

MODIFICATIONS OF THE HUMIC ACID FRACTION IN A SOIL TREATED WITH COMPOSTED MUNICIPAL REFUSE

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SUMMARY

The effects on the humic acid fraction of a soil after three years of compost application in a field experiment has been studied. Most of the analytical parameters, such as elementary composition, functional group contents, E_4/E_6 ratios and spectral characteristics seem to be quite useless for evaluating differences between the structure of the humic acids isolated from soil before and after the application of compost. However, chemical degradations reveal that representative components of the organic matter from compost such as fatty acid series were retained in loosely linked forms in the humic acid fraction of the soil.

INTRODUCTION

As supplies of farmyard manures have diminished and the resources of other organic substrates are quite exhausted in Spain, the incorporation in agricultural lands of compost from municipal refuse, is receiving increasing attention. These composts, which are normally obtained by an aerated pile process, differ considerably from other organic amendments due to the complex nature of the prime material, which contains lignins, cellulose, fats, tannins, plastic debris, etc.

Several important limitations with regard to the agricultural use of city refuse composts have been described (ref. 12), although their effect on the composition of the soil organic matter has received little attention. Due to the high levels of organic matter in these materials (ref. 3), which may in part persist in the soil for relatively long periods, their repeated application could affect the status of the soil humic fraction, as has been proved in the case of sewage sludges (ref. 4).

In a previous work on the changes in the lipid fraction of a soil, resulting from three years of compost application (ref. 5) an accumulation of n-alkane and n-fatty acid series bonded to the organic-mineral soil complex

was detected. The object of this investigation was to determine in the same field experiment the effects of the compost amendment on the humic acid fraction of soil. Our approach involved the isolation and characterization by non-destructive and degradative methods of the humic acid-like fraction from the compost (defined in operational terms as 'the compost organic matter soluble in alkali but precipitated by mineral acids') and the humic acids extracted from the original soil and the compost-amended soil.

MATERIAL AND METHODS.

Characteristics of the raw refuse, collected from the metropolitan area of Sevilla (Southern Spain), as also chemical analyses of the derived compost used in this experiment, were previously reported (ref. 3). The compost was annually applied at rates of 14 metric tons/ha over three years, together with 500 Kg/ha of a complex NPK (15-15-15) fertilizer, to plots of a Xerofluvent (1.5% C) where shorgum or wheat were cultivated.

The procedures for the extraction of humic acids from compost (HA-C) and soil before (HA-S-b) and after (HA-S-a) application of the compost were published elsewhere (refs. 5-6). Elemental analysis and functional group determinations of the extracted humic acids were carried out according to methods previously described (ref. 7).

Infrared spectra were recorded on KBr pellets (1 mg of HA per 300 mg of KBr) on a Perkin Elmer 377 spectrometer. E_4/E_6 ratios were determined by measuring optical densities of humic acid solutions (12 mg of HA in 100 ml of 0.05 N NaHCO_3) at 465 and 665 nm on a Pye Unicam 1800 spectrophotometer.

The ^{13}C -NMR solution spectra were obtained from 150 mg of the freeze-dried humic acid samples dissolved in 3 ml of 0.5N NaOH. These were taken on a Bruker MSL 300 spectrometer at 75.4 MHz under continuous broad band decoupling conditions with 90 RF pulses and pulse delays of 0.5 s; 30,000 free induction decays were accumulated for each sample.

The humic acid samples were degraded with potassium persulfate at acid pH, and the non-degraded residues were methylated with diazomethane and further submitted to alkaline permanganate oxidation according to methods previously reported (ref. 8-9). The ethyl acetate soluble degradation products from permanganate were fractionated by Sep-Pak cartridges using progressively hexane, hexane-chloroform (1:1) and chloroform. Experimental conditions for GC-MS studies and methods for identification of components in the oxidation products mixture were previously reported (ref. 10). Relative amounts of volatile components were expressed as percentages of the most abundant component of each fraction measured on peak heights.

RESULTS AND DISCUSSION

Results of elemental and functional group analysis and E_4/E_6 parameters for compost (HA-C) and soil humic acids (HA-S-b, HA-S-a) are shown in Table 1, although with no aim to comparison of soil HA's and the humic acid-like compost fraction. Little differences was observed in the elementary composition of the two soil humic acids, although the C,H, and N percentages were found to be slightly higher in the HA-S-a, all values falling into the typical range found for soil HA's (ref. 11). However, these differences should not be discussed in structural terms due to the high complexity of the humic materials (ref. 12).

