

### *Abstract*

Chemical characterization of acid sulphate soils of Upper Kuttanad, Kerala was done to study its present nutrient status due to the impact of heavy flood that occurred in 2018. Extreme acidity is the major issue with this type of soil. Among the collected soil samples, 53.33 per cent of soil samples fall under very strongly acidic group (4.5 to 5) and 33.33 per cent comes under strongly acidic category (5.1 to 5.5). Lower values of EC in Upper Kuttanad indicate that this area is less affected by saltwater intrusion. More than 90 per cent of the samples were rich in organic carbon content. Among the major nutrients, 40 per cent of the soil samples recorded low available P content ( $<10 \text{ kg ha}^{-1}$ ). The availability of potassium, calcium, and magnesium increased with flooding. Almost all the samples collected from the acid sulphate soils of Upper Kuttanad showed high available sulphur status. It ranged from 20.20 to 3361.50  $\text{mg kg}^{-1}$ . The hike in micronutrient status showed the impact of flooding in these locations. The cation exchange capacity of the collected soil ranged from 5.92 to 30.64  $\text{cmol (+) kg}^{-1}$  and showed a positive correlation with organic carbon (0.779\*\*\*), available potassium (0.571\*) and available iron (0.717\*). This paper helps in understanding the present nutrient status in acid sulphate rice soils of Upper Kuttanad after the flood and adoption of suitable management practices.

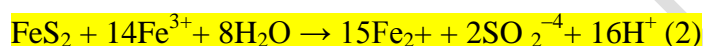
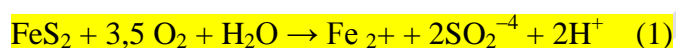
**Keywords :** *Acid sulphate soil, Upper Kuttanad, Flood, Available nutrients, Organic carbon, Micronutrients, Cation exchange capacity*

### **Introduction**

Kuttanad, the low-lying tract in Kerala State of south-west India, is a place where rice cultivation is mainly practised below mean sea level. Kuttanad, "the rice bowl of Kerala covers an area of 874  $\text{km}^2$  distributed with in Alappuzha , Kottayam and Pathanamthitta districts and lying 0.6 to 2.2 m below mean sea level. The area extends from 9°17' to 9°40' N latitude and 76°19' to 76°33' E longitude on the west coast of Kerala. Based on the flood incidence, salt water intrusion and acidity, Kuttanad has been divided into 7 agro-ecological zones, viz., Upper Kuttanad, Lower Kuttanad, Kayal lands, North Kuttanad, Coastal Kuttanad, Purakkad kari and Vaikam kari (Thampatti, 1997)

Soils in these regions are extremely acidic due to the deposit of pyrites or sulphidic material in the subsurface layers of soil. Due to the deposition of sulphidic materials, Kuttanad is included under the great group sulfaquents and the subgroup Typic Sulfaquents. Extreme acidity, high organic matter content and presence of Fe and Al ions in the soil affect plant growth by reducing the uptake of elements like phosphorus.

The main problem found in acid sulphate soil is low soil pH (<3.5) due to pyrite content (FeS<sub>2</sub>), jarosite content [KFe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>] and high concentrations of Al and/or Fe. However, the agricultural activities can oxidize pyrite layer. When the pyrite is dry, the pyrite layer will oxidize and release sulfuric acid so that soil becomes very acidic. Each pyrite molecule under oxidized conditions will produce 16 moles of H<sup>+</sup> ions through the following reaction (Ratmini and Suprihatin 2023).



Kerala State receives very high rainfall during the monsoon season. In August 2018, the State received a terrific rainfall of nearly 2346.6 mm against the normal value of 1649.5 mm causing much havoc to entire Kerala except Kasargod district. Vishnu *et al.* (2019) found that 36 percent excess rainfall occurred during this period led to widespread floods and landslides events. The soils of Kerala, exposed to this devastating flood in this incessant rainfall experienced great damage to the soil environment in different ways. Besides heavy agricultural losses, soil fertility and productivity have been disturbed, the exposed soils were eroded and various kinds of debris accumulated on farm fields. The top soil in the hills and upland areas have been removed in the flash flood and plantations were completely destroyed. Physical, chemical and biological properties of the soil were highly altered. In this circumstances chemical characterisation of acid sulphate soils of Upper Kuttanad is inevitable and this paper will help in understanding the distribution and availability of macro and micronutrients in Upperkuttanad in post-flood scenario.

