

Original Paper

Role of clay cation exchange capacity, location of charge, and clay mineralogy on potassium availability in Indian Vertisols

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Abstract

Precise information on the location of charge in clay minerals and their charge density in smectite-dominant soils is rare. The present study was undertaken with three benchmark Vertisols to establish the relationship between the clay cation exchange capacity (CEC), charge density, as well as the location of charge in smectitic soil clay minerals and their relationship with potassium (K) fixation and release. Potassium fractions and their threshold levels in the Vertisols were determined by standard methods. Soils were segregated into silt, total clay and fine clay fractions for X-ray diffraction analysis and fine clay fractions were used to determine the CEC using standard methods. The Hofmann-Klemen effect (HK) and modified Greene-Kelly test was done with the fine clay to determine the CEC of the tetrahedral sheet. Subsequently, the CEC of the octahedral sheet was calculated as the difference between total CEC and the tetrahedral CEC. The results showed that ~60–64% of the total CEC is attributed to the tetrahedral layers. The tetrahedral CEC that is proportional to the tetrahedral charge density was significant and negatively correlated with K release threshold values and all fractions of K. The tetrahedral CEC contributed more toward the K fixation and release than the octahedral CEC. The study shows that the dominant presence of high-charge smectites in the fine clay fractions of these Vertisols contributed to the tetrahedral CEC and consequently to the charge density of these soils, which implied a tendency to fix K easily and release it with greater difficulty compared to soils with low-charge smectites.

Keywords: charge density; K fixation and release; octahedral CEC; smectites; tetrahedral CEC; Vertisols

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Introduction

The world's population is increasing day by day, and is predicted to reach around 9.7 billion by 2050. Therefore, it is necessary to amplify food grain production to feed the future demand of the increasing population. It is well known that the application of potassium (K) fertilizer not only increases the yield and quality of food grains, but also improves nitrogen (N) fertilizer use efficiency, which helps in increasing the yield of the crops and in reducing environmental pollution (Yin et al., 2023). The intensive cropping system used for a long time without application of K fertilizer may cause modifications in K-bearing clay minerals which adversely affect the K supply for plant uptake and, consequently, soil health (Barré et al., 2008a; Sanyal et al., 2014; Das et al., 2019; Das et al., 2022). Therefore, to manage K nutrients properly and maximize plant uptake, it is necessary to increase the effectiveness of both available soil K and applied

fertilizer K. Hence, prior knowledge of the K-supplying capacity, clay mineralogy, and layer charge characteristics are necessary, as they play an important role in K fixation and release and ultimately plant uptake and yield (Wakeel et al., 2022). There are a large number of references that deal with this topic, but very few that focus on the relative importance of cation exchange capacity (CEC) of smectite-dominant soil clays and their layer charge characteristics related to potassium availability.

Layer charge is an elementary structural property of clay minerals such as vermiculites, montmorillonites, and beidellites (Lagaly and Weiss, 1976; Lagaly, 1982). Layer charge is used to determine the physical as well as chemical characteristics of soils. Also, it indicates a mineral's ability to hold cations and to adsorb water and other polar organic molecules (Christidis, 2011). The swelling behavior of K-bearing minerals also depends on the location of charge in clay minerals. Beidellites are smectites with >50% of their total charge as tetrahedral charges, and montmorillonites are those smectites having <50% of their total charge as tetrahedral charges (Borchardt, 1989). Potassium release and fixation by clay minerals in soils are vital processes affecting plant availability (Bouabid et al., 1991; Taiwo et al., 2018; Shakeri and Abtahi, 2019). The impact of clay mineralogy on K availability

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has attracted substantial attention from mineralogists and soil scientists (Gurav et al. 2018; Gurav et al., 2019; Gurav et al., 2021).

The charge magnitude and charge location between octahedral and tetrahedral sheets are crucial attributes that impact K fixation and release by 2:1 layer silicate minerals (Florence et al., 2017). Clay minerals are the most important indicators in the assessment of K availability. The underlying phenomenon of the location of charge and charge characteristics on K availability is still unclear. Knowledge of the clay mineralogy as well as location of charge in clay minerals has significant and practical inferences for the use of fertilizers, for application and for management. To understand and interpret the results of fertility experiments, specifically in development of fertilizer recommendations, the soil mineralogy–soil fertility relationship is an elementary component (Kome et al., 2019).

It appears from review that the anomaly regarding ammonium acetate-extractable K is also related to the mineralogy of smectite, notwithstanding the fact that vermiculite and mica are the proven sources for adsorption–desorption of K in shrink-swell soils (Raheb and Heidari, 2011). The weathering of primary minerals releases various nutrients, including K^+ , to the soil solution. The *in situ* reduction of Fe^{3+} to Fe^{2+} in layer silicate minerals also occurs, and creates a climate responsible for K^+ fixation. This is because numerous changes are invoked in the physicochemical properties of the minerals in soil, i.e. swellability in water, electrical charge and surface area (Stucki et al., 1984; Shen and Stucki, 1994). The smectites participate in the exchange of K and difference with illite or mica as for example is that the exchange is more reversible due to lower charge. It has been reported that the smectites with high charge are capable of adsorbing K (Malla and Douglas, 1987). Therefore, the aim of this study was to understand whether the K dynamics in shrink-swell soils is restricted to vermiculite and micas only, or is also extended to high-charge smectites.

The present work aimed to relate the location of charge and CEC of clay minerals with K availability in shrink-swell soils (vertisols) of India. Knowledge of the mineralogical characteristics of the soil may help to develop a comprehensive understanding of K and other nutrient management in the Vertisols of India and elsewhere. The actual reason behind the anomalous behavior of neutral normal ammonium acetate-extractable K in Vertisols may also be resolved after gaining knowledge of the mineralogical characteristics of these soils. Keeping this in mind, the present work attempted to understand the relationship between the location of charge in soil

clay smectites and release threshold levels of K and different forms of K.

