Cultivation-Induced Effects on the Organic Matter in Degraded Southern African Soils

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We studied quantitative and qualitative changes in soil organic matter (SOM) due to different land uses (reference woodland versus cultivated) on six soils from Tanzania (Mkindo and Mafiga), Zimbabwe (Domboshawa and Chikwaka), and South Africa (Hertzog and Guquka). Structural characteristics of the humic acids (HAs) were measured by Curie-point pyrolysis–gas chromatography/mass spectrometry (P_y–GC/MS) and solid-state ^{13}C nuclear magnetic resonance (CPMAS ^{13}C NMR) spectroscopy. Significant changes in concentration and composition of SOM were observed between land uses. Losses of organic carbon after cultivation ranged from 35% to 50%. Virgin soils showed large proportions of colloidal humus fractions: humic acids (HAs) and fulvic acids (FAs) but negligible amounts of not-yet decomposed organic residues. The change in land use produced a contrasting effect on the composition of the HAs: a noteworthy "alkyl enhancement" in Mkindo soil and "alkyl depletion" in Chikwaka and to a lesser extent in Domboshawa. The remaining soils displayed only minor alterations.

Keywords ^{13}C NMR, Curie-point pyrolysis, soil management, soil respiration, tropical soils

Introduction

In most southern African soils, increasing human population and the requirement for improved nutrition have led to the transformation of forest soils for agricultural purposes. Much of the increased agricultural output has relied on the exploitation of reserves of soil organic matter (SOM) that occurs as land is brought into production. Although tropical soils are not necessarily low in SOM in comparison to temperate soils (Greenland, Wild, and Adams 1992), the breakdown rates of SOM could be significantly faster in the Tropics (Jenkinson and Anayaba 1977; De Ridder and van Keulen 1990). On the other hand, SOM levels largely depend on the management systems applied by farmers, and most of them use practices that reduce rather than build up SOM concentration. Thus, severe losses of soil carbon (C) as a result of cultivation in southern African soils are well documented (Pardo, Giampaolo, and Almendros 1997; Solomon, Lehmann, and Zech 2000; Nandwa 2001; Zingore et al. 2005).

Simply maintaining or increasing SOM may not necessarily lead to increased nutrient availability or productivity (Martius, Tiessen, and Vlek 2001). Changes associated with the transformation from a natural ecosystem to an agroecosystem not only affect the quantity of SOM but also could affect its chemical composition (Almendros, Zancada, and Pardo 2005; Dieckow et al. 2005; Gerzabek et al. 2006). This fact is important, because SOM quality, in the sense of the extent to which it can be mineralized, is a major determinant of soil C storage and rate of release of available nutrients.

Curie-point pyrolysis–gas chromatography/mass spectrometry (P_y–GC/MS) is currently considered not only useful for routine characterization of humic substances (Schulten and Schnitzer 1992; Dorado et al. 2003a) but also shows a high sensitivity versus the concentration and transformation degree in soil of lignins and for specific alkyl compounds (Schulten, Leinweber, and Reuter 1992; Schulten, Monreal, and Schnitzer 1995), and these features could be highly responsive for the impact of land use. On the other hand, nondestructive techniques, such as the solid-state ^{13}C nuclear magnetic resonance (CPMAS ^{13}C NMR) spectroscopy that provides quantitative information about different organic chemical groups, have also been used to evaluate the effects of soil management on the composition of SOM (Almendros, Zancada, and Pardo 2005; Knicker et al. 2006; López et al. 2008). Based in these complementary methods, some authors (Dorado et al. 2003b; Dieckow et al. 2005) have reported substantial differences in the chemical composition of the SOM as a result of soil management.

In African soils, little effort has been done to asses the resilience or, conversely, the vulnerability of the soils after local management practices, and in particular to establish to which extent long-term cultivation affects SOM composition. In this research, attention has been paid to establishing the influence of land-use changes (reference woodland versus cultivated land) on the concentration and composition of SOM in several representative agricultural soils located in Tanzania, Zimbabwe, and South Africa.

Materials and Methods

Areas and Sampling

The topsoil samples collected for the laboratory analysis (0–10 cm) were taken from cultivated and the adjacent woodland areas (virgin, uncultivated soils) as part of the INCO-DEV project ICA4-CT-2001-10058. The sampling points were uniformly distributed along zigzag paths. Up to ten individual samples collected from each analytical unit (up to 25 m^2) were used to prepare four composite samples. Two soils were selected in Tanzania: Mkindo (MK) located in Mvomero district, classified as Eutric Fluvisol (FAO-UNESCO 1989) and Mafiga (MF) located at Sokoine University Farm in Morogoro district, classified as Ferric Lixisol. Mkindo has been cultivated for 10 years under subsistence farming without the use of mineral fertilizers, and MF has been cultivated for more than 30 years with periodic fallows and regular fertilizer use. In South Africa, the soils were collected in the Eastern Cape Province, Guquka (GQ), located below the escarpment of the Amatola Mountains and classified as Ferric Luvisol, and Herzog (HZ), in the northern part of the Kat River Basin and classified as Haplic Luvisol. Both soils have been cropped with maize for more than 20 years under smallholder agriculture. In Zimbabwe, the sampling sites were located in the Central region near Domboshawa (DW) and Chikwaka (CK) villages and classified as Chromic Luvisol and Ferric Luvisol respectively. The soils selected in Zimbabwe have been cultivated since 1974 under the conditions of small-holding with occasional fertilizer inputs.