## Materials and Method

The present study entitled "Chemical characterization of acid sulphate rice soils of Upper Kuttanad of Kerala" was carried out at College of Agriculture, KAU during Oct- Jan, 2019. A total of fifteen soil samples were collected from Pavookara, Veeyapuram, Payippad, Karuvatta of Alappuzha and Thiruvarp village of Kottayam district. Details of locations are given in (Table 1).

**Table 1: Details of locations**

SI No.	Block /Panchayath/ village	Name of the padav	Latitude	Longitude
	<b>Pavukara</b>			
1		Ariyodi padashekaram (1)	9.323066133074462	76.52112998999655
2		Ariyodi padashekaram (2)	9.323414065875113	76.52080971747637
3		Ariyodi padashekaram (3)	9.32342127431184	76.52046228758991
4		Panthalattipadam (1)	9.324274216778576	76.51800530031323
5		Panthalattipadam (2)	9.324298272840679	76.51756642386317
	<b>Veeyapuram</b>			
6		Kattakuzhi, Maelpadam (1)	9.325750730931759	76.46919714286923
7		Kattakuzhi, Maelpadam (2)	9.3249811020763516	76.4676930103451
8		Veeyapuram state seed farm (1)	9.322019568644464	76.4618010353297
9		Veeyapuram state seed farm (2)	9.322077655233443	76.46131597459316
	<b>Payippad</b>			
10		Prayatterippadam (1)	9.321848535910249	76.4577947370708
11		Prayatterippadam (2)	9.3216404132545	76.45756758749485
12			9.320900542661548	76.45257147029042
	<b>Karuvatta</b>			
13		Vellookaripadam	9.320897608995438	76.43266185186803
	<b>Thiruvarpu</b>			
14		Muppaykaripadam	9.5893772598356	76.47217825055122
15		Malaraikkal, J block	9.557558675296605	76.49141463451087

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Soil sampling were done by random sampling method and core sampler were used to take samples from 0–20 cm depth without disturbing the reduced condition. 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.

### **Characterization of soil samples**

Soil samples collected from the paddy fields of Upper Kutanad regions were analysed for estimating pH, EC, OC, Available N, P, K, Ca, Mg, S, Fe, Mn, Cu, Zn and CEC. The procedures adopted for the characterization of soil samples are detailed below. Soil reaction (pH) was determined in a 1:2.5 soil-water suspension potentiometrically using a pH meter (Jackson, 1958). Electrical conductivity (EC) was estimated in the supernatant liquid of the soil-water suspension (1:2.5) used for pH estimation with the help of a conductivity meter (Jackson, 1958). Organic carbon was estimated by wet digestion method (Walkley and Black) and expressed as per cent organic carbon after doing correction for incomplete oxidation. Available nitrogen was determined by alkaline potassium permanganate ( $\text{KMnO}_4$ ) method by Subbiah and Asija (1956). The soil was mixed with  $\text{KMnO}_4$  solution and distilled using kjeldahl distillation unit to liberate ammonia which was condensed and absorbed in known volume of boric acid ( $\text{H}_3\text{BO}_3$ ) with mixed indicator to form ammonium borate. This ammonia was determined volumetrically by titration with standard acid ( $\text{H}_2\text{SO}_4$ ).

Available phosphorus was extracted using Bray No. 1 extractant (Bray and Kurtz, 1945) which was widely used as an index of available P in acid soil. Available potassium, calcium and magnesium in the soil samples were extracted using neutral normal ammonium acetate. The potassium content in the extract was estimated by flame photometry (Jackson, 1958). Calcium and magnesium content were estimated in an atomic absorption spectrophotometer (Model: Perkin Elmer-PinAAcle 500). Available sulphur was extracted by using 0.15%  $\text{CaCl}_2$  (Tabatabai, 1982) and estimated by turbidimetry (Massoumi and Cornfield, 1963) using a spectrophotometer (Model: Systronics 169). Available micronutrients were analysed using 0.1M HCl extractant and concentrations of micronutrients (Fe, Mn, Zn and Cu) were measured using AAS (Sims and Johnson, 1991).

