soil management can have a marked effect on the SOM stock as a result of the interactions between detrital input and mineralization mediated by soil microorganisms (Tate, 1987). Several studies in the past have shown that deforestation and cultivation of native tropical soils often lead to accelerated SOM turnover, and thereby to depletion of nutrients (N, P, and S) present as part of complex organic polymers. Therefore, understanding processes that govern SOM dynamics in tropical soils is essential from the viewpoint of long-term sustainability of agriculture and influence on atmospheric CO_2 concentration and greenhouse effect.

Despite the importance of SOM in subhumid and humid tropical soils, very little information is available on the complex biological, chemical, and physical processes involved during decomposition and humification of organic substrates in physically separated-size fractions and on the factors influencing these processes. Information about the impact of land use changes on the amount and composition of organic substrates such as lignin, carbohydrates, and amino sugars in particle-size separates can eventually improve the knowledge of organic matter dynamics in tropical ecosystems.

Johansson (1986) indicated that a considerable proportion of the terrestrial C is present in the form of lignin and carbohydrates and that SOM is predominantly derived from their decomposition. Lignin decomposes slowly and represents a recalcitrant fraction in soil and litter (Guggenberger et al., 1994). During decomposition of lignin, intramolecular bonds between phenylpropanoid components of the lignin are severed and oxidized, and phenolic derivatives are released. As biodegradation progresses, the fractions derived from lignin in soil become increasingly acidic (carboxylic) (Haider, 1992; Kögel-Knabner, 1993). Thus, acid to aldehyde ratio of phenolic moieties can be used to esti-

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Abbreviations: $(Ac/Al)_V$, mass ratios of acid to aldehyde for the vanillyl; $(Ac/Al)_S$, mass ratios of acid to aldehyde for syringyl units; ANOVA, analysis of variance; CEC, cation-exchange capacity; (Fuc + Rha)/(Ara + Xyl), the ratio of fucose + rhamnose to arabinose + xylose; (Gal + Man)/(Ara + Xyl), the ratio of galactose + mannose to arabinose + xylose; GlcN/GalN, the ratio of glucosamine to galactosamine; GlcN/MurA, the ratio of glucosamine to muramic acid; LSD, least significant difference; NMR, nuclear magnetic resonance; SOC, soil organic C; SOM, soil organic matter; S/V, the ratio of syringyl to vanillyl; VSC, the sum of vanillyl, syringyl and cinnamyl units.

mate the extent of lignin biotransformation (Zech and Kögel-Knabner, 1994; Solomon et al., 2000a).

The primary C input into forest-derived soils is, however, holocellulose (cellulose and hemicellulose), which makes up approximately half of the dry weight of leaves (Haider, 1992). Plant-derived sugars, especially pentose polymers (arabinose and xylose) serve as the major source of energy and C for soil microorganisms. In turn, the microorganisms synthesize primarily hexose polymers (e.g., galactose, mannose, fucose, rhamnose) and release them into the soil (Oades, 1984; Murayama, 1984). Both the concentrations and compositions of saccharides can, therefore, be used to assess plant–microbe relationship in SOM dynamics. However, they cannot provide information about the microbial origin of organic substrates in the soil (Zhang et al., 1997). On the other hand, amino sugars are derived from different groups of soil microorganisms (Sowden and Ivarson, 1974; Parson, 1981; Zhang et al., 1998). Hence, the amount of hexosamines and muramic acid and their ratios (glucosamine to galactosamine [GlcN/GalN] and glucosamine to muramic acid [GlcN/MurA]) can serve as useful indicators for bacterial and fungal contribution to SOM (Zhang et al., 1998; Amelung et al., 1999a).

Specific wet-chemical degradation procedures and subsequent chromatographic separation and detection of individual components are suitable to elucidate the nature of primary and secondary resources of SOM. However, they usually fail to characterize the complex structure of the humified stable compounds of SOM (Kögel et al., 1988). In contrast, ^{13}C NMR spectroscopy can provide unparalleled structural information on the humic substances from many different sources (Preston, 1987) and can supplement the results obtained by degradative wet-chemical methods (Kögel-Knabner, 1997).

Therefore, the objectives of the present study were (i) to characterize phenolic, carbohydrate and amino sugar signatures in bulk soils and size separates, and (ii) to investigate the influence of land use changes on the chemical and structural composition of SOM in the subhumid highland ecosystems of southern Ethiopia. The results from the wet-chemical methods were supplemented by solution ^{13}C NMR spectroscopy.

MATERIALS AND METHODS

Site Description

The present research was conducted at the southwestern highlands (Wushwush) and the southeastern Rift Valley escarpment (Munesa) of Ethiopia. Wushwush is located at 7° 19′ N lat. and 36° 07′ E long. The altitude of the area is 1900 m above sea level. Mean annual temperature is 18°C with an average annual precipitation of 1800 mm. Geologically, the area is associated with Jimma Volcanics with abundant rhyolites and trachybasalts. The soils of the area are classified as Plinthaquic Paleudalfs (Soil Survey Staff, 1999), with clayey texture and dark reddish brown color. The Wushwush natural forest is mainly composed of *Olea africana* (Mill.), *Syzygium guineense* (Guill. ex Perr. Gmel.), *Cordia africana* (Lam.), *Croton macrostachys* (Hochst. ex Rich.), and *Ficus vasta* (Forsk.) The Munesa site is located at 7° 35′ N lat. and 38° 45′ E long. Mean annual temperature is 19°C with an average annual precipitation of 1250 mm. Parent materials of the Munesa area are of volcanic origin, principally trachytes and basalts with ignimbrites and pumices at the rift valley floor. The escarpment extends from 2100 to 3200 m and the plain descends gradually to the Rift Valley lakes at 1600 m above sea level. The soils of the area are classified as Typic Palehumults (Soil Survey Staff, 1999), with clayey texture and very dark reddish brown color. The natural vegetation of the Munesa site ranges from the *Arundinaria alpina* (K. Schum.), *Hagenia abyssinica* (Bruce ex J.F. Gmel.), *Croton macrostachys* (Hochst. ex Rich.), *Podocarpus falcatus* (Thunb. ex Mirb.), *Olea hochstetteri* (Baker.) dominated forest on the escarpment to *Acacia* woodlands (*Acacia tortilis* (Forsk ex Hayne), *Acacia abyssinica* (Hochst. ex Benth.) and *Acacia seyal* (Delile) in the semi-arid lowlands.

The land-use systems studied at the Wushwush site were natural forest, tea plantations (35 yr old) and fields cultivated for 25 yr, while at the Munesa site *Podocarpus* natural forest, *Cupressus* plantations (25 yr old) and fields cultivated for 30 yr were investigated. There is no well established fertilization program in the tea plantations. Depending on fertilizer availability, up to 100 kg ha^{-1} Urea or NPK (50:10:20) were applied every 3 to 5 yr as a side dressing. In the cultivated fields of both sites, maize (*Zea mays* L.) was grown without fertilizer inputs. However, during the intermittent dry periods, sorghum (*Sorghum bicolor* L. Moench) was grown at Munesa. The plowing depth both at the Wushwush and Munesa sites varies between 10 to 12 cm. Crop residues that remain on the cultivated fields are normally collected and used as animal feed at both sites.

After considering the depth of cultivation in the region, we used a core sampler (200-cm^3 core volume at each subsite) and collected soil samples in three replicates from the upper 10 cm of the different land-use systems in April 1998. This helps to minimize differences, which may arise because of the dilution of SOM because of mixing of the surface soil with that of the subsoil through cultivation. We selected three representative fields from each land-use system, and from each site collected nine subsamples in a radial sampling scheme (Wilding, 1985). A composite sample was then prepared from the subsamples. The samples were air-dried and sieved (<2 mm) prior to fractionation and chemical analysis.

Particle-Size Fractionation

Particle-size fractionation was done on <2-mm material (bulk soil) according to Amelung et al. (1998). After removing visible root remnants, 30 g of soil was ultrasonically treated with an energy input of 60 J mL^{-1} using a probe type sonicator (Branson Sonifier W-450) in a soil/water ratio of 1:5 (w/v). The coarse-sand size separates (250–2000 μm) were isolated by wet sieving. To completely disperse the remaining material in the <250-μm suspension, ultrasound was again applied with an energy input of 440 J mL^{-1} in a soil/water ratio of 1:10 (w/v). The clay-size separates (<2 μm) were separated from the silt (2–20 μm) and fine sand (20–250 μm) size separates by repeated centrifugation. The silt-size separates were separated from the fine-sand size separates by wet sieving. Coarse- and fine-sand separates were combined and finally all size separates were dried at 40°C before grinding them for chemical analysis. The recovery of size separates after ultrasonic dispersion, wet sieving, and centrifugation ranged from 97 to 98% of the initial soil mass.

Chemical Analysis

Carbon and N contents of bulk soils and particle-size separates were analyzed by dry combustion with a C/H/N/S-ana-

Table 1. Selected physical and chemical characteristics of surface soils (0–10 cm) in the subhumid highlands of southern Ethiopia.