Soil Chemical and Mineralogical Analysis

The soils were air dried and sieved to pass a 2-mm sieve. The pH was measured in a 1:2.5 (w/w) soil/water suspension. Available phosphorus (P) was determined following the Bray and Kurtz (1945) procedure. Available calcium (Ca), potassium (K), and magnesium (Mg) were extracted with 1 mol dm^{-3} ammonium acetate (NH_4Ac) (pH 7) and the available micronutrients with diethylenetriaminepentaacetic acid (Lindsay and Norwell 1978). The SOM was determined by the Walkley and Black method (Nelson and Sommers 1982) and the effective cation exchange capacity (ECEC) by the method described by Juo, Ayanlaja, and Ogunwale (1976). The oxide content was determined by extraction with dithionite–citrate–bicarbonate (Mehra and Jackson 1960) with iron (Fe), aluminium (Al), and manganese (Mn) being measured in the extracts by inductively coupled plasma–atomic emission spectrometry. Clay minerals were identified by x-ray powder diffraction. These characteristics are given in Table 1 where each value represents the average of four samples.

Soil Humus Fractions

Methods described by Dabin (1971), Merlet (1971), and Duchaufour and Jacquin (1975) have been used for the isolation and quantitative analysis of the soil humus fractions. The sequential extraction procedure includes the previous removal of soil lipid (petroleum ether 60–70 °C, 12 h in Soxhlet extractor). Then, separation of the not-yet-decomposed organic particles (free SOM) was carried out by flotation in 2 mol dm^{-3} phosphoric acid (H_3PO_4). The soil residue resulting after centrifugation was successively extracted with 1 mol dm^{-3} sodium pyrophosphate ($Na_4P_2O_7$) followed by extraction with 0.1 mol dm^{-3} sodium hydroxide (NaOH), five times each. Aliquots of the total humic extract obtained were precipitated with H_2SO_4 (1:1 by vol) and used for quantitative determination of the acid-soluble fulvic acid (FA) and the acid-insoluble humic acid (HA). The soil residue was treated three times with a mixture of 60 mmol dm^{-3} sodium hydrosulfite ($Na_2S_2O_4$) and 1 mol dm^{-3} hydrochloric acid (HCl)–hydrofluoric acid (HF) (1:1 by vol) at 60 °C to remove Al and Fe oxides and the clay, respectively. The final residue was treated with 0.1 mol dm^{-3} NaOH to obtain the insolubilized extractable humin, consisting of humic substances stably associated to the soil mineral matrix.

P_y–GC/MS

Analytical pyrolysis of the HAs was performed with a Curie-point pyrolyser unit (Horizon Instruments) attached to a Varian Saturn 2000 gas chromatography–mass spectrometry (GC/MS) system (Varian Inc., Palo Alto, Calif.). Humic acid samples finely grounded in an agate mortar and deposited on ferromagnetic wires were heated at Curie temperature of 510 °C for 5 s. The interface temperature of the pyrolysis unit was set at 250 °C, and the GC oven was set from 50 to 100 °C at 32 °C min^{-1} and then up to 320 °C to a rate of 6 °C min^{-1}. The GC injector, equipped with a liquid CO_2 cryogenic unit, was set from –30 °C (1 min) to 300 °C at 20 °C min^{-1}. A 25 m × 0.32 mm × 0.4 μm fused-silica capillary column coated with CPSil and He as carrier gas were used. The identification of the compounds in the chromatogram was based on previously published data and further comparisons with mass spectral libraries.

Table 1

General characteristics of the studied soils (U = uncultivated, C = cultivated)

