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Availability indices of calcium and magnesium in soils of Kerala

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Abstract
Calcium and magnesium are indispensible as secondary nutrients for plant growth. Availability of these nutrients to plants depends on the form and quantity present in soil. Soils of Kerala pose the problem of acidity due to high rainfall and leaching of bases causing widespread deficiency of these nutrients. A study was conducted to characterize the soils of the state with respect to availability indices and major fractions of calcium and magnesium contributing to plant available pool. The availability of calcium and magnesium increased with pH, cation exchange capacity and decreased with increase in exchangeable aluminium. The mean per cent contribution of different fractions to total calcium was in the order exchangeable > mineral > acid soluble > water soluble > organic complexed, whereas in the case of magnesium, it was mineral > acid soluble > exchangeable > water soluble > organic-complexed fractions. Exchangeable calcium and water soluble magnesium were the sole forms contributing directly to the available pool.

Key words: Available pool, Calcium, Fractions, Kerala soils, Magnesium.

Intoduction

The soils in the state of Kerala formed under tropical humid climate vary widely with land form, vegetation and hydrology. Distinct types of lateritic soils, colluvial and alluvial deposits and sandy soils varying widely in physical and chemical properties have been formed as influenced by the above factors (Krishnan et al., 1996). High rainfall in a bi-modal pattern resulted in leaching of calcium and magnesium and subsequent accumulation of iron, aluminium and manganese in the upper soil layers. However, the rain shadow areas in the high ranges and low rainfall areas in the eastern parts of Palakkad district derived neutral to slightly alkaline soil. Soils formed by the alluvial and colluvial deposits by rivers originating from the Western Ghats and emptying into the so called *kayal* lands have properties influenced by both deltaic deposition and tidal influence of Arabian Sea. The soil of these special zones (*Kuttanad*, *Pokkali*, *Kole* and *Kaipad*) have developed as acid saline/ potentially acid sulphate soil with very low pH and high content of bases (Nair et al., 2013).

Based on the variations in soil, landform, rainfall, length of growing period and vegetation, the state is divided into five agro-ecological zones viz., Coastal plains, Midland laterites, Foot hills, High hills and Palakkad plains, and further sub-divided into 23 agro-ecological units (AEUs) (Nair et al., 2011). Kerala is thus covered by a wide spectrum of soil and hence requires location specific management techniques. Deficiency of calcium and magnesium is found to affect the yield of many crops with no response to optimum doses of nitrogen, phosphorus and potassium. They are recognized as major yield limiting parameters in the highly weathered tropical acid soils. :Hence a study was conducted to unravel the availability

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indices, forms of the nutrient in soil and their contribution to available pool and understand the intricacies involved in maintaining optimal nutritional status of calcium and magnesium in soils of different agro-ecological units of Kerala.

Material and methods

Soil samples from 0-20 cm depth were collected from sixty nine locations in different agro-ecological units of the state. Soil samples were air-dried and sieved through 2 mm and characterized for pH, electrical conductivity (EC), organic carbon, effective cation exchange capacity (ECEC), and available (Av) nutrient status following standard procedures.

Different fractions of calcium and magnesium in the soil samples were determined following the sequential fractionation procedure outlined by Mokwunye and Melsted (1972). One gram of sample was crushed and passed through a 35 mesh sieve and subjected to successive treatments. Exchangeable fraction (Ex) was extracted with 1N neutral ammonium acetate and the residue was oxidized with 10% H_2O_2 solution to extract organic-complexed (Or-c) fraction. Further it was treated with 1N HNO_3 to remove the Acid-soluble (Ac-s) fraction. The residue was then digested with tri-acid mixture to decompose the Mineral (Min) fraction.

Total content was determined on separate sample by digesting with 70% $HClO_4$ following the procedure of Jackson (1958) and water soluble fraction was estimated by the modified procedure of Baruah et al. (2011).

