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Characteristics of Humic and Fulvic Acid and Other Chemical Properties of Some Peat Materials in Eastern Anatolia

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Abstract: Humic Acids (HA) and Fulvic Acids (FA) extracted from different peat materials have been characterised by chemical methods. The chemical properties of HA and FA showed differences depending on the source from which they were obtained. Compared with the peat materials, the cation exchangeable capacity (190.20 cmol_c kg⁻¹), organic matter (40.83%), total N (2.83%), exchangeable potassium (850 mg kg⁻¹) of Sığırılı (S) materials were greater than those of other materials. But Na (28 mg kg⁻¹), Fe (85 mg kg⁻¹), Zn (24 mg kg⁻¹) Cu (4 mg kg⁻¹) and Mn (6.24 mg kg⁻¹) contents of Erzurum (E) material were greater than those of other materials. The chemical properties of HA and FA showed differences depending on source and climatic condition from which they were obtained. Organic C and nitrogen contents of humic acid were greater than FA. Most of the total acidity of humic acid consists of COOH group, but with few exceptions, fulvic acid mainly consists of phenolic-OH.

Key words: Humic substances, macro-micro element, organic matter, peat material, total acidity

INTRODUCTION

Organic materials such as peat materials and organic wastes when added to the soil have a major effect on its physical, chemical and biological properties^[1-3]. This effect depends on Organic Matter (OM) sources and qualities both of which are governed by climatic conditions, nature of plant material and soil type^[2,4].

Knowledge of carbon dynamics and organic matter quality is therefore essential for understanding the sustainability of different agricultural systems, the global carbon cycle, element leaching causing water pollution and soil depletion and the ability of soil to withstand physical damage such as compaction and erosion^[3].

An important strategy for recycling organic deposition is their use in agriculture as fertiliser and as an organic amendment in intensively-cropped, organic farming and organic depleted soils^[5]. Indeed, OM plays a fundamental role in conditioning soil properties. Organic matter can be divided into non-humic and humic substances. Non-humic substances include those with still-recognisable chemical characteristics of their precursors (e.g. polysaccharides, proteins, lipids, etc.), while humic substances are defined as a general category of naturally occurring, biogenic, heterogenous organic substances that can generally be characterised as yellow to black in colour, high molecular weight and refractory^[6]. Since the bioavailability of OM Soil Organic Matter (SOM) is controlled by chemical structure of OM and

physical protection offered by the soil matrix and minerals^[7], the chemical characteristics of OM are important to understanding the dynamics of SOM in C cycling. Humic substances are known as its most important fraction since they are directly involved in the slow release of nutrients high cation capacity, pH buffer capacity and heavy metals^[8]. Therefore the recycling of organic wastes through their application for the soil can be an important and promising practise for agricultural activities. The soil has almost unlimited capacity to accept large quantities of those materials and transform them through processes leading to humic substances. Part of this newly formed organic matter (humic acid and the other humic substances) has a great influence on soil fertility^[9], due to its carboxyl and phenolic-OH groups that interact with various soil components. A better understanding of the chemical and physical characteristics of these acids is necessary to comprehend the transformations the acids will undergo after different times in the soil environment.

Many studies were point to the favourable effect that humic substances have on plant growth. These substances can either have a direct effect such as absorption of the humic compounds by the plant, affecting certain enzymatic activities, membrane permeability, etc.^[10,11] or an indirect (changes in the soil structure, increased cationic capacity, stimulation of microbiological activity the capacity to solubilize or complex certain soil ions) effect on the plant^[12,13].

