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Soil acidity and exchange chemistry in soils of southern Karnataka

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Abstract : Two surface soil samples representing acidic Ultisol and Entisol were analyzed to study the nature of soil acidity and exchange chemistry. The soils under study were sandy loam to sandy clay loam in texture with low pH, CEC and base saturation. The negative values of ΔpH in both the soils indicate that the soils carry net negative charge under natural soil pH conditions. The low ZPC values recorded for these acid soils were low which might be due to high organic matter in the surface soils. The negative pH (KCl)-ZPC values indicate highly weathered nature of these acid soils. The variation in the values of the ZPC, ΔpH, surface potential and pH (KCl)–ZPC values is attributed to the varying contents of organic matter, clay, Fe and Al oxides and hydroxides and dominance of kaolinite clay in these soils. The values of total potential acidity, pH dependent acidity and total acidity were very high, exchange and extractable acidity values were very low thus contributing little towards total potential and total acidity. The pH dependent acidity contributed more than 94 per cent towards total potential acidity. The extractable acidity value was higher than exchange acidity. The values of hydrolytic acidity were higher than exchange and extractable acidity. The lime requirement (LR) values for the soils revealed that LR as estimated by Adams - Evans buffer method, Incubation method, SMP buffer method and exchangeable Ca method were higher than those determined by other methods in Sirsi soil whereas LR as estimated by SMP–buffer method was higher than that determined by other methods in case of Mudigere soil.

Additional key words: *Soil acidity, Lime requirement, Charge characteristics, Ultisols and Entisols*

Introduction

The soils of southern Karnataka are, in general, acidic with poor base saturation and low exchange capacity. Free oxides of Fe and Al and kaolinite clays dominate in these soils. The productivity potential of these soils is limited. Further, there is a concern that the severity of soil acidity may increase because of poor management and heavy rainfall (Krishnamurthy Rao and Ramaiah 1993; Ananthanarayana and Ravindra 1998). Soil acidity is usually defined in terms of KCl extractable (permanent) and pH dependent acidity (Coleman and Thomas 1967). The permanent acidity is also ascribed to isomorphous substitution whereas the second type is ascribed to the polymers of Fe and Al, the kaolinite clays and the organic matter. The proportional amount of these two types of acidities determines the production potential, phosphate fixation and lime requirement of soils.

The humid climate of the region profoundly favours intensive weathering, culminating in the formation of minerals of constant surface potential at the expense and/or alteration of minerals with constant surface charge. Progressive leaching of the bases, originally present, results in residual accumulation of sesquioxides, which in turn gives rise to variable nature of these soils. A comprehensive knowledge of chemical and exchange behaviour of these soils is essential for sound management appraisal. In the present investigation, an attempt has been made to know the nature of acidity and exchange characteristics in an Ultisol and Entisol of southern Karnataka.

Materials and Methods

Surface soil samples (0 to 15 cm) representing acidic Ultisol and Entisol were collected respectively from Mudigere and Sirsi falling under hilly agro-climatic zone (zone 9) in southern Karnataka. Rainfall in both the locations varied from 1500 to 3800 mm and 3000 to 4500 mm, respectively (Dhanorkar and Ananthanarayana 2002). Mudigere soil was collected from a sapota orchard whereas Sirsi soil was collected from a cultivated rice fallow.

Physicochemical and exchange properties

Soil pH was measured in 1:2.5 soil - water and soil - 1N KCl suspensions. Soils were analyzed for organic carbon by the method of Walkley and Black as described by Tan (1995), particle size distribution by international pipette method (Piper 1966) and CEC by neutral normal ammonium acetate method (Jackson, 1973). Free iron and aluminium oxides were determined by citrate-bicarbonate-dithionate (CBD) procedure as described by Mehra and Jackson (1960). Surface charge density (SCD) was determined by X-ray diffractometry (Ananthanarayana and Ravindra 1998) Effective CEC is determined by the summation of exchangeable cations extracted by 1*N* NH_4OAc and extractable Al^{3+} by 1*N* KCl solution. Lime potential was obtained by subtracting 1.14 from pH (0.01 M $CaCl_2$).

