

Seat of Charge in Clay Smectites of Some Vertisol Maharashtra

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Abstract: In view of scanty information about the position of charge in smectites for soils of Maharashtra in particular, and India in general an attempt has been made to locate seat of charge of some Vertisol clays by determining the reduced cation exchange capacity (CEC_R) of smectitic clays. Six benchmark Vertisols from Maharashtra namely, Linga (P1), Loni (P2), Asra (P3), Paral (P4), Kalwan (P5) and Nimone (P6) from Nagpur, Yavatmal, Amravati, Akola, Nashik and Ahmednagar districts, respectively were chosen for the study. Fine clays were separated from the soils and their original CECs (CEC_{UT}) were determined by exchange with neutral normal $MgCl_2$ followed by $CaCl_2$ and $BaCl_2$. Greene-Kelly test was performed by treating these clays with 3N LiCl. The Li-clays were also treated with the above metal chlorides in the same order to get the reduced CECs.

Methods were formulated to calculate the actual CEC. The tetrahedral CEC decreased with increasing depth of soil for Linga, Asra, Kalwan and Nimone, whereas opposite trend was observed for Loni and Paral. The octahedral charge increased with depth for all except for Asra and Paral. The study indicated that cation exchange capacity determination appeared to be an accurate and less time-consuming approach to measure charge reduction. It can be used to locate seat of charge and also to study changes in the proportion of tetrahedral and octahedral charge during the pedogenetic processes of soil formation.

Vertisols are dominated by smectitic group of clay minerals (Pal and Deshpande, 1987; Bhattacharyya *et al.*, 1993; Ray *et al.*, 2003; Deshmukh, 2009; Bhople, 2010). Natural smectites have various chemical compositions having non-equivalent substitutions of central atoms in the octahedral and/or tetrahedral to generate a net negative charge on the layer that is

balanced by hydrated exchangeable cations e.g. Ca^{2+} , Mg^{2+} , Na^+ , etc. Ideally the charge in the layer silicate minerals should be either in the 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).

Vertisols are dominated by smectitic group of clay minerals. These clays hold a number of cations like Ca^{2+} , Mg^{2+} , Na^+ , K^+ , etc. Natural smectites have various chemical compositions having non-equivalent substitutions of central atoms in the octahedral and/or tetrahedral to generate a net negative charge on the layer that is balanced by hydrated exchangeable cations e.g. Ca^{2+} , Mg^{2+} , Na^+ , etc. The negative charge on smectite layers is recognized as one of the most important characteristics of 2:1 phyllosilicates (Komadel et al., 2005). The exchange of cations has been explained on the basis of the electrokinetic theory of ion exchange. According to this theory, the adsorbed cations forming the outer shell of the ionic double layer are supposed to be in a state of oscillation, when suspended in water, forming a diffuse double layer. Due to these oscillations, some of the cations move away from the surface of clay micelle. In the presence of solution of an electrolyte, cations of the added electrolyte slip in between the inner negative layer and outer oscillating positive ion. The electrolyte cation is then adsorbed on the micelle and the surface cation remains in solution. Thus exchange of cation takes place (Grim, 1953).

Cation exchange capacity (CEC) usually expressed in milliequivalents per 100g of soil. Its SI unit $\text{cmol(p+)}\text{kg}^{-1}$ soil/clay is a measure of the quantity of readily exchangeable cations, neutralizing negative

charge in the soil. These charges may be viewed as being balanced by either (i) an excess of ion of opposite charge or a deficit of ions of like charge, or (ii) the excess of ions of opposite charge over those of like charge (Bolt et al., 1976). The negative charges in soil constituents are derived from isomorphous substitution within the structure of layer silicate minerals, broken bonds at mineral edges and external surfaces, dissociation of acidic functional groups in organic compounds, amorphous materials and the preferential adsorption of certain ions on the particle surfaces (Rhoades and Krueger, 1968).

