

Calculating Charge Density of Clays : an Improved Method

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Abstract: Two benchmark Vertisols from Maharashtra, viz. Linga series (Typic Haplusterts in Nagpur district) and Pahur series (Sodic Haplusterts in Yavatmal district) of Maharashtra were chosen for the study. The fine clay fractions are dominated by smectite with small amounts of vermiculite. Reduced CECs of the fine clays were determined after the Greene-Kelly test. CEC and calculated surface charges are distributed in both the tetrahedral and octahedral layers of which the former (65%) is higher than the latter (35%). However, the proportion of octahedral CEC and charge increases (44%) with the deduction of the contribution of vermiculite and chlorite CEC from the tetrahedral (corrected) CEC. The CEC and charge distribution exhibited fairly good relationship with some soil properties such as, fine clay, COLE, moisture retention at 1500 kPa, hydraulic conductivity and pH. The study also indicated that determination of reduced CECs from Greene-Kelly test is an effective means of measuring the octahedral and tetrahedral CECs and also for calculating the charge of soil clays. The Pahur soils could be more prone to hydroxy-interlayering owing to its higher tetrahedral charge than Linga soils. The surface area method overestimates the calculation of charge from CEC than formula weight method. In India, the black soils occupy about 116 m ha (Bhattacharyya *et al.*, 2009) of which about 30 m ha is in Maharashtra and about 8.04 m ha is in Vidarbha region. These soils are developed in alluvium derived from weathering of Deccan basalt (Pal *et al.*, 2006). The black soils of the Deccan Trap are rich in plagioclase feldspars and yield dioctahedral smectite as its first weathering product (Pal and Deshpande, 1987; Pal *et al.*, 1989; Bhattacharyya *et al.*, 1993). Earlier review on the Vertisols of India indicate that black soils of India are dominated by beidellite-nontronite type of minerals (Ghosh and Kapoor, 1982). However, fine clay smectite when subjected to the Greene-Kelly test (Greene-Kelly, 1953) by heating clays with Li and subjecting to glycerol solvation, expands to about 18 Å and contracts to ~9.5 Å indicating this to be a mixture of beidellite/ nontronite and montmorillonite in which the amount of the former is more than the latter (Pal and Deshpande 1987; Ray *et al.*, 2003).

There are only scanty information on the origin and nature of charge of smectites in Vertisols of India (Pal and Deshpande

1987b; Bhattacharyya *et al.*, 1993; Ray *et al.*, 2003). Thus information on charge characteristics of Vertisols may be helpful to

identify the smectite species in the mineralogy class instead of the group name i.e. smectite. Apart from the alkylammonium method to determine the layer charge of soil clays (Lagaly, 1994; Ray *et al.*, 2003), there are some other indirect methods to determine the layer charge density of soil clays. Among them some methods involve CEC values that can be used to calculate the charge density. In the present study, however, two methods viz., surface area method and formula weight method were evaluated for their accuracy in calculating charge density from reliably drawn CEC values.

Materials and Methods

Two benchmark Vertisols were selected from Maharashtra for the study. One was Linga soil series (P1) (very fine, smectite, hyperthermic Typic Haplusterts) from Nagpur district and the other one was Pahur soil series (P2) (very fine, smectite, hyperthermic Sodic Haplusterts) from Yavatmal district.

Analyses of soil properties

Some soil physical and chemical properties such as total clay and fine clay contents, COLE, moisture retention, saturated hydraulic conductivity (sHC), pH, exchangeable K, etc. were analysed by standard methods (Jackson, 1973; Piper, 1966). Fine clays were separated from soil by size segregation method of Jackson (1979) following the removal of cementing

agents. Only fine clays were considered in this study as they are fine clays are the dominant fractions of these soils' smectites are the dominant minerals in these clays. Some properties are presented in table 1.

Mineralogical analysis by X-ray diffractometer

The fine clay (<0.2 μm) fractions of each horizons of two pedons were analysed for qualitative mineralogy by X-ray diffraction (XRD) techniques. For identification of clay minerals, the fine clay fractions were subjected to XRD of the parallel oriented samples using a Philips X'Pert Pro diffractometer with Ni filtered Cu-K α radiation at a scanning speed of 2°2 θ /min. Different thermal pre-treatments of the K-saturated samples were given to distinguish and confirm the type of mineral present. Greene-Kelley (1953) test was also performed on these fine clays to distinguish between montmorillonite and beidellite / nontronite.