		Mafiga			Mkindo			Chikwaka			Domboshawa			Hertzog			Guquka		
		U	C		U	C		U	C		U	C		U	C		U	C	
Minerals[a]		K; S; I; G	K; S	LSD	I; K; Cl	S; I; K	LSD	K; I	K; I	LSD	K; I	K; I	LSD	Mi	Mi	LSD	I	I	LSD
pH (H_2O)		6.4	6.6	0.7	6.8	7.8	0.1	6.1	5.3	0.1	6.1	5.3	0.3	7.3	7.9	0.3	5.4	5.4	0.2
pH (KCl)		5.0	5.2	0.7	5.4	6.0	0.1	4.5	4.1	0.1	4.7	4.1	0.2	5.9	6.9	0.1	4.0	4.2	0.2
N	(g kg^{-1})	1.1	0.8	0.4	0.9	0.6	0.2	0.3	0.3	0.1	0.8	0.5	0.2	1.4	0.7	0.3	0.4	0.4	0.1
C	(g kg^{-1})	12.3	8.3	2.1	16.3	7.6	2.4	6.7	3.8	1.2	10.2	6.3	0.9	16.1	7.7	0.7	10.1	6.1	1.2
C/N	(g kg^{-1})	123	10.8	2.6	18.1	12.7	0.6	22.3	12.7	1.6	12.8	12.6	2.1	11.3	10.2	2.5	25.3	15.3	4.6
P	(mg kg^{-1})	5.6	6.3	1.4	27	2.0	2	0.5	1.8	0.2	1.2	4.5	0.8	30	30	5	0.9	0.8	0.3
Ca	(mg kg^{-1})	1367	1047	303	1293	693	226	145	87	15	285	160	26	1720	1400	95	250	280	22
K	(mg kg^{-1})	243	275	35	208	90	8	27	37	6	128	107	17	392	370	22	55	105	14
Mg	(mg kg^{-1})	303	217	25	106	268	24	27	<0.1	0.7	33	8	4	440	260	24	36	34	9
Fe	(mg kg^{-1})	48	26	9	210	101	6	14	15	1.3	28	24	3	114	53	14	19	27	5
Mn	(mg kg^{-1})	191	93	34	144	43	3	11	42	3.1	89	109	8	427	310	39	37	46	5
Zn	(mg kg^{-1})	0.7	0.2	0.2	0.6	1.9	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	2.0	0.8	0.5	<0.1	<0.1	<0.1
Cu	(mg kg^{-1})	2.0	0.63	1.3	2.0	2.4	1.5	<0.1	<0.1	<0.1	0.2	0.5	0.2	4.0	2.4	0.2	0.8	1.0	0.3
ECEC[b]	(mmolc kg^{-1})	101	69	21	81	103	12	11	6	3	21	13	5	133	102	5	18	20	2
Ca	(mmolc kg^{-1})	68	52	9	65	35	11	7	4	2	14	8	4	86	70	5	13	14	3
K	(mmolc kg^{-1})	6.2	7.0	3.5	5	2.0	0.2	0.7	1.1	0.2	3.3	2.7	0.9	10.1	9.5	0.6	1.4	2.7	0.6
Na	(mmolc kg^{-1})	1.3	0.9	0.2	1	44	2.4	0.3	0.3	0.1	0.4	0.4	0.2	0.2	0.4	0.2	0.9	0.4	0.2
Mg	(mmolc kg^{-1})	25.3	9.4	1.3	9	22	1.9	2.2	0	1.2	2.7	0.6	0.8	37	21	2	3.0	2.8	0.4

H	(mmolc kg^{-1})	<0.1	<0.1	<0.1	0.6	<0.1	3.2	0.15	0.28	0.1	0.13	0.37	0.2	<0.1	<0.1	<0.1	0.4	0.2	0.2
Al	(mmolc kg^{-1})	<0.1	<0.1	<0.1	0.1	0.1	0.1	0.06	0.05	<0.1	0.06	0.14	0.1	<0.1	<0.1	<0.1	0.2	0.1	0.2
ESP[c]	(%)	1.3	1.3	0.2	1.4	43	1.4	3.14	4.91	1.1	1.90	2.60	0.6	0.05	0.4	0.2	4.8	2.1	0.5
SiO_2	(g 100 g^{-1})	59	61	3	54	54	2	56.1	64.3	3	65.8	51.4	5	74	79	4	76	74	6
Al_2O_3	(g 100 g^{-1})	17	15	3	13	15	3	6.3	7.4	1.2	10.6	10.9	2.8	12	10	1.2	5	4	1.4
Fe_2O_3	(g 100 g^{-1})	6.9	4.4	0.6	3	4.0	1.1	0.5	1.0	0.3	1.7	2.2	0.8	3.9	2.7	0.6	3	2	0.9
MnO	(g 100 g^{-1})	0.1	0.1	<0.1	0.07	0.03	0.01	0.03	0.05	<0.1	0.06	0.08	<0.1	0.1	0.1	<0.1	0.1	0.1	<0.1

[a] Cl, chlorite; G, goethite; K, kaolinite; I, illite; Mi, mica; S, smectite.
[b] ECEC, effective cation exchange capacity.
[c] ESP, % Na saturation.

CPMAS ^{13}C NMR Spectroscopy

The solid-state ^{13}C NMR spectra were acquired with a Bruker MSL 100 instrument (2.3 Tesla) at 25.1-MHz cross-polarization / magic angle spinning (CPMAS) performed at 4 kHz. At least 10,000 free induction decays for each spectrum were accumulated. The pulse repetition rate was 5 s, and the contact time was 1 ms. A sweep width of 37.5 kHz and an acquisition time of 0.016 s were adjusted. The chemical shift range of the NMR spectrum was referred to tetramethylsilane (= 0 ppm). Under these conditions, it is considered that this technique provides quantitative integration values in the different spectral regions (Fründ et al. 1989).

