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Short Communication

PHENOLICS AND THE EXCHANGE CAPACITY OF HUMIC MATERIALS†

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Sivapalan and Sivasubramaniam (1979) examined the effect of plant residues of varying phenolic contents on the humus status of a tea soil. Their results supported the view that polyphenols are one of the main skeletal constituents of soil humic substances. Since phenols are believed to play a dominant role in the formation and composition of humus (Flaig *et al.*, 1975), I have examined the contribution of phenolics to the exchange capacity of humic matter by studying the effect of phenol-rich and phenol-poor plant residues on the acidity groups of the soil humic constituents.

An essential requirement in the analysis of these acidity groups is the obtaining of low-ash preparations of fulvic acid (FA) and humic acid (HA). A number of methods have been proposed to achieve this (Goh, 1970; Whitby and Schnitzer, 1978), but most methods produced either low yields of FA or did not lower the ash content sufficiently. They were also laborious and time-consuming.

I have developed a simple and satisfactory method to achieve this.

Experimental details of the plant materials, the green-house procedures and analytical methods were reported by Sivapalan and Sivasubramaniam (1979). Briefly, soil was incubated with plant residues of varying phenolic contents for 4-12 months before analysis for various constituents. The treatments were replicated thrice in a randomized block design. Samples from the three replicates were mixed and the composite sample used for this study.

On the basis of their phenolic contents, the first four treatments in Table 1 namely Tea shoot tips, Mature tea leaf, Mixture and Black tea, have been classified as phenol-rich residues while the last four treatments, viz. Dadap leaf, Mana grass, Guatemala grass and Tobacco leaf, have been referred to as phenol-poor residues (Sivapalan and Sivasubramaniam, 1979).

Improved procedure to fractionate and purify humic constituents

The fractionation and purification of FA was based on the methods of Goh (1970) and Sequi *et al.* (1972), while the purification of HA was based on the method of Griffith and Schnitzer (1975) with certain modifications (Fig. 1).

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The wet HA was washed once by stirring with 0.2 N H_2SO_4, centrifuged and the HA residue shaken with 0.5% HCl HF solution (Griffith and Schnitzer, 1975) for 18 h separated by centrifugation, dialysed against distilled water for 24 h and freeze dried.

"True" humic fractions of FA

After the precipitation of HA from an alkaline extract of HM, the supernatent FA fraction contains significant amounts of non-humic material in addition to the true FA's which are phenolic condensation products (Schnitzer, 1977). These