Hofmann and Klemen (1950) examined reference smectites to determine relationship between Li-uptake, cation exchange capacity and octahedral layer charge after Li-saturation and heating at 250°C . They also observed a loss of exchangeable Li and reduction of layer charge when Li saturated montmorillonite was heated at low temperatures ($200\text{--}300^{\circ}\text{C}$). The mechanism of charge reduction advocated by Hofmann and Klemen (1950) by Greene-Kelly (1953) invoked migration of Li ions into the vacant octahedral sites until the octahedral charge imbalance was neutralized. Thus, a lower limit to total charge was set by tetrahedral substitution plus terminal edge sites. Jaynes and Bigham (1987) reported that direct measurement of exchangeable Li after heating led to over

estimation of charge reduction due to entrapment of Li in collapsed interlayers. Tettenhorst (1962) was of the view that Li moves into the hexagonal cavities of the Si-O network but not into the octahedral sheet. Lim and Jackson (1986) reported that non-exchangeable Li in excess of reduction of cation exchange capacity ranged from 4 to 21 meq/100g in a series of standard smectites.

Brindley and Erten (1971) determined the CEC of Wyoming montmorillonite ("Volclay") after Li-treatment by measuring Li-displaced with ammonium acetate. They found no leveling of CEC at a value corresponding to tetrahedral layer charge. Farmer and Russell (1967) reported that charge reduction and Li-retention in heated Li-montmorillonites could be partially reversed by treatment with NH_3 . Calvet and Prost (1971) opined from the interpretations of IR data and suggested that Li remaining in the hexagonal cavities is in a transitional state prior to movement into the octahedral sheet. Relationship between Li uptake, charge reduction, and octahedral charge has also been disputed. They also observed that total charge reduction to be equal to the octahedral charge. An attempt has been made to locate seat and distribution of charge of some Vertisol clays of Maharashtra by using cation exchange capacity method of fine clays with the aid of mechanism of charge reduction advocated by Hofmann and Klemen.

Materials and Methods

Six Benchmark Vertisols from Maharashtra namely Linga (P1), Loni (P2), Asra (P3), Paral (P4), Kalwan (P5) and Nimone (P6) from Nagpur, Yavatmal, Amravati, Akola, Nashik and Ahemadnagar districts respectively were chosen for the study.

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 sites have been blocked by Li). Samples were saturated with 3N LiCl (AR, Merck) solution (pH 7.0), mixed uniformly and kept overnight. 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 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) may be computed from the difference between untreated CEC (CEC_{UT}) and CEC due to tetrahedral charge (CEC_T) as follows:

$$CEC_O = CEC_{UT} - CEC_T$$

Results and Discussion

Cation exchange capacities of original untreated fine clays

The fine clays were saturated with 1N $MgCl_2$ (AR Merck, Germany) and then exchange with 1N $CaCl_2$ (AR Merck, Germany). The extracted solution which is saturated with Mg^{2+} ions is the magnesium exchange capacity ($MgEC_{UT}$) of the original untreated samples.

The total CECs of original untreated fine clays with respect to Mg^{2+} ion ($MgEC_{UT}$) ranged from 93.1 to 107.5 $cmol(p^+) kg^{-1}$ for P1, 90.0 to 118.4 $cmol(p^+) kg^{-1}$ for P2, 75.5 to 113.2 $cmol(p^+) kg^{-1}$ for P3, 69.9 to 79.6 $cmol(p^+) kg^{-1}$ for P4, 67.2 to 76.0 $cmol(p^+) kg^{-1}$ for P5 and 66.4 to 80.0 $cmol(p^+) kg^{-1}$ for P6 respectively (Table 1). Pedons 1, 2 and 3 showed higher CEC values. In pedons 4, 5 and 6 whereas no definite trend was observed. For soil smectites similar values also reported by Jaynes and Bigham (1987) and Kapse (2007).