Materials and methods

Soil sample collection and soil analysis

The current study was undertaken on three benchmark soils and well-recognized soil series indicating that Vertisols developed on basaltic alluvium and spread in diverse agroecological regions of India (Table 1). Soil classification, depth, location, climate, and selected soil properties of these benchmark soils are presented in Table 1. The pH of the soil was analyzed in soil water suspension in a ratio of 1:2 and measured using a pH meter (Jackson, 1958). The pipette method allows determination of the particle-size distribution, which is used to determine the texture (Jackson, 1979). The soil samples were first treated with 1 N sodium acetate (AR, Merck, Germany) (pH 5.0) to dissolve $CaCO_3$, then with 30% H_2O_2 (AR, Merck, Germany) to oxidize organic matter, and lastly by citrate-bicarbonate-dithionite treatment to remove free iron oxides (Mehra and Jackson, 1960). Sand (2000–50 μm) was separated by the wet sieving method, and silt, clay, and fine clay fractions of the soil were separated by the size segregation method (Jackson, 1979). The fine clay separated from the soil was again treated with H_2O_2 to remove the organic carbon, if any, so that the contribution of organic matter toward CEC of fine clay samples was negligible. The fine clays were treated with 1 N NaCl solution and the excess salt was removed by washing with ethanol and stored for further analysis.

Potassium fractions in soil

Exchangeable K was determined by extracting the soil with 1 N ammonium acetate (1:10) and shaking for 30 min at 200 oscillations min^{-1} (Khudsen et al., 1982). The water-soluble K (WS-K) was determined from the soil-water mixture (1:5 ratio) after shaking for 1 h (Dhawan and Mishra, 1968). The non-exchangeable K was determined using two methods: (1) using 1 N HNO_3 (AR, Merck, Germany) (1:10) and boiling the soil for 10 min (Wood and Deturk, 1940); and (2) using sodium tetraphenyl borate (Schulte and Corey, 1965). Total K was determined by digesting the soil sample with HF (hydrofluoric acid) in an ETHOS-D microwave digester followed by analysis with a flame photometer (Elico, India) (Jackson, 1958).

Table 1. Benchmark soils classification, depth, location, parent material, climate, and selected properties of soil

Benchmark soil/Soil series	Depth (cm)	Classification	State	Location	Agroecological zone	pH	Soil texture			
							Sand (2000-50 μm)	Silt (50-2 μm)	Clay (<2 μm)	Fine clay (<0.2 μm)
Kheri	141	Typic Haplusterts	Madhya Pradesh	23°14'N, 79°56'E	Sub-humid (moist)	Neutral to alkaline	6–18*	30–40	45–54	27–35
Panjari	150	Typic Haplusterts	Maharashtra	21°01'N, 79°03'E	Sub-humid (dry)	Alkaline	0.2–0.6	31–44	55–69	42–54
Teligi	157	Sodic Haplusterts	Karnataka	15°37'N, 76°54'E	Semi-arid (dry)	Alkaline	4–10	21–30	61–74	33–56

*Values in the table are profile ranges.