TABLE 1

Elemental analysis¹, content of oxygen-containing functional groups², and E_4/E_6 values of the humic acids from composts (HA-C), untreated soils (HA-S-b), and compost-amended soil (HA-S-a)³

Sample	% Ash	C	H	N	O	Total acidity	COOH groups	Phenolic OH	E_4/E_6
HA-C	3.2	56.2	7.1	6.2	30.4	5.0	1.5	3.5	4.5
HA-S-b	1.1	45.7	3.6	4.3	46.4	6.5	3.2	3.3	4.1
HA-S-a	1.8	49.7	4.1	4.7	41.5	6.3	3.1	3.2	5.0

¹ on moisture-free, ash-free basis.

² meq.g⁻¹

³ mean values for the different composts applied during the field experiments
Phenolic OH= total acidity-COOH acidity.

The high N content in HA-C suggests that protein material present in the refuse is incorporated, in loosely joined forms, in the humic acid fraction during the maturing process of the starting material, which is consistent with the lack of N-containing substances in the free organic components isolated by solvent extraction from this compost (ref. 3), and the presence of amino acid N in substantial concentrations after mild hydrolysis.

The content of functional groups in the soil HA before and after amendment show no indication of effect attributable to the compost, since the values are quite constant and similar to those reported for an average soil HA (ref. 11). The HA-C sample showed lower values of total acidity and COOH groups, as an indication of its different nature.

Considering the E_4/E_6 ratios, there are certain differences in molecular sizes (ref. 13) between the soils HA's, and therefore the effect of compost amendment can be considered as negligible. In general, the classical parameters for HA characterization seem to be quite useless to evaluate differences between the soil humic samples.

Fig. 1 shows the IR spectra of the three samples. The main distinguishing characteristics of the IR spectrum of HA-C are a broad band near 1530 cm^{-1} and 1040 cm^{-1} , which are respectively attributed to the peptide linkage of proteins and the C-O stretching of polysaccharide substances, and strong bands in the $2950\text{-}2840\text{ cm}^{-1}$ region, corresponding to methylene and methyl C-H stretching vibrations. These bands could arise mainly from the long alkyl chains of fatty acids (ref. 4), and also from long-chain alkanes, which were detected among the free organic compounds present in the compost (ref. 3).

It is likely that part of such compounds were incorporated in the humic fraction of the compost during the composting processes or were co-extracted with them. HA-S-b and HA-S-a IR spectra (Fig. 1) show poor resolution and the few typical absorption bands for soil HA's. The bands corresponding to aliphatic C-H ($2950\text{-}2840\text{ cm}^{-1}$) and polysaccharide material (1040 cm^{-1}) are, however, more pronounced in the HA-S-a, which may indicate a relatively higher aliphatic character of this HA, as a probable result of the incorporation of compost components to its structure.



Fig. 1. IR spectra of the humic acids before (HA-S-b) and after (HA-S-a) the compost treatment, and from compost (HA-C).

Unexpectedly, these differences were less apparent by comparison of the solution ^{13}C -NMR spectra (Fig. 2) of the HA's before and after compost amendment. The spectra appear different at first sight, but a closer inspection shows that they are qualitatively and quantitatively very similar, the most pronounced differences being the the much higher resolution and signal/noise ratio of the AH-S-b sample. Some minimal differences observed in the aliphatic region (0-100 ppm), particularly changes in band intensity ratios, should not be considered as an effect due to the application of compost.

The assignment of the various clearly resolved absorption signals through the 0-200 ppm range is identical to that previously reported for other soil HA's (ref. 14-15) and compost HA's (refs. 10 and 16).

In view of the relative insensibility of the physicochemical parameters and the non-destructive spectroscopic methods to evidentiare changes in the HA from the compost-amended soil, the samples were studied by chemical degradations.

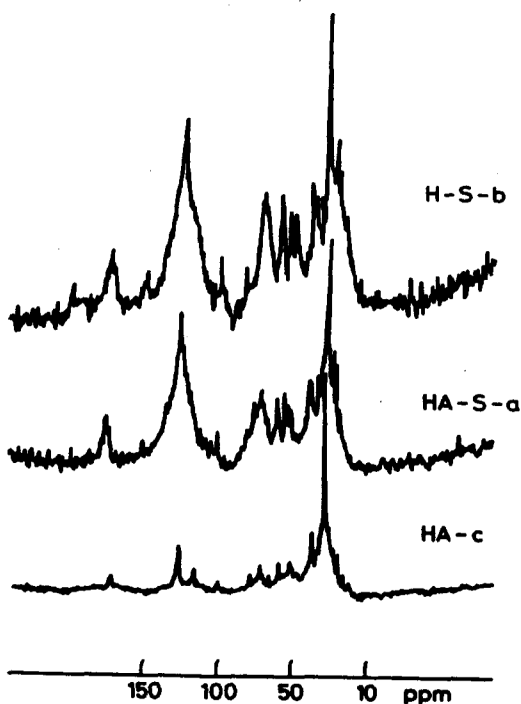


Fig. 2. ^{13}C -NMR spectra of the humic acids before (HA-S-b) and after (HA-S-a) the compost treatment, and of compost (HA-C).

