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Nano-Effect of Clay minerals on Human Papilloma Virus-Warts

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Abstract: *Clay minerals form 16% of earth minerals and their micro structure make it useful materials used in different medical fields because of it adsorption or absorption for different organic materials. The object of this research is to detect antiviral efficacy of clay minerals on human papilloma virus. Types of Clay mineral structures, major elements and trace elements were determined by X-ray, flame photometer and atomic absorption analysis respectively. Four types of Clay minerals were topically applied against warts of HPV. Montmorillonite showed the best effect on the warts (remove 100% of warts). Mixture of kaolinite, montmorillonite, and illite gave lower effect (remove 80% of warts). Kaolinite alone showed moderate effect (remove 66.6% of warts) whereas Kaolinite with organic materials showed low effect (remove 22.2% of warts). More studies are needed to study the effect of clay minerals against others HPV types which cause cancerous warts in a high ratio all over the world.*

Keywords*: Clay minerals, M HPV-warts, Kaolinite, Montmorillonite,*

Clay minerals make up about 40% of minerals in sedimentary rocks andregard as the main constituent of soils representing 16% of earth minerals (Skinner *et al.,* 2019; Khoury, 2002). Clay minerals regard as a nano structure because it consist of grains less than 2 µm in diameter arranged in sheet-like structure (tetrahedral and octahedral cations) originated to form sheets or layers (Potts, 1987; Choi, 2005). The main classes of clay minerals are; Kaolinite (two layer minerals, T-O), the Smectite, such as montmorillonite, illite (three layer minerals, T-O-T), and the Chlorite (four layerminerals, T-O-T O T-O-T) (Beall and Goss, 2004). Clay minerals have been used for a long time in many applications, such as industrial, agricultural, pharmaceutical and medicinal applications (Kenzevich, 2008; Khurana *et al.,* 2016). From medicinal view, clay minerals were used internally and externally. External applications includes, both dermopharmacy and dermacosmotics, treatment of many skin diseases such as eczema, psoriasis, rashes, acne, healing of wounds and burns (Gomes and Silva, 2007; López-Galindo *et al.*, 2011).

Montmorillinite can absorb water molecules in between the T-O-T sheets causing expanding of clay minerals when they are exposed to water giving biological activities of adsorption for organic materials (Karata *et al.*, 2017; Trckova, *et al.*, 2004). Kaolinite not absorb water molecules, thus not expand and used in ceramic industry (Awad *et al.*, 2017). Illites are non-expanding clays due to the presence of cations such as Mg and Ca that prevents the entrance of water molecules in to the structure, but these cations can be substitute with K, and Na to give new biological applications (Garrison *et al.*, 1999).

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Many studies were explained the nano ability of clay minerals to adsorb or absorb viral ions proteins and genomes (Duarte-Silva *et al.,* 2014; Haydel *et al*, 2007). Other studies referred to the effect of nano silica and their neural charges, large surface area that allow binding to different viral trace elements, proteins and nucleic acid (Luo *et.al*, 2003; Beck, 2001). The nano crystal sites of clay minerals contain high surface in small area (800 m^2/ gm), thus the clay minerals have a large sorption and ionic exchange capacity (Homoky *et al*., 2016; Khoury, 2002). High consideration was given to the antiviral action of the trace elements of clay minerals which bind by different nano mechanisms at several sites of viruses such as, proteins (enzymes) and nucleic acids (Gyawu, *et al*, 2008).

Human papillomavirus (HPV) belong to double-stranded DNA viruses with more than 100 genotypes. It is includemany types that cause cancers. Each year it causes 450,000 infectionwith mortality reached 50% (Parkin, 2006). HPV causes high impact on women causing cervical cancer worldwide. It was recorded that 75% of patients ages 15 to 49 years infected with one genital HPV in the united states (Lowndes, 2006). HPV stimulate formation of warts which causecause frustration to patients (Meinek *et al*, 2002). There are many types of warts which formed in different sites of the body such as flat, plantar, coalesced mosaic, filiform, periungual, anogenitaland oral warts (Brederode and Engel, 2001).

HPV genotype belong to papillomaviridae with 12 genera, beta HPV cause epidermodys plasticverruciform is in nono-genital HPV-lesion (Chang, *et al,* 2002). HPV-1,2,4,27,57 and 65 are associated with common warts whereas HPV-3, 10,28 and 41 are found in flat warts (Payal, *et al*, 2006; Lipke, 2006). Many different trails seek to treat HPV warts including chemicals, pharmaceutical, surgical and physical treatments but not gave complete recovery. Almost all treatments (Surgery, Lazer, Carbon Dioxide (CO2) Laser , Pulsed Dye Laser, Glutaraldehyde, Formaldehyde, Nitric acid, Nitrogen, Folic acid, formic acid, salicylic acid, cryotherapy, Garlic Extracts, Cantharidin, Hot Water, Exothermic Patches, Ultrasound Hyperthermia, Radiofrequency Ablation, Bleomycin, Podophyllin, Podophyllotoxin, Immunotherapy such as; Oral Zinc Sulphate, intralesionalinjection of interferon, 5-Fluorouracil, Cimetidine, Levamisole, Imiquimod, Vaccines and Antiviral Drugs such as; Cidofovir) have low rate effect but companioned with pain, side effects, and high costs (Bhat *et al*., 2001).

The importance of this study comes from the using of safe, available, cheap and non toxic clay minerals which have been used all over the world as cosmetics and remedies. This research aim to study the possibility of using clay minerals as antiviral agent to remove warts caused by HPVfor the first time. Identification of HPV-warts types, classify their response to clay minerals application and interpretation of nano-mechanical action of clay minerals against HPV-warts.

Materials and Methods

Clay minerals preparation

Clay minerals were collected from three sites in Jordan; Dead Sea, Azraqu, and Mahis in addition to Al-shwra site in Musol/ Iraq. Clay minerals were crushed, milled, and stored in dry place until separation.

Separation of clay minerals

There are different methods for separation such as pipette method and hydrometer methods (Kaufman, 2006). A pipette method was used for the determination of sand, silt and clay content. The details of the pipette procedures of separation are as follows: From the origin sample 15 gm of clay minerals was taken and placed in graduated cylinder (1000 ml). Na-hexametaphosphate (calgon) as a dispersing agent

5.5 gm was added then the cylinder completed with distilled water and the mixture was stirred. The sample was placed for 24 hours to be sure that flocculation does not occur, at the room temperature (approximately 24 °C). The sample was mixed with a plunger unit homogeneity, the moment that mixing stop is time zero and the analysis has started. The initial aliquot from the cylinder (after one minute) was removed using 20ml pipette. Depending on standard table the size fractionation was completed (Van and fripiate, 1979).

Determination of clay mineral types by X-ray Diffraction

Clay minerals were analyzed by X-Ray diffractometer (Philips PW 1390) to determine the chemical structure of clay and the main components of clay in each site. Determination of clay minerals is depending on diffraction and Braggs low. X-rays can be diffracted from component of crystalline clay mineralswhich have regular atomic structure. Braggs low ($n\lambda=2d \sin\theta$), gathers many factors including the d-spacing (d) in angstrom, the angle of diffraction (2-theta angle) in degree, and the wave length of X-ray (λ). The diffraction pattern can determine an unknown elements or identify the atomic structure of known mineral (Potts, 1987).

Chemical digestion of clay minerals

Chemical analysis by using digestion pump methods was performed to determine the major and the trace elements in the four types of clay minerals, this method include the following steps: From each clay sample (Haswa, Iraqi, Azraq and Dead sea) 0.2000 gram was placed into specific container (resistant to high temperature, pressure and chemical reaction of strong acids). For each sample 5 ml of hydrofluoric acid and 5 ml of aquaregia were added. The container was screwed well and inserted into the steel-pump. The steel-pump then placed inside the oven at 105 °C for 2-3 hours. The pump was cooled and transferred into volumetric flask which containing three grams of boric acid (to neutralize the acidity of acids). Add 100 ml of distill water and shacked well. From each sample 10% and 1% dilution were prepared.

Determination of major and trace elements in clay minerals types

Standardization

Both Na and Kand other major elements percentages in the four types of clay minerals were determined using six materials as standard criteria; Nose, Granite, Millinite, Corderite, Tonalite, and Garbo. The percentage of Na and K and other major elements were determined byflame photometer (Sherwood-159). By using The percentages of other major elements (Fe, Ca, Mg, Mn, Si, and p as oxides forms) and the trace elements in ppm (Cu, Co, Cr, Zn, Ni, Ba, Pb, Sr, and Rp) were determined by the Atomic absorption spectrometer (AAS320N UK) following the procedure described by Hutchison (1974).

Patients questionnaire

Eight patients infected with coetaneous HPV-warts were subjected to this study in the lab of microbiology/college of Science/university of Jordan/Amman from July 8/ 2008 to October 11/ 2008. The patients questionnaires were taken from patients including; Patient number, Date of sampling, Address, Region, Age, Sex, Marital state and Job.

Warts characterization

There are many types of benign warts (nongenital warts) include; common, periungual, flat, and filiform or planter warts, based on location and shape (Sturlberg and Hutchinson, 2003). Each wart was characterized, measured and recorded.

Warts treatment

In-vivo application of clay minerals types on warts-HPV

From each type of clay minerals 2 grams were mixed with sufficient distillated-sterilized water enough to form semi-solid poultice for each wart, eachwartcovered with the clay poultice and lefttodry thoroughly (15-30 min), the solidified poulticethenrubbed completely to remove all poultice away. The sizes, elevation and shape of each wartwastested each week, if the warts were not recovered repeat the application once again for 2-6 weeks.

Results and Discussion

Determination of clay mineral types by X-ray

The result of x-ray analysis revealed four types of clay minerals according to sites of collection (Table 1).

Table 1. *Types of clay minerals according to their sites*

Site of collection	Type of clay mineral
Jordan/Azraq	Kaolinite
Jordan/Haswa	Montmorillinite
Jordan/Dead sea	Kaolinite and Organic materials
Iraq/Mosul/Al-showra	Kaolinite, Montmorillinite, and Illite

Determination of major and trace elements in clay minerals types

Flame photometer analysis

By using flame photometer analysis the percentage of Na, K and other major element were determined according to standard criteria.

Standardization

Both Na and K percentages in the four types of clay minerals were determined using five materials as standard criteria (Table 2).

Table 2. *Sodium and K content in standard materials and their correlation coefficient*

Materials	Na %	K%	r- ratio
Nose	7.33	8.82	0.998
Granite	3.0	5.06	
Millinite	5.68	3.36	
Corderite	2.85	2.67	
Tonalite	3.77	2.44	
Gabro	1.35	0.84	

According to standard criteria the percentages of Na and K were determined in the four types of clay minerals (Table 3).

Atomic absorption photometr analysis

The percentages of major elements (Table 4) (Fe, Ca, Mg, Mn, Si, and p) as oxides forms and the trace elements (Table 5) in ppm (Cu, Co, Cr, Zn, Ni, Ba, Pb, Sr, and Rp) were determined using atomicabsorption.

Patients questionnaires

Patients questionnaires were collected and arranged as in Table 6.

Warts characterization

From 8 patients, 37 warts of different patients were characterized and classified according to their features (Hoon *et al*, 2005; Leman and Benton, 2000) (Table 7). Verruca vulgaris (common warts) were found in 7 patients infected with HPV whereas only one patient showed filiform wart type.

Application of clay minerals types on HPV-warts

The 37 warts were classified into four groups and treated with the four types of clay minerals (Table 8). Montmorillinite (Jordan/Haswa) gave the best effect (100% recovery)(Fig. 1). Kaolinite, Montmorillinite, and Illite (Iraq/Mosul/Al-Showra) gave lowereffect (80% recovery of warts) (Fig. 2). Kaolinite (Jordan/Azraq) revealed moderate removing (66.6%) of warts (Fig.3). On the other hand Kaolinite and organic materials (Jordan/Dead sea) revealedthe lower percentage of wart removing (22.2%)(Fig. 4). Different removing of HPV-warts occurred within 2-6 weeks.

This ability of clay minerals to react with HPV and any other biomass is related to four main features;The first one is the presence of different clay classes, each class has its specific

Table 3. *Sodium and K content in the four types of clay minerals using flame spectrophotometer*

Site of collection	Type of Clay mineral	Na (%)	K%
Jordan/Azraq	Kaolinite	0.35	1.40
Jordan/Haswa	Montmorillinite	2.82	2.25
Jordan/Dead sea	Kaolinite and Organic materials	4.06	1.81
Iraq/Mosul/Al-showra	Kaolinite Montmorillinite, and Illite	0.355	1.19

Table 4. *Contents of major elements in the four types of clay minerals using atomic absorption photometer*

Type of Clay mineral	Major elements					
	Fe	Ca	Mg	Mn	Si	P
Kaolinite/Jordan/Azraq	7.82	0.12	0.39	0.007	33.44	0.001
Montmorillinite/Jordan/Haswa	8.12	4.62	5.22	0.034	24.99	0.098
Kaolinite and Organic materials/Jordan/Dead sea	2.15	13.59	5.63	0.037	55.77	0.091
Kaolinite, Montmorillinite, and Illite (Iraq/Mosul/Al-showra)	4.45	17.99	3.718	0.094	61.77	0.10

Table 5. *Percentages of trace elements determined in the four types of clay minerals using atomic absorption photometer.*

Type of Clay mineral	Trace elements								
	Cu	Co	Cr	Zn	Ni	Ba	Pb	Sr	Rp
Kaolinite (Jordan/Azraq)	0.0	0.15	0.33	0.13	0.11	0.0	0.15	0.0	0.0
Montmorillinite (Jordan/Haswa)	0.0	0.12	0.88	0.11	0.20	0.0	0.10	0.0	0.0
Kaolinite and Organic materials (Jordan/Dead sea)	0.0	0.40	0.19	0.10	0.60	0.0	0.20	0.0	0.0
Kaolinite, Montmorillinite, and Illite (Iraq/Mosul/Al-Showra)	0.0	0.01	0.38	0.18	0.20	0.0	0.40	0.0	0.0

Table 6. *Patients questionnaires*

Patient number	Date of sampling	Address	Infected region	Age/year	Sex	Marital state	Job
1	8.7.08	Madaba/Jordan	Left hand	20	Male	single	student
2	14.7.08	AmmanJordan	Left hand/finger	34	Male	Married	laborer
3	14.7.08	Azraq/Jordan	Head front	36	Male	single	Securityman
4	8.10.08	AmmanJordan	Left hand/finger	51	Male	single	Secretariat office
5	9.10.08	Al-Aqaba/Jordan	Right hand/finger	27	Male	Married	Cleaning laborer
6	11.10.08	Azraq/Jordan	Head	40	Male	Married	Securityman
7	14.10.08	AmmanJordan	Left leg/thumb	48	Female	Married	House keeper
8	24.10.08	AmmanJordan	Rright leg/thumb	6	Female	single	student

Table 7. *HPV-Warts characterization*

Patient Number	Type of warts	Sites of warts	Number of warts	Diametermm	Previous treatment
1	Verruca vulgaris (Common warts)	Left hand finger	2	5-10	Lazer, Surgery, Nitric acid
2	Verruca vulgaris	Left hand finger	3	5-12	Nitrogen Folic acid
3	Filliform	Head front	3	1-2	Lazer, Surgery, Nitric acid
4	Verruca vulgaris	Left hand finger	1	4	none
5	Verruca vulgaris	Right hand finger	4	1-5	Lazer, Surgery, Nitric acid
6	Verruca vulgaris	Head	2	4	Nitrogen Surgery
7	Verruca vulgaris	Left leg thumb	21	2-12	Lazer, Surgery, Nitric acid, Nitrogen, Folic acid
8	Verruca vulgaris	Right leg thumb	1	2	none

Table 8. *Percentage effect of clay minerals types on HPV-warts within 2-6 weeks*

Type of clay mineral	Number of tested warts in each group	Warts recovery	
		Number	%
Montmorillinite (Jordan/Haswa)	9	9	100
Kaolinite, Montmorillinite, and Illite (Iraq/Mosul/Al-Showra)	10	8	80
Kaolinite (Jordan/Azraq)	9	6	66.6
Kaolinite and Organic materials (Jordan/Dead sea)	9	2	22.2

chemical structures and thus give different mechanism to react with different organic materials in eukaryotic, prokaryotic organisms and viruses (Schiffenbouer and Stotzky, 2005). Second feature of clay minerals is the possibility of elements substitution in the clay components (Al for Si and Mg for Al) (Skinner *et al.,* 2019), this create negative charges which allow the interlayer cations such as Na, K, Mg and Ca to enter and cause new binding with virus. This feature make clay minerals as a good reactant with many biological system (Lipson and Stotzky, 2002; William and Moll, 2001). Third is the presence of silica (with its neutral charges) as a nano structure in clay minerals create an attractive power for viruses and other organic materials (Blaser *et al.,* 2019). Fourth character of clay minerals is their high content of trace elements which may react with viral organic materials and cause different modifications in viruses (Charlotte *et al.,* 2005). Trace elements types in clay minerals may reach 29-34 types. The most important elements are; selenium, zinc, copper, cobalt, manganese, molybdenum, Iron and nickel (Melinda *et. al*, 2004).

This study showed that topical application of Montmorillinite-(Jordan/Haswa) poultice on HPV-warts gave high effect with 100% of recovery (Fig. 1). This ability is due to its expanding feature when mixed with water and when water is removed by drying the size of Montmorillinite-poultice is considerably reduced and this reduction creates high absorption power lead to pull free viral episomes from the warts cells into the nano-structure of Montmorillinite. This feature was illustrated by Schiffenbouer and Stotzky, 2005. In addition to this physical absorption power, there is a chemical reaction represented by the huge number of neutral charges in nano-structure of silica in side Montmorillinite which react with different cations of viral proteins and genome. Borrego-Sánchez *et al.,* 2018; Bogden, and Oleske, 2007 recorded that this chemical reaction occur between silica and organic materials.

In this studyflame spectrophotometer and atomic absorption photometer analysis of montmorillonite showed the presence of both major and trace elements with different ratios (Table 3, 4, and 5), major elements include; Na, K, Fe, Ca, Mg, Mn, Si and P. (Marchetti *et al* in 1999; Iannuccelli *et al*., 2015) also revealed that major elements; Mg, Mn gave inhibition effect on poliovirus. The trace elements in the four types of clay minerals in this study represented by Co, Cr, Zn, Ni, and Pb. These trace elements cause impact on viral proteins and genomes by creates many reactions leads to nano- modification of organic materials of HPV and thus block the genetic replication and protein assembly of HPV and end up to warts vanishing. These result come in agreement with Chaturved *et al*, in 2004; Iannuccelli *et al*., 2015; Marchetti*, et al* in 1999 studies which revealed that most trace elements have biological applications of clay minerals. Different studies showed that the trace elements such as; zinc, selenium, manganese may effect on viral proteins or genomes in many pathogenic viruses such as; HPV, Herpes simplex virus Varicella-zoster virus, Hepatitis A, B, C, D and E viruses, Human immune-difficiency virus (HIV), Measles virus, Semliki forest virus, Ebola virus, Coxsackie B virus, Influenza virus, Avian myeloblastosis viruses, and Polioviruses (Bogden, and Oleske 2007; Johanson *et al*, 2006; Chen *et al*, 2006; Charlotte *et al*, 2005; Lee *et al,* 2003; Goyal, and Gerba, 1979; Yoshinaka *et al,* 2000; Meschke *et al,* 2003; Moore *et al*, 1981).

The second type of clay mineral that gave 80% efficiency against HPV-warts was the mixture of Kaolinite, Montmorillinite, and Illite (Iraq/Mosul/Al-Showra). The ratio of recovery was reduced to 80% compared to Montmorillinite-Jordan/Haswa. This reduction may be due to the presence of mixture of three types of clay minerals and each type has its specific nano-mechanism. Kaolinite clay is a non-expanded when mixed with water whereas Montmorillonite expanded when mixed with water and adsorb or absorb HPV from warts.Illites are non-expanding clays due to the presence of cations such as Mg and Ca that prevents the entrance of water molecules in to the structure (Garrison *et.al*, 1999). In addition to that both Montmorillinite and Illitespossess major and trace elements (Table 3,4 and 5) which interfere with HPV replication and assembly. Previous study recorded that Montmorillonite and Illites are used as cosmetics to recover lipodystrophies, acne and cellulite, from skin due to their large area, plasticity, nano size, and no toxicity (Park *et al.,* 2016; Carretero, 2002). The third type (kaolinite) gave 66.6% of recovery, this reduction in the efficiency may be because kaolinite is not expanded when mixed with water thus its effect on HPV depend only on reactions between neutral charges of silica and HPV proteins and genome in addition to the effect of major and trace element (Table 3, 4 and 5) on HPV proteins and genome. Similar results but on other viruses were recorded in previous study (Trckova *et al*, 2004).

The fourth type of clay minerals (Kaolinite and organic materials) showed the lower effect against HPV-warts (22.2%). The reason may be due to the non-expanding feature of kaolinite, thus absorption not occur and the effect of major and trace elements were affected considerably by the presence of high ratio of organic materials which react with kaolinite elements and prevent most reactions between major and trace elements of kaolinite and human papilloma viral organic materials. Previous study showed that each of kaolinite, montmorillonite, and illite can inactivate bacteriophage (type T2) and poliovirus (Type1) by pulling viruses on clay particles. There are many types of viral removal mechanisms such as, activation of a clay-cation-virus bridge, high capacity of Surface exchange, change of particle size and shape, and substitution of isomorphous which affect the virus-adsorption activity on a clay and adsorption reached its maximum within 15 minutes (George *et al* 1968). Another study provided essential information for the ability of kaolinite and bentonite to remove viruses by adsorption from aqueous solutions (Vasiliki I and Constantinos, 2010)

Conclusions

This study recorded for the first time that clay minerals have a considerable nano effect on HPV-warts through their topical application. Application of Montmorillinite alone give high efficiency against HPV which leads to total recovery of HPV-warts. Thus Montmorillinite can be used as a safe, cheap, painless, available and efficient antiviral agent against HPV-warts. Mixture of Montmorillinite, kaolinite and Illite also can be used to get rid of most HPV-warts. Kaolinite alone also can be used to remove more than half of HPV-warts. The presence of organic materials with kaolinite reduced the action of kaolinite toward the HPV particles or genomes and reduce its efficiency against HPV-warts. This study open the door for future application of different clay minerals against different types of cancerous genital-HPV-warts that

Conflict of Interest

Author declares that he introduced this article (Nano-Effect of Clay minerals on Human Papilloma Virus-Warts) to Clay Research and that he has read/ approved the final version of the paper and understood that the full responsibility for all presented data in the article belongs to him, and he is solely responsible for any conflict of interest (related to subjects included in his work, financial, consultant, institutional and other aspects).

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Soil Chemical and Mineralogical Characteristics under Major Land Use Systems on Upper Brahmaputra Valley of Assam

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Abstract: *Study of two typical pedons representing forest and tea growing soils of upper Brahmaputra valley of Assam showed that soils were very deep, moderately well drained, brown to yellowish brown in colour with redoximorphi features like mottles in the subsoil. The soils were acidic and the pH of the soil ranged from 4.5 to 5.3. The surface soil under tea was more acidic (pH 4.5) than the soils under forest (pH 4.8). However, pH of the subsurface soil under tea was higher than that of the soils under forest. The organic carbon content was relatively higher in forest soil (12.7 g kg^{-1}) than the tea soil (5.6 g kg^{-1}). The CEC of clays indicated its association with the mineralogical composition of clays. Exchangeable Al^{3+} contributed largely towards exchangeable acidity and it is high at the surface under tea soils and at the sub-surface under forest soils. The forest soils are high in exchangeable acidity, pH dependent acidity and total potential acidity. The mineralogical studies indicated the dominance of kaolin followed by mica, smectite and vermiculite in both the soils. The study also suggested that kaolin was relatively higher in tea growing soil whereas the forest soil had relatively higher mica, smectite and vermiculite. There is no significant variation both in chemical and mineralogical properties.*

Keywords: *Clay mineralogy, Forest soils, Soil acidity, Soil characteristics, Soil organic carbon, Tea soils.*

The natural resources of our country is under severe threat due to alarming increase in population including both human and cattle resulting in severe degradation with large scale change in the land use/land cover of the country. This is again aggravated due to the competing demands and needs of the society which imparts tremendous pressure on the limited and shrinking land resources viz., soil, water, forest vegetation, bio-diversity etc. Deforestation for the purpose of agriculture is a common practice in the undulating and hilly landscapes of north-eastern states. To conserve the precious natural resources, it is imperative to have the soil resource data base and maintain the health of these natural resources for its sustenance in terms of better agricultural production.

In north-eastern India, tea, coffee, rubber etc. have been traditionally grown adjoining to the forest on undulating uplands and hill slopes. The luxuriant growth of the forest vegetation may influence the soil characteristics due to the differences in uptake and release of different nutritional elements through leaf, litter fall. Initially, the tea growing areas were mostly under forest and gradually with the increase of population, deforestation took place which ultimately makes room for tea cultivation in these areas.

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In Hollongapara Reserve forest at Mariani, Jorhat district, Assam on upper Brahmaputra valley, it is observed that tea grows well surrounding the forest areas which in fact helps in protecting the dense forest area. As the area is under the same climatic condition and parent materials, it is expected that the changes in vegetations may definitely have some impact on soil characteristics. Several workers studied the tea growing soils (Ray and Mukhopadhyay, 2012; Karak *et al.* 2015; Borah 1996; Gangopadhyay *et al.* 2016) and also forest soils (Gangopadhyay *et al.* 2011; Nayak *et al.* 2002; Gangopadhyay *et al.* 1999) in the north-eastern part of India. However, the information of the soils supporting tea and forest in a contiguous area especially in the upper Brahmaputra valley of Assam is meager. Hence the present study has been undertaken to characterize the soils on upper Brahmaputra valley of Assam under two widely occurring land use systems.

Materials and Methods

The study area represents gently sloping undulating upland of Hollongapara Reserve Forest covering 11.57sq.km area and surrounding tea growing areas occupying 13.24 sq. km area (Das *et al.*, 2019) by 2011 at Mariani, Jorhat district, on the upper Brahmaputra valley of Assam (Fig. 1). The soils mostly developed from the alluvium carried and deposited by the river Brahmaputra. The geological formations are mainly sedimentary rocks with sandstone, shale and clay of the Surma, Tipam and Duptila groups (Krishnan, 1982). The study area belong to the humid subtropical climate with high annual precipitation of 2250 mm. The mean annual maximum and minimum temperature is 28.7°C and 17 °C. The soil moisture and temperature regimes are 'Udic' and 'Hyperthermic' respectively.

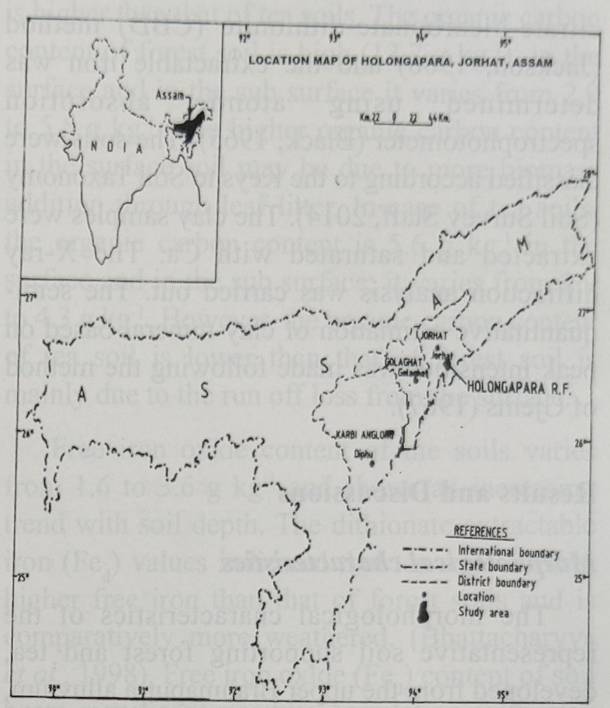

Fig. 1. Location map of the study area

During the reconnaissance soil survey work at 1:50,000 scale, 20 soil profiles under both the land uses were studied at Mariani, Jorhat district, Assam. Out of that, one typical representative soil profile from Hollongapara Reserve Forest area supporting luxuriant growth of Hollong trees and one adjoining tea growing areas were considered for the present study following the standard methods as outlined in the Soil Survey Manual (Soil Survey Division Staff, 1995). The pedons were exposed under two different land use systems in a contiguous area for morphological studies and the horizon wise soil samples were collected, air-dried and processed (2 mm sieve) for various analyses following standard methods (Black, 1965; Jackson, 1973).

Total potential acidity of soil ($BaCl_2$-triethanolamine buffered at pH 8.0) was determined following the method of Peech *et al.*, (1962). Exchangeable acidity and exchangeable Al^{3+} was determined by leaching the soil with unbuffered 1(N) KCl solution (Black, 1965). Acidity due to variable charge (pH dependent) was computed by difference between total potential acidity and exchangeable acidity. The free oxides of iron in soils were determined by citrate-bicarbonate-dithionite (CBD) method (Jackson, 1966) and the extractable iron was determined using atomic absorption spectrophotometer (Black, 1965). The soils were classified according to the Keys to Soil Taxonomy (Soil Survey Staff, 2014). The clay samples were extracted and saturated with Ca. The X-ray diffraction analysis was carried out. The semi-quantitative estimation of clay mineral based on peak intensities was made following the method of Gjems (1967).

Results and Discussions

Morphological characteristics

The morphological characteristics of the representative soil supporting forest and tea, developed from the upper Brahmaputra alluvium, are presented in Table 1. The soils are deep, brown to yellowish brown in the surface and dark yellowish brown to brownish yellow in the sub surface indicating better drainage condition. However, presence of mottles in the lower most layer indicates moderately well drained condition (Gangopadhyay *et al*., 2011). The forest soils from Hollongapara reserve forest are brown (10YR 5/3) at the surface and dark yellowish brown (10YR 4/4) to yellowish brown (10YR 6/6) at the subsurface to subsoil, loam in texture whereas the tea soils are yellowish brown (10YR 5/6) to brownish yellow (10YR 6/6), sandy loam in texture. The forest and tea growing soils are to some extent developed in terms of colour as well as structure forming cambic subsurface diagnostic horizon.

Physical and chemical characteristics

The physical and chemical characteristics of soils are presented in Table 2. The texture of the soils varied from loam (P1) to sandy loam (P2) in the surface horizons (Table 2). The coarser surface horizon indicates erosion and / or illuviation / in-situ formation of soil. Among the particle size fractions, sand is the dominant constituent in the tea soils while silt is dominant in the forest soil. The clay content of both the forest and tea growing soil increases with depth with the development of cambic subsurface diagnostic horizon.

