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ABSTRACT

The effects on the structural features of humic acids (HA) from dryland farming soils under long term management practices have been approached by analytical pyrolysis (Curie-point pyrolysis-gas chromatography/mass spectrometry, Py-GC/MS). The field experiments (started in 1987) include conventional, minimum and no-tillage plots, as well as non cultivated plots. The HA isolated from the various plots showed significant differences in their pyrolytic behaviour, in particular regarding the total abundances of alkyl pyrolysis compounds (fatty acids, alkenes and alkanes). The occurrence of very short-chain fatty acids (C_5 to C_{11}) in uncultivated plots could be indicative of constitutional alkyl structures in the relictual HA from undisturbed soil. The effect of soil tillage managements substantially increased total abundances of fatty acids in plots under conservation practices (mainly no-tillage).

The HAs from uncultivated soils showed the greatest percentages of alkanes and alkenes. This was associated to the increased proportions of even C-numbered alkene homologues from C_{12} to C_{18}, possibly related to the incorporation of microbial compounds during the humification process. High percentage of alkylbenzenes and catechols were also characteristic of the uncultivated plots. The increased proportions of methoxyphenols, in special of the syringyl (dimethoxyphenyl) type compounds, in HAs from plots subjected to conventional tillage pointed out to humification processes based on progressive alteration of plant lignins. From the viewpoint of soil quality, the results suggest comparatively advanced

transformation stages of the HA from uncultivated plots, which means that conservation tillage practices seems to lead to increasing soil C levels, at expenses of the accumulation of comparatively recent organic matter derived either from altered lignins and/or microbial biomass.

Keywords: Humic acid; Soil organic matter; Dryland management; Minimum tillage; No-tillage; Curie-point pyrolysis

1. Introduction

Current agroecological research is paying increasing attention to the assessment of soil quality descriptors useful in forecasting sustainability of productive fields [1–4]. Among such descriptors total soil C has been considered a key parameter to assess soil, since it is generally accepted that soil organic matter (SOM) influences many soil properties related to its productivity, including water holding capacity, bulk density, aggregate stability, cation exchange and biological activity [5,6]. However, at this respect, a new trend deal with the convenience of studying the quality of SOM instead of only considering the total amount of soil organic C. In fact, even the quantitative composition of the major SOM fractions (i.e., free organic matter, humic acid (HA), fulvic acid (FA), humin) shows a limited value as indicator of soil perturbation processes [7–9]. In addition, it has also been suggested that in agricultural soils under contrasted tillage practices the different fractions may have similar turnover rates [10].

One recognized way to approach the quality of SOM is the study of the different organic fractions at a molecular level. At this respect, the potential of analytical pyrolysis in analysing the molecular composition of soil organic matter, with similar success than alternative, time-consuming, wet chemical methods has been largely recognized [9,11].

In fact, previous pyrolytic analyses has succeeded in revealing the impact of no-till cropping systems on the composition of SOM, whereas complementary spectroscopic data (CP/MAS ^{13}C NMR measurements) failed in showing substantial effect due to the cropping systems [12].

In the present study, a pyrolytic assessment of the impact of tillage practices on dryland farming systems from Central Spain is carried out. The field experiment, involving conventional, minimum and no-tillage as well as uncultivated plots, was designed in 1987. To date, no previous molecular-level characterization of the differences in the organic matter composition was done in this long-term experimental field.

Due to the massive incorporation of crop residues in agricultural fields subjected to minimum tillage practices, and in order to preclude trivial pyrolytical results mainly reflecting the quantitative contribution by non-decomposed crop residues (accumulated in the fractions referred to as free organic matter and humins) the study was focused in the comparatively stabilized HA fraction, which is considered to display a recalcitrant nature, mainly after its interaction with the mineral fraction.

2. Experimental

2.1. Field location and experiment design

The CSIC experimental farm "La Higueruela" (UTM coordinates: zone 30; 4434290 m N; 377738 m E) under semi-arid continental climate (average temperatures of 6^{o}C and 23^{o}C in winter and summer, respectively; mean annual rainfall, *ca*. 400 mm, with a extended dry season from June to September [13]) is located in Toledo, Central Spain. The soil samples were collected from the 20 upper cm of a Calcic Haploxeralf [14] with loam-sandy texture (total sand = 783 $\pm$ 29 g kg^{-1}, clay = 135 $\pm$ 22 g kg^{-1}).

The experiment to compare the effect of different tillage systems was a randomized block design with three replications and two blocks. Plot size was 40 · 9 m. The tillage treatments consisted of: i) conventional plow tillage (CT), i.e., tilling the soil with mouldboard plow to a 20–22 cm depth, then using a rotovator; ii) chisel (minimal) tillage (MT), i.e., chiselling the soil to a depth 14–16 cm and using the rotovator before sowing; iii) no-tillage (NT), i.e., implementing direct drilling. In the NT plots, volunteer barley plants and weeds were sprayed with 0.54 kg ha^{-1} glyphosate [*N*-(phosphonomethyl) glycine] before seeding with a triple-disk seed drill.

Samples from uncultivated plots near the experimental plots, with typical Mediterranean shrub consisting mainly of *Retama sphaerocarpa* (L.) Boiss and dense herbaceous layer, were also taken as a reference in order to assess the impact of the above agricultural practices.

2.2. Soil general analyses

Air-dried soil samples were homogenised to 2 mm. The chemical analyses included determination of pH (water suspension, 1:2.5 w:w), total N (micro-Kjeldahl digestion), available P [15], and available Na, K, Ca and Mg (1 *M* NH_4OAc [pH = 7] extraction). Oxidizable soil C was determined according to Walkley and Black method [16].