Land use	Bulk density	pH		CEC†	BS	Fe_d‡	Fe_o§	Al_d†	Al_o§
	$Mg\ m^{-3}$	H_2O	KCl	$cmol_c\ kg^{-1}$ soil	%	$g\ kg^{-1}$			
				Wushwush					
Natural forest	**0.69**	**6.4**	**5.5**	**37**	**69**	**6.7**	**0.60**	**0.96**	**0.25**
Tea plantation	**0.87**	**5.7**	**4.5**	**25**	**35**	**6.5**	**0.70**	**0.97**	**0.32**
Cultivation	**0.89**	**5.7**	**4.7**	**26**	**46**	**5.8**	**0.83**	**0.77**	**0.30**
				Munesa					
Natural forest	**0.62**	**7.6**	**6.8**	**52**	**98**	**2.5**	**0.30**	**0.38**	**0.15**
***Cupressus* plantation**	**0.77**	**7.4**	**6.6**	**40**	**96**	**2.5**	**0.36**	**0.32**	**0.18**
Cultivation	**1.04**	**5.6**	**4.5**	**27**	**51**	**3.4**	**0.71**	**0.40**	**0.21**

† Cation-exchange Capacity.

‡ Fe_d and Al_d, dithionite-citrate-bicarbonate extractable Fe and Al.

§ Fe_o and Al_o, oxalate extractable Fe and Al.

lyzer (Elementar Vario EL Hanau, Germany). The pH-H_2O and pH-KCl were determined in 1:2.5 soil/water (w/v) suspension using a glass electrode. Cation-exchange capacity (CEC) was determined with 1 *M* NH_4OAc (pH = 7.0) according to Avery and Bascomb (1974). Dithionite-citrate-bicarbonate extractable Al and Fe (Al_d, Fe_d) were determined after double extractions at 70°C for 15 min as described by Mehra and Jackson (1960). Oxalate-extractable Al and Fe (Al_o, Fe_o) were determined using atomic absorption spectrometer (Varian AAS-400, Varien Techtron, Mulgrave, Victoria, Australia) after extraction for 2 h with 0.2 *M* ammonium oxalate at pH = 3 in darkness (Blume and Schwertmann, 1969). Selected soil physical and chemical characteristics are shown in Table 1.

Phenolic-Carbon Constituents

The amount and stage of oxidative decomposition of lignin in bulk soils and particle-size separates were estimated using the system of lignin parameters obtained from alkaline CuO-oxidation (Hedges and Ertel, 1982). Samples were oxidized with CuO and 2 *M* NaOH for 2 h at 170°C under a N_2 atmosphere. Lignin-derived phenols generated upon CuO-oxidation were analyzed as O-methyloxime trimethylsilyl derivatives by capillary gas-liquid chromatography (HP 6890, HP Ultra 2 fused silica column, 25 m, Hewlett Packard, Palo Alto, CA) equipped with an FID detector. Ethylvanillin was added as an internal standard before extraction and phenylacetic acid before derivatization to determine the recovery of ethylvanillin. Intact lignin moieties (vanillin, syringyl, and cinnamyl units; VSC) were estimated by the sum of vanillyl (vanillin and vanillic acid), syringyl (syringaldehyde and syringic acid), and cinnamyl (ρ-coumaric acid and ferulic acid) units. Absolute lignin contents cannot be determined, because the contribution of VSC-lignin to the total lignin remains unknown (Amelung et al., 1999b).

Carbohydrate-Carbon Constituents

Determination of neutral sugars and uronic acids was conducted according to Amelung et al. (1996). Individual neutral sugars and acidic sugars were liberated from noncellulosic soil carbohydrates with 4 *M* trifluoroacetic acid (TFA) at 105°C for 4 h. The hydrolysates were filtered through glass fiber filters and dried using a rotary evaporator. The samples were purified by percolation through XAD-7 and Dowex 50 resin columns (Fluka chemic GmbH, Neu-Ulm, Germany). Myoinositol was added as the first internal standard before hydrolysis and 3-O-methylglucose was added as a second internal standard prior to derivatization to determine the recovery of the myo-inositol. The resulting hexoses, pentoses, and uronic acids were converted to O-methyloxime trimethylsilyl derivatives and separated by gas-liquid chromatography.

Amino Sugar-Carbon Constituents

Amino sugars, i.e., glucosamine, galactosamine, mannosamine, and muramic acid were determined according to the method of Zhang and Amelung (1996). Samples from bulk soils and particle-size fractions were hydrolyzed with 6 *M* HCl at 105°C for 8 h. Before hydrolysis, myoinositol was added as the first internal standard. The final organic phase was dried with N gas at 45°C and finally dissolved in 300 μL of ethyl acetate-hexane (1:1). Identification and quantification of amino sugars was conducted by capillary gas-liquid chromatography. As a recovery standard, 3-O-methylglucose was used.

Nuclear Magnetic Resonance Spectroscopy

For liquid-state ^{13}C NMR measurements, the soils were extracted three times with 0.1 *M* NaOH and 0.4 *M* NaF at a ratio of soil/extraction solution of 1:5 (w/v). The sample size was adjusted to ensure a minimum yield of 200 mg of organic C in the extracts. The extraction procedure followed the outline of Schnitzer (1982), as modified by Sumann et al. (1998). Replacement of 0.1 *M* $Na_4P_2O_7$ by 0.1 *M* NaOH-0.4 M NaF mixture does not affect the ^{13}C-NMR spectra of alkali-extracts, rather it improves extraction yield compared with extractions using only 0.1 *M* $Na_4P_2O_7$ (Sumann et al., 1998). The combined extracts were dialyzed (molecular weight cutoff, MWCO, 12 000–14 000 Da) and freeze-dried. Liquid-state ^{13}C NMR spectra were obtained on a Bruker Avance DRX 500 NMR spectrometer (Bruker Instruments, Billerica, MA). About 150 mg of the freeze-dried material was dissolved in 3 mL of 0.5 *M* NaOD in a 10-mm NMR tube. Conditions for ^{13}C NMR were: spectrometer frequency, 125.77 MHz; inverse-gated decoupling; acquisition time, 0.33 s; delay time, 1.67 s; and line-broadening factor, 100 Hz. This factor was used to enhance the characteristic broad signals of extracted organic matter. Chemical shifts were given in parts per million relative to the resonance of an external standard of TSP (3-[trimethylsilyl] propionic acid). The signal areas were calculated by electronic integration and signal assignments were made according to literature data (Kögel-Knabner, 1997).

Statistics

Statistical analysis of the data was carried out on the replicates by one-way ANOVA. If the main effects were significant at $P < 0.05$, a post hoc separation of means was done by univariate least significant difference (LSD) test. Statistical analysis was conducted with STATISTICA 5.1 for Windows (StatSoft Inc., Tulsa, OK).

RESULTS AND DISCUSSION

Soil Organic Carbon and Nitrogen Contents

The content of total SOC in the surface soils (0–10 cm) varied from 38 to 85 g kg^{-1} soil at Wushwush and 38 to 103 g kg^{-1} soil at the Munesa sites, whereas the amount of total soil N ranged from 3.7 to 7.8 g kg^{-1} soil and 3.3 to 8.2 g kg^{-1} soil at the two sites, respectively (Table 2). The amount of SOM in the surface soils of these subhumid tropical highland ecosystems is larger than the amounts reported for lowland humid tropical forest soils (Veldkamp, 1994; Van Noordwijk et al., 1997). However, they compare positively with the results of Möller et al. (2000) for humid tropical mountain ecosystems of northern Thailand. The large amount of SOM in the surface soils of these subhumid tropical highland forest ecosystems could possibly be attributed to the relatively slower decomposition of SOM because of the cool mountainous climate compared with the humid tropical lowland ecosystems with higher annual precipitation and temperature and to differences in litter quality.

Agricultural management of virgin soil induces a drastic change in the equilibrium of SOM attained under undisturbed conditions, and thereby affects the quantity and quality of SOM especially in the near-surface layers (Tate, 1987). In the present study, the amounts of both total SOC and N in the surface soils significantly decreased ($P < 0.05$) following land-use changes (Table 2). At the Wushwush site, forest clearing and 25-yr continuous low-input cropping led to the depletion of 55% of the total SOC and 52% of total N, whereas 30 yr of cultivation at the Munesa site resulted in a 63 and 60% reduction of the total SOC and N in the bulk soils, respectively. These results are comparable with the results of Skjemstad et al. (1986) for cultivated subtropical Vertisols of Australia and with our results from cultivated Luvisols of northern Tanzania (Solomon et al., 2000a). The depletion of SOM in the continuously cultivated soils may be attributed to the drastic reduction of organic matter input and to the tillage practices, which frequently exposes aggregates to physical disruption by rapid wetting and rain drop impact as well as through shearing by agricultural implements. The net effect of which is the loss of SOM through the stimulation of oxidation and exposure of the originally inaccessible organic matter to the attack of soil microorganisms. The average losses of total SOC and N depleted because of clear-cutting and establishment of the tea (51 and 49%) and the *Cupressus* (27 and 13%) plantations, however, were lower than those from the cultivated fields, respectively. This may be attributed to the higher organic matter input through the use of pruned plant parts as a mulch at the tea plantations and through litter-fall after senescence at the *Cupressus* plantations. In addition, the less frequent mechanical disturbance at the plantations than the continuously cultivated fields may also contribute to the relatively lower SOM depletion from the plantations. In contrast, the C/N ratios in bulk soils of the different land use systems of the two sites did not significantly differ (Table 2).