Table 1. *Morphological characteristics of soils*

Hori-zon	Depth(m)	Colour (m)	Mottle colour (m)	Texture	Structure	Consistency	Boundary
			Forest soil				
Pedon 1. Hollongapara Reserve Forest Soil							
A	0-0.09	10YR5/3	-	1	f1sbk	sh, fr, ssps	cs
Bw1	0.09-0.32	10YR4/4	-	1	m1sbk	- fr, ssps	gs
Bw2	0.32-0.60	10YR5/6	-	1	m2sbk	- fr, ssps	gs
Bw3	0.60-0.90	10YR6/6	7.5YR4/4	1	m2sbk	- fr, ssps	gs
Bw4	0.90-1.20	10YR6/6	7.5YR4/4	1	m2sbk	- fr, ssps	
			Tea soil				
Pedon 2. Hollongapara Tea Soil							
Ap	0-0.13	10YR5/6	-	sl	m1sbk	sh, fr, ssps	gs
Bw1	0.13-0.50	10YR4/6	-	sl	m1sbk	- fr, ssps	gs
Bw2	0.50-0.80	10YR4/6	-	sl	m1sbk	- fr, ssps	gs
Bw3	0.80-1.09	10YR6/6	5 YR4/6	sl	f1sbk	- fr, ssps	cs
Bw4	1.09-1.32	10YR5/6	5 YR4/6	sl	f1sbk	- fr, ssps	

All the soils are acidic in nature with pH ranging from 4.5 to 4.8 (very strongly acidic) at the surface and 4.5 to 5.3 (very strongly acidic to strongly acidic) in the sub-surface (Table 2). The presence of acidic parent materials, leaching of bases due to increasing precipitation and presence of appreciable amount of exchangeable Al^{3+} (Gangopadhyay *et al.*, 2016) increases the acidity of these soils. The tea soils are highly acidic at the surface and it gradually decreases with the increase in soil depth. However, in case of forest soils, no definite trend of variation in soil pH was observed. However, in the subsurface, pH of the tea soil is relatively higher compared to that of the forest soil. The pH (KCl) is lower than pH (H_2O) by 0.6 to 1.2 units and the negative Δ pH of the soils (pH KCl – pH H_2O) indicated that all the studied soils contain considerable amount of reserve acidity (Bleeker and Sageman, 1990). This also further indicated that sufficient amount of exchangeable aluminium or complexed slowly exchangeable aluminium was present in these soils (Karmakar, 2014). The lower Δ pH in Ap horizons (-0.8 to -1.2) is due to the presence of higher organic carbon (OC) (Eswaran and Bin, 1978).

The organic carbon content of the forest soil is higher than that of tea soils. The organic carbon content of forest soil is high (12.7 g kg^{-1}) in the surface and in the sub surface it varies from 2.9 to 5.5 g kg^{-1}. The higher organic carbon content in the surface soil may be due to more biomass addition through leaf litter. In case of tea soils, the organic carbon content is 5.6 g kg^{-1} in the surface and in the sub surface; it varies from 2.9 to 4.3 g kg^{-1}. However, the organic carbon content of tea soil is lower than that of forest soil is mainly due to the run off loss from the surface.

Free iron oxide content of the soils varies from 1.6 to 3.6 g kg^{-1} and shows an increasing trend with soil depth. The dithionate extractable iron (Fe_d) values indicated that tea soils contain higher free iron than that of forest soils and is comparatively more weathered. (Bhattacharyya *et al.*, 1998). Free iron oxide (Fe_d) content of soil bears significant positive correlation with clay (r= 0.769, p <0.01) and pH (r= 0.576, p<0.01) indicating translocation of clay and iron oxide under acidic condition.

Exchangeable characteristics

The soils are low in CEC (Table 3) and it varies from [4.0 to 6.5 cmol (p^+) kg^{-1}] indicating that the soils are poor in nutrient holding capacity

Table 2. *Soil characteristics*

Horizon	Depth (m)	Sand	Silt (%)	Clay	pH_w	pH_{KCl}	ΔpH	O.C. gkg^{-1}	Fed gkg^{-1}
Hollongapara Reserve Forest soil									
A	0-0.09	37.9	45.6	16.5	4.8	4.0	0.8	12.7	1.8
Bw1	0.09-0.32	36.6	44.9	18.5	4.6	3.9	0.7	5.5	1.8
Bw2	0.32-0.60	37.8	42.7	19.5	4.5	3.9	0.6	4.3	1.9
Bw3	0.60-0.90	33.6	44.4	22.0	4.7	3.9	0.8	2.9	2.9
Bw4	0.90-1.20	30.5	44.5	25.0	4.8	3.9	0.9	2.9	3.6
Hollongapara Tea soil									
Ap	0-0.13	61.0	23.5	15.5	4.5	3.6	0.9	5.6	1.6
Bw1	0.13-0.50	59.8	23.7	16.5	4.6	3.6	1.0	4.3	3.0
Bw2	0.50-0.80	59.5	23.0	17.5	4.7	3.6	1.1	3.7	2.5
Bw3	0.80-1.09	61.3	21.2	17.5	5.0	3.8	1.2	2.9	2.5
Bw4	1.09-1.32	62.3	18.7	19.0	5.3	4.1	1.2	3.1	2.9

Table 3. *Exchangeable characteristics of the soils*

Horizon	Depth (m)	CEC [cmol(p$^+$) kg^{-1}]	Exchangeable bases cmol (p$^+$) kg^{-1}				B.S. (%)	Clay CEC	Exch. Ca^{2+}/ Mg^{2+}
			Ca^{2+}	Mg^{2+}	Na$^+$	K$^+$			
Hollongapara Reserve Forest soil (.Fine-loamy, mixed, hyperthermic, Humic Dystrudept)									
Pedon 1. Fine-loamy, mixed, hyperthermic, Humic Dystrudepts									
A	0-0.09	6.3	1.0	0.6	0.2	0.1	30	38	1.6
Bw1	0.09-0.32	5.3	1.0	0.5	0.2	0.1	26	28	2.0
Bw2	0.32-0.60	5.1	0.4	0.3	0.2	0.1	20	22	1.3
Bw3	0.60-0.90	5.9	0.4	0.1	0.1	0.1	12	26	4.0
Bw4	0.90-1.20	6.5	0.6	0.5	0.2	0.1	21	26	1.2
Hollongapara Tea soil									
Pedon 2. Coarse-loamy, mixed, hyperthermic, Fluventic Dystrudepts									
Ap	0-0.13	4.6	0.7	0.1	0.3	0.1	25	30	7.0
Bw1	0.13-0.50	4.8	0.9	0.6	0.3	0.1	39	29	1.5
Bw2	0.50-0.80	4.6	0.9	0.5	0.3	0.1	29	26	1.8
Bw3	0.80-1.09	4.0	1.5	0.7	0.2	0.1	63	23	2.1
Bw4	1.09-1.32	4.8	2.6	1.1	0.3	0.2	86	25	2.3

and contain low activity clay minerals (Bhattacharyya et al., 1994). The clay CEC value of the soils ranges from 22 to 38 indicating heterogeneity of mineralogical composition of clays with more than 50% kaolin hydroxyl interlayered vermiculite minerals (Bhattacharyya *et al.*, 2013). CEC of soil bears significant positive correlation with clay (r= 0.499, p<0.01) and free iron oxide (r=0.672, p<0.01). Among the exchangeable bases, Ca^{2+} is the dominant cation followed by Mg^{2+}, Na$^+$ and K$^+$ in both the pedons. The higher amount of exchangeable bases in the surface soil may be due to phytocycling of the nutrients released from decomposition of the leaf and litter fall. The distribution of exchangeable cations in these soils indicate that in case of forest soil, the exchangeable bases are high at the surface due to the accumulation and decomposition of the leaf, litters on the forest floor and it decreases with the increase in soil depth due to the recycling of bases by the plants. In case of tea soils, the ratio of extractable Ca^{2+} and Mg^{2+} in most of the soils shows decreasing trend with the increase in soil depth, indicating the leaching of the bases with percolating water into the lower layers. Extractable Ca^{2+} / Mg^{2+} ratio of the forest soils are higher in comparison to that of tea soils indicating higher recycling of bases in case of forest soils. The soils are low to medium in base status and the base saturation of soil varies from 12 to 86 per cent. In case of tea soil, the surface soils are low in bases and it is high in the lower most layers indicating leaching of bases to the lower layers.

Soil acidity

Exchangeable acidity

The exchangeable acidity of the soils, mostly constituted by exchangeable Al^{3+}, varies from [0.4 to 4.1 cmol (p+) kg^{-1}] (Table 4). In case of forest soil, the exchangeable acidity is comparatively low [1.5 cmol (p+) kg^{-1}] at the surface and it increases with the increase in soil depth whereas in tea soils, its value is low and reverse trend is observed. In soils with a pH value of less than 5, preponderance of exchangeable aluminium was reported from north-eastern regions (Bhattacharyya *et al.*, 1994). The exchangeable Al^{3+} contributes major share towards exchangeable acidity in all the soils. But the amount of exchangeable Al^{3+} is much higher in tea soil in comparison to that of forest soil where the contribution of exchangeable Al^{3+} ions is more than H^{+} which is amply supported by the high OC content and low pH values (Bhattacharyya *et al.*, 1994; Bhattacharyya *et al.* 2003a). Relatively low exchangeable Al^{3+} in the surface horizon of forest soils is mainly due to mobilization of Al^{3+} by its complexes with organic acids produced by the decomposition of leaf-litter in the surface horizons and subsequent downward movement and adsorption of these complexes by clay minerals in the sub-surface horizons (Schnitzer and Skinner 1963). The exchangeable acidity was relatively higher in the sub-surface horizons within a profile which may be due to higher amount of clay in the subsurface horizons. Exchangeable acidity of soil bears significant positive correlation with pH ($r=0.739$, $p<0.01$) and exchangeable H^{+} ($r= 0.417$, $p>0.05$).

pH dependent acidity

The pH dependent acidity of the forest soil contributes about 76.2 to 91.3 per cent of the total potential acidity and is relatively high in comparison to that of tea soil which contributes about 42.9 to 66.7 per cent of the total potential acidity (Table 4). The pH dependent charge may arise from the structural –OH groups at the corners and edges of soil clay minerals, which dissociates into H^{+} ions in slightly acid to alkaline pH range. Borah (1996) also reported that pH dependent acidity constituted more than 83% of the total potential acidity in the surface soils (0-15 cm) of tea growing areas of the Brahmaputra valley of Assam.

The total potential acidity of the soil is high in case of forest soil and comparatively low in tea soils (Table 4). The higher value of total potential acidity in the surface horizons of the soils is mainly due to higher content of organic matter (Borah1996).

Table 4. *Soil Acidity*

Horizon	Depth (m)	Exch. H^{+}	Exch. Al^{3+}	Exch. Acidity	Total potential acidity	pH dependent acidity
		c mol (p+) kg^{-1}				
			Forest soil			
Pedon 1. Fine-loamy, mixed, hyperthermic, Humic Dystrudepts						
A	0-0.09	0.6	0.9	1.5 (8.7)	17.2	15.7 (91.3)
Bw1	0.09-0.32	0.7	1.8	2.5 (17.1)	14.6	12.1 (82.9)
Bw2	0.32-0.60	0.3	2.7	3.0 (18.6)	16.1	13.1 (81.4)
Bw3	0.60-0.90	0.2	3.1	3.3 (14.2)	23.2	19.9 (85.8)
Bw4	0.90-1.20	0.2	3.9	4.1(23.8)	17.1	13.1 (76.2)
			Tea soil			
Pedon 2. Coarse -loamy, mixed, hyperthermic, Fluventic Dystrudepts						
Ap	0-0.13	0.5	2.2	2.7 (41.5)	6.5	3.8 (58.5)
Bw1	0.13-0.50	0.3	2.2	2.5 (43.1)	5.8	3.3 (56.9)
Bw2	0.50-0.80	1.1	1.4	2.5 (431)	5.8	3.3 (56.9)
Bw3	0.80-1.09	0.4	0.8	1.2 (33.3)	3.6	2.4 (66.7)
Bw4	1.09-1.32	0.4	tr	0.4 (57.1)	0.7	0.3 (42.9)

Note : The parenthesis indicate percentage of total potential acidity.

Clay mineralogy

The mineralogical analysis of clay fraction of surface and subsurface soils was carried out to identify the dominant minerals present in both the pedons (Fig. 2 to 5). The X-ray diffractograms indicated that mineralogy of all the samples were more or less similar. The Ca-saturated samples of all the clays have a characteristic peak at 1.4-1.5 nm region indicating the presence of 2:1 mineral in the soils. On glycolation, this 1.4 nm peak partially shifted to 1.7 to 1.8 nm region indicating the presence of smectite in the sample. The characteristic peak at 1.0 nm region and its persistence during glycolation and K-treatment and heating at 550°C indicated the presence of mica in the sample. Presence of 0.7 nm peak in all the clay samples confirmed the presence of kaolin in the samples. This was further confirmed by the disappearance of this peak during the K-saturation at 550°C. However, the nature of the 0.7 nm peak and its behavior to K-saturated and heated samples indicated that it is not a true kaolin but interstratified with 2:1 mineral. This is common in the soils of the sub-tropical India (Bhattacharyya *et al*,1993, Chandran *et al*., 2000).

The presence of trace amount of vermiculite was also observed in all the samples. This was confirmed by the increase in intensity of the 1.0 nm peak of mica during K-saturation and heating of the samples from 25 to 300°C. It was noticed that on K-saturation the 1.4 nm peak did not readily shifted to 1.0 nm region at ambient temperature but shifted slowly at 110 to 300°C. This indicated that the 2:1 mineral is hydroxy-interlayered. The persistence of a small 1.4 nm peak in some samples during K-saturation and heating at 550°C also indicated chloritization of the smectite and vermiculite layers.

Semi quantitative analysis of the forest and

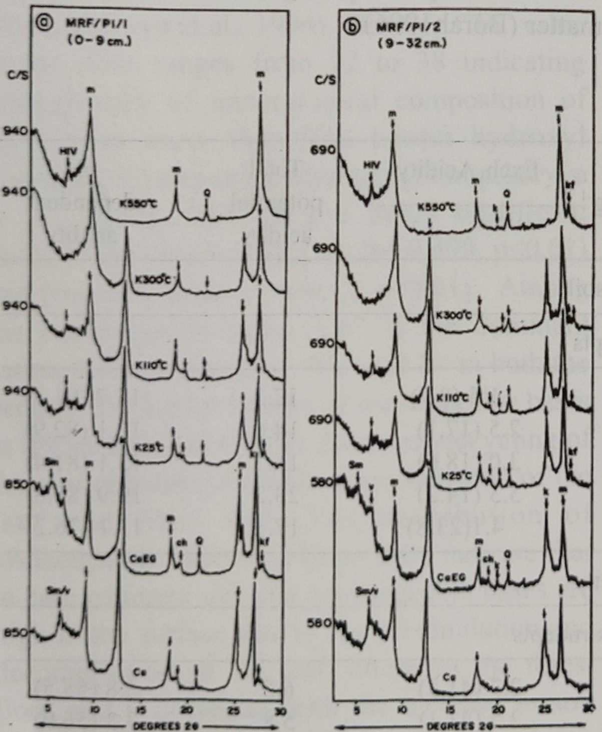

Fig. 2. *Representative x-ray diffractograms of clay fraction of Holongapara Forest soils m-mica, k-kaolin, sm-smectite, v-vermicullite, ch-chlorite, q-quartz, pf–plagioclase fieldspar, kf-potash fieldspar, HIV-hydroxy-interlayered-vermiculite*

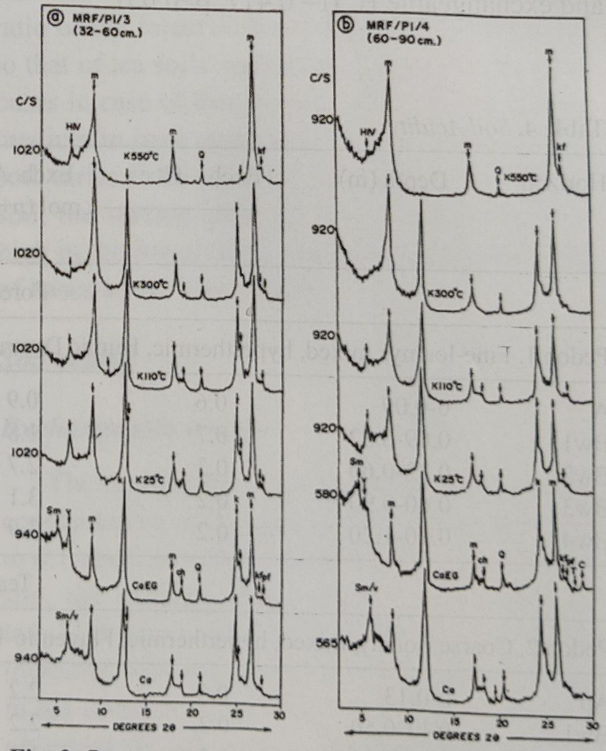

Fig. 3. *Representative x-ray dittractograms of clay fraction of Holongapara Forest soils m-mica, k-kaolin, sm-smectite, v-vermicullite, ch-chlorite, q-quartz, pf-plagioclase feldspar, kf-potash feldspar, HIV-hydroxy-interlayered-vermiculite, t-talc, c-calcite*

tea soils (Table 5) indicates that mica and kaolin are the dominant minerals in these soils. However, mica content is comparatively higher in forest soil while kaolin content is higher in tea soil. Smectite and vermiculite content is comparatively higher in forest soil while chlorite is relatively higher in tea soil.

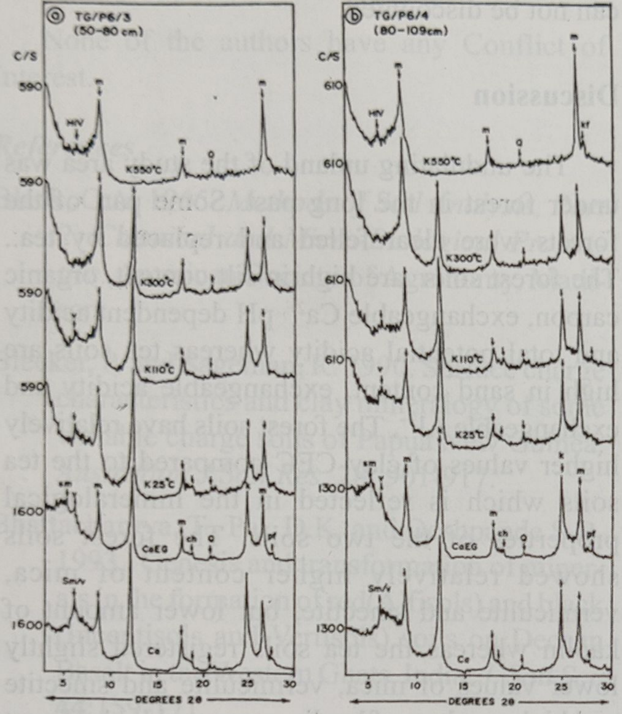

Fig. 4. *Representative x-ray diffractograms of clay fraction of Tea soils*

m-mica, k-kaolin, sm-smectite, v-vermicullite, ch-chlorite, q-quartz, pf-plagioclase feldspar, kf-potash feldspar, HIV-hydroxy-interlayered-vermicullite, t-talc, c-calcite

Genesis of the soils

The 1.0 nm peak of mica is broader and more asymmetrical towards low angles in the clay fractions indicating the replacement of interlayer K of mica. Presence of mica, mixed-layer minerals (1.0-1.4 nm), vermiculite and smectite indicates that these minerals appeared to have originated from mica. During the early stage of weathering, mica involved in its expansion to 1.0-1.4 nm minerals with concurrent formation of vermiculite. As the weathering continued, progressive build up of the 1.0-1.4 nm minerals, followed by the formation of vermiculite and smectite appears to have occurred. Kaolin has developed at the expense of smectite through smectite kaolin intermediate phase. The lack of evidence of such an intermediate phase in other pedons may be due to the dilution effect with the subsequent enrichment of kaolin formation (Herbillon *et al.* 1981). However, the formation of kaolin from the weathering of feldspars may

Table 5. Semi-quantitative analysis of clay minerals in the soils

Depth(m)	Horizon	Texture	Mineral abundance in clay fraction (in percent)										001/
			m	k	ch	V	sm	q	kf	Pf	t	c	002
						Forest soil							
0-0.09	A	1	40	45	1	6	6	1	1	-	-	-	2.0
0.09-0.32	Bw1	1	38	42	1	6	11	2	-	-	-	-	2.8
0.32-0.60	Bw2	1	36	45	2	7	8	1	-	1	-	-	3.5
0.60-0.90	Bw3	1	31	45	1	8	9	2	1	1	1	1	1.4
						Tea Soil							
0-0.13	Ap	sl	30	46	2	4	5	1	2	1	-	-	2.3
0.13-0.50	Bw1	sl	40	48	1	4	5	1	1	1	-	-	2.1
0.50-0.80	Bw2	sl	33	50	2	8	5	1	-	1	-	-	1.7
0.80-1.09	Bw3	sl	35	48	1	8	6	1	-	1	-	-	2.3
1.09-1.32	Bw4	sl	38	50	2	4	4	1	-	1	-	-	1.9

m- mica (Illite), k- Kaolin, ch- chlorite, v- Vermiculite, sm- Smectite, q- Quartz, kf- Potash feldspar, pf – Plagioclase feldspar, t – Talc, c – Calcite.

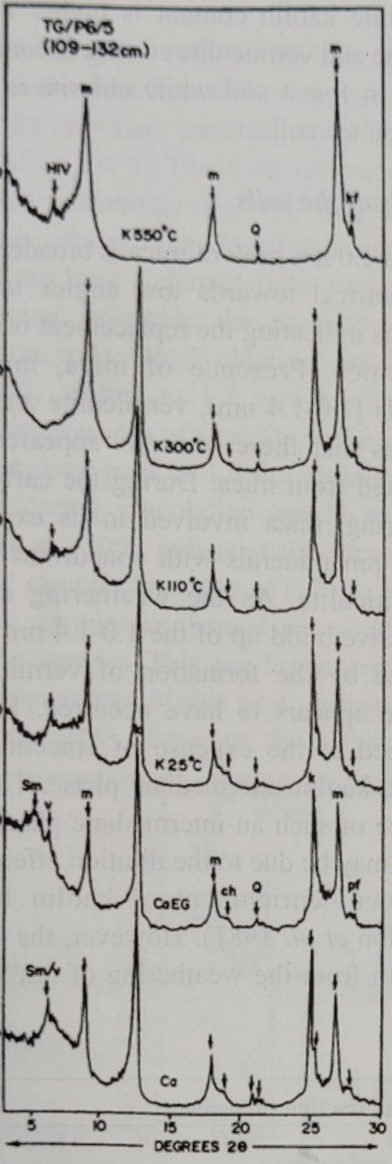

Fig. 5. *Representative x-ray diffractograms of clay fraction of Tea soils*
m-mica, k-kaolin, sm-smectite, v-vermicullite, ch-chlorite, q-quartz, pf-plagioclase feldspar, kf-potash feldspar, HIV-hydroxy-interlayered-vermicullite

not be totally ruled out.

The similarity in the mineralogy within the pedons, indicates that the weathering of minerals might have taken place in the source area and that the minerals were transported and deposited as alluvia in the valley. However, considering the extent of pedogenesis in these alluvium derived soils developed under hyperthermic, humid climate (Chakravorty, 1977), the possibility of *in-situ* weathering of micas, especially biotite, during post depositional period can not be discounted.

Discussion

The undulating upland of the study area was under forest in the long past. Some part of the forests were clear felled and replaced by tea.. The forest soils are high in silt content, organic carbon, exchangeable $Ca^{2+,}$ pH dependent acidity and total potential acidity whereas tea soils are high in sand content, exchangeable acidity and exchangeable Al^{3+}. The forest soils have relatively higher values of clay CEC compared to the tea soils which is reflected in the mineralogical properties of the two soils. The forest soils showed relatively higher content of mica, vermiculite and smectite, but lower amount of kaolin whereas the tea soils registered slightly lower values of mica, vermiculite and smectite and higher values of kaolin compared to the forest soils. This may be attributed to the transformation of mica and smectite to kaolin under relatively higher weathering conditions prevailing in tea growing soils. This can also be supplemented with the fact that the tea soils had higher exchangeable aluminium. After conversion of the forest land to tea, kaolin may have formed at the expense of smectite through smectite-kaolin intermediate phase. The smectite-kaolin and mica-vermiculite mixed layer minerals are responsible for the formation of mixed layer kaolin phase in view of the fact that the climatic conditions of the region persisted to remain under per-humid sub-tropical conditions wherein the weathering of the tea soils was hastened by the change in land use.

Contribution of Authors

First author conducted soil survey field work and laboratory analysis of soils, interpreted data and prepared manuscript. Second author

contributed in the interpretation of the clay mineralogical data and editing of the manuscript.

Conflict of Interest

None of the authors have any Conflict of Interest.

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Abbreviations used as per Soil Survey Division Staff (1995)

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Cracking Clay Soils of Middle Indo-Gangetic Plains of Bihar, India: Characteristics and Mineralogy

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Abstract: *Three typical pedons representing the undulating upland and old alluvial plain of Aurangabad district, Bihar under middle Indo-Gangetic plain were undertaken for this study. The soils were very deep, well to moderately well drained, dark grayish brown to light olive brown in colour and silty clay loam to silty clay in texture. Soils were slightly acidic to slightly alkaline in reaction (pH 6.2 to 8.4), medium to high in organic carbon (6.3 to 12.0 g kg*$^{-1}$*), medium in CEC [16.5 to 22.0 c mol (p*$^{+}$*)kg*$^{-1}$*] with medium to high in base saturation (62 to 88%). The soils developed deep and wide cracks which resembled to Vertisols / Vertic properties found in other parts of the country with respect to texture, periodic opening and closing of cracks in the subsurface but have dissimilarity with respect to slickenside development, wedge shaped structure and colour. XRD studies indicated that the presence of sufficient amount of smectite and kaolinite-smectite interstratified clay minerals in these soils are responsible for shrink-swell character of the soils.*

Keywords*: Aurangabad district soils; Clay mineralogy – Bihar; Soils – Bihar; Vertisols.*

The Indo-Gangetic Plains (IGP), the most extensive fluvial plains, of the country possesses major share of the total food grains production. After Green Revolution, there was a challenge of increasing food grain production to support the increasing population of the country. Increasing use of fertilizers and, over exploitation of soil resources in this region, affect the food production system which lead to adverse change in soil properties. (Bhattacharyya and Mandal, 2009). The pressure directed towards north and northeast is responsible for the formation of the landform of IGP. Due to change in the course of the rivers towards southeast and east (Parkash *et al*., 2000), a series of terraces, bars and meandering scarce are formed in IGP resulting in micro high and micro low areas on the apparently smooth topography (Pal *et al*., 2003; Singh *et al.*, 2006). Thus the rainfed region of IGP possesses various constraints like undulating topography, moisture stress, soil degradation, inherent soil and climatic constraints and their management that restricts crop production significantly.

The morphological, physical, chemical and mineralogical characteristics of soils are essential to address different soil related issues. Soil clays play a very crucial role not only to increase the availability of soil moisture to the plants but also hold and release some of the essential nutrients to the plant and therefore information on mineralogical make up of the soil is also important towards the management of natural resources. Aurangabad district of south Bihar, under middle Indo-Gangetic plain, represents a transitional zone in respect of geology, climate

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and agriculture. It represents two geological formations viz., a fringe of Chhotanagpur plateau representing Indian Peninsula composed mainly of Archaean granite and gneissic rocks covering the southern part of the district and, the Indo-Gangetic alluvial plains in the north. The soils of Chhotanagpur plateau, developing on undulating topography experience varying degrees of soil erosion, scarcity of ground water, drainage congestion, poor soil fertility and rainfed agriculture. Inceptisols was the dominant soil in the district followed by Alfisols and Entisols (Gangopadhyay *et al*, 2013). Some soils have medium to high clay content, wide cracks at surface and sub-surface horizons during rabi season affecting soil moisture storage. The study area was initially drained by the Son River which was originating from Amarkantak, Chhattisgarh carrying weathered basaltic alluvium (Deccan trap) which may be the reason for developing cracking clay soils in presence of significant amount of smectite clay (Mourya *et al.* 2014). Such soils resembled to the Vertisols developed from basalt and occurring in other parts of the country with respect to texture, periodical opening and closing of cracks and sub-surface colour but neither have slickenside nor wedge shaped structure or characteristic colour at surface layer. Several workers (Pal 2017; Srivastava *et al.* 2015; Pal *et al.* 2009 and 2012; Dasog *et al.* 1988) have extensively studied the cracking clay soils of the black soil region of India (BSR). Ray *et al.* (2006) reported that the occurrence of smectite for the development of Vertisols in Indo- Gangetic Plains of West Bengal was primarily derived from the alluvium of Rajmahal trap. However such studies in the soils of Bihar is limited (Diwakar and Singh 1994) and therefore, effort has been made to study the characteristics of the cracking clay soils of Aurangabad district of South Bihar.

Materials and Methods

Three representative pedons developed from the upper and lower reaches of undulating upland (P1 and P2) and old alluvial plain (P3) of middle Indo-Gangetic plains from Aurangabad district, south Bihar were selected for the study. The district falls under hot dry sub humid agro climate with dry summers and cool winters and suffers from climatic extremities with mean maximum temperature of 36.6^{o} C and mean minimum temperature as 9.2^{o} C in January. The annual precipitation is within the range of 1000 to 1200 mm with 'Hyperthermic' moisture regime and 'Ustic' temperature regime.

The morphological properties of soil profiles were studied (Soil Survey Division Staff, 1995), and horizon wise samples were collected and characterized for physical and chemical properties following standard procedure (Black, 1965; Jackson, 1973) and classified as per USDA soil classification (Soil Survey Staff, 2014). For mineralogical analysis, the clay samples were separated following International pipette method (Jackson, 1979). The calcium and potassium saturated and ethylene glycol solvated clay samples were heated to 25^{0}C, 110^{0}C, 300^{0}C and 550^{0}C for X-ray diffraction (XRD) studies with a Philips diffractometer using Ni-filtered Cu-$K_{\acute{a}}$ radiation and at a scanning speed of 2^{o}2θ m^{-1} analysis to identify the minerals. The semi-quantitative estimation of clay mineral was performed following the standard procedure as outlined by Gjems (1967).

