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Characterisation of soil humic and fulvic acids from different land use systems in shrink swell soil series of western Maharashtra

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Abstract
This study examines humic substances in different land use systems across Rahuri, Pather, and Babulgaon soil series, investigating total acidity and acidic functional groups in humic acid (HA) and fulvic acid (FA). The highest total acidity (7.10 me g^{-1}), carboxylic group (4.40 me g^{-1}), and phenolic group (2.70 me g^{-1}) for HA were observed in Babulgaon series. Similarly, Fulvic acid in Babulgaon series exhibited the highest total acidity (9.25 me g^{-1}) and carboxylic group (6.45 me g^{-1}), while the phenolic group (3.95 me g^{-1}) peaked in Rahuri series. Surface soil in Babulgaon consistently displayed higher mean values for total acidity, carboxyl, and phenolic groups compared to Pather and Rahuri series. This trend persisted irrespective of soil series and land use, with these groups decreasing with increasing soil depth. Analyzing the impact of land use, guava orchard soils had the highest mean total acidity, carboxyl, and phenolic content for both HA and FA. Agriculture-cultivated lands followed, while fallow lands exhibited the lowest mean values. In conclusion, guava orchards exert a significant influence on soil properties, and specific numerical values highlight variations in humic substances across soil series and land use types.

Keywords: Rahuri, Pather, Babulgaon, guava, depth, humic, fulvic, acidity, carboxyl, phenolic

Introduction

Humic substances are colloidal compounds characterized by high specific surface area and surface charge, exerting significant control over the mobility of heavy metals and pesticides within the soil matrix. They play a crucial role in chelation and complexation reactions with metal ions, contribute to nutrient cycling, enhance aggregate structure, improve soil buffering capacity, and interact with minerals, oxides, metal ions, and organic compounds (Gautam *et al.*, 2021) [2]. The soil, as the largest organic carbon reservoir, stores more than three times the carbon compared to atmospheric and biotic pools, with humic substances representing the recalcitrant carbon pools within the soil organic matter (Galantini *et al.*, 2014; Wiesmeier *et al.*, 2019) [1, 6]. Functional groups, specific arrangements of atoms or bonds within a compound, are pivotal in chemical reactions (Schnitzer, 1965) [4]. These groups play a critical role in chelation and complexation reactions with metal ions, influencing the mobility and availability of these ions in soil. Additionally, functional groups contribute to the development of charges on organic colloids, enhancing the availability of metal ions for plant uptake by safeguarding the chelated ions from undesirable chemical reactions (Tewari, 2018) [5].

Total acidity, indicating the presence of carboxylic and alcoholic groups, constitutes one-third of the total acidity. Carboxylic groups, found in amino acids, oxalic acid, and acetic acid, are essential in cellular respiration. Phenolic groups, consisting of aromatic rings with one or more hydroxyl (OH) groups, regulate soil organic matter decomposition and nutrient cycling. Our research aimed to assess the impact of various land use systems on depth wise humic substances in the examined soils and characterize the humic components. This proposed technique proves valuable for understanding soil organic substances, especially when evaluating the influence of environmental changes on the soil.

Materials and Methods
The present investigation was carried out in the guava orchards of farmer's field at Rahata, Ahmednagar district.
The age of guava orchards was around 15-25 years. Guava orchards, conventionally cultivated land and fallow land of three major soil series of Rahuri, Pather and Babulgaon were selected to conduct this experiment. The soils of the farm belong to the broad group of black soils with variation in depth, colour, texture and other morphological characteristics. The vegetation in study area was categorized on the basis of varied land use in different soil order of Entisol, Inceptisol and Vertisol. In this study, three different land use patterns in three different soil series were selected as 1) Fallow land 2) Conventionally cultivated land 3) Perennial horticulture land (guava orchard). The composite soil samples from specified horizons *viz*., A_p horizon in Rahuri series, A_p, Bw_1 and B_{w2} horizons in Pather soil series, A_P, B_{w1}, B_{wss1}, B_{wss2} horizons in Babulgaon soil series were collected from soil profiles from each soil series in each land use system. The soil samples thus obtained were subjected to various functional group analyses, and the results obtained have been presented in table 1 and 2.