Electrochemical properties

Delta pH (Δ pH) is obtained by taking the difference between pH measured in 1*N* KCl and water (Sen *et al.* 1997). Zero point of charge (ZPC) was determined by salt titration (ST) method as described by Sakurai *et al.* (1988) and charge - pH curves were plotted for all the soils. Surface potential was calculated by simplified Nernst type relation using ZPC and soil pH (Gast 1977).

Forms of soil acidity

Total potential acidity was determined by $BaCl_2$ – TEA solution buffered at pH 8.0 ± 0.02 and exchange acidity by 1 *M* KCl extract. The pH dependent acidity was calculated as the difference between these two. Total acidity was determined by 1*N* NaOAc solution buffered at pH 8.2 and extractable Al was determined by leaching the soil with NH_4OAc buffered at pH 4.8 and Al in the extract was determined calorimetrically using Aluminon. Hydrolytic acidity was obtained as the difference between total acidity and extractable acidity (Baruah and Barthakur 1998).

Lime requirement

Lime requirement (LR) of the soils was determined by five methods, *viz.*, incubation method of Dunn (1941), exchangeable Ca titrimetric method of Puri (1962), buffer methods of Adams and Evans (1962) and Shoemaker *et al.* (1961) and LR by CEC-TEB concept.

Results and Discussion

Physicochemical properties of the soils

The data on physicochemical properties are presented in Table 1. The texture of Mudigere soil was sandy loam (sand content, 60.3%) whereas Sirsi soil was sandy clay loam (sand content 56.4% and clay content 33.2%). The dominant clay in these soils is kaolinite with SCD values of 1.90 and 1.80 meq cm^{-2} respectively, in Mudigere and Sirsi soils (Ananthanarayana and Ravindra 1998). The pH was acidic in both the soils (pH ranging between 5.05 to 5.39). The Mudigere soil had medium (6.8 g/kg^{-1}) and Sirsi soil had high (13.7 g/kg^{-1}) organic carbon contents. The free iron and aluminium oxide contents were high in both the soils due to higher solubility of Fe and Al in acidic environment of these soils. The value of lime potential was 2.74 in Mudigere soil and 3.61 in Sirsi soil. The CEC and ECEC values were low due to relatively low clay content and coarser texture, acidic parent material, low exchangeable bases and Kaolinite clay minerals.

Table 1. Physicochemical properties of the soils

Particulars	Ultisol	Entisol
Location Details	**Mudigere, Chikmagalur District, Karnataka**	**Sirsi, Uttara Kannada District, Karnataka**
Sand	60.3	56.4
Silt	18.0	10.4
Clay	21.7	33.2
Textural Class	sl	scl
Surface Charge Density (SCD) (meq cm^{-2})	1.90	1.80
Soil Group	Ustic Haplohumults	Aquic Ustorthents
pH	5.05	5.39
Organic Carbon (g kg^{-1})	6.8	13.7
Fe_2O_3 (%)	2.72	3.63
Al_2O_3 (%)	0.17	0.09
Lime Potential	2.74	3.61
Exchangeable Al^{3+} [cmol(p^+)kg^{-1}]	0.40	0.20
Extractable Al^{3+} [cmol(p^+)kg^{-1}]	0.74	0.51
Sum of exchangeable bases [cmol(p^+)kg^{-1}]	2.37	2.56
CEC [cmol(p^+)kg^{-1}]	12.31	12.90
ECEC [cmol(p^+)kg^{-1}]	3.11	3.07
% Al saturation of ECEC	23.79	16.61
Base saturation (%)	27.40	26.82

Sirsi soil. The CEC and ECEC values were low due to relatively low clay content and coarser texture, acidic parent material, low exchangeable bases and Kaolinite clay minerals. The percent Al saturation of ECEC was higher in Mudigere soil (30.95%) than in Sirsi soil (22.94%).

The base saturation percentage was almost similar in both the soils (27.40 and 26.82%, respectively).

Electrochemical properties of the soils

The electrochemical properties of the soils are resented in Table 2. The pH (water) values were higher than the pH (KCl) values. The pH values of Mudigere and Sirsi soils in water were 5.05 and 5.39, respectively and pH values of the two series in 1*N* KCl were 3.65 and 4.46, respectively.

Table 2. Electrochemical properties of the soils.