Results and Discussion

Morphological characteristics

The soils are very deep, well to moderately well drained, dark grayish brown (2.5 Y 4/2) to light olive brown (2.5Y 5/4) colour in the surface and dark grayish brown (2.5 Y 4/2) to olive brown (2.5Y 4/4) colour in the subsurface (Table 1). The brownish colour of the soil indicates better drainage condition. The soil varies from silty clay loam to silty clay in texture and medium moderate sub angular blocky to strong coarse sub angular blocky structure. The soils were hard when dry, friable to firm when moist and slightly sticky and slightly plastic to sticky plastic when wet. Iron and calcium concretions were observed in the soils of pedon 1 and 2 while in pedon 3 only iron concretions were noticed. Presence of deep and wide cracks along with pressure faces was observed up to a depth of 75-110 cm. Soils of Pedon 2 was calcareous in nature whereas other two pedons (Pedons 1 and 3) were non-calcareous. The significant illuviation of clay and deep and wide cracks up to a depth of 75 to 110 cm with pressure faces are common in these soils.

Soil Characteristics

Among the soil separates, silt was the dominant constituent in all the soils followed by clay and sand (Table 2). The silt content varied from 47.1 to 62.5 percent at the surface and 44.2 to 54.8 percent in the subsurface and showed a decreasing trend with soil depth. Clay content of soils varied from 29.7 to 48.4 percent at the surface and 38.6 to 53.7 percent in the subsurface. The clay content showed an increasing trend with depth indicating the eluviations of clay from the surface layer (Gangopadhyay *et al.* 1999). The

Table 1. *Morphological characteristics of soils of Aurangabad district, Bihar.*

Horizon	Depth (cm)	Colour (m)	Texture	Structure	Consistency	Concretions	Efferve-scence	Boun-dary	Cracks/ other features
Pedon 1. Dadhpa series: Soil of gently sloping upper_ reaches of undulating upland									
Ap	0-12	2.5Y4/4	sicl	Pudd-led	h,fr, ssps	Fe Caf f c f	-	gs	3-5 cm_wide
Bt1	12-39	2.5Y4/4	sicl	c2sbk	- fi, sp	Fe Caf m c f	-	cs	cracks upto
Bt2	39-75	2.5Y4/4	sic	m2sbk	- fr, s p	Fe Caf m m f	-	cs	75cm
Bt3	75-120	2.5Y4/4	sic	m2sbk	- fr, s p	Fe Caf m m f	-	gs	Pressure faces
Bt4	120-150	2.5Y 4/4	sic	m2sbk	- fr, s p	Fe Caf m m f	-		Pressure faces
Pedon 2. Gurdi series: Soil of very gently sloping lower reaches of undulating upland									
Ap	0-13	2.5Y4/2	sic	Pudd-led	h, fi, sp	Fe - c f	e1	gs	4-6 cmwide
Bw	13-30	2.5Y4/2	sic	c3sbk	- fi, sp	Fe Cac f m f	e1	cs	cracks upto
Bt1	30- 65	2.5Y4/2	sic	m2sbk	- fi, sp	Fe Cam f c m	e1	gs	100cm
Bt2	65-110	2.5Y4/2	sic	m2sbk	- fi, sp	Fe Cam f c m	e1	gs	
Bt3	110- 150	2.5Y4/2	sic	m2sbk	- fi, sp		e1		
Pedon 3.Karma series: Soil of very gently sloping old alluvial plain									
Ap	0-13	2.5Y5/4	sic	Pudd-led	h, fr, ss ps	-	-	gs	3-5 cm wide
Bw1	13-45	2.5Y4/4	sic	m2sbk	- fr, ss ps	Fe (c f)	-	gs	cracks upto
Bw2	45-70	2.5Y4/4	sic	m2sbk	- fi, s p	Fe (c f)	-	gs	110cm
Bw3	70-110	2.5Y4/4	sic	m2sbk	- fi, s p	Fe (m f)	-	gs	
Bw4	110-150	2.5Y4/4	sic	m2sbk	- fi, s p	Fe (m f)	-		

Note:Texture:sicl-siltyclayloam, sic-siltyclay; Structure:m2sbk-Moderatemediumsubangularblocky, c2sbk-medium coarse subangular blocky, c3sbk- strong coarse subangular blocky; Consistency (dry): h-Hard; Consistency (moist): fr-Friable,fi-Firm, Consistency (wet): ss ps -Slightly sticky and slightly plastic, s p - Sticky and plastic, Effervescence: e1- slight. Boundary:cs-Clearsmooth, gs-Gradualsmooth.

illuviation of clay in subsoils is common in all the pedons but the increase is not sufficient enough to qualify for argillic subsurface diagnostic horizon in pedon 3, instead they qualify for cambic horizon.

The soils were slightly acidic (pH 6.2) to neutral (pH 7.1) at the surface and neutral (pH 6.9) to moderately alkaline (pH 8.4) in the subsurface and it showed an increasing trend with depth (Table 2). The higher pH of the soils in the subsurface may be due to the release of bases, mainly calcium from the basic parent materials. pH (KCl) were lower than pH H_2O in all the soils and the negative Δ pH (pH KCl – pH H_2O) is assigned to, the absence of net positive charge and presence of considerable amount of reserve acidity (Chandran *et al*, 2004). Organic carbon content of soils varied from 7.0 to 12.0 g kg^{-1} at the surface and 1.6 to 3.4 g kg^{-1} at the subsurface and it showed a decreasing trend with depth indicating that fluvial activity is absent in the recent past. The anaerobiosis and associated chemical and biochemical processes due to submergence under rice cultivation is supposed to be the reason for high organic carbon content of the soil at the surface (Sehrawat, *et al*, 2005).

The soils are medium in cation exchange capacity (CEC) and it varies from 16.5 to 22.0 cmol (p^+) kg^{-1} (Table 3). The medium CEC value of the soils indicated the presence of illite (mica) and kaolinite interstratified with 2:1 minerals in the soils. The Clay CEC value (39 to 55) reflects the presence of significant amount of smectite clay minerals in these soils (Soil Survey Staff, 2014). Among the exchangeable bases, Ca^{2+} is the dominant cation followed by Mg^{2+}, Na^+ and K^+. The increasing value of exchangeable Ca^{2+}/Mg^{2+} ratio with depth indicates considerable recycling of bases particularly Ca^{2+} in these soils. Soils are moderately base saturated and the base saturation varied from 62 to 88 Percent.

Mineralogical properties of the soils

The mineralogical analysis of clay samples

Table 2. *Characteristics of soils*

Horizon	Depth (cm)	Sand	Silt (%)	Clay	pH (H_2O)	pH (KCl)	Δ pH	Organic carbon (%)
Pedon 1. Dadhpa series : Soil of gently sloping upper reaches of undulating upland								
Ap	0-12	7.8	62.5	29.7	7.1	5.9	-1.2	12.0
Bt1	12-39	6.6	54.8	38.6	7.5	6.9	-0.6	2.8
Bt2	39-75	5.3	51.9	42.8	8.0	6.3	-1.7	1.8
Bt3	75-120	5.3	54.0	40.7	8.4	6.3	-2.1	1.6
Bt4	120-150	4.6	52.5	42.9	7.8	6.5	-1.3	2.6
Pedon 2. Gurdi series: Soil of very gently sloping lower reaches of undulating upland								
Ap	0-13	3.4	53.3	43.3	6.2	6.6	0.4	8.6
Bw	13-30	2.4	53.1	44.5	7.2	6.7	-0.5	3.4
Bt1	30- 65	2.1	44.2	53.7	7.8	6.7	-1.1	2.0
Bt2	65-110	2.9	50.5	46.6	8.1	6.8	-1.3	2.0
Bt3	110- 150	2.9	48.1	49.0	8.4	6.6	-1.8	2.2
Pedon 3. Karma series: Soil of very gently sloping old alluvial plain								
Ap	0-13	4.5	47.1	48.4	6.6	5.1	-1.5	7..7
Bw1	13-45	3.5	46.9	49.6	6.9	5.5	-1.4	3.5
Bw2	45-70	3.6	47.2	49.2	7.1	5.6	-1.5	2.9
Bw3	70-110	3.2	46.5	50.3	7.1	5.8	-1.3	2.7
Bw4	110-150	3.1	49.6	47.3	7.1	5.8	-1.3	2..3

collected from subsurface layer was carried out to identify the mineralogical properties of soils. The X-ray diffractograms indicated that the mineralogy of Pedon 1 and Pedon 3 was almost similar (Fig. 1 & 3). The Ca-saturated samples of all the clays has a characteristic peak at 1.4 - 1.5 nm region indicating presence of 2:1 mineral in the samples. The Ca-saturated clay samples after glycolation results in the shifting of 1.4 nm peak to 1.7 to 1.8 nm region indicating the presence of smectite in the sample (Fig. 1 & 2). The characteristic peak at 1.0 nm region and its persistence during glycolation and K-treatment and heating at 550 °C indicated the presence of mica in the sample. Presence of 0.7 nm peak in all the clay samples confirmed the presence of kaolinite as the clay minerals. The disappearance of this peak during the K-saturation at 550 °C also confirmed the presence of Kaolinite. However, the nature of the 0.7 nm peak and its behavior to the K-saturated and heated samples indicated the presence of Kaolinite interstratified with 2:1 mineral instead of true Kaolinite. Similar results were found in the soils of the tropical India (Bhattacharyya *et al*, 1993; Chandran *et al*., 2000, 2013; Pal *et al*, 2009).

The presence of trace amount of vermiculite was also observed in all the samples. This was confirmed by the increase in intensity of the 1.0 nm peak of mica during K-saturation and heating of the samples from 25 to 300°C. It was noticed that on K-saturation the 1.4 nm peak did not readily shifted to 1.0 nm region at ambient temperature but shifted slowly at 110 to 300°C. This indicated that the 2:1 mineral is hydroxy-interlayered. The persistence of a small 1.4 nm peak in some samples during K-saturation and heating at 550°C also indicated chloritization of the smectite and vermiculite layers.

Semi-quantitative analysis of clay minerals (Table 4) indicates that in Pedon1, kaolinite is the dominant clay mineral (36.2%) followed by smectite (29.2%) and illite (18.8) and hence qualifies for "mixed" mineralogy. In Pedon 2, smectite (52%) is followed by mica (21.2%) and

Table 3. *Exchange characteristics of soils*

Horizon	Depth (cm)	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Sum	CEC	B.S. (%)	Ca^{2+}/ Mg^{2+}	Clay CEC
					cmol(p$^+$)kg^{-1}					
Pedon 1. Dadhpa series : Fine, mixed, hyperthermic, Vertic Haplustalfs										
Ap	0-12	9.6	1.5	0.5	0.5	12.1	16.5	73	6.4	55
Bt1	12-39	10.8	1.6	0.9	0.3	13.6	17.9	76	6.7	46
Bt2	39-75	12.4	1.7	1.6	0.3	16.0	19.4	82	7.3	45
Bt3	75-120	12.4	1.6	2.2	0.3	16.5	18.6	88	7.7	45
Bt4	120-150	11.8	1.6	2.5	0.3	16.2	19.6	82	7.3	45
Pedon 2. Gurdi series: Fine, smectitic, hyperthermic, Vertic Endoaqualfs										
Ap	0-13	11.2	1.3	0.5	0.4	13.4	21.5	62	8.6	49
Bw	13-45	12.2	1.4	1.2	0.4	15.2	21.4	71	8.7	48
Bt1	30-65	13.1	1.6	1.7	0.5	16.9	22.0	77	8.2	41
Bt2	65-110	13.4	1.6	1.9	0.5	17.4	21.6	80	8.4	46
Bt3	110-150	13.7	1.6	2.1	0.5	17.9	21.7	82	8.5	44
Pedon 3. Karma series: Fine, mixed, hyperthermic, Vertic Haplustepts										
Ap	0-13	10.9	1.6	0.1	0.9	13.5	19.6	69	6.8	40
Bw1	13-45	12.0	1.6	0.1	0.5	14.2	19.4	73	7.5	39
Bw2	45-70	12.6	1.6	0.1	0.5	14.8	19.8	75	7.8	40
Bw3	70-110	13.0	1.7	0.2	0.5	15.4	20.0	77	7.6	40
Bw4	110-150	12.7	1.7	0.1	0.5	15.0	19.5	77	7.4	41

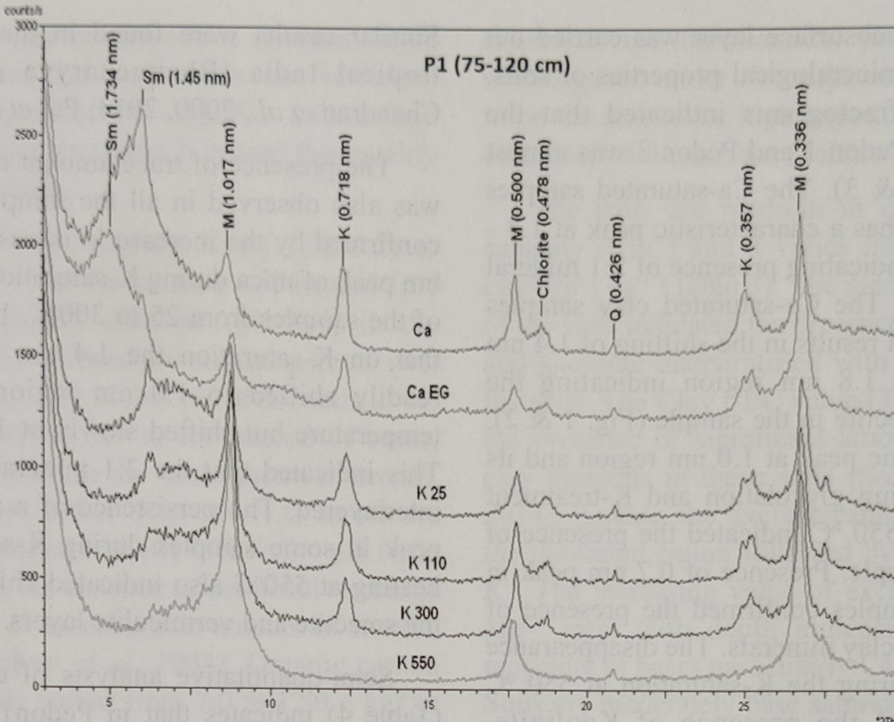

Fig. 1. *Representative X-ray diffractogram of clay fraction of pedon 1 (Bt3 horizon: 75-120 cm) (Ca=Ca saturated, CaEg=Ca saturated and glycolated, K25/110/300/550 = K saturated and heated to 25,110,300,550°C respectively. Sm-smectite, Vm-vermiculite, Ch-chlorite, M-mica, K -kaolinite).*

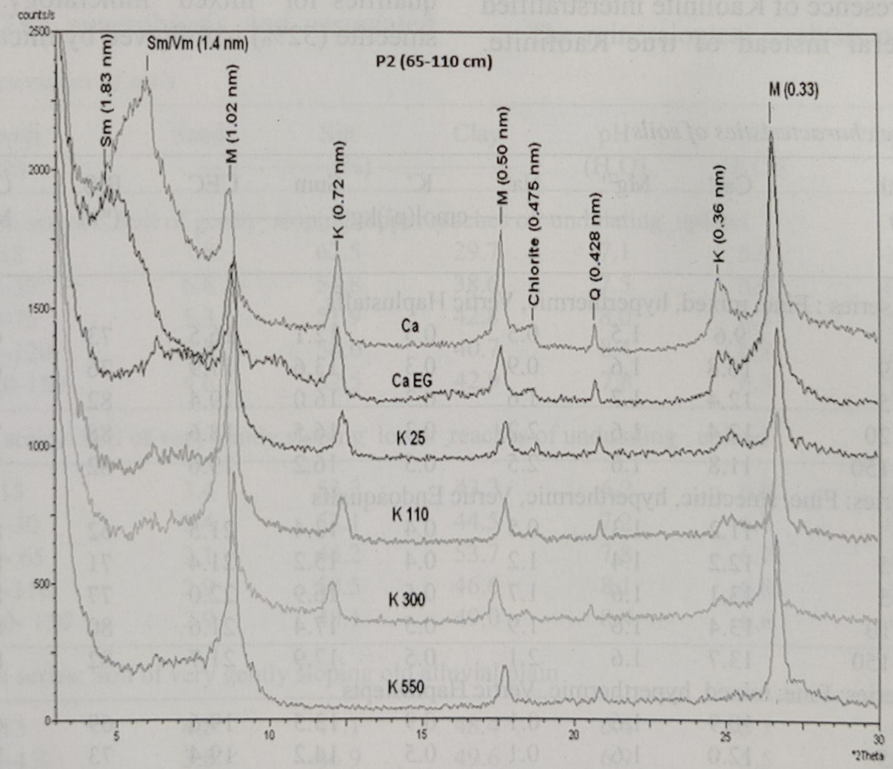

Fig. 2. *Representative X-ray diffractogram of clay fraction of pedon 2 (Bt2 horizon: 65-110 cm) (Ca=Ca saturated, Ca-Eg=Ca saturated and glycolated, K25/110/300/550 = K saturated and heated to 25,110,300,550°C respectively. Sm-smectite, Vm-vermiculite, Ch-chlorite, M-mica, K -kaolinite).*

kaolinite (18.2%) and it qualifies for "smectitic" mineralogy; and Pedon 3 qualifies for "mixed" mineralogy as it contains kaolinite (32.6%), mica (29.6%) and smectite (25.5%). All pedons show vertic properties due to the presence of higher amount (25-52%) of smectite. Shirsath *et al.*, (2000) found the minimum threshold value of 20 percent smectite for the initiation of vertic properties in shrink-swell soils.

Table 4. *Semi-quantitative analysis of clay samples*

Pedon No.	Mineral name	% present
P1	Smectite	29.2
	Vermiculite	Tr*
	Mica	18.8
	Kaolinite	36.2
	Chlorite	Tr*
P2	Smectite	52.0
	Vermiculite	Tr*
	Mica	21.2
	Kaolinite	18.2
	Chlorite	Tr*
P3	Smectite	25.5
	Vermiculite	Tr*
	Mica	29.6
	Kaolinite	32.6
	Chlorite	Tr*

* Traces

Ray *et al.* (2006) reported the occurrence of Vertisols in the Bengal basin part of IGP which is otherwise dominated by micaceous minerals. They concluded that sufficient amount of smectite required for the development of Vertisol was brought down as alluvium from weathering basalt of Rajmahal trap by the eastern flowing rivers of the past before they were shifted to the south in the late Holocene period. In the study area, the archean granite and gneisses of Chotanagpur Plateau is reported to have the dotted presence of basalt and basaltic materials. At places the presence of partially weathered phylites below the residuum of basalt was also observed. In addition, the Son River which originating from Amarkantak, Chhattisgarh have carried weathered

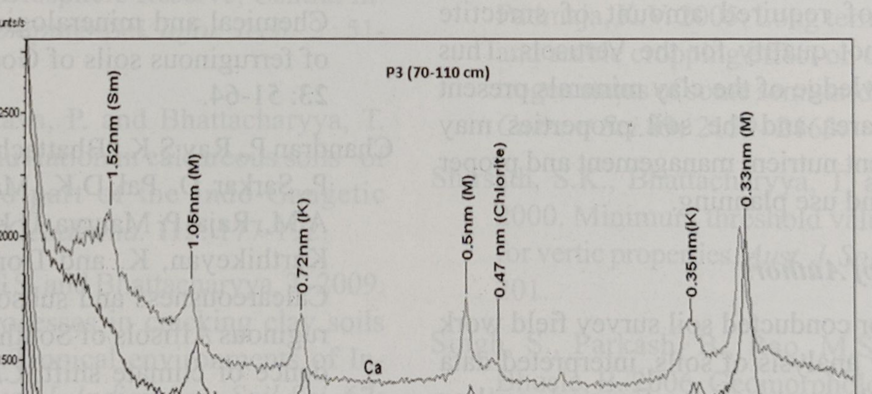

Fig. 3. *Representative X-ray diffractogram of clay fraction of pedon3 (Bw3 horizon: 70-110 cm) (Ca= Ca saturated, CaEg= Ca saturated and glycolated, K25/110/300/550 = K saturated and heated to 25,110,300,550°C respectively. Sm-smectite, Vm-vermiculite, Ch-chlorite, M-mica, K -kaolinite).*

basaltic alluvium (Deccan trap). The smectite in these soils might have developed from these basaltic materials and is responsible for the development of isolated parcels of cracking clay soils in Aurangabad district.

Conclusions

The study area of middle Indo-Gangetic plain of Aurangabad district, Bihar was initially drained by Son River which was originating from Amarkantak, Chhattisgarh carrying weathered basaltic alluvium (Deccan trap) which may be the reason for developing deep and wide cracks in these soils with the increasing content of smectitic clay minerals. Such soils resembled to the Vertisols mapped elsewhere in other parts of the country with respect to texture, periodical opening and closing of cracks and sub-surface colour but the absence of slickenside development, wedge shaped structure, probably due to lack of required amount of smectite minerals, do not qualify for the Vertisols. Thus adequate knowledge of the clay minerals present in the study area and the soil properties may help for efficient nutrient management and proper agricultural land use planning.

Contribution of Authors

First author conducted soil survey field work and laboratory analysis of soils, interpreted data and prepared manuscript. Second author contributed in the interpretation of the clay mineralogical data and the third author contributed for editing of the manuscript.

Conflict of Interest

None of the authors have any Conflict of Interest.

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Predicament in Identifying Clay Palygorskite in Vertisols of Chhattisgarh Basin, India

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Abstract: *Earlier research on non-saline and non-sodic shrink-swell soils (Typic Haplusterts) of semi-arid climates (SAT) of western Maharashtra exhibited poor hydraulic properties due to the presence of clay palygorskite, which causes a remarkable reduction in crop yield. Similar impairment of hydraulic properties is recently observed also in non-saline and non-sodic deep shrink-swell soils (Typic Haplusterts) of sub-humid dry (SHD) climate of Chhattisgarh Basin of central India. In contrast to poor crop productivity of SAT Typic Haplusterts, SHD Typic Haplusterts are cultivated to rice as a prosperous agricultural land use plan. To confirm the possible presence of palygorskite as the causative factor in impairing the hydraulic properties of Typic Haplusterts of Chhattisgarh Basin, X-ray diffraction (XRD) technique was used to identify palygorskite in their clay fractions (< 2μm). Identification of clay palygorskite in Indian shrink-swell soils (Vertisols and their intergrades) by XRD method has not always been straight forward or might have been overlooked because of its low content, and also due to lack of sharp characteristic peak at 1.05 nm. It is also apprehended that its presence could be destroyed due to the chemical pre-treatments that are routinely applied to separate soil clay fractions. Often the identification of palygorskite in the pre-treated clay fractions is fraught with difficulty as no distinct peak at 1.05 nm is observed at a scanning speed of $2^{0}2\theta\ min^{-1}$. To circumvent this predicament, water-dispersible clays (WDC) of SHD Typic Haplusterts were used for XRD analysis. Presence of a broad peak around 1.05 nm was observed, which was further resolved by slow-scanning at a speed of $1^{0}2\theta\ min^{-1}$ and $0.5^{0}2\theta\ min^{-1}$. In the scanning speed of $0.5^{0}2\theta\ min^{-1}$, palygorskite peak at 1.05 nm was relatively well resolved than by scanning speed of $1^{0}2\theta\ min^{-1}$. By the use of deconvolution method, the identification problem of the peak at 1.05 nm for palygorskite was much better resolved. Palygorskite mineral creates some unique physical and chemical properties of soils, such as a decrease in sHC (< 10 mm hr^{-1}) and exchangeable Ca/Mg ratio with pedon depth, and an increase in soil base saturation (> 100). The results of the present study suggest that these unique soil properties would be enough to ensure the presence of palygorskite in Vertisols even when XRD facilities are not available. Its presence poses a challenge to pedologists/ soil mappers, which demands a new initiative to classify palygorskite containing Vertisols at a higher categorical level for the benefit of various stakeholders, farmers' communities of rain-fed regions in particular.*

Keywords: *Palygorskite mineral; Vertisols; Identification of palygorskite*

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Palygorskite belongs to phyllosilicate minerals with a ribbon-like structure, which is formed from two inversed silica tetrahedral sheets and a magnesium-rich octahedral sheet between them (Singer, 2002). Thus, palygorskite mineral is structurally distinct from the typical 1:1 and 2:1-layer structure and has fibrous morphology in contrast to the platy morphology of most other clay minerals. Such an arrangement makes alternate hollow channels, which allow penetrations of solutes into the structure (Shirvani *et al*., 2006). This mineral is a common clay mineral of the Calcic/Gypsic soils developed in arid regions worldwide (Heystek and Schmidt, 1953; Yaalon *et al*., 1966; Eswaran and Barzanji, 1974; Hutton and Dixon, 1981; Sombroek, 1981; Patil and Surana, 1992). Clay minerals are beneficial for plants and animals. But there is some like palygorskite whose presence impairs soil physical properties to affect soil quality (Bhattacharyya *et al*., 2018). An early review of the mineralogy of the Indian soils (Sarma and Sidhu, 1982) reported the presence of palygorskite in some Indian western desert soils of Rajasthan. Recently, its existence is noted in Vertisols developed in the alluvium of the weathering Deccan basalt (Pal *et al*., 2003; Hiller and Pharande, 2008; Zade *et al*., 2017; Bhattacharyya *et al*., 2018), and in parent materials derived from red clay boles (Kolhe *et al*., 2011) in the central and western Peninsular India in the states of Maharashtra and Gujarat. These soils were under both rainfed and irrigated agriculture. The presence of palygorskite was also reported as the detrital origin from marine sedimentary rocks in calcic soils of western Thar Desert of Rajasthan (Hameed *et al*., 2018).

Despite the possibility of inheritance of palygorskite from the intertrappean sediments sandwiched between the Deccan trap flows in Andhra Pradesh (Siddiqui, 1967), Karnataka and Gujarat where palygorskite occurs in lacustrine sediments of high basicity under arid conditions induced and influenced by Deccan volcanism (Kolhe *et al*., 2011), reports on the occurrence of palygorskite in cracking clay soils of Indian semi-arid tropics (SAT) environment was rarely made in the last few decades. However, in recent years, its presence in Indian soils is reported (Bhattacharyya *et al*., 2018; Hameed *et al*., 2018). Lack of report on the presence of palygorskite in Indian soils maybe because of its destruction during the preparation of clay samples for the regular clay mineralogical analysis, which involves the removal of cementing agents (organic matter, $CaCO_3$ and free Fe_2O_3) (Sombroek, 1981), especially when soils contain meagre amounts of this mineral. Such difficulty was experienced by Zade *et al*. (2017) for Vertisols where only water without the removal of cementing agents was used to disperse soil clays (<2 µm) for identification of palygorskite by the XRD technique. However, many times XRD analyses of water-dispersible soil clays of non-sodic and non-zeolitic and poorly drained Vertisols (Typic Haplusterts) of SAT. parts of the Indian state of Maharashtra do not show a very distinct and characteristic peak of palygorskite at 1.04-1.05 nm; instead, it shows a broad and low-intensity peak around 1.05 nm at the low angle side of the 1.0 nm peak of mica (Pal *et al*., 2003; Kolhe *et al*., 2011; Zade *et al*., 2017), and such soils generally show a sharp decrease in exchangeable Ca/Mg ratio with pedon depth due to downward movement of Mg ions from the palygorskite mineral. Mg enrichment on soil exchange sites ultimately impairs the drainage due to reduction in saturated hydraulic conductivity (sHC) (< 10 mm hr^{-1}), which would restrict the free entry of air and water. Therefore, yields of deep-rooted crops are severely affected (Zade, 2007) due to inadequate amounts of stored soil moisture and its subsequent release between the rains during the crop growth under rain-fed conditions (Kadu *et al*., 2003). Moreover, these SAT soils may turn out to be waterlogged during monsoon or if irrigation is introduced.

In contrast to the above, a recent field visit by our team members at the ICAR-NBSS & LUP confirmed the wide occurrence of Vertisols in the sub-humid dry (SHD) bioclimatic environment of Chhattisgarh basin of central India, where long-duration rice is being cultivated by direct-seeded method for decades under rain-fed conditions. Even though the water is a major limiting factor in growing crops under rainfed conditions, economically viable rice cultivation on Vertisols (Typic Haplusterts) of Chhattisgarh Basin proves a fact that the soils have been providing sufficient soil moisture between the rains. In Typic Haplusterts of this basin, retention of soil water is not governed by the dispersion of soil colloids by the abundance of Na$^+$ ions on the soil exchange complex (NBSS&LUP, 2016). Earlier research on Typic Haplusterts of the SAT. climate showed a sharp decline in sHC (< 10 mmhr^{-1}) with pedon depth due to enrichment of Mg^{2+} ions on exchange sites provided by palygorskite mineral (Zade *et al*., 2017). Enrichment of Mg^{2+} along with Ca^{2+} ions on the soil exchange complex (exchangeable Ca/Mg $\leq$ 2) cause dispersion of clay colloids that restricted the free entry of rainwater into the soil profile and held a significant positive correlation with WDC and exchangeable magnesium percentage (EMP) (Zade *et al*., 2017). This unique observation led us to presume that Typic Haplusterts of SHD Chhattisgarh Basin may have palygorskite mineral which helps in holding the sufficient amount of rainwater standing on the soil surface (an essential requirement for rice cultivation) and makes the growing of rice crop possible under rain-fed situation as a very successful agricultural enterprise. In order to confirm the presence of palygorskite in Vertisols of Chhattisgarh Basin, it is necessary to identify palygorskite precisely by XRD. Therefore, in the present study, two extensively occurring Typic Haplusterts of Chhattisgarh basin were selected for precise tracing out of the small amount of palygorskite by XRD.

Materials and Methods

Collection of soil samples

Two Vertisols (Typic Haplusterts) representing two soil series (Dhadhi, Pedon1, and Badwa Kapa, Pedon 2) were selected from the Bemetara district of the Chhattisgarh Basin. Both the pedons were formed in the alluvium of the weathering Deccan Basalt (D.B.) overlying on the gypsiferous purple shale geology of Maniari formation in the riverine (Mukherjee *et al*., 2014). These soils are being cultivated with rice for the last 40 years. Their other details are presented in (Table 1).