Cation exchange capacity of clays

The method used by Jaynes and Bigham (1987) was followed for the determination of reduced CEC of the lithium saturated and heated at 250°C (Li-250) clay samples. The reduced CEC would give the values of tetrahedral CEC (as the octahedral soils have been blocked by Li). Samples were saturated with 3N LiCl (AR, Merck) solution (pH 7.0), mixed uniformly and kept overnight.

Table 1. *Some properties of the soils*

Horizon	Depth (cm)	Total clay	Fine clay	Moisture retention 1500 kPa	HC (cm/h)	COLE	pH 1:2 H ₂ O	Extrac-table (cmol(p+) kg ⁻¹)
				←————— (%) —————→				
<i>Linga Series, Katol, Nagpur (Typic Haplusterts)</i>								
Ap	0-16	54.9	41.0	31.0	2.3	0.2	8.1	1.3
Bw1	16-44	60.6	38.8	27.6	2.8	0.2	8.2	0.5
Bw2	44-69	62.4	41.7	27.4	2.5	0.2	8.3	0.4
Bss1	69-102	67.3	39.2	27.2	1.8	0.2	8.3	0.4
Bss2	102-128	67.7	45.2	28.8	2.8	0.3	8.3	0.5
Bss3	128-150	68.2	45.2	39.8	2.6	0.3	8.2	0.4
<i>Pahur series, Yavatmal (Sodic Haplusterts)</i>								
Ap	0-19	55.6	36.8	26.9	1.0	0.2	8.3	1.0
Bw1	19-40	54.8	36.7	27.4	0.8	0.1	8.4	0.4
Bss1	40-78	60.9	36.5	31.7	0.3	0.1	8.6	0.3
Bss2	78-122	57.7	32.2	26.7	0.3	0.1	8.6	0.5
Bss3	122-150	65.9	43	30.2	0.3	0.2	8.9	0.4

The treatment was repeated 3 more times. Subsequently the excess salt was removed by washings first with 50 per cent methanol and then with pure methanol until the EC was between 40-55 $\mu\text{mhos cm}^{-1}$. A centrifuge was used for these treatments. The Li-saturated samples were then transferred into previously dried and weighed silica crucibles with minimum amount of water. Later they were kept in a furnace at 250°C for 16 hours and their weights recorded, so as to express the data on an oven-dry basis (110°C) or at 250°C. The CEC of these samples were

determined by exchange with MgCl_2 . This CEC is the tetrahedral CEC (CEC_T). The original fine clays were also treated with MgCl_2 to get their CEC. The octahedral CEC (CEC_O) was determined by the difference between CEC of untreated fine clay (CEC_{UT}) and the tetrahedral CEC. Details of these methods are given in Kapse (2007).

Calculation of charge from CEC

Ideally the charge in the layer silicate minerals should be either in the

Table 2. *Semi-quantitative estimates of minerals in fine clays of the soils*

Horizon	Depth (cm)	Clay minerals (%)					
		Smectite	Vermiculite	Chlorite	Kaolin	Mica	Quartz
<i>Linga</i>							
Ap	0-16	82	14	4 (Tr)	1 (Tr)	<1 (Tr)	<1 (Tr)
Bw1	16-44	87	10	4 (Tr)	1 (Tr)	<1 (Tr)	<1 (Tr)
Bw2	44-69	87	9	5 (Tr)	1 (Tr)	<1 (Tr)	<1 (Tr)
Bss1	69-102	87	9	4 (Tr)	1 (Tr)	<1 (Tr)	<1% (Tr)
Bss2	102-128	87	9	4 (Tr)	1 (Tr)	<1 (Tr)	<1 (Tr)
Bss3	128-150	88	9	3 (Tr)	1 (Tr)	<1 (Tr)	<1 (Tr)
<i>Pahur</i>							
Ap	0-19	85	11	5 (Tr)	1 (Tr)	<1 (Tr)	<1 (Tr)
Bw1	19-40	88	10	3 (Tr)	1 (Tr)	<1 (Tr)	<1 (Tr)
Bss1	40-78	88	10	3 (Tr)	1 (Tr)	<1 (Tr)	<1 (Tr)
Bss2	78-122	90	7	4 (Tr)	1 (Tr)	<1 (Tr)	<1 (Tr)
Bss3	122-150	90	8	2 (Tr)	1 (Tr)	<1 (Tr)	<1 (Tr)

tetrahedral sheet or octahedral sheet, but it is usually observed that the charge is distributed over both the sheets (Foster, 1960; Schultz, 1969; Malla and Douglas, 1987). To find the location of charge in the lattice of clay minerals, the relationship between CEC and charge has been utilized to calculate the charge density by the following two methods.

