

Soil Acidity and its Distribution in laterite soils of Northern Kerala: A descriptive analysis

Abstract

Soil acidity is one of the major constraints of crop production in tropical soils. A study was conducted to examine different forms of soil acidity, contribution of each fraction to total acidity and distribution of exchangeable Al^{+3} , exchangeable H^{+} detrital laterite rice wetlands of Kerala. Among the series, the Kalikkadavu series reported the highest exchangeable acidity with a mean of 1.66 ± 0.23 meq/100g at a depth of 0-15 cm. Soils from Angadipuram series showed high values for exchangeable hydrogen with a mean of 0.71 ± 0.87 meq/100g and a range of 0.2- 3 meq/100g. Kalikkadavu series reported a high value for exchangeable hydrogen with a mean value of 1.29 ± 0.23 meq/100g. Regarding potential acidity, Nanminda series reported the highest with a mean value of 40.2 meq/100g. Descriptive statistics of pH dependent acidity data revealed highest acidity for Nanminda series in surface layer with a mean value of 39.27 ± 1.77 meq/100g while in subsurface soils, Arathil series has reported the highest with a mean value of 32.21 ± 3.28 meq/100g. From the paired t-test analysis, significant variations of potential acidity and pH-dependent acidity were observed across surface and subsurface while exchangeable acidity, exchangeable Al^{+3} , exchangeable H^{+} have shown non-significant variation. Hence, we recommend a proper soil management system that lowers the surface and subsoil acidity in low-pH soil. Again, for best effects in terms of biomass production and economic crop yields, amelioration of soil acidity should be followed by optimum plant nutrient inputs.

Keywords: Exchangeable acidity, Exchangeable aluminium, Exchangeable hydrogen, Potential acidity, pH dependent acidity

1. Introduction

Soil acidity is one of the major constraints of crop production in tropical soils. Around 50% of all world arable land is occupied by acidic soils and in many agricultural systems, the issue of soil acidity has gotten worse in recent years (Dai *et al.*, 2017). It has reached an alarming level in Indian soils, reducing the yield of most of the crops. The soils of Kerala are acidic-ferruginous in nature and are lateritic in origin. Detrital laterites are formed through partial or complete consolidation of lateritic material. The leaching of silica, alkali, alkaline earth metals, and the subsequent enrichment of either iron or aluminium or both, during tropical weathering, are major processes involved in laterite formation (Prasad and Parthasarathy, 1993).

Soil acidification is predominantly due to the weathering of acidic rocks, precipitation of H^+ ions, atmospheric deposition of acidifying gases like ammonia, nitric acid, and hydrochloric acid, application of acid-forming fertilisers like urea, ammonium salts, and sulphur rich amendments, by crop removal, root exudation and by organic matter decomposition process (Goulding, 2016). Soils show buffering action against acidification either by the dissolution of basic rocks, carbonates, the replacement of exchangeable cations by basic cations, the dissolution of aluminium (Al) bearing and manganese minerals, or by the dissolution of iron-bearing minerals (Goulding, 2016).

The major soil-related constraints of laterite soils are the acidity and toxicity of metals like iron (Fe), Al, and manganese (Mn) (Yadav *et al.*, 2017). The presence of high concentrations of these metals in soil hinders the absorption of other nutrients leading to poor nutrient use efficiency. Soil acidity impairs nutrient uptake, microbial activity, nitrogen fixation, and organic matter decomposition in the soil. Crop growth is severely affected by soil acidification. Plant roots are injured by the high concentration of aluminium ions in very acidic soils. To cope with this, different crops show different tolerant mechanisms. Hence a suitable nutrient management system that reduces acidity and the toxic level of metals prevalent in low-pH soil will certainly improve the crop yield (Yadav *et al.*, 2017).