Reduced CECs of the fine clays

Hofmann and Klemen (1950) effect is characterized by a loss of exchangeable Li and a reduction of layer charge when Li-saturated montmorillonite was heated at low temperatures (200°-300°C). The mechanism of charge reduction advocated by Hofmann and Klemen and later by Greene-Kelly (1953) involved migration of Li ions into vacant octahedral sites until the octahedral charge imbalance was neutralized. The blocked octahedral layer position has thus no contribution towards CEC. After Lithium treatment, the CEC as well as charge are likely to reduce. Lithium saturation and heating caused the colour of dioctahedral minerals to darken. The colour of the samples under study changed from nearly off white to dark grayish brown.

As expected, all the six pedons showed reduction in CEC following Li-saturation and heating at 250°C (Lim and Jackson, 1986). The CEC measured after Greene-Kelly test is the reduced CEC (CEC_R) or the CEC contributed by the tetrahedral layer (CEC_T). The difference between the CEC of the original untreated samples and the CEC_T would give the CEC contributed by octahedral layer (CEC_O). The reduced Li exchange capacity ($LiEC_R$) values obtained by exchanging Li^+ ions with Mg^{++} ions (Fig 3.8) of P1 to P6 ranges from 31.0 to 127.0 $cmol(p^+) kg^{-1}$. Similarly the $MgEC_R$ (= $MgEC_T$) values obtained by exchanging

Mg²⁺ ions by Ca²⁺ ions for P1 to P6 ranges from 39.2 to 96.3 cmol(p+) kg^{-1} . The CaEC_R values obtained by exchanging Ca²⁺ ions by Ba²⁺ ions for P1 to P6 varies from 26.8 to 76.0 cmol(p+) kg^{-1} . Barring only two horizons, one from Kalwan and another from Nimone soils, the LiEC_R values are higher than the MgEC_R values (Table 1). This may be due to entrapment of Li in the interlayer region in a manner similar to K fixation observed in K-saturated and heated clay smectites and vermiculites (i.e. collapsed interlayers). Lithium fixation probably affected the results of Brindley and Erten (1971) who also reported charge reduction in montmorillonite (on the basis of exchangeable Li) that exceeded the octahedral charge. By washing the samples with diluted MgCl₂, the collapsed interlayers were effectively re-expanded and the entrapped Li was released, thereby giving irregular results (Jaynes and Bigham, 1987). The Mg²⁺ ions were exchanged by Ca²⁺ ions as the latter is a better exchanger than the former because clays saturated with highly hydrated cations are themselves more highly hydrated and are more difficult to coagulate than clays saturated with less hydrated cations (Weigner, 1935). Thus the zeta potential of Ca²⁺ ion is less than Mg²⁺ ion thus favouring better exchange of the latter. Further when Ca²⁺ ions are exchanged by Ba²⁺ which replaces the Ca²⁺ ions with ease (being less hydrated) resulting in higher values of CaEC_R. Differences between the reduced

values LiEC_R and MgEC_R for each sample can be attributed to Lithium entrapped in the interlayer region in a manner similar to the K-fixation observed in heated, k-saturated smectites (i.e. collapsed interlayers). The collapsed interlayers were effectively re-expanded and entrapped Li which was released by extended washing with dilute MgCl₂ solution. The MgEC_R values seem to be more stable indicator and appears to give a reliable picture and reasonably quantitative indicator for exchange studies done with clays. Similar results were also obtained by Jaynes and Bigham (1987). Consequently, the difference between total CEC (untreated) and MgEC_R (reduced) (Table 1) is hence forth used as a measure of net charge reduction following Li-saturation and heating.

Distribution of corrected CECs of the fine clays

It appears that tetrahedral charge is over estimated which may be due to the fact that the CEC contributed by vermiculite and chloride may have been included with tetrahedral charge. Some previous workers (Kapse, 2007 and Ray et al., 2009) have worked out a relationship between the content of vermiculite (V) and chlorite (Ch) from XRD analysis and the non-exchangeable Lithium CEC (LiEC_{NE}) obtained by treating mild acid to the Lithium treated and heated followed by Mg treated fine clays. Thus it was envisaged to deduct the contribution of V+Ch (towards total