The soil properties were correlated and the parameters with significant correlation coefficients with available calcium and magnesium were considered for regression analysis as described by Cox (1987) using SPSS software. The contribution of different fractions of calcium and magnesium to available pool was estimated with the help of path coefficient analysis in OPSTAT package.

Results and discussion

Soil characteristics

The range and mean values of soil properties studied are presented in Table 1. The wide variations in the soil characteristics have been contributed by the varying conditions under which the soils were developed. The extremely lower values of soil pH and higher values of electrical conductivity, organic carbon, potassium, magnesium, sulphur, iron, and boron were contributed by the soils categorized as acid saline or potentially acid sulphate soils. These soils lying at or below sea level are characterized with high content of organic matter, salinity, and acidity and are classified as special zone soils under AEU 4 (*Kuttanad*), AEU 5 (*Pokkali*), AEU 6 (*Kole*) and AEU 7 (*Kaipad*). Near neutral pH and high content of available calcium and high cation exchange capacity were observed in soils of rain shadow areas comprising of AEU 17 (Marayur hills), AEU 18 (Attapady hills), AEU 19 (Attapady dry hills) and AEU 23 (Palakkad eastern plains)

Table 1. Range and mean values of soil properties

Soil property	Range	Mean	Soil property	Range	Mean
pH (1:2.5)	3.03 - 6.99	1.69	Available copper (mg kg^{-1})	0.55-13.93	3.64
EC (dSm^{-1})	0.03-13.66	43.21	Available zinc (mg kg^{-1})	0.04-11.00	2.11
Organic carbon (%)	0.3-10.72	225.70	Available boron (mg kg^{-1})	0.04-5.20	0.55
Available phosphorus(kg ha^{-1})	1.59-388.42	527.74	ECEC ($cmol^{(+)}kg^{-1}$)	0.71-14.58	5.79
Available potassium (kg ha^{-1})	23.52- 1025	182.36	Exchangeable calcium ($cmol^{(+)}kg^{-1}$)	0.26-11.64	2.77
Available calcium (mg kg^{-1})	73.10 - 1725	171.35	Exchangeable magnesium ($cmol^{(+)}kg^{-1}$)	0.13-5.64	1.44
Available magnesium (mg kg^{-1})	9.56- 1931	135.64	Exchangeable potassium ($cmol^{(+)}kg^{-1}$)	0.03-2.18	0.24
Available sulphur (mg kg^{-1})	0.89-3894	171.35	Exchangeable sodium ($cmol^{(+)}kg^{-1}$)	0.03-5.65	0.29
Available iron (mg kg^{-1})	8.84- 1033	135.64	Exchangeable aluminium ($cmol^{(+)}kg^{-1}$)	0- 9.02	0.75
Available manganese (mg kg^{-1})	0.79-148.7	27.34	Anion exchange capacity ($cmol^{(-)}kg^{-1}$)	0.95-10.68	5.25

which can be attributed to low rainfall and presence of mixed layer lattice clays with dominance of vermiculite/montmorillonite. The dominant cation in the exchange complex was found to be calcium followed by magnesium in all soils except in soils of AEU 4, 5 and 7 where aluminium followed by magnesium and calcium were the dominant cations. The mean values of anion exchange capacity of soils from different AEUs varied from 0.95 to 10.68 cmol (-) kg^{-1}. Higher values of AEC were recorded in lateritic soils with dominance of 1:1 type layer lattice silicates and hydroxides and hydrous oxides of iron and aluminium.

Available calcium (Av Ca)

Available calcium status in soil samples collected from different AEUs varied from 73.1 to 1725 mg kg^{-1}. Twenty seven per cent of soils studied were deficient (< 300 mg kg^{-1}) in available calcium. Calcium deficiency was pronounced in the soils of *Onattukara* sandy plains (AEU 3), and AEUs covering south and central lateritic soils (AEU 8, 9, 10) and south and central foot hills (AEU 12). Deficiency of calcium was negligible in soils of Marayoor hills (AEU 17), Attapady hills (AEU 18 and 19), Palakkad central and eastern plains (AEU 22 and 23). Higher status of calcium was recorded in soils receiving less rainfall due to reduced leaching losses which was well reflected in the near neutral pH.