The major forms of acidity are exchangeable acidity, potential acidity, and pH-dependent acidity. Furthermore, exchangeable H^+ and exchangeable Al^{3+} in the soil also contribute to total acidity. Recent studies reported that pH-dependent and hydrolytic acidities contribute nearly 86 to 99 and 77 to 97 percent of the total potential acidity and total acidity, respectively, with little (0.8 to 22.6%) contribution of exchangeable acidity. While the exchangeable acidity ranges from 0.79 to 7.61 $cmol(p^+) kg^{-1}$ and is mostly constituted by exchangeable Al^{3+} in high-acid soils (Gangopadhyay *et al.*, 2016). Exchangeable sites and soil solutions are predominated by exchangeable Al^{3+} (Byju and Thomas, 1999). All these forms of acidity show close correlations with organic C and forms of Al in soils but negative correlations with soil pH (Chand and Mandal, 2000). In laterite soils, the total potential acidity is quite high and accounts for severe acidity problems. Most of the components of acidity are significantly and positively correlated with cation exchange capacity (Sangtam *et al.*, 2017). Regarding the distribution over the profile, exchangeable acidity and exchangeable Al are usually higher in the upper layers compared to subsoils.

Al in soils exists in various chemical forms from soluble ionic species in the soil solutions to being a basic structural component of secondary clay minerals such as kaolinite and vermiculite. The solubility of Al is highly pH-dependent and an increase in soil pH alleviates its toxicity. Al is adsorbed on organic and mineral colloidal surfaces, amorphous and crystalline forms of hydroxy-Al as well as Al polymerized on clay surfaces and between clay inter-layer. In acid soils, an appreciable portion of the cation exchange capacity is

satisfied by Al ions. Whilst these Al ions are referred to as exchangeable Al⁺³, they are a mixture of monomeric Al ions [Al⁺³, AlOH⁺², Al(OH)₂⁺] with an average charge per Al between 2 and 3, which decreases as pH increases (Thakuria *et al.*, 2016).

For sustainable agricultural development and meeting the ever-increasing food demand, it is imperative to identify effective soil amendments to reduce soil acidification. Lime application is one strategy that has been widely adopted to reduce the problems brought on by soil acidity. Though liming has been reported to be very effective to combat soil surface acidity, it is ineffective in reducing subsurface soil acidity as it moves slowly through the soil profiles. Gypsum is thus recommended to ameliorate subsurface acidity in Kerala soils. Hitherto there is a plethora of research on soil acidity, limited works have been carried out to study acidity in detrital laterite of tropical soils. Hence, the current study was conducted to examine different forms of soil acidity, contribution of each fraction to total acidity and distribution of exchangeable Al⁺³ and exchangeable H⁺ in detrital laterite rice wetlands of Kerala.