Horizon	Depth (cm)	LiEC _R	MgEC _{UT} Total CEC	MgEC _R Tetrehedral CEC	MgEC _O Octahedral CEC	CaEC _{UT}	CaEC _R	Li-trapped in the interlayer =(LiECR- MgECR)
<div> <div></div> <div>cmol(p+)kg⁻¹</div> <div></div> </div>								
P1: Linga Series, Nagpur (Typic Haplustert)								
Ap	0-16	84.6	99.0	83.3	15.6	80.3	76.0	1.3
Bw1	16-44	87.0	93.1	76.3	16.8	65.0	56.6	10.7
Bw2	44-69	77.3	97.2	69.6	27.6	69.4	60.9	7.7
Bss1	69-102	78.6	99.6	69.5	30.1	74.1	60.8	9.1
Bss2	102-128	81.1	107.5	62.4	45.1	80.5	59.3	18.7
Bss3	128-150+	81.9	99.9	64.8	35.1	82.5	62.7	17.1
P2: Loni Series, Yavatmal (Typic Haplustert)								
Ap	0-14	104.4	90.0	75.2	14.8	71.9	55.4	29.2
Bw1	14-36	113.6	95.2	63.9	31.3	75.3	48.9	49.8
Bw2	36-65	127.0	114.0	69.8	44.2	88.5	42.5	57.3
Bss1	65-99	114.3	118.4	96.3	22.1	91.5	60.1	18.0
Bss2	99-144	127.0	101.5	56.4	45.2	84.0	32.6	70.6
Bss3	144-160	105.9	116.9	76.1	40.8	88.8	47.7	29.8
P3: Asra Series, Amravati (Sodic Haplustert)								
Ap	0-14	87.4	100.1	64.1	36.0	81.5	63.6	23.3
Bw1	14-40	73.2	94.2	64.9	29.4	77.2	51.7	8.3
Bw2	40-59	110.0	87.3	74.6	12.8	70.0	51.0	35.4
Bss1	59-91	102.6	75.5	70.4	5.1	61.2	56.9	32.2
Bss2	91-125	90.4	113.2	69.6	43.5	91.0	63.9	20.7
Bss3	125-150	118.4	78.3	57.9	20.4	83.1	57.3	60.5
P4: Paral Series, Akola (Sodic Haplustert)								
Ap	0-9	96.7	69.9	60.6	9.3	54.6	33.6	36.1
Bw1	9-35	130.1	77.5	57.9	19.5	69.7	42.0	72.2
Bss1	35-69	118.1	79.6	63.2	16.5	56.7	32.4	55.0
Bss2	69-105	121.1	79.5	63.9	15.7	60.4	51.9	57.3
Bss3	105-132	86.3	76.3	71.3	5.1	67.2	62.0	15.1
Bss4	132-150	120.2	72.8	70.0	2.8	63.0	33.6	50.2

contd...

P5: Kalwan Series, Nashik (Sodic Haplustert)

Ap	0-20	90.7	72.2	62.0	10.2	46.8	34.4	28.7
Bw1	20-48	110.4	77.5	75.6	1.9	47.3	37.6	34.8
Bss1	48-70	89.8	76.0	62.6	13.5	60.2	55.6	27.2
Bss2	70-88	68.3	73.6	55.7	17.9	54.3	49.0	12.7
Bw2	88-133	67.5	72.3	50.7	21.7	41.4	34.3	16.9
Bw3	133-154	18.9	67.2	39.2	28.0	30.9	26.8	-20.3

P6: Nimone Series, Ahemadnagar (Sodic Haplustert)

Ap	0-13	31.0	66.4	65.6	0.8	49.7	42.7	-34.6
Bw1	13-38	71.6	80.0	59.1	21.0	70.0	48.6	12.5
Bw2	38-55	74.5	79.2	54.5	24.7	63.6	49.1	20.0
Bss1	55-94	76.3	79.1	54.4	24.7	59.9	41.0	21.9
Bss2	94-128	92.0	67.7	52.0	15.7	70.5	36.4	40.0
Bw/Bc	128-150+	87.4	68.5	47.8	20.8	59.5	28.6	39.7