The interrelationship between the soil characteristics and available calcium was analysed through correlation and quantified through regression after excluding the special zone soils as these soils with unique properties like low pH, high EC, high content of basic and acidic cations are likely to have a biased influence. Available calcium had significant positive correlations with pH (0.73**), EC (0.28*), exchangeable (exCa) calcium (0.89**), potassium (0.34*), magnesium (0.77**), sulphur (0.36**), and ECEC (0.87**) and significant negative correlations with available boron (-0.36**) and exchangeable aluminium (-0.43**). Step wise regression analysis including soil parameters significantly correlated with available calcium yielded the following equations

AvCa = 114.64 + 0.66 exCa (adj R^2 = 0.79) ......(1)

AvCa = -530.36 + 0.53 exCa + 136.06 pH (adj R^2 = 0.83) ……...(2)

AvCa = - 428.77 + 0.45 exCa + 107.45 pH + 0.95 AvMg (adj R^2 = 0.85) ....(3)

AvCa = -187.90 + 0.90 exCa + 65.00 pH + 2.20 AvMg - 86.10 ECEC (adj R^2= 0.86) …..…(4)

Exchangeable calcium alone accounted for 79 per cent variations in available calcium content in soil. Inclusion of pH, available magnesium and ECEC could improve the predictability of available calcium to 86 per cent.

Available magnesium (Av Mg)

In comparison to calcium, the deficiency of available magnesium was more aggravated and widespread. Available magnesium status in soil samples collected from different AEU's varied widely from 9.56 to 1931 mg kg^{-1}. Around sixty-seven per cent of soils were deficient (< 120 mg kg^{-1}) in magnesium. This might be due to the predominance of coarse textured soils, well drained condition and intense leaching losses, and less addition of inputs supplying the nutrient to soil. In comparison to calcium, magnesium is less strongly bound to soil colloids due to its higher hydrated ionic radii and hence easily leached off. The higher values of available magnesium were found in the special zone soils of AEU 4, 5, 6 and 7 which can be related to the presence of soluble salts of magnesium due to sea water inundation. High content of available calcium, magnesium and sulphur was reported by Beena and Thampatti (2013) in the soils of *Kuttanad*. Another exception to the widespread deficiency of magnesium was recorded in the soils of Attapady hills (AEU 18 and 19) and central and eastern plains of Palakkad (AEU 22 and 23), which can be attributed to low rainfall and near neutral pH.

Correlation coefficients between different soil properties worked out after excluding the special zone soils showed available magnesium to have significant positive correlations with pH (0.62**), EC (0.31*), available calcium (0.77**), sulphur (0.38**), zinc (0.52**),exchangeable calcium (0.71**), magnesium (0.94**), ECEC (0.84**) and PBS (0.49**) and a negative correlation with available boron (-0.47**) and exchangeable aluminium (-0.37**).The significant positive correlations between exchangeable calcium and magnesium, pH and ECEC and negative correlation with exchangeable aluminium confirmed that as the ECEC of the variable charged soils increased with pH, calcium and magnesium being the dominant cations on the exchange complex, significantly influenced their availability in soil. On the contrary as the pH decreased, dominance of exchangeable alumiunium increased thus reducing the availability of calcium and magnesium.

Step wise regression analysis including soil parameters significantly correlated with available magnesium yielded the following equations

Av Mg = 27.75 + 0.47 exMg (adj R^2 = 0.87 ……..……(5)

AvMg = 16.183 + 0.39 Mg + 0.05 AvCa (adj R^2 = 0.90 ……..….(6)

AvMg = 22.644 + 0.49 exMg + 0.09 AvCa - 8.96 ECEC (adj R^2 = 0.91) ……..…..(7)

Similar to that of available calcium, variability in available magnesium could be explained to the tune of 87 per cent by exchangeable magnesium alone. Further inclusion of available calcium and ECEC could improve the predictability to 91 per cent. A complementary effect of available calcium and magnesium in soil is understood from the regression analysis.