Soil C Mineralization Curves

The soil respiratory activity was measured in the laboratory to assess the stability against biodegradation and the mineralization kinetics of the SOM under comparable conditions. Samples of 20 g of soil were homogenized to 2 mm and kept into 250-cm^3 Erlenmeyer flasks with rubber stoppers perforated with inlet and outlet polyethylene tubes. The samples were moistened to 60% of the soil water-holding capacity at atmospheric pressure and incubated at 27 ± 1 °C (Chone, Jacquin, and Yaghi 1973). The carbon dioxide (CO_2) released during the incubation was measured daily by connecting the outlet tube to a Carmhograph-12 (Wösthoff GmbH, Germany) CO_2 analyzer and the inlet tube to a soda-lime column supplying CO_2-free air. The mineralization of the SOM was expressed in relative terms, that is, taking into account that each soil had a different SOM content (mg C released per kg of soil and per day).

Results and Discussion

Characteristics of the SOM under Native Woodland and under Cropping

Under reference woodland, the six soils studied presented low amounts of soil organic carbon (SOC), which ranged from 6.7 g C kg^{-1} (CK) to 16.3 g C kg^{-1} (MK) (Table 1). With regard to the composition of the SOM in these uncultivated soils (Figure 1), the most significant differences were the negligible amount of free particulate organic matter in MF soils; the large relative proportion of alkali-soluble HAs in MK soils; the dominance of extractable humin over nonextractable humin in CK and HZ soils (indicating prevailing soil matrix interactions playing an effective role in the insolubilization of SOM); and the small proportions of FAs in MF, MK, DW, and GQ soils, which contrast with the preferential accumulation of FA fractions in CK and HZ where the low HA/FA ratio (data not shown) pointed to typical tropical biogeochemical C cycle.

After cultivation, severe losses of SOC were produced in all the soils (Table 1) representing a minimum of 32% (MF) and a maximum of more than 50% (MK and HZ sites). Similar decreases in SOC have been reported in other African soils (Lobe, Amelung, and Du Preez 2001; Solomon, Lehmann, and Zech 2000; Nandwa 2001; Zingore et al. 2005). Land use also affected the composition of the SOM. In all the soils, cultivation caused a relative increase in the proportions of one or two humin fractions (i.e., extractable humin and nonextractable humin), suggesting enhanced organomineral interactions (Figure 1). In other words, cultivation changed the selective accumulation patterns of insoluble SOM in practically all soils. Thus, the trend in Zimbabwean (DW and CK) and South African (HZ and GQ) soil samples was the relative increase of the clay-oxide-associated humin

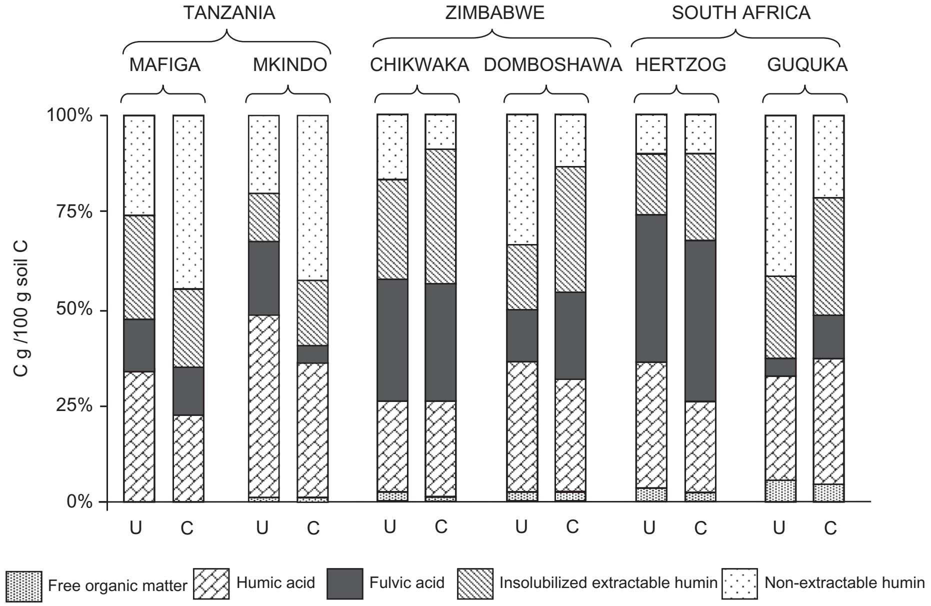

Figure 1. SOM fractions (percentage of total soil C) in uncultivated and cultivated sites. U, uncultivated; C, cultivated.

as regards the other insoluble SOM forms whereas in Tanzanian soils (MF and MK) the nonextractable humin was a major fraction.