2.3. Soil organic matter fractionation and humic acid purification

The isolation and quantitative analysis of the soil organic fractions included the previous removal of the not-yet decomposed organic particles (*free organic matter*), which was separated by flotation in 2 *M* H_3PO_4. The resulting soil residue was treated with 0.1 *M* $Na_4P_2O_7$ and 0.1 *M* NaOH, and the extraction was repeated up to 5 times with each solution. After centrifuging (2600 *g*) the successive suspensions obtained with the use of these extractants, the supernatant fractions were aggregated and the final volume was measured. Aliquots were taken from this total extract for quantitative determination of the C in the acid-insoluble HA separated after dropwise precipitation with H_2SO_4 (1:1 by vol.) whereas the acid-soluble FA was determined as the difference in C concentration with the whole humic extract [17, 18].

For preparative isolation of the HAs, the remaining humic extract was precipitated (pH = 1) with 12 *M* HCl. The precipitate (HA) was redissolved in 0.25 *M* NaOH and centrifuged (43 500 *g*) to remove the particulate impurities. The resulting sodium humate solution was reprecipitated with HCl overnight, purified with 1 *M* HCl-HF, dialysed in cellophane bags for one week against distilled water, and desiccated at 36 ^{o}C.

2.4. Spectroscopic characteristics of the humic acids

The optical densities at 465 nm (E_4) and 665 (E_6) nm of HAs were determined from solutions of 200 mg C L^{-1} of HA in 0.02 *M* $NaHCO_3$ [19] with a Shimadzu UV-240 spectrophotometer. The E_4 is classically considered to be related with the aromaticity of HAs [20,21], whereas the E_4/E_6 ratio gives information about the polydispersity of the HAs [22].

2.5. Curie-point pyrolysis-gas chromatography/mass spectrometry

The HAs were analysed by Py-GC/MS in a Horizon Instruments unit attached to a Varian Saturn 2000 gas chromatography-mass spectrometry system (GC/MS). The samples on ferromagnetic wires were heated at the Curie temperature of 510 °C for 5 s. The pyrolytic interface was set to 250 °C, and the chromatographic temperature was programmed from 50 to 100 °C at 32 °C min^{-1} and then up to 320 °C using a rate of 6 °C min^{-1}. In order to enhance the chromatographic resolution, a liquid CO_2 cryogenic unit, fitted to the injection port, was adjusted from –30 °C (1 min) to 300 °C at 20 °C min^{-1}. A 25-m · 0.32 mm · 0.4 ⌠m fused-silica capillary J&W CP-Sil 5 CB column (Agilent Technologies Spain S.L., Las Rozas, Madrid) was used.

The pyrolysis compounds were identified on basis to their electron impact mass spectra (70 eV) and by comparison with those in the Wiley (1986) spectral database. The ion traces for the main series of homologous compounds were obtained (e.g., 85 for alkanes, 69 for alkenes, 60 for fatty acids). In the case or aromatic compounds reconstructed ion chromatograms displaying the joint intensity of the major diagnostic fragments, in general [M^+] and [$M^+ – CH_3$], were used to identify the expected pyrolysis products in the whole chromatogram (e.g., m/z 109+124 for guaiacol, m/z 139+154 for syringol, etc).

2.6. Data analyses

For comparison purposes, the amounts of the different compounds were considered to be proportional to the peak areas of the total ion chromatographic trace. These data were subjected to multivariate analyses in order to recognize some trends in the compound assemblages released for the HAs from the different experimental plots. The variables (descriptors) processed were the main groups of pyrolysis products from soil HAs, whereas the observations (samples, individuals) were the different spatial replications of the HAs isolated from soils managed with the different tillage systems. The program used (correspondence analysis, two-way table, no supplementary observations [23]) converts the original frequency table into a plot in which samples and variables are depicted as points in the space defined by factorial axes.

3. Results and discussion

Several general analytical characteristics of the soils are illustrated in Table 1, showing differences due to management. Thus, some significant ($P < 0.05$) improvements in soil fertility with conservation tillage practices were noted. Available P and K in minimum and no-tillage plots were in significantly higher concentrations as regards to conventional tillage plots. The conservation practices also lead to significant increase in soil organic C as regards conventional tillage, mainly with no-tillage, where the C content was found even higher than in the uncultivated soil. In addition, a relative enrichment of the different humus fractions (HA+FA) was found after conservation practices—very significant in the case of no-tillage plots—with respect to conventional ones. Furthermore, the increased values of the HA/FA ratio in minimum and no-tillage plots betrays a trend for accumulation of the HA fraction in the soil managed with these tillage systems. On the other hand, the values for non-extractable humin (highest values in the uncultivated plots) point to progressive insolubilisation of the organic matter in soils under conservation practices (mainly in no-tillage).

The lower E_4 values of the HAs from no-tillage plots as regards uncultivated plots could indicate that surface straw mulch has led to soil enrichment in comparatively young and aliphatic organic matter. In this sense, the changes observed in the E_4/E_6 ratio—an index considered to decrease with the molecular size of humic macromolecules [22]—point out to microbial fragmentation of the humic like substances in no-tillage plots when compared with uncultivated plots.

Changes in HA characteristics after tillage were also observed, particularly the lower HA/FA ratio and the higher E_4/E_6 ratio, than in the minimum tillage system, both suggesting a lower molecular size of soil humic fractions with conventional tillage than with the minimum tillage system.

Table 2 shows the major Curie-point pyrolysis products released from the HA samples expressed as total abundances (relative percentage area of total ion chromatogram). All of them yielded series of alkyl compounds (mainly series of fatty acids, alkenes and alkanes) as well as aromatic compounds (mainly phenols and alkylbenzenes) as major compounds.

The most important difference in terms of tillage was observed in the distribution patterns of alkyl compounds.

The homologous series of alkenes and alkanes peaks eluting as doublets are frequently considered to be derived from non-hydrolyzable aliphatic polymers, such as cutan and suberan. This would lead to hypothesize that most of these compounds could derive from biopolyester domains in the HA structure more than being individual fatty acids trapped in humic substances as free or esterified acids, as frequently reported in the literature [24].