Examination of physically fractionated-size separates showed that only 4 to 13% of the total SOC and 2 to 9% of the total N were found in the sand-size separates. The SOM associated with the silt contained 29 to 52% of SOC and 25 to 40% of soil N, while most of the SOM was bound to the clay-size separates (40 to 63% of the total SOC and 56 to 71% of the total soil N) (Fig. 1). Besides the reactivity and specific charge characteristics of clay minerals and associated oxides and hydroxides, the higher active surface area controls the enrichment of SOM in the finer-size separates (Zech et al., 1997a). The C/N ratios of the size separates of both soils decreased with decreasing particle-size from 22.4 in the sand to 8.8 in the clay-size separates, reflecting a progressive SOM humification with decreasing diameter (Fig. 1). This was also revealed by the electron microscopy of organic matter associated with representative size separates of the soils under investigation. The scan-

Table 2. Amounts of soil organic C (SOC), total N, and phenolic, carbohydrate, and amino sugar signatures in soils of the different land use systems.

Land use	SOC	N	C/N	VSC†	Ac/Al_V‡	Ac/Al_S‡	S/V§	Non-cellulosic carbohydrates	(Gal+Man)/(Ara+Xyl)¶	(Fuc+Rha)/(Ara+Xyl)#	Amino sugars	(GluN)/(GalN)††	(Glu/N)/(MurA)‡‡
	—— g kg^{-1} soil ——			g kg^{-1} SOC				g kg^{-1} SOC			g kg^{-1} SOC		
								Wushwush					
Natural forest	85a§§	7.8a	10.8ns	25.9a	0.36b	0.55b	0.84a	141a	0.86a	0.42a	91a	1.31	11.5
Tea plantation	42b	4.0b	10.4ns	24.1a	0.39b	0.59a	0.89a	113b	0.72b	0.30b	41b	2.36	20.2
Cultivation	38b	3.7b	10.2ns	16.6b	0.52a	0.61a	0.62b	92b	0.66c	0.25b	39b	2.37	20.8
								Munesa					
Natural forest	103a	8.2a	12.6ns	23.3a	0.34b	0.45b	0.85a	153a	0.89a	0.45a	70a	1.42	12.5
Cupressus plantation	71b	7.1b	10.0ns	21.2a	0.28c	0.69a	0.22c	122b	0.86a	0.38b	54b	2.03	15.5
Cultivation	38c	3.3c	11.8ns	17.9b	0.44a	0.72a	0.79b	79c	0.56b	0.29c	32c	2.45	21.4

† VSC, vanillyl + syringyl + cinnamyl.

‡ $(\text{Ac/Al})_V$ and $(\text{Ac/Al})_S$, acid to aldehyde ratio of vanillyl and syringyl.

§ S/V, syringyl to vanillyl ratio.

¶ (Gal+Man)/(Ara+Xyl), galactose + mannose to arabinose + xylose.

(Fuc+Rha/Ara+Xyl), fucose + rhamnose to arabinose + xylose.

†† (GluN/GalN), ratio of glucosamine to galactosamine.

‡‡ (GluN/MurA), glucosamine to muramic acid; ns, not significant.

§§ Within one site, letters along the column indicate significant differences between mean values of the different land use systems at $P < 0.05$ ($n = 3$).

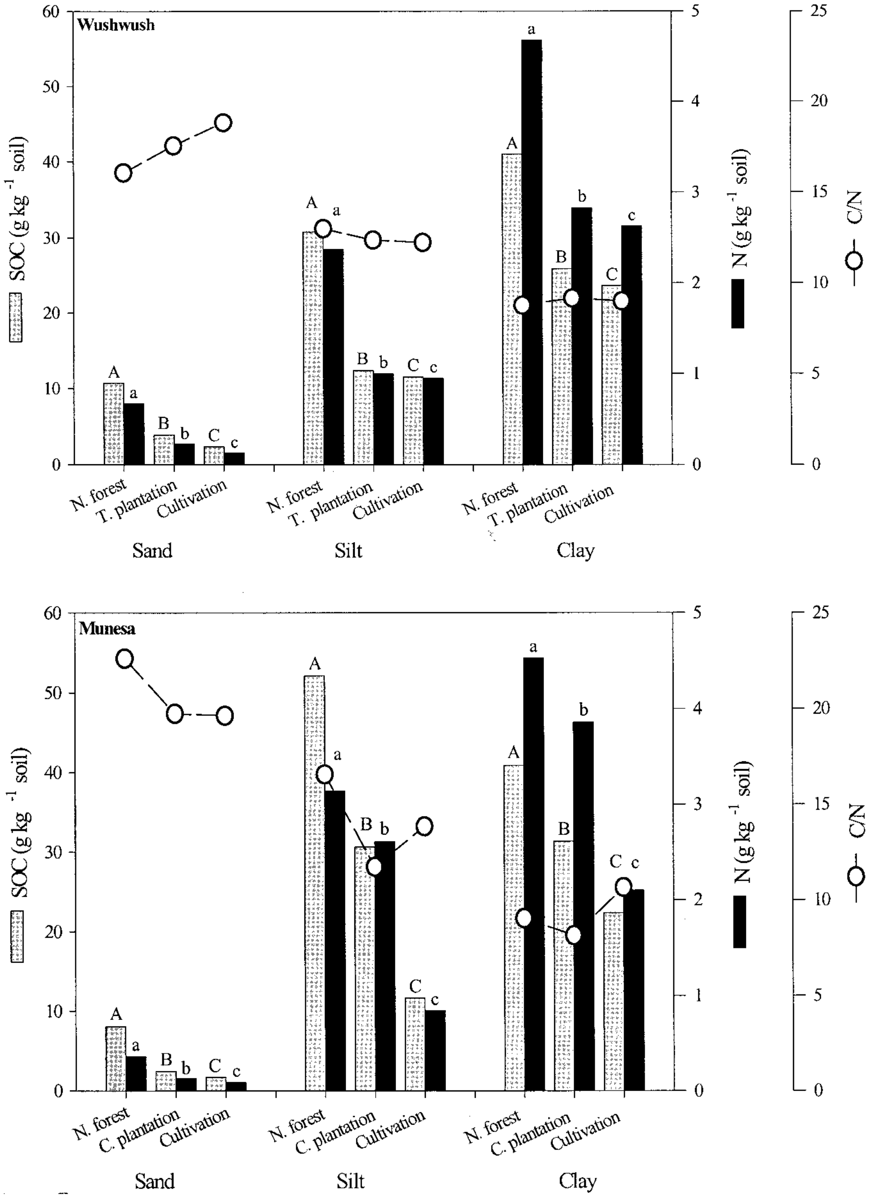

Fig. 1. Soil organic carbon (SOC) and total N contents and C/N ratios in size separates of the different land-use systems at the Wushwush and Munesa sites. Letters above the bars indicate significant differences between mean values of the same size separates of the different land use systems at $P < 0.05$; N. forest, natural forest; T. plantation, Tea plantation; C. plantation, *Cupressus* plantation.

ning electron microscope micrographs showed that the SOM associated with the sand-size separates was composed of undecomposed and macromorphologically identifiable particulate plant residues (coarse sand) as well as partially decomposed organic debris (fine sand). The SOM associated with the silt- and clay-size separates, however, was composed of completely decomposed organic structures and microbial residues (Fig. 2).

Long-term continuous cropping markedly reduced the amount of SOM in all size separates at the Wushwush and Munesa sites. The largest depletion of SOC (78 and 79%) and N (81 and 75%) because of continuous cultivation occurred from particulate SOM associated with the sand-size separates at both sites, respectively (Fig. 1). The silt separates of the Wushwush and Munesa sites lost on average 63 and 78% of the SOC and 60 and 73% of the N, respectively, indicating that the SOM associated with the silt-size separates of these tropical soils is also quite labile. The clay-bound SOM lost on the average only 42 and 44% of the SOC and 42 and 53% of the N after 25 and 30 yr of cultivation, respectively. Compared with the cultivated fields, relatively lower average losses of SOC (63 and 69%) and N (67 and 64%) were obtained from the SOM associated with the sand, the silt (60 and 41%, SOC; 58 and 17% N) and the clay-size (36 and 22%, SOC; 38 and 14% N) separates of the tea and *Cupressus* plantations, respectively. The relatively lower depletion of SOC and N from clay-size separates of the cultivated fields and plantations indicated that the SOM bound to the clay was more stable than that found in the sand and silt-size separates of these tropical soils. This may be attrib-