In the first oxidation step the percentage of materials removed by persulfate, a mild oxidative reagent, accounted for 30% in HA-C, 28% in HA-S-b and 32% in HA-S-a, while no residues were obtained after completion of the oxidation with permanganate.

TABLE 2

Compounds identified amongst the persulfate oxidation products of the samples

	HA-C	HA-S-b	HA-S-a
α, ω dicarboxylic aliphatic acids	C5-C6	-	-
n-fatty acids	C14-C26	C15-C19	C12-C22
monounsaturated fatty acids	-	-	C16:1/C18:1
branched fatty acids	C16-C18	C18	C14-C19
alkyl phthalates	++	-	-
phenolic acids	-	+	+
benzenecarboxylic acids	-	+	+

The amount of amino acids and sugars released by persulfate were small compared with the quantities released from more vigorous acid hydrolysis (unpublished results). HA-C and HA-S-a contain higher amounts of N and carbohydrates, and these compounds contribute to their higher degradation percentages. In Table 2 the different kinds of oxidation products released by persulfate are shown. There were remarkable differences between the soil HA's, the HA-S-a yielding a higher variety of saturated, unsaturated and branched fatty acids, and overall higher concentrations of such compounds. This is illustrated in the histograms of Fig. 3, where the distribution of n- and branched fatty acids in the three samples is presented.

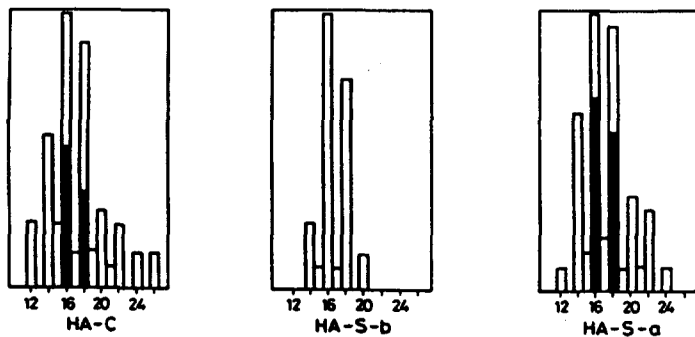


Fig. 3. Distribution of the saturated and unsaturated (black bars) fatty acids after persulfate degradation of humic acids before (HA-S-b) and after (HA-S-a) the compost treatment, and of compost (HA-C).

It has been suggested (ref. 8) that persulfate may attack the most accessible or more easily degradable portion of the humic materials. On the other hand, fatty acids are known to be loosely held or physically adsorbed compounds that may be extracted from humic materials following saponification (ref. 17). Moreover, HA's can retain or fix significant amounts of hydrophobic compounds, including dialkyl phthalates (ref. 18).

It may be assumed that the aliphatic compounds present in high quantities in the easily degradable portion of the HA-S-a, are derived from the lipid fraction of the compost, both free or loosely joined to its humic fraction.

Table 3 shows the distribution of products resulting from the permanganate oxidation of the persulfate residues. The soil HA samples yield relatively large amounts of di- and polysubstituted single aromatic structures, in addition to C16 and C18 fatty acids and n-alkanes in the range C14-C31 (in the hexane soluble fraction). The most noticeable difference between the soil HA's is the greater amount and variety of short-chain dicarboxylic aliphatic acids in the HA-S-b, which may be also considered a consequence of the compost application.

TABLE 3

Compounds identified amongst the permanganate oxidation products of the persulfate degradation residues.

	HA-C	HA-S-b	HA-S-a
α, ω dicarboxylic aliphatic acids	C4-C12	C5-C7	C4-C11
n-alkanes *	-	C14-C26	C14-C31
n-fatty acids	-	C16/C18	C16/C18
phenolic acids	-	+	+
benzenecarboxylic acids	-	+++	+++

* In the hexane soluble fraction.