Morphological, physical and chemical properties of soils

The morphological properties of the two pedons were described following the Soil Survey Manual (Soil Survey Division Staff, 2017). Horizon-wise soil samples were collected and processed for laboratory analyses. The particle-size distribution was determined using the

Table 1. *Details of the soil profile locations*

	Pedon 1 (P1)	Pedon 2 (P2)
Location	Dhadi Series, Bemetara District, Chhattisgarh.(21.91413°N, 81.46403°E)	Baduwa Kapa Series, Bemetara District, Chhattisgarh.(22.014316°N, 81.481168°E)
Classification	Very fine, smectitic, hyperthermic, *Typic Haplusterts*	
Mean annual rainfall (mm)	1310	
Land use	Rice (*Oryza sativa*) for the past 40 years.	
Geology	Purple Shale	
Parent material	Basaltic alluvium overlying Purple Shale	

International pipette method after the removal of the cementing agents. Sand (2000-50µm), silt (50-2 µm) and clay (< 2 µm) fractions were separated after dispersion according to the size segregation procedure of Jackson (1979). For the collection of water-dispersible clays (WDC), 10 g soil was added to distilled water in a shaking bottle and shaken for eight hours, transferred to a cylinder, and the volume made up to 1000 ml. Aliquots were taken to collect the clay fractions following the international pipette method. The coefficient of linear extensibility (COLE) was determined following the procedure of Schafer and Singer (1976). The pH, electrical conductivity (EC), organic carbon (OC), $CaCO_3$ equivalent, CEC and exchangeable Na^+ and K^+ were determined by standard methods on < 2 mm fractions (Richards, 1954; Jackson, 1973). Exchangeable Ca^{2+} and Mg^{2+} were determined following the 1 *N* NaCl solution extraction method (Piper, 1966). The saturated hydraulic conductivity (sHC) was determined by the constant head method (Klute and Dirksen, 1986). The semi-quantitative estimates of the clay minerals in the < 2 µm fractions, were done (data in the table not shown) following the methods of Gjems (1967) and Datta and Sastry (1993).

X-ray diffraction analysis

X-ray diffraction analysis of the clay fraction (< 2µm) was carried out after preferred orientation on a glass slide with either Ca or K using a Philips diffractometer (X'Pert PRO, M/s PAN alytical) with Ni-filtered CuKα at a scanning speed of 2°2θ/min, and the minerals were identified using the diagnostic method of Jackson (1979). The treatments followed were: (a) Ca-saturated - air-dried, (b) CaEG: Ca saturated, and ethylene glycol solvated, (c) K-25°C: K saturated at 25°C, (d) K-110⁰C: K saturated, and heated to 110°C, (e) K-300⁰C: K saturated and heated to 300°C and (f) K-550⁰C: K saturated and heated to 550°C. Because of apprehensions expressed about the destruction of palygorskite during the removal of cementing agents by chemical pre-treatments (Sombroek,1981; Zade, 2007), WDC was subjected to XRD- analysis alongside the pre-treated clays to gain knowledge on the extent of destruction of palygorskite peak at 1.04-1.05 nm by chemical pre-treatments. Because of the presence of small amounts of palygorskite, the XRD scans of clay fractions were captured at various scanning speeds, i.e., at 2°2θ/min, 1°2θ/min and 0.5°2θ/min so that the peak at 1.04-1.05 nm could be deciphered with ease.

Deconvolution and curve fitting of XRD profile

Although the width of XRD peak of a particular order of reflection from a plane of clay mineral is a combination of several factors like instrumental broadening, broadening due to small particle size, crystal effect, and strain in the crystal (Reynolds Jr., 1989), peak overlapping also causes considerable peak broadening. Peak overlapping is evident in interstratified and mixed-layer minerals which are common in the majority of the agricultural soils (Datta *et al.*, 2015; Liu *et al.*, 2017). Peak broadening is measured by the intensity and width of one line (full width at half maximum, FWHM) (Klug and Alexander, 1974). Broadening in XRD peaks caused by particle size and crystal strain can be determined by unfolding of broadening effects using a least square method of curve fitting through parameter optimization called 'Deconvolution' (Datta, 1996). For this, oriented X-ray diffractograms (3-10°2θ) were deconvoluted following the procedure as described by Velde and Barré (2009) and Datta *et al.* (2015). The diffractograms were fitted to a standard equation by High Score-XRD software (PANalytical).

Further, the effect of instrumental broadening has been eliminated from the observed XRD peak and was corrected after necessary smoothening to eliminate the angular variation of X-ray scattering. After this, the peaks were resolved into individual peaks by fitting, so that areas of overlapping peaks could be calculated. Following this technique, the diagnostic peak of palygorskite at 1.04-1.05 nm could be resolved.

Results

Physical and chemical properties

The soils (Typic Haplusterts) are very deep (0-150 cm), exhibit high shrink-swell potential (COLE value ≥ 0.20), and are clayey (50 to 70% clay), moderately calcareous (< 7 % $CaCO_3$), and have CEC ranging from 40 to 50 cmol (p+) kg^{-1}. These soils are relatively well enriched with OC. The weighted mean value of OC. in the 0-30 cm in Pedon P1 is 0.6 % whereas in Pedon P2 it is 0.8% (Tables 1 and 2).

Both the Vertisols are non-saline (< 0.5 dsm^{-1}) and non-sodic (pH ≤ 8.5; ESP < 15, Richards, 1954) but are very poorly drained as evidenced from their sHC values; the weighted mean value of sHC in the 0-100cm soil depth of Pedon 1is 0.07 cm hr^{-1} and 0.19 cm hr^{-1} in Pedon 2. It is intriguing that even when the exchange sites of both the soils are enriched with Ca and Mg, in contrast to the normal trend in Vertisols, the ratio of exchangeable Ca/Mg decreases sharply with pedon depth and their base saturation is > 100 % (Table 3). Such unique physical and chemical properties suggest the critical role of Mg in the dispersion of clay colloids and halting the free entry of rainwater into the soil profile. Similar chemical and physical properties are often observed in Vertisols that contain palygorskite mineral (Zade *et al*., 2017; Pal, 2019).

Clay mineralogical composition of Typic Haplusterts

Mineralogical composition of the clay fractions (<2 µm) of both P1 and P2 is identical and composed of smectite (60-70%), kaolin (12-22 %), mica (5-10 %) and hydroxy interlayered vermiculite (HIV) plus pedogenic chlorite (PCh) (2-5 %) (Fig. 1). In both the soils, the 1.4 nm peak of Ca saturated samples expand to about 1.7 nm on ethylene glycol solvation, suggesting the presence of smectite. Still a little hydroxy interlayered as evidenced from its tailing at the

Table 2. *Size class, particle diameter (at fine earth fraction; < 2mm) and COLE of the studied Vertisols*

Horizon	Depth (cm)	Size class and particle diameter (µm) Sand (2000-50)	 Silt (50-2)	 Clay (<2)	COLE
			(% of < 2 mm)		
Pedon 1 (P1): Dhadi Series					
Ap	0-14	1.7	40.6	60.1	0.26
Bw	14-37	1.1	38.7	59.3	0.20
Bss1	37-60	1.4	35.4	64.9	0.20
Bss2	60-88	1.8	35.4	60.1	0.19
Bss3	88-115	1.0	45.4	52.9	0.25
Bss4	115-162	1.0	39.5	58.2	0.25
Pedon 2 (P2): Baduwa Kapa Series					
Ap	0-8	5.9	32.0	60.0	0.20
Bw	8-27	5.6	40.9	52.5	0.20
Bss1	27-50	5.0	39.8	54.6	0.19
Bss2	50-70	4.4	35.4	61.9	0.18
Bss3	70-98	3.1	34.5	61.5	0.21
Bss4	98-136	2.5	30.8	66.6	0.18
Bss5	136-154	2.5	35.9	66.3	0.20

low angle side of the mica peak when heated to 550°C (Fig. 1). On K saturation at 25°C, the intensity of 1.4 nm peak got reduced but enhanced that of 1.0 nm peak of mica, and on further heating the K-saturated samples from 110-300°C, the peak of 1.0 nm gets further reinforced, indicating the presence of HIV. At 550°C, the K-saturated sample showed a peak around 1.3 nm, suggesting the presence of PCh. Mica, present in the soils is composed of both muscovite and biotite since the ratio of peak heights of 001 and 002 is > 1 (1.92 and 2.15 for P1 and P2, respectively) (Kapoor, 1972).

Mineral identification from deconvoluted XRD diagram

The deconvoluted Ca-EG graph of pre-treated P1 clays at 3-10°2θ region showed the presence of a distinct peak at 1.72 nm of smectite and peaks at 1.43, 0.99 and 0.92 nm represented traces of vermiculite/chlorite (Vm/Ch), mica and zeolite, respectively (Fig 2). In the case of P2 soil clays, the 1.77 and 1.66 nm peaks are resolved after deconvolution, which correspond to smectite and hydroxy interlayered smectite, respectively (Fig 2). Although the peaks at 1.01, 1.04 and 1.08 nm alongside the peak of mica at 0.99 nm indicated the presence of palygorskite (Moore and Reynolds, 1989; Singer, 2002; Œrodoñ, 2006), no distinct peak of palygorskite at 1.05 nm was visible in the pre-treated clay samples (Fig 1); instead, a broad and moderate peak around 1.05 nm was observed.

In contrast to the XRD results of the pre-treated soil clays, a distinct peak at 1.04 nm of palygorskite but smaller in size along side the peak of mica at 0.99 nm was observed in the deconvoluted CaEG treated samples of WDC of both the soils when scanned at a speed of 0.5°2θ/min (Fig 3). The similar peak at 1.04 nm was not noticed when the WDC samples were scanned at a speed of 1°2θ/min. The P1 soil clays (< 2µm) contain< 2 % palygorskite. In P2 soil clays, a small and broad peak of 1.03 nm was observed when clays were scanned at 2°2θ/min, but a similar peak was not noticed in P1 soil clays. The P2 soil clays contain 2.0-2.5 % palygorskite.

When the K-saturated WDC were heated from 110°C to 300°C, palygorskite peaks at 1.02,

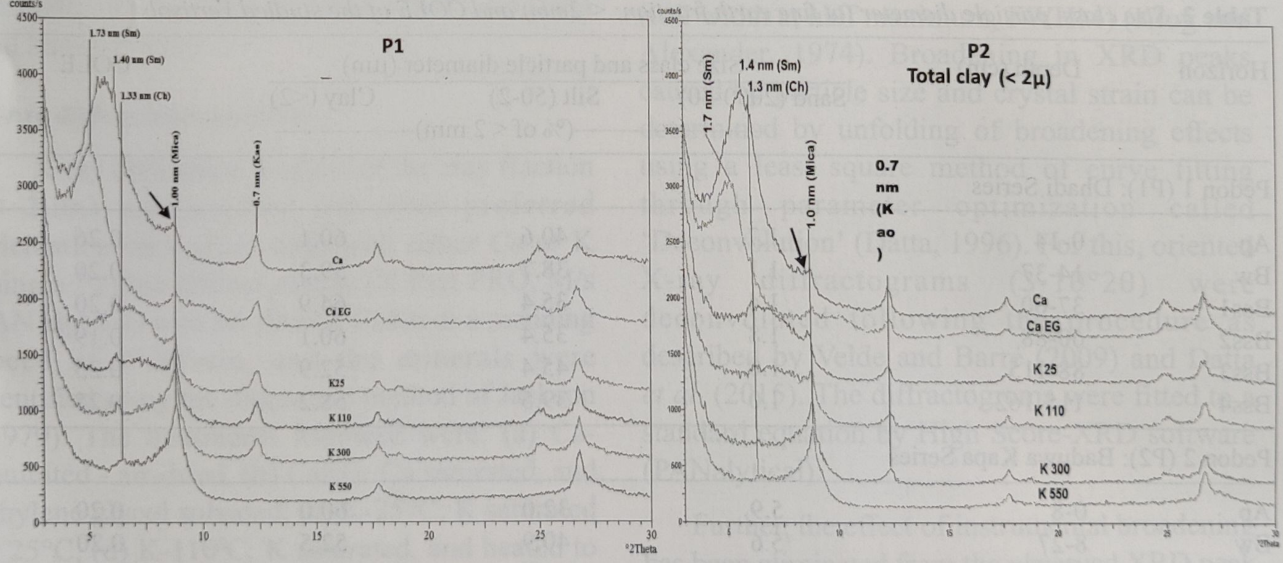

Fig 1. *X-ray diffractogram of pre-treated total clay (<2 µm) fraction derived from P1 and P2 soil. Scanning speed 2°2θ/min. Different treatments are, (a) Ca: Saturated with Ca and air-dried at room temperature (25°C), (b) CaEG: Ca saturated and ethylene glycol solvated, (c) K 25: K saturated at 25°C, (d) K 110: K saturated and heated to 110°C, (e) K 300: K saturated and heated to 300°C, (f) K 550°C: K saturated and heated to 550°C. Sm: Smectite, Ch: Chlorite. Kao-Kaolin,*

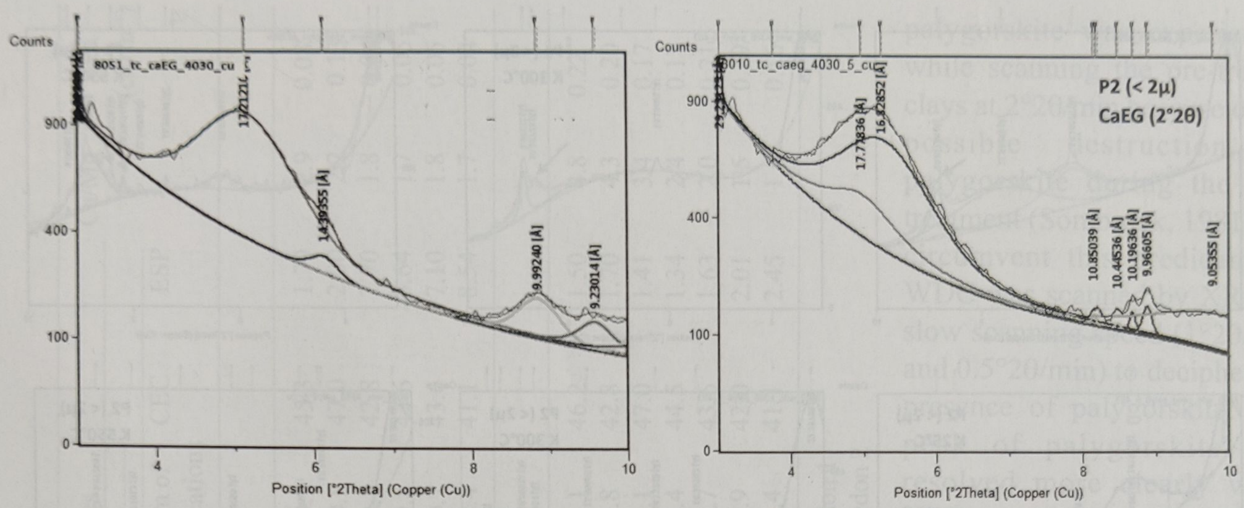

Fig. 2. *Deconvoluted XRD graph of pre-treated clay fractions (<2 θm) derived from P1 and P2 soil. Scanning speed 2°2θ/min.*

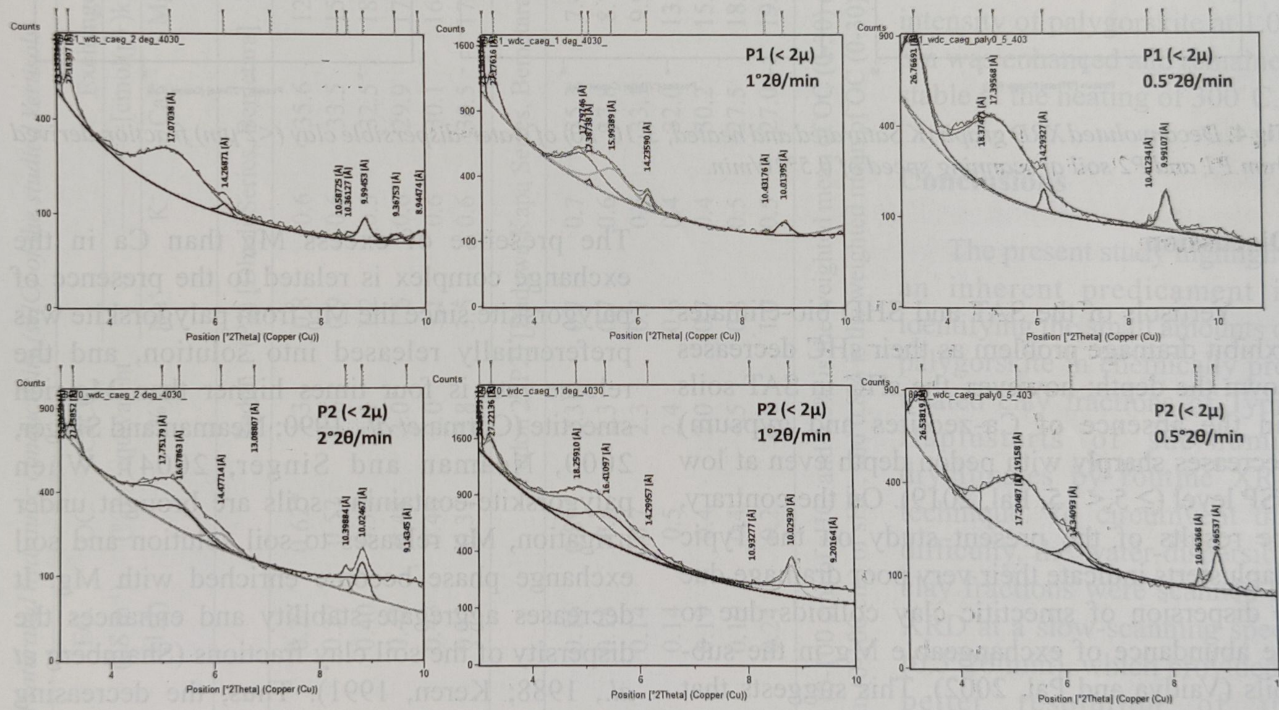

Fig. 3. *Deconvoluted XRD graph (Ca saturated and glycolated, Ca EG treated; 3-10°2θ) of water-dispersible clay (<2 µm) fraction derived from P1 and P2 soil at scanning speed of 2°, 1°, 0.5°2θ/min, respectively.*

1.03, 1.05 and 1.07 nm were observed (Fig 4), which overlapped to that of mica (1.00 nm). As proposed by Nathan (1970), heating the K saturated samples to higher temperature showed a marked increase in 1.05 nm peak which was observed at 300 ˚C in the present study (Fig 4). Although the heating of palygorskite yields a loss of water and causes an initial decrease in d_{001} reflection from 1.05 nm to 0.94 nm (Van Scoyoc *et al.*, 1979), such a peak shift was not observed in the present study.

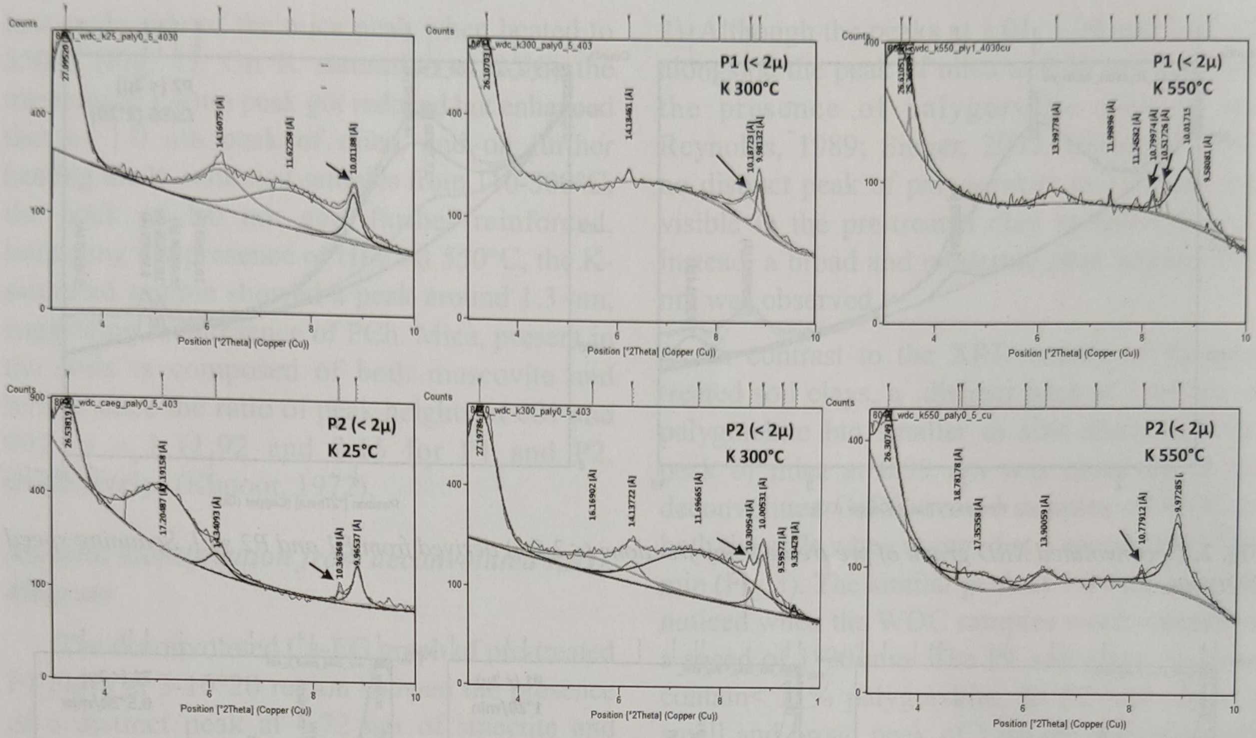

Fig 4. *Deconvoluted XRD graph (K Saturated and heated; 3-10°2θ) of water-dispersible clay (<2 μm) fraction derived from P1 and P2 soil at scanning speed of 0.5°2θ/min.*

Discussion

Vertisols of the SAT and SHD bio-climates exhibit drainage problem as their sHC decreases down the depth; however, the sHC in SAT soils (in the absence of Ca-zeolites and gypsum) decreases sharply with pedon depth even at low ESP level (≥ 5,< 15, Pal, 2019). On the contrary, the results of the present study on the Typic Haplusterts indicate their very poor drainage due to dispersion of smectitic clay colloids due to the abundance of exchangeable Mg in the sub-soils (Vaidya and Pal, 2002). This suggests that the saturation of exchange complex of Vertisols not only with Na $^{+}$ ions but also with Mg^{2+} ions blocks small pores of the soils (Pal *et al.* 2006). Richards (1954) grouped Ca^{2+}, and Mg^{2+} ions in USDA Handbook No. 60 as both these divalent cations are expected to improve the soil structure. However, Alperovitch *et al.* (1981) reported that the presence of exchangeable Mg governs sHC and clay dispersion of sodic smectitic soils containing a very lesser amount of free $CaCO_3$. The presence of excess Mg than Ca in the exchange complex is related to the presence of palygorskite since the Mg from palygorskite was preferentially released into solution, and the release rate is four times higher than Mg-rich smectite (Corma *et al.*, 1990; Neaman and Singer, 2000, Neaman and Singer, 2004). When palygorskite-containing soils are brought under irrigation, Mg releases to soil solution and soil exchange phase become enriched with Mg. It decreases aggregate stability and enhances the dispersity of the soil clay fractions (Shainberg *et al.*, 1988; Keren, 1991). Thus, the decreasing depth distribution of Ca/Mg ratio and Ca/(Na+Mg) ratio and the concomitant decrease in sHC in normal (non-saline and non-sodic) cracking clay soils like Typic Haplusterts of the present study appears to be related to high Mg-rich chemical environment due to the presence of small amounts of clay palygorskite.

The predicament in the straightforward identification of very small to small amounts of

Table 3. *Chemical properties and saturated hydraulic conductivity (sHC) of the studied Vertisols*

Horizon	Depth (cm)	pH (1:2)	EC. (dS m^{-1}) (1:2)	OC. (%)	CaCO$_3$ equivalent (%)	Exchangeable bases [cmol(p+)kg^{-1}] Na$^+$	K$^+$	Ca^{2+}	Mg^{2+}	Sum of base cations	CEC	ESP	Ca/Mg	sHC (cm hr^{-1})
Pedon 1 (P1) [Dhadi Series, Bemetara]														
Ap	0-14	8.1	0.22	0.62*	1.3	0.8	0.6	35.6	12.2	49.2	45.3	1.79	2.9	0.08*
Bw	14-37	8.3	0.27	0.57	1.6	0.9	0.6	33.5	15.5	50.5	47.0	2.00	2.2	0.13
Bss1	37-60	8.3	0.40	0.39	1.1	1.2	0.5	32.5	18.5	52.7	42.8	2.70	1.8	0.04
Bss2	60-88	8.5	0.42	0.48	3.0	1.6	0.6	29.9	17.7	49.8	43.6	3.64	1.7	0.05
Bss3	88-115	8.6	0.43	0.46	2.0	3.1	0.6	30.1	16.9	50.7	43.6	7.10	1.8	0.05
Bss4	115-162	8.7	0.43	0.37	2.8	3.5	0.6	30.5	17.8	52.4	41.1	8.54	1.7	0.04
Pedon 2 (P2) [Baduwa Kapa Series, Bemetara]														
Ap	0-8	8.1	0.16	0.8**	2.3	0.7	0.7	35.3	7.4	44.1	46.2	1.50	4.8	0.22**
Bw	8-27	8.2	0.18	0.8	2.3	0.7	0.6	37.8	8.7	47.8	42.8	1.70	4.3	0.20
Bss1	27-50	8.3	0.14	0.7	2.3	0.7	0.5	33.1	9.9	44.1	47.0	1.41	3.4	0.17
Bss2	50-70	8.4	0.14	0.5	2.4	0.6	0.4	32.0	13.5	46.4	44.5	1.34	2.4	0.17
Bss3	70-98	8.4	0.19	0.4	2.0	0.7	0.4	30.2	15.3	46.7	43.6	1.63	2.0	0.21
Bss4	98-136	8.5	0.19	0.4	4.5	0.8	0.5	27.5	18.1	46.9	42.0	2.01	1.5	0.19
Bss5	136-154	8.5	0.24	0.2	6.6	1.0	0.5	27.0	19.9	48.4	41.1	2.45	1.4	0.16

*0.07 cmhr^{-1} is the weighted mean (0-100 cm) of sHC, and 0.6% is the weighted mean of OC (0-30) cm of Pedon 1

**0.19 cmhr^{-1} is the weighted mean (0-100 cm) of sHC, and 0.8% is the weighted mean of OC (0-30) cm of Pedon 2

palygorskite was experienced while scanning the pre-treated clays at 2°2θ/min because of the possible destruction of palygorskite during the pre-treatment (Sombroek, 1981). To circumvent this predicament, WDC was scanned by XRD in slow scanning speed (1°2θ/min and 0.5°2θ/min) to decipher the presence of palygorskite. The peak of palygorskite was resolved more clearly when XRD scans of WDC were taken at 0.5°2θ min^{-1} rather than 2° or 1°2θ min^{-1}. The peak intensity of palygorskite at 1.04 nm was enhanced and remained stable at the heating of 300° C.

Conclusions

The present study highlights an inherent predicament in identifying the small amounts of palygorskite in chemically pre-treated clay fractions of Typic Haplusterts of sub-humid dryclimates by routine XRD technique. To circumvent this difficulty, the water-dispersible clay fractions were scanned by XRD at a slow-scanning speed (0.5°2θ/min), which provided a better resolution of the palygorskite peak at 1.05 nm than those scanned at 1°2θ/min. Employing the deconvolution method, further resolution of the peak was obtained. Presence of palygorskite even in small amounts may be comprehended with some certainty by some unique and in herently associated soil properties such as a decrease of exchangeable Ca/Mg with pedon depth, base saturation > 100 and sHC < 10 mmhr^{-1}. Thus, even in the absence of XRD facilities to identify palygorskite, these soil properties would be enough to confirm its presence even in the presence of Ca-zeolites (Pal, 2019). Because of its adverse effect on crop yield in SAT Typic Haplusterts as against its beneficial influence in raising economically viable rice production in SHD Typic Haplusterts, a new research initiative to classify palygorskite containing soils at the higher categorical level is warranted to help farming communities of rain-fed regions at their micro-level agricultural land use plans (Pal *et al.,* 2012).

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Credit authorship

Conceptualization, R.P., K.K. and P.C.; methodology, R.P.; investigation, R.P., D.V., S.S. and S.S.G.; writing original draft preparation, R.P.; writing review and editing, R.P., K.K., P.C., D.V., S.S. and P.T.; visualization, R.P., P.T., K.K., D.V., S.S. and P.C.; supervision, R.P., P.C. and P.T. All authors have read and agreed to the published version of the manuscript.

Conflict of interest

The authors declare no conflict of interest that could have appeared to influence the work reported in this paper.

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Plant Available Water Capacity (PAWC) for Deep-Rooted Crops in Cracking Clay Soils (Vertisols) of Semi-Arid Central India

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Abstract: *Smectite is the dominant clay mineral in the cracking clay soils (mainly Vertisols) in the semi-arid tropical (SAT) region (Vidarbha and Marathwada).Amongst the crystalline clay minerals, smectite has the highest soil moisture retention capacity depicted as the available water between field capacity and wilting point, which increases with soil depth. But in SAT Vertisols of Vidarbha and Marathwada regions, the release of this soil water is unavailable to deep-rooted crops, causing loss of crop yield is frequently observed. Thus, the water holding between33 and 1500 kPa tension is not in reality available soil moisture in these soils. The release of soil moisture is, however, seriously constrained by the dispersion of smectitic clay colloids due to the presence of both Mg and Na ions on soil exchange complex. In reality, in calcareous Vertisols of non-sodic nature, soil moisture is held at 100 kPa while in calcareous Vertisols of sodic nature it is held at 300 kPa. Based on this field observation the concept of plant available water content, which relates to profile water content, was adopted earlier to calculate the plant available water capacity (PAWC) considering the soil moisture held between 100-1500 kPa for non-sodic and 300-1500 kPa for sodic soils. This pragmatic PAWC method showed a significant positive correlation between the PAWC and the yield of cotton (lint + seed) of 32 Vertisols of the Vidarbha region, however, it did not address the status of soil moisture release at higher tensions. It is apprehended that at higher tensions, the release of soil moisture is not enough during the dry period of the season that can prevent the extension of vertical cracks in the slickensided horizons at deeper depth of 100 cm and beyond. Less amount of soil water in the subsoils is due to the decrease of saturated hydraulic conductivity(sHC) with depth preventing the free flow of rainwater in the subsoils. This makes subsoils as more water constraint horizons but enriches subsoils with pH > 8.0, more amount of* Mg^{2+} *and* Na^{+} *ions on soil exchange complex. Such Vertisols do not support the second crop during the winter months. In view of this predicament in agricultural land use plan of SAT Vertisols, the present study was undertaken to understand the cause and effect relationship between soil moisture and relevant soil parameters that prevent the release of soil moisture at higher tensions. In order to find an insight into this queer issue, soil moisture retention and release curves at 33, 100, 300, 500, 800, 1000 and 1500 kPa, were obtained for each genetic horizon of 33 representative Vertisols of Vidarbha and Marathwada region. In Vidarbha, Vertisols are Aridic/Typic/Sodic Haplusterts and Calciusterts, and in Marathwada, they*

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are Typic/ Sodic Haplusterts. Moisture tension curves indicate that the release of water beyond 800 kPa is negligible. Failure in the release of soil water beyond 800 kPa is due to the dispersion of fine clay size smectite (< 200 nm) consisting primarily of nano-size smectite (<100 nm), caused by the Mg^{2+} and Na^{+} ions present on the soil exchange complex. The dispersed nano-size smectite blocks the macropores and simultaneously increase the micropores, where soil moisture is held very tightly. In the present study, PAWC calculation was done considering the soil water held between 100-800 kPa for soils of non-sodic nature, and for sodic soils, it was between 300-800 kPa. The revised PAWC data showed a better significant positive correlation with yields of cotton on farmers' field, in comparison to correlation obtained earlier. Thus, it stands as a robust index parameter of soil abiotic stress in SAT environment. This unique parameter having a legacy to major pedogenetic processes in SAT Vertisols. In Indian states under SAT, PAWC emerges as a formidable biophysical parameter for evaluation of rain-fed Vertisols for growing deep-rooted crops.