Qualitative Features of Soil Humic Acid Fraction

CPMAS ^{13}C NMR Spectroscopy. CPMAS ^{13}C NMR spectroscopy allows elucidation and quantification of different structures in humic substances (Preston, Newman, and Rother 1994; Skjemstad et al. 1997). Figure 2 shows that most of the uncultivated soils studied displayed intense peaks in the 110- to 180-ppm range, suggesting dominant aromatic character associated with intense biogeochemical activity expected from humid subtropical climate in most of the sites. In the case of temperate soils in European countries, the ^{13}C NMR spectra suggest that lignin is the major macromolecule contributing to aromatic structures (Tinoco, Almendros, and Gonzalez Vila 2002). In our tropical soils, however, this situation occurs only in DW and to a lesser extent in GQ and HZ (additional marked peaks at 153 ppm and 57 ppm for metoxyl/amino structures), whereas in the other soils the extremely high maturity, aromatization, and demethoxylation of the SOM suggested intense diagenetic transformations and/or accumulation of black-carbon-type oxidized C forms.

With regard to the effect of cultivation, a progressive pattern between two extreme situations was observed: some soils (DW, and to a lesser extent HZ and GQ) showed mainly raw organic matter, pointing to residual lignocellulosic material from fresh plant biomass. Conversely, in the MF site where HAs in the uncultivated soil showed intense aromatization, demethoxylation, and dealkylation, the major effects of cultivation were oxidation and accumulation of aliphatic structures. The Mkindo site presented before cultivation the lowest signal intensity for aliphatic structures and the lowest concentration of carboxyl

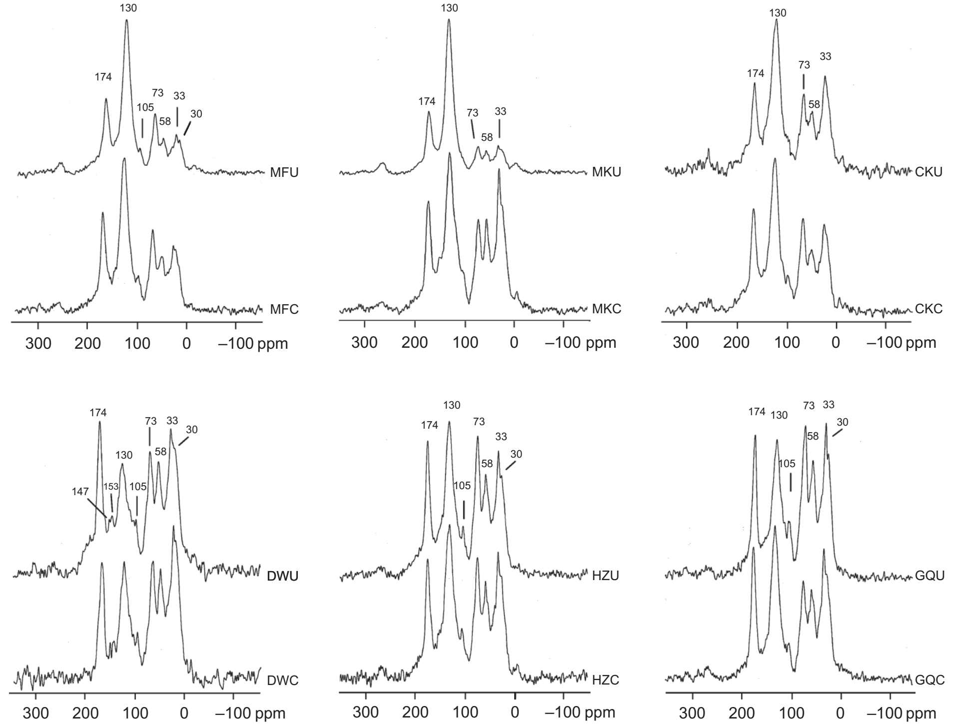

Figure 2. Solid-state ^{13}C NMR spectra of soil humic acids showing the effect of cultivation. MAU, Mafiga uncultivated; MAC, Mafiga cultivated; MKU, Mkindo uncultivated; MKC, Mkindo cultivated; CKU, Chikwaka uncultivated; CKC, Chikwaka cultivated; DWU, Domboshawa uncultivated; DWC, Domboshawa cultivated; HZU, Hertzog uncultivated; HZC, Hertzog cultivated; GQU, Guquka uncultivated; and GQC, Guquka cultivated.

groups, whereas after cultivation it displayed an important aliphatic increase in the HA fraction. Chikwaka was resilient with regard to cultivation effects: the dominant aromatic domain coexisted with aliphatic structures including carbohydrate and alkyl compounds. These results suggested contrasting conditions for HA formation and also a differential response to clearing and cultivation.

Pyrolysis–GC/MS. Pyrolysis–GC/MS has been widely used in the structural characterization of the humic substances (Martin 1975; Schnitzer and Schulten 1995). Table 2 shows the cumulative abundance of the different groups of compounds. The soils studied showed a conspicuous series of alkyl compounds, mainly alkanes and alkenes, that revealed microbial metabolism and selective preservation of alkyl biomacromolecules (cutans, suberans). In addition, there was unexpectedly low amounts of fatty acids that were only present in the uncultivated soils from Zimbabwe (CK and to a lesser extent in DW), and these amounts decreased to zero after cultivation.