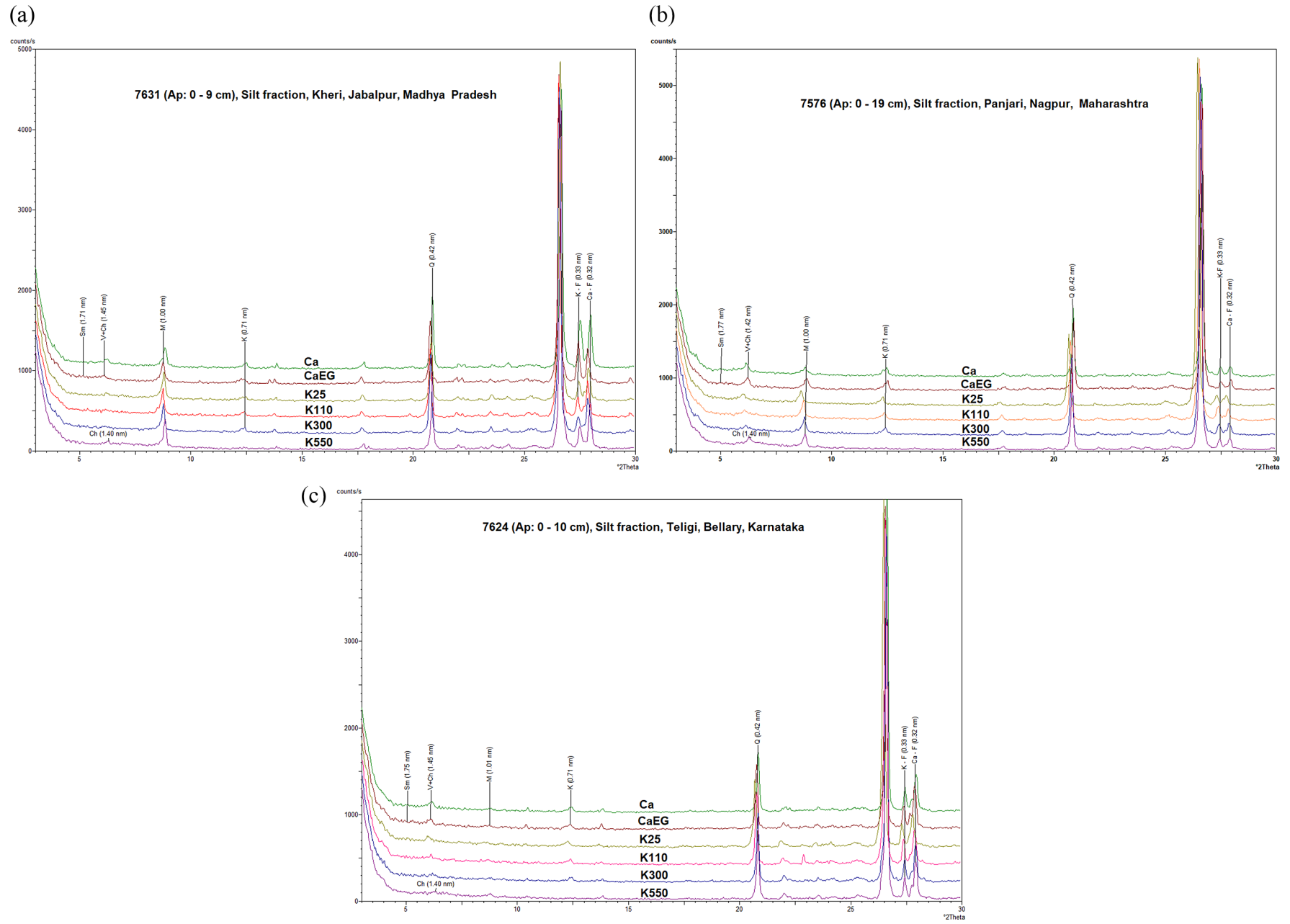


Figure 1. X-ray diffractograms of silt fractions (50–2 μm): (a) Kheri series; (b) Panjari series; (c) Teligi series. Ca = Ca-saturated; CaEG = Ca-saturated plus ethylene glycol vapor; K-saturated and heated to 25, 110, 300, 550°C; Sm = smectite, V+Ch = vermiculite plus chlorite; Ch = chlorite; M = mica; K = kaolinite; K-F = potassium feldspars; Ca-F = calcium feldspar; Q = quartz.

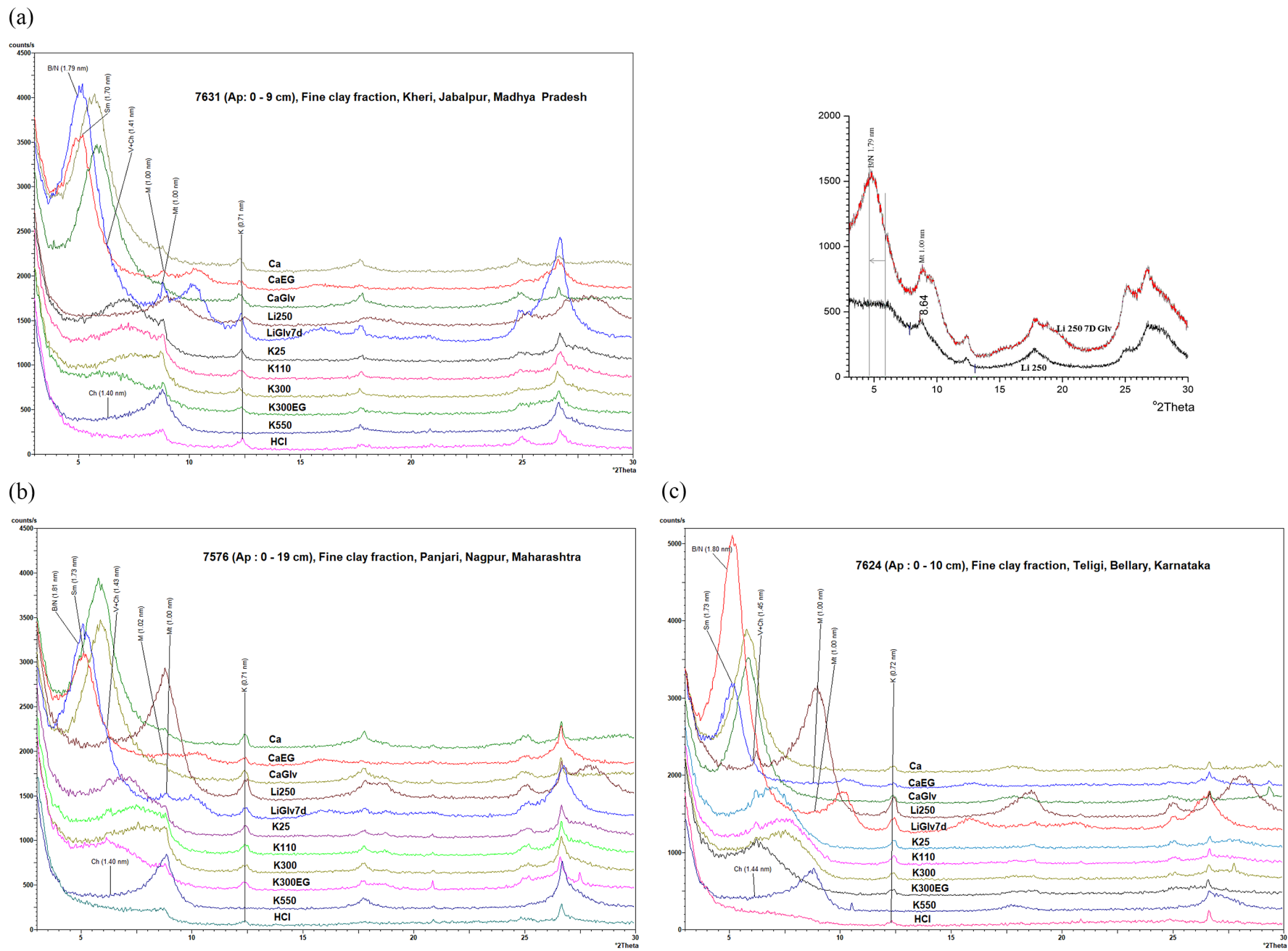


Figure 2. X-ray diffractograms of fine clay fractions (<0.2 μm). (a) Kheri series: (i) X-ray diffractograms of fine clay for Greene-Kelly test; (b) Panjari series; (c) Teligi series. Ca = Ca-saturated; CaEG = Ca-saturated plus ethylene glycol vapor; CaGLV = Ca-saturated plus glycerol vapor; Li = Li-saturated and heated to 250°C (16 h); LiGLV = Li-saturated and heated to 250°C plus glycerol vapor; K saturated and heated to 25, 110, 300, 550°C. K300EG = K-saturated plus ethylene glycol vapor and heated to 300°C; HCl = 6 N HCl-treated fine clays; Sm = smectite, B-N = beidellite-nontronite; V+Ch = vermiculite plus chlorite; M = mica; Mt = montmorillonite; K = kaolinite; F = feldspars.