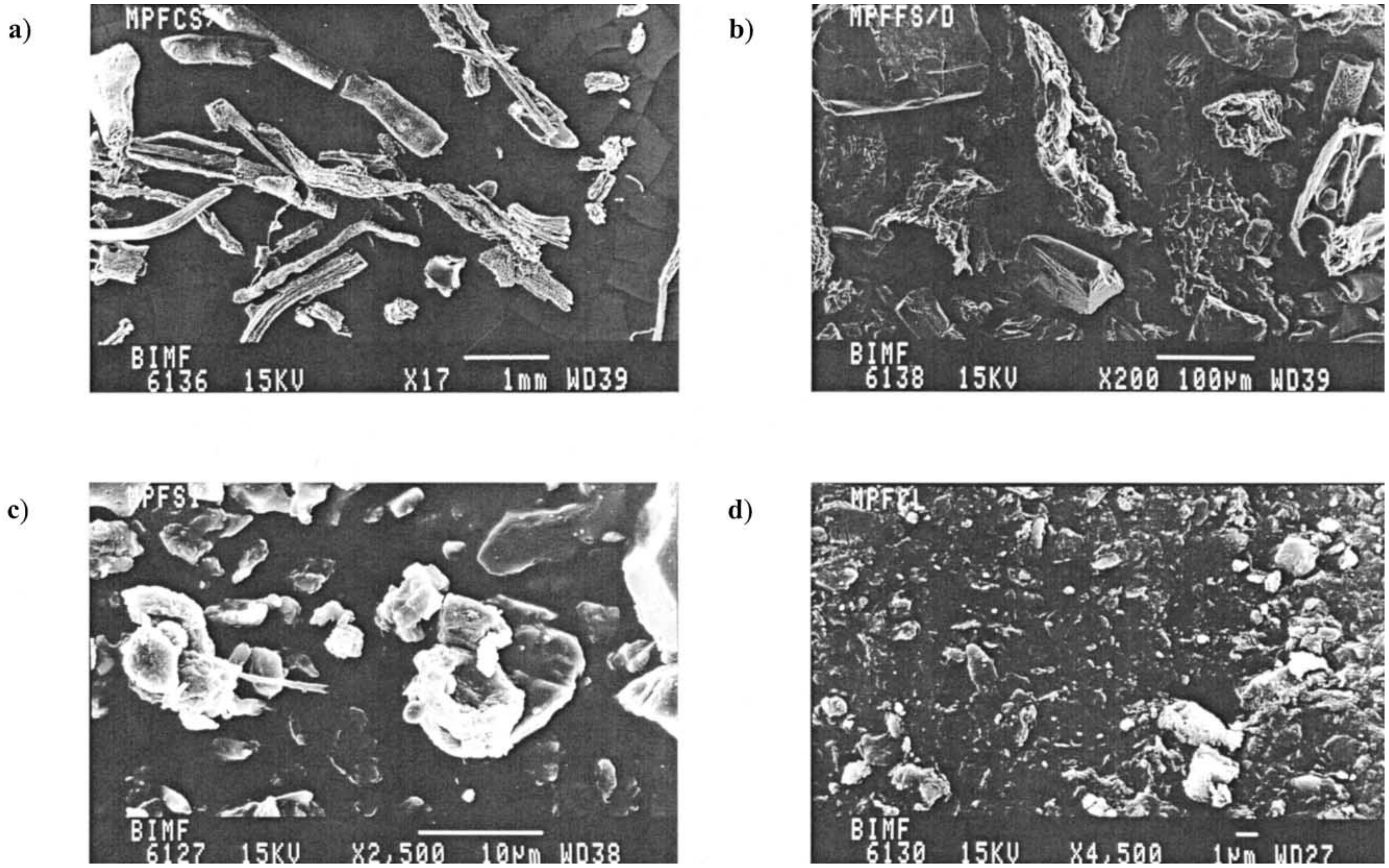

Fig. 2. Scanning electron microscope micrographs (acceleration voltage = 15 kV) of organic matter associated with (a) coarse sand (2000–250 μm), (b) fine sand (250–20 μm), (c) silt (20–2 μm) and (b) clay (<2 μm) size separates of soils from the natural forest of the Munesa site.

uted to physical and chemical stabilization of the SOM against biodegradation by the clay and clay associated sesquioxides (Zech et al., 1997a).

Phenolic Signature

The concentration of lignin-derived C (g VSC kg^{-1} SOC) and patterns of the total phenolic-C moieties in the surface soils (0–10 cm) differed significantly ($P < 0.05$) under the different land use systems. As shown in Table 2, soils of the natural forests at the Wushwush and Munesa sites had the largest concentrations of lignin-derived phenols followed by the plantations and cultivated fields. Alterations of the chemical structure of the vanillyl and syringyl moieties during lignin decomposition often results in increased acid to aldehyde ratios of vanillyl $[(Ac/Al)_V]$ and syringyl $[(Ac/Al)_S]$ units and decreased S/V quotient (Kögel et al., 1988). In the present study, the $(Ac/Al)_{V,S}$ ratios generally decreased in the order: cultivation > plantation > natural forest. The S/V ratio in the bulk soils, however, increased in the order: cultivation < tea plantation < natural forest at the Wushwush and cultivation < natural forest < *Cupressus* plantation at the Munesa sites. These results indicated that the VSC-lignin in the natural forest and plantations was less oxidized than the lignin in the cultivated fields. The lowest S/V ratio found in bulk soil and size separates of the *Cupressus* plantations may be attributed to the inherently lower proportion of syringyl units in the gymnosperm lignin (Sarkanen and Ludwig, 1971).

The highest average proportion of VSC-lignin in particle-size separates was found in the particulate SOM associated with the sand (53 and 57%) followed by the SOM in the silt (34 and 33%) and clay (13 and 10%) size separates at the Wushwush and Munesa sites, respectively (Fig. 3). The $(Ac/Al)_{V,S}$ ratios increased with decreasing particle-size at both sites, whereas the opposite was true for the ratio of S/V units, suggesting a progressive lignin degradation and selective loss of syringyl units in the order: sand < silt < clay, independent of the land use systems. The relative amount and patterns of phenolic-C moieties in these soils are comparable with those obtained in temperate (Guggenberger et al., 1994; Glaser, et al., 2000) and tropical soils (Zech et al., 1997b; Guggenberger et al., 1999; Solomon et al., 2000a).

Since the major proportion of lignin is particulate, management effect on the concentrations of total phenolic-C moieties in size separates were most apparent in the particulate SOM associated with sand followed by the silt-size separates of the soils under investigation. According to Fig. 3, significantly lower ($P < 0.05$) concentrations of VSC-lignin were found in SOM associated with the sand-size separates of the cultivated fields than the natural forests of both sites. Relatively higher yields of phenolic CuO-oxidation products were also obtained in the silt-size separates of the natural forests compared with the cultivated soils. These results concur positively with the results of Solomon et al. (2000a) where a higher depletion of VSC-lignin was obtained from the sand- and silt-size separates of arable soils than the corresponding size separates of native woodland soils of northern Tanzania. Compared with the cultivated soils, lower $(Ac/Al)_{V,S}$ ratios and higher S/V ratio (except in *Cupressus* plantations) were found in the sand- and silt-size separates of the natural forests followed by soils under plantations at both sites. These results indicated that the VSC-lignin in the sand- and silt-size separates of the cultivated fields was more altered than the lignin in the same size separates of the natural forests or the plantations. The concentration and patterns of VSC-lignin in the clay-size separates appeared to be little affected by land use changes.

Carbohydrate Signature

The total concentrations of noncellulosic carbohydrates (g kg^{-1} SOC) significantly decreased in the order: natural forest > plantation > cultivation at the Wushwush and Munesa sites (Table 2). Microorganisms synthesize little if any pentoses, while xylose and arabinose are ubiquitous constituents of plant cells (Oades, 1984). Therefore, individual quotients of sugar monomers can be used to estimate the relative contribution of microbial-derived saccharides to the soil carbohydrate composition. Murayama (1984) and Oades (1984) used the ratios of hexoses to pentoses [galactose (Gal) + mannose (Man)]/[arabinose (Ara) + xylose (Xyl)] and deoxyhexoses to pentoses [fucose (Fuc) + rhamnose (Rha)]/[arabinose (Ara) + xylose (Xyl)] to estimate the contribution of plant-derived and microbially synthesized sugars to the soil monosaccharide composition. The (Gal + Man)/(Ara + Xyl) and (Fuc + Rha)/(Ara + Xyl) ratios in the bulk soils of the natural forests at the Wushwush and Munesa sites were higher than those from corresponding plantations and cultivated fields (Table 2). These results indicated the presence of higher proportions of microbial-derived carbohydrates in SOM of the natural forests compared with the SOM in the plantations and cultivated fields. Higher amounts of microbial-derived saccharides in forest than arable soils were also reported by Guggenberger et al. (1994) in Germany, Guggenberger et al. (1999) in Costa Rica, and Solomon et al. (2000a) in Tanzania. However, these authors reported higher concentration of TFA-hydrolyzable saccharides in the cultivated than in the forest soils. The lower carbohydrate concentrations in the arable soils of our sites may be attributed to the lower biomass input as a result of competitive use of crop residues (e.g., for animal feed, construction material, or cooking) coupled with the rapid depletion of monosaccharides because of accelerated mineralization of the original (forest-derived) SOM following clear-cutting and long-term continuous cultivation under the subhumid tropical highland environment. This suggestion is supported by our natural ^{13}C abundance studies, where only about 25 and 55% of the SOC in cultivated soils of the Wushwush and Munesa sites was derived from maize (C_4) crop residues, while the remaining SOC at both sites was of forest (C_3) origin (Solomon et al., 2000, unpublished data).