2. Materials and Methods

2.1. Study site

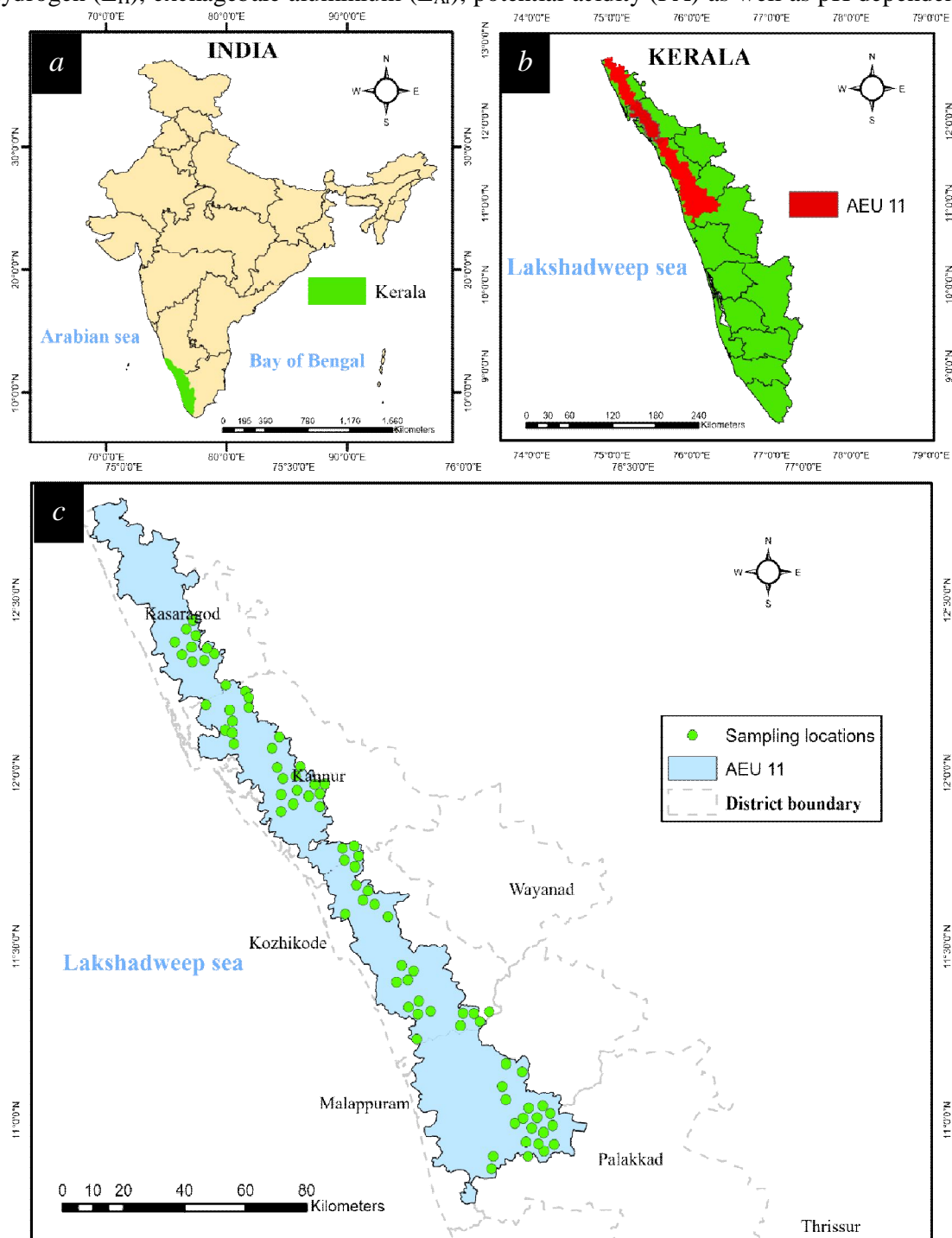
Laterite soils of Kerala are the products of intensive and long-lasting tropical rock weathering intensified by high and seasonal rainfall, and with isohyperthermic temperature regimes as per US Soil Taxonomy under the humid tropical environment result in the formation of sesquioxide-rich soils with poor base content and low fertility. A catenary series of soils, from fully weathered Ultisols in high ranges, plateaus, and midland plains to recently developed Entisols and Inceptisols in the deltaic and coastal areas, can be inferred from the unique topography with evergreen vegetation under high rainfall. Thus the entire state of Kerala is covered by soil orders with a significant share constituted by Ultisols. The study area comprises eight major benchmark soil series viz Angadipuram, Naduvattom, Kunnamangalam, Nanminda, Kalikkadavu, Arathil, Kunnathura, and Payalam of Agroecological Unit 11 (AEU 11) under the order Ultisol and geo-referenced soil samples were collected from detrital laterite paddy wetlands at two different depths (Fig.1).

2.2 Soil Sampling

After a preliminary survey 160 geo-referenced soil samples were collected from the rice-based detrital laterites derived wetlands ie, from the surface and subsurface depths of 0-15 cm (80 samples) and 15-30 cm (80 samples) respectively. Samples were collected during the period from December 2020 to February 2021. Profiles were dug and composite soil samples were collected from six randomly selected locations. Undisturbed soil samples were collected from the same locations for the determination of bulk density. After quartering, the samples were sealed in plastic bags with proper labelling. Soils were dried in shade, powdered with a wooden mallet, sieved, and stored in polythene bags to characterize the physical, chemical, and biological parameters

2.3 Soil analysis

Standard procedures were followed to estimate exchangeable acidity (E_a), exchangeable hydrogen (E_H), exchangeable aluminium (E_{Al}), potential acidity (PA) as well as pH dependent



acidity (PDA). Sum of total H^+ and Al^{+3} retained on the soil exchange complex equals the exchangeable acidity of the soil. The ions exchanged by neutral salt solution were extracted by shaking 20g of soil in 50 ml 1N KCl solution for 30 minutes. After filtering the extract, 20 ml of extract was titrated against 0.025 N NaOH with phenolphthalein as an indicator. Before titration, the measured quantity of filtrate was heated to the boiling temperature to drive off carbon dioxide.