Potassium release threshold level in the soil

Potassium release threshold levels (RTL) in soil were obtained using 2 g of soil (<2 mm) in a 0.01 M CaCl₂ solution by sustaining the distinct soil:solution ratios of 1:2, 1:4, 1:5, 1:10, 1:15, 1:25, 1:50, 1:100, 1:150, 1:200, and 1:400 (Datta and Sastry, 1988; Datta and Sastry, 1989). The soil sample was placed in a polypropylene centrifuge tube and polypropylene bottle and 0.01 M CaCl₂ solution was added to each tube and bottle. After thorough shaking, the stoppered tubes and bottles were kept for 24 h. The sample was centrifuged to a clear supernatant liquid which was removed and analyzed for K using a flame photometer. The content of the solution was determined by multiplying the K concentration with the volume of the solution. After equilibration, the K present in the exchangeable form was determined by extracting the same sample with neutral normal ammonium acetate. The amount of neutral normal ammonium acetate-extracted K was corrected by subtracting the amount of K present in the entrapped solution due to a portion of the solution becoming trapped in the soil after syphoning out the transparent supernatant solution (which was known from the volume of siphoned solution) (Gurav et al., 2018). The versenate titration method was used to evaluate the calcium plus magnesium in the soil solution. The K-Ca activity ratio of the equilibrated solution was calculated using the formula below:

$$AR = \frac{a_K}{\sqrt{a_{Ca} + a_{Mg}}} = \frac{c_K}{\sqrt{c_{Ca} + c_{Mg}}} = \frac{f_K}{\sqrt{f_{Ca} + f_{Mg}}}, \quad (1)$$

where, *a* is activity, *c* is concentration, and *f* denotes the activity coefficient of the ion concerned. Beckett's (1964) equation was used to calculate the activity ratio of K as follows:

$$\text{Log} \frac{f_K}{\sqrt{f_{Ca} + f_{Mg}}} = \frac{0.5\sqrt{I}}{1 + \sqrt{I}} - 0.086C_{Cl}, \quad (2)$$

where *I* is the ionic strength and *C_{Cl}* is the concentration of chloride. Curves were drawn by plotting *K_T* (solution K plus exchangeable K) against (i) activity ratio, and (ii) K concentration for all the soil:solution ratios. Threshold values for K release regarding activity ratio and K concentration were determined graphically from (i) and (ii), respectively.

Qualitative and quantitative mineralogy

The silt (50–2 μm) (Fig. 1) and fine clay fractions (<0.2 μm) (Fig. 2) were subjected to X-ray diffraction (XRD) analysis (wavelength 3–30°2θ; X-ray diffractometer from Malvern Panalytical, UK) using Ni-filtered CuKα radiation at a scanning speed of 2°2θ min⁻¹ as outlined by Jackson (1979). The identification of minerals was carried out following the procedures by Jackson (1979) and Harward et al. (1969). Semi-quantitative estimates of

clay minerals were made using the method defined by Gjems (1967) with some modifications suggested by Kapoor (1972) (Tables 2 and 3). This method uses a set of theoretical background curves which is a hyperbola. These background curves were placed under the diffractometer curves, and the hyperbola giving the best fit, at both high and low angles. This was drawn on the diffractograms and used as the background curve. Reflection intensities were estimated from the areas of the reflections lying above the background on the diffractograms by means of a planimeter. The figures obtained by planimetry of the curves were converted to indices or percentages using the total reflection area above background in the ethylene glycol-treated samples. This was first carried out on the untreated sample, and the same background curve was then used for ethylene glycol-treated samples. As a modification, the same background curve was used for both solvated and ignited samples (Kapoor, 1972). Although this technique of estimating the background is based on assumptions such as uniform scattering from samples treated by different methods, it provides reproducibility in the treatment of the curves, which in a comparative study is of vital importance. The calculation of the intensity percentage for the various clay mineral groups was carried out by the following equation, where *x* is the intensity of the individual reflection or reflection group and *y* is the corresponding intensity percentage:

$$\text{Montmorillonite} : y_1 = \frac{x_1}{\sum x} * 100, \quad (3)$$

and *x*₁ is the intensity of a (1.4–1.7) nm reflection in the glycol-treated sample, minus the intensity of a (1.4–1.7) nm reflection in the untreated sample when present; $\sum x$ is the sum of the intensities for the reflections from and including 1.0 nm to and including 1.7 nm in the ethylene glycol-treated sample, plus an eventually negative value for the vermiculite reflection.

The Hofmann–Klemen effect (Hofmann and Klemen, 1950) modified by Greene-Kelly (1953) and Lim and Jackson (1986) was performed on fine clay samples. The fine clay samples were saturated with 3 N LiCl (AR, Merck, Germany) solution (pH 7.0) and allowed to stand overnight. The fine clay samples were saturated with 3 N LiCl three more times, washed with ethanol to remove excess salt, dried, and stored for analysis. The glycerol solvation of the Li-saturated samples was prolonged for up to 7 days to perform X-ray diffraction of the samples (Fig. 2) (Ray et al., 2003) to allow sufficient time for the expansion of the smectite interlayers.