Keywords : *Cotton yield; Maharashtra; revised plant available water content (PAWC); SAT Vertisols; soil moisture curves; Vidarbha and Marathwada.*

The cracking clay soils of India (Vertisols and their intergrades) occupy 76.4 m ha out of which 35.5% area falls in the state of Maharashtra (Mandal *et al*., 2014). The majority of cracking clay soils in the semi-arid tropical (SAT) parts of central India, are rainfed. They support cropping sequences of sorghum / pigeon pea, cotton / pigeon -pea, and cotton/sorghum/ soybean. These types of cropping patterns usually combine crops with different maturity lengths, drought-sensitive with drought-tolerant crops, cereals with legumes, and cash crops with food crops and are cultivated under hyperthermic to iso-hyperthemic temperature and ustic soil moisture regimes (Swindale, 1989; Pal *et al*., 2012a, b). These agricultural land-use patterns highlight that Vertisols, a relatively homogeneous major soil group in India, support a variety of crops to be grown in subhumid moist (SHM), subhumid dry (SHD), semi-arid moist (SAM) and semi-arid dry (SAD) bio-climates, especially in the Maharashtra state of central India (Pal *et al*., 2012a, b). Although the smectite rich Vertisols, well known to enhance the water holding capacity both at 33kPa and 1500 kPa, have limitations that restrict their full potential to grow both rainy season (*kharif*) and winter (*rabi*) crops. This dismal agricultural situation is observed in very fine/ fine, smectitic, iso-hyperthermic family of Aridic / Sodic Haplusterts of Amravati and Sodic Haplusterts of Akola districts of Vidarbha region of Maharashtra. In Vertisols under SAT areas of central India, cultural operations using a handheld or animal-drawn implements are difficult because of lack of adequate moisture and poor porosity in the subsoil's regions. Thus, the roots of annual crops cannot penetrate to the deeper depths (NBSS&LUP-ICRISAT, 1991). These unfavourable physical properties compel the farmers to grow only one season crop in SAD Vertisols (Aridic / Sodic Haplusterts) of the western part of the Amravati district and the adjoining Akola district. But in SHD Vertisols (very fine, smectitic, hyperthermic family of Typic Haplusterts/ Calciusterts) of Nagpur district, both rainy and winter crops are grown with limited irrigation (Kadu, 1997; Vaidya, 2001; Pal *et al* 2012a, b). Similar cracking clay soils (Typic Haplusterts and Sodic Haplusterts) are also widely occurring in Marathwada region of Maharashtra, which are no better than those of Vidarbha region in growing deep-rooted crops (Zade, 2007).

Deep-rooted crop (cotton) on Aridic Haplusterts (exchangeable sodium percentage, ESP >5, but < 15) and Sodic Haplusterts (ESP ≥ 5, < 15, Balpande *et al*., 1996 or > 15, Richards, 1954) of Vidarbha region has poor productivity (Kadu,1997; Vaidya, 2001). Kadu *et al*. (2003) tried to identify bio-physical factors that decrease the yield of cotton on farmers' field in 29 Vertisols derived from basaltic-alluvium of the Vidarbha region in central India. The yield of deep-rooted crops under rainfed conditions on Vertisols depends mostly on the amount of rain stored in the soil profile and the extent to which this soil water is released during crop growth. The available water content (AWC), calculated from moisture retained between field capacity (33kPa) and permanent wilting point (1500 kPa), indicated that Sodic Calciusterts can hold sufficient amount of water as that of Typic/Aridic Haplusterts; however, a non-significant negative correlation exits between cotton yield and AWC (Kadu *et al.*, 2003). This anomalous situation suggests that the water determined in the laboratory as AWC is not fully released during the crop growth period. The reason is the presence of Na^+ ions on exchange complex of Aridic Haplusterts and Sodic Haplusterts/Calciusterts with ESP > 5 but < 15. Therefore, the AWC so estimated in the laboratory is an overestimation (Gardner *et al.*, 1984) and does not reflect the real soil moisture condition in the field. Kadu (1997) and Vaidya (2001) made repeated careful estimations of moisture during June to September after cessation of rains and they observed that moisture remains at 100 kPa for Typic Haplusterts and Aridic Haplusterts (ESP >5 but < 15). But for Sodic Haplusterts, moisture remains at 300kPa as the downward movement of rain water is governed by hydraulic properties of Vertisols (Kadu, 1997). The saturated hydraulic conductivity (sHC) of soils decreases rapidly with depth, and for Aridic/Sodic Haplusterts the decrease is sharper (ESP > 5, Pal *et al.,* 2009). This conclusion is supported by a significant positive relationship between ESP and AWC, and a significant negative correlation between cotton yield and ESP. On the other hand, a significant positive correlation between yield and exchangeable Ca/Mg (Kadu *et al.*, 2003) indicates that a dominance of Ca^{2+} ions in the exchange sites of Vertisols is required to improve the hydraulic properties for a favourable growth and final yield of crops. Following the observation of Kadu *et al.* (2003), Deshmukh *et al.* (2014) attempted to suggest a pragmatic method to estimate the AWC and plant available water capacity (PAWC), which were estimated at 100-1500 kPa for non-sodic and 300-1500 kPa for sodic soils. They observed a significant correlation between PAWC with cotton yield data collected from the farmers' field from 32 Vertisols of Vidarbha region. This unique relation suggests that newly developed PAWC concept needs to be favoured as an important biophysical parameter in evaluating rainfed Vertisols (without soil modifiers) for deep rooted crops. However, calculating the AWC between 100/300 kPa and 1500 kPa as the lower and upper limit, respectively, does not enlighten us about the quantum of soil water releases with the increase in applied tension from 100/300 kPa to 1500kPa. It appears that moisture release at higher tensions (say at 800 kPa and beyond), especially in the subsoils may be very insignificant as suggested by earlier research (NBSS&LUP-ICRISAT, 1991; Kadu, 1997). Therefore, this important issue needs a fresh research attempt in view of lowering of sHC with pedon depth in SAT Vertisols. The nature and content of clay minerals, and the nature of the exchangeable cations are the deciding parameters for sHC and the retention and release of soil water (Pal, 2017). Dispersion of clay colloids by Mg causes a reduction in sHC, which further drastically reduced in the presence of ESP ≥ 5 (Balpande, 1993; Kadu, 1997, Vaidya, 2001; Zade, 2007). Therefore, it is quite likely that the dispersed clays would cause an increase in the number of small pores by blocking the large ones. The small pores would then retain more amount of moisture held by Mg- and Na- clays, and thus the release of moisture would be highly restricted. There is a general lack of soil depth wise soil moisture data in literature at different tensions (100, 300, 500, 800,1000 and 1500 kPa) in SAT Vertisols of Vidarbha and Marathwada regions. After gaining such data set, it would be possible to ascertain the exact higher limit of moisture tension by which the maximum amount of soil water would be released for its availability for crop growth. Therefore, there is a need to develop the pragmatic method of actual PAWC, which may have a better correlation with crop yields.

In view of the above scenario, the present study was undertaken by selecting representative Vertisols (Typic Calciusterts and Typic/Aridic/ Sodic Haplusterts) of Vidarbha and Marathwada regions with the following objectives.

1. To estimate available water at tensions of 33, 100, 300, 500, 800, 1000 and 1500 kPa for each horizon of the soils of Vertisols and also to follow the nature of moisture release curve of each horizon with pedon depth.
2. To relate the closure of moisture release at the higher tension with some relevant soil physical and chemical properties.
3. To develop a revised PAWC method by calculating soil moisture held between 100/ 300 kPa and the specific higher tension after which release of soil moisture is not significant.
4. To propose the revised PAWC method as an important biophysical parameter in evaluating rainfed Vertisols for deep-rooted crops, based on improved relation between PAWC and cotton yield data collected from farmers' field.

Materials and Methods

Selection of Vertisols

In the present study, 44 Vertisols were studied in Vidarbha and Marathwada region in recent decades (Balpande, 1993; Kadu, 1997, Vaidya, 2001; Zade, 2007). For brevity, a total of 10 representative Vertisols from the districts of Nagpur (Pedons 1 and 2), Amravati (Pedon 3) and Akola (Pedon 4) from the Vidarbha region, and Parbhani (Pedon 5), Jalna (Pedon 6), Osmanabad (Pedon 7), Latur (Pedon 8), Aurangabad (Pedon 9) and Beed (Pedon 10) were selected (Table 1) to collect their depth wise soil moisture data at different tensions in Vertisols for proposing a revision of the existing PAWC calculation (Deshmukh *et al.*, 2014). For the proposed revision, cotton yield data collected earlier from farmers' field from Vidarbha (Kadu *et al.*, 2003; Deshmukh *et al.*, 2014) and the data set of the Marathwada region (Zade, 2007) were utilized, and statistical analysis was made between PAWC and cotton yield from 33 Vertisols. All the soils are developed in basaltic alluvium of the Deccan Basalt and occur in alluvial plains of 1-2% slopes. Pedons 1- 4 represent ustic soil moisture and hyperthermic temperature regime whereas Pedons 5-10 represent ustic soil moisture but isohyperthemic temperature regime (Table 1).

Typical management of soils for cotton and estimates of yield: A total of 33 Vertisols under study are deep-ploughed (30 cm) once in two to three years. In each summer before onset of monsoon, two to three blade harrow is used. Cotton cultivation is followed with 4 months of fallow during February to May each year. After rains frequent blade harrowing is carried out to create the necessary tilth for sowing. Generally, every 2 years, organic manure is added. Improved cultivars are hand-sewn at a depth of about 5 cm on marker intersection points at appropriate times with the inter-row spacing of 75 ± 90 cm. The intercultural operations were carried out by two to three hoeing and hand weeding for removal of weeds, soil aeration and to adsorb maximum moisture from receding rains, as well as to function as dust mulch during the post-rainy season. Insect and pest were controlled with 1 to 2 spraying of insecticide and pesticide. The first inter-row cultivation is done 20 ± 25 days after sowing. The inorganic fertilizers @ 18:18:10 Kg ha^{-1} were applied at the time of sowing. Half dose of nitrogen (urea) @ 25 Kg ha^{-1} was applied 45 to 60 days after sowing. Yield of cotton (as representative of deep-rooted crops), was collected on the 33 Vertisols. Yield data are 10-year averages for Vertisols covering an area of about 200 hectares in each village of Vidarbha and Marathwada region. Eight to ten farmers from each village was periodically contacted to collect the yield data during the last two decades. The variation in yield between the years was about 40%.

Analytical methods: Morphological properties of pedons were studied as per Soil Survey Manual (Soil Survey Division Staff, 1995; Bhattacharyya *et al*., 2009) and horizon wise samples were collected for laboratory analysis. Both sphenoid and slickensides observed in the field confirm the presence of slickensided B horizon (Bss) and thus classified as Vertisols (Soil Survey Staff, 1999)

The bulk density of soil was determined using core samplers (Richards, 1954). The moisture retention and release behaviour within the available range of 33, 100, 300, 500, 800, 1000 and 1500 kPa were measured on < 2-mm size sample using pressure plate membrane apparatus as per method outlined by Richards (1954). PAWC was determined by using the formula suggested by Gardner *et al*. (1984), modified by Coughlan *et al*. (1987) shown below.

$$1.\ \mathrm{AWC} = \frac{(W_{max} - W_{dry})}{\mathrm{DW}} \ \mathrm{x\ BD\ x\ Depth\ (100\ cm)}$$

$$2.\ \mathrm{PAWC} = \sum_{Z=0}^{Z=RD} \mathrm{AWC\ x}\ \Delta Z$$

Where,

W_{max} = gravimetric water content (g g^{-1}) at the upper soil storage limit (0.33 bar),

W_{dry} = gravimetric water content after the plant water extraction i.e. lower soil state storage limit (15 bar),

BD = bulk density of Wmax (0.33 bar),

RD = Rooting depth,

Table 1. *Geographic location of representative Vertisols of Vidarbha and Marathwada region and their classification as per US Taxonomy*

Pedon No	Village	District	Region/State/Mean Annual Rainfall (MAR)	Soil classification
1	Sooli	Nagpur	Vidarbha, Maharashtra, 1060 mm	Very fine, smectitic, hyperthermic family of Typic Haplusterts
2	Brahmpuri	Nagpur	Vidarbha, Maharashtra, 1060 mm	Very fine, smectitic, hyperthermic family of Typic Calciusterts
3	Pusada	Amravati	Vidarbha, Maharashtra, 974 mm	Very fine, smectitic, isohyperthemic family of Aridic Haplusterts
4	Paral	Akola	Vidarbha, Maharashtra, 794 mm	Very fine, smectitic, isohyperthemic family of Sodic Haplusterts
5	Chandaj	Parbhani	Marathwada, Maharashtra, 957 mm	Very fine, smectitic, isohyperthemic family of Typic Haplusterts
6	Kalegaon	Jalna	Marathwada, Maharashtra, 840 mm	Fine, smectitic, isohyperthemic family of Sodic Haplusterts
7	Nali Wadgaon	Osmanabad	Marathwada, Maharashtra, 809 mm	Fine, smectitic, isohyperthemic family of Sodic Haplusterts
8	Gategaon	Latur	Marathwada, Maharashtra, 802 mm	Very fine, smectitic, isohyperthemic family of Typic Haplusterts
9	Bhalegaon	Aurangabad	Marathwada, Maharashtra, 782 mm	Fine, smectitic, isohyperthemic family of Sodic Haplusterts
10	Patrud	Beed	Marathwada, Maharashtra, 685 mm	Fine, smectitic, isohyperthemic family of Typic Haplusterts

ΔZ = depth increment,

DW = density of water (approximately 1g cm^{-3})

The particle size distribution was determined as per the International Pipette method after the removal of calcium carbonate, organic matter and free iron oxides. Sand (2000-50µm), silt (50-2µm), total clay (<2 µm) fractions were separated according to the size segregation procedure of Jackson (1979). For the collection of water-dispersible clays (<2 µm) (WDC), 10 g soil was added to distilled water in a shaking bottle and shaken for eight hours, transferred to a cylinder, and the volume made up to 1000 ml. Aliquots were taken to collect the clay fractions following the international pipette method. The WDC was determined by the International Pipette method. Saturated hydraulic conductivity (sHC) was determined by constant head permeameter (Richards, 1954). The $CaCO_3$, pH, cation exchange capacity (CEC), and exchangeable bases were determined following standard methods (Richards, 1954; Jackson, 1973). Extractable Ca and Mg were determined following the method of 1N Na Cl solution extraction (Piper, 1950).

Undisturbed soil blocks 8 cm long, 6 cm wide, and 5 cm thick were collected from the soil horizons, and thin sections were prepared by the methods of Jongerius and Heintzberger (1975). They were described according to the nomenclature of Bullock *et al*. (1985).

Results and Discussions

Physical and chemical properties of soils under study (Table 2) indicate that Vertisols are deep to very deep (> 100 cm), fine (> 40 to < 50% clay) to very fine (> 50 to < 82% clay) textured, moderately to highly calcareous (< 5 to < 25%), non-saline, moderately to highly alkaline (pH < 8.5 to 9.6). They are moderately well, and poorly to very poorly drained soils, and their exchange sites are mostly dominated by Ca^{2+} and Mg^{2+} cations followed by Na^+ and K^+ ions. In general, CECs of soils are higher than 50 and often show a value nearing 80 cmol (p^+) kg^{-1}, except in soils of fine textural class (Pedons 6,7,9,10). Soils are highly base saturated, but in soils of Marathwada region, the base saturation (BS) often exceeds > 100, indicating the presence of Ca-zeolites (Zade, 2007; Zade *et al*., 2017)). The depth distribution pattern of exchangeable Ca and Mg in soils indicates that in Typic/Aridic Haplusterts and Typic Calciusterts, the exchangeable Mg percentage (EMP) increases while in Sodic Haplusterts both exchangeable sodium percentage (ESP) and EMP increase (Table 2; Fig.1a-f). The depth distribution of clay indicates the gradual increase of clay in the Bss horizons, suggesting an active clay illuviation process in Vertisols (Table 2) (Pal *et al*., 2009; 2012a). This pedogenic process can only be operative when clay particles remain in dispersed or deflocculated form (Pal *et al*., 1994, 2009, 2012a). The calcareous Vertisols under the present study are slightly to highly alkaline (pH ≥ 8.0, Table 2) and contain a considerable amount of water dispersible clay (WDC), which increases with depth with a maximum accumulation in the Bss horizons (Fig.1 a-f). This indicates that the dispersion of clay smectite is possible under slightly acidic to moderately alkaline pH conditions at a very low electrolyte concentration (Pal *et al.,* 2012a) that ensure a pH higher than the zero point of charge required for a full dispersion of clay (Eswaran and Sys, 1979). The increasing trend of WDC with pedon depth (Fig.1 a-f) of Typic/Aridic Haplusterts and Typic Calciusterts and also of Sodic Haplusterts indicate that the dispersion of clay can be caused by magnesium ion as that of sodium ions in the exchange complex (Yadav and Girdhar, 1981; Rengasamy *et al.,* 1986; Magar, 1990; Kadu *et al.,* 1993; Balpande *et al*., 1996; Vaidya and Pal, 2002). This is in contrast to the grouping of Ca^{2+} and Mg^{2+} ions together by the United States Salinity Laboratory (Richards, 1954) since both

Table 2. *Some relevant physical and chemical properties of representative Vertisols*

Horizon	Depth (cm)	pH (1:2)	$CaCO_3$ %	Clay (< 2µm)%	Extractable bases (cmol(p+)/kg)				CEC cmol (p+)/kg	Base saturation (%)
					Ca	Mg	Na	K		
Pedon 1 (Sooli, Nagpur): Very fine, smectitic, hyperthermic family of Typic Haplusterts										
Ap	0-15	8.1	4.4	52.8	32.6	11.6	0.3	0.9	46.5	98
Bw1	15-38	8.1	3.9	57.2	34.0	11.4	0.3	0.8	50.4	92
Bw2	38-62	8.1	3.8	61.6	32.4	14.8	0.4	0.8	52.2	93
Bw3	62-89	8.1	3.7	61.9	30.6	17.4	0.6	0.8	50.4	98
Bss	89-133	8.1	3.7	65.0	28.2	21.8	0.6	0.9	53.9	96
BC	133-150	8.2	17.0	65.6	21.4	24.6	0.7	0.9	53.9	88
Pedon 2 (Brahmpuri, Nagpur): Very fine, smectitic, hyperthermic family of Typic Calciusterts										
Ap	0-14	8.1	3.8	63.0	35.0	15.8	1.3	0.9	57.5	92
Bw1	14-33	8.0	2.0	66.8	40.8	14.2	1.5	0.8	59.1	96
Bw2	33-51	8.0	7.5	67.3	38.6	14.8	1.5	0.8	60.4	92
Bss1	51-92	8.0	9.4	68.4	38.4	17.6	1.1	0.8	62.7	92
Bss2	92-136	8.0	16.1	56.5	26.6	18.2	0.9	0.7	52.8	87
BC	136-155	8.0	9.2	46.4	25.6	20.4	0.8	0.8	48.2	98
Pedon 3 (Pusada, Amravati): Very fine, smectitic, isohyperthemic family of Aridic Haplusterts										
Ap	0-13	8.0	7.0	72.6	47.1	12.8	0.3	0.7	67.8	90
Bw1	13-35	8.0	8.6	75.9	45.5	14.6	0.34	0.5	67.8	90
Bw2	35-59	8.0	9.1	81.4	49.9	14.5	0.39	0.4	66.1	99
Bss1	59-94	8.0	7.4	82.2	49.0	15.3	0.52	0.4	66.1	99
Bss2	94-140	8.0	7.5	81.2	44.3	19.7	0.60	0.4	68.9	95
Pedon 4 (Paral, Akola): Very fine, smectitic, isohyperthemic family of Sodic Haplusterts										
Ap	0-16	8.1	8.7	65	41.5	6.1	0.3	1.76	60.5	83
Bw1	16-39	8.4	10.0	66	39.1	11.5	1.4	0.69	60.0	88
Bw2	39-75	8.6	8.4	63	35.2	10.8	3.5	0.93	63.4	86
Bss1	75-118	8.7	9.5	66	36.1	10.3	5.4	0.89	70.3	82
Bss2	118-144	8.6	10.0	65	30.0	14.8	7.2	0.92	64.2	84
Bss3	144-150	8.7	15.0	59	22.6	15.7	6.9	0.69	48.5	94
Pedon 5 (Chandaj, Parbhani): Very fine, smectitic, isohyperthemic family of Typic Haplusterts										
Ap	0-13	8.2	6.7	63.9	52.3	10.9	0.5	1.9	61.8	106
Bw1	13-28	8.3	6.3	68.6	55.9	9.7	0.3	1.3	59.1	114
Bw2	28-45	8.3	6.5	69.6	54.9	10.6	0.3	1.1	57.5	117
Bss1	45-75	8.2	6.8	69.6	54.2	12.1	0.3	1.0	50.6	134
Bss2	75-108	8.3	6.7	70.1	51.9	14.1	0.4	1.2	56.8	119
Pedon 6 (Kalegaon, Jalna): Fine, smectitic, isohyperthemic family of Sodic Haplusterts										
Ap	0-14	8.8	15.0	41.6	36.7	18.1	0.8	1.2	51.7	110
Bw1	14-36	8.9	14.2	46.4	32.9	21.1	2.8	0.9	54.5	106
Bw2	36-57	9.3	14.4	47.3	29.5	22.4	4.5	0.8	53.3	107
Bss1	57-87	9.3	15.5	48.7	21.1	27.3	7.2	1.4	54.4	105
Bss2	87-114	9.2	17.0	44.1	18.5	25.9	9.9	0.8	50.9	108
C	114-130	9.6	24.4	13.5	12.6	14.7	5.6	0.1	21.8	153
Pedon 7 (Nali Wadgaon, Osmanabad): Fine, smectitic, isohyperthemic family of Sodic Haplusterts										
Ap	0-13	8.5	12.7	49.7	**25.2**	18.1	**1.4**	0.7	45.4	100
Bw1	13-33	8.6	13.5	51.6	23.1	22.1	1.9	0.4	47.1	101
Bw2	33-53	8.9	13.6	56.7	21.0	27.3	2.9	0.4	51.7	100
Bss1	53-82	9.1	13.8	62.1	17.0	34.1	2.5	0.6	56.5	96
Bss2	82-99	9.2	13.5	61.1	19.4	35.6	3.1	0.4	58.4	100
Bss3	99-150	8.9	18.9	67/4	20.3	35.8	2.8	0.7	55.8	107

Table 2. *Continued ....*

Horizon	Depth (cm)	pH (1:2)	$CaCO_3$ %	Clay (< 2μm)%	Extractable bases (cmol(p+)/kg)				CEC cmol (p+)/kg	Base saturation (%)
					Ca	Mg	Na	K		
Pedon 8 (Gategaon, Latur) : Very fine, smectitic, isohyperthemic family of Typic Haplusterts										
Ap	0-14	8.2	1.9	72.8	55.8	12.6	0.5	1.1	78.9	88
Bw1	14-34	8.4	3.6	73.4	56.6	12.5	0.5	1.0	75.0	94
Bw2	34-55	8.5	4.6	77.2	58.3	13.8	1.3	1.0	80.6	92
Bss1	55-84	8.4	4.6	74.4	55.4	15.1	1.0	0.8	78.4	92
Bss2	84-120	8.6	4.4	79.0	51.3	17.4	0.7	0.8	78.4	90
Bss3	120-150	8.4	7.9	80.4	49.5	16.3	0.4	0.4	68.9	97
Pedon 9 (Bhalgaon, Aurangabad) ; Fine, smectitic, isohyperthemic family of Sodic Haplusterts										
Ap	0-12	8.8	12.3	29.7	20.1	14.6	5.4	1.9	34.0	124
Bw1	12-33	9.1	13.5	36.8	15.3	17.0	5.9	1.5	37.1	107
Bw2	33-62	9.1	14.2	38.9	13.4	16.6	9.2	1.5	41.6	97
Bss1	62-88	9.0	14.7	41.6	14.2	17.8	11.5	1.8	40.8	111
Bss2	88-123	8.8	11.7	51.0	12.3	22.0	14.7	1.4	44.4	113
Bss3	123-150	8.9	12.8	46.4	11.2	23.0	21.3	1.5	40.9	139
Pedon 10 (Patrud, Beed): Fine, smectitic, isohyperthemic family of Typic Haplusterts										
Ap	0-14	8.5	11.8	42.8	47.8	10.4	0.7	1.7	55.1	110
Bw1	14-28	8.5	12.2	49.2	44.1	13.7	0/4	0.9	54.5	108
Bw2	28-43	8.5	10.2	48.4	45.4	15.9	0.2	1.3	62.7	100
Bss1	43-85	8.6	9.9	49.1	39.1	18.7	0.5	1.6	56.6	106
Bss2	85-130	8.5	11.8	51.1	36.2	23.5	0.1	0.8	52.6	115
Bss3	130-150	8.5	10.2	58.6	37.8	21.6	0.6	1.9	60.4	102

these ions were assumed to improve the soil structure. Dispersion of clay colloids has impaired the hydraulic properties (sHC) of Vertisols. The sHC decreases rapidly with depth in Typic/Aridic Haplusterts and Typic Calciusterts to Sodic Haplusterts, but the decrease was sharper in Sodic Haplusterts because of their subsoil sodicity (Fig.1 a-f). The decreased sHC restricts vertical and lateral movement of water in the subsoils. During the very hot summer months, this would result in much less water in the subsoil of isohyperthemic temperature regime (SAD bioclimate) (Pal *et al.* 2001; 2012a). This is evident from the deep cracks (> 0.5 cm) cutting through the Bss horizons in Vertisols of drier climates (Fig. 2a, b) associated with the formation of calcareous and sodic soils. Generally, cracks in non-sodic soils (Typic/Aridic Haplusterts and Typic Calciusterts) of hyperthermic temperature regime (SHD bioclimate) extend down to the slickenside zones around 40-50 cm depth (Fig. 2a, b) and show strong plasma separation even when the exchange sites are enriched with Ca^{2+} ions followed by Mg^{2+} (Fig. 3a, c). However, in Sodic Haplusterts with subsoil sodicity alongside high EMP, the less amount of soil water during the shrink-swell cycles restrict the swelling of smectite resulting in weaker plasma separation (Fig.3 b, d). However, in both the state of plasma separation, the presence of macro-and micropores could not be discerned under soil thin section studies. Highly clayey Vertisols under study have nearly 30 to 50 % of fine clay particles (< 0.2μm or < 200 nm), which preferentially translocate downward in the subsoil regions and make clay illuviation process possible in Vertisols (Balpande, 1993; Kadu, 1997, Vaidya, 2001; Zade, 2007; Pal *et al*., 2003). Recent research indicates that fine clay particles (< 200 nm), consist of more than 95 % of < 100 nm size clay particles (Paul *et al*., 2020), show an increasing trend with pedon depth to make the clay

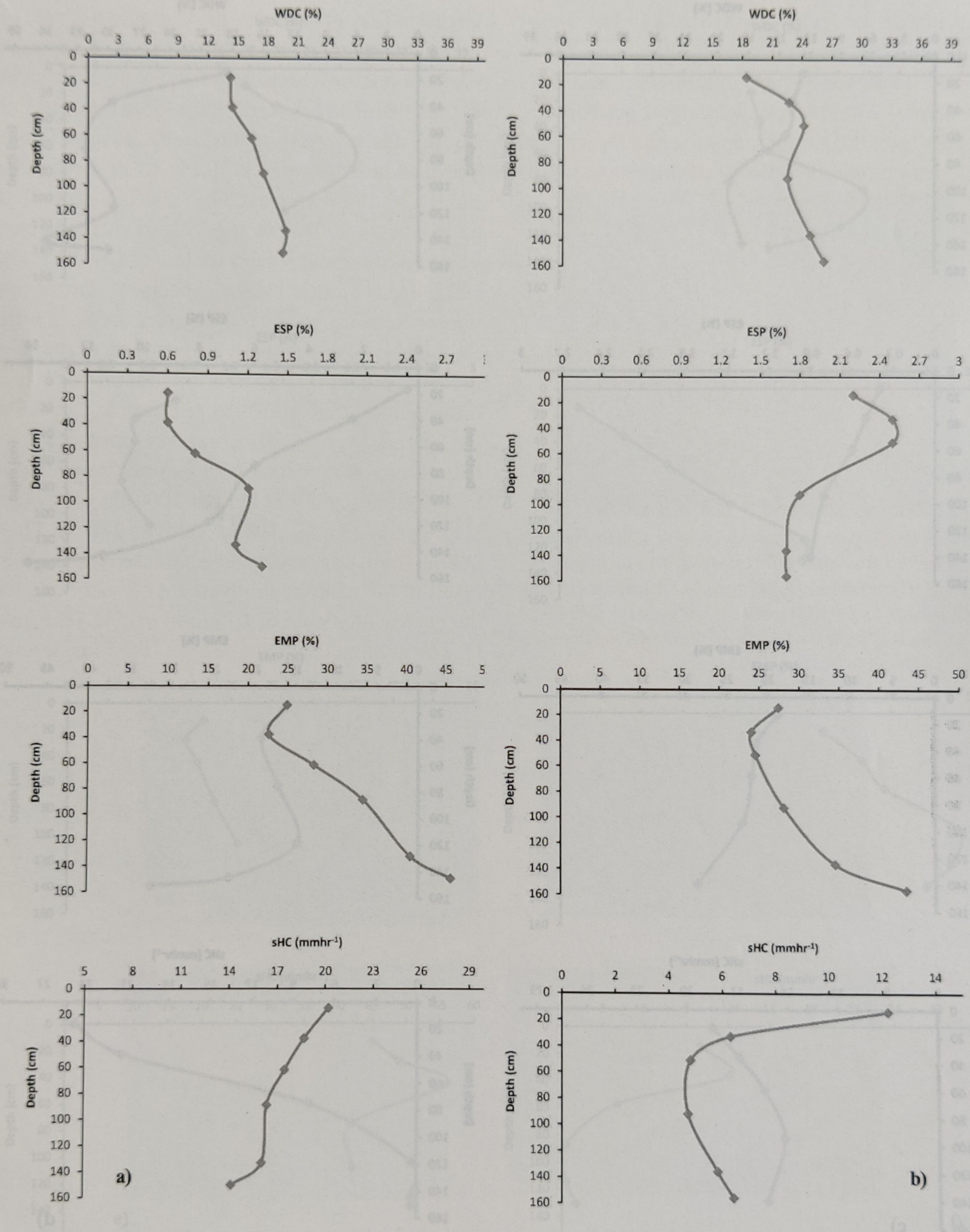


Fig. 1. *Depth distribution patterns of WDC, ESP, EMP and sHC of representative Vertisols of Vidarbha region a) Pedon 1 and b) Pedon 2*

