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Mineralogical Characteristics and Potassium Quantity/ Intensity Relation in Three Indus River Basin Soils

MOHAMMAD SALEEM AKHTAR* and JOE BORIS DIXON†
Department of Soil Science and SWC
Arid Agriculture University, Rawalpindi, Pakistan
Email: msakhtar@uaar.edu.pk

Mineral characteristics in the Indus basin are less understood making it difficult to extrapolate the field experimental results. The clay layer charge and other mineral characteristics were determined and related to potassium (K) quantity/intensity (Q/I) relation as an index for potassium bioavailability. Three soils, namely: (1) Gujranwala, fine-loamy, mixed, hyperthermic Typic Haplustalf; (2) Peshawar, fine-silty, mixed, hyperthermic Haplocalcidic Haplustept and (3) Lyallpur, fine-silty, mixed, hyperthermic Ustic Haplocambid, which vary in profile development, were sampled at diagnostic horizons and fractionated into sand (+50 µm), silt (50-2 µm), coarse clay (2-0.2 µm) and fine clay (< 0.2 µm) size separates. Mineralogy of each size-separate was examined by X-ray diffraction; layer charge of the fine clays phyllosilicates by the alkylammonium exchange method (nC = 5 to 18); and di- *vs.* trioctahedral structural nature by an assay of $Fe^{2+} + Mg^{2+}$. For the same samples, K Q/I parameters were determined from K adsorption isotherm fitted to Langmuir equation. The sand and silt fractions contained mica (both di- and trioctahedral), quartz, feldspars and chlorite. The shale derived Peshawar soil had smaller and lesser mica and more chlorite than the alluvial Gujranwala and Lyallpur soils. The coarse clay had mainly mica, kaolinite and smectite and in addition, chlorite and quartz in case of semi-arid Peshawar and Layllpur soils. The fine clay was composed of mainly smectite, mica and kaolinite. Most clay particles had layered structure with discrete boundaries as seen under transmission electron micrograph. The clays from Peshawar and Layllpur soils had 2 to 3 times greater $Fe^{2+} + Mg^{2+}$, low layer charge density smectite (fine clay) compared to the Gujranwala which also had partially opened mica (wedges) seen with HRTEM. The Layllpur and Peshawar soils although had less potassium buffering capacity but had 2 to 4 times greater K^+ activity in 0.002 M $CaCl_2$ solution than the Gujranwala and showed potassium release as opposed to adsorption in the later soil. The study will help to explain the results of field experiments and extrapolation to other soils.

Key Words: Alluvial soils, Clay layer charge, Potassium Q/I parameters, Soil mica type and distribution.

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†Department of Soil and Crop Science, Texas A&M University, College Station, Texas, 77843 (USA); E-mail: j-dixon@tamu.edu

INTRODUCTION

Bioavailability of soil potassium is a function of release from soil mica and K-feldspar and fixation by partially weathered mica and high layer-charge smectite in soil clays. Bioavailable K is critical in field crop production in many soils. Potassium release from the soil minerals occurs only when solution concentration is low and depends upon nature of crystal structure of these minerals[1,2]. The critical K concentration of equilibrium solution-below which the interlayer K is released - is greater for trioctahedral mica (biotite) compared to a dioctahedral (muscovite)[3]. Biotite weathers first and faster to transforms to vermiculite than muscovite[4-6]. Added K is retained and fixed irreversibly by partially weathered mica and vermiculite[7,8]. Since natural soils vary in mineral composition with varying characteristics of component minerals, the information on soil mineral composition and characteristics of mineral structure helps to understand soil K status and crop plant response to fertilizer K[9].

Layer charge density and charge distribution on octahedral *versus* tetrahedral sheet has been correlated with K-selectivity of smectite[10,11]. Over the conventional techniques[12], *n*-alkylammonium cation exchange has been extensively used to determine layer charge of soil and reference clays[13,14]. Some later studies intercalated the clays with one specific alkylammonium (nC 12) cation and partitioned samples into high and low smectites[15,16]. However, intercalation with different chain length alkylammonium cation with number of carbon (nC) in the range of 5 to 18 may indeed show a gradual transition in spacing between 1.36 to 1.77 nm or higher. Then, assuming random interstratification of mono-layer (1.36 nm) and bi-layer (1.77 nm) structures, calculation of layer charge heterogeneity would be possible using Mering's method[17].

Layer charge density by *n*-alkylammonium after blocking the charge originating from tetrahedral sheet done by saturation with Li and heating[18] allows studying local effects in the octahedral sheet structure but it may result in reorientation of the OH group in clay structure[19]. Alternatively, an analysis of divalent octahedral cations such as Mg^{2+} and Fe^{2+} can provide better information on the charge distribution and structural configuration. Stucki and Anderson[20] proposed scheme for quantitatively determination of Fe^{2+} in the presence of Fe^{3+} by dissolving clays in a solution containing redox reagent that reacts immediately with released Fe^{2+}.

Mineral composition of representative soils of Indus River Basin has been documented[21] but further characterization of the mineral has not been documented. The crystal structure of mica or feldspar, layer charge density and charge distribution on the soil smectite and other characteristics of minerals are less well understood. The field crop response to K fertilizer is erratic and cannot be extrapolated to other soils until detailed mineral characteristics are known. The objectives were (1) to identify mineral phases and determine their characteristics important for bioavailability of K and (2) to determine effect of soil mineral composition, clay layer charge characteristics and nature of mica on K Q/I relation parameters.