Particulars	Ultisol	Entisol
Location	Mudigere	Sirsi
pH (water)	5.05	5.39
pH (KCl)	3.65	4.46
Δ pH [pH (KCl) – pH (water)]	- 1.40	- 0.93
Zero Point Charge (ZPC) [ST-ZPC]	4.10	4.90
Surface potential (mv. at 25^0 C)	- 53.10	- 31.86
pH (KCl) – ZPC	- 0.45	- 0.44

Table 3. Forms of acidity and lime requirement of the soils

	Particulars	Ultisol	Entisol
Location		Mudigere	Sirsi
Forms of Acidity [c mol (p^+) kg^{-1}]	Total potential acidity	8.60	16.60
	Exchange acidity	0.50	0.25
	pH dependent acidity	8.10	16.35
	Total acidity	3.60	6.80
	Extractable acidity	0.74	0.51
	Hydrolytic acidity	2.86	6.29
Lime requirement [t ha^{-1}]	Adams - Evans buffer method	2.46	4.67
	Incubation method	2.13	4.20
	SMP buffer method	6.47	5.84
	Exchangeable Ca method	2.80	4.48
	CEC-TEB method	2.31	2.00

The ΔpH values for both the experimental soils were negative, - 1.40 and - 0.93 for Mudigere and Sirsi soils, indicating that the soils were negatively charged. Roopa and Ananthanarayana (2001) also reported negative ΔpH values in some acid soils of Karnataka indicating thereby that the soil under natural pH carries a net negative charge, which can however, be increased by increasing the pH (addition of lime).

One of the most important characteristics of soils dominated by variable charge clays is the ZPC (Zero Point Charge) or pH, at which value of the net charge of the variable charge component is zero (Sakurai *et al.* 1988). The evaluation of ZPC enables to predict the soil response to the changes in the surrounding conditions and fertilizer applications in the field.

The ZPC values of the experimental soils were 4.1 and 4.9 for Mudigere and Sirsi soils, respectively (Fig. 1). Roopa and Ananthanarayana (2001) reported ZPC values varying from 3.9 to 5.5 in some acid soils (Entisols and Inceptisols) of Karnataka. Sen *et al.* (1997) reported ZPC values of 2.4 to 3.2 in some surface acidic soils of Assam. Comparatively lower ZPC values observed for the experimental soils might be due to the higher organic matter in the surface soils. High organic matter in the surface keeps the ZPC low and therefore soil pH is low and at the same time keeps the negative SCD high. Majority of acid soils of Karnataka have variable charge. The lesser ZPC values indicate that the permanent charge carried by the soil clay minerals was lower than the surface negative charge (Ananthanarayana and Ravindra 1998).

Negative surface potential values for the experimental soils were obtained from the relationship, $\Psi_0 = 59$ (ZPC - pH) (Sparks 1986). The values were different t for the soils due to difference in organic matter content, sesquioxides content and clay content in the soils. The negative surface potentials of -53.10 mv and – 31.86 mv were recorded for the Mudigere and Sirsi soils under study. Roopa and Ananthanarayana (2001a) reported negative surface potential values varying from -36.6 to -131.0 mv at 25^0C at natural pH for the acid soils in various agro climatic regions of Karnataka. Sen *et al.* (1997) and Datta *et al.* (2000) also reported negative surface potentials for various acid soils and they attributed it to the varying organic matter and sesquioxides contents of soils.

The pH (KCl) - ZPC values for the experimental acid soils of Mudigere and Sirsi were -0.45 to -0.44,