The total abundances of C_{14} to C_{18} fatty acids (mainly palmitic) were significantly ($P < 0.05$) higher in cultivated plots compared to the uncultivated ones (Fig. 1). This fact could be interpreted as an aliphatic enhancement of the HA structure at expenses of acids > C_{14} of recent origin from plants or microorganisms. In all cases, the most important effect of soil tillage on the proportions of fatty acids was a relative increase in their total abundances in the plots under conservation practices compared to plots with conventional tillage (Table 2). This agree with the findings by Sleutel et al. [25], who described larger proportions of free fatty acids, sterols, and N-containing compounds in reduced tillage soils than in the conventional tillage soil.

In addition to the *n*-chain alkanes, the 60 m/z ion trace from the three chromatograms (Fig. 1) clearly suggests peaks due to bacterial *iso*- and *anteiso*- C_{15} acids before the *n*-C_{15} (to much lower extent, and only in some samples, similar doublets for branched fatty acids seem to elute before the peaks for C_{17} and C_{13} *n*-acids). Assuming that these *b*-fatty acids are not inherited from aliphatic biomacromolecules but derive from microbial metabolism, the differences between their total abundances in terms of soil management could be interpreted. Compared to the conventional tillage plots, the plots subjected to practices of no tillage and minimum tillage showed proportions of these bacterial acids higher than for the corresponding *n*-chain acids, which could be interpreted as an enhanced size of the microbial biomass degrading the crop wastes left to decompose on these plots.

As a difference to fatty acids, the alkane homologue series (C_8 to C_{22}) showed no differences attributable to agricultural practices. Apparently, alkane compounds behaved relatively stable against microbial activity and consequently less responsive to perturbations produced in cultivated plots. Due to the relatively short chain of the alkanes, this could be justified by a biodegradation compensated for by a continuous microbial production, although the comparatively complex *n*-alkane degradation pathways, generating fatty acid intermediates ought not to be ruled out. As regards the alkene series, it was found a substantial proportion of even C-numbered homologues from C_{12} to C_{18} in uncultivated plots, possibly derived from from the above-indicated accumulation of alkanes from microbial activity [26].

Total abundances of alkanes and alkenes were significantly ($P < 0.05$) higher in HAs from uncultivated than in cultivated plots (Fig. 2) and qualitative differences were observed when the data from alkyl compounds were examined by means of multivariate data analysis. Figure 3 illustrates alkene/alkane distributions versus chain length after correspondence analysis of a data matrix including HA samples, using as descriptors the total abundances of pyrolytic alkyl compounds. The main changes in the fatty acid pattern observed in the plane defined by the two first axes (up to 92% total variance explained) caused by the agricultural practices (Fig. 3a) were a relative increase in proportions of fatty acids with comparatively high C-number (from C_{12} to C_{18}) in cultivated plots, and the concomitant increase of the proportions of short-chain fatty acids (up to C_{11}) in the uncultivated soil.

The alkanes and alkenes (Fig. 3b, c) did not show clear trends in terms of tillage systems but some tendency observed to relative accumulation of short-chain alkanes C_8 and C_9 in uncultivated plots could be pointing out to an origin of these compounds from cutans, suberans or epicuticular waxes which could be a major source of the aliphatic moiety of the HA.

The total abundances of alkylbenzenes, commonly described as typical fragments of HAs

[27], and considered as indicator of stability of the soil organic matter in soils under different management practices [28] were higher in uncultivated as regards to cultivated plots (Fig. 2). These compounds behaved also differently as regards the tillage system, showing low relative proportions under minimum and no-tillage systems.

The patterns of phenolic compounds also showed substantial changes depending on soil management practices. Most of the phenols (up to 8% of the total volatile products) showed methoxyl substitutions typical of the lignin structural units (Table 2), which inform about the preservation extent of this biomacromolecule in different soil conditions [29,30]. Therefore, an increase in the yields of methoxyphenols in plots with conventional tillage (Fig. 2) point out to prevailing processes of formation of HAs based on direct transformation of plant lignin. In addition, the high syringyl/guaiacyl ratio (data not shown) calculated for these HAs could betray to comparatively rapid incorporation of lignin to the HA fraction when the soil is managed with conventional tillage in comparison with conservation tillage or uncultivated plots. As a whole, the pyrolytic results suggest that the continuous incorporation of crop waste on soil surface of reduced tillage plots would lead to somewhat higher inputs of microbial metabolites as starting materials for HA formation. In fact, the guaiacyl-type lignins have higher degree of internal cross-linking than those of syringyl-type, showing comparatively higher resistance to biodegradation [31].

These results could be compared with those found in HAs from soils under different tillage practices [32], showing an increase in the relative amounts of aromatic structures in minimum tillage plots. In this study, analytical pyrolysis lead to a more accurate differentiation between the origin of the aromatic moieties (Fig. 2) reflecting a dual origin of aromatic structures in HAs, either consisting of methoxyl-containing non-decomposed lignin structures or comparatively more condensed aromatic structures yielding alkylphenols upon pyrolysis [33].

Total abundances of catechols upon pyrolysis was higher in uncultivated soil than in soil under conservation tillage, as could correspond to the most intense oxidative transformation of the lignin in the former. Conversely, the lowest relative amounts of catechols amounts were found in the HAs from conventional tillage plots.

Figure 4 illustrates some significant ($P < 0.05$) trends in the methoxyphenol pattern depending on tillage systems. It was observed the relative increase in the relative proportions of syringyl-type (methyl-, ethyl-, vinyl- and propenyl-) methoxyphenols from HAs in plots under conventional tillage and the concomitant increase of the guaiacyl-type compounds in no-tillage and uncultivated plots. This would betray the intense lignin demethoxylation expected in comparatively mature humus from undisturbed soil. Similar patterns were found in no-tillage plots, where crop wastes are not mechanically incorporated to the soil, and leave to decompose in the surface. On the opposite site, the significant increase in the total abundancs of methoxyphenols and the frequent occurrence of syringyl-type phenols in HAs from conventional tillage plots with respect to reduced tillage and uncultivated plots is probably pointing out to active incorporation to HAs of slightly-transformed lignin from crop wastes. As expected, the HAs from plots subjected to minimum tillage showed average methoxyphenol composition, their most diagnostic feature—apart from the balanced syringyl/guaiacyl composition—being the dominance of non-alkylated methoxyphenols, which depict a specific, intermediate fate of lignin alteration in these plots.