Fig. 1 Maps depicting the map of India (a), Agro Ecological Unit 11 (b), and location map of samples in AEU 11(c)

The titre value was noted at the end point of pink colour (Baruah and Barthakur, 1997). Exchangeable Al^{+3} was determined in the extract by titration with NaOH after complexing Al with 1N NaF. It was then titrated against 0.025N H_2SO_4 till the pink colour disappeared. The exchangeable H^+ is expressed as the difference between exchangeable acidity and exchangeable Al^{+3} .

Potential acidity is comprised of all the components of acidity. Ten grams of soil was weighed into 250 ml conical flasks, then 100ml extracting solution (0.5N $BaCl_2$, 0.055N triethanolamine adjusted to a pH 8-8.2) was added. It was then shaken for half an hour and allowed to stand overnight. The contents was then filtered through Whatman No. 42 filter paper. The leaching of soil was continued by adding small amounts of extracting solution. Then the leachates were transferred to 250 ml volumetric flask and the volume was made up. After transferring to 500 ml conical flasks, 5 drops of mixed indicator solution were added. Then it is titrated against 2N HCl to a pink end point. A blank value was also recorded by titrating 250ml of the original extracting solution against 2N HCl (Baruah and Barthakur, 1999). pH dependent acidity is expressed as the difference between total acidity and exchangeable acidity.

2.4 Statistical analysis

The mean and standard deviation (SD) were calculated using the R-based web application GRAPES (Gopinath *et al.*, 2021). Descriptive analysis was carried out to find the mean value and standard deviation. Paired t-test was applied to examine the relationship between soil parameters at two distinct depths. The Grapes Agril software package was used to perform paired t-tests. ArcGIS 10.2 software was used to create location map.

3. Results and discussion

Exchangeable acidity refers to hydrogen and aluminum ions retained on the exchange complex of the soil. It is that form of acidity of the soil which is adsorbed as Al^{+3} and H^+ ions, along with Ca^{+2} , Mg^{+2} , K^+ , and Na^+ , that is in equilibrium with the soil solution (Behera and Shukla, 2015). The E_a of soil samples collected from detrital laterite is described in Table.1. Among the series, it was found that the Kalikkadavu had the highest value with a mean of 1.66 ± 0.23 meq/100g at a depth of 0-15 cm. Few samples of the Angadipuram series also reported a high E_a of 3.75 meq/100g. This might be due to the presence of cations like H^+ and Al^{+3} in the exchangeable sites. The Al^{+3} present in soil solution and exchangeable sites undergo hydrolysis and generate more H^+ ions. Along with the innate acidity of laterite soils, indiscriminate use of nitrogen fertilizers in paddy fields, such as ammonium sulphate, ammonium nitrate, and urea are the major reasons for high E_a in these series.

Table. 1 Descriptive statistics summary of exchangeable acidity (meq/100g) at two different depths of 0-15 cm and 15-30 cm. Data are depicted as means \pm standard error

	0-15 cm		15-30 cm	
	Mean \pm SD	Range	Mean \pm SD	Range
Angadipuram	1.54 ± 1.11	0.87 - 3.75	0.9 ± 0.31	0.75 - 1.75
Naduvattom	1.27 ± 0.44	0.87 - 1.87	1.56 ± 0.06	1.5 - 1.62
Kunnamangalam	1.49 ± 0.15	1.25 - 1.75	1.59 ± 0.145	1.37 - 1.88

Nanminda	0.94 ± 0.06	0.87-1	0.96 ± 0.145	0.75 - 1.13
Kalikkadavu	1.66 ± 0.23	1.37 - 1.87	1.59 ± 0.167	1.37 - 1.87
Arathil	1.01 ± 0.11	0.87 - 1.13	1.59 ± 0.06	1.5 - 1.63
Kunnamthura	1.36 ± 0.09	1.25 - 1.39	1.51 ± 0.11	1.37 - 1.63
Payalam	1.037 ± 0.10	0.87 - 1.13	1.012 ± 0.09	0.87 - 1.13