The degree of microbial alteration of lignin can be demonstrated by the syringil to guayacil ratio (S/G) of the HAs. Among the soils studied, only in DW and HZ it was possible to calculate this ratio (Table 2). In these soils, this index tended to increase after cultivation (to a greater extent in HZ), and this clearly indicated that the effect of cultivation is an enrichment of raw organic matter reflected by the low alteration degree of the residual

Table 2
Groups of compounds released by Curie-point pyrolysis of humic acids from uncultivated (U) and cultivated (C) Southern African soils

	Mafiga		Mkindo		Chikwaka		Domboshawa		Hertzog		Guquka	
Compounds	U	C	U	C	U	C	U	C	U	C	U	C
G-type	0.0	0.0	0.0	1.3	8.5	0.0	1.2	0.7	0.5	0.2	0.0	0.0
S-type	0.5	0.2	0.0	3.0	0.2	0.0	0.7	1.6	0.8	1.8	0.0	0.0
S/G ratio	—	—	—	2.3	0.0	—	0.6	2.2	1.7	8.4	—	—
Phenols	0.0	0.0	0.0	16.5	7.8	0.0	4.0	6.4	4.9	2.5	0.0	0.0
Catechols	0.0	0.0	0.0	5.5	0.0	0.0	0.7	0.0	0.0	0.0	0.6	0.0
Naphthalenes	5.8	2.2	0.0	10.0	2.7	0.7	4.1	6.8	3.8	12.6	7.4	0.0
Aromatic	5.8	2.2	0.0	32.0	10.5	0.7	8.9	13.2	8.7	15.1	8.0	0.0
Fatty acids	0.0	0.0	0.0	0.0	1.8	0.0	0.5	0.0	0.0	0.0	0.0	0.0
Total Alkanes	13.0	12.9	0.0	15.5	20.3	0.0	21.7	14.6	12.6	20.3	6.1	66.6
Alkanes >C20	0.0	0.0	0.0	3.5	4.2	0.0	6.2	1.0	1.1	2.7	0.0	0.0
Alkanes <C20	13.0	12.9	0.0	12.0	16.1	0.0	15.5	13.6	11.5	17.6	6.1	66.6
Total Alkenes	23.1	17.5	0.0	22.3	33.7	0.0	26.9	12.9	21.1	18.3	4.6	0.0
Alkenes >C20	0.0	0.0	0.0	4.5	8.7	0.0	6.3	0.0	0.0	0.0	0.0	0.0
Alkenes <C20	23.1	17.5	0.0	21.5	31.5	0.0	24.6	12.9	21.1	18.3	4.6	0.0

Note. Percentage of total volatile products.

lignin. In fact, because demetoxylation is a typical behaviour of lignin in the course of its transformation into humic substances, the relative increase of dimethoxyphenols (Syringyl) versus metoxyphenols (Guaiacyl) is a surrogate indicator of the degree of integrity of plant lignin accumulated in soils (Solomon, Lehmann, and Zech 2000; Dorado et al. 2003a).

In general, the most important effects of the change in land use were found in the *O*-alkyl domain (selected pyrograms are shown in Figure 3). In MK, that under woodland showed the lowest signal intensity for aliphatic structures and the lowest concentration of carboxyl groups, cultivation induced an intense "alkyl enhancement," whereas in CK and to a lesser extent in DW an important "alkyl depletion" was observed, which is frequent in temperate countries (Tinoco, Almendros, and Gonzalez Vila 2002). The remaining soils studied (MF, HZ, and GQ) displayed only minor alterations.

Soil Respiratory Activity

Potential changes in the performance of the soil biogeochemical system after clearing and cultivation are to a large extent summarized by the in vitro mineralization curves of the soils under controlled laboratory conditions (Figures 4 and 5). Figure 4 shows the soil respiration curves of uncultivated and cultivated soils (recorded during the first 3 weeks of the experiment) after the periodic analysis of CO_2 in the atmosphere of the flasks incubated under aerobic conditions. Compared to soils under temperate climates (Friedel et al. 2006; Tinoco, Almendros, and Gonzalez Vila 2006), respiration rates were low in all the soils studied; the data, however, were in the same range of those obtained in other African soils (Almendros, Giampaolo, and Pardo 2001). In the mineralization curves, it is usual to consider progressive mineralization stages. According to the data in Figure 4, we could consider in all the soils the following stages: (1) A rapid CO_2 release at the beginning of the experiment (1–3 days). This stage would correspond to the early microbial degradation of the readily degradable substances concomitant with the rapid colonization of the external aggregate surfaces exposed to microorganisms after homogenization of the soil samples. (2) An intermediate stage (4–10 days) that would be more representative of a stabilized respiration after the laboratory mechanical disturbance of the soil material. (3) A final stabilization stage that continued until the end of the experiment, probably more representative of the long-term C mineralization in the soil.