Charge from surface area

$CEC = S \times \sigma$, where S = specific surface and σ = surface charge density

$\sigma = (CEC \times 10) / 780$, where $780 \text{ m}^2 \text{ g}^{-1}$ is the specific surface area for smectite mineral (Grim, 1953).

Charge from formula weight

$\sigma = CEC \times 738 \times 10^{-5}$ considering 738g as the formula weight of smectites.

Results and Discussion

XRD analysis of the fine clay

The fine clay fraction is mostly composed of smectite with small amount of vermiculite and chlorites (in traces) and traces of mica, kaolin and quartz (Figs. 1 and 2). Some of the smectites are also chloritized. On glycolation the 1.4 nm peak expanded to about 1.7 nm indicating the presence of smectites. On K-saturation at 25°C the smectite peak shifted to 1.1 to 1.2 nm, which is characteristic of

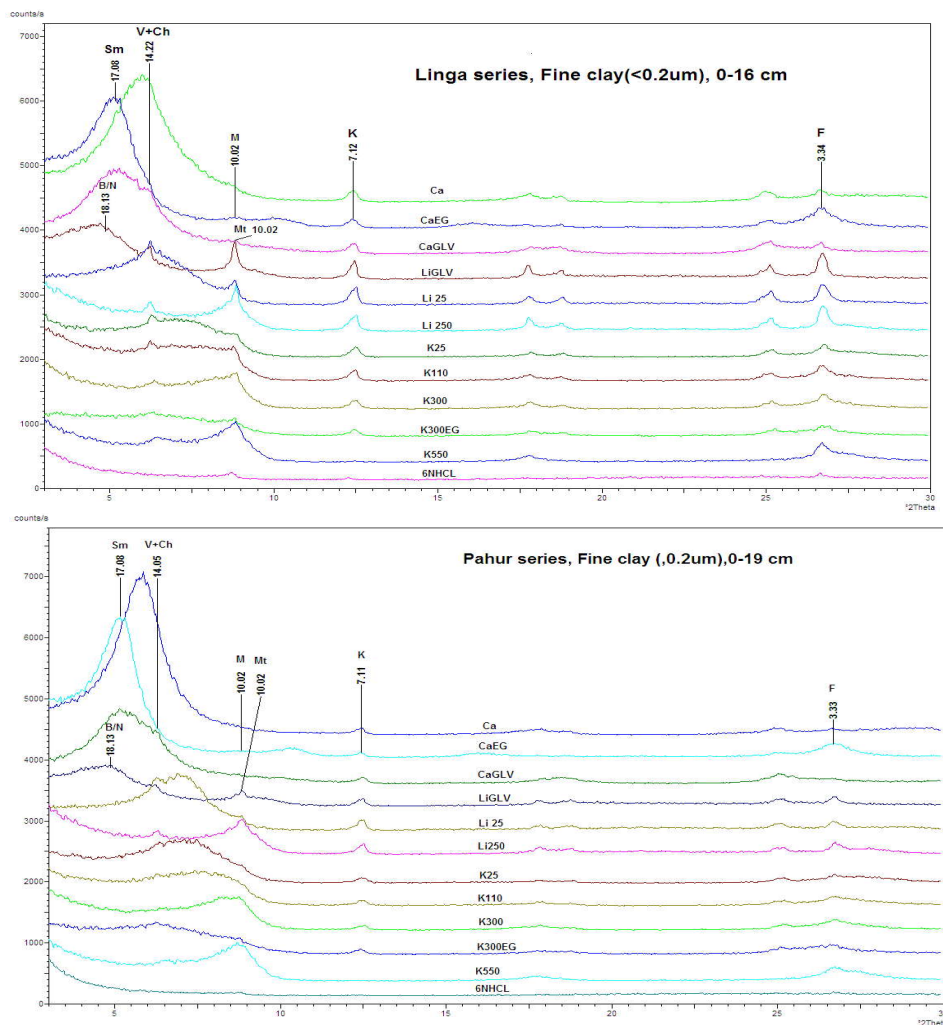


Fig. 1. X-ray diffractograms of fine clay fractions ($<0.2 \mu\text{m}$); Ca=Ca saturated; CaEG=Ca saturated plus ethylene glycol vapour; CaGLV=Ca-saturated plus glycerol vapour; Li=Li-saturated and heated to 250°C (16h), LiGLV=Li-saturated and heated to 250°C plus glycerol vapour; K-saturated and heated to 25, 110, 300, 550 $^{\circ}\text{C}$. K300EG= K-saturated at heated to 300°C plus ethylene glycol vapour; 6N HCl = HCl treated fine lays; Sm=Smectite, B/N=beidellite/nontronite; V+Ch = vermiculite plus chlorite; M = mica; Mt = montmorillonite; K = Kaolinite; F = Feldspars; (a) Linga series surface horizon; (b) Pahur series surface horizon