LiEC_R = reduced lithium exchange capacity ; MgEC_{UT} = Total or untreated magnesium exchange capacity; MgEC_R = Tetrahedral or reduced magnesium exchange capacity; MgEC_O = Octahedral magnesium exchange capacity; CaEC_{UT} = Total or untreated calcium exchange capacity; CaEC_R = Tetrahedral or reduced calcium exchange capacity

CEC) from the tetrahedral CEC to obtain a better relation between the octahedral and tetrahedral CEC values (Table 1, Fig. 1). This is expected to give a better representation of the tetrahedral charge and is henceforth mentioned as corrected tetrahedral CEC (MgEC_{CT}). The distribution of corrected total (or untreated), tetrahedral and octahedral CEC of fine clays is shown in figure 2 for all six pedons. Similarly the proportion of weighted mean of tetrahedral and octahedral (corrected) CECs are about 65% and 35%, respectively for P1, 63% and 37% for P2, 69% and 31% for P3, 81% and 19% for P4, 74% and 26% for P5 and for P6 69% and 31%, (Fig. 2, a to f). After

correction the proportion of octahedral CEC value has increased compared to the uncorrected one, though the tetrahedral CEC value continued to dominate the interlayer exchange complex. The tetrahedral CECs (MgEC_{CT}) decreased down the depth (Table 2) for pedons 1, 3, 5 and 6 whereas opposite trend was observed for pedons 2 and 4. The octahedral CEC (MgEC_O) on the other hand showed an increase in trend except in pedon 4 as both the data are complementary to each other (Kapse, 2007). When CEC values were corrected the percent octahedral CEC increased with depth except for pedons 3 and 4 (Table 2).



Fig. 2: Proportion of corrected tetrahedral CEC (CEC_{CT}) and octahedral CEC (CEC_{CO}) of fine clays for (a) Linga (b) Loni (c) Asra (d) Paral (e) Kalwan (f) Nimone soils in terms of weighted mean of the whole profile

Table 2. *Untreated (Total), tetrahedral and octahedral CEC and corresponding corrected CEC of fine clays*

Hori-zon Depth (cm)	Mg EC _{UT}	Mg EC _T	Mg EC _O	Vermi- culite (%)	Chlorite (%)	Contribution of V and Ch in CEC		Corrected Total CEC	Corrected tet CEC	CEC _{cr} (%)	CEC _{Co} (%)		
	cmol (p+)kg ⁻¹			d	e	f	g	h	i	j	k	l	
	a	b	c										
	V	CH	V+Ch										
cmol (p+)kg ⁻¹													
P1:Linga Series, Nagpur (Typic Haplustert)													
Ap	0-16	99.0	83.3	15.6	9	5	14	2	15.5	83.5	67.8	81	19
Bw1	16-44	93.1	76.3	16.8	11	3	17	1.2	17.7	75.4	58.6	78	22
Bw2	44-69	97.2	69.6	27.6	11	2	17	0.8	17.3	79.9	52.3	65	35
Bss1	69-102	99.6	69.5	30.1	9	4	14	1.6	15.1	84.5	54.4	64	36
Bss2	102-128	107.5	62.4	45.1	9	3	14	1.2	14.7	92.8	47.7	51	49
Bss3	128-150+	99.9	64.8	35.1	10	3	15	1.2	16.2	83.7	48.6	58	42
P2:Loni Series, Yavatmal (Typic Haplustert)													
Ap	0-14	90.0	75.2	14.8	14	0	21	0	21	69.0	54.2	79	21
Bw1	14-36	95.2	63.9	31.3	15	0	23	0	22.5	72.7	41.4	57	43
Bw2	36-65	114.0	69.8	44.2	6	0	9	0	9	105.0	60.8	58	42
Bss1	65-99	118.4	96.3	22.1	5	0	7.5	0	7.5	110.9	88.8	80	20
Bss2	99-144	101.5	56.4	45.2	9	0	14	0	13.5	88.0	42.9	49	51
Bss3	144-160	116.9	76.1	40.8	7	0	11	0	10.5	106.4	65.6	62	38
P3:Asra Series, Amravati (Sodic Haplustert)													
Ap	0-14	100.1	64.1	36.0	5	0	7.5	0	7.5	92.6	56.6	61	39
Bw1	14-40	94.2	64.9	29.4	9	0	14	0	13.5	80.7	51.4	64	36
Bw2	40-59	87.3	74.6	12.8	12	0	18	0	18	69.3	56.6	82	18
Bss1	59-91	75.5	70.4	5.1	6	0	9	0	9	66.5	61.4	92	8