Chemical fractionation of calcium and magnesium

The mean values of calcium and magnesium in various fractions in soils of different AEUs are given in Tables 2 and 3. The water soluble fraction (WS Ca) of calcium accounted for 0.13 to 36.17 per cent of total calcium while water soluble magnesium

Table 2. Mean values of fractions of calcium (mg kg^{-1}) in soils from different AEUs of Kerala

	WSCa	ExCa	Or-cCa	Ac-sCa	MinCa	TotCa
AEU 1 Southern coastal plain	53.50	539.3	24.08	79.90	250.4	1027
AEU 2 Northern coastal plain	13.86	172.2	26.10	16.60	181.2	417.0
AEU 3 Onattukara sandy plain	10.73	121	25.60	41.09	93.00	325.5
AEU 4 *Kuttanad*	118.2	384.6	90.30	102.9	202.6	1005
AEU 5 *Pokkali*	518.5	500.5	40.00	69.30	301.7	1434
AEU 6 *Kole* lands	36.20	1099	22.60	153.4	232.7	1584
AEU 7 *Kaipad*	261.50	615.70	15.80	145.70	333.60	1828
AEU 8 Southern laterites	13.35	228.85	32.50	16.40	174.70	480.80
AEU 9 South central laterites	10.39	597.31	43.70	95.20	246.80	1091
AEU 10 North central laterites	9.95	178.95	21.50	82.90	89.20	417.0
AEU 11 Northern laterites	8.49	322.31	21.30	105.60	145.00	665.0
AEU 12 South and central foothills	8.45	102.30	20.40	39.40	65.40	258.0
AEU 13 Northern foothills	8.95	410.45	26.10	19.10	128.00	661.0
AEU 14 Southern high hills	13.91	364.29	16.70	137.40	89.20	643.5
AEU 15 Northern high hills	3.83	1153.17	45.40	82.20	1587.00	2981
AEU 16 Kumily hills	14.30	564.60	63.30	154.30	208.20	1032
AEU 17 Marayur hills	34.41	777.59	39.80	36.50	160.20	1066
AEU 18 Attapady hills	57.49	766.11	49.20	66.30	1600.00	2855
AEU 19 Attapady dry hills	65.67	531.33	34.60	113.40	1020.00	1775
AEU 20 Wayanad central plateau	8.39	153.51	12.90	184.20	81.40	465.0
AEU 21 Wayanad eastern plateau	6.83	353.47	26.30	84.90	126.20	663.5
AEU 22 Palakkad central plains	8.38	640.72	38.10	90.60	154.80	1019
AEU 23Palakkad Eastern Plains	7.39	1263.01	68.60	211.10	206.90	1775

WSCa, Water soluble calcium; ExCa, exchangeable calcium; Or-cCa, organic complexed calcium; Ac-sCa, acid soluble calcium; MinCa, mineral calcium; TotCa. Total calcium

Table 3. Mean values of fractions of magnesium(mg kg^{-1}) in soils from different AEUs of Kerala