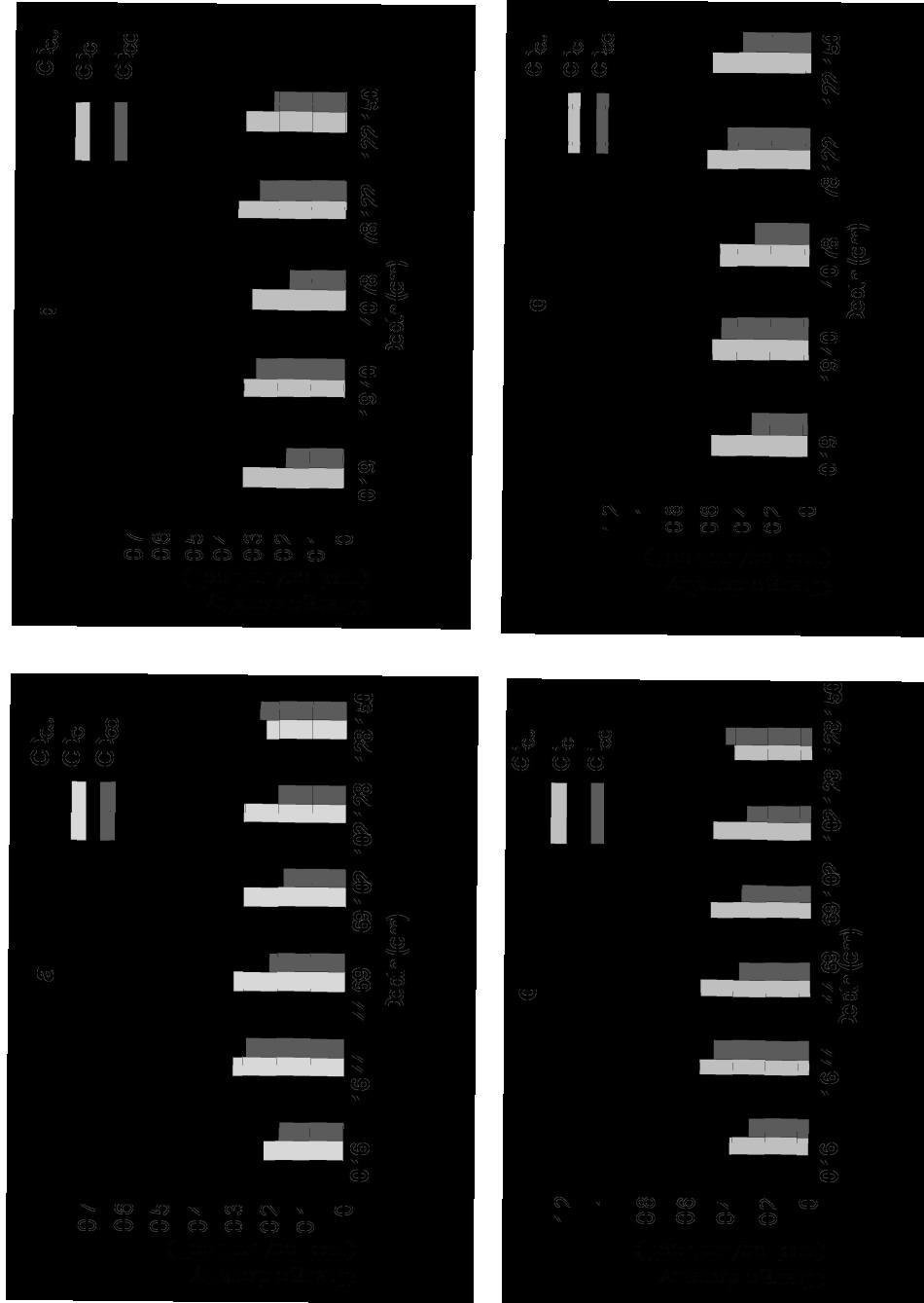


Fig.2. Distribution of corrected total (CD_{CUP}), tetrahedral (CD_{CT}) and octahedral (CD_{CO}) charge densities of fine clays for (a) Linga soils by formula weight method, (b) Linga soils by surface area method, (c) Pahur soils by formula weight method, (d) Pahur soils by surface area method.

smectite (Pal and Deshpande, 1987). The shifting of the 1.0 nm peak of K-saturated and heated (300°C) sample on glycolation to 1.4 nm indicates its low charge density (Bhattacharyya *et al.*, 1993). The presence of 0.72 and 0.35 nm peaks in Ca-saturated and glycolated sample and 0.72 nm peak in K-saturated and heated (300°C) sample and its disappearance at 550°C and retention of the peak at 0.72 nm after treating with HCl indicate the presence of kaolin. The smectite was found to be a little chloritized as evidenced by the broadening towards the low angle side of 1.0 nm peak in K-saturated sample after subsequent heating to 550°C. Such chloritization is common in black soils (Pal and Deshpande, 1987; Pal *et al.*, 1989; Balpande, 1993; Kadu, 1997; Pal *et al.*, 2000). A weak peak of 0.97 nm followed by 0.48 nm peaks indicates the presence of small amount of mica in these horizons.