Table 1: Sampling location and their meteorological information^[30]

Location	Meteorological data ¹			
	Min. temp. (°C)	Max. temp. (°C)	Mean temp. (°C)	Mean rain (mm)
Erzurum (E)	-32.3	32.9	5.2	390.2
Sığırlı (S)	-30.5	35.6	5.0	394.2
Toparlak (T)	-33.0	32.4	4.7	393.6
Sarıkamış (Sa)	-30.5	33.8	5.2	393.7
Dumlu (D)	-30.4	31.8	5.8	398.5
Erzincan (Er)	4.2	30.9	10.8	380.8
Ardahan (A)	-30.2	31.2	5.1	360.2

¹The meteorological information is based on 73 years

The effect which humic substances have on nutrient absorbance generally depends on their origin, type and concentration in the nutrient solution and on the species and variety of plant treated. The mechanisms by which the nutrients are absorbed by the plants and the interactions between the plant and culture medium are two factors which substantially influence the effect of humic substances on nutrient absorption. If the nutrients are absorbed by an active mechanism (metabolic process) the humic substances can inhibition absorption, since they tend to complex the ions^[14,15]. Conversely, if the same ions are absorbed by means of a passive mechanism (diffusion through the tissues, translocation, etc.), the humic substances either do not intervene at all in the absorption or have a positive effect^[14,16].

Organic matter sources such as peat material area of Turkey are approximately 25.000 ha. Characteristics of peat materials of Turkey vary based on climatic condition, botanical contents, topography, water quality and origin, drainage condition of the area.

The objectives of this study were to (I) assess the nutrient contents suitability of some organic material for plant breeding, (ii) determine an optimum application rate of peat material to mineral soil, (iii) evaluate and compare the chemical characteristics of some peat materials in Eastern Anatolia before they were added to soil.

MATERIALS AND METHODS

Twenty samples of each seven peat materials (0-40 cm depth) were collected in the region of Eastern Anatolia shown in Table 1. The samples were dried at room temperature to workable water content and then passed through a 2 mm sieve before chemical analysis. Exchangeable cations (K, Ca, Mg, Na) and Cation Exchange Capacity (CEC) Page *et al.*^[17] pH and electric conductivity^[18], organic C and organic matter^[19], total nitrogen^[20] and plant available phosphorus were^[21] determined. For the total heavy metal concentration, a known quantity (1 g) sample was digested with 10 mL of concentrated HNO₃ as described by Zorpas *et al.*^[22]. After

digestion, the samples were vacuum filtered and the filtrate was used to determine the heavy metal concentration by atomic spectrophotometer (a Perkin Elmer 360 spectrophotometer was used). Humic substances were extracted using 0.1 N NaOH for 24 h according to Schintzer *et al.*^[23].

For the determined total acidity; 100 mg of humic preparation in a 125 mL ground-glass stoppered Erlenmeyer flask, add 20 mL of 0.20 N Ba (OH)₂ solution. Simultaneously, set up a blank consisting of add 20 mL of 0.20 N Ba (OH)₂ only. Displace the air in each flask by N₂, stopper flask carefully and shake the system for 24 h at room temperature. Following this, filter the suspension, wash the residue thoroughly with CO₂-free distillate water and titrate the filtrate plus washing potentiometrically with standard 0.5 N HCl solutions to pH 8.4^[24].

For the determined carboxyl groups; 100 mg of humic preparation in a 125 mL ground-glass stoppered Erlenmeyer flask, add 10 mL of 1 N (CH₃COO)₂Ca solution and 40 mL of CO₂-free distillate water. Setup blank simultaneously, consisting of add 10 mL of 1 N (CH₃COO)₂Ca solution and 40 mL of CO₂-free distillate water only. After shaking for 24 h at room temperature, filter the suspension, wash the residue with CO₂-free distillate water, combine the filtrate and the washing and titrate potentiometricall with standard 0.1 N NaOH solutions to pH 9.8^[24]. Phenolic hydroxyls were ascribed to the difference between total acidity and carboxyl groups.

RESULTS AND DISCUSSION

The analytical data differed among the materials are shown that the moisture of S was the lowest in the all of the materials, pH values of E was the slight alkaline while T, Er, Sa, S and A had an acidic pH and D had neutral pH (Table 2).