	WSMg	ExMg	Or-cMg	Ac-sMg	MinMg	TotMg
AEU 1 Southern coastal plain	20.74	41.36	4.25	270.72	642.90	1064
AEU 2 Northern coastal plain	3.87	24.63	7.20	153.50	190.50	382.0
AEU 3 Onattukara sandy plain	3.77	15.03	11.60	21.80	118.10	176.5
AEU 4 *Kuttanad*	255.70	121.00	26.40	659.70	1374.00	3264
AEU 5 *Pokkali*	1465.00	313.00	45.80	605.70	2385.00	5055
AEU 6 *Kole* lands	9.82	163.48	3.30	966.70	1650.00	2894
AEU 7 *Kaipad*	815.00	207.00	14.70	486.50	1197.00	2848
AEU 8 Southern laterites	3.47	53.23	11.10	66.30	335.40	482.5
AEU 9 South central laterites	4.77	77.73	14.50	424.80	2484.00	3210
AEU 10 North central laterites	3.46	44.24	10.00	164.50	412.00	659.5
AEU 11 Northern laterites	4.34	123.16	10.00	172.70	1270.00	1641
AEU 12 South and central foothills	2.94	42.31	8.70	118.70	315.90	510.5
AEU 13 Northern foothills	2.81	61.69	11.00	31.40	1205.00	1554
AEU 14 Southern high hills	5.30	74.30	15.90	616.00	1302.00	2028
AEU 15 Northern high hills	3.74	168.96	14.50	324.20	2498.00	3590
AEU 16 Kumily hills	7.65	119.35	30.10	861.40	352.20	1535
AEU 17 Marayur hills	16.40	142.70	19.90	191.70	2536.00	4038
AEU 18 Attapady hills	29.70	104.50	25.90	911.90	1191.00	2455
AEU 19 Attapady dry hills	32.19	159.21	14.50	1181	2595.00	4171
AEU 20 Wayanad central plateau	3.26	38.34	8.60	84.30	589.80	801.5
AEU 21 Wayanad eastern plateau	2.20	105.80	4.70	42.90	832.10	1015
AEU 22 Palakkad central plains	1.86	180.94	8.80	249.30	1490.00	1981
AEU 23 Palakkad eastern plains	3.22	358.68	16.40	669.10	1708.00	2811

(WS Mg) contributed about 0.09 to 28.98 per cent of total magnesium. Water soluble calcium and magnesium was considerably high in the lowlands of AEU 4, 5, and 7 due to marine influence. Exchangeable calcium (Ex Ca) accounted for 26.83 to 72.95 per cent of total calcium while exchangeable magnesium (Ex Mg) was about 2.42 to 21 percent of total magnesium content. Organic-complexed calcium (Or-c Ca) accounted to 0.86 to 8.99 per cent of total calcium and the corresponding fraction of magnesium (Or-c Mg) contributed about 0.12 to 6.57 per cent of total magnesium. Mokwunye and Melsted (1972) also reported that only a small fraction of total magnesium occurred as organic complexed in soil.

The acid soluble fraction is the measure of the potentially available/non exchangeable forms present in soil while the mineral fraction is associated with the more resistant primary minerals and clay lattice structure of the soils (Hailes et al., 1997). The acid soluble calcium (Ac-s Ca) contributed to about 2.32 to 39.61 per cent of total calcium while acid soluble fraction of magnesium (Ac-s Mg) accounted to 2.02 to 56.12 per cent of total magnesium. The mineral fraction of calcium (Min Ca) accounted for 11.60 to 57.48 per cent of total calcium and mineral magnesium (Min Mg) had a per cent contribution of 22.95 to 81.98 of total magnesium. The total calcium (Tot Ca) ranged from 258 to 3161.75 mg kg^{-1} and total magnesium (Tot Mg) ranged from 176.5 to 5055 mg kg^{-1} in the soils from different AEUs of Kerala.

The mean per cent contribution of different fractions to total calcium was in the order exchangeable > mineral > acid soluble > water soluble > organic complexed fractions whereas in case of soil magnesium it was observed as mineral > acid soluble > exchangeable > water soluble > organic complexed. Ananthanarayana and Rao (1979) and Jayaganesh et al. (2011) also reported mineral magnesium followed by acid soluble magnesium to be the dominant fractions in lateritic soils of south India. The acid soluble and mineral fractions of magnesium were found to be higher than the corresponding fractions of calcium in all the soils. Consequently the total magnesium was higher than calcium in most soil types. This might be due to the dominance of hydroxy interlayered vermiculites and interstratified micas in soils of Kerala (Chandran et al., 2005). Unlike magnesium, calcium is not included in the structure of clay minerals due to bigger ionic size.