Semi-quantitative estimates of the minerals in the fine clay fractions of P1 and P2 are shown in table 2. Smectite is the dominant mineral (82-90%) with small amount of vermiculite (7-14%) and pedogenic chlorite, mica, kaolin and quartz in traces. Smectite content in both the pedons increases slightly with depth, while the vermiculite content decreases with depth. Pedogenic chlorites are also found to decrease with depth. Pahur soils have slightly higher amount of smectites than Linga soils whereas the vermiculite content is higher in Linga soils. These values

may reflect upon the reduced CECs of the fine clays discussed latter.

Determination of seat of charge

The Greene-Kelly test (1953) (Hofman-Klemen effect) distinguishes between montmorillonite and beidellite/nontronite by glycerol solvation of the Li-saturated samples whereby the former collapses to 0.95 nm and the latter expands to about 1.8 nm (Pal and Deshpande, 1987; Kalbande *et al.*, 1992; Bhattacharyya *et al.*, 1993; Kapse, 2007).

Table 3. Untreated and Li-treated CECs (reduced CECs) of the fine clays

Depth (cm)	Horizon	CEC _T	CEC _{UT}	CEC _O
		← cmol(p+) kg ⁻¹ →		
<i>P1 : Linga series</i>				
0-16	Ap	53.5	77.5	24.0
16-44	Bw1	58.9	95.6	36.7
44-69	Bw2	58.3	86.5	28.2
69-102	Bss1	54.2	80.6	26.4
102-128	Bss2	54.0	78.4	24.4
128-150	Bss3	45.0	78.4	33.4
<i>P2 : Pahur series</i>				
0-19	Ap	64.0	91.3	27.3
19-40	Bw1	62.0	103.4	41.3
40-78	Bss1	58.0	83.4	25.8
78-122	Bss2	60.7	101.0	40.3
122-150	Bss3	59.8	92.8	33.0