Cation exchange capacity of Lithium-250 clays (CEC_L)

The CEC of the Li-saturated fine clay samples (lithium saturated and heated at 250°C) was determined using the procedure of Jaynes and Bigham (1987). The total CEC (CEC_{Tot}) of fine clay samples was determined from the Li-saturated samples, whereas the

Table 2. Semi-quantitative estimate of clay minerals in soil silt fraction (50–2 μm)

Soils	Clay minerals (%)							
	Sm	Vm	Chl	K	M	Q	K-F	Ca-F
Kheri series	Tr*	Tr	Tr	Tr	Tr	35–47*	14–28	18–23
Panjari series	Tr	Tr	Tr	6–8	6–8	51–59	9–13	9–15
Teligi series	Tr	Tr	Tr	Tr	Tr	41–50	14–19	23–29

*Values in the table are profile ranges. Tr = traces; Sm = smectite; Vm = Vermiculite; Chl = chlorite; K = kaolin; M = mica; Q = quartz; K-F = K feldspars; Ca-F = Ca feldspars.

Table 3. Semi-quantitative estimate of clay minerals in fine clay fraction (<0.2 μm) of soils

Soils	Clay minerals (%)						
	B-N	Mt	Vermiculite	Chlorite	Kaolin	Mica	Feldspar
Kheri series	59–70	7–12	9–13*	Tr	Tr	Tr	Tr
Panjari series	64–76	5–8	10–14	Tr	Tr	Tr	Tr
Teligi series	66–81	2–7	9–13	Tr	Tr	Tr	Tr

*Values in the table are profile ranges. B-N = beidellite-nontronite; Mt = montmorillonite.

tetrahedral CEC (CEC_T) was obtained from Li-saturated and heated at 250°C, designated here as Li-250. The Li-250 samples represented the decreased CEC due to the migration of Li^+ into vacant octahedral sites, with the Li^+ compensated negative charge arising from ionic substitutions in the octahedral sheet (Gaudin *et al.*, 2004; Petit *et al.*, 2006; Petit *et al.*, 2008; Mano *et al.*, 2014; Fonteneau *et al.*, 2020). A 100 mg Li-250 fine clay sample was weighed in a centrifuge tube and about 5 mL of 1 N MgCl_2 (AR Merck, Germany) (pH 7.0) was added. The centrifuge tubes were kept in a sonicator for dispersion of the sample for ~4–5 days. After complete dispersion of the samples, these were centrifuged, and the supernatant was collected in a 100 mL volumetric flask. Three more treatments of 1 N MgCl_2 were given, and supernatant liquid was collected in the same volumetric flask. Two more washings of 0.01 N MgCl_2 were given and the supernatant liquids were collected in the same volumetric flask and the volume was made up to the 100 mL mark with distilled water. Li values in the samples were determined using an inductively coupled plasma emission spectrophotometer. This value of Li represented the reduced LiCEC (LiEC_R). The same centrifugates were saturated with 1 N CaCl_2 (AR Merck, Germany) (pH 7.0) and allowed to stand overnight as described above, and the same procedure was followed to collect the supernatant liquid. The Mg in solution was determined using an inductively coupled plasma emission spectrophotometer which represented the reduced MgCEC. These values correspond to the tetrahedral CEC (CEC_T). The octahedral CEC (CEC_O) was determined from the difference between total CEC (CEC_{Tot}) and tetrahedral CEC (CEC_T) as follows: $\text{CEC}_O = \text{CEC}_{\text{Tot}} - \text{CEC}_T$.

Statistical analysis

All statistical analyses were performed using the SPSS (10.0) software package (SPSS Inc., Chicago, USA). Simple linear regression analyses were applied to evaluate the relationship between total K (K_T) extracted with K concentration and activity ratio. The Pearson correlation coefficient examined the significant correlation between all the other parameters.

Results

Mineralogy of the silt (50–2 μm) and fine clay fraction (<0.2 μm) of soil

The XRD analysis of the silt fractions (50–2 μm) of all soils indicated the presence of smectite, vermiculite, chlorite, kaolin, mica, quartz, and feldspar. A representative X-ray diffractogram of silt for all soils is presented in Fig. 1. The presence of smectite in the silt fraction of soil is indicated by a peak at 1.4 nm that displaced to ~1.7 nm after solvation with ethylene glycol (EG). The presence of vermiculite was ascertained by the 1.4 nm peak in CaEG-treated samples and reinforcement of the 1.0 nm peak of the K-treated

samples at 25°C and 110°C. The presence of kaolin was ascertained by K-saturation, and heating up to 300°C, and this peak disappeared after subsequent heating to 550°C. The persistence of a 1.38 nm peak after heating to 550°C for 1 h indicated the presence of pedogenic chlorite. The peak at 0.42 nm indicates the presence of quartz in all samples. The feldspar peaks were detected between 0.318 and 0.319 nm for Ca feldspar and at 0.325 nm for K feldspar. Quartz is the dominant mineral in all pedons followed by feldspar, kaolin, mica, chlorite, vermiculite, and smectite (Table 2).

The fine clay fraction was mostly composed of smectite with small amounts of vermiculite and chlorites (in traces) and traces of mica, kaolin, and quartz (Fig. 2). The presence of smectite in the fine clay fraction of soil is indicated by a peak at 1.4 nm that displaced to about 1.7 nm after solvation with EG (Pal and Deshpande, 1987). On K-saturation at 25°C, the smectite peak shifted to 1.1–1.2 nm, which is characteristic of smectite. The shifting of the 1.0 nm peak of K-saturated and heated (300°C) sample on glycolation to 1.4 nm indicates that the smectites are of low charge (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) and its disappearance at 550°C and reappearance of the peak at 0.72 nm after treating with HCl indicate the presence of kaolin. The smectite in these soils was found to be a little aluminized smectite in the form of hydroxyl aluminium interlayered smectite (also known as chlorite) as evidenced by the broadening of a 1.0 nm peak in the K-saturated sample toward the low angle side after heating to 550°C. Such aluminized smectite is common in black soil (Kadu, 1997; Pal *et al.*, 2000). A weak peak of 0.97 nm followed by 0.48 nm peaks indicates the presence of a small amount of mica in these fractions.

