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Characterisation of acidity in Kole lands (AEU 6) of Kerala

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Abstract
The acidity characteristics of acid sulphate soils in the Kole lands of Thrissur district of Kerala were studied in detail by collecting surface soil samples at 0-30 depth from 25 locations, including Puzhakkal, Mullessery, Andhikkad, and Cherpu blocks. Around eight% of the soil samples fall under ultra-acid category (pH <3.5) and 20% come under extremely acidic (pH 3.5-4.5) category. Potential acidity showed higher values compared to other acidity fractions. It ranged from 5.8 to 34.4 meq 100 g^{-1}, followed by pH dependent acidity, which ranged from 5.17 to 26.92 meq 100 g^{-1}. Contribution of different fractions of acidity towards potential acidity showed that around 60.71 to 94.19% of acidity is contributed by pH dependent acidity, followed by exchangeable acidity (5.81-39.29). Active acidity showed the least contribution towards potential acidity and it accounted for 0.06-2.71%. Each acidity fraction is important in accessing the acidity in acidsulphate soil, and this paper aims to reveal the importance of the estimation of operationally defined acidity fractions such as actual acidity, potential sulfidic acidity, and retained acidity for the assessment of acidity hazards in acidsulphate soils and thereby their management.

Keywords: Kole, acid sulphate soils, pH, potential acidity, exchangeable acidity, pH dependent acidity, active acidity

Introduction
Kole lands, a part of Vembanad Kole, is one of the major wetland systems on the south-west coast of India. Kole land comes under the special agro-ecological unit (AEU 6), which is delineated to represent the waterlogged soils below MSL with an area of 13,632 ha. They are the low-lying tracts located 0.5 to 1 m below mean sea level, situated between 10° 20’ to 10° 40’ N latitude and 75° 58’ to 76° 11’ E longitude. The climate is tropical humid monsoon type, with a mean annual temperature of 27.6 °C and a rainfall of 2902 mm. Hydromorphic soils are often underlain by potential acid sulphate sediments and unique hydrological conditions characterise the unit. Seawater ingress to Kole is controlled through bunds and barrages to facilitate rice cultivation. Coconut is grown on the uplands and bunds of the area and rice in the lowlands.

The soils of these regions are extremely acidic (acid sulphate soils) and fall under the subgroup Teric Sulfohemists due to the presence of sulphuric horizons within 50 cm of the surface with a pH less than 3.5. They are acid sulphate soils that are mainly organic. Sulfidic materials in these soils are exposed to oxidation and extreme soil acidity affects nutrient uptake and the physiology of plants and microorganisms. Apart from H^+ ions, presence of Fe, Al, and Mn also contributes to soil acidity. In acid sulphate soil, oxidation of sulphur compounds results in the development of potential acidity. One part of potential acidity is contributed by exchangeable acidity which develops due to the H^+ and Al^{3+} ions in the soil colloids. So assessment of acidities such as potential acidity, exchangeable acidity and active acidity and the contribution of these acidities to potential acidity should be considered for the effective management of acid sulphate soil. This paper will help in the evaluation of different acidities in acidsulphate soils of Kole lands of Thrissur district and there by helps in the adoption of suitable management strategies.

Materials and Method
Surface (0–15 cm) samples of acid sulphate soils of Kole lands were collected during the season Oct-Jan from the acid sulphate soils of Thrissur district. A total of 25 samples from different locations of Kole land (AEU 6) including Puzhakkal, Mullessery, Andhikkad and Cherpu blocks, were collected using a core sampler without disturbing the reduced condition

as far as possible. The collected samples were immediately sealed in a polythene cover and labelled with the location details and additional information if any. The geographic coordinates of sampling sites were recorded using GPS (Table 1).