Bss2	91-125	113.2	69.6	43.5	7	0	11	0	10.5	102.7	59.1	58	42
Bss3	125-150	78.3	57.9	20.4	12	0	18	0	18	60.3	39.9	66	34
P4:Paral Series, Akola (Sodic Haplustert)													
Ap	0-9	69.9	60.6	9.3	10	2	15	0.8	15.8	54.1	44.8	83	17
Bw1	9-35	77.5	57.9	19.5	6	1	9	0.4	9.4	68.1	48.5	71	29
Bss1	35-69	79.6	63.2	16.5	8	2	12	0.8	12.8	66.8	50.4	75	25
Bss2	69-105	79.5	63.9	15.7	6	1	9	0.4	9.4	70.1	54.5	78	22
Bss3	105-132	76.3	71.3	5.1	4	2	6	0.8	6.8	69.5	64.5	93	7
Bss4	132-150	72.8	70.0	2.8	10	2	15	0.8	15.8	57.0	54.2	95	5
P5:Kalwan Series, Nashik (Sodic Haplustert)													
Ap	0-20	72.2	62.0	10.2	5	2	7.5	0.8	8.3	63.9	53.7	84	16
B	20-48	77.5	75.6	1.9	8	0	12	0	12	65.5	63.6	97	3
Bss1	48-70	76.0	62.6	13.5	8	0	12	0	12	64.0	50.6	79	21
Bss2	70-88	73.6	55.7	17.9	8	0	12	0	12	61.6	43.7	71	29
Bk	88-133	72.3	50.7	21.7	8	0	12	0	12	60.3	38.7	64	36
Bw3	133-154	67.2	39.2	28.0	9	0	14	0	13.5	53.7	25.7	48	52
P6:Nimone Series, Ahmadnagar (Sodic Haplustert)													
Ap	0-13	66.4	65.6	0.8	5	0	7.5	0	7.5	58.9	58.1	99	1
Bw1	13-38	80.0	59.1	21.0	9	0	14	0	13.5	66.5	45.6	69	31
Bw2	38-55	79.2	54.5	24.7	5	0	7.5	0	7.5	71.7	47.0	66	34
Bss1	55-94	79.1	54.4	24.7	9	0	14	0	13.5	65.6	40.9	62	38
Bss2	94-128	67.7	52.0	15.7	9	0	14	0	13.5	54.2	38.5	71	29
Bw/Bc	128-150+	68.5	47.8	20.8	6	0	9	0	9	59.5	38.8	65	35

1. $MgEC_{UT}$ = Total or untreated magnesium exchange capacity; 2. $MgEC_T$ = Tetrahedral or reduced magnesium exchange capacity; 3. $MgEC_O$ = Octahedral magnesium exchange capacity; 4. V = Vermiculite (%); 5. Ch = Chlorite (%); 6. V+Ch = Vermiculite plus chlorite (%); 7. $MgEC_{CUT}$ = Corrected total magnesium exchange capacity; 8. CEC_{CT} = Corrected tetrahedral CEC (%); 9. CEC_{CT} = Corrected tetrahedral CEC (%); 10. CEC_{CO} = Corrected octahedral CEC (%)