Cation exchange characteristics

The total cation exchange capacity is a measure of the total capacity of soil to hold exchangeable cations. It involves edge, interlayer, and planar surface charges. The total CEC for clays with completely open interlayer space, like smectites and vermiculites, is equal to their edge and interlayer charges. The interlayer charge for these clays represents >90% of the total charge (Lagaly *et al.*, 1981; Bouabid *et al.*, 1991). The total CEC of soil fine clays varied from 79 to 107 $\text{cmol}(\text{p}^+) \text{kg}^{-1}$ fine clay in all the soils. The tetrahedral CEC represented the tetrahedral interlayer charge plus edge charge. In our studied soils the tetrahedral CEC varied from 56 to 69 $\text{cmol}(\text{p}^+) \text{kg}^{-1}$ whereas the octahedral CEC varied from 17 to 45 $\text{cmol}(\text{p}^+) \text{kg}^{-1}$. The data in Table 4 show that all the three soils have >50% of the total CEC as tetrahedral CEC or tetrahedral charge (Table 3). Similar results were also observed by Boubid *et al.* (1991). Borchardt (1989) reported that smectites having >50% of their total charge (tetrahedral CEC) as a tetrahedral charge are called beidellites and those <50% of tetrahedral charge are called montmorillonites. In our studied sites we found all the three soils had >50% of total CEC as a tetrahedral CEC having high beidellite-nontronite content in soil (Table 3).

Table 4. Total, tetrahedral, and octahedral cation exchange capacity of studied soils

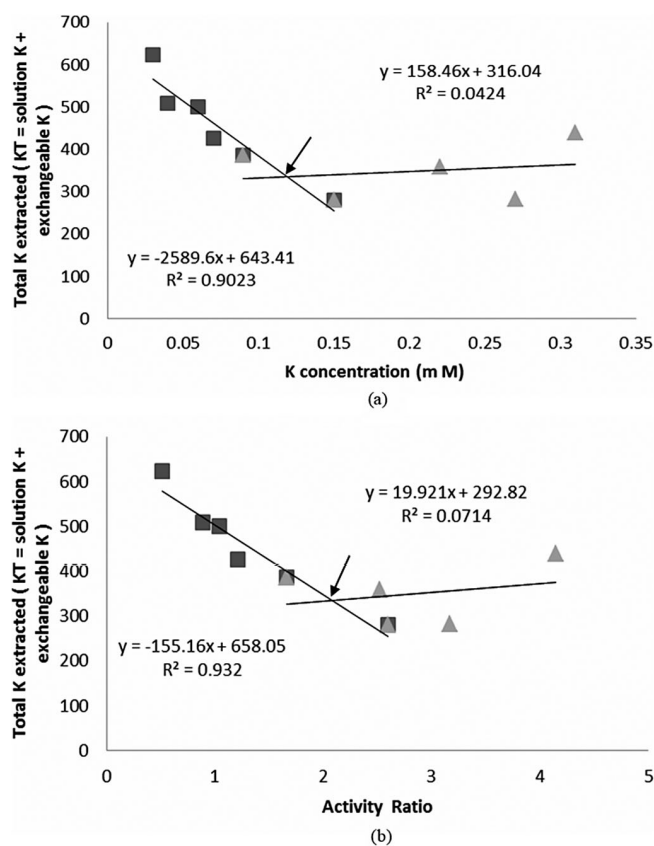
Soils	Total CEC	Tetrahedral CEC	Octahedral CEC	Tetrahedral CEC (%)	Octahedral CEC (%)
	(cmol(p ⁺) kg ⁻¹)				
Kheri series	79–105*	56–66	23–41	63–71	29–36
Panjari series	85–107	62–69	17–45	58–80	20–41
Teligi series	89–100	65–67	24–36	64–73	26–35

*Values in the table are profile ranges.

Table 5. Fractions of soil potassium (kg ha⁻¹)

Soils	WS-K	Exch-K	Non-exchangeable K		Total K
			HNO ₃ K	NaBPh ₄ K	
Kheri series	8–24*	456–661	1981–2682	1330–2078	12320–24640
Panjari series	7–20	438–735	1384–2874	1162–1705	11200–15680
Teligi series	4–22	206–560	269–1345	296–1202	5600–13440

WS-K = water-soluble K; *Exch-K = exchangeable K. *Values in the table are profile ranges.

**Figure 3.** Relationship of total K (K_T) extracted with (a) K concentration and (b) activity ratio for Kheri soil series, Jabalpur, Madhya Pradesh, India.

Relationship between location of charge, forms of potassium, K release and clay minerals

The amounts of various fractions of K and the amount of K present in the soil are important in assessing K availability (Table 5). The total K content in the Kheri series was high compared with the other series. This is because that soil has a high K-feldspar content

compared with the other two series (Fig. 1; Table 2). K transport to roots by mass flow is generally low due to its quite low concentration in soil solution (Table 5). The relationships of total K, K concentration, and activity ratio were drawn for the three soils, and the relationship for the Kheri soil series was presented (Fig. 3). K extractability was consistent up to a point (arrow marked in

Table 6. Threshold K levels for potassium release in terms of K concentration and activity ratio

Soils	K concentration (mM)	Activity ratio
Kheri series	0.043–0.11*	0.9–2.08
Panjari series	0.044–0.049	0.70–0.79
Teligi series	0.034–0.062	0.69–1.74

*Values in the table are profile ranges.