The cation exchangeable capacity (190.20 cmol_c kg⁻¹), exchangeable potassium (62 g kg⁻¹), available phosphorus (850 mg kg⁻¹), total N (2.83%) and organic matter content (40.83%) of S were much greater than those of the other materials. Available Na (32 mg kg⁻¹), Fe (85 mg kg⁻¹), Zn (24 mg kg⁻¹) Cu (4 mg kg⁻¹) and Mn (6.24 mg kg⁻¹) contents of Erzurum (E) material were greater than those of other materials (Table 2).

Among the sources, nitrogen contents of HA and FA was the maximum for E followed by Sa>S>A>T>D>Er, S>Sa>D>T>A>Er, respectively (Table 3). That the highest nitrogen and lowest organic carbon contents of E materials was probably due to the greater content of humified organic matter caused by a longer period of decomposition. That the lowest nitrogen content but the

Table 2: Some characteristics of original peat materials

Locution	Moisture (%)	pH (1/3)	EC (dS m ⁻¹)	CEC (cmol, kg ⁻¹)	Org. Matter (%)	Organic C (%)	Total N (%)	Ca (mg kg ⁻¹)
Erzurum (E)	70.50±3.4	7.25±0.12	1.04±0.09	122.60±6.25	36.60±4.28	21.91±2.28	1.70±0.21	35.60±5.10
Sığırlı (S)	62.30±2.8	5.18±0.22	0.84±0.05	190.20±8.12	40.83±6.17	20.14±3.15	2.83±0.09	28.31±6.30
Toparlık (T)	67.20±2.4	4.72±0.10	1.05±0.08	118.30±14.60	28.86±3.56	16.69±1.78	1.41±0.12	20.20±13.80
Sarıkamış (Sa)	68.50±2.0	5.90±0.08	0.40±0.06	165.20±13.24	18.60±7.11	13.90±1.05	2.21±0.14	32.62±10.15
Dumlu (D)	71.20±3.6	6.54±0.17	0.76±0.05	105.14±10.12	25.25±2.65	16.40±2.22	1.65±0.10	38.40±3.20
Erzincan (Er)	71.14±2.8	4.32±0.13	0.38±0.06	148.35±16.37	38.20±3.68	24.31±1.89	1.98±0.13	23.70±3.60
Ardahan (A)	74.25±2.3	5.20±0.12	0.44±0.05	122.04±11.10	33.20±4.12	18.13±1.92	0.98±0.15	39.41±4.10

Table 2: Continued

	Mg (mg kg ⁻¹)	K (g kg ⁻¹)	P (mg kg ⁻¹)	Na (mg kg ⁻¹)	Fe (mg kg ⁻¹)	Zn (mg kg ⁻¹)	Cu (mg kg ⁻¹)	Mn (mg kg ⁻¹)
Erzurum (E)	12.83±1.5	30.00±2.43	480±21.55	28±1.20	85±6.12	24.00±0.66	4±0.05	6.24±1.20
Sığırlı (S)	7.11±1.3	62.00±5.64	850±13.22	15±2.15	58±4.17	9.00±0.89	1±0.02	4.13±1.10
Toparlık (T)	11.83±2.4	51.00±3.72	540±26.95	12±1.24	72±3.52	20.00±1.12	3±0.02	3.55±1.40
Sarıkamış (Sa)	6.29±2.0	44.00±5.13	830±14.66	24±1.32	36±2.12	8.00±0.15	2±0.07	3.16±0.84
Dumlu (D)	15.62±1.6	18.00±3.17	620±28.60	32±1.66	63±3.21	16.00±0.24	3±0.06	5.25±1.90
Erzincan (Er)	24.80±1.5	29.00±3.45	260±33.34	6±1.10	42±5.12	12.00±0.14	1±0.03	1.10±0.45
Ardahan (A)	9.64±2.2	32.12±2.74	790±12.15	27±2.14	12±2.88	6.14±0.18	4±0.07	2.40±0.45