In particular, this is due to the generation of protons from the oxidation of NH_4^+ to NO_3^- in the nitrification process and also through urea hydrolysis (Cai *et al.*, 2015). Low exchangeable acidity in the Nanminda series could be due to the efficient recycling of exchangeable sites with basic cations. Also, the alkalinity of amendments added to soils followed by the decarboxylation of organic anion and ammonification of organic N might be the major reasons for the low in E_a , although nitrification of mineralized N could generate protons to some degree (Cai *et al.*, 2015). At subsurface levels, Kalikkadavu, Arathil, and Kunnamthura series had the highest value of 1.59 meq/100g. Lower down the profile, a slight increase in E_a had been observed in subsurface soils except for the Angadipuram, Kalikkadavu, and Payalam series. The application of soil amendments also has an important role in the dynamics of E_a within and between the soil horizons (Mathew *et al.*, 2022).

Table. 2 Descriptive statistics summary of Exchangeable H^+ (meq/100g) at two different depths of 0-15 cm and 15-30 cm. Data are depicted as means ± standard error.

	0-15 cm		15-30 cm	
	Mean ± SD	Range	Mean ± SD	Range
Angadipuram	0.71 ± 0.87	0.2 - 3	0.33 ± 0.29	0.15 - 1.15
Naduvattom	0.45 ± 0.44	0.23 - 1	0.78 ± 0.17	0.35 - 0.95
Kunnamangalam	0.31 ± 0.03	0.28 - 0.38	0.37 ± 0.07	0.28 - 0.78
Nanminda	0.17 ± 0.05	0.1 - 0.23	0.19 ± 0.03	0.15 - 0.23
Kalikkadavu	0.38 ± 0.07	0.3 - 0.48	0.4 ± 0.05	0.35 - 0.48
Arathil	0.19 ± 0.04	0.1 - 0.23	0.21 ± 0.03	0.13 - 0.23
Kunnamthura	0.37 ± 0.07	0.28 - 0.48	0.83 ± 1.29	0.35 - 4.5
Payalam	0.4 ± 0.08	0.23 - 0.48	0.42 ± 0.05	0.3 - 0.48

Table 2. depicts the descriptive statistics of E_{H^+} of soil samples. The surface soils, from Angadipuram series showed high values for E_{H^+} with a mean of 0.71 ± 0.87 meq/100g and a range of 0.2- 3 meq/100g. The Kunnamthura series had the highest E_{H^+} in subsurface soils, with a mean value of 0.83 ± 1.29 meq/100g. The high concentration of Al^{+3} accelerates E_{H^+} concentration in soil. Presence of Al^{+3} causes an acidic regime by hydrolysis reactions as it goes through the soil solution since the hydrolysis of aluminum generates hydrogen ions.

Table. 3. Descriptive statistics summary of exchangeable Al^{+3} (meq/100g) at two different depths of 0-15 cm and 15-30 cm. Data are depicted as means ± standard error

	0-15 cm		15-30 cm	
	Mean ± SD	Range	Mean ± SD	Range
Angadipuram	0.83 ± 0.69	0.5 - 2.75	0.57 ± 0.03	0.55 - 0.6
Naduvattom	0.83 ± 0.05	0.77 - 0.87	0.78 ± 0.18	0.67 - 1.27

Kunnamangalam	1.18 ± 0.17	0.93 - 1.45	1.22 ± 0.16	0.9 - 1.43
Nanminda	0.77 ± 0.08	0.65 - 0.88	0.77 ± 0.14	0.55 - 0.95
Kalikkadavu	1.29 ± 0.23	1-1.58	1.19 ± 0.18	1 - 1.53
Arathil	0.83 ± 0.11	0.65 - 0.95	1.38 ± 0.07	1.28 - 1.5
Kunnanthura	1.05 ± 0.21	0.78 - 1.55	0.69 ± 1.26	0.35 -1.25
Payalam	0.64 ± 0.12	0.4 - 0.83	0.6 ± 0.11	0.4 -0.73