Table 7. Correlation between forms of potassium, release threshold values with total CEC, tetrahedral CEC and octahedral CEC

Parameters	CEC (cmol(p ⁺) kg ⁻¹)		
	CEC _{Tot}	CEC _T	CEC _O
WS-K	-0.230	-0.584**	0.012
Exch-K	-0.079	-0.498*	0.128
HNO ₃ K	0.017	-0.352	0.163
NaBPh ₄ K	-0.239	-0.522*	0.023
Total K	-0.169	-0.236	0.073
K concentration	0.270	-0.306	0.401
Activity ratio	-0.530*	-0.514*	-0.321

WS-K = water-soluble K; *Exch-K = exchangeable K. **Correlation is significant at the 0.01 level; *correlation is significant at the 0.05 level.

Fig. 3) below which total K extracted rose exponentially, suggesting that intermediate K was released from wedge zones (Datta, 2005).

The 'threshold K' level is simply the limiting value of the variable (plotted along the *x*-axis), below which the total K rises dramatically (Fig. 3) and becomes parallel to the *y*-axis, and can be expressed in terms of K concentration (C_t) and activity ratio (AR_t). Labile K is the amount of K corresponding to a constant value of K_T above the threshold value, which could be smoothly extracted by 1 N ammonium acetate solution. These threshold values could be used as a guidance tool for the nature of potassium-bearing clay minerals in the soil. The threshold values were significantly different for each of the three soils (Table 6).

Compared with these values, there is no similarity in release threshold K levels in terms of exchangeable K, activity ratio, and concentration for the Kheri, Panjari, and Teligi soil series (Table 6). All aspects of release threshold K levels, viz. activity ratio, and concentration, narrate the K-releasing propensity of soil and are linked with one another (Gurav et al. 2018). The Greene-Kelly test (1953) (Hofmann–Klemen effect) was done to distinguish between montmorillonite and beidellite-nontronite. The Li-saturated samples heated at 250°C for 16 h gave distinct peaks at ~0.95–1.1 nm and 1.79–1.81 nm in the fine clay samples of all soils. According to the corresponding X-ray intensities, it is suggested that the fine clays of these soils are a combination of beidellite-nontronite and montmorillonite, with a more significant proportion of the former (Fig. 2a(i); Table 3).

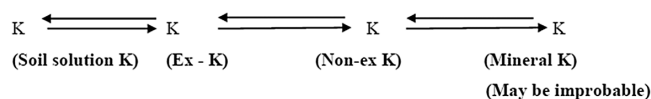
In the present study, significant negative correlations between water-soluble K/exchangeable K and tetrahedral CEC suggests that tetrahedral CEC reduces plant-available K. In contrast, the relationships between octahedral CEC, and forms of K, were not in good agreement (Table 7). This indicates that the weathering environment that produced these soil smectites tends to produce smectites with significant tetrahedral isomorphous

substitutions. The closer proximity of tetrahedral CEC to the interlayer retains K more effectively than octahedral CEC (Bouabid et al., 1991). The simple correlation between release threshold values regarding K concentration, activity ratio, and CEC was studied. It is observed that there is a significant negative correlation between total CEC and tetrahedral CEC, with threshold values (AR) (Table 7).

Discussion

Potassium availability to plants is regulated in soils by its relatively weak adsorption onto non-specific charged sites (planar), stronger (wedge zones) adsorption by the clay, and its fixation in non-exchangeable form in the structure of the clay crystals (Rao and Rao, 1996; Gurav et al., 2018). The soluble, exchangeable and non-exchangeable fractions of K are inter-related by a dynamic equilibrium. The driving force for this equilibrium is largely a function of clay composition, while the magnitude of the process is a function of clay content of soil. As growing season is limited in most cases, a high uptake rate for large crop yields can only be maintained with high flux rates of nutrients to the plant roots. Therefore, mineralogy plays an important role in potassium-supplying capacity of a particular soil (Gurav et al., 2018). The fine clay fraction of soils in the Teligi series have large beidellite-nontronite contents with a high tetrahedral CEC (Table 4). This has also been supported by the fact that the Greene-Kelly test permits one to evaluate the proportions of both tetrahedral and octahedral charges of dioctahedral smectites and vermiculites having an appreciable amount of charge in the tetrahedral sheet (Malla and Douglas, 1987). The smectites present in the fine clay fraction of Teligi soil have high tetrahedral CEC and high total CEC (Table 4). This resulted in low exchangeable and non-exchangeable K (Table 5), as well as low release threshold K (Table 6). Therefore, the smectites with a high tetrahedral CEC are likely to have more K retention (Coulombe et al., 1996; Gurav et al. 2021; Winsor, 2021). Similar results were also observed by Akhtar and Dixon (2009), who reported that soils having high charge density smectites adsorb higher K than the soils having low charge density smectites.

The fractions of soil K in the order of their availability to plants and microbes are: solution K > exchangeable K > non-exchangeable K > mineral K (Sarkar et al., 2013). Most of the K in soil is found in K-bearing micas and feldspars; only a small portion of soil K is generally held in solution or exchangeable forms. Potassium uptake by plants gives rise to the release of K from the exchangeable site, first by desorption from the exchangeable fraction and later from the interlayer of non-exchangeable K, which results in the reduction of K in the soil solution. Furthermore, there is a fundamental relationship between soil NH₄⁺ and K⁺ as one is a compliment to the other. An adequate amount of ammonium may be accountable for the exchange of K by ammonia in shrink-swell soils (Pal et al., 2012). It is envisaged that the K is released to the plant in the following manner:



However, shrink-swell soils may not follow a similar kind of dynamic equilibrium as these soils contain a considerable amount

of smectite minerals, which are known not to have K selectivity. Notwithstanding this fact, it is amply clear that smectite behaves differently in various environments depending upon its charge density (Christidis et al., 2023; Mills et al., 2023). Tessier and Pedro (1987) that the smectites with a charge of >0.45 electrons per half unit cell are high-charge smectites. Cations such as K^+ and NH_4^+ are not freely exchangeable when the layer charge exceeds this value. The higher charge developed due to the imbalance may establish a gradual affinity for the adsorption–desorption of K (Bajwa, 1980; Laird et al., 1987; Tessier and Pedro, 1987). Singh and Heffernan (2002) also deduced that the high-charge smectites were present in vertisols, where a considerable proportion of the charge originates in the tetrahedral layer, which has a large capacity to fix K^+ and NH_4^+ .