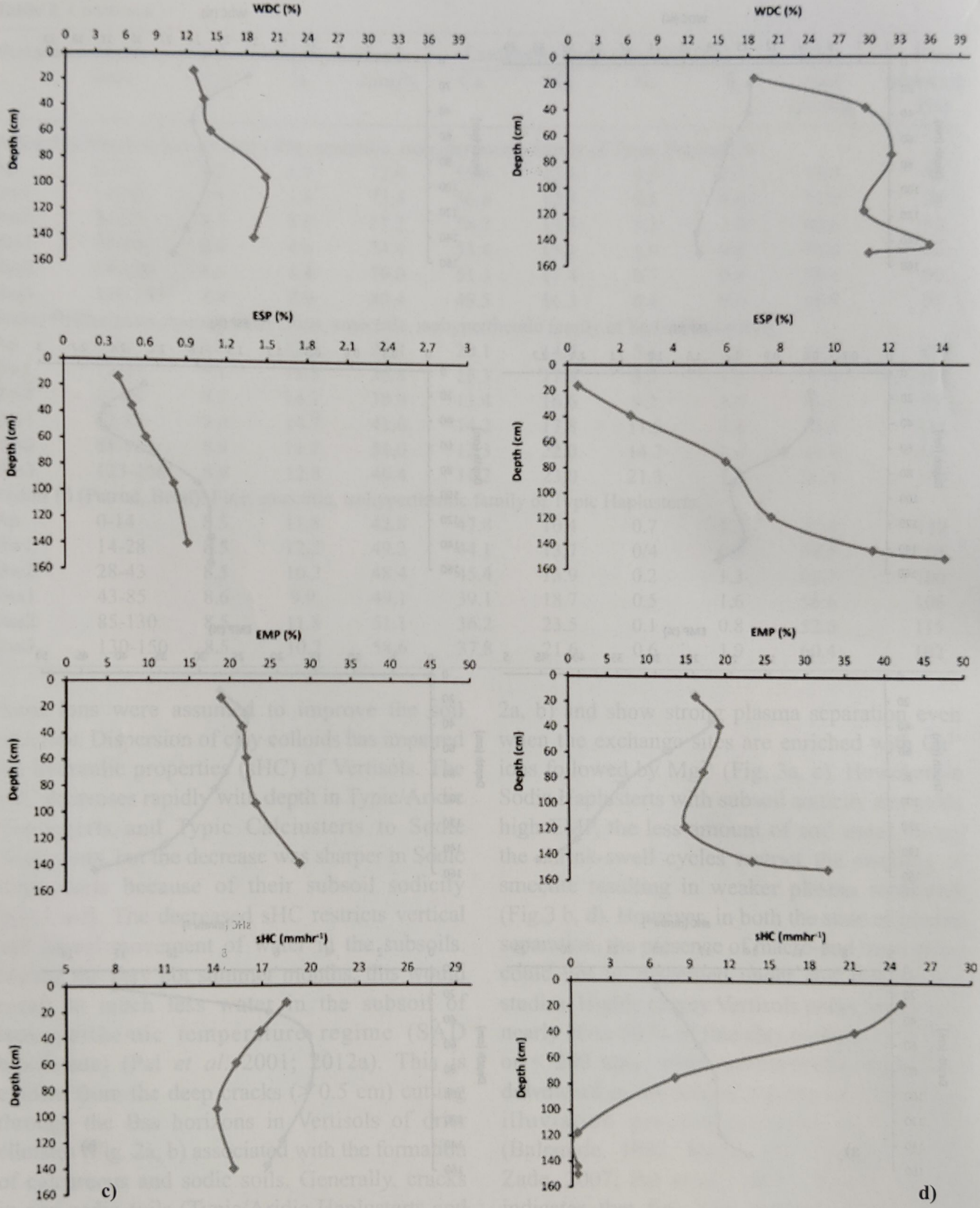


Fig. 1. *Depth distribution patterns of WDC, ESP, EMP and sHC of representative Vertisols of Vidarbha region c) Pedon 3 and d) Pedon 4.*

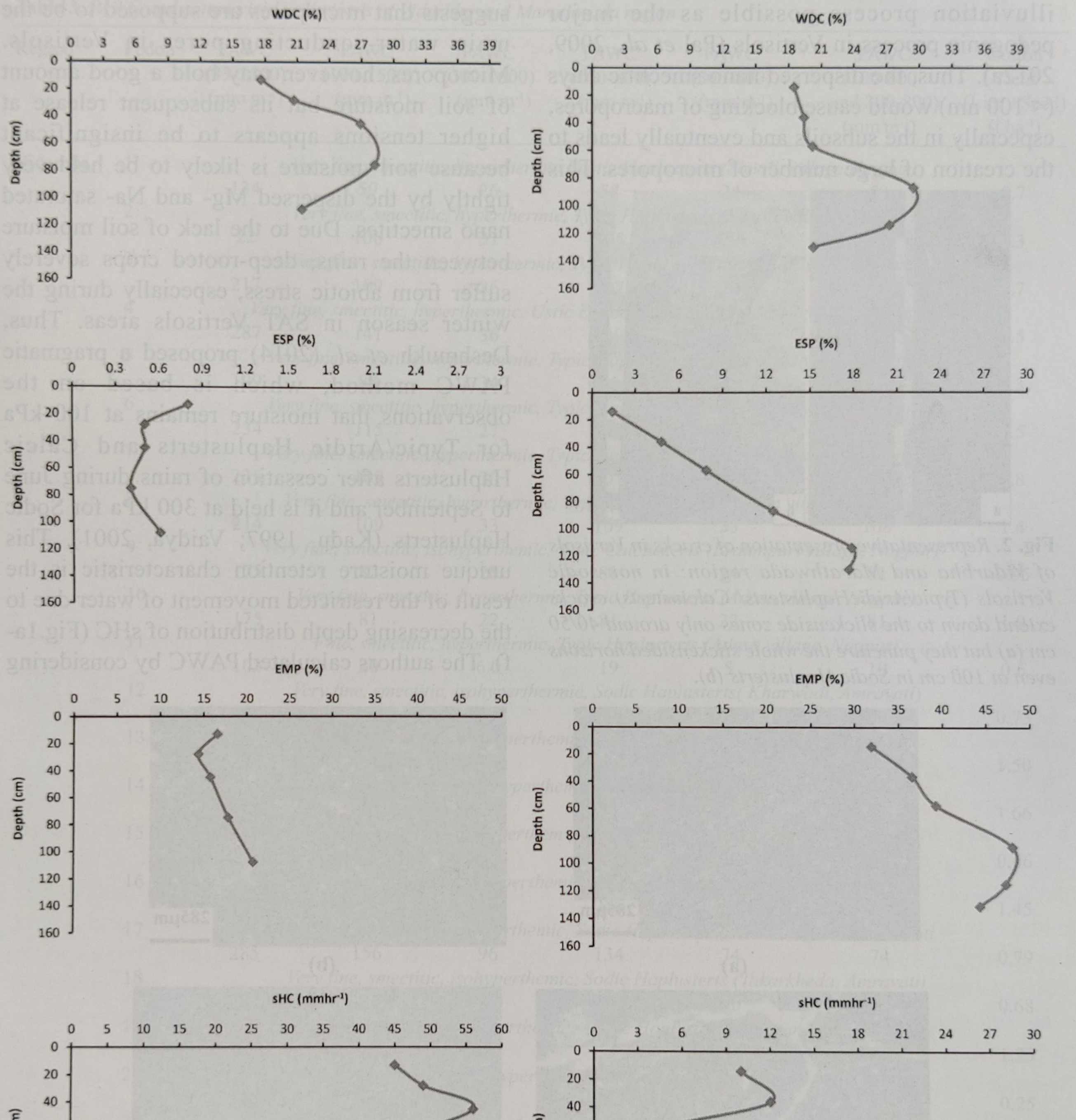


Fig. 1. *Depth distribution patterns of WDC, ESP, EMP and sHC of representative Vertisols of Marathwada region e) Pedon 5 and f) Pedon 6.*

illuviation process possible as the major pedogenic process in Vertisols (Pal *et al*., 2009, 2012a). Thus, the dispersed nano smectitic clays (< 100 nm) would cause blocking of macropores, especially in the subsoils and eventually leads to the creation of large number of micropores. This suggests that micropores are supposed to be the main water-conducting pores in Vertisols. Micropores, however, may hold a good amount of soil moisture but its subsequent release at higher tensions appears to be insignificant because soil moisture is likely to be held very tightly by the dispersed Mg- and Na- saturated nano smectites. Due to the lack of soil moisture between the rains, deep-rooted crops severely suffer from abiotic stress, especially during the winter season in SAT Vertisols areas. Thus, Deshmukh *et al.* (2014) proposed a pragmatic PAWC method, which is based on the observations that moisture remains at 100 kPa for Typic/Aridic Haplusterts and Calcic Haplusterts after cessation of rains during June to September and it is held at 300 kPa for Sodic Haplusterts (Kadu, 1997; Vaidya, 2001). This unique moisture retention characteristic is the result of the restricted movement of water due to the decreasing depth distribution of sHC (Fig.1a-f). The authors calculated PAWC by considering

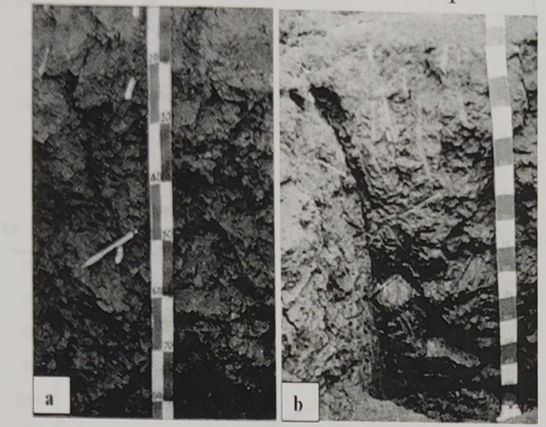
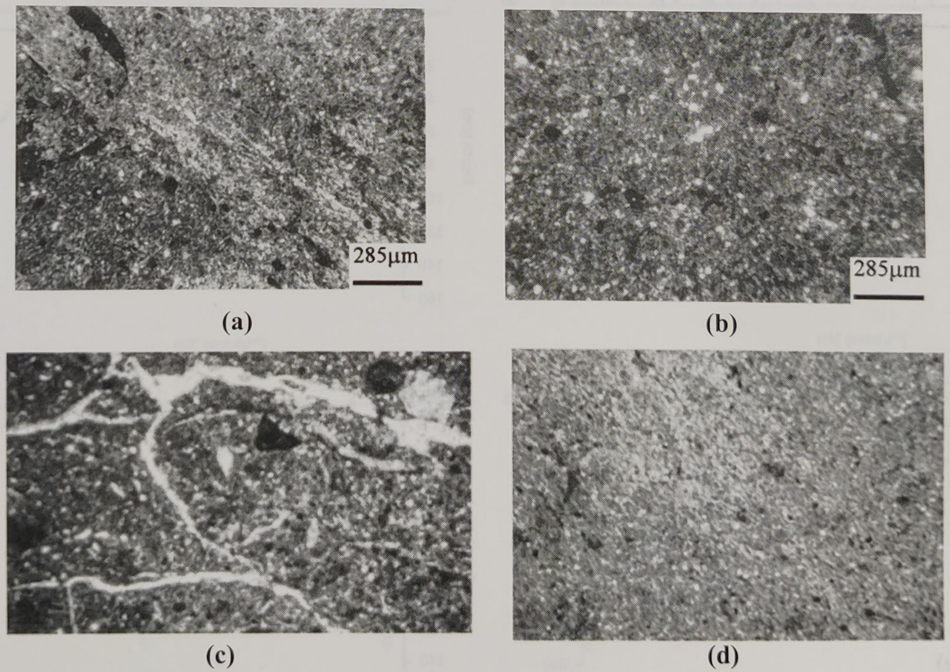


Fig. 2. *Representative presentation of cracks in Vertisols of Vidarbha and Marathwada region: in non-sodic Vertisols (Typic/AridicHaplusterts/ Calciusterts) cracks extend down to the slickenside zones only around 40/50 cm (**a**) but they puncture the whole slickensided horizons even at 100 cm in Sodic Haplusterts (**b**).*



(a) (b)

(c) (d)

Fig. 3. *Representative photograph of plasmic fabrics in cross polarized light. (a) Strong plasma separation with parallel-striated b-fabric of the Bss horizon of Typic/Aridic Haplusterts/Typic Calciusterts of Vidarbha region. (b)Weak plasma separation with mosaic-speckled plasmic fabric of the Bss horizon of Sodic Haplusterts of Vidarbha region. (c) Strong plasma separation with reticulate b-fabric of the Bss horizon of Typic Haplusterts of Marathwada region. (d) Weak plasma separation with mosaic-speckled plasmic fabric of the Bss horizon of Sodic Haplusterts of Marathwada region.*

Table 3. *PAWC and cotton yield in Vertisols of Vidarbha and Marathwada region*

Region	Pedon	PAWC (33-1500) (mm m^{-1})	PAWC (100-1500) (mm m^{-1})	PAWC (300-1500) (mm m^{-1})	PAWC (100-800) (mm m^{-1})	PAWC (300-800) (mm m^{-1})	*PAWC (100-800 and 300-800) (mm m^{-1})	Cotton Yield (Lint +Seed) (t ha^{-1})
Vidarbha	1.	*Very fine, smectitic, hyperthermic,Leptic Haplusterts (Sonoli, village,Nagpur)*						
		134	59	26	58	24	58	0.7
	2.	*Very fine, smectitic, hyperthermic, Typic Haplusterts (Sonoli village, Nagpur)*						
		22	106	31	105	29	105	1.3
	3	*Very fine, smectitic, hyperthermic, Typic Haplusterts (Sonoli village, Nagpur)*						
		217	109	26	107	24	107	1.7
	4	*Very fine, smectitic, hyperthermic, Ustic Endoaquert (Madhaisawangi village, Nagpur)*						
		287	141	36	139	33	139	1.5
	5	*Very fine, smectitic, hyperthermic, Typic Haplusterts (Dhapewada village, Nagpur)*						
		199	88	34	85	31	85	1.3
	6	*Very fine, smectitic, hyperthermic, Typic Haplusterts (Dhapewada village, Nagpur)*						
		234	115	27	114	26	114	1.5
	7	*Very fine, smectitic, hyperthermic, Typic Haplusterts (Dhapewada village, Nagpur)*						
		235	109	30	107	28	107	1.8
	8	*Very fine, smectitic, hyperthermic, Typic Haplusterts (Nilgaon village, Nagpur)*						
		214	109	33	109	33	108	1.4
	9	*Very fine, smectitic, isohyperthemic, Typic Calciusterts (Brahmpuri village, Nagpur)*						
		175	82	26	81	24	81	0.95
	10	*Very fine, smectitic, hyperthermic, Typic Haplusterts (Adasa village, Nagpur)*						
		175	81	22	81	22	81	1.0
	11	*Fine, smectitic, hyperthermic, Typic Haplusterts (Adasa village, Nagpur)*						
		103	20	6.0	19	5	19	0.6
	12	*Very fine, smectitic, isohyperthermic, Sodic Haplusterts(Kharwadi, Amravati)*						
		270	198	80	188	69	69	0.75
	13	*Very fine, smectitic, isohyperthemic, Aridic Haplusterts (Wadura, Amravati)*						
		214	140	70	125	56	125	1.50
	14	*Very fine, smectitic, isohyperthemic, Aridic Haplusterts (Pusda, Amravati)*						
		144	90	23	93	26	93	1.66
	15	*Very fine, smectitic, isohyperthemic, Aridic Haplusterts (Khanapur,Amravati)*						
		131	66	33	60	27	60	0.66
	16	*Very fine, smectitic, isohyperthemic, Aridic Haplusterts (Walgaon, Amravati)*						
		157	94	40	88	34	88	1.45
	17	*Very fine, smectitic, isohyperthemic, Sodic Haplusterts (Khartalegaon , Amravati*						
		285	156	96	134	74	74	0.79
	18	*Very fine, smectitic, isohyperthemic, Sodic Haplusterts (Takarkheda, Amravati)*						
		209	136	95	131	90	90	0.68
	19	*Very fine, smectitic, isohyperthemic, Aridic Haplusterts (Purnanagar, Amravati)*						
		185	92	61	85	54	85	1.25
	20	*Fine , smectitic, isohyperthemic, Sodic Haplusterts (Sait, Amravati)*						
		246	209	49	205	44	44	0.25
	21	*Very fine, smectitic, isohyperthemic, Aridic Haplusterts (Gawarkheda, Amravati)*						
		212	174	67	182	75	182	1.20
	22	*Very fine, smectitic, isohyperthemic, Sodic Haplusterts (Ritpur, Amravati)*						
		266	172	104	164	97	97	0.50
	23	*Very fine, smectitic, isohyperthemic, Sodic Haplusterts (Yawali, Amravati)*						
		250	154	101	145	91	91	0.65
	24	*Very fine, smectitic, isohyperthemic, Sodic Haplusterts (Antora, Amravati)*						
		296	241	125	233	116	116	0.60
	25	*Very fine smectitic, hyperthermic, Typic Haplusterts (Linga Series : Katol, Nagpur)*						
		337	123	112	52	41	52	0.68

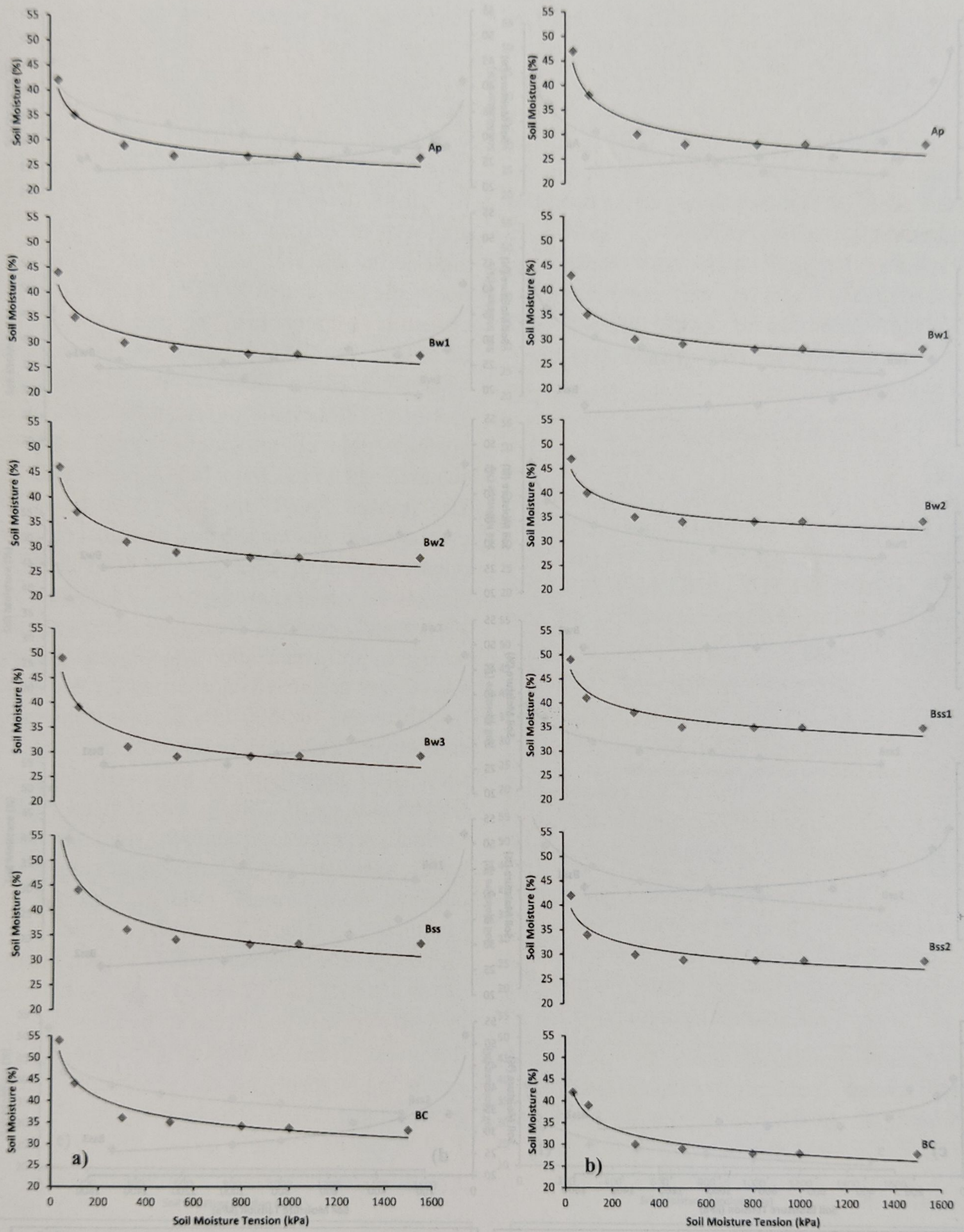
Table 3. *Continued ....*

Region	Pedon	PAWC (33-1500) (mm m^{-1})	PAWC (100-1500) (mm m^{-1})	PAWC (300-1500) (mm m^{-1})	PAWC (100-800) (mm m^{-1})	PAWC (300-800) (mm m^{-1})	*PAWC (100-800 and 300-800) (mm m^{-1})	Cotton Yield (Lint +Seed) (t ha^{-1})
	26	*Very fine smectitic, isohyperthemic, Sodic Haplusterts (Asra Series, Asra,Amravati)*						
		315	102	90	44	33	33	0.50
	27	*Very fine smectitic, isohyperthemic, Sodic Haplusterts (Paral series, Paral, Akola)*						
		341	127	114	64	52	52	0.55
Marathwada	28	*Very fine, smectitic, isohyperthemic, Typic Haplusterts (Chandaj, Parbhani)*						
		247	122	92	79	48	79	1.30
	29	*Fine, smectitic, isohyperthemic, Sodic Haplusterts (Kalegaon, Jalna)*						
		298	210	153	164	106	106	1.25
	30	*Fine, smectitic, isohyperthemic, Sodic Haplusterts (Nali Wadgaon, Osmanabad)*						
		245	149	105	108	64	64	1.00
	31	*Very fine, smectitic, isohyperthemic, Typic Haplusterts (Gategaon, Latur)*						
		219	156	93	116	53	116	1.25
	32	*Fine, smectitic, isohyperthemic, Sodic Haplusterts (Bhalegaon, Aurangabad)*						
		427	270	171	202	103	103	1.05
	33	*Fine, smectitic, isohyperthemic, Typic Haplusterts (Patrud, Beed)*						
		238	137	85	94	43	94	1.00

*These are the PAWC values of Leptic/Aridic/Typic/Sodic Haplusterts/Calciusterts considered for correlation studies with the yield of cotton.

the available water at 100-1500 kPa for non-sodic and 300-1500 kPa for sodic soils. Based on a significant positive correlation between PAWC and yield of cotton, they proposed this method as a pragmatic one. However, it still remains uncertain about the amount of water release at higher tensions due to creation of micropores by the Mg- and Na-saturated nano smectites in the subsoils of Vertisols of non-sodic and sodic nature. In order to resolve this issue, a revisit on the exiting PAWC method (Deshmukh *et al.*, 2014) becomes necessary to obtain the depth-wise soil moisture curves at different tensions of Typic/Aridic Haplusterts, Typic Calciusterts and Sodic Haplusterts. In the following, results obtained for soil moisture at different tensions for the representative Vertisols of both SHD and SAD bioclimates are presented and discussed to propose the revised method of PAWC.

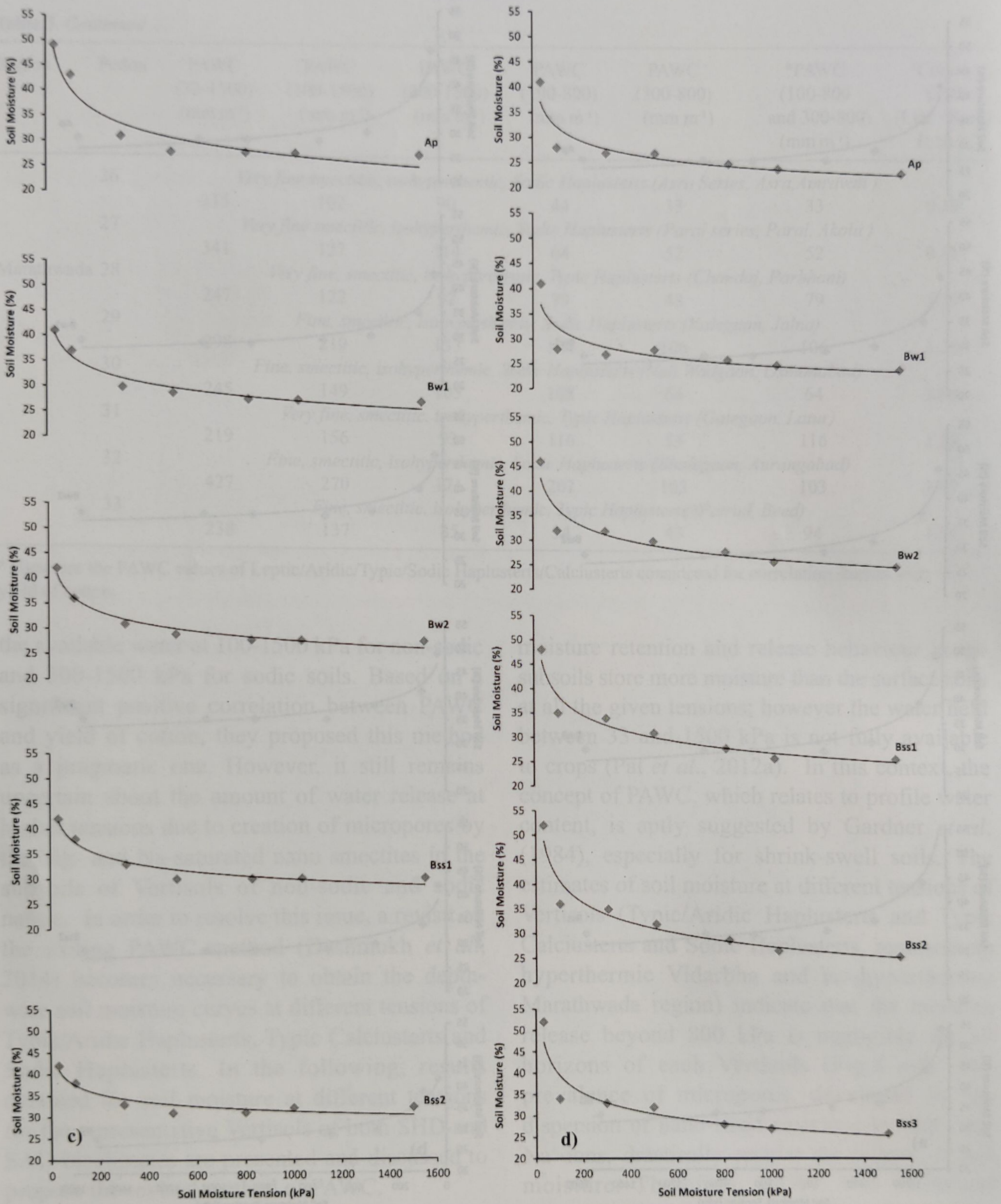
Many researchers in the recent past (Kadu, 1977; Vaidya, 2001; Zade, 2007) after conducting moisture retention study at 33, 100, 500, 800, 1000 and 1500 kPa for a large number of shrink-swell soils (nearly 35 pedons), indicated that the moisture retention and release behaviour in the subsoils store more moisture than the surface soils at all the given tensions; however the water held between 33 and 1500 kPa is not fully available to crops (Pal *et al.*, 2012a). In this context, the concept of PAWC, which relates to profile water content, is aptly suggested by Gardner *et al.* (1984), especially for shrink-swell soils. The estimates of soil moisture at different tensions of Vertisols (Typic/Aridic Haplusterts and Typic Calciusterts and Sodic Haplusterts, representing hyperthermic Vidarbha and iso-hyperthermic Marathwada region) indicate that the moisture release beyond 800 kPa is negligible for all horizons of each Vertisols (Fig.4 a-f). The prevalence of micropores, developed by the dispersion of nano-sized smectites by Mg^{2+} and Na^{+}-ions, drastically restrict the release of soil moisture. Therefore, PAWC was estimated considering available water (AW) between 100-800 kPa for Vertisols of non-sodic nature and for Vertisols of sodic nature, AW was considered between 300-800 kPa (Table 3). The revised PAWC shows a better significant positive



Pedon 1 (Sooli, Nagpur): Very fine, smectitic, hyperthermic family of Typic Haplusterts