Compared to the surface soils, E_{H^+} of subsurface soils showed a slight variation. In the Angadipuram series, a marginal decrease in E_{H^+} was observed while in the Kunnanthura series a marginal increase in E_{H^+} was observed. At a depth of 0-15 cm, the Kalikkadavu series reported a high value for E_{Al} (Table 3.) with a mean value of 1.29 ± 0.23 meq/100g. At 0-15 cm, Arathil series have reported high E_{Al} with a mean value of 1.38 ± 0.07 meq/100g. Few samples recorded very high E_{Al} of 2.75 meq/100g in surface soils. Regarding variation across the soil profile, E_{Al} slightly decreased in all series except Arathil and Kunnamnagalam series. As per the findings of Kostenko (2015) the exchange acidity is mainly formed due to exchangeable aluminum and is characteristic of all the soils developed from clayey texture. The low value of E_{Al} in Payalam series might be due to strong complex formation with organic carbon in soil. Also, the application of soil amendments may also cause a reduction in E_a as well as E_{Al} (Mathew *et al.*, 2022). Lime application is one strategy that has been widely adopted to reduce the problems brought on by soil acidity. Lime neutralises the H^+ generated from Al^{3+} hydrolysis, as well as that present in the soil solution. In laterite soils, liming, dolomite, and, gypsum application has ameliorating action since it reduces the soil pH, exchangeable Al, and exchangeable acidity in laterite soils (Srinivasan *et al.*, 2016). The variation of E_{H^+} observed in eight soil series and within a soil profile might be due to the hydro thermic conditions of wetlands, the type of vegetation, and the pedogenic process affecting the acidic and basic components of soil adsorption complex (Kostenko, 2015).

Table. 4. Descriptive statistics summary of Potential acidity (meq/100g) at two different depths of 0-15 cm and 15-30 cm. Data are depicted as means ± standard error

	0-15 cm		15-30 cm	
	Mean ± SD	Range	Mean ± SD	Range
Angadipuram	20.6 ± 4.01	16 - 26	7.25 ± 0.16	6.9 - 7.5
Naduvattom	11.8 ± 3.19	6.0 - 18.0	7.54 ± 0.21	7.2 - 7.9
Kunnamangalam	26.6 ± 4.12	20 - 34	27 ± 4.74	18 - 34
Nanminda	40.2 ± 1.75	38 - 42	28 ± 3.89	24 - 36
Kalikkadavu	35.8 ± 2.57	32 - 40	14.8 - 5.27	6.0 - 22.0
Arathil	13.8 ± 1.48	12.0 - 16.0	33.8 ± 3.33	28.0 - 38.0
Kunnanthura	34.2 ± 3.33	30.0 - 40.0	18.2 ± 2.57	12.0 - 20.2

Payalam	33 ± 2.70	28.0 - 38.0	26.8 ± 2.34	24 - 30
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Potential acidity is referred to the buffer capacity of soil or resistance to changes in pH. Table 4. depicts the descriptive statistics of PA of soil samples. In surface layer of soils, Nanminda series reported highest PA with a mean value of 40.2 meq/100g. Some samples of the Kalikadavu series also reported a very high PA of 40 meq/100g. Usually, the higher the clay and organic matter content, the greater the buffer capacity. Hence, more lime is needed to change the pH of the soil with a high buffering capacity than soil with a low buffering capacity soil. At 15-30 cm, Arathil series reported high a PA of 33.8 ± 3.33 meq/100g. High PA in Arathil series might be due to Al³⁺ and H⁺ on the exchange complex. Lower down in the profile, PA decreased except in the case of Arathil and Kunnamangalam series. Low PA in these soils is due to sandy fraction and low organic matter in lower layers (Gangopadhyay *et al.*, 2016).