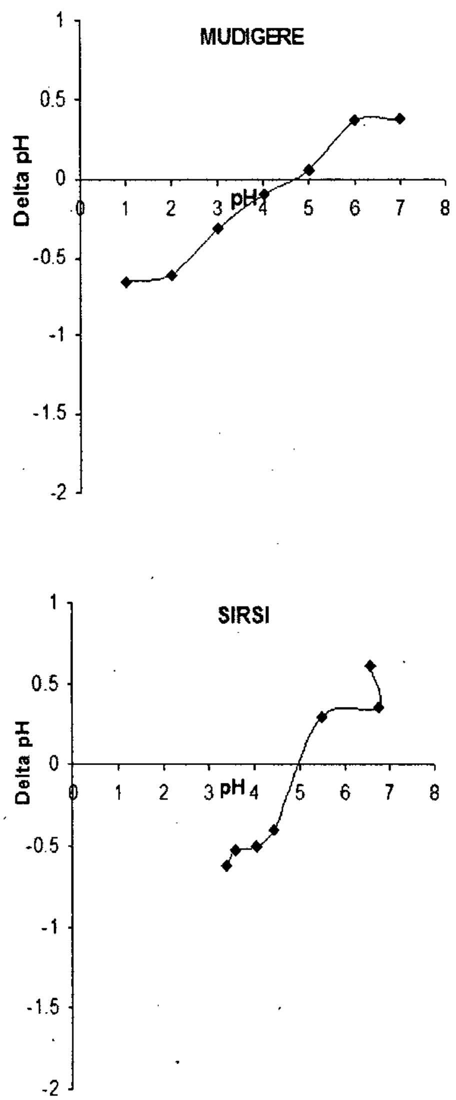

Fig. 1. ZPC curves of Mudigere and Sirsi soils

respectively. The values were different for the soils due to varying contents of organic matter, Fe and Al oxides and clay contents of the soils. These negative values indicate the highly weathered nature of these acid soils. Datta *et al.* (2000) also reported pH (KCl) - ZPC values varying from - 1.41 to - 0.60 for different acid soils of West Bengal suggesting that the soils are generally in advanced stages of pedogenic development.

Forms of acidity and lime requirement for the soils

The different forms of acidity are presented in table 3. Between the two soils, the values of total potential acidity, pH dependent acidity, total acidity and the hydrolytic acidity were higher in Sirsi soil than in Mudigere soil. But the values of exchange and extractable acidities were higher in former than those in the latter. The extractable acidity was more than exchange acidity. In both the soils, pH dependent acidity contributed 94 to 98 per cent towards the pool of total potential acidity whereas the exchange acidity contributed a very little (less than 1 to 5%).

Higher contribution made by pH dependent acidity may be due to high content of Fe and Al oxides and organic matter in the soils (Misra *et al.* 1987). The higher total potential acidity may also be due to higher percentage of organic matter in the soil, which contributed to total acidity through their functional groups like carboxylic and phenolic hydroxyl groups (Das *et al.* 1991).

Lime requirement of a soil is the amount of liming material, which must be applied to a soil to raise its pH from an initial acid condition to a level selected for near optimum plant growth. In the present study, five LR methods were used and the corresponding recorded LR values are presented in table 3.

It was observed that LR as estimated by Adams - Evans buffer method, Incubation method, SMP buffer method and exchangeable Ca method were higher than CEC – TEB method in Sirsi soil, whereas LR as estimated by SMP – buffer method was higher than those estimated by other methods in case of Mudigere soil. High LR value of 6.47 t ha^{-1} by SMP buffer method was noticed in Mudigere soil whereas LR by other methods varied between 2.31 to 2.80 t ha^{-1}. In case of Sirsi soil, the LR values ranged between 4.20 to 5.84 t ha^{-1} by all the methods except LR by CEC-TEB, which recorded 2 t ha^{-1}.

Ananthanarayana and Manjunatha Prabhu (1992) reported LR values of 0.60 to 2.5 t ha^{-1} and 1.0 to 4.1 t ha^{-1} by exchangeable Ca method and SMP buffer method for some acid soils of Chickmagalur district, Karnataka state, where the extractable acidity is 1 to 2 cmol (p^+) kg^{-1}.

LR of Sirsi soil is higher than that of Mudigere soil even though the latter has lower pH. This is attributed to the higher magnitude of total potential acidity, total acidity and high organic matter content in Sirsi soil which contributed for higher buffering capacity of the soil. This is also revealed by the correlation studies.

pH related negatively and organic matter related positively with LR of both the soils. The negative relation between pH and LR is due to the fact that pH measures only the intensity factor of soil acidity, but the chemistry of liming involved the replacement of exchangeable H^+ from the exchange complex as well as the free H^+ ions in the soil solution. Hence, unless the extent of potential acidity is assessed, the lime recommendation based on only pH will be misleading. Dadhwal and Tripathi (1986) and Ananthanarayana and Manjunatha Prabhu (1992) also made similar observations in some acid soils of Himachal Pradesh and Karnataka, respectively.

Positive relationship between LR and organic matter is due to the contribution of organic matter to pH dependent charges provided through the dissociation of hydroxyl and carboxyl groups of humus. Sharma and Tripathi (1989) also reported similar findings from their studies on acid soils of India.

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