In addition, and considering that conventional tillage plots showed lower C/N ratio and comparatively higher proportions of methoxyphenols than plots under the other soil management practices, the above differences could be interpreted as a higher performance of the lignin biodegradation processes in the N-limited systems, a circumstance widely reported in the literature [34].

Figure 5 summarizes the effects of the different tillage managements based on the whole pyrolytic data processed by multivariate data treatment. The correspondence analysis suggests an increase after cultivation in the proportions of fatty acids (mainly in plots under conservation tillage) and phenols (mainly in plots under conventional tillage). On the other hand, the uncultivated plots show a HA pattern more similar to those from undisturbed semiarid soils. This could be reflecting comparatively higher maturity degree, with comparatively low proportions of lignin-derived methoxyphenols and the substantial proportions of alkanes, alkenes, alkylbenzenes and catechols.

4. Conclusions

In general, maturity surrogates of the HAs (e.g., aromaticity, intense transformation of lignins), defined by spectroscopic analyses and descriptors based in their pyrolytic behaviour, were comparatively higher in uncultivated than in cultivated plots. In spite of conservation practices lead to significantly increased levels of soil organic C, we found the highest diagenetic transformation of the HAs in undisturbed or minimum tillage plots. This is explained in terms of rapid incorporation of relatively unaltered organic fractions derived either from microbial biomass or plant biomacromolecules to the soil HA fraction in conventional tillage plots. On the other hand, comparatively intense biodegradation and humification processes in the uppermost soil layer of undisturbed soil have led to some common patterns with reduced tillage plots. This situation could be considered as a consequence of the environmental constraints in semiarid Mediterranean scenarios, where pyrolytical characterization of HAs could successfully betray accumulation of raw organic materials in those treatments receiving continuous inputs of crop residues such as the conservation tillage practices.

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Figure legends

Figure 1. Mass fragmentograms showing the intensity of the *m/z* 60 ion, characteristic for fatty acids, in pyrograms from humic acid isolated from uncultivated soil and soils managed with conventional, minimum and no-tillage systems. Carbon number of the homologous compounds is indicated on the peaks.

Figure 2. Cumulative values for the main groups (relative peak areas as regards total ion chromatogram) of pyrolysis products from humic acid of uncultivated soil (U) and soils managed with different tillage systems: conventional (CT), minimum (MT) and no-tillage (NT). Error bars indicate the standard deviations between replicated spatial samples. Within a subplot, bars labelled with the same letter are not significantly different at $P < 0.05$.

Figure 3. Correspondence analyses showing changes in the distribution patterns of: **a)** fatty acids, **b)** alkanes and **c)** alkenes, in terms of the tillage systems (bold labels): CT = conventional tillage; MT = minimum tillage; NT = no-tillage; U = uncultivated. Error bars indicate the variability ranges defined by triplicate runs; average values (centroids) are drawn with circles. The percentage of the total variance accounted for by the two first components is shown in the corresponding axis. Compounds are indicated by their C atom number.

Figure 4. Correspondence analysis showing changes in the distribution patterns of methoxyphenols in terms of the tillage systems (bold labels): CT = conventional tillage; MT = minimum tillage; NT = no-tillage; U = uncultivated. Error bars indicate the variability ranges defined by triplicate runs; average values (centroids) are drawn with circles. The percentage of the total variance accounted for by the two first components is shown in the corresponding axes.

Figure 5. Correspondence analysis of cumulative data of all types of pyrolysis compounds, showing the effects of tillage practices (bold labels: CT = conventional tillage; MT = minimum tillage; NT = no-tillage; U = uncultivated) on the relative yields of the main groups of

pyrolysis compounds. Error bars indicate the variability ranges defined by triplicate runs; average values (centroids) are drawn with circles. The percentage of the total variance accounted for by the two first components is shown in the corresponding axes.

Table 1

General analytical characteristics in uncultivated soil (U) and soils managed with conventional tillage (CT), minimum tillage (MT) and no-tillage (NT) systems

	CT	MT	NT	U	*LSD* [a]
Total organic C (g kg^{-1})	5.6	7.1	12.5	11.5	1.0
Total N (g kg^{-1})	0.7	0.7	1.3	1.2	0.2
C/N ratio	8.6	10.1	9.6	9.9	2.3
pH	5.1	5.7	5.0	7.2	0.7
Available K (mg 100 g^{-1})	22	30	39	44	8
Available Ca (mg 100 g^{-1})	171	170	116	251	24
Available Na (mg 100 g^{-1})	4	3	2	1	2
Available Mg (mg 100 g^{-1})	26	25	20	20	6
Free organic matter (g C kg^{-1})	0.6	0.4	0.9	1.0	0.2
Humic acid (HA) (g C kg^{-1})	0.5	1.1	2.6	1.2	0.3
Fulvic acid (FA) (g C kg^{-1})	0.9	1.2	3.3	3.1	0.4
Non-extractable humin (g C kg^{-1})	3.6	4.3	5.7	6.3	0.5
HA/FA ratio	0.57	0.92	0.79	0.39	0.33
E_4 (optical density of HA at 465 nm)	0.95	1.03	0.76	1.13	0.35
E_4/E_6 optical density ratio	4.93	4.50	5.06	4.55	0.85

[a] Least significant difference at $P = 0.05$.