The effects of the application of compost on the humic acid fraction of soil seems to be limited to the incorporation of aliphatic material to the more easily degradable portion, as revealed by persulfate degradation and, to a lesser extent, by the permanganate results. On the other hand, the relative contribution of the free lipid components or the humic acid fraction of the refuse cannot be deduced from our results. However, the observation that hydrophobic materials are present in the soil HA fraction for as long as three years after the application of compost suggest that these materials become resistant to biodecomposition and can accumulate in the soil, producing potential long-term negative effects upon decomposition processes, inorganic N immobilization and plant growth (refs. 19-21).

REFERENCES.

- C. Tietjen, Principal problems of the use of city waste for crop production and soil conservation, Organic materials as fertilizers, FAO Soils Bull., 27 (1975) 211-216
- H. Kick. Les aspects de l'utilisation des composts de ville dans l'agriculture, Int Conf. on Compost, Office of Environment, Ministry of Public Works and City Planning, Madrid, 1980, 13 pp.
- F.J. Gonzalez-Vila, C. Saiz-Jimenez and F. Martin, Identification of free organic chemicals found in composted municipal refuse, J. Environ. Qual., 11 (1982) 251-254.
- S.A. Boyd, L.E. Sommers and D.W. Nelson, Changes in the humic acid fraction of soil resulting from sludge application, Soil Sci. Soc. Am. J., 44 (1980) 1179-1186.
- F.J. Gonzalez-Vila, F. Martin and T. Verdejo, Changes in the lipidic fraction of soil after municipal refuse application, Agrochimica, 29 (1985) 210-219.
- F.J. Gonzalez-Vila, C. Saiz-Jimenez and F. Martin, Comparative studies of humic acids extracted with alkaline agents, Agrochimica, 18 (1974) 164-172.
- F. Martin, C. Saiz-Jimenez and A. Cert, Pyrolysis-gas chromatography-mass spectrometry of soil humic fractions. The low boiling point compounds, Soil Sci. Soc. Am. J., 41 (1977) 1114-1118.
- F. Martin, C. Saiz-Jimenez and F.J. Gonzalez-Vila, The persulfate oxidation of a soil humic acid, Soil Sci., 132 (1981) 200-203.
- S.U. Khan and M. Schnitzer, Permanganate oxidation of humic acids extracted from a gray wooded soil under different cropping systems and fertilizer treatments, Geoderma, 7 (1974) 113-120.
- F.J. Gonzalez-Vila and F. Martin, Chemical structural characteristics of humic acids extracted from composted municipal refuse, Agric. Ecosyst. Environ., 14 (1985) 267-278.
- M. Schnitzer, Recent findings on the characterization of humic substances extracted from soils from widely different climatic zones, Proc. Symp. on Soil Organic Matter studies, Braunschweig, West Germany, September 6-10, 1976, IAEA, Vienna, 1977, pp. 117-131.
- M.H.B. Hayes and R.S. Swift, The chemistry of soil organic colloids, in: D.J. Greenland and M.H.B. Hayes (eds.), The Chemistry of Soil Constituents, John Wiley, Chichester, 1978, pp. 179-216.
- Y. Chen, N. Senesi and M. Schnitzer, Information provided on humic substances by E_4/E_6 ratios, Soil Sci. Soc. Am. J., 41 (1977) 352-358.
- F. J. Gonzalez-Vila, H.D. Lüdemann and F. Martin, ^{13}C -NMR structural features of soil humic acids and their methylated, hydrolyzed and extracted derivatives, Geoderma, 31 (1983) 3-15.
- C.M. Preston and B.A. Bracewell, Carbon-13 nuclear magnetic resonance for a humic and a fulvic acid: signal to noise optimization, quantitation and spin-echo techniques, Soil Sci., 139 (1985) 88-96.
- R. Fründ, F.J. Gonzalez-Vila, H.D. Lüdemann and F. Martin, Comparison of the solid state CPMAS and solution carbon-13-NMR spectra of humic acids extracted from composted municipal refuse. Submitted for publication to Agric. Ecosyst. Environ.
- M. Schnitzer and J.A. Neyroud, Alkanes and fatty acids in humic substances. Fuel, 54 (1975) 17-19.
- S.U. Khan and M. Schnitzer, The retention of hydrophobic organic compounds by humic acid, Geochim. Cosmochim. Acta, 36 (1972) 745-754.
- R.A. Terry, D.W. Nelson and L.E. Sommer, Carbon cycling during sewage sludge decomposition in soils, Soil Sci Soc. Am. J., 43 (1979) 494-501.
- E.G. Beauchamp, Y.C. Soon and J.R. Moyer, Nitrate production from chemically treated sewage sludges in soil, J. Environ. Qual., 8 (1979) 557-563.
- F. J. Stevenson, Humus Chemistry, John Wiley and Sons, New York, 1982, 443 pp.