Table 4. Untreated, reduced (Tet), octahedral and corrected CECs of fine clays

Horizon (cm)	CEC _{UT}	CEC _T	CEC _O	Vermi- culite (%)	Chlorite (%)	Contribution of V and Ch in CEC _T			Corrected tet CEC =(Tet CEC -CEC V+ Ch)	CEC CEC Tet Oct. (%) (%)		
						V	CH	Ch				
Linga Series, Katol, Nagpur (Typic Haplusterts)												
Ap	0-16	77.5	53.5	24	14	4	21	1.6	22.6	30.9	56	44
Bw1	16-44	95.6	58.9	36.7	10	3	15	1.2	16.2	42.7	54	46
Bw2	44-69	86.5	58.3	28.2	9	5	13.5	2.6	15.5	42.8	60	40
Bss1	69-102	80.6	54.2	26.4	9	4	13.5	1.6	15.1	39.1	60	40
Bss2	102-128	78.4	54.0	24.4	9	4	13.5	1.6	15.1	389	61	39
Bss3	128-150	78.4	45.0	33.4	9	3	13.5	1.2	14.7	30.3	48	52
Pahur series, Yavatmal (Sodic Haplusterts)												
Ap	0-19	91.3	64.0	26.3	10.5	5	15.75	2	17.75	46.3	63	37
Bw1	19-40	103.4	62.1	41.3	9.5	3	14.25	1.2	15.45	46.6	53	47
Bss1	40-78	83.4	58.1	25.4	9.5	2.5	14.25	1	15.25	42.8	62	42
Bss2	78-122	101.0	60.7	40.3	7	3	10.5	1.2	11.7	49.0	55	45
Bss3	122-150	92.8	59.8	33.0	8	2	12	0.8	12.8	47.0	58	42

Table 5. Charge densities of the fine clays calculated from the corrected CEC values

Horizon Depth (cm)	CEC (cmol(p+) kg ⁻¹)			Charge density (mol eq/unit cell)						
	CEC _{CT}	CEC _O	Total	Formula weight method			Surface area method			
				CEC _T	CEC _O	Total	CEC _T	CEC _O	Total	
<i>Linga series, Nagpur (Typic Haplusterts)</i>										
Ap	0-16	30.9	24	77.5	0.22	0.18	0.40	0.39	0.30	0.69
Bw1	16-44	42.7	36.7	95.6	0.31	0.27	0.58	0.54	0.47	1.01
Bw2	44-69	42.7	28.2	86.5	0.31	0.21	0.52	0.54	0.36	0.90
Bss1	69-102	39.1	26.4	80.6	0.28	0.17	0.45	0.50	0.34	0.84
Bss2	102-128	38.8	24.4	78.4	0.28	0.19	0.47	0.49	0.32	0.81
Bss3	128-150	30.2	33.4	78.4	0.22	0.24	0.46	0.38	0.43	0.81
<i>Pahur series, Yavatmal (Sodic Haplusterts)</i>										
Ap	0-19	46.2	26.3	91.3	0.34	0.20	0.54	0.59	0.35	0.94
Bw1	19-40	46.6	41.3	103.4	0.34	0.30	0.64	0.59	0.53	1.12
Bss1	40-78	42.8	25.4	83.4	0.31	0.19	0.50	0.54	0.33	0.87
Bss2	78-122	48.9	40.3	101.0	0.36	0.29	0.65	0.62	0.51	1.13
Bss3	122-150	47.0	33.0	92.8	0.34	0.25	0.59	0.60	0.42	1.02

The Li-saturated samples and heated at 250°C for 16 h (Lim and Jackson, 1986) gave a peak around 0.95 nm for montmorillonite and 1.4 nm peak for beidellite/nontronite, which expanded to 1.8 nm on glycerol salvation (Figs.1 and 2). All the fine clay samples of P1 and P2 gave distinct peaks at \approx 0.95 nm and 1.8 nm. This indicates that the fine clays are a mixture of beidellite/nontronite and montmorillonite in which the amount of the former is more as indicated by the respective X-ray intensities (Pal and Deshpande, 1987).