Table 2

Relative amounts[a] of the major pyrolysis products of humic acids isolated from uncultivated soil (U) and soils managed with conventional tillage (CT), minimum tillage (MT) and no-tillage (NT) systems

	CT	MT	NT	U	*LSD* [b]
Alkylbenzenes					
Methylbenzene (toluene)	0.77	0.76	0.65	1.46	0.45
Styrene	0.44	0.24	0.19	0.72	0.33
C_3-Alkylbenzene	0.34	0.20	0.13	0.91	0.22
C_4-Alkylbenzene	0.44	0.23	0.39	0.13	0.34
C_5-Alkylbenzene	0.00	0.02	0.06	0.00	0.08
Catechols					
Catechol	0.00	0.22	0.24	1.21	0.14
Methylcatechol	0.00	0.09	0.00	0.00	0.04
C_2-Catechol	0.00	0.02	0.00	0.00	0.02
Phenols					
Phenol	0.89	0.59	0.27	1.39	0.33
Methylphenol (cresol)	0.39	0.25	0.26	0.17	0.20
C_2-Alkylphenol	0.16	0.05	0.12	0.18	0.14
C_3-Alkylphenol	0.00	0.04	0.11	0.00	0.09
C_4-Alkylphenol	0.00	0.02	0.04	0.00	0.05
Methoxyphenols					
Guaiacol	1.25	0.81	0.50	0.69	0.76
Methylguaiacol	0.26	0.26	0.22	0.39	0.17
Ethylguaiacol	0.38	0.25	0.53	0.50	0.12
Vinylguaiacol	1.41	1.16	1.43	0.90	1.12
Syringol	0.65	0.48	0.33	0.19	0.57
Methylsyringol	0.14	0.12	0.10	0.13	0.08
Propenylguaiacol	0.12	0.12	0.10	0.14	0.12
Acetoguaiacone	0.59	0.33	0.23	0.23	0.28
Ethylsyringol	0.47	0.22	0.11	0.19	0.15
Vinylsyringol	0.43	0.24	0.26	0.18	0.16
Propenylsyringol	0.14	0.13	0.11	0.08	0.13
Acetosyringone	0.55	0.41	0.61	0.68	0.50
Polycyclic aromatic					
Naphthalene	0.00	0.00	0.02	0.00	0.02
Methylnaphthalene	0.00	0.00	0.02	0.00	0.03
C_2-Alkylnaphthalene	0.00	0.00	0.03	0.00	0.04
Alkenes					
C_8-Alkene	0.03	0.03	0.00	0.16	0.09
C_9-Alkene	0.13	0.03	0.12	0.25	0.07
C_{10}-Alkene	0.16	0.09	0.15	0.32	0.10

C_{11}-Alkene	0.10	0.05	0.07	0.20	0.09
C_{12}-Alkene	0.96	0.18	0.06	1.03	0.15
C_{13}-Alkene	0.24	0.14	0.20	0.27	0.22
C_{14}-Alkene	0.68	0.41	0.17	1.33	0.86
C_{15}-Alkene	0.17	0.11	0.13	0.14	0.09
C_{16}-Alkene	0.79	2.29	1.91	4.20	1.72
C_{17}-Alkene	0.76	0.76	0.60	0.36	0.24
C_{18}-Alkene	2.29	1.75	1.58	6.12	1.11
C_{19}-Alkene	0.29	0.12	0.12	0.23	0.43
C_{20}-Alkene	0.04	0.55	0.59	0.31	0.71
C_{21}-Alkene	0.09	0.20	0.07	0.23	0.19
C_{22}-Alkene	0.00	0.55	0.00	0.74	0.34
Alkanes					
C_8-Alkane	0.23	0.46	0.52	1.10	0.39
C_9-Alkane	0.20	0.32	0.22	0.86	0.30
C_{10}-Alkane	0.04	0.04	0.05	0.04	0.06
C_{11}-Alkane	0.27	0.07	0.15	0.35	0.20
C_{12}-Alkane	0.17	0.07	0.07	0.19	0.08
C_{13}-Alkane	0.11	0.27	0.18	0.16	0.18
C_{14}-Alkane	0.16	0.11	0.37	0.50	0.15
C_{15}-Alkane	0.13	0.16	0.13	0.26	0.07
C_{16}-Alkane	0.31	0.20	0.32	0.25	0.20
C_{17}-Alkane	0.66	0.31	0.46	0.46	
C_{18}-Alkane	0.70	0.57	0.57	0.92	0.36
C_{19}-Alkane	0.59	0.35	0.54	0.66	0.51
C_{20}-Alkane	0.24	0.19	0.36	0.93	0.49
C_{21}-Alkane	0.09	0.34	0.02	0.39	0.18
C_{22}-Alkane	0.00	0.58	0.00	0.40	0.20
Fatty acids					
Heptanoic acid	0.23	0.07	0.14	0.18	0.21
Octanoic (caprylic) acid	0.79	0.28	0.66	0.81	0.13
Nonanoic (pelargonic) acid	1.02	0.44	0.44	1.05	0.57
Decanoic (capric) acid	0.38	0.31	0.33	0.23	0.14
Undecanoic acid	0.10	0.02	0.09	0.98	0.08
Dodecanoic (lauric) acid	0.96	0.59	0.77	0.26	0.38
Tridecanoic acid	0.22	0.22	0.11	0.13	0.16
Tetradecanoic (myristic) acid	3.87	3.70	4.06	0.25	1.27
iso-Pentadecanoic acid	1.56	3.35	1.47	0.41	2.09
anteiso-Pentadecanoic acid	1.83	2.87	2.56	0.90	0.37
Pentadecanoic acid	0.83	1.52	1.34	0.25	0.79
Hexadecanoic (palmitoleic) acid	0.66	1.74	2.13	0.00	1.25
Hexadecanoic (palmitic) acid	14.30	18.84	24.88	0.32	8.41
iso-Heptadecanoic acid	0.45	1.87	0.61	0.00	0.91
anteiso-Heptadecanoic acid	0.48	1.08	0.48	0.00	1.36
Heptadecanoic (margaric) acid	0.33	0.27	0.80	0.00	0.24

Octadecenoic (oleic) acid	1.68	0.69	1.25	0.73	2.02
Octadecanoic (stearic) acid	0.81	0.66	1.66	0.00	1.47
Nonadecanoic acid	0.00	0.07	0.00	0.11	0.12
2-Propenoic acid, 3-(4-methoxyphenyl)-	0.85	0.00	1.01	3.39	1.83
Eicosanoic (arachidic) acid	0.00	0.16	0.00	0.00	0.17

[a] Percentage of the total peak area in the total ion chromatogram (compounds representing less than 00.02% are not shown).