Pedon 2 (Brahmpuri, Nagpur): Very fine, smectitic, hyperthermic family of Typic Calciusterts

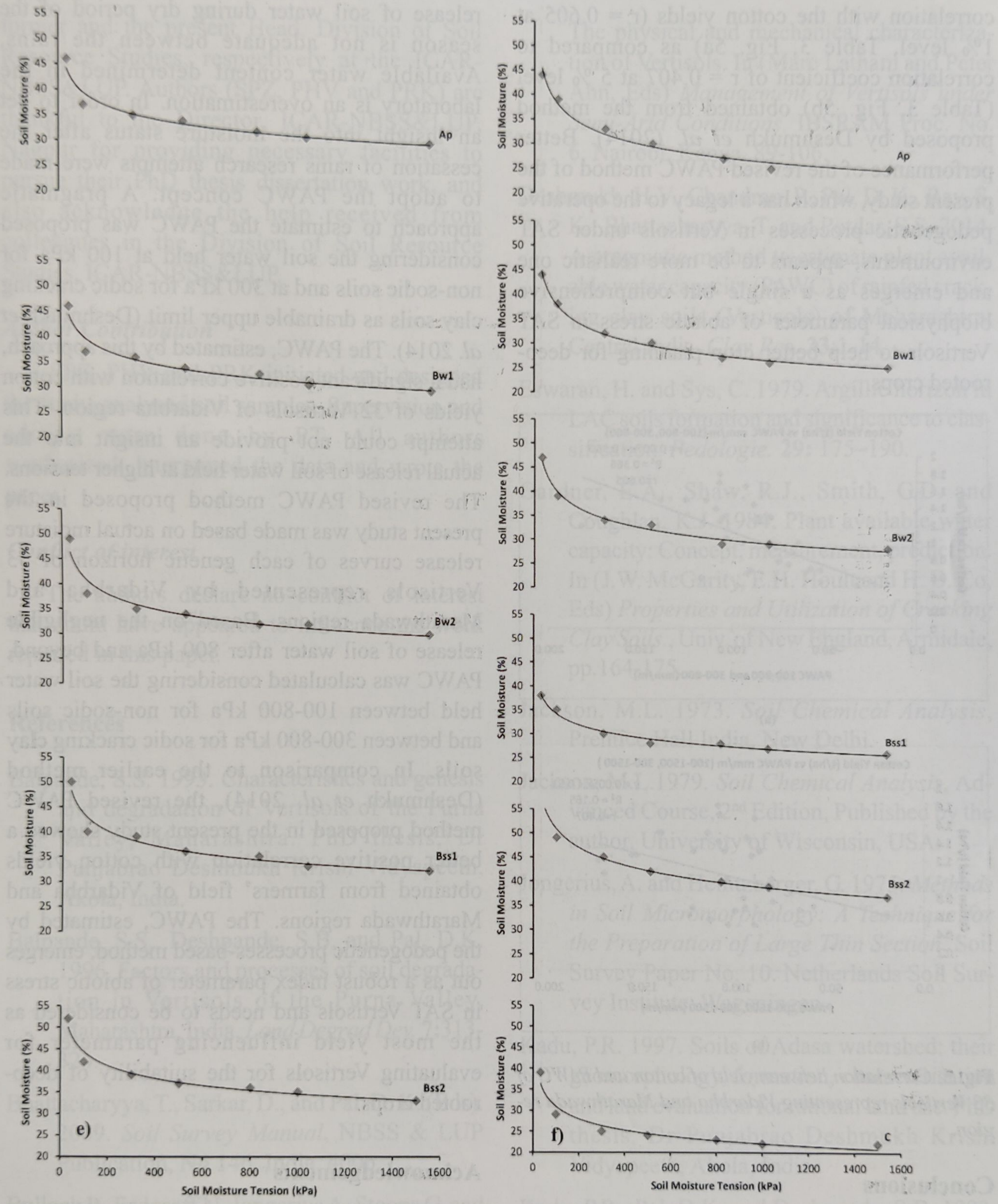
Fig. 4. *Release of soil moisture at different tensions of representative Vertisols of Vidarbha region a) Pedons 1 and b) Pedon 2.*



Pedon 3 (Pusada, Amravati): Very fine, smectitic, Isohyperthermic family of Aridic Haplusterts

Pedon 4 (Paral, Akola): Very fine, smectitic, Isohyperthermic family of Sodic Haplusterts

Fig. 4. *Release of soil moisture at different tensions of representative Vertisols of Vidarbha region c) Pedons 3 and d) Pedon 4.*



Pedon 5 (Chandaj, Parbhani): Very fine, smectitic, isohyperthemic family of Typic Haplusterts

Pedon 6 (Kalegaon, Jalna): Fine, smectitic, isohyperthemic family of Sodic Haplusterts

Fig. 4. *Release of soil moisture at different tensions of representative Vertisols of Marathwada region e) Pedons 5 and f) Pedon 6.*

correlation with the cotton yields (r = 0.605 at 1% level, Table 3, Fig. 5a) as compared to correlation coefficient of r = 0.407 at 5 % level (Table 3, Fig. 5b) obtained from the method proposed by Deshmukh *et al.* (2014). Better performance of the revised PAWC method of the present study, which has a legacy to the operative pedogenetic processes in Vertisols under SAT environments, appears to be more realistic one and emerges as a single but comprehensive biophysical parameter of abiotic stress in SAT Vertisols to help better crop planning for deep-rooted crops.

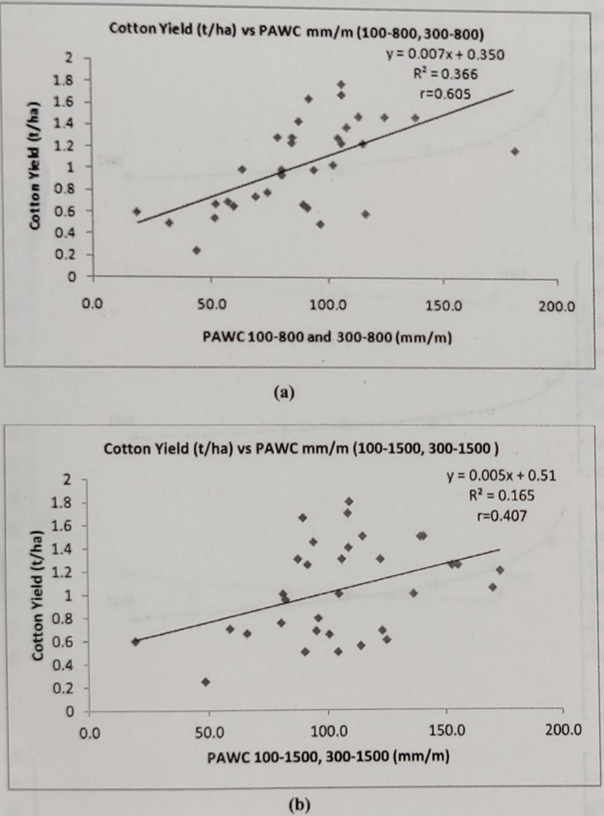


Fig. 5. *Correlation between yield of cotton and PAWC of 33 Vertisols representing Vidarbha and Marathwada region.*

Conclusions

The deep cracking clay soils (Vertisols) of SAT parts of Maharashtra, with special reference to Vidarbha and Marathwada regions, do not support growing deep-rooted crop because the release of soil water during dry period of the season is not adequate between the rains. Available water content determined in the laboratory is an overestimation. In order to get an insight into the moisture status after the cessation of rains research attempts were made to adopt the PAWC concept. A pragmatic approach to estimate the PAWC was proposed considering the soil water held at 100 kPa for non-sodic soils and at 300 kPa for sodic cracking clay soils as drainable upper limit (Deshmukh *et al.* 2014). The PAWC, estimated by this approach, had a significant positive correlation with cotton yields of 32 Vertisols of Vidarbha region. This attempt could not provide an insight into the actual release of soil water held at higher tensions. The revised PAWC method proposed in the present study was made based on actual moisture release curves of each genetic horizon of 33 Vertisols represented by Vidarbha and Marathwada regions. Based on the negligible release of soil water after 800 kPa and beyond, PAWC was calculated considering the soil water held between 100-800 kPa for non-sodic soils and between 300-800 kPa for sodic cracking clay soils. In comparison to the earlier method (Deshmukh *et al.* 2014), the revised PAWC method proposed in the present study showed a better positive correlation with cotton yields obtained from farmers' field of Vidarbha and Marathwada regions. The PAWC, estimated by the pedogenetic processes-based method, emerges out as a robust index parameter of abiotic stress in SAT Vertisols and needs to be considered as the most yield influencing parameter for evaluating Vertisols for the suitability of deep-rooted crops.

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Author Contribution

SPZ, PHV and PRK initiated and designed the study, analysed soil samples. Supervision and editing were done by PT. All authors synthesized, interpreted the data and wrote the paper.

Conflict of interest

The authors declare no conflict of interest that could have appeared to influence the work reported in this paper.

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Mineralogy Class of Indian Cracking Clay Soils (Vertisols and intergrades) in the US Soil Taxonomy: A Critical Appraisal

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Abstract: *Soil Taxonomy (USDA) places cracking clay soils (CCS) (Vertisols and vertic intergrades) into the smectitic mineralogy class. Smectite is a group name consisting of montmorillonite, beidellite and nontronite.Numerous studies, especially undertaken at the ICAR-NBSS&LUP, Nagpur over the last few decades, established that the layer charge of smectites in reality reflect that of specimen bentonite (montmorillonite). Therefore, it would be prudent to revise the mineralogy class of the CCS as 'montmorillonitic' instead of the present class as 'smectitic'. The presence of palygorskite as one of the other minerals, is quite common in the Deccan Basalt derived alluvial parent materials of the CCS. Despite the problem in identification of small amounts of this mineral by X-ray diffraction analysis, simple method, based on the unique depth distribution of exchangeable Ca, Mg, Na, Ca/Mg, and base saturation ≥ 100, is in place to ascertain its presence. Remarkable reduction in hydraulic properties in the subsoils, observed due to the presence of palygorskite, is expected to impair the productivity of the CCS under rain-fed conditions of the semi-arid climates (SAT). This important edaphological issue can be well highlighted if the mineralogy class of the CCS containing palygorskite is revised as 'montmorillonitic-palygorskitic' instead of only 'montmorillonitic'. Such revision will help pedologists/soil mappers to guide the SAT farming communities to raise agricultural crops. This critical appraisal is prepared for its acceptance in the US Soil Taxonomy, which is a dynamic and an open-ended system, and has provision to accommodate any new concepts developed over time through concerted global research efforts to make the system more rational, understandable and meaningful for the soils of tropical India.*

Keywords: *Deccan Basalt alluvium; Indian Vertisols and vertic intergrades; Montmorillonitic mineralogy class; montmorillonitic-palygorskitic mineralogy class.*

Realizing the importance of clay minerals, Soil Taxonomy (United States Department of Agriculture, USDA) advocated a diagnostic mineralogical class in soil classification. The field of soil mineralogy has grown greatly and much of this growth can be attributed to the expansion of agricultural research in general. During the 1950's and early 1960's the mineralogy sections of the soil survey laboratories made major contributions to soil taxonomy (Soil Survey Staff, 1975) while helping to define the various diagnostic horizons and features (Cady and Flach, 1997). The genesis of clay and other minerals are products of interactions of parent materials with climate and other factors and processes of soil formation, they are dependent on the climate and consequent intensity of weathering; accumulation and losses of substance within the soil profile, and often related to its landscape features; vegetation and the duration of these

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influences. However, only in certain combinations of circumstances, soil forming processes exhibit their effects on the clay mineralogy viz. in Oxisols, Vertisols and Andosols (Newman, 1984). In many other soil types, mineralogy is not a dominant characteristic as the soils contain mixture of clay minerals inherited from the parent material and partly from the alteration by soil forming processes (Jackson, 1969). In the early period of growth of soil mineralogy. the USDA emphasized on building up relations to field problems in soil survey. During the development of soil mineralogy, synthesis was made on the observations from different geographical areas, and also on the particular characteristics of previously studied soils (Cady and Flach, 1997). Soon after the adoption of the US Soil Taxonomy (USST) in 1969 to classify the Indian soils, relent less research efforts on the genesis and transformation of clay and other minerals during the last few decades by the Indian pedologists and mineralogists provided insights into several aspects of five pedogenetically soil orders (Alfisols, Mollisols, Ultisols, Vertisols and Inceptisols) with a special attention on their mineralogy. The advancement of soil mineralogy helped to measure the relatively subtle processes related to pedology of the present and past geological periods (Pal, 2017, 2019a) and its impact in rationalizing the soil taxonomic database, especially at the family level of classification with a view to make USST (Soil Survey Staff, 1999) more rationale, understandable, and meaningful for Indian tropical soils (Bhattacharyya *et al*., 2015). The present critical appraisal is exclusively focussed on the existing family level 'smectitic mineralogy class' of Vertisols and intergrades in USST (Soil Survey Staff, 1999).

Parent material and climate in the formation of smectitic CCS

The unique morphology of CCS is caused by typical shrinking and swelling properties of the smectite clay minerals and thus, attracted attention of both pedologists and edaphologists all over the world. Vertisols are an important natural agricultural resource in many countries including Australia, India, China, the Caribbean Islands and the USA (Pal *et al*., 2012a). Although they appear to be a relatively homogenous soil group and occur in a wide range of climatic environments globally, they show considerable variability in their uses and crop production (Pal *et al*., 2012b). As in several parts of the world, Vertisols also occur in wider climatic zones in India. They are humid tropical (HT), sub-humid moist (SHM), sub-humid dry (SHD), semi-arid moist (SAM), semi-arid dry (SAD) and arid dry (AD) climatic environments (Table 1). In total, they occupy 8.1% of the total geographical area of the Indian sub-continent (Table 1). The majority of the Indian CCS are developed in the alluvium of weathering Deccan Basalt, covering an area of 500,000 km ^{2} (Duncan and Pyle, 1988). Additionally, outside the Deccan basalt region of the peninsula, in the states of Punjab, Bihar, Jharkhand and West Bengal, Vertisols and their vertic intergrades occur in SHM, SHD and SAM climates (Pal *et al*., 2010; Nayak *et al*., 2017), but they are not mappable at the 1:250,000 scale. Research work at the ICAR-NBSS&LUP, established a fact that the smectitic parent material in CCS of the Indo-Gangetic alluvial plains of Punjab, Bihar, and West Bengal (Singh *et al*., 1998; Ray *et al*., 2006a; Pal *et al*., 2010; Srivastava *et al*., 2015), and in the metamorphic rock terrain in Jharkhand (Nayak *et al*., 2017), and Andhra Pradesh (Pal and Deshpande, 1987a) is the weathering product of plagioclase feldspar as the first weathering product of the Deccan Basalt (Pal and Deshpande, 1987b). It is estimated that that 100 g of Vertisols of the Peninsular India may contain 40–50 g of low charge dioctahedral smectite (Pal *et al*., 2012a), which cannot be generated at the expense of plagioclase in the prevailing dry climates (Bhattacharyya *et al*., 1993; Pal *et al*., 2012a). Indian Vertisols contain muscovite and biotite mica in the silt and clay fractions but the dioctahedral smectite (DOS) cannot be formed at the expense of muscovite (dioctahedral mica) because the weathering of muscovite is very sensitive to potassium levels in soil (Pal, 2003). On the other hand, biotite converts to trioctahedral vermiculite(TOV) in dry climates (Pal, 2003); thus, the simultaneous formation of DOS and TOV from mica is very unlikely (Pal *et al*., 1989; Ray *et al*., 2006a). As the prevailing sub-humid and semi-arid climates facilitate the formation of $CaCO_3$ from plagioclase (Pal *et al*., 2012c), mica may not yield as much DOS, required for the typical morphological manifestation (slickensides and deep cracking) in Vertisols. Thus, the large quantity of DOS formed under a previous humid climate regime in the source area as an alteration product of plagioclase, which was brought down as alluvium by the rivers in the lower topographic situations in the landscape (Pal *et al*., 1989; Srivastava *et al*., 1998, 2015; Pal *et al*., 2012c), where its crystallinity was preserved in the non-leaching environment of the latter sub-humid to dry climates (Pal *et al*., 2009, 2012c).

Smectite species in CCS and its influence in selected soil bulk properties

Although montmorillonite, beidellite and nontronite as smectite species are often reported in CCS, montmorillonite and beidelliteare the most commonly mentioned. But reports of nontronite are rare (Coulombe *et al*., 1996); however, its presence was reported in Vertisols of Upper Volta (Trauth *et al*., 1967). Coulombe *et al*. (1996), however, opined that despite the presence of an appreciable amount of iron in soil smectites, they seldom qualify as nontronite. An earlier review on the mineralogy of Indian CCS

Table 1. *Distribution of Vertisols in different states of India under broad bioclimatic systems* [a]

States	Bio-climate[b]	Area(mha)(%)[c]
Uttar Pradesh	SAM, SHD	0.41 (0.12)
Punjab	SAM[e]	
Rajasthan	AD	0.98 (0.30)
Gujarat	AD, SAD, SAM	1.88 (0.57)
Madhya Pradesh	SAM, SHD, SHM[d]	10.75 (3.27)
Maharashtra	SAD, SAM, SHD, SHM[d]	5.60 (1.70)
Andhra Pradesh	SAD, SAM, SHD	2.24 (0.68)
Karnataka	AD, SHD, SHM, H	2.80 (0.85)
Tamil Nadu	SAD, SAM, SHD, SHM, H	0.91 (0.28)
Puducherry and Karaikal	SHM	0.011 (0.003)
Jharkhand	SHM, SHD	0.11 (0.034)
Orissa	SHM, SHD, H	0.90 (0.28)
West Bengal	SHD, SHM[e]	
Bihar	SHM[e]	
India		26.62 (8.10)

[a] Adapted from Bhattacharyya *et al*. (2009).

[b] AD: arid dry: 100-500 mm MAR (mean annual rainfall); SAD: semi-arid dry: 500-700 mm MAR; SAM:semi-arid moist: 700-1000 mm MAR; SHD: subhumid dry: 1000-1200 mm MAR; SHM: subhumid moist: 1200-1600 mm MAR; H: Humid: 1600-2500 mm MAR.

[c] Parentheses indicate percent of the total geographical area of the country.

[d] In addition Vertisols occur in HT climate (>2500 mm MAR) in Madhya Pradesh and Maharashtra but they are not mappable in 1:250,000 scale (Bhattacharyya *et al*., 1993, 2005, 2009; Pal *et al*., 2012b).

[e] In the states of Punjab, Bihar, and West Bengal, Vertisols and Vertic intergrades also occur in SHM, SHD, and SAM climates (Pal *et al*., 2010) but they are not mappable in 1:250,000.

by Ghosh and Kapoor (1982) indicated that the CCS clays are dominated by beidellite–nontronite type minerals based on smectite formulae, which however, is not infallible one (Sawhney and Jackson, 1958). During the last three decades, x-ray diffraction (XRD) analysis of large numbers of fine clay smectites of Indian CCS (Pal *et al.*, 2000, 2003, 2012a; Bhattacharyya *et al.*, 1993, 2005; Pal, 2003, 2017) indicates the presence of fairly well crystalline low charge DOS (as evidenced by their higher order reflections, though short and broad) with small to moderate amounts of hydroxy-interlayer (HI) material in the smectite interlayers, alongside a small amount of vermiculite. Therefore, assigning smectite species even in presence of a small quantity of such HI materials and vermiculite would affect the charge and sum relationships using smectite formulae. Therefore, soil researchers of the ICAR-NBSS & LUP, Nagpur further characterized the fine clay smectites by several diagnostic analytical methods such as (1) the Green-Kelly test to identify the smectite species in the smectite group of clay minerals, (2) their expansion towards the intercalation of non-polar organic solvents, and (3) collapsing behaviour to K saturation and heating and further glycol solvation. In addition, they were also characterized by determining their layer charge and seat of charge in their tetrahedral and octahedral layers. These diagnostic analytical tools helped in characterising the exact smectite species in the smectite group of swelling minerals (Bhattacharyya *et al.*, 1993,2005; Pal *et al.*, 2000, 2003; Pal, 2003.2017, 2019a, b).

The Greene-Kelly test (Greene-Kelley, 1953; Hoffman–Klemen effect) confirmed the presence of both montmorillonite and beidellite inthe fine-clay fractions of Indian CCS developed in basaltic alluvium,and the former dominates over the latter (Bhattacharyya *et al.*, 1993; Kapse *et al.*, 2010; Murthy, 1988; Pal and Deshpande, 1987b); however, on glycerol vapour treatment (Harward *et al.*, 1969), the clay smectites expand to approximately 1.9 nm, indicating only the presence of montmorillonite (Fig. 1). It becomes obvious that the beidellite used by Harward *et al.* (1969) could not be expanded to about 1.9nm with glycerol vapour because the solvation energy for the glycerol molecule was less than the attractive force of layers for the interlayer Ca/ Mg. It is felt that the beidellite studied by Harward *et al.* had apparently a higher tetrahedral charge than the Indian fine clay smectites. In other words, fine-clay smectite of Indian CCS is nearer to montmorillonite in the montmorillonite–beidellite series. It is known that nontronite would behave like beidellite in these tests. The clay smectite releases considerable iron in solution as it is unstable under HCl treatment. Therefore, it was concluded that the smectite in Indian CCS is nearer to the montmorillonite of the montmorillonite–nontronite series (Pal and Deshpande, 1987b; Pal, 2017).

Fine clay smectite expands beyond 1.4 nm after glycolation of the K-saturated and heating samples (300 °C; Fig. 1), confirming its low-layer charge density, which is also evidenced by its no K-selectivity (Fig. 2, Pal and Durge, 1987). This unique property suggests that NH_4^+ions also being nonhydrated monovalent cation with almost the same ionic radius as K, is not expected to be adsorbed/fixed in the interlayers of smectites. Therefore, K fertilisers when added in the CCS as a basal dose, the K^+ ions would be adsorbed/ fixed by vermiculite of the CCS (Fig. 3, Pal and Durge, 1987). This reaction would make the NH_4^+ ions from N fertilisers more labile for ready assimilation by growing plants (Pal *et al.*, 2012a) and thus, the addition of K may not cause a reduction in crop yield, as experienced elsewhere with high charge smectite (Chen *et al.*, 1989). Despite having the highest surface area, little hydroxy-interlayered smectite (Fig.1) plays a small role in the adsorption of added negatively charged phosphate ions in Vertisols (Pal *et al.*, 2012a).

The CCS contain> 25 to < 65 % fine clay

fractions (< 0.2 μm or < 200 nm), which consist of > 50 to < 85 % in the total clay fraction (< 2 μm) of the CCS (Pal *et al.*, 2003). It is noted that the fine clay low charge DOS often contain > 90% of < 0.1 μm or < 100 nm nano clays, which are much less hydroxy-interlayered than in the coarser clay smectites (Paul *et al.*, 2020a). Therefore, even at low level of exchangeable sodium percentage (ESP $\leq$ 5 but< 15) alongside moderate amount of exchangeable magnesium percentage (EMP), the abundance of nano clay DOS causes a high level of dispersion and swelling (COLE $\leq$ 0.20, Pal *et al.*, 2009) to the extent that impairs saturated hydraulic conductivity (sHC) to < 1 cm hr^{-1} of CCS of semi-arid tropical (SAT) climates (Balpande *et al.*, 1996; Kadu *et al.*, 2003; Pal *et al.*, 2006; Zade *et al.*, 2017)). It is interesting to note that even after long-term cultivation of horticulture and agriculture crops including rice for > 30 years, the soil organic carbon (SOC) content in the 0-30 cm depth of CCS endowed with low charge nano DOS, seldom crosses 1%, suggesting their inertness in the enhancement of SOC (Pal, 2019b; Paul *et al.*, 2020a).

Seat of charge in tetrahedral and octahedral layers and layer charge of smectite

The qualitative knowledge on the charge density of clay smectites is not enough to relate quantitatively to the above discussed important edaphological issues of the Indian CCS.

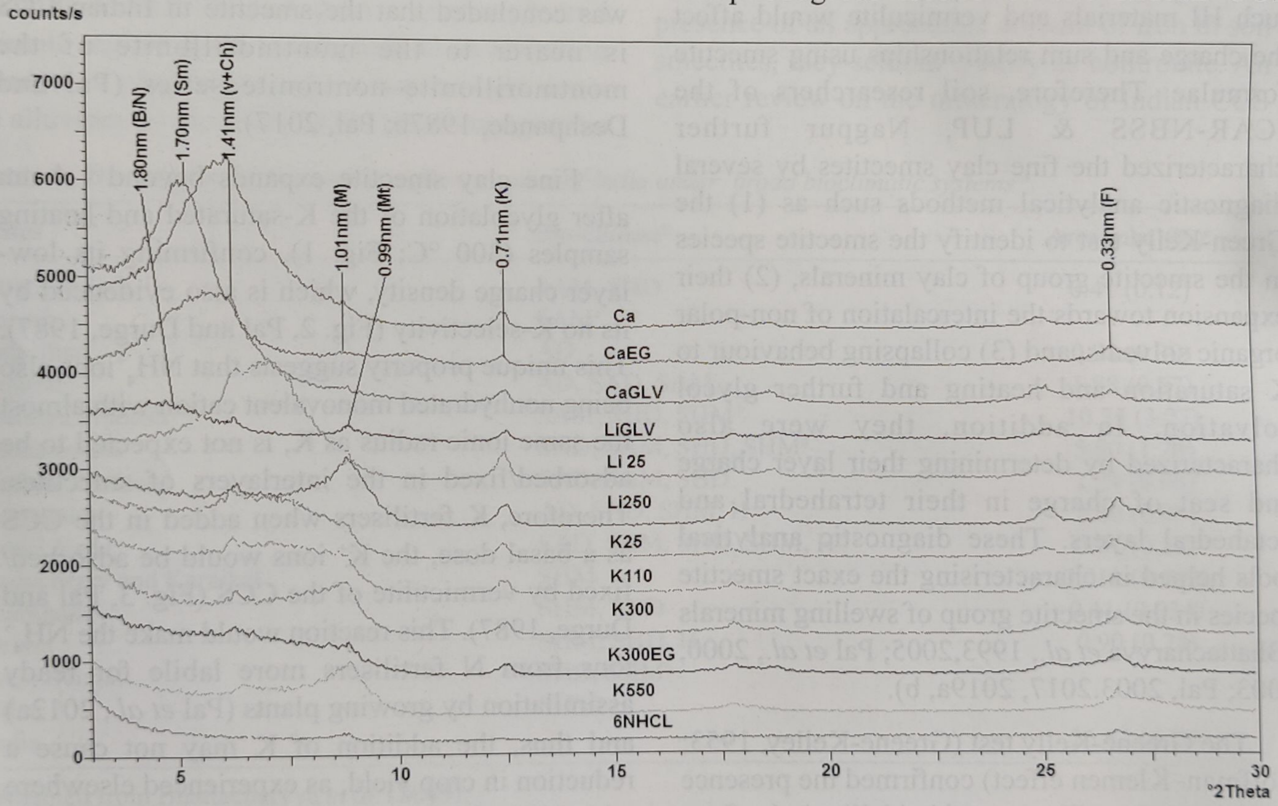

Fig. 1. *Representative X-ray diffractograms of fine clay fractions (<0.2μm) of the Bss horizons of Vertisols of central India; Ca = Ca saturated; Ca-EG = Ca saturated plus ethylene glycol vapour treated; CaGLV = Ca-saturated plus glycerol vapour treated; Li = Li-saturated and heated to 25°C, 250°C (16h), LiGLV 30-D = Li-saturated and heated at 250°C plus glycerol vapour treated and scanned after 30 days; K25/110/300/550°C= K-saturated and heated to 25, 110, 300, 550°C; K300EG = K-saturated and heated to 300 °C plus ethylene glycol vapour treated; 6NHCl = 6N HCl treated fine clays; Sm = Smectite, B/N = beidellite/nontronite; V + Ch = vermiculite plus chlorite; M = mica; Mt = montmorillonite; K = Kaolinite; F = Feldspars.*

Adapted from Pal *et al.* (2003) and Bhople (2010).

Therefore, the determination of their layer charge remains a fundamental requirement in relating to the soil properties. 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 (Ray *et al.*, 2003; Pal *et al.*, 2012a). It is essential to locate seat of charge and also to study changes in the proportion of tetrahedral and octahedral charge during the pedogenic processes of soils. Information about the position of charge in smectites of Indian CCS was made using cation exchange capacity (CEC) method of fine clays (< 200 nm) through a mechanism of charge reduction (Hofmann and Klemen, 1950) by Kapse *et al.* (2010) and Bhople *et al.* (2011). Their results indicate that the charge is distributed in both tetrahedral and octahedral layers of which the contribution of the former is higher (>50%) than the latter (Table 2). However, it is more important to determine the layer charge of smectite minerals, required to relate the important soil properties. Theoretically, this parameter should range between 0.3 and 0.6 electrons per half unit cell in smectites. Tessier and Pedro (1987), however, reported that high-charge smectite (between 0.45 and 0.60 electrons per half unit cell), is common in soils. Several researchers (Bardaoui and Bloom, 1990; Chen *et al.*, 1989) also reported the presence of smectite

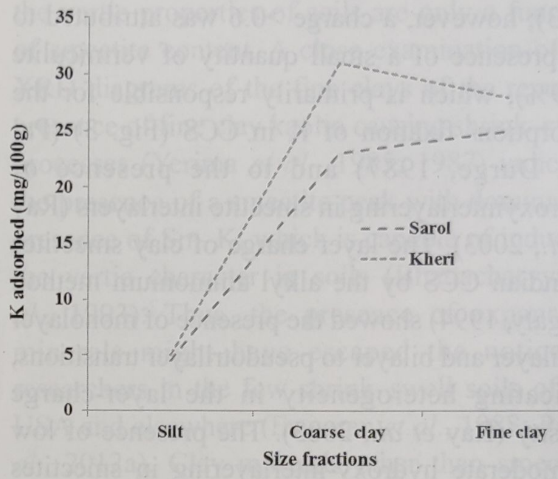

Fig. 2. *Adsorption of added K in silt (50-2um), coarse clay (2-0.2um), fine clay (<0.2um) fractions of representative SAT Vertisols, showing no selectivity for K by the fine clay fractions, dominated by low charge smectite.* Adapted from Pal and Durge (1987).