Cation exchange capacity of fine clays

The values of CEC of untreated fine clay (CEC_{UT}) for P1 ranged from 77 to 95 cmol(p+)kg⁻¹ and for P2 it ranged from 83 to 103 cmol(p+)kg⁻¹, respectively. The total values for Pahur fine clays are slightly higher than Linga fine clays and matches well with their semi-quantitative contents (Table 3). Jaynes and Bigham (1986) also reported similar values for soil smectites. The Greene-Kelly test enabled the Li⁺ ions to occupy the vacant octahedral position and thus there is no contribution of this layer towards CEC. The CEC measured after Greene-Kelly test

is the reduced CEC or the tetrahedral CEC (CEC_T). The reduced CEC values obtained for P1 and P2 ranges from 45.0 to 58.9 $cmol(p+)kg^{-1}$ and 58.1 to 64.0 $cmol(p+)kg^{-1}$, respectively.

The variation of tetrahedral (CEC_T) and octahedral (CEC_O) CEC is represented in table 3. Pahur soils seem to hook higher charge reduction compared to Linga soil clays. To obtain a better relation between the CEC_O and CEC_T values, it was envisaged that the contribution of vermiculite and chlorite towards tetrahedral CEC should be deducted to get values of CEC contributed only by smectites (Table 4). These values show that the difference between the corrected tetrahedral CEC (CEC_{CT}) and the corrected octahedral CEC (CEC_{CO}) has decreased after correction, though the CEC_{CT} values (56-58%) remained higher than CEC_{CO} values (42-44%).

Distribution of charge density

The charge densities were calculated only with the corrected CECs which are presented in table 5. The surface area method gave relatively higher octahedral charge than the formula weight method. The data also show that similar to CEC data the tetrahedral charge is higher than octahedral charge (Fig. 2). As the CEC is directly proportional to the charge density, the proportion of weighted mean of charge densities in octahedral and tetrahedral layers show a similar trend. The

charges at tetrahedral site by both the methods are much higher than the octahedral sites for the two soil clays. The tetrahedral charge of Pahur clays are higher than Linga soil clays. According to Pauling's rule the charges are balanced over the shortest possible distances (Pauling, 1960). Therefore, to balance the tetrahedral charge, the soil clay may become more prone to hydroxy-interlayering. This should result in a decrease in COLE, increase in ESP, decrease in moisture holding capacity and increase in availability of nutrients like K^+ and NH_4^+ (Ray *et al.*, 2004). The Pahur soils showing

Table 6. Relationship between tetrahedral charges (calculated by the two methods) and some soil properties

Sr. No.	Parameter	Correlation values (r)	
		Corrected charge density (tetrahedral)	
		Formula weight method	Surface area method
		CEC_T	CEC_T
1.	FC %	0.81	0.65
2.	COLE	0.65	0.72
3.	SHC	0.34	0.60
4.	1500 kPa	-0.68	-0.70
5.	pH	0.62	0.63
6.	Ex. K	0.14	0.11

higher tetrahedral charge may be more prone to hydroxy-interlayering and sodicity hazards than Linga soils.

The charges calculated by the two methods are not similar because the contribution of charge due to external surface has also been included in case of surface area method. Moreover, fine clays contain as much as 90% smectite and thus the estimate of surface area could be greater than $780 \text{ m}^2 \text{ g}^{-1}$ (considered in this study for the calculation of charge density), which could bring the values closer to that obtained by formula weight method.

Relation of CEC and charge characteristics with some soil properties

An attempt was made to correlate the charge calculated and some soil properties. The corrected tetrahedral charge calculated by both formula weight and surface area methods were found to be significantly correlated with fine clay, COLE, saturated hydraulic conductivity (sHC) and pH (Table 6) and significantly negative correlation with moisture retention (1500 kPa). Good agreement was not obtained with exchangeable K for the obvious reasons that the vermiculite and chlorite component in the tetrahedral CEC/charge was deducted to obtain the sole smectite charge and also it is known that smectites are not selective towards K (Pal and Durge, 1987). The exercise of calculating charge has been useful in understanding the direct relationship

between CEC and charges of soil clays which in turn is intrinsically related to some soil properties, especially those related to shrink-swell phenomena of Vertisols.

Conclusion

The formula weight method provides lower values of charge than surface area method. The values by latter method are also much higher than contemporary methods (Lagaly, 1994; Ray *et al.*, 2003). The study showed that reliably drawn cation exchange capacity data can help to calculate the charge (by formula weight method) of soil clays which are quick to determine and values are closer to those determined by other methods. Finally it elucidates that the CEC and surface charge governs some properties of these soils, which in turn influences the use and management of Vertisols of semi-arid tropics.

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