[b] Least significant difference at $P = 0.05$

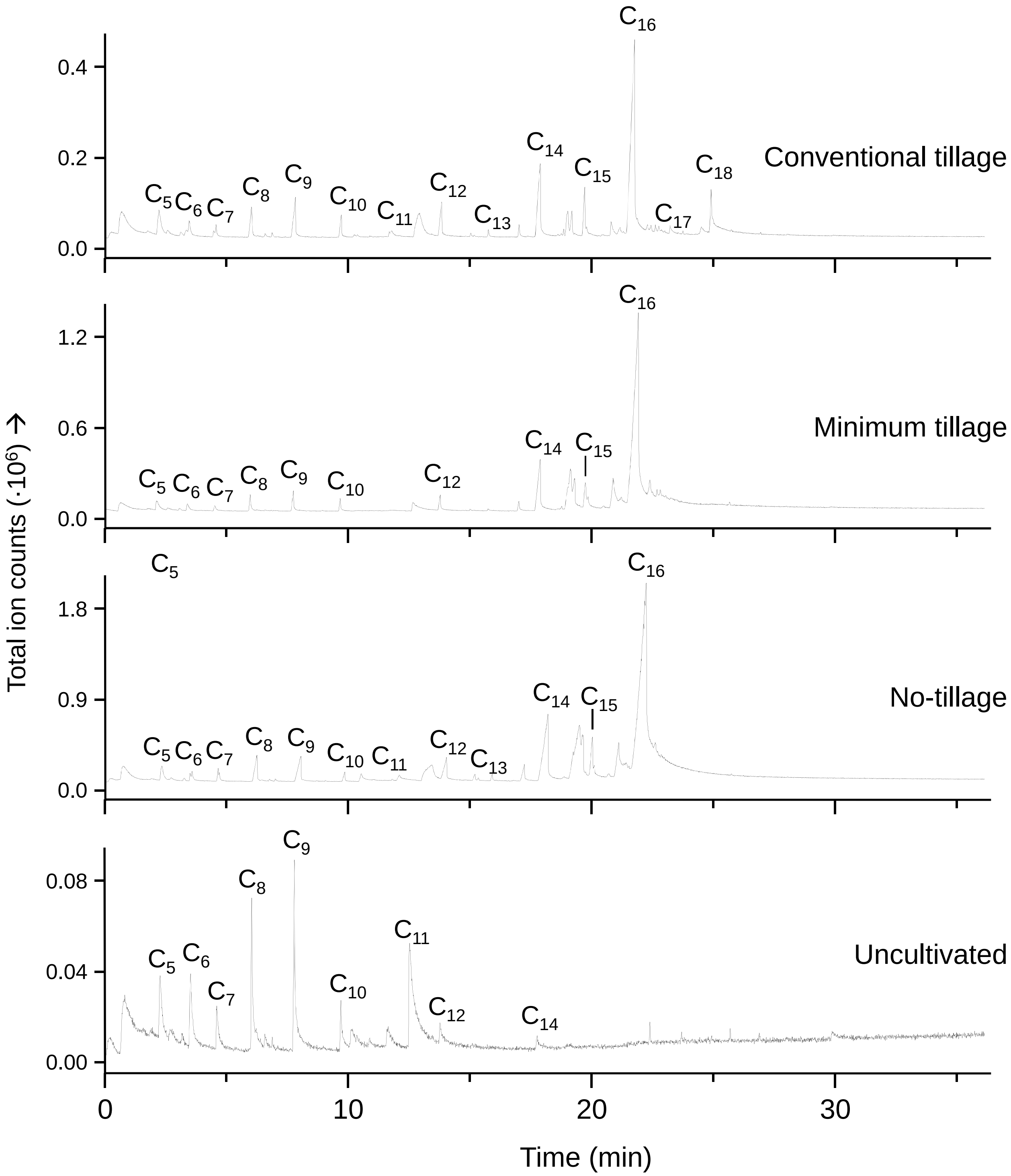


Figure 1. Mass fragmentograms showing the intensity of the *m/z* 60 ion, characteristic for fatty acids, in pyrograms from humic acid isolated from uncultivated soil and soils managed with conventional, minimum and no-tillage systems. Carbon number of the homologous compounds is indicated on the peaks.