Barium chloride extractable cations were determined by following the procedure of Hendershot and Duquette (1986). The cations present in the exchangeable sites in the soil were replaced by Barium. Estimation of cations in the extract (Ca, Mg, Al, Fe, Mn, Cu, Zn, Na and K) was done using AAS. Since the lowland soils are high in water soluble cations, the deduction of water soluble fraction from barium chloride extractable cations was carried out to avoid over estimation. Water-soluble cations were estimated by the modified procedure of Baruah et al. (2011).

## Results

Chemical characterisation of soil samples from Upper Kuttanad is given in the Table 2. Soil reaction or pH is the single most informative measurement that can be made to determine soil characteristics. The pH of the collected soil varied from 4.63 to 6.49 with a mean of 5.13. The lowest value, 4.63 was reported by Muppaykaripadam of Thiruvarpur village and highest value, 6.49 was reported by Prayatterippadam of Payeppad. Among the collected soil samples, 53.33 percent of soil samples fall under very strongly acidic group (4.5 to 5) and 33.33 percent fall under strongly acidic category (5.1 to 5.5) and 6.67 percent fall under moderately (5.6 to 6) and slightly acidic category (6.1 to 6.5).

The electrical conductivity of the soil samples varied from 0.04 to 0.97 with a mean value of 0.26 dS m<sup>-1</sup>. Soil samples from the state seed farm, Veeyapuram panchayath reported the lowest EC content and J block padashekaram of Thiruvarpur showed highest value for EC.

The organic carbon content of the collected soil samples varied from 0.42 to 4.33 percent with a mean content of 2.35 percent. Almost all the samples were rich in organic carbon content. Collected soil samples from Upper Kuttanad showed a variation in available nitrogen content. It varied from 170.72 to 480.45 kg ha<sup>-1</sup> with a mean value of 264.11 kg ha<sup>-1</sup>. The lowest value was reported in Ariyodi padashekaram of Pavukara village and highest value was reported by Muppaykaripadam of Thiruvarpur. Almost 73.33 percent of soil samples showed low available nitrogen content (<280 kg ha<sup>-1</sup>) whereas 26.67 percent showed available nitrogen in medium range (280-560 kg ha<sup>-1</sup>).

The available phosphorus content in acid sulphate soil ranged from 2.14 to 118.29 kg ha<sup>-1</sup> with a mean value of 38.73 kg ha<sup>-1</sup>. Ariyodi padashekaram of Pavukara village showed lowest value for available P whereas Panthalattipadam of Pavukara showed the highest value. Gradation in available P status revealed that almost 40 percent of the soil samples recorded

low available P content ( $<10 \text{ kg ha}^{-1}$ ), 13.33 per cent of the collected soil samples were in the medium range ( $10\text{-}25 \text{ kg ha}^{-1}$ ) and 46.67 percent of soil samples recorded high value for available p status ( $>25 \text{ kg ha}^{-1}$ ).

Available potassium ranged from  $34.11$  to  $769.25 \text{ kg ha}^{-1}$  with a mean value of  $215.72 \text{ kg ha}^{-1}$ . Among the collected soil samples, 33.33 per cent were under low range for available potassium ( $<120 \text{ kg ha}^{-1}$ ) in which Ariyodi padashekaram of Pavukara showed available K content of  $34.11 \text{ kg ha}^{-1}$ . 40 percent of soil samples fall under the medium range ( $120\text{-}280 \text{ kg ha}^{-1}$ ) and 26.67 percent of soil samples fall under high for available potassium ( $>280 \text{ kg ha}^{-1}$ ).