Considering the quantitative values of CO_2 release (Figure 5), the total maximum respiratory activity in the uncultivated soils corresponded to HZ soil (South Africa), whereas the lowest respiratory activity was observed in CK and MF, with both soils showing similar values. The effect of cultivation on soil respiration showed different results. In HZ, GQ, and DW, there was a clear decrease in the total CO_2 emission after cultivation. In CK, in contrast, no important effect was observed. In both MF and MK sites, there was an increase in the mineralization rates after cultivation. These results completely coincide with the changes in the composition of the SOM shown in the ^{13}C NMR spectra (Figure 2). In fact, the aliphatic enhancement observed in MK soils after cultivation was reflected by a significant increase in the respiratory activity. This effect could have been favored by changes in soil structure and biological activity associated with management practices.

Conclusion

The results obtained in this study suggested contrasting conditions for HA formation and also a differential response to clearing and cultivation. The cultivation-induced aliphatic

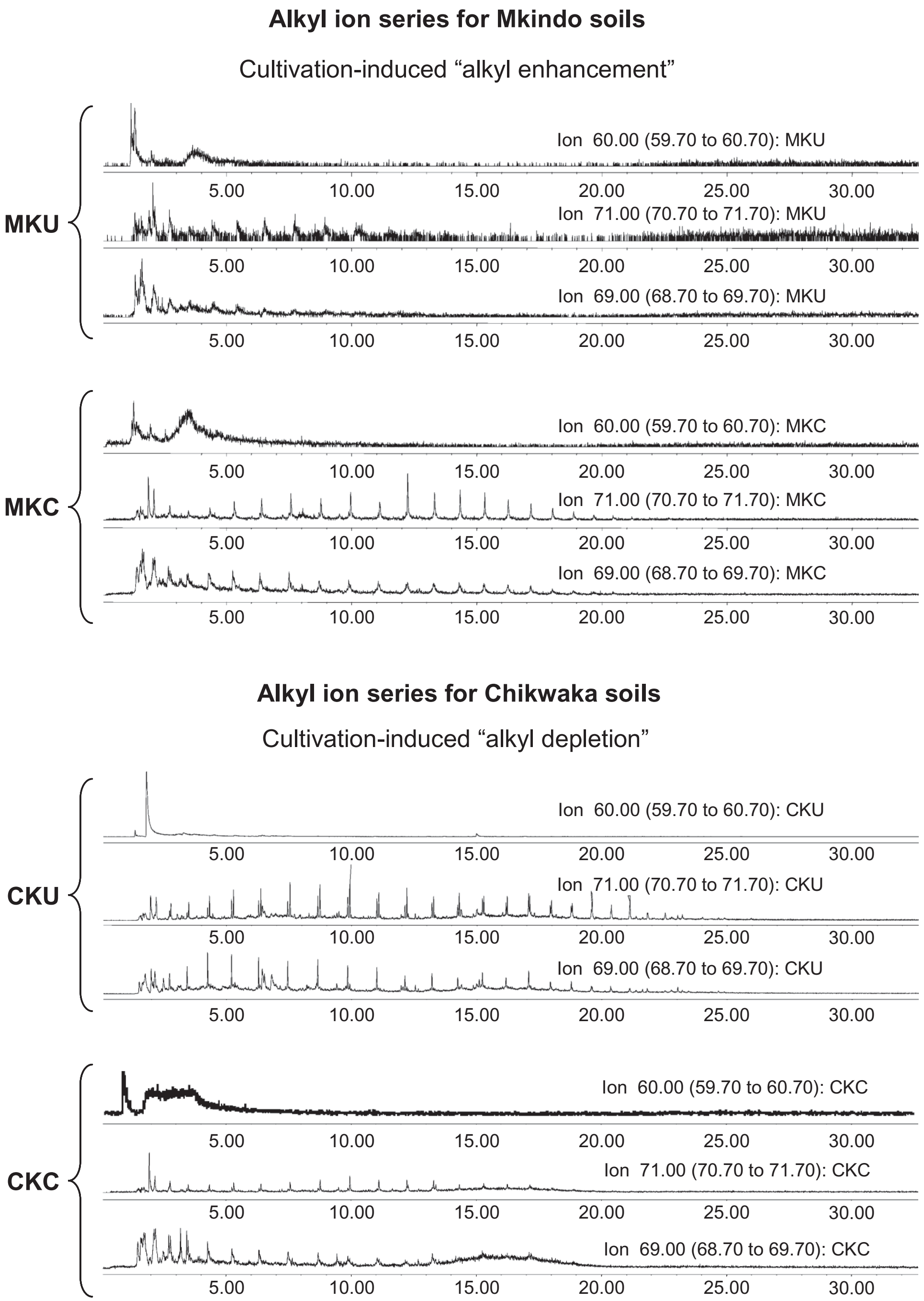

Figure 3. Alkyl ion series from chromatographic traces corresponding to Curie point pyrolysis products from humic acids of selected soils. MKU, Mkindo uncultivated; MKC, Mkindo cultivated; CHU, Chikwaka uncultivated; and CKC, Chikwaka cultivated.