Contribution of fractions to available pool of calcium and magnesium

The available pool of calcium was significantly and positively correlated to all fractions except water soluble fraction, and the available pool of magnesium had significant positive correlation with all fractions except acid soluble fraction. Path analysis offers a clear picture on the direct and indirect effect of different fractions on available pool.

The path coefficients of different fractions of calcium depicted in Table 4, reveal that the direct effect of exchangeable calcium on available pool was very high and positive. The direct effects of organic-complexed and acid soluble fractions were negligible while the indirect effects through exchangeable calcium were moderate and positive. The direct effect of mineral calcium was moderate and negative while its indirect effect through exchangeable calcium was moderate and positive. The direct effect of total calcium and indirect effect through exchangeable calcium was very high and positive. This indicates that the immediate solid phase of calcium controlling its availability in soil is the exchangeable fraction. All other fractions influence the available pool positively through the exchangeable fraction.

The path coefficients showing the direct and indirect effects of fractions of magnesium on available pool in soil are presented in Table 5. The direct effect of water soluble magnesium on available magnesium was very high and positive while the indirect effect of WS Mg through exchangeable magnesium was positive but low. The direct effect of exchangeable magnesium was positive and moderate while its indirect effect through water soluble magnesium was positive and high. The direct effects of organic-complexed and mineral fraction on available magnesium were negligible while their indirect effect through water soluble magnesium was moderate to very high and positive and through exchangeable magnesium was low and positive. The direct effect of total magnesium was low and negative while the indirect effect through water soluble magnesium was very high and positive and through exchangeable magnesium was low and positive. Hence it is evident that in the case of magnesium, the available pool was directly and indirectly influenced by the water soluble fraction. This might be due to the high mobility of magnesium in soil as it is loosely bound to the exchange sites of soil clays and tend to exist in solution. Halstead et al. (1958) reported that for a given amount of exchangeable calcium and magnesium, more magnesium than calcium is found in the water-soluble form.

Table 4. Path coefficients of fractions of calcium to available calcium in soil

	ExCa	Or-cCa	Ac-sCa	MinCa	TotCa	Correlation coefficients
ExCa	**0.579**	0.020	-0.031	-0.110	0.502	0.96**
Or-cCa	0.268	**0.043**	-0.018	-0.059	0.252	0.49**
Ac-sCa	0.269	0.011	**-0.068**	-0.009	0.255	0.46**
MinCa	0.268	0.011	-0.003	**-0.236**	0.458	0.50**
TotCa	0.500	0.019	-0.030	-0.187	**0.581**	0.88**

(Values on diagonal are direct effects and values on horizontal lines are indirect effects)

Table 5. Path coefficients of fractions of magnesium to available magnesium in soil

	WSMg	ExMg	Or-cMg	MinMg	TotMg	Correlation coefficients
WSMg	**0.831**	0.103	0.050	0.025	-0.050	**0.96****
ExMg	0.344	**0.249**	0.031	0.051	-0.067	**0.61****
Or-cMg	0.536	0.100	**0.077**	0.037	-0.063	**0.69****
MinMg	0.235	0.142	0.032	**0.089**	-0.099	**0.40****
TotMg	0.393	0.158	0.045	0.084	**-0.106**	**0.57****

(Values on diagonal are direct effects and values on horizontal lines are indirect effects)

From the study it can be concluded that in all soils of Kerala, except soils from AEU 4, 5 and 7, calcium and magnesium are the dominant cations in the exchange complex of soils. Calcium mainly resides in exchangeable form, whereas magnesium is reserved in the mineral form. Only a small portion of calcium and magnesium in soil is complexed with organic colloids. All fractions of calcium except water soluble fraction had significant positive correlation with available calcium but the immediate solid phase directly controlling the availability in soil is the exchangeable fraction. All fractions of magnesium except acid soluble fraction had significant positive correlation with available magnesium and contributed to the available pool through water soluble fraction.

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