Table 3: Functional group content of humic and fulvic acids

Locution	HA Organic		FA Organic		HA Nitrogen		FA Nitrogen		Total acidity (meq g ⁻¹)		COOH (meq g ⁻¹)		Phenolic-OH (meq g ⁻¹)	
	C content (%)	C content (%)	C content (%)	C content (%)	content (%)	content (%)	content (%)	content (%)	HA	FA	HA	FA	HA	FA
Erzurum (E)	18.4±2.10	14.4±1.12	11.16±1.68	3.65±0.20	7.37±1.25	6.77±0.88	3.25±0.14	2.92±0.22	4.12±0.42	3.85±0.23				
Sığırlı (S)	34.2±2.30	19.6±0.15	9.25±1.18	3.21±0.52	6.39±0.83	5.96±1.05	4.15±0.18	4.00±0.34	2.24±0.30	1.96±0.19				
Toparlık (T)	32.4±1.88	28.3±2.14	7.12±5.7	2.14±0.62	7.26±0.79	6.63±0.92	5.48±0.26	4.25±0.44	1.78±0.12	2.38±0.24				
Sarıkamış (Sa)	36.3±3.15	21.2±1.82	10.14±3.8	3.20±0.78	6.40±1.12	5.53±0.68	3.45±0.42	2.95±0.18	2.92±0.14	2.60±0.14				
Dumlu (D)	26.6±4.51	15.1±1.16	5.78±1.9	2.60±0.11	8.86±1.10	7.80±0.42	3.62±0.23	3.05±0.16	5.24±0.31	4.75±0.17				
Erzincan (Er)	39.8±2.12	16.2±0.18	2.32±1.13	1.15±0.21	12.42±0.86	9.87±0.66	8.28±0.58	6.12±0.69	4.14±0.22	3.75±0.28				
Ardahan (A)	29.4±3.12	18.2±1.10	8.62±2.11	1.98±0.18	6.70±1.10	4.78±0.51	3.15±0.33	3.74±0.14	2.13±0.18	2.44±0.11				

highest level of organic carbon contents of Er materials might be attributed not only to the shorter period decomposition but also the slow humification process of Er material. The results suggest that Er samples are characterised by a low degree of condensation and humification compared with the other samples^[8]. The carboxylic group contents, as a consequence, the total acidity of humic acid materials were higher than the fulvic acid in all of the materials (Table 3). All these findings are close values found by other authors for similar materials^[25,26].

Most of the total acidity of humic acid consist of COOH group, but with few exceptions fulvic acid consist of phenolic-OH (Table 3). In several studies were obtain similar results. But some values for those parameters were, generally, higher than those other studies for similar organic materials. This may be attributed to the use of different methods for extraction and purification of humic and fulvic acid and determination of functional groups^[27].

The humic acid of S material had higher concentrations of carboxylic groups than the other materials (Table 3). This could be attributed to the fact that organic materials led to as increase in carboxylic group of humic acid^[28] which play an important role in exchange reactions^[29].

The results show that chemical properties of humic acid varied depending on the source from which they were obtained. The application to soil of peat materials produced by the controlled biological transformation of organic wastes is a traditional practice required for the sustainable management of productive systems. Currently, there is a large variety of easily available organic materials, the characteristics of which must be quarantined for their safe agricultural use. Organic substances in soil can have a direct physiological effect on plant growth. Some compounds, such as certain phenolic acids, have phytotoxic properties; other, such as the auxins, enhance plant growth. Under certain conditions, substances toxic to plants can arise either directly or indirectly during the decomposition of plant residues in soil. Furthermore application of partially humified organic wastes to the soil maybe caused harmful effects because of any nature affects, to a measurable degree, the composition and chemistry of soil. Therefore, various organic materials should initially be subjected to appropriate treatment to minimise adverse effects on soil properties and to optimise their fertility functions before applied to soil. Determining peat chemical properties of Eastern Anatolia is very important because of topographic and botanical conditions, drainage case and including organic matter quality.

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