Secondary nutrients like available calcium, magnesium and sulphur also varied among different locations. Available calcium status ranged from  $197.10$  to  $2581.35 \text{ mg kg}^{-1}$  with a mean of  $714.76 \text{ mg kg}^{-1}$ . Among the soil samples collected, Ariyodi padashekaram of Pavukara reported very low available Ca content and Prayatterippadam of Payippad reported very high value for available Ca status. Around 20 percent of soil samples showed low available Ca content ( $<300 \text{ mg kg}^{-1}$ ) whereas 80 percent of the collected soil samples showed high Ca content ( $>300 \text{ mg kg}^{-1}$ ). Available magnesium content ranged from  $39.22$  to  $372.51 \text{ mg kg}^{-1}$  with a mean value of  $139.23 \text{ mg kg}^{-1}$ . Ariyodi padashekaram of Pavukara showed low available Mg content and J block of Thiruvarpur reported high for available Mg status. More than 50 percent of soil samples showed low for available Mg ( $<120 \text{ mg kg}^{-1}$ ) and 46.67 percent showed high levels of available Mg ( $>120 \text{ mg kg}^{-1}$ ).

Almost all the samples collected from the acid sulphate soils of Upper Kuttanad showed high value for available S status. It ranged from  $20.20$  to  $3361.50 \text{ mg kg}^{-1}$  with a mean value of  $1257.27 \text{ mg kg}^{-1}$ . The lowest values were reported by the state seed farm of Veeyapuram and the highest values were reported by Kattakuzhi, Maelpadam of Veeyapuram.

Among the micronutrients, Fe, Mn, Cu and Zn reported very high values in all the collected soil samples. Kattakuzhi, Maelpadam of Veeyapuram showed very high values for available Fe and Mn. Available Fe ranged from  $104.74$  to  $2817.99 \text{ mg kg}^{-1}$  with a mean content of  $933.70 \text{ mg kg}^{-1}$ . In the case of available Mn, values ranged from  $2.38$  to  $247.07 \text{ mg kg}^{-1}$  with a mean value of  $44.01 \text{ mg kg}^{-1}$ . Vellookaripadam of Karivatta reported very low value for available Cu and Zn. Available Cu ranged from  $2.30$  to  $35.69 \text{ mg kg}^{-1}$  with a mean value of  $11.86 \text{ mg kg}^{-1}$ . Available Zn ranged from  $1.03$  to  $21.37$  with a mean value of  $8.64 \text{ mg kg}^{-1}$ . Cation exchange capacity of the collected soil ranged from  $5.92$  to  $30.64 \text{ cmol (+)}$

kg<sup>-1</sup> with a mean value of 18.87 cmol (+) kg<sup>-1</sup>. Soil samples collected from Veeyapuram reported a low CEC of 5.92 cmol (+) kg<sup>-1</sup> and the highest CEC of 30.64 cmol (+) kg<sup>-1</sup>.

## Discussion

More than half of the soil sample collected from acid sulphate soils of Upper Kuttanad falls under very strongly acidic group. According to Ghosh *et al.*, (2019), acidsulphate soils are characterised by extreme acidity and presence of sulphide minerals. These sulphide minerals (in the form of iron pyrites) present in these soils and/or sediments along with organic matter are rapidly oxidized in presence of air. Oxidations of sulphide layers in soil, may be due to natural (e.g. drought, draining or irrigation during cultivation) or human induced (e.g. land use change, drainage, groundwater withdrawal) interventions, resulting in the generation of sulphuric acid, and consequently causing soil acidification.

Soil salinity is characterized in terms of the concentration and composition of the soluble salts and is most commonly measured in the laboratory as the electrical conductance of the saturation extract in dSm<sup>-1</sup> (Corwin 2021). The electrical conductivity of all the collected soil samples were below 1.00 dSm<sup>-1</sup>. Lower values of EC in Upper Kuttanad indicate that this area is less affected by saltwater intrusion. Even though the salt intrusion is low in Upper Kuttanad, this area is vulnerable to flooding (Thampatti, 1997). Shilpa (2022) reported that low EC values reported at RRS, Vyttila compared to other locations during high saline phase might be due to the controlled sea water intrusion into the field and also it being located far away from the brackish water.

Almost all the samples were rich in organic carbon content. Pisharody and Brito-Mutunayagam (1967) observed that organic carbon in rice soils of Kerala varied from 0.03 to 2.86 percent with the highest in Kuttanad soils. The general trend was a decrease in organic carbon with depth. Tampatti (1996) reported the presence of undecomposed organic matter in Upper Kuttanad, which coincides with a high CN ratio that will go above 10. From the correlation matrix (Table 3) it is very clear that organic carbon showed a strong positive correlation with available potassium (0.514\*). Grealish and fitzpatrick (2013) mentioned one of the feature comprising acid sulphate soil properties is the presence of organic-rich materials/peats and clays.