Characterization of Humic and Fulvic Material by Chemical Methods (Functional Group Analysis)
Total Acidity: Fifty milligrams of HA/FA and blank were taken in stoppered flasks and 20 ml of 0.2 N Ba $(OH)_2$ was added. The flasks were shaken for 24 h at room temperature. The suspension was filtered and the residue was washed with CO_2-free distilled water. The filtrate and washings were titrated against 0.5 N HCl to pH 8.4 potentiometrically. Identical blanks were maintained simultaneously.

Carboxyl Groups (COOH)
For this, fifty milligrams of HA/FA were taken in a stoppered flask to which 10 ml of 1 N $(CH_3COO)_2$ Ca and 40 ml of CO_2-free distilled water was added. A blank was also set up simultaneously. After shaking at room temperature for 24 h, the suspension was filtered and the residue was washed with CO_2-free distilled water. The filtrate and washings were titrated potentiometrically with standard 0.1 N NaOH to pH 9.8.

Phenolic-OH groups: The phenolic-OH groups were calculated as the difference between total acidity and carboxylic group acidity.

Phenolic-OH groups = (Total acidity) - (-COOH acidity) (me g^{-1})

Results and Discussion
Characterization of Humic Substances (Functional groups)
The depth wise total acidity and acidic functional group contents of humic acid and fulvic acid as influenced by soil series, land use and soil depth are presented in tables 1 and 2. The perusal of data revealed that the highest total acidity (7.10), carboxylic group (4.40), phenolic group (2.70) for humic acid was observed in the surface soil of guava orchards in Babulgaon series. Further, it revealed that the highest total acidity (9.25 me g^{-1}) and carboxylic group (6.45 me g^{-1}) of fulvic acid was maximum in surface soil of guava orchards in Babulgaon series and the phenolic group (3.95 me g^{-1}) was maximum in surface soil of guava orchards in Rahuri series.

Table 1: Effect of different land use on depth wise total acidity, carboxyl and phenolic group in humic acid of Rahuri, Pather and Babulgaon soil series

Soil series (order)	Land Use	Tr. No.	Treatment	Total acidity	COOH	Phenolic OH
				(me g^{-1})		
Rahuri (Entisol)	Fallow	1	EFD_1	3.70	2.05	1.65
	Agriculture (cultivated)	2	EAD_2	5.20	3.35	1.85
	Guava orchard	3	EGD_3	6.60	4.20	2.40
Pather (Inceptisol)	Fallow	4	IFD_1	3.90	2.50	1.40
		5	IFD_2	3.10	1.75	1.35
		6	IFD_3	2.00	1.15	0.85
	Agriculture (cultivated)	7	IAD_1	5.00	3.15	1.85
		8	IAD_2	4.20	2.70	1.50
		9	IAD_3	3.30	1.80	1.50
	Guava orchard	10	IGD_1	6.90	4.25	2.65
		11	IGD_2	6.00	3.90	2.10
		12	IGD_3	5.20	3.55	1.65
Babulgaon (Vertisol)	Fallow	13	VFD_1	3.90	2.20	1.70
		14	VFD_2	3.20	1.60	1.60
		15	VFD_3	2.70	1.10	1.60
		16	VFD_4	2.30	0.80	1.50
	Agriculture (cultivated)	17	VAD_1	5.35	3.40	1.95
		18	VAD_2	4.70	2.95	1.75
		19	VAD_3	3.80	1.95	1.85
		20	VAD_4	3.40	1.85	1.55
	Guava orchard	21	VGD_1	7.10	4.40	2.70
		22	VGD_2	6.10	4.05	2.05
		23	VGD_3	5.40	3.85	1.55
		24	VGD_4	4.50	2.65	1.85
			Max	7.10	4.40	2.70
			Min	2.00	0.80	0.85
			Mean	4.38	2.64	1.73
			SD	1.43	1.09	0.41
			CV	32.66	41.46	23.64

Table 2: Effect of different land use on depth wise total acidity, carboxyl and phenolic group in fulvic acid of Rahuri, Pather and Babulgaon soil series