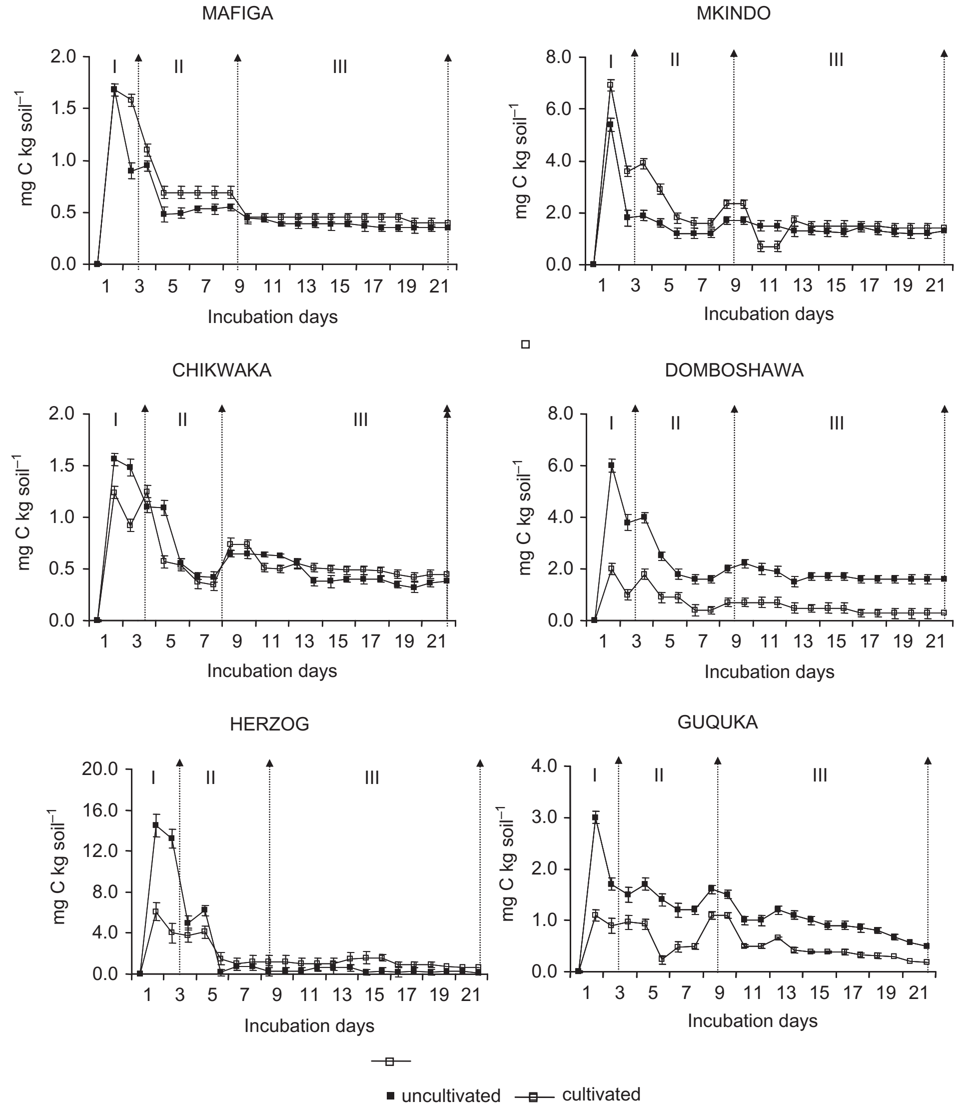

Figure 4. Soil respiration curves (soil C released as CO_2) of cultivated and uncultivated soils during the first 21-day incubation period. Error bars indicate standard deviations of replicated spatial sampling.

enhancement was observed to concur in exceptionally aromatic HAs, whereas aromatization after cultivation was noted in humic acids, where structural modifications as regards biomacromolecules were less pronounced. From the agronomical viewpoint, it is interesting to point out that several soils in the wide area studied show some virtual resilience attributable either to the presence of matured organic matter in biogeochemically active scenarios (e.g., CK soil) or to selective preservation of lignocelluloses biomass (e.g., DW soil), where cultivation had some effect more similar to those soils in temperate countries with a preferential degradation of aliphatic structures in SOM.

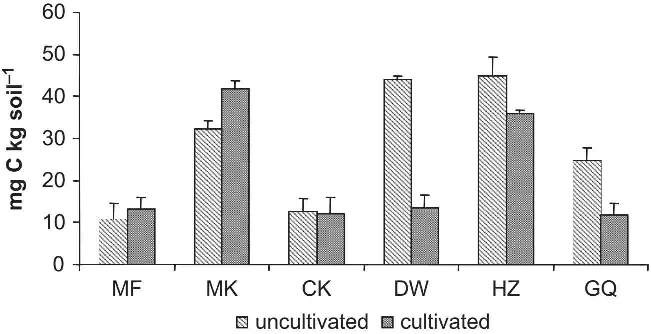

Figure 5. Cumulative mineralization of uncultivated and cultivated soils during the first 21-day laboratory incubation. Error bars indicate standard deviations of replicated spatial sampling.

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