Table. 5 Descriptive statistics summary of pH-dependent acidity (meq/100g) at two different depths of 0-15 cm and 15-30 cm. Data are depicted as means ± standard error

	0-15 cm		15-30 cm	
	Mean ± SD	Range	Mean ± SD	Range
Angadipuram	19.06 ± 3.5	14.7 - 25.2	6.35 ± 0.35	5.45 - 6.75
Naduvattom	10.53 ± 3.35	4.25 - 16.5	5.97 ± 0.22	5.7 - 6.4
Kunnamangalam	25.11 ± 4.16	18.5 - 32.65	25.41 ± 4.77	16.38 - 32.5
Nanminda	39.27 ± 1.77	37 - 41.13	27.03 ± 3.93	23.12 - 35.25
Kalikkadavu	34.14 ± 2.53	30.6 - 38.5	13.21 ± 5.25	4.5 - 20.63
Arathil	12.78 ± 1.53	1.53 - 15.13	32.21 ± 3.28	26.5 - 36.34
Kunnanthura	31.56 ± 5.72	18.13 - 38.62	16.68 ± 2.63	37 - 18.63
Payalam	31.96 ± 2.65	27.13 - 36.87	25.78 ± 2.31	23 - 29

From the descriptive statistics of data (Table.5), Nanminda series reported highest PDA in surface soil with a mean value of 39.27 ± 1.77 meq/100g while in subsurface soils, Arathil series has found to have a high PDA with a mean value of 32.21 ± 3.28 meq/100g. The high PDA in the Arathil series might be due to high PA prevailing in the soil Table 4. Down the profile, PDA decreased in all soil series. The variations in organic matter content, microbial activity, and soil respiration across the horizon might be some of the major reasons for the PDA fluctuations (Zhang *et al.*, 2019). In acidic soils rich in Fe and Al, the contribution of exchangeable acidity to total acidity decreases as the Fe and Al oxide coatings on the clay surfaces reduce the quantity of exchangeable acidity (Yerima *et al.*, 2020). Hence, PDA has a major contribution to total potential acidity.

Table. 6. Summary of Paired t-test analysis of soil parameters at two depths (0-15 cm and 15-30 cm). E_a -Exchangeable Acidity, E_H – Exchangeable Hydrogen, E_{Al}- Exchangeable Aluminium PA-Potential Acidity, PDA-pH dependent acidity. S-Significant, NS-Nonsignificant

	Mean		p-value	p value	Significance
	0-15 cm	15-30 cm			

E_a	1.45	1.34	0.64	0.52	NS
E_H	0.37	0.44	0.48	0.28	NS
E_{Al}	1.08	0.89	1.05	0.29	NS
PA	27.0	20.43	4.65	0.031	S
PDA	25.55	19.08	4.65	0.031	S

The summary of paired t-test analysis of soil parameters at two depths (0-15 cm and 15-30 cm) is depicted in Table. 6. It is evident from the table that potential acidity and pH-dependent acidity had significant variations across 2 depths while E_a, E_H, and E_{Al} have shown non-significant variation. It is evident from Table. 3 that the exchangeable Al in these soils decreased with depth. The high amounts of sesquioxide coatings may be reducing the amount of extracted exchangeable Al leading to low exchangeable Al in lower horizons (Yerima *et al.*, 2020). The decrease in PA and PDA in the lower layers might be due to a decrease in the levels of organic matter, and exchangeable cations like Ca⁺² and Mg⁺², which is in agreement with Zhou *et al.* (2019).

4. Conclusion

From the current study, the major forms of acidity such as exchangeable acidity, potential acidity, and pH-dependent acidity were found to be high and showed variation in the major lateritic soil series of northern Kerala. The patterns in which each fraction contributed to the total acidity varied within the series and down the profile. A close relation between exchangeable aluminium and exchangeable hydrogen with acidity forms were observed. The potential acidity and pH-dependent acidity had significant variations across surface and subsurface depths while exchangeable acidity, aluminium, and hydrogen have showed non-significant variation. We recommend a proper soil management system that lowers the surface and subsoil acidity and the toxic level of metals prevalent in low-pH soil. Again, for best effects in terms of biomass production and economic crop yields, amelioration of soil acidity should be followed by optimum plant nutrient inputs.

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6. Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

7. Author contributions

SREELAKSHMI. M. M: Conceptualization, Methodology, Formal analysis, Investigation, Writing- Original draft, Critical Review and Editing, Visualization, Validation, Project Administration

APARNA. B: Conceptualization, Methodology, Resources, Validation, Project Administration, Supervision

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