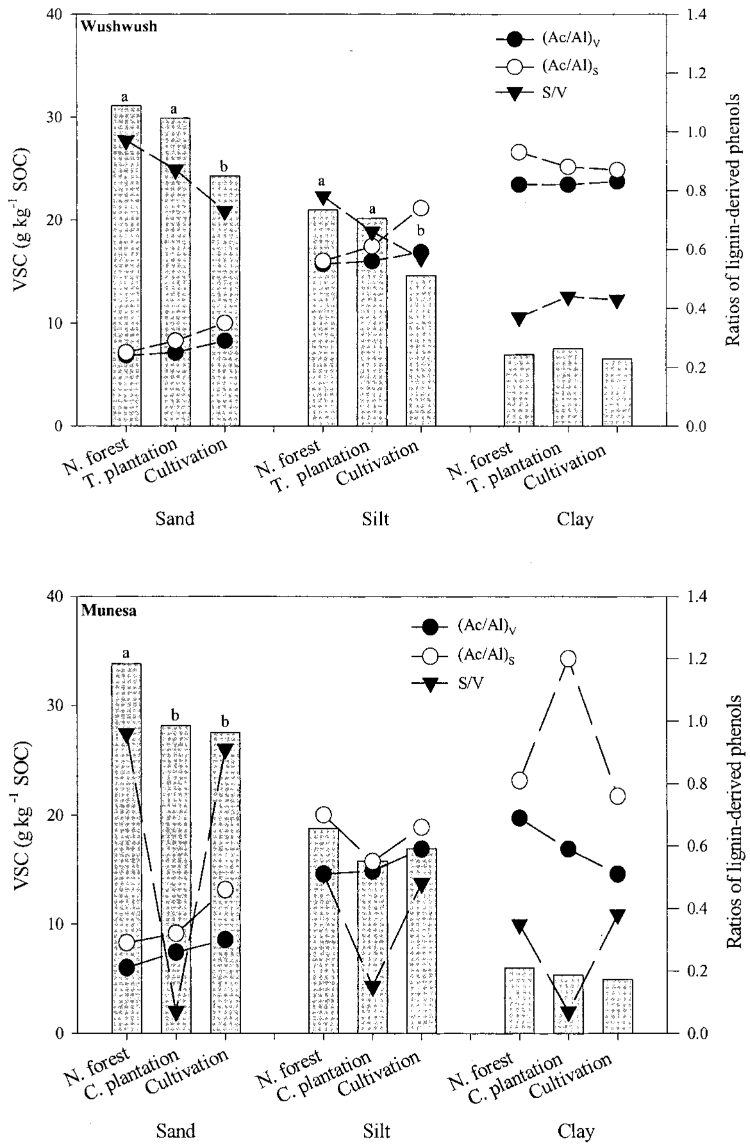

Fig. 3. Average concentrations of CuO-oxidation products (VSC) and ratios of lignin-derived phenols in size separates of the different land use system at the Wushwush and Munesa sites. VSC, vanillyl+syringyl+cinnamyl; $(Ac/Al)_{V,S}$, acid to aldehyde ratio of vanillyl and syringyl; S/V, syringyl to vanillyl ratio; letters above the bars indicate significant differences between mean values of the same size separates of the different land use systems at $P < 0.05$; bars without letters are not significant; N. forest, natural forest; T. plantation, Tea plantation; C. plantation, *Cupressus* plantation.

The highest percentage of total TFA-hydrolyzable soil saccharides was found in the clay-bound SOM (50 and 49%) at the Wushwush and Munesa sites, respectively (Fig. 4). The carbohydrates in the silt-size separates comprised on average 30 and 32%, whereas carbohydrates associated with the sand-size separates contained 20 and 19% of the total soil monosaccharides at the two sites, respectively. The ratios of hexoses to pentoses and deoxyhexoses to pentoses in physically separated-size separates increased in the order: sand < silt < clay. These results indicated greater contribution of microbial-derived sugars (galactose, mannose, fucose, and rhamnose) to saccharide spectrum of the clay, while plant-derived saccharides (arabinose and xylose) dominated the monosaccharide composition of the sand-size separates. Our results are inline with the results of Zech et al. (1997b) for soils of Argentina, Amelung et al. (1999c) for soils of North American prairie, Guggenberger et al. (1999) for soils of Costa Rica, and Glaser, et al. (2000) for the mountain soils of Khyrgyzia.

The impact of land use changes on soil carbohydrate concentrations was visible in all size separates. According to Fig. 4, significantly lower concentrations of noncellulosic carbohydrates were generally found in SOM associated with the size separates of the continuously cultivated fields and plantations compared with the corresponding size separates of the natural forests ($P < 0.05$), with the exception of the clay-size separates of the *Cupressus* plantations. Moreover, the ratios of hexoses to pentoses and deoxyhexoses to pentoses in size separates of the cultivated fields and plantations were generally lower than those in the natural forests,

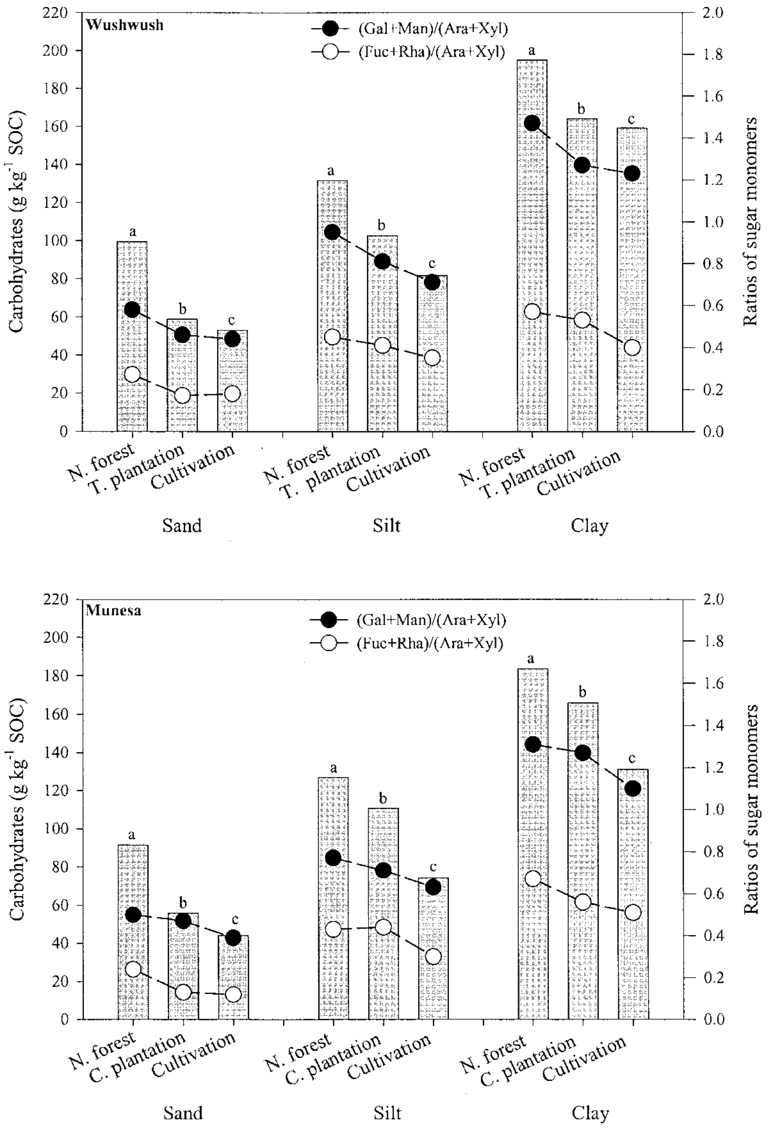

Fig. 4. Average concentrations of noncellulosic carbohydrates and ratios of sugar monomers in size separates of the different land-use systems at the Wushwush and Munesa sites. (Gal + Man)/(Ara + Xyl), galactose + mannose to arabinose + xylose; (Fuc + Rha/Ara + Xyl), fucose + rhamnose to arabinose + xylose; Letters above the bars indicate significant differences between mean values of the same size separates of the different land use systems at $P < 0.05$; N. forest, natural forest; T. plantation, Tea plantation; C. plantation, *Cupressus* plantation.

indicating depletion of microbial-derived carbohydrates from the SOM associated with size separates of these tropical soils following land use changes.