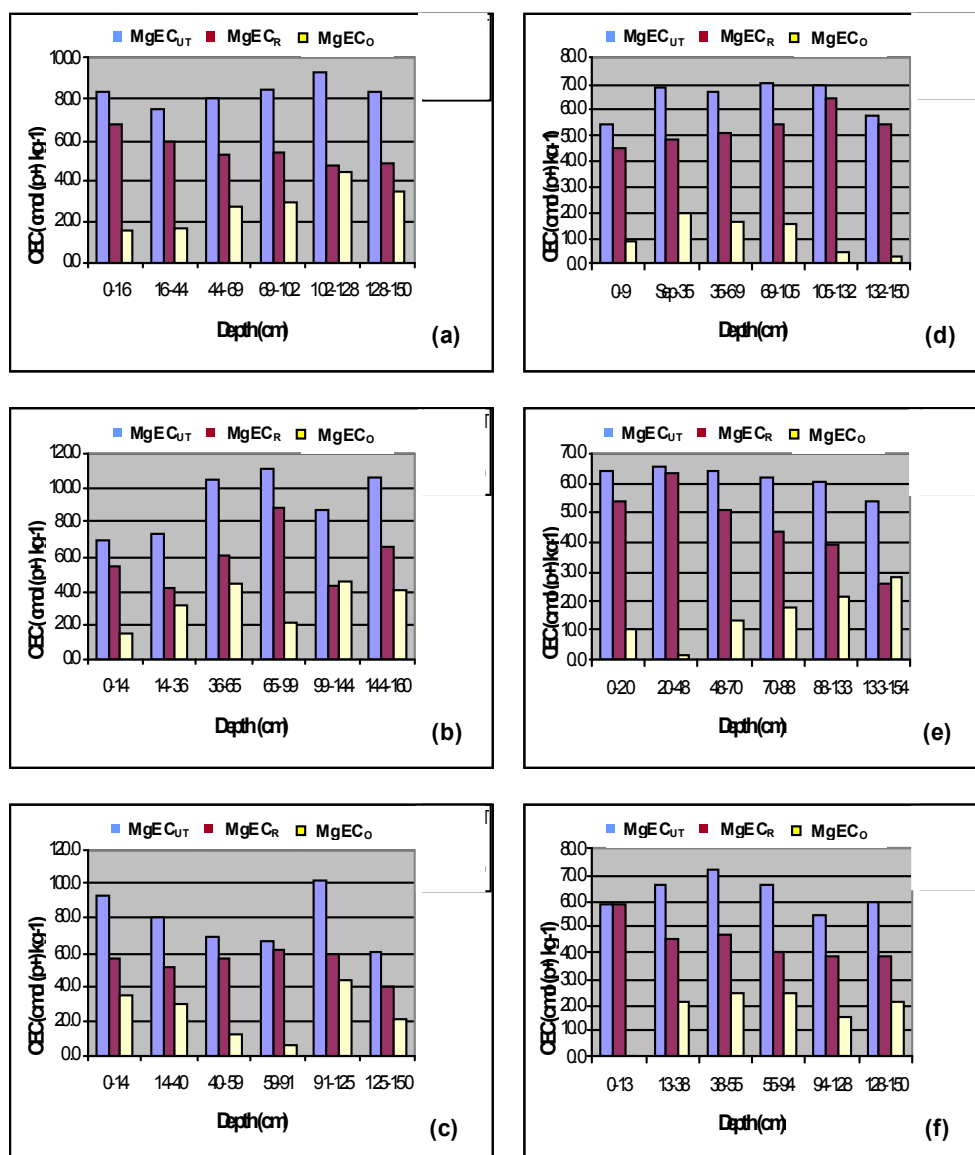


Fig.1: Distribution of corrected total CEC (CEC_{UT}), tetrahedral CEC (CEC_{CT}) and octahedral CEC (CEC_{CO}) of fine clays for (a) Linga (b) Loni (c) Asra (d) Paral (e) Kalwan (f) Nimone soil fine clays

This data shows that the tetrahedral charge is more at surface and decreases down the depth. These results are in agreement with Kapse (2007) and Ray et al. (2002).

Conclusion

Cation exchange capacity determination appeared to be a more accurate and less time-consuming approach to measure charge reduction. Because CEC reduction was found to be equivalent to octahedral charge. It might also be used to locate seat of charge and to study changes in the proportion of tetrahedral to octahedral charge during weathering.

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