Table 2. *CECs (total, tetrahedral and octahedral) and the contribution of tetrahedral and octahedral CECs to total CEC of fine clay smectites of some representative benchmark Vertisols of central India.*[1]

Horizon	Depth (cm)	CEC - Total cmol(p+) kg^{-1}	CEC Tetrahedral cmol(p+) kg^{-1}	CEC$_{\text{Octahedral}}$ cmol(p+) kg^{-1}	Contribution of CEC$_{\text{Tetrahedral}}$ to CEC$_{\text{Total}}$(%)	Contribution of CEC$_{\text{Octahedral}}$ to CEC$_{\text{Total}}$(%)
Linga Series: Nagpur: Maharashtra: Typic Haplusterts						
Ap	0-16	83	68	15	82	18
Bw1	16-44	75	59	16	78	22
Bw2	44-69	80	52	28	65	35
Bss1	69-102	84	54	30	64	36
Bss2	102-128	93	48	45	52	48
Bss3	128-150	84	49	35	58	42
Nimone Series: Ahmednagar: Maharashtra: Sodic Haplusterts						
Ap	0-13	59	58	1	98	2
Bw1	13-38	66	46	20	69	31
Bw2	38-55	72	47	25	65	35
Bss1	55-94	66	41	25	62	38
Bss2	94-128	54	38	26	70	30
Bw/Bc	128-150	59	39	20	66	34

[1] Adapted from Kapse *et al.*, (2010); Bhople *et al.* (2011)

in Vertisols with a layer charge in the range of vermiculite (0.6–0.9 electrons per half unit cell). Clay smectite in representative Indian CCS also showed a high layer charge (0.28 to 0.78 mol electrons/$(SiAl)_4O_{10}(OH)_2$). The low-charge smectite constitutes >70% in them (Ray *et al.*, 2003); however, a charge >0.6 was attributed to the presence of a small quantity of vermiculite (5–9%), which is primarily responsible for the adsorption/ fixation of K in CCS (Fig. 3) (Pal and Durge, 1987) and to the presence of hydroxyinterlayering in smectite interlayers (Ray *et al.*, 2003). The layer charge of clay smectites in Indian CCS by the alkyl ammonium method (Lagaly, 1994) showed the presence of monolayer to bilayer and bilayer to pseudotrilayer transitions, indicating heterogeneity in the layer-charge density (Ray *et al.*, 2003). The presence of low to moderate hydroxy-interlayering in smectites is more common in CCS smectites in peninsular India (Pal, 2003; Pal and Deshpande, 1987b). Ray *et al.* (2002) observed that higher the tetrahedral charge, greater is the probability that hydroxy-interlayers will form in fine clay smectites. The hydroxyinterlayers prevent the determination of the layer charge by the alkylammonium method (Lagaly, 1994) by obstructing the normal intrusion of alkylammonium ions into interlayers (Ray *et al.*, 2006b), which causes the overestimation of the layer charge of core lattice mineral. Thus, Ray *et al.*(2006b) observed the removal of HI was almost complete by using the 0.25 N EDTA solution (pH 7.0), and obtained the weighted-average layer charge of the pre-treated clays from 0.40 to 0.46 mol (–)/$(Si, Al)_4O_{10}(OH)_2$. After the EDTA treatment, the charge rangedfrom 0.27 to 0.33 mol (–)/ $(Si, Al)_4O_{10}(OH)_2$, a value ranges close to the layer charge of Wyoming bentonite (montmorillonite species of the smectite group of layer silicate minerals) (Thakare *et al.*, 2013).

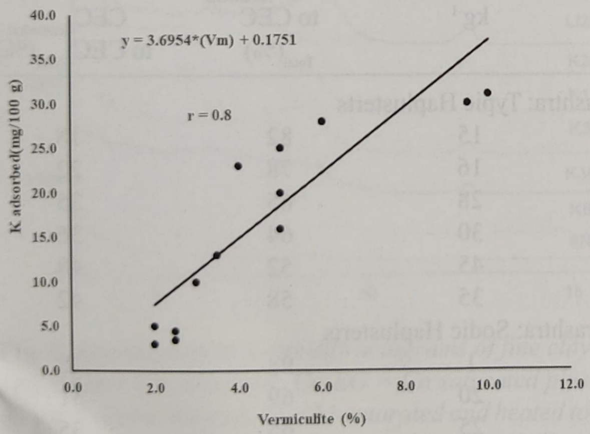

Fig. 3. *Relation between K adsorbed and vermiculite content of the silt, coarse clay and fine clay fractions of representative SAT Vertisols, suggesting vermiculite being the prime K adsorbing mineral in these fractions,* Adapted from Pal and Durge (1987)

'Montmorillonitic' instead of 'smectitic': A rational mineralogy class of CCS

Soil Survey Staff (1994) stipulated the montmorillonitic mineralogy of soils (hitherto proxying for the smectite group of clay minerals) is associated with vertic properties when smectite exceeds 50% of the total mineral content in the < 2 μm clay fraction. Later on, a qualitative smectite mineralogy class was proposed by the Soil Survey Staff (1998, 1999) for the soils that contain more smectite by weight than any other single clay mineral. This requirement provided a means by which smectite can reflect a quantitative dimension of the vertic properties of soils. By XRD analysis, quantitative determination of minerals in the soil clay fractions is difficult, and it yields only their semi-quantitative estimates and is also not straight forward when minerals are in the interstratified phase. To circumvent this problem, the chemical method of Alexiades and Jackson (1965) offers an effective way to determine the smectite content in soil clays quantitatively. Following this classical chemical method, Shirsath *et al.* (2000) observed a remarkable relationship between marked shrink–swell properties and smectite content in the clay fraction (< 2μm). Vertic properties with a linear extensibility (LE) of 6 in CCS correspond to a minimum threshold value of 20% clay smectite (Fig. 4). This relation advocates that only smectitic soils should be considered CCS in the US Taxonomy. However, in view of the affirmative establishment of exclusive presence of montmorillonite as one of the species of smectite in CCS developed in the alluvium of the Deccan Basalt, it would be wise to assign the 'montmorillonitic' mineralogy class of CCS, which has inherent link in influencing some of the above discussed important physical, chemical and mineralogical properties of Vertisols and vertic intergrades.

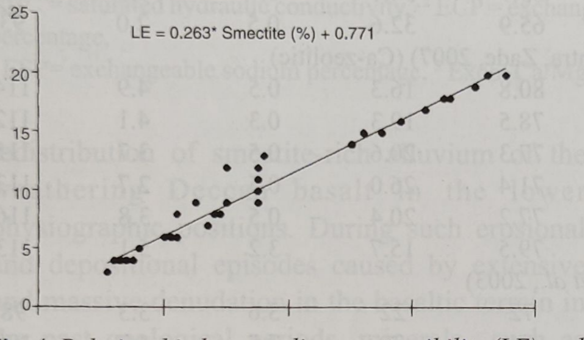

Fig. 4. *Relationship between linear extensibility (LE) and smectite content of soils with vertic characters.* Adapted from Shirsath *et al.* (2000)

Influence of other non-smectitic clay minerals in CCS

Smectite is considered the major mineral in CCS, with kaolinite being of secondary importance (Hajek, 1985). In contrast, kaolinite has been reported to be abundant in some Vertisols in El Salvador (Yerima *et al.*, 1985, 1987) and Sudan (Yousif *et al.*, 1988). In addition to kaolinite, several other non-expanding clay minerals such as micas, chlorites, palygorskite and vermiculites, are mentioned as associated clay minerals in Vertisols and their vertic intergrades (Hajek, 1985; Coulombe *et al.*, 1996; Heidari *et al.*, 2008). As a matter of fact, surface properties of soils primarily govern their shrinking and swelling phenomena, which however are extremely manifested in smectitic soils whereas other soils containing all other clays may shrink and swell with variations in moisture content (Borchardt, 1989). However, it is well known that kaolin, micas, chlorites, palygorskite and vermiculite do not expand on solvation and thus these minerals do not exhibit any swelling phenomenon. This was demonstrated by Bhattacharyya *et al.* (1997) who concluded that the vertic properties of soils are only a function of smectite content. A close examination of the XRD diagrams of the fine clays of the reported presence of fine clay kaolin causing shrink–swell processes (Yerima *et al.*, 1985; 1987) indicates the presence of a smectite peak with dominating presence of Sm–K, which is capable of inducing the vertic character in soils (Bhattacharyya *et al.*, 1993). Thus, the presence of expansible minerals might have escaped the notice of researchers in the few shrink–swell soils of the USA and elsewhere (Eswaran *et al.*, 1988; Pal *et al.*, 2012a). Clay minerals other than smectite, are also beneficial for plants and animals but not the palygorskite clay mineral because it affects the quality of soils by impairing their hydraulic properties (Zade, 2007; Pal, 2017; Bhattacharyya *et al.*, 2018). In recent years,the presence of palygorskite is noted in CCS (Aridic/Typic /Sodic Haplusterts) developed in the alluvium of the weathering Deccan basaltin the central and western Peninsular India in the states of Maharashtra (Hiller and Pharande, 2008; Kolhe *et al.*, 2011; Zade *et al.*, 2017), Gujarat (Pal *et al.*, 2003), Rajasthan (Pal *et al.*, 2003) and Chhattisgarh (Paul *et al.*, 2020b) (Table 3). Palygorskite clay mineral is related to the intertrappean sediments sandwiched between the Deccan trap flows in Andhra Pradesh (Siddiqui, 1967), Karnataka and Gujarat (Shrivastava *et al.*, 2000) where palygorskite occurs in lacustrine sediments of high basicity under arid conditions induced and influenced by Deccan volcanism (Shrivastava *et al.*, 2000). Such highly calcareous, palygorskitic and alkaline sediments are red in colour and often referred to as red bole in Maharashtra (Kolhe *et al.*, 2011). Pal and Deshpande (1987b) and Bhattacharyya *et al.* (2018) reported a major phase, or phases, of

Table 3. *Some physical and chemical properties of CCS containing palygorskite*

Horizon	Depth (cm)	pH 1:2	CaCO$_3$ %	sHC^1 mm/hr	ECP^2	EMP^3	ESP^4	Exch. Ca/Mg^5	BS^6 %
Pedon 1: Kesapur (Sodic Haplusterts, Hingoli, Maharashtra, Kolhe *et al.*, 2011)									
Ap	0-14	9.1	12.0	0.8	51	42.0	16.4	1.2	110
Bw1	14-29	9.1	11.8	0.3	43	43.5	26.5	0.9	113
Bw2	29-49	9.4	14.4	0.4	36	43.3	30.4	0.8	110
Bw3	49-71	9.3	16.6	0.2	31	47.2	37.5	0.6	116
Bss1	71-103	9.0	15.9	0.4	32	46.2	37.5	0.7	116
Bss2	103-155+	8.5	10.7	2.2	37	44.4	36.5	0.8	119
Pedon 2: Sawargaon Deoni (Typic Haplusterts, Latur, Maharashtra, Zade, 2007) (Ca-zeolitic)									
Ap	0-14	7.2	0.9	6	62.9	34.8	0.5	1.8	93
Bw1	14-30	7.0	2.2	2	63.9	33.5	0.7	1.9	95
Bw2	30-54	6.7	0.9	4	63.9	34.1	0.7	1.9	94
Bss	54-90	7.0	1.6	4	65.9	32.6	0.5	2.0	93
Pedon 3: Kajal Hipperga (Typic Haplusterts, Latur, Maharashtra, Zade, 2007) (Ca-zeolitic)									
Ap	0-10	7.9	4.7	6	80.8	16.3	0.5	4.9	114
Bw1	10-34	8.0	4.1	9	78.5	19.3	0.3	4.1	112
Bw2	34-66	8.1	5.6	7	77.3	20.6	0.5	3.7	115
Bss1	66-89	8.2	5.8	7	71.4	26.0	0.5	2.7	113
Bss2	89-112	8.4	6.9	9	77.2	20.4	0.5	3.8	116
C	112-131	8.6	21.1	—	79.5	15.7	3.2	5.1	113
Pedon 4: Jhalipura (Typic Haplusterts, Kota, Rajasthan, Pal *et al.*, 2003)									
Ap	0-12	8.3	0.9	8	72	22	3.6	3.3	98
Bw1	12-31	8.3	5.7	15	84	20	2.5	4.2	108
Bw2	31-48	7.7	5.4	7	80	23	1.5	3.5	105
Bss1	48-74	8.1	5.9	6	86	21	1.6	4.1	110
Bss2	74-110	8.3	7.3	13	71	33	1.6	2.1	106
Bss3	110-148	8.1	7.1	14	81	24	1.9	3.4	109
Bss4	148-165	8.4	7.1	30	76	30	4.2	2.5	112
Pedon 5: Semla (Aridic Haplusterts, Rajkot, Gujarat, Pal *et al.*, 2003) (Ca-zeolitic)									
Ap	0-17	7.8	15.4	23	68	30	1.4	2.3	102
Bw1	17-42	7.8	18.2	42	73	34	2.2	2.1	110
Bw2	42-57	7.9	18.6	21	58	41	4.9	1.4	105
Bss1	57-86	7.9	14.5	17	70	32	4.5	2.2	108
Bss2	86-115	7.9	17.2	32	57	41	6.3	1.4	108
Bss3	115-144	7.9	17.7	9	61	35	3.4	1.7	101
Bc	144-155	8.0	23.3	12	48	45	7.7	1.1	101
Pedon 6: Sokhda (Sodic Calciusterts, Rajkot , Gujarat, Pal *et al.*, 2003, 2012a) (Ca-zeolitic)									
Ap	0-11	8.2	21.9	32	76	35	3.6	2.2	118
Bw1	11-37	8.4	21.4	30	74	32	4.4	2.3	113
Bw2	37-63	8.7	21.5	15	63	46	9.1	1.4	120
Bss1	63-98	8.8	22.0	4	49	47	16.2	1.0	115
Bss2	98-145	8.6	21.6	2	42	51	28.0	0.8	123
BC	145-160	8.5	11.6	21	36	43	31.3	0.8	112
Pedon 7: Dhadi (Typic Haplusterts, Bemetara, Chhattisgarh, Paul *et al.*, 2020b)									
Ap	0-14	8.1	1.3	0.8	78	27	1.8	2.9	109
Bw	14-37	8.3	1.6	1.3	71	33	2.0	2.2	107
Bss1	37-60	8.3	1.1	0.4	76	43	2.7	1.8	123
Bss2	60-88	8.5	3.0	0.5	68	40	3.6	1.7	114

Table 3. *Continued...*

Horizon	Depth (cm)	pH 1:2	$CaCO_3$ %	sHC[1] mm/hr	ECP[2]	EMP[3]	ESP[4]	Exch. Ca/Mg[5]	BS[6] %
Bss3	88-115	8.6	2.0	0.5	69	39	7.1	1.8	116
Bss4	115-162	8.7	2.8	0.4	74	43	8.5	1.7	127
Pedon 8: Baduwa Kapa (Typic Haplusterts, Bemetara, Chhattisgarh, Paul *et al.*, 2020b)									
Ap	0-8	8.1	2.3	2.2	76	16	1.5	4.8	95
Bw	8-27	8.2	2.3	2.0	88	20	1.7	4.3	112
Bss1	27-50	8.3	2.3	1.7	70	21	1.4	3.4	94
Bss2	50-70	8.4	2.4	1.7	73	30	1.3	2.4	104
Bss3	70-98	8.4	2.0	2.1	68	35	1.6	2.0	107
Bss4	98-136	8.5	4.5	1.9	65	43	2.0	1.5	117
Bss5	136-154	8.5	6.6	1.6	65	48	2.4	1.4	118

[1]sHC = saturated hydraulic conductivity, ,[2] ECP = exchangeable calcium percentage, [3] EMP = exchangeable magnesium percentage,
[4] ESP= exchangeable sodium percentage, [5] Exch. Ca/Mg =Exchangeable Ca/Mg, [6] BS = percent base saturation.

redistribution of smectite-rich alluvium of the weathering Deccan basalt in the lower physiographic positions. During such erosional and depositional episodes caused by extensive and massive denudation in the basaltic terrain in the past geological periods, minerals such as quartz, K-feldspar, chlorite and micas that have no legacy to the Deccan basalt, were incorporated due to the exhumation of other rock formations that underlie the Deccan basalt (Pal and Deshpande, 1987b). It is quite likely that during such episodes, the palygorskite-rich clay sediments of the intertrappean were also exhumed and became a part of smectite rich alluvial parent material for the formation of CCS (Bhattacharyya *et al.*, 2018).

The presence of palygorskite (the most magnesium-rich of the common clay minerals) is thus common in Typic Haplusterts, Sodic Haplusterts and Sodic Calciusterts in association with Typic Haplusterts that contain no palygorskite in CCS of peninsular India (Zade, 2007; Kolhe *et al.*, 2011) and elsewhere (Heidari *et al.*, 2008). These calcareous and non-sodic and sodic soils with and without Ca-zeolites, show interesting physical and chemical properties in terms sHC, pH, ECP, EMP, ESP, and Exch. Ca/Mg (Table 3). The depth distribution of sHC in the first 100 cm in Sodic Haplusterts (Pedons 1 and 6) indicates a sharp reduction alongside the enrichment of both ESP and EMP in the subsoils where EMP is more than ECP, and thus Exch. Ca/Mg shows a value < 1 in pedon 1, and < 2 in pedon 6 (Table 3). Despite being Ca-zeolitic, the sHC in the subsoils of pedon 6 is < 5 $mmhr^{-1}$, suggesting the adverse effect of EMP mediated through the release of Mg^{2+} ions from palygorskite clay mineral. In non-zeolitic Sodic Haplusterts (Pedon 1), the adverse effect of EMP on sHC reduction is more severe as evident from their poor Exch. Ca/Mg (< 1). In contrast to sodic soils, non-sodic CCS like Aridic/Typic Haplusterts in the first 100 cm soil depth show a decrease in sHC < 5 $mmhr^{-1}$ in pedon 2, <10 $mmhr^{-1}$ in pedon 3, < 20$mmhr^{-1}$ in pedon 4, < 20 $mmhr^{-1}$ in pedon 5 and < 2 $mmhr^{-1}$ in pedons 7 and 8. The dispersibility of clay colloids impairing the sHC of Vertisols is generally an effect of ESP in the presence or absence of soil modifiers (Pal *et al.*, 2012a); however, in Aridic/Typic Haplusterts the reduction in sHC is due to increase in EMP with concomitant decrease in ECP and Exch. Ca/Mg in the subsoils (Table 3). The BS of such CCS ≥ 100 indicates the enrichment of Mg^{2+} ions due to the presence of palygorskite. Neaman *et al.* (1999) probed the influence of clay mineralogy on disaggregation in some palygorskite-, smectite-, and kaolinite-containing soils (ESP<5) of the Jordan and Betshe'an valley in Israel and reported that palygorskite is the most disaggregated of the clay minerals, and its fibre does not associate into aggregates in soils and suspensions even when the soils were saturated with Ca^{2+} ions. This particular property of palygorskite makes its fine size particles move downward in the profile preferentially over smectite and eventually clog the soil pores (Neaman and Singer, 2004). The downward movement of fine palygorskite particles causes higher EMP than ECP in the subsoils of Aridic/ Typic Haplusterts (Table 3), which causes dispersion of the clay colloids. This interaction causes drainage problems, which gets further aggravated on irrigation, presenting a predicament for crop production. Identification of clay palygorskite in Indian CCS by XRD method has not always been straight forward. When it is present in moderate amounts, it is detected well (Fig.5). But its presence in low amounts may often be overlooked due to lack of sharp characteristic peak at 1.05 nm (Fig. 6). Additionally, its presence could be destroyed due to the chemical pre-treatments that are routinely applied to separate soil clay fractions. To circumvent this predicament, water-dispersible clays of CCS are used for XRD analysis (Zade *et al.*, 2017) and the broad peak around 1.05 nm was resolved by slow-scanning at a speed of $1^{0}2\theta$/minute and $0.5^{0}2\theta$/minute, which can be betterresolved using the deconvolution method (Paul *et al.*, 2020b). The results of the present study suggest that the unique depth distribution of sHC, ECP, EMP, Exch. Ca/Mg and BS $\geq$ 100 (Table 3), especially in subsoils of the CCS of SAT climate would be enough to ensure the presence of palygorskite even when XRD facilities are not available (Pal, 2019b) so that its presence does not escape the attention of the soil researchers. In view of their poor sHC that

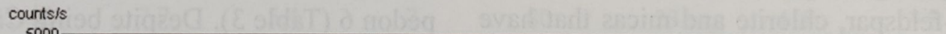

Fig. 5. *Representative X-ray diffractograms of total clay fractions of Sodic Haplusterts (Pedons 1 and 6) (Sm=smectite, Sm/Vm=smectite or vermiculite, Pk=palygorskite, Ca = calcium saturated; CaEG = Ca-saturated and ethylene glycolated; K25°/K110°/K300°/K550° = K saturated and heated at 25, 110, 300 and 550°C. K300°EG= K saturated and heated at 300° and ethylene glycolated).* Adapted from Kolhe et al (2011).

causes inadequate plant available water content resulting in loss of soil productivity (Kadu *et al.*, 2003; Zade, 2007; Deshmukh *et al.*, 2014), non-sodic and calcareous Indian CCS (Aridic/Typic Haplusterts) with palygorskite minerals must be considered naturally degraded soils (Pal *et al.*, 2012a). Thus, they stand for a new initiative to classify them at a higher categorical level for the benefit of various stakeholders, farming communities of rain-fed regions in particular. A revision in their mineralogy class as 'montmorillonitic-palygorskitic'instead of only 'montmorillonitic', would be an appropriate approach so that pedologists/ soil mappers highlight the severe drainage problem in both non-sodic and sodic CCS with and without Ca-zeolites.

Conclusions

In view of the recent research conducted at ICAR-NBSS&LUP, in proper characterisation of smectite clay mineral in Indian CCS as a low charge di-octahedral montmorillonite species of the smectite group of clay minerals, the current 'smectitic' mineralogy class stands for a revision as 'montmorillonitic'. Such mineralogy class is more compatible with certain important physical, chemical and mineralogical properties of the CCS developed in the alluvium of the weathering Deccan Basalt.

Among the other clay minerals, presence of Mg- rich palygorskite is very common in the Deccan Basalt derived alluvial parent materials of the CCS in peninsular India. It releases enough of Mg^{2+} ions that cause a remarkable reduction in hydraulic conductivity in subsoils that impairs the soils' productivity. Despite the predicament in the identification of small amounts of clay palygorskite by XRD method, its presence can be easily confirmed by unique depth distribution of ECP, EMP, Exch. Ca/Mg and BS ≥ 100. In CCS with and without Ca-zeolites, the presence of palygorskite clay mineral needs to be

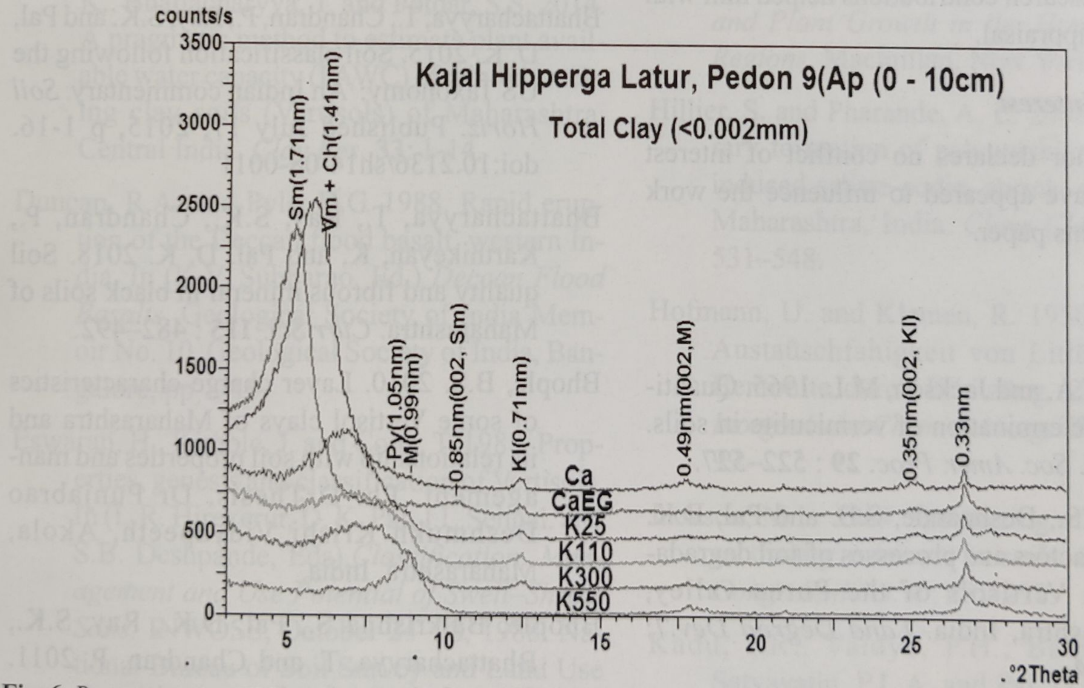

Fig. 6. *Representative XRD patterns of the total clay fraction of Aridic/Typic Haplusterts (Pedons 2-5 and 7-8). Ca=Ca saturated, CaEG=Ca saturated and ethylene glycolated, K25/110/300/550°C=K saturated and heated to 25°C, 110°C, 300°C and 550°C, Sm=Smectite, Vm=Vermiculite, Ch=Chlorite,Py=Palygorskite, M=Mica, Kl=Kaolin.*Adapted from Zade *et al.* (2017).

highlighted at a higher categorical level of soil classification and therefore, mineralogy class as 'montmorillonitic-palygorskitic' instead of only 'montmorillonitic' would be a wise proposal. This modified mineralogy class will help pedologists/soil mappers to highlight the palygorskite induced drainage problem as an important predicament in raising agricultural crops under rain-fed conditions. Thus, the decisive feature of soil classification will remain compatible with the crop performance, which indicates the nature of soil much more explicitly than by proposing any other arbitrary definition and nomenclature (Hilgard, 1906).

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Conflict of Interest

The author declares no conflict of interest that could have appeared to influence the work reported in this paper.

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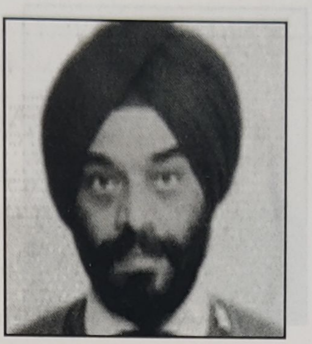
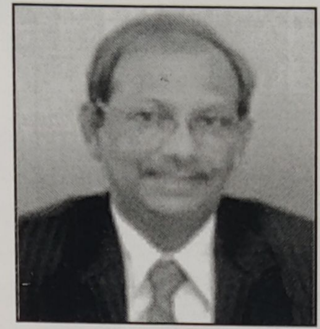
Obituary – Dr. Charan Singh Walia



The Clay Minerals Society of India deeply mourn the untimely demise of one of her valuable member Dr. Charan Singh Walia on13 December 2020 in New Delhi. He retired as a Principal Scientist at the ICAR-National Bureau of Soil Survey & Land Use Planning (NBSS&LUP), Delhi Regional Centre in April 2014. He did his M.Sc. with major in Soil Science from Punjab Agricultural University, Ludhiana in 1978 and completed his Ph.D. in Soil Science from Indian Agricultural Research Institute in 1993. In 1978, he joined in prestigious Agricultural Research Service of the Indian Council of Agricultural Research, and got his placement at the NBSS&LUP Regional Centre - Jorhat and later shifted to its Regional Centre – Delhi. He was pioneer in carrying out soil survey and classification in the north eastern region, and successfully mapped and profoundly placed soils of the north eastern region in Soil Taxonomy. He has published numerous research articles and reports on the soils of the north eastern region, which are being cited extensively. At the NBSS&LUP's Regional Centre in Delhi, he had done excellent work on soil survey and land evaluation and handled large number of research projects sponsored by the Department of Science & Technology, Government of India. His extensive contribution to the soil resources in states of Uttar Pradesh, Uttara Khand and Haryana under Soil Resource Mapping of India mega project earned him laurels. He served the Society in various capacities and had always been a great support to her annual conventions. He had always been a milk of human kindness. He carried with him a jovial nature and helpful disposition.

Obituary – Dr. Dipak Sarkar



The Clay Minerals Society of India deeply mourn the passing away of one of her former President, a Fellow and Honorable member Dr. Dipak Sarkar on 24 December 2020 in Kolkata. He was born on 15 January 1952 in Calcutta (now, Kolkata). He obtained his B.Sc.Ag.(Hons) from Kalyani University in 1971, and then moved to the Indian Agricultural Research Institute from where he received M.Sc. and Ph.D. with major in Soil Science and Agricultural Chemistry. He joined Agricultural Research Service of the Indian Council of Agricultural Research in 1978, and rose to the prestigious apex position of Director of ICAR-National Bureau of Soil Survey & Land Use Planning (NBSS&LUP), Nagpur in 2005. He contributed immensely to natural resource appraisal, monitoring and management towards land use planning and generated soil and soil based thematic maps using geoinformatics. He contributed to National Mission Project on Soil Resource Mapping of Eastern States as Team Leader. He harmonized land degradation database of the country in association with NRSC, ISRO, CSSRI and CSWCRTI. His contribution towards soil nutrient mapping for the states of Jharkhand, West Bengal, Assam at specified grid intervals towards Site Specific Nutrient Management (SSNM) deserves special mention. His study on "Status, Causes and Impacts of Arsenic Contamination in Ground Water in parts of West Bengal *viz-a-vis* Management of Agricultural System" improved our understanding of arsenic toxicity in ground water-soil-plant-animal-human continuum. He had visited Soil Survey and Land Resource Centre (SSLRC), Silsoe, United Kingdom and worked with Prof. Peter Bullock, Chief of Soil Survey & Mapping, UK. He was a member of the Indian delegation to Brazil. He published more than 150 scientific papers in journals of high repute, several books, book chapters, popular articles and research and technical bulletins. He has successfully guided 4 research students for Ph.D. Degree. He was honoured with Soil Conservation Society of India special award (2009), Shriram award of the Fertilizer Association of India (2011– 2012), and was elected as Fellows of the Indian Society of Soil Science (2003), National Environmental Science Academy (2003), West Bengal Academy of Science & Technology (2000), Indian Society of Coastal Agricultural Research (2007), Institute of Chemist (1991). He served as President for Agriculture & Forestry Sciences Section, 93rd Indian Science Congress, Clay Minerals Society of India, and Indian Society of Soil Survey and Land Use Planning, and as Chairman, International Conference on "Environment & Development" in the session "Control of Pollution (Soil and Plants)" in 2004.

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