Soil series (order)	Land Use	Tr. No.	Treatment	Total acidity	COOH	Phenolic OH
				(me g^{-1})		
Rahuri (Entisol)	Fallow	1	EFD_1	5.50	3.25	2.25
	Agriculture (cultivated)	2	EAD_2	7.35	4.85	2.50
	Guava orchard	3	EGD_3	9.20	5.25	3.95
Pather (Inceptisol)	Fallow	4	IFD_1	5.60	4.10	1.50
		5	IFD_2	4.80	3.35	1.45
		6	IFD_3	4.25	2.90	1.35
	Agriculture (cultivated)	7	IAD_1	7.25	4.95	2.30
		8	IAD_2	6.45	4.50	1.95
		9	IAD_3	5.45	3.55	1.90
	Guava orchard	10	IGD_1	8.90	5.65	3.25
		11	IGD_2	8.20	5.20	3.00
		12	IGD_3	7.40	4.85	2.55
Babulgaon (Vertisol)	Fallow	13	VFD_1	5.80	3.95	1.85
		14	VFD_2	5.05	3.30	1.75
		15	VFD_3	3.90	2.20	1.70
		16	VFD_4	3.60	2.05	1.55
	Agriculture (cultivated)	17	VAD_1	7.35	5.05	2.30
		18	VAD_2	6.90	4.90	2.00
		19	VAD_3	6.25	4.35	1.90
		20	VAD_4	5.65	4.05	1.60
	Guava orchard	21	VGD_1	9.25	6.45	2.80
		22	VGD_2	8.45	6.25	2.20
		23	VGD_3	7.60	5.90	1.70
		24	VGD_4	7.15	5.30	1.85
			Max	9.25	6.45	3.95
			Min	3.60	2.05	1.35
			Mean	6.44	4.33	2.10
			SD	1.63	1.19	0.63
			CV	25.36	27.41	29.91

Soil series and depth

The results showed that surface soil of Babulgaon soil series recorded relatively higher mean values of total acidity, carboxyl and phenolic group of humic acid (5.45, 3.33 and 2.12 meq g^{-1}, respectively) compared to that of Pather (5.27, 3.30 and 1.97 me g^{-1}, respectively) and Rahuri soil series (5.17, 3.20 and 1.97 me g^{-1}, respectively). According to the findings, the mean value of total acidity, carboxyl and phenolic group of fulvic acid recorded in surface soil of Babulgaon series was 7.47, 5.15 and 2.32 me g^{-1}, respectively. Then for Pather and Rahuri soil series was (7.25, 4.90 and 2.35, respectively) and (7.35, 4.45 and 2.90 me g^{-1}, respectively). The results further revealed that total acidity, carboxyl and phenolic group showed decreasing trend with successive increase in soil depth irrespective of soil series and land use pattern.

Land use

The highest mean total acidity, carboxyl and phenolic content of humic acid (5.98, 3.86 and 2.12 me g^{-1}, respectively) were detected in the soils of guava based land use followed by agriculture cultivated land (4.37, 2.64 and 1.73 me g^{-1}, respectively) while the lowest mean (3.10, 1.64 and 1.46, respectively) were measured for the fallow land. The similar trend was associated with the functional groups of fulvic acid, the soil of guava orchard recorded maximum mean values of total acidity, carboxyl and phenolic content of fulvic acid (8.27, 5.61 and 2.66 me g^{-1}) followed by agriculture land (6.58, 4.53 and 2.06 me g^{-1}, respectively) and the minimum was recorded in fallow land (4.81, 3.14 and 1.68 me g^{-1}, respectively). Soils from the three land use systems (Table 1 and 2) lead us to assert that the introduction of guava trees in cropping pattern over a prolonged number of years has not only had a strong impact on the physico-chemical and biological properties of the soil but also on HA and FA associated functional groups.

Conclusion

- Guava orchards exhibit the highest mean values for total acidity, carboxyl, and phenolic content in both humic acid (HA) and fulvic acid (FA), suggesting a significant influence on soil properties. Agriculture-cultivated lands follow a similar trend, while fallow lands consistently show the lowest mean values.
- Surface soil of Babulgaon series consistently records higher mean values of total acidity, carboxyl, and phenolic groups in both HA and FA, compared to Pather and Rahuri series. Total acidity, carboxyl, and phenolic groups exhibit a decreasing trend with successive increase in soil depth, irrespective of soil series and land use pattern.
- The introduction of guava trees in cropping patterns over an extended period significantly influences the physico-chemical and biological properties of the soil, particularly affecting HA and FA-associated functional groups.

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