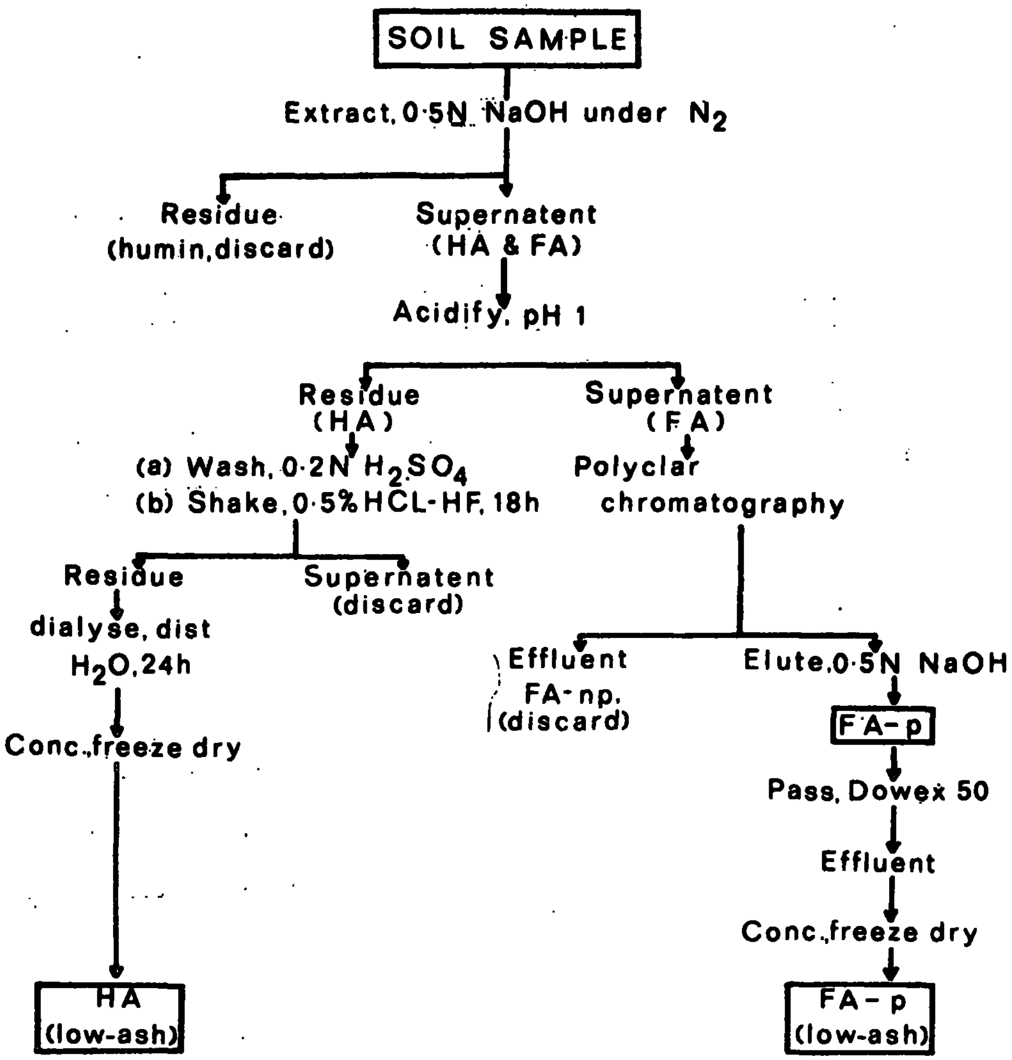

Fig. 1 — Improved scheme for the fractionation and purification of soil humic constituents.

TABLE 1 — *Yield and ash content of purified humic fractions*

Treatment	*Yield of purified humic fraction (% of original HM)* FA-p	HA	*Ash (%)* FA-p	HA
Tea shoot tip	20.98	13.97	1.62	5.55
Mature tea leaf	22.67	12.06	1.19	6.08
Mixture*	18.19	13.39	1.24	6.14
Black tea	21.07	13.34	0.28	7.06
Spent tea leaf	13.38	12.12	0.50	4.98
Dadap leaf	14.95	10.06	0.80	3.80
Mana grass	13.38	10.24	1.79	5.01
Guatemala grass	16.24	11.28	0.51	3.21
Tobacco leaf	13.34	10.71	0.58	5.10
Control	18.07	10.17	0.22	3.08
Average	17.23	11.73		

*Mixture—Tea shoot tip and Mature tea leaf mixed in the ratio 1:1

two fractions of FA could be separated on Polyclar (PVP) which is a specific adsorbent for phenolics (Loomis, 1975). The fraction retained on the Polyclar column, referred to as FA-phenolic (FA-p), is the true FA, while the effluent, referred to as FA-nonphenolic (FA-np) is the non-humic fraction. The FA fraction also contains large amounts of Na_2SO_4 which too would pass into the effluent FA-np fraction. Thus the use of Polyclar ensures the elimination of both the non-humic as well as the bulky inorganic contaminants.

The FA-p retained on the column was eluted with 0.5 N NaOH and the eluate immediately passed through a Dowex 50 (H) cation exchange column connected in sequence by a Quickfit arrangement. The effluent was collected and freeze-dried.

Purification of FA-np

To the FA-np fraction collected off the Polyclar column, NaOH pellets were added to raise the pH to about 4.5-5.0, when flocculation occurred. This has been attributed to Al impurities (Sequi *et al.*, 1972). Repeated centrifugation was necessary to remove the flocculated fraction, after which the solution was passed through Dowex 50 (H) cation exchange column. The effluent was concentrated to a small volume, dialyzed against distilled water for 48 h and freeze dried.

Total acidity and carboxyl groups were determined by the methods of Schnitzer and Gupta (1965), organic C and ash by those of Jackson (1958) and Goh (1970) respectively. Duplicate determinations of the above were carried out and the means reported.