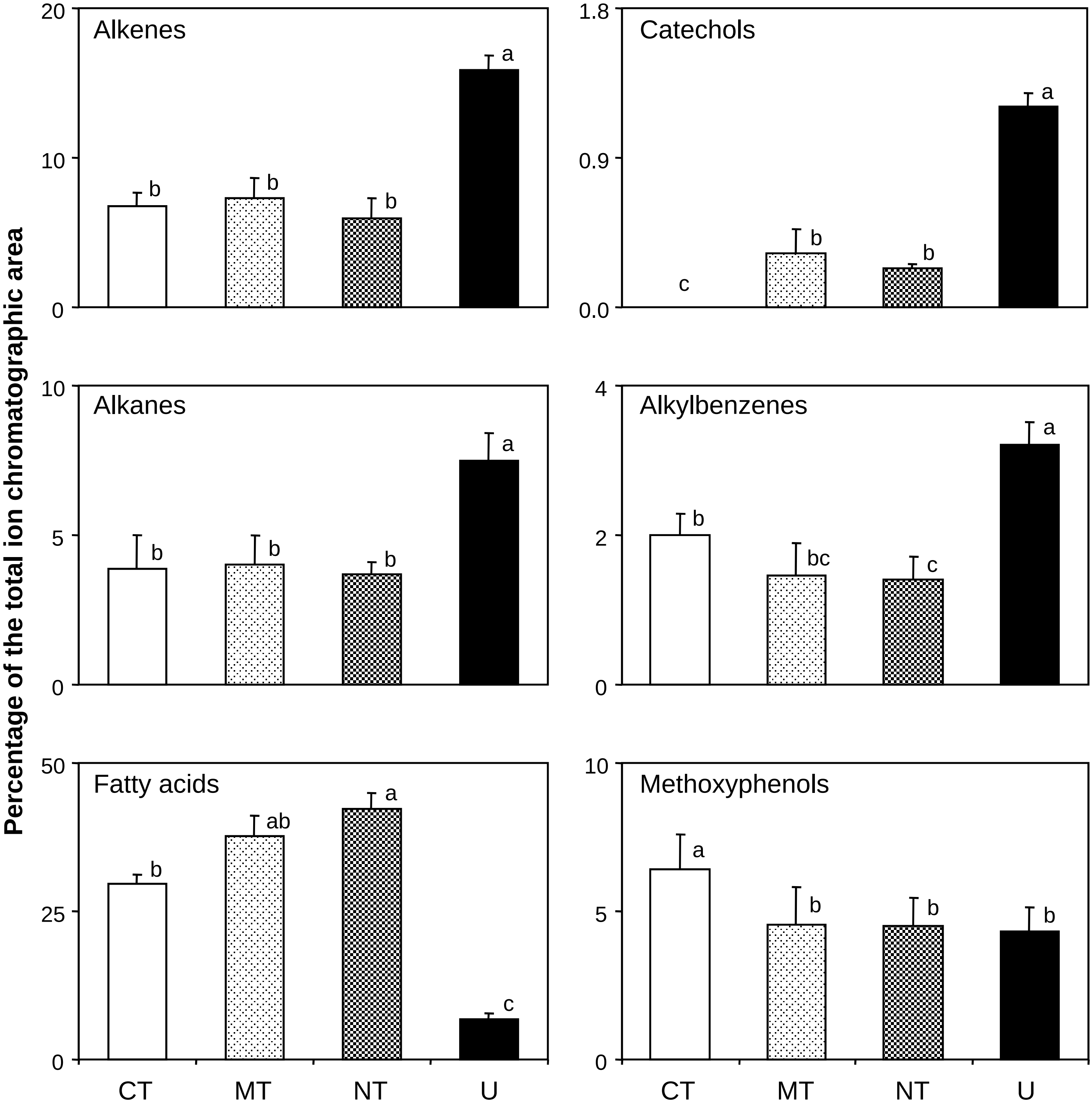
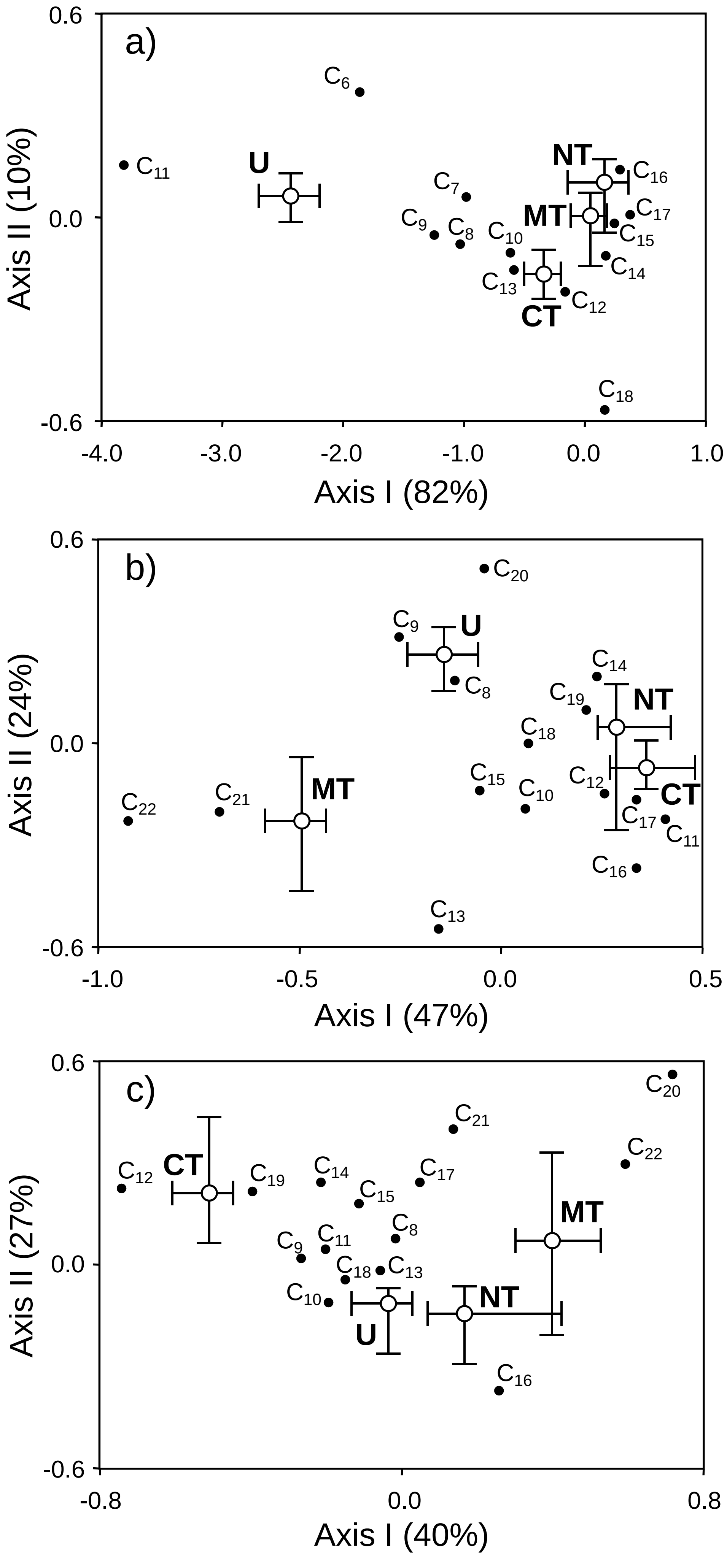