Table 1: Details of location

Sl. No.	Block Panchayath	Name of the padav	Latitude	Longitude
	Puzhakkal			
1		Ombhathumuri	10.5388409	76.13906906
2		Kadavil Kole	10.53661602	76.13957137
3		Tharishukarimbhana	10.56263914	76.13734197
4		Thiruthinthazham	10.52917236	76.13602653
	Mullessery			
5		Elavathur padav	10.548477489	76.11158816
6		Pavuttai	10.54846971	76.11164069
7		Paenakam	10.54846971	76.11164069
8		Madhukkara Vadak	10.54256294	76.10847816
9		Manalpuzha	10.53127679	76.11027264
10		Ealamudha	10.52624243	76.11253097
11		Ponnamudha	10.52010278	76.1124
12		Madhukkara thaek	10.5263955	76.11373393
13		Vadakkaekonchira	10.51278386	76.1050413
14		Thaekkaekonchira	10.50984444	76.10706667
	Andhikkad			
15		Manalur thazham	10.48155876	76.1259133
16		Rajmut	10.47160556	76.13000833
17		kodayatti	10.47236667	76.14218056
18		Andhikkad Kole padav	10.41724	76.15161
19		Variyam	10.50356264	76.14399707
20		Chaladipazham Kole	10.49946645	76.13556275
21		Pallippuram	10.4475075	76.16566891
22		Alapad	10.44732349	76.16606763
23		Pulle	10.45271856	76.155571726
24		Jubeli thuravur padav	10.45254638	76.19610909
	Cherpu			
25		Erumakuzhi	10.45251545	76.19628747

Soil samples collected from the paddy fields of Kole regions were analysed for estimating acidity fractions including active acidity, pH-dependent acidity, potential acidity, exchangeable acidity, exchangeable Al^{3+} and exchangeable H^{+}.

Soil reaction (pH)
Soil reaction was determined in a 1:2.5 soil-water suspension potentiometrically using a pH meter (Jackson, 1958) [5].

Active acidity
Active acidity was estimated by recording the pH of ten gram soil sample equilibrated with 25 ml of 0.01 $CaCl_2$ solution (1:2.5 soil-solvent ratio) (Jackson, 1973) [4].

Exchangeable acidity
Exchangeable acidity is the sum total of H^{+} and Al^{3+} retained on the soil exchange complex. It constitutes a significant part of the total acidity. It is the acidity exchanged by an un-buffered neutral salt solution. i.e., KCl. Weigh 20 g soil in a conical flask. Add 50 ml of 1 N KCl solution and shake the suspension for 10 minutes. Filter the suspension and then transfer 20 ml of the filtrate into a titration flask and heat it to boiling temperature to drive off the CO_2. Add 2-3 drops of phenolphthalein indicator and titrate the solution against 0.1 N NaOH until a pink coloration is obtained (Baruah and Barthakur, 1999) [1].

Potential acidity
Potential acidity refers to the exchangeable plus residual acidity contained in a soil as referenced to a given pH value. It is determined using barium chloride triethanolamine procedure. Add 100 mL extracting buffer {0.5 N $BaCl_2$, plus triethanolamine (pH 8–8)} to 10 g of soil taken in a conical flask. Then the contents were shaken for half an hour and allowed to stand overnight. Filtered the contents through Whatman No. 42 filter paper and continued the leaching of soil by adding a small amount of extracting solution. Then transfer the leachate to a 250 ml volumetric flask and make up the volume with the extracting solutions. Pour the leachate into a conical flask and add a few drops of mixed indicator. Titrate against standard 0.2 N HCl until pink coloration is obtained. Perform a blank titration, keeping all the conditions identical for standardisation and estimation (Baruah and Barthakur, 1999) [1].

pH dependent acidity
It is calculated by subtracting exchangeable acidity from potential acidity.

Exchangeable aluminium
Exchangeable Al^{3+} in the KCl extract was determined by adding 5 ml of freshly prepared 1 N NaF and kept it for 5 minutes and then titrated against 0.025 N H_2SO_4 till the pink colour disappears.

Result and Discussion
The acidity characteristics are given in Table 2. The pH of the soil ranged from 3.1 to 6.42 with a mean value of 4.98. The

lowest pH of 3.31 was reported by Tharishukarimbhana of Puzhakkal block and highest pH of 6.42 was reported by Thiruthinthazham padav of Puzhakkal block. The pH values of the collected samples showed that approximately eight% of the soil samples are ultra-acidic (pH 3.5) and 20% are extremely acidic (pH 3.5-4.5) and very strongly acidic (pH 4.5-5). Among the samples collected, 16% are strongly acidic (pH 5.1-5.5) and 32% are moderately acidic (pH 5.6–6). Only four percent of soil samples fall under slightly acidic category.