The yields of the purified humic fraction expressed as percentages of the original humic matter (HM) in the respective soil samples (Sivapalan and Sivasubramaniam, 1979) are shown in Table 1. The purified FA'ps ranged from 13.34 to 22.67%

of the initial HM with an average value of 17.23%, while the purified HA's ranged from 10.06 to 13.97% of the original HM with an average value of 11.73%. The ash content of HA's ranged from 3.08 to 7.06% while that of FA-p's varied from 0.22 to 1.62%.

Analysis of the FA-np fractions was discontinued after the assay of the first three samples revealed that the recovery of FA-np was only about 3.60% of the original content of HM, and that the ash content was on an average about 38.70%. However, for the samples analyzed, the "total acidity" averaged 0.80 m-equiv g^{-1}, of which carboxyl acidity constituted 0.68 m-equiv g^{-1}.

"Total acidity" of the FA-p's ranged from 2.92 to 3.23 m-equiv g^{-1} while that of HA's ranged from 1.09 to 1.45 m-equiv g^{-1} (Table 2). In each case carboxyl groups accounted for most of the acidity. The "total acidity" per g of purified material was not related to the phenolic nature (i.e. phenol-rich or phenol-poor) of the decomposing plant residues. In fact, addition of plant material has not affected the "total acidity" per g of purified FA-p or HA, in relation to even the "control" treatment. The effect of plant residues, if any, on "total acidity" characteristics of the soil would therefore appear to depend mainly on the relative content of these humic fractions in the soil.

TABLE 2 — *Analysis of acidity groups in purified humic fractions (m-equiv g^{-1} oven-dry basis)*

	FA-p			*HA-*		
Treatment	*Total acidity*	*Carboxyl*	*Phenolic OH*	*Total acidity*	*Carboxyl*	*Phenolic OH*
Tea shoot tips	2.92	2.81	0.11	1.33	0.92	0.41
Mature tea leaf	3.27	3.04	0.23	1.11	0.91	0.20
Mixture	2.98	2.83	0.15	1.20	0.88	0.33
Black tea	3.23	3.17	0.06	1.17	0.92	0.25
Spent tea leaf	3.06	3.02	0.04	1.09	0.94	0.15
Dadap leaf	3.07	3.02	0.05	1.20	1.00	1.19
Mana grass	2.98	2.91	0.07	1.25	0.93	0.32
Guatemala grass	3.03	2.96	0.07	1.45	1.01	0.42
Tobacco leaf	3.07	2.90	0.17	1.34	0.98	0.36
Control	3.08	2.94	0.15	1.25	1.00	0.25

"Total acidity" in initial FA-p and HA

From the "total acidity" value per g purified preparation FA-p or HA and its per cent C content, the "total acidity" per mg C of purified preparation was calculated. This value was then used to estimate the "total acidity" of the FA-p and HA initially present in the soil samples, since the initial content of these individual fractions have been reported earlier as mg C g^{-1} soil (Sivapalan and Sivasubramaniam, 1979). These values (corrected for 100 g soil) are presented in Table 3 and provide a more realistic picture of the acidity groups per unit of soil. The relative contributions of FA-p and HA are clearly seen, and these on an average amount to 5.05 and 0.69 m-equiv $(100\ g)^{-1}$ soil respectively. This data therefore underlines the importance of the fulvic acid fraction in "total acidity" considerations of the soil.

TABLE 3 — *"Total acidity" contents in original humic fractions*

Treatment	*Total acidity m-equiv 100 g^{-1} Soil* FA-p	HA	*Sum total acidity m-equiv 100 g^{-1} soil*
Tea shoot tip	5.94	0.81	6.75
Mature tea leaf	5.02	0.69	5.71
Mixture	5.41	0.66	6.07
Black tea	5.20	0.80	6.00
Spent tea leaf	4.86	0.54	5.41
Dadap leaf	4.45	0.68	5.14
Mana grass	4.71	0.69	5.40
Guatemala grass	4.54	0.74	5.28
Tobacco leaf	5.00	0.70	5.70
Control	4.87	0.50	5.37
Average	5.00	0.69	

In Table 3, the sum of each pair of "total acidity" values will be referred to as "sum total acidity", and it will be apparent that this unit may be taken as a measure of the cation exchange capacity (CEC) of HM present in 100 g soil. This data, shown in Table 3, indicates that soils treated with phenol-rich residues, in general, are associated with a higher CEC value of HM.

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