Amino Sugar Signature

Significantly higher ($P < 0.05$) total amino sugar concentrations (g kg^{-1} SOC) were found in bulk soils of the natural forests compared with the plantations and cultivated fields (Table 2). The apparent depletion of amino sugars may be attributed to accelerated mineralization of hexosamines and muramic acid upon forest clearing and subsequent low-input agricultural management under the subhumid tropical highland environment. Glucosamine is an important constituent of the fungal cell wall (Chantigny et al., 1997; Zhang et al., 1998, 1999), while in terrestrial ecosystems muramic acid uniquely originates from bacteria (Kenne and Lindburg, 1983; Amelung et al., 1999a). Sowden and Ivarson (1974) demonstrated that little if any galactosamine is synthesized by fungi during fungi-inoculated incubation experiments. Hence, the ratios of both glucosamine to galactosamine (GlcN/GalN) and glucosamine to muramic acid (GlcN/MurA) were used to assess the fate of bacterial- and fungal-derived SOM in these tropical soils. According to Table 2, the patterns of amino sugars in the soils under investigation were considerably influenced by land use changes. The ratios of both GlcN/GalN and GlcN/MurA increased in the order: natural forest < plantation < cultivation at the Wushwush and Munesa sites. The higher GlcN/GalN and GlcN/MurA ratios in the continuously cultivated fields and plantations compared with the corresponding natural forests indicated higher depletions of galactosamine and muramic acid than glucosamine because of land-use changes. Rapid losses of galactosamine and muramic acid compared with glucosamine because of agricultural manage-

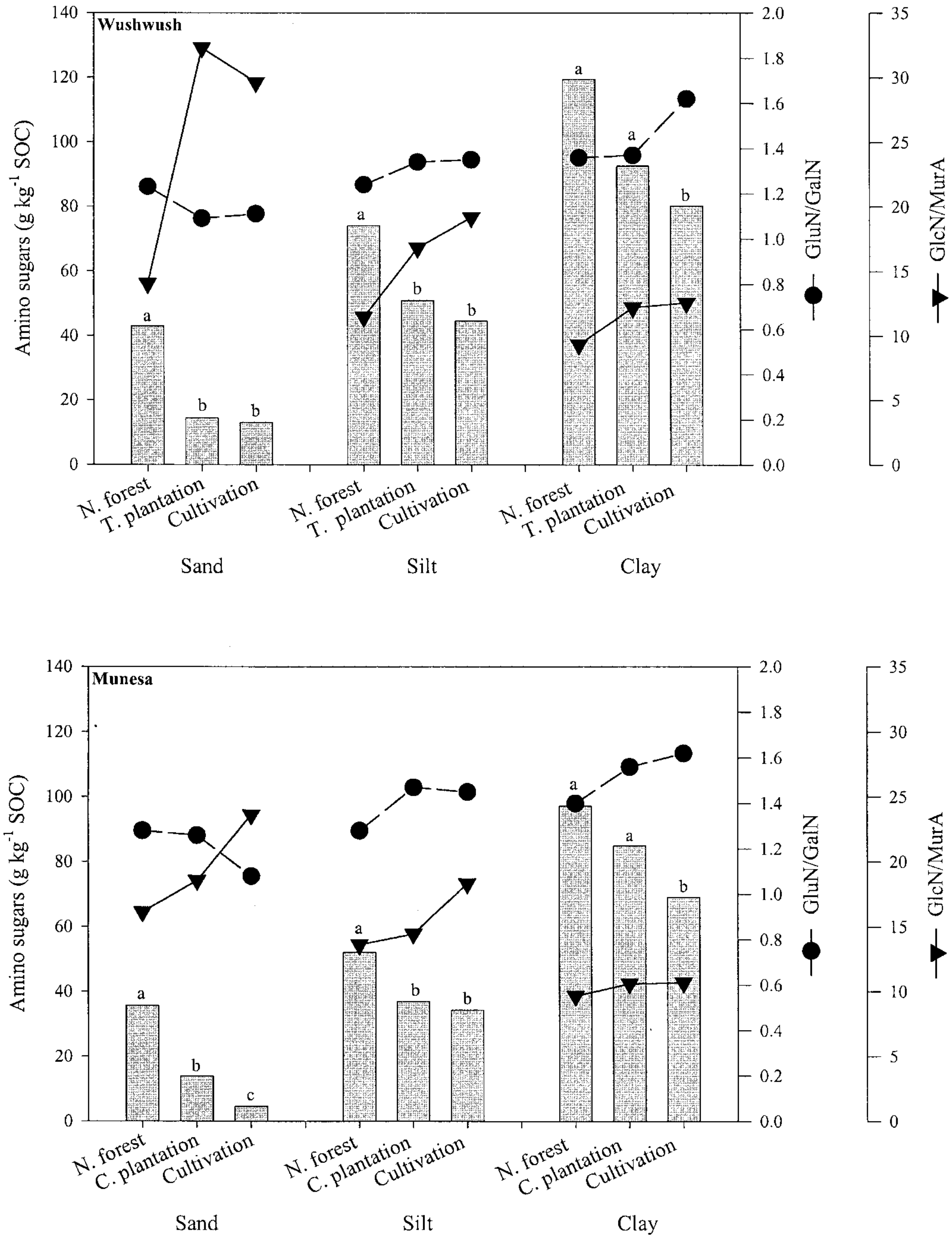

Fig. 5. Total amino sugar concentrations and ratios of glucosamine to galactosamine (GlcNl + GalN) and glucosamine to muramic acid (GluN + MurA) in size separates of the different land use systems at the Wushwush and Munesa sites. Letters above the bars indicate significant differences between mean values of the same size separates of the different land use systems at $P < 0.05$; N. forest, natural forest; T. plantation, Tea plantation; C. plantation, *Cupressus* plantation.

ment of native soils were also reported by Zhang et al. (1997, 1999) in North America and by Solomon et al. (2000b) in northern Tanzania. The results of the present investigation further supports the suggestion by these authors that bacterial-derived amino sugars (galactosamine and muramic acid) are less stable compared with fungal-derived glucosamine in arable soils. The relative stability of glucosamine compared with galactosamine and muramic acid may be ascribed to the fact that it is the constituent of the recalcitrant glomaline, a glycoprotein produced in the soil by arbuscular mycorrhizal fungi (Wright and Upaghyaya, 1996; Zhang et al., 1998). The higher concentration of glucosamine might be partly explained by the enhanced growth of fungi in a slightly more acidic environment under the investigated arable soils than under the native forest vegetation.

The distribution of amino sugars in size separates of the soils under study was similar to that observed for the total SOC. Accordingly, the SOM in the clay (56 and 60%) was enriched in amino sugars compared with the silt (32 and 29%) and sand (12 and 11%) size separates (Fig. 5). These results show that microbial contri-

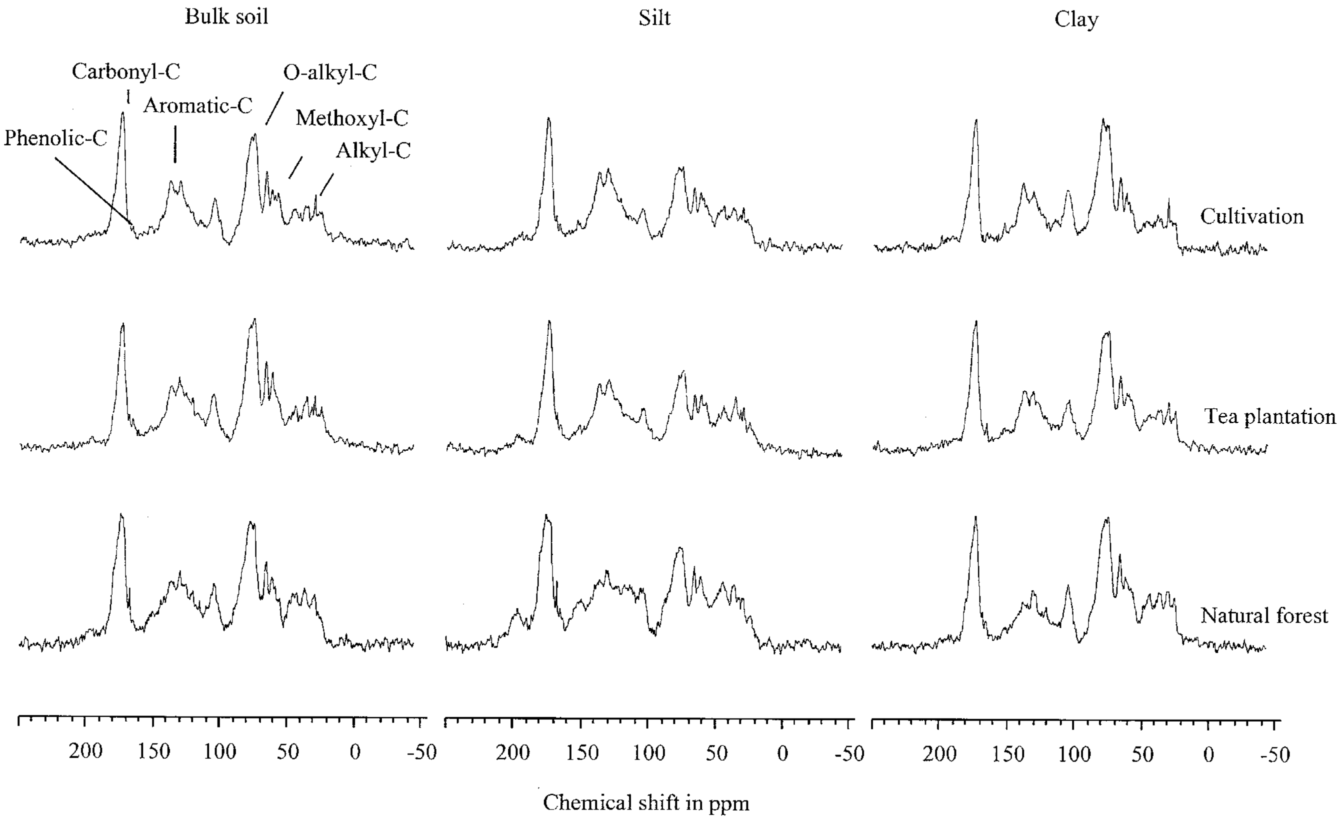

Fig. 6. Solution ^{13}C NMR spectra of alkali-extractable organic matter in bulk soil and size separates of the different land use systems at the Wushwush site.

bution to the total organic matter accumulation increased with decreasing particle-size. Amino sugar ratios were used to evaluate the pattern of bacterial- and fungal-derived amino sugars among particle-size separates of the studied tropical soils. According to Fig. 5, the GlcN/GalN ratio increased in the order: sand < silt < clay, whereas the GlcN/MurA ratio decreased with decreasing particle-size, the highest being in the sand-size separates. The amounts and patterns of amino sugars in these soils are consistent with the results of Zhang et al. (1997, 1998), Amelung et al. (1999a) for North American soils, and with our results for soils from northern Tanzania (Solomon et al., 2000b). The relative enrichment of muramic acid in the clay compared with the silt- and sand-size separates may be attributed to the increased stabilization of this bacterial-derived amino sugar with decreasing size separates. However, galactosamine was enriched in the sand compared with the silt- and clay-size separates, which might suggest that this amino sugar is most likely synthesized at an early stage of SOM decomposition (Zhang et al., 1998).