Table 2: Acidity parameters of soil samples

Sample No.	pH	Ex. Acidity	Potential acidity	Ex. Al^{3+}	Ex H^+	pH dependent acidity	Active Acidity
1	4.52	5.17	25.40	4.34	0.83	20.23	3.92
2	5.99	0.66	5.87	0.46	0.20	5.21	4.28
3	3.31	2.89	29.81	1.67	1.22	26.92	3.40
4	6.42	0.63	5.80	0.34	0.29	5.17	4.38
5	5.36	1.23	10.40	0.89	0.34	9.17	3.55
6	4.92	4.49	22.60	3.11	1.38	18.11	3.46
7	3.8	8.11	23.45	5.78	2.33	15.34	3.79
8	5.15	2.77	18.20	0.89	1.88	15.43	3.65
9	5.26	2.16	17.50	1.78	0.38	15.34	3.79
10	5.12	3.04	18.91	2.45	0.59	15.87	3.97
11	4.92	1.56	18.12	1.05	0.51	16.56	4.99
12	3.73	8.23	34.40	5.23	3.00	26.17	3.46
13	5.81	0.98	15.29	0.45	0.53	14.31	3.49
14	4.99	3.63	20.40	2.67	0.96	16.77	3.70
15	5.87	0.77	12.30	0.43	0.34	11.53	4.21
16	3.49	9.42	26.37	5.46	3.96	16.95	3.49
17	4.53	1.89	20.86	0.38	1.51	18.97	3.78
18	5.75	1.22	15.70	0.78	0.44	14.48	3.66
19	5.98	0.73	11.90	0.42	0.31	11.17	3.73
20	5.84	0.86	14.60	0.34	0.52	13.74	3.56
21	5.84	0.79	13.60	0.44	0.35	12.81	3.97
22	3.91	8.9	29.12	5.23	3.67	20.22	3.80
23	4.31	6.44	27.61	4.33	2.11	21.17	3.79
24	3.99	7.23	18.40	4.67	2.56	11.17	3.71
25	5.7	1.09	15.80	0.87	0.22	14.71	3.60

Acidity fractions

Exchangeable acidity or salt replaceable acidity, which develops due to hydrogen (H^+) and aluminium (Al^{3+}) ions on the soil colloids of collected soil samples ranged from 0.63 to 9.42 with a mean content of 3.4 meq 100 g^{-1}. The lowest exchangeable acidity of 0.63 meq 100 g^{-1} was reported by Thiruthinthazham padav of Puzhakkal block and highest was reported by Rajmut padav of Andhikkad block. Exchangeable acidity which is mainly contributed by exchangeable Al^{3+} and exchangeable H^+ concentrations also varied among the soil samples. Exchangeable Al^{3+} ranged from 0.34 to 5.78 meq 100 g^{-1} with a mean content of 2.18 meq 100 g^{-1}. Chaladipazham Kole padav of Andhikkad block showed the lowest exchangeable Al^{3+} content and Paenakam padav of Mullessery block showed the highest content of 5.78 meq 100 g^{-1}. Exchangeable H^+ which contributes to the exchangeable acidity ranged from 0.2 to 3.96 meq 100 g^{-1} with a mean content of 1.22 meq 100 g^{-1}. The lowest content of exchangeable H^+ was reported by Kadavil Kole padav of Puzhakkal block and the highest content was reported by Rajmut padav of Andhikkad block. Exchangeable Al^{3+} content is greater than exchangeable H^+.