Kabeerathumma and Patnaik (1980) reported that acid sulphate soils had moderate to high content of total N (0.095 to 0.37 per cent) and organic carbon (1.4 to 8.4 per cent). The carbon and nitrogen contents are rather high and decrease with depth. In the correlation matrix (Table 3), available nitrogen showed a strong positive correlation with organic carbon

content (0.562\*). Yli-Halla et al. (2020) reported that besides causing acidification, acid sulphate (AS) soils contain large nitrogen (N) stocks and are a potential source of N loading to waters and nitrous oxide (N<sub>2</sub>O) emissions.

Mathews and Jose (1984) reported a low content of available phosphorus in acid rice soils of Kerala. It was only 4.79 ppm in laterite and 3.84 ppm in *kari* soils. Irene (2014) reported that the available phosphorus in Ponnani kole is medium and it is significantly and positively correlated with electrical conductivity. Minh et al. (2023) reported low availability of phosphorus or Phosphorus shortage is prevalent, as are iron, aluminum, or manganese toxicities and high fixation of phosphorus is caused mainly by the clay fraction's high free ferric oxide (Fe<sub>2</sub>O<sub>3</sub>) content, which fixes phosphate ions into inaccessible forms. Pareek and Mathur (1969) found higher concentrations of available phosphorus in the surface layers. This was attributed to the distribution pattern of organic matter, pH, sesquioxides and clay content in the soils as well as the requirements of the crop and the rooting depth. Though the soils were deficient in available K, they are well supplied with total K and nonexchangeable K (Thampatti, 1997). Beena and Manorama (2013) reported high content of potassium in the acid sulphate soils of Kuttanad ranging from 142.1 mg kg<sup>-1</sup> to 326.4 mg kg<sup>-1</sup>. In the correlation study (Table 3) potassium showed a strong positive correlation with available nitrogen (0.671\*\*) and cation exchange capacity (0.571\*).

According to Irene (2014), under acidic conditions, the exchangeable K, Ca and Mg in solid phase are released into the solution phase. Thus, the bioavailability of these cations is increased upon flooding. Sulphate sulphur in acid sulphate soil is controlled by levels of sulfide minerals as well as past and current land-use activities (Nayman 2023). Money (1961) reported that the sub-soil clay in the Kari soils of Kuttanad contains high amount of organic matter and are rich in sulphur compounds. Surface soils contain total sulphur (1.92 per cent), subsoil (3.13 per cent) and wood fossils (6.10 per cent).

Micronutrient status during the pre-flooded situation in Upper kuttanad of Kerala reported very low value, which was in accordance with the result of (Irene 2014). But after the flood in 2018, there was a hike in its status. In the correlation analysis (Table 3), available Fe showed positive correlation with available Mn (0.747\*\*), organic carbon (637\*) and available nitrogen (654\*\*). Available Mn showed a positive correlation with available Zn (0.695\*\*). Available Cu showed a positive correlation with available sulphur (0.563\*). The correlation matrix (Table 3) showed a strong positive correlation between CEC and organic

carbon (0.779<sup>\*\*\*</sup>) (Fig 1), available potassium (0.571\*), and available iron (0.717). Organic carbon contributes more to CEC. Higher values of CEC in acid sulphate soils of Kuttanad is mainly due to the presence of clay and organic matter (Thampatti, 1996).

## Conclusion

Chemical characterization of the acid sulphate soils of Upper Kuttanad reveals that the distribution of nutrients and its sufficiency range. Most of the soil falls under very strongly acidic group with high content of organic carbon. Almost 40 per cent of the soil samples recorded low in available P content. Among the secondary nutrients, almost all the samples from the different locations showed very high values for available sulphur. The hike in micronutrient status showed the impact of flooding in these locations. This characterization is the basic study that will help to sort out the effect of acidity on the availability of nutrients and their interaction, followed by its management.