Comparisons of size separates of the different land-use systems indicated that forest clearing and subsequent agricultural management significantly reduced ($P < 0.05$) the total amino sugar concentrations in size separates of the cultivated fields and plantations (Fig. 5). The largest losses of hexosamines and muramic acid occurred from the sand followed by the silt-size separates of the cultivated fields and plantations. Land use changes also influenced the relative accumulation of the different amino sugars in SOM associated with the size separates. With the exception of GlcN/GalN ratio in sand-size separates of the natural forests, higher GlcN/GalN and GlcN/MurA ratios were found in SOM asso-

Table 3. Distribution of C species in alkali-extracts of bulk soil and particle-size separates of the different land use systems at the Wushwush site.

Separate	Land use	Alkyl-C	Methoxyl-C	O-Alkyl-C	Aromatic-C	Phenolic-C	Carbonyl-C	Aromaticity†	Aryl-O/Aromatic-C
		%							
Bulk soil	Natural forest	17.7	3.8	32.6	21.0	5.0	19.8	0.32	0.24
	Tea plantation	20.3	4.1	34.0	20.6	4.2	16.9	0.30	0.20
	Cultivation	19.9	4.1	31.3	20.8	3.4	20.4	0.31	0.17
Silt	Natural forest	19.1	3.9	26.0	22.4	6.5	22.1	0.37	0.29
	Tea plantation	20.4	3.8	25.2	25.0	4.6	21.0	0.37	0.18
	Cultivation	18.3	4.0	25.8	26.3	5.2	20.4	0.40	0.20
Clay	Natural forest	22.8	4.1	35.4	16.1	3.3	18.2	0.24	0.21
	Tea plantation	18.7	3.8	35.3	19.5	3.9	18.8	0.29	0.20
	Cultivation	14.2	3.8	39.9	19.7	4.0	18.3	0.29	0.20

† Aromaticity = (aromatic-C+phenolic-C)/(alkyl-C+methoxyl-C+O-alkyl-C+aromatic-C+phenolic-C).

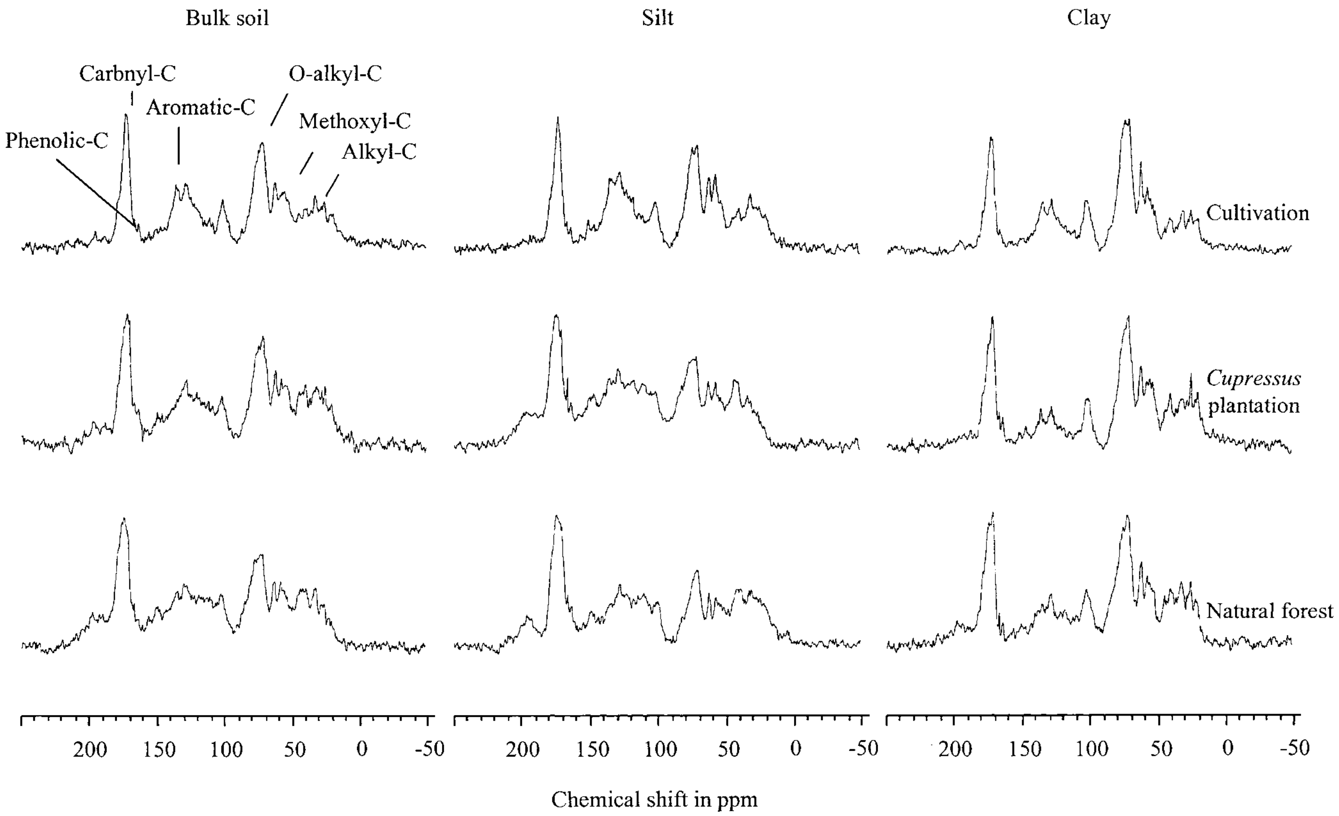

Fig. 7. Solution ^{13}C NMR spectra of alkali-extractable organic matter in bulk soil and size separates of the different land use systems at the Munesa site.

ciated with size separates of the cultivated fields and plantations than those from the natural forest sites, indicating the presence of higher proportions of bacterial-derived amino sugars (galactosamine and muramic acid) in the undisturbed soils. These result imply that agricultural management changed the relative distribution of bacterial- and fungal-derived amino sugars in the sand-, silt-, and clay-size separates, regardless of the different degree of SOM alteration among the size separates.

Carbon-13 Nuclear Magnetic Resonance Spectroscopy

Liquid-state ^{13}C NMR spectra of alkali-extracts in bulk soils of the Wushwush and Munesa sites are shown in Fig. 6 and 7. The spectra revealed multiple peaks between $\delta = 0$ to 50 ppm, thus indicating a highly heterogeneous composition of alkyl-C species. The resonances between $\delta = 50$ and 60 ppm may be assigned to methoxyl C in lignin as well as to C in amino acids (Baldock et al., 1990). The O-alkyl-C region ($\delta = 60$ to 110 ppm) was dominated by carbohydrates which generally produce signals around $\delta = 61$ ppm (C_6), $\delta = 70$ to 90 ppm (C_2 to C_5) and at $\delta = 102$ ppm (anomeric C). Broad signals between 110 to 145 ppm were because of protonated and C-substituted aryl-C, while resonances between $\delta = 145$ to 160 ppm arose from O-substituted aryl (phenolic) C and are indicative of lignin-derived compounds (Kögel-Knabner, 1997). The carbonyl-C ($\delta = 160$ to 200 ppm) was dominated by resonances because of carboxylic-C around $\delta = 175$ ppm. The NaOH-NaF solution extracted 26 to 32% of the total SOC in bulk soils and particle-size separates of these tropical soils.

The proportions of major functional groups in alkali-

Table 4. Distribution of C species in alkali-extracts of bulk soil and particle-size separates of the different land use systems at the Munesa site.