According to Vietch (1904) [10], exchangeable acidity is that portion of the soil acidity that can be replaced with a neutral, unbuffered salt such as KCl, $CaCl_2$, or NaCl and is due almost entirely due to monomeric Al^{3+} ions. Harward and Coleman (1954) [2] and Low (1955) [6] demonstrated the importance of Al^{3+} in the exchangeable portion of soil acidity. Their work showed that the exchangeable acidity extracted from clays was almost entirely due to Al^{3+}. In the case of soils where organic matter is an important contributor to CEC, it appears that a higher proportion of the exchangeable acidity is H^+ (Yuan, 1959, 1963), [11-12] because Al is extremely difficult to extract from organic matter. It appears that much of the H^+ that is apparently exchangeable from organic soils arises from the hydrolysis of Al^{3+} which is difficult to replace with KCl. The presence of Fe and Al hydrous oxides reduces the exchange acidity. Among the Fe and Al hydrous oxides, Al oxide is more effective in reducing exchange acidity.

Potential acidity, which is the sum of exchangeable acidity and pH-dependent acidity, ranged from 5.8 to 34.4 meq 100 g^{-1} with a mean value of 18.46 meq 100 g^{-1}. Thiruthinthazham of Puzhakkal block showed the lowest potential acidity (5.8 meq 100 g^{-1}) and Madhukkara thaek of Mullessery block reported the highest potential acidity (34.4 meq 100 g^{-1}). The pH-dependent acidity, which is one of the parameters contributing to the potential acidity ranged from 5.17 to 26.92 meq 100 g^{-1} with a mean content of 15.88 meq 100 g^{-1}. Thiruthinthazham padav of Puzhakkal block showed lowest pH dependent acidity and Tharishukarimbhana padav of Puzhakkal block showed highest pH dependent acidity. The active acidity which is extracted by means of $CaCl_2$ ranged from 3.4 to 4.99 with a mean of 3.81. The lowest active acidity was reported by Tharishukarimbhana padav of Puzhakkal block and the highest active acidity was reported by Ponnamudha padav of Mullessery block.

Among the acidity fractions, potential acidity recorded higher values and this is because of the subsurface accumulation of pyrite. Pyrite with a size of less than 2µm will undergo oxidation very easily and leads to the release of sulphuric acid and thereby increases the acidity of acid sulphate soil (Subramonia Iyer, 1989) [7]. Another important factor determining the acidity of acid sulphate soil is organic matter. H^+ ions containing functional groups present in organic matter contribute to different kinds of acidity (Beena and Manorama, 2013) [3]. Among the acidity fraction, pH-dependent acidity also seems to be higher than all the other forms; this may be due to the presence of high amount of clay, organic carbon and Fe and Al oxides (Sharma *et al*., 1987) [9].

Contributions of different acidity fractions to potential acidity is showed in the figure (1). The contribution of pH-dependent acidity to potential acidity ranged from 60.71 to 94.19% with a mean value of 84.18% whereas the contribution of exchangeable acidity ranged from 5.81 to 39.29% with a mean% of 15.82. The contribution of exchangeable acidity (which arises due to the isomorphus substitution) to potential acidity is very low in acid sulphate soil. In soils containing appreciable organic matter, the proportion of exchangeable acidity is generally low for two reasons. First, most of the acidity of organic matter is ionized only by raising the pH, i.e., it is truly a weakly ionized acid. Second, in acid soils much of the ionized CEC of organic matter is countered by Al, Fe or both which are not easy to exchange (Thomas and Hargrove, 1984) [8]. Active acidity contributes very little towards potential acidity and it ranged from 0.06 to 2.71%.

Correlation analysis

Results of the correlation analysis are given in Table 3. pH shows a strong negative correlation with all the acidity fractions. pH shows a strong negative correlation with exchangeable acidity (-0.849***), potential acidity (-0.797***), pH-dependent acidity (-0.804***), exchangeable Al^{3+} (-0.812***), and exchangeable H^+ (-0.82***). Active acidity shows a positive correlation with pH but is not significant. Exchangeable acidity showed a significant positive correlation with exchangeable Al^{3+} (0.977***) and exchangeable H^+ (0.928***). Ferrugineous soils are those that have undergone severe leaching and accumulation of acid-forming ions like H^+ and Al^{3+}, which has led to the development of soil acidity. They are typically created in humid tropical climates with high rainfall. The high CO_2 content and low redox potential (Eh) had an impact on the soil pH. Anaerobic decomposition of organic materials results in the production of organic acids (Beena and Manorama, 2013) [3]. Potential acidity shows a strong positive and significant correlation with exchangeable acidity (0.671***), exchangeable Al^{3+} (0.67***), exchangeable H^+ (0.598**), and pH-dependent acidity (0.837***). Acidity produced by the oxidation of pyrite is mainly potential acidity, which is stronger than other acid fraction. Active acidity showed a negative correlation with pH dependent acidity (-0.422*).