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	pH	EC (dSm <sup>-1</sup> )	OC (%)	Av N(kg/ha)	Av P (kg/ha)	Av K (kg/ha)	Av Ca (mg/kg)	Av Mg(mg/kg)	Av S(mg/kg)	Av Fe(mg/kg)	Av Mn(mg/kg)	Av Cu(mg/kg)	Av Zn(mg/kg)	CEC (cmol(+) kg <sup>-1</sup> )
1	4.76	0.09	0.42	170.72	15.67	34.11	197.10	39.22	719.37	721.66	7.12	3.54	5.14	14.14
2	5.08	0.05	1.89	263.20	2.14	86.59	446.13	61.63	725.66	889.25	8.22	7.18	5.22	13.58
3	4.85	0.06	1.38	219.32	97.04	90.58	519.03	84.46	3239.49	759.24	15.28	10.59	7.42	13.49
4	5.95	0.08	2.96	176.72	118.29	103.68	979.43	98.91	1277.78	561.66	27.25	12.91	8.26	15.75
5	5.56	0.13	3.91	402.01	53.76	769.25	729.61	163.55	57.16	1512.48	8.84	3.67	5.73	25.59
6	5.07	0.06	1.16	171.58	3.50	84.32	462.87	94.41	943.43	398.16	44.69	19.85	20.52	5.92
7	4.91	0.31	4.33	368.29	45.12	146.44	850.46	212.77	3361.50	2817.99	247.07	17.04	19.34	30.64
8	5.17	0.04	0.49	208.30	4.58	170.84	410.15	80.63	1219.66	104.74	7.27	9.94	1.38	13.72
9	4.70	0.18	2.47	221.01	2.41	204.01	1024.43	91.77	20.20	569.49	12.96	6.49	5.62	18.72
10	6.49	0.55	2.40	249.05	2.15	309.91	2581.35	192.63	763.68	1030.04	136.63	9.09	11.11	23.30
11	5.22	0.23	2.80	244.43	5.20	231.71	765.00	98.04	1418.05	1290.80	89.68	4.30	21.37	20.66
12	4.91	0.23	3.42	248.24	79.75	170.53	573.58	129.88	2839.15	1056.29	25.19	35.69	7.99	23.31
13	4.85	0.31	2.16	221.04	77.92	150.55	271.33	142.20	81.14	466.58	5.17	2.30	1.03	13.05
14	4.63	0.55	2.32	480.45	18.16	344.60	618.12	225.86	43.58	1608.93	22.34	16.37	5.14	26.68
15	4.74	0.97	3.07	317.30	55.21	338.72	292.88	372.51	2149.19	218.21	2.38	18.92	4.28	24.50
<b>Mean</b>	5.13	0.26	2.35	264.11	38.73	215.72	714.76	139.23	1257.27	933.70	44.01	11.86	8.64	18.87

**Table 2: Chemical characteristics of soil samples from Upper Kuttanad****Table 3: Correlation analysis**

	pH	EC	OC	Av N	Av P	Av K	Av Ca	Av Mg	Av S	Av Fe	Av Mn	Av Cu	Av Zn	CEC
pH	1													
EC	-0.046	1												
OC	0.163	0.363	1											
Av N	-0.157	0.482	0.562*	1										
Av P	0.041	-0.012	0.35	-0.052	1									
Av K	0.251	0.327	0.514*	0.671**	-0.018	1								
Av Ca	0.783***	0.21	0.261	0.036	-0.181	0.216	1							
Av Mg	-0.042	0.929***	0.541*	0.625*	0.13	0.473	0.129	1						
Av S	-0.14	0.066	0.25	-0.06	0.429	-0.318	-0.093	0.174	1					
Av Fe	0.005	0.068	0.637*	0.654**	-0.017	0.259	0.222	0.211	0.273	1				

Av Mn	0.277	0.151	0.462	0.219	-0.139	-0.058	0.506	0.224	0.424	0.747**	1			
Av Cu	-0.165	0.238	0.282	0.12	0.255	-0.136	-0.064	0.322	0.563*	0.101	0.122	1		
Av Zn	0.177	-0.088	0.269	-0.044	-0.211	-0.138	0.254	-0.036	0.346	0.467	0.695**	0.195	1	
CEC	0.054	0.579*	0.779***	0.783***	0.059	0.571*	0.328	0.664**	0.215	0.717**	0.495	0.231	0.09	1

UNDER PEER REVIEW

Fig 1: Relation between CEC AND OC