Separate	Land use	Alkyl-C	Methoxyl-C	O-Alkyl-C	Aromatic-C	Phenolic-C	Carbonyl-C	Aromaticity†	Aryl-O/Aromatic-C
		%							
Bulk soil	**Natural forest**	**19.7**	**4.1**	**26.7**	**20.0**	**6.2**	**23.4**	**0.34**	**0.31**
	***Cupressus* plantation**	**23.2**	**3.8**	**27.9**	**19.7**	**4.3**	**21.2**	**0.30**	**0.22**
	Cultivation	**21.2**	**5.1**	**29.9**	**21.1**	**3.2**	**19.5**	**0.30**	**0.15**
Silt	**Natural forest**	**24.5**	**3.2**	**20.0**	**22.0**	**5.3**	**25.0**	**0.36**	**0.24**
	***Cupressus* plantation**	**16.1**	**3.3**	**26.0**	**23.8**	**6.9**	**23.9**	**0.40**	**0.29**
	Cultivation	**20.4**	**4.9**	**27.8**	**24.4**	**4.1**	**18.2**	**0.35**	**0.17**
Clay	**Natural forest**	**22.0**	**4.1**	**35.7**	**14.4**	**3.1**	**20.8**	**0.22**	**0.21**
	***Cupressus* plantation**	**26.2**	**4.9**	**33.7**	**11.5**	**2.7**	**21.0**	**0.18**	**0.23**
	Cultivation	**18.4**	**4.6**	**39.9**	**16.7**	**2.9**	**17.5**	**0.24**	**0.17**

† Aromaticity = (aromatic-C+phenolic-C)/(alkyl-C+methoxy-C+O-alkyl-C+aromatic-C+phenolic-C).

extracts of bulk soils under investigation are listed in Table 3 and 4. According to Table 3 and 4, O-alkyl-C in the $\delta = 60$ to 110 ppm region of the spectra was the dominant C functional group in bulk soils of the Wushwush (33%) and Munesa (29%) sites. The dominance of carbohydrates in liquid-state ^{13}C NMR spectra of tropical soils has also been reported by Guggenberger et al. (1999) and Möller et al. (2000). Almost equal proportions of alkyl-C (19 and 21%), protonated and C-substituted aryl-C (21 and 20%) and carbonyl-C (19 and 21%) structures were identified by ^{13}C NMR spectroscopy of alkali-extracts in bulk soils of the two sites, respectively. The average proportions of the phenolic-C amounted to 4% at the Wushwush and 5% at the Munesa sites, while methoxyl-C made up 4% of the total alkali extractable SOM at both sites.

Compared with the results of degradative wet-chemical techniques, solution ^{13}C NMR spectroscopy of the alkali-extracts did not reveal clear differences in relative abundance of the various C functional groups among the contrasting land use systems (Fig. 6 and 7 and Table 3 and 4). This is in accordance with previous studies where, despite large losses in SOM contents following land use changes, ^{13}C NMR spectroscopy failed to show significant differences in the structural make-up of SOM (Skjemstad et al., 1986; Guggenberger et al., 1999). The absence of clear differences in the spectra of the different land use systems might be because of the fact that alkali-extractable organic substance used for liquid-state ^{13}C NMR spectroscopy represents only a small portion of the total SOM (Guggenberger et al., 1995; Amelung et al., 1999b). On the contrary, wet-chemical degradation methods rely on accessibility of the reagent to the organic compounds of interest (Tanaka et al., 1992), and thus exhibit the impact of land use changes better than solution ^{13}C NMR spectroscopy. However, in analogy to the results of CuO-oxidation, a slightly higher proportion of phenolic-C was generally obtained by ^{13}C NMR spectroscopy in alkali-extracts of the natural forest soils than the plantations and cultivated fields (Table 3 and 4). Moreover, the phenolic-C contents as estimated by the ratio of O-aryl-C to aromatic-C decreased in the order: natural forest > plantation > cultivation, indicating that the contribution of phenolic-C moieties to the total aromatic C decreased following forest clearing and cultivation. This is consistent with the oxidative degradation of lignin as indicated by the higher $(\mathrm{Ac/Al})_{\mathrm{V,S}}$ and lower yields of CuO-oxidation products in the bulk soil samples of the cultivated soils than the corresponding natural forest soils.

The stacked solution ^{13}C NMR spectra (Fig. 6 and 7) and relative proportions of different functional groups (Table 3 and 4) in particle-size separates indicated the presence of relatively higher proportions of protonated and C-substituted aryl-C and O-substituted aryl-C in the silt than in the clay-size separates of both sites. Thus, SOM associated with the silt-size separates showed higher aromaticity (0.38 and 0.37) compared with SOM in the clay-size separates (0.27 and 0.21) of the Wushwush and Munesa soils, respectively. In addition, the average ratio of O-aryl-C to aromatic-C in the silt appears to be higher than that in the clay-size separates of the two sites, respectively. These results are inline with results previously reported by Randall et al. (1995) and Guggenberger et al. (1995). According to Guggenberger et al. (1995), the decline of O-aryl-C to aromatic-C ratio with progressive lignin degradation from coarser- to finer-size separates reflects decreased input of lignin to the total aromatic C region in the course of SOM humification. Liquid-state ^{13}C NMR spectra of the clay-size separates were enriched (37 and 36%) in O-alkyl-C structures compared with the silt (26 and 25%) size separates at the Wushwush and Munesa sites, respectively. This supports our results from the wet-chemical analysis, where the highest relative enrichment of microbial-derived saccharides (hexoses and deoxyhexoses) was obtained in the clay-size separates. Our results also concur positively with the results of Baldock et al. (1990), who demonstrated using incubation experiments of a uniformly labeled ^{13}C glucose that utilization of glucose by soil microorganisms resulted in the synthesis and accumulation of predominantly O-alkyl-C, alkyl-C, and carboxylic-C in clay-size separates. However, the differences in the average proportions of alkyl-C and carbonyl-C structures in the silt- and clay-size separates of our sites were small and variable.

Comparisons of signal intensities and relative distribution of functional groups in alkali-extractable SOM associated with the silt- and clay-size separates exhibited only minor differences among the different land use systems (Fig. 6 and 7 and Table 3 and 4). The silt-size separates of natural forests showed slightly higher ratios of O-aryl-C/aromatic-C than those from the cultivated fields, suggesting a relative enrichment of refractory, C-substituted aryl-C in the silt-size separates of the cultivated soils. In addition, the solution ^{13}C NMR spectra of the alkali extracts from the size separates of the cultivated fields and tea plantations exhibited distinct signals at 135 and 177 ppm compared with the corresponding natural forests. The presence of intense signals in the above mentioned regions have also been reported by Möller et al. (2000) in alkali extracts of forest soils from northern Thailand. These authors used 10 Hz line-broadening and mellitic acid as a standard and found out that these sharp peaks originate from mellitic (benzenehexacarboxylic) acid. Glaser et al. (1998) pointed out that mellitic acid is not produced by oxidation of organic materials obtained by common humification reactions but it rather is the product of the oxidation of charred plant materials. Spectra recorded with a line-broadening of 10 Hz from the alkali-extracts of size separates of the soils under investigation also indicated the presence of small but distinct mellitic acid signals in silt and clay separates of the cultivated fields and tea plantations (spectra not presented). These results may suggest the contribution of pyrogenic-C to the total SOC of the cultivated and plantation sites.

CONCLUSIONS

Physical fractionation of the soils under investigation into sand-, silt-, and clay-size separates, coupled with wet-chemical analysis indicated the presence of three distinct SOM pools which are markedly different in the amount, composition and turnover of the organic matter associated with them. Thus, this study demonstrated the value of combining physical fractionation with degradative wet-chemical analysis in evaluating land use effects on the SOM properties of tropical soils. It also highlighted the importance and limitations of integrating solution ^{13}C NMR spectroscopy to such studies.

Forest clearing and subsequent low-input agricultural management led to significant depletion of total SOC and N in bulk soils and size separates of these tropical soils. Compared with the continuously cultivated fields, lower depletion of SOM occurred from plantations. The phenolic-C signature indicated that VSC-lignin in the continuously cultivated soils was at a more advanced stage of oxidation than the lignin in the plantations and natural forests. The carbohydrate and amino sugar signatures indicated pronounced depletions of both the TFA-hydrolysable monosaccharides and hexosamines and muramic acid following land use changes. The largest depletion occurred from the labile SOM associated with sand. However, substantial amounts of these organic substrates were also lost from the stable SOM fractions. Particularly SOM associated with the silt was quite susceptible to land use changes, and that at least in the soils under study represents a moderately labile SOM pool. The results of liquid-state ^{13}C NMR spectroscopy showed pronounced difference in C-functional groups among the silt- and clay-size separates. On the contrary, differences between land-use systems appeared to be very small. Protonated and C-substituted aryl-C and O-substituted aryl-C were more prominent in the silt than in the clay separates. In contrast, O-alkyl-C groups were dominant C structures in the clay compared with the silt-size separates, corroborating with results of the degradative wet-chemical analysis of these tropical soils.

Based on our results, it is possible to conclude that deforestation of remnant natural forests and subsequent agricultural management not only influenced the amount but also the chemical composition of SOM in these tropical soils. These have a negative impact on soil fertility, and thereby endanger sustainability of agriculture in the fragile ecosystems of southern Ethiopian highlands. Therefore, there is a need to develop appropriate soil and agronomic practices to overcome the current depletion of SOM and to ensure sustained agricultural production without environmental degradation in the region.

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