Table 3: Correlation analysis

	pH	Ex. Acidity	Ex.Al^{3+}	Ex. H^+	Potential Acidity	pH dependent Acidity	Active acidity
pH	1						
Ex. Acidity	-0.849***	1					
Ex.Al^{3+}	-0.812***	0.977***	1				
Ex. H^+	-0.82***	0.928***	0.828***	1			
Potential Acidity	-0.797***	0.671***	0.67***	0.598**	1		
pH dependent Acidity	-0.804***	0.623***	0.579**	0.63***	0.837***	1	
Active acidity	0.327	-0.301	-0.258	-0.341	-0.356	-0.422*	1

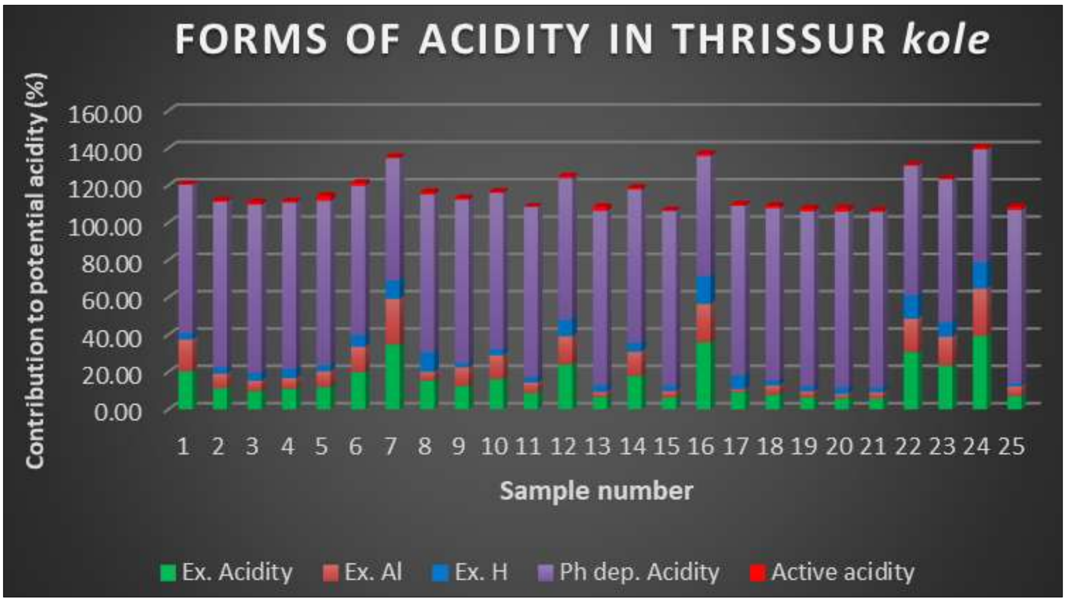

Fig 1: Contribution of different fractions of acidity to potential acidity

Conclusion

In acid sulphate soil, apart from the soil reaction, pH (1:2.5 soil water suspension) there are other acidity fractions that should be considered for accessing the acidity. Among the acidity fractions, potential acidity is higher than the other fractions and pH-dependent acidity contribute more towards the potential acidity, whereas the contribution of exchangeable acidity is very low. In the case of exchangeable acidity, which develops due to exchangeable Al^{3+} and exchangeable H^+, most of the acidity is contributed by exchangeable Al^{3+}. The highest value of pH dependent acidity is mainly due to the presence of clay, Fe and Al oxide and organic matter. The contribution of active acidity to potential acidity is very low compared to the other acidity fractions. So assessment of acidity hazards in acid sulphate soils requires the estimation of operationally defined acidity fractions such as potential acidity, exchangeable acidity, pH dependent acidity, exchangeable Al^{3+} exchangeable H^{+} and active acidity.

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