The significant negative correlation between threshold values regarding activity ratio and tetrahedral CEC indicates that high tetrahedral CEC is responsible for K fixation in these soils. However, when the charge is concentrated more in the octahedral sheet (indicating it to be dominantly montmorillonitic), the smectites (montmorillonite) owing to low charge do not adsorb and/or exchange K and it is more reversible compared with those smectites having higher charge in the tetrahedral layer dominated by beidellite/nontronite minerals (Pal and Durge, 1987). The present study also shows similar results as there is no significant correlation between K threshold values and octahedral CEC. However, as the layer charge increases, with higher charge in the tetrahedral layer, the affinity toward K also increases. The summation of tetrahedral as well as octahedral CEC in a simple correlation (Table 7) made improvements in r -value (-0.530^*) compared with those of tetrahedral CEC (-0.514^*) alone. Even though octahedral CEC inherently is not correlated with release threshold values, it is partially responsible for the total interlayer charge density, and thus K release. Malla and Douglas (1987) reported that the smectites with a layer charge equal to or greater than 0.45 electrons per half-unit cell contribute to K retention. The results are similar to those of past researchers who reported the affinity of charge toward K (Bajwa, 1980; Ghosh and Kapoor, 1982; Tessier and Pedro, 1987; Akhtar and Dixon, 2009).

Knowledge of the clay mineralogy of soil is necessary for tailored nutrient management of soils and a good understanding of other related properties, particularly those concerned with K (Gurav et al. 2018; Kome et al., 2019; Biswas et al., 2021; Gurav et al. 2021; Das et al., 2022). In the present study, the soils of the Teligi series were observed to contain high beidellite–nontronite in their fine clay fraction (Table 3) and also have a low release threshold K (Table 6). These results support the proposition that smectites entrap various quantities of K depending upon the source and magnitude of their layer charge (Alexiades and Jackson, 1965). Coulombe et al. (1996) reported that the montmorillonite and beidellite–nontronite theoretically have the same layer charge but are located in the octahedral and tetrahedral sheets, respectively. Beidellite will tend to hold interlayer cations more strongly than montmorillonite due to its proximity to negatively charged sites. Many authors have reported high tetrahedral-charged smectites in vertisols (Chen et al., 1989; Badraoui and Bloom, 1990; Righi et al., 1998; Singh and Heffernan, 2002; Vingiani et al., 2004; Chittamart et al., 2010). Furthermore, Coulombe et al. (1996) stated that there are clay minerals that show a high affinity for K due to their high layer charge. Shadfan (1983) observed that, in the Vertisols of Jordan, the K status is not only influenced by mica but also influenced by interstratified clay minerals such as mica–smectite.

The nature and relationship between the charge characteristics and clay minerals showed that smectite also affects the K contribution to the different plant available pools in the studied soils. Furthermore, beidellite species of smectite soil clays are greater fixers for added K than vermiculite clays, and fixation is not appreciable in clays consisting of montmorillonite (Ross and Cline, 1984; Ruhlicke, 1985).

Singh and Heffernan (2002) reported that the significance and location of charge in swelling clay minerals are important in the adsorption and fixation of K^+ and NH_4^+ . The present study shows a sufficient data set (Fig. 2; Table 7) which indicates that the high tetrahedral CEC in smectites may be able to fix and release potassium for its availability to plants. Furthermore, many researchers reported that consideration of clay mineralogy and quantity–intensity analysis of K in experimental sites enhances the prediction of crop yield response to K fertilization (Breker et al., 2019; Ranjbar et al., 2019). The availability, fixation, and release of K in shrink–swell soils (Vertisols and their intergrades) depend upon their K-supplying capacity, charge density, location of charge, mineralogical composition, and cation exchange capacity of smectite, etc. Differences in these mineralogical properties would bring about variations in different forms of K, and thus the K availability as well as K uptake by plants. This is the model study that explained how location of charge may help to develop a comprehensive understanding of the various properties of shrink–swell soils and also the K and other nutrient management in these soils.

Conclusions

Smectite is the dominant mineral in fine clay fractions of all three soil series in which beidellite–nontronite type may be dominating over montmorillonite type in the montmorillonite–beidellite series. All three vertisols showed a greater tetrahedral CEC than octahedral CEC. This tetrahedral CEC was directly but negatively related to K release threshold values and thus had implications for K release in these shrink–swell soils. The tetrahedral CEC maintained a significant negative relationship with all fractions of K, indicating that the increase in tetrahedral CEC resulted in more K fixation in the mineral assemblage. This fact suggests that smectites with a high tetrahedral CEC have a greater capacity to adsorb and fix K in shrink–swell soils. The results of this research may stimulate new research endeavors to provide probable reasons for K response not only in Indian Vertisols but also elsewhere, even though soil test values for available K are high. This suggests a need to revisit the existing neutral normal ammonium acetate method for determining available K concerning their location of charge characteristics and mineralogical properties, which can serve as the basis for tailored K nutrient management strategies in these soils. This information will also be helpful for soil testing laboratories and fertilizer industries to modernize agriculture with the latest knowledge. Additional research needs to be conducted to determine the significance of charge characteristics on K fixation/release in soils with different mineralogical classes, considering other factors such as conventional potassium management and crop uptake.

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