Figure 2. Cumulative values for the main groups (relative peak areas as regards total ion chromatogram) of pyrolysis products from humic acid of uncultivated soil (U) and soils managed with different tillage systems: conventional (CT), minimum (MT) and no-tillage (NT). Error bars indicate the standard deviations between replicated spatial samples. Within a subplot, bars labelled with the same letter are not significantly different at $P<0.05$.



gure 3. Correspondence analyses showing changes in the distribution patterns of: **a)** fatty acids, **b)** alkanes and **c)** alkenes, in terms
e tillage systems (bold labels): CT= conventional tillage; MT= minimum tillage; NT= no-tillage; U= uncultivated. Error bars indicate th
ariability ranges defined by triplicate runs; average values (centroids) are drawn with circles. The percentage of the total varian

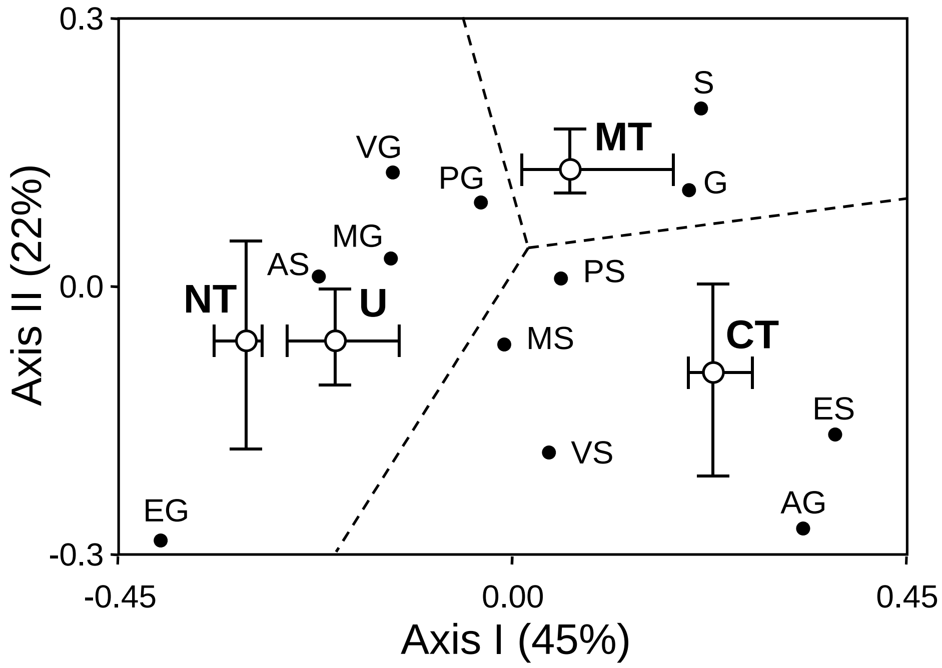


Figure 4. Correspondence analysis showing changes in the distribution patterns of methoxyphenols in terms of the tillage systems (bold labels): CT= conventional tillage; MT= minimum tillage; NT= no-tillage; U= uncultivated. Error bars indicate the variability ranges defined by triplicate runs; average values (centroids) are drawn with circles. The percentage of the total variance accounted for by the two first components is shown in the corresponding axes.

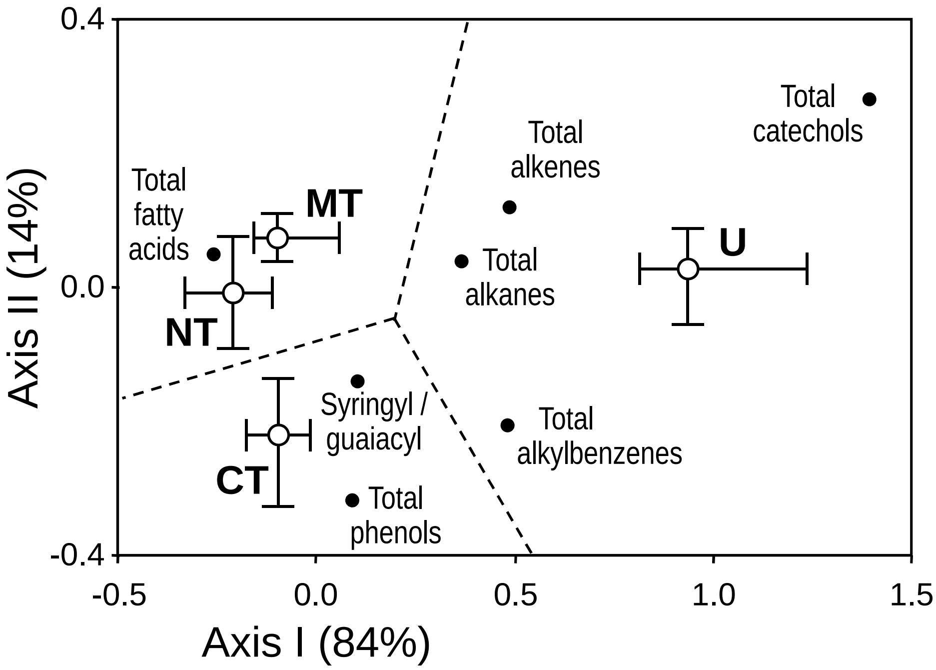


Figure 5. Correspondence analysis of cumulative data of all types of pyrolysis compounds, showing the effects of tillage practices (bold labels: CT = conventional tillage; MT = minimum tillage; NT = no-tillage; U = uncultivated) on the relative yields of the main groups of pyrolysis compounds. Error bars indicate the variability ranges defined by triplicate runs; average values (centroids) are drawn with circles. The percentage of the total variance accounted for by the two first components is shown in the corresponding axes.