EXPERIMENTAL

The study area comprised of (1) Pleistocene alluvial terraces comprising of mixed mineralogy calcareous material derived from variety of sedimentary rocks and (2) piedmont alluvial plain derived mainly from mix of sandstone and calcareous red shale (Fig. 1). The Gujranwala and Lyallpur soils were sampled from the Pleistocene terraces. The Gujranwala occurs in subhumid moisture regime. It is one of the better developed soils in the area which showed signs of greater weathering (decalci-fication to 150 cm, segregation of Fe and Mn oxides as nodules and clay cutans at 66 to 180 cm profile depth). Lyallpur soil occurs in the semi-arid part of the terraces. From the piedmont alluvial plain the Peshawar soil was sampled, which occurs in semi-arid environment. The Gujranwala is classified as fine-loamy, mixed, hyperthermic Typic Haplustalf; Peshawar as fine-silty, mixed, hyperthermic Haplocalcidic Haplustept and Lyallpur as fine-sillty, mixed, hyperthermic Ustic Haplocambid. Gujranwala and Lyallpur soils also receive sediments with river-diverted water used for irrigation.

Particle size fractionation: Bulk samples were taken from each diagnostic horizon, air-dried and crushed to pass through a 2 mm sieve. The samples were fractionated into sand (+50 μm), silt (50-2 μm), coarse clay (2-0.2 μm) and fine clay (< 0.2 μm) after removing soil $CaCO_3$, organic matter and iron oxides by chemical treatments[22]. Soil $CaCO_3$ was removed by treatment with 1 N NaOAc buffered to pH 5 at 75 °C for 0.5 h; soil organic matter was removed by 30 mL 100 mL H_2O_2 at 70 to 80 °C and iron oxides with citrate-bicarbonate dithionite (Na-citrate to $NaHCO_3$ ratio 1:8) buffered at pH 7.3. The soil suspension was dispersed in 0.02 M Na_2CO_3 solution (pH 9.5) by a 30 s sonification. The sand was separated by wet sieving through a 0.51 μm nominal pore size screen and silt by 5 repeated sonification and centrifugation washes. From the remaining clay suspension, the coarse clay and fine clay were separated by 5 repeated sonification and high speed centrifugation washes. The sand and silt fractions were dried in oven at 70 ºC. The clays were dialyzed to remove salt and freeze-dried.

Mineralogical identification and characterization: The sand was powdered finely in a pestle and mortar in the presence of acetone. Randomly oriented powder mounts of the sand and silt were X-rayed at a scanning speed of $1^\circ\ 2\theta\ min^{-1}$ by using a $CuK\alpha$ radiation. 50 mg portions of each clay fraction were saturated with Mg^+ and K^+ by washing 5 times with respective 1.0 N solution of Mg and K chloride followed by 95 % (v/v) ethanol washings to remove interstitial salts. Slurries of Mg- and K-saturated clays were pippetted onto glass and Vycor glass slides, respectively, and allowed to air-dry and achieve preferential orientation of constituent layered silicates. X-ray diffraction of the each clay mount was carried out initially after air-drying and after spraying 10 % (v/v) glycerol/water solution on Mg-saturated clay mounts (*i.e.*, glycerol salvation) and after heating the K-saturated clays at 350 and 550 ºC for 2 h. Each sample was irradiated at a scanning speed of $1^\circ\ 2\theta$ per min on a Philips X-ray diffractometry.

Vermiculite and smectite in the clay fractions were determined quantitatively from Ca/Mg and K/NH_4 exchange capacity[22]. The clay was saturated with Ca by repeated washing with 1 N $CaCl_2$ solution and the exchangeable Ca was displaced by Mg by repeated washing with 1 N $MgCl_2$ solution. Similarly, K/NH_4 was determined by saturating the same clay with K by repeated washing with 1 N KCl solution. The K-saturation clay was heated at 105 °C and exchangeable K was displaced[22] by 1 N NH_4Cl. The displaced Ca and K were assayed by atomic absorption spectrophotometer. Vermiculite was calculated assuming CEC 140 $cmol_c\ kg^{-1}$ vermiculite and smectite assuming 105 $cmol_c\ kg^{-1}$ smectite. Five $cmol_c$ CEC kg^{-1} sample was ascribed to the edge surfaces and subtracted in each case.

For total chemical analysis, the coarse and fine clays were digested in HF at room temperature and assayed for K, Ca, Al, Si, Fe, Ti, Mn and Na by an ICP. Ferric and ferrous in the coarse and fine clay were determined by 1,10-phenanthroline reagent[23]. Mica in the clay fraction was calculated assuming 10 % K_2O in mica crystals and assuming mica was the only source of K, which seemed valid as there was no X-ray diffraction line for feldspar in the clay X-ray diffraction patterns.

Layer charge density was determined for the soil fine clays from the upper 4 genetic horizons of each soil and four reference clays. N-alkylammonium cation ($C_nH_{2n+1}NH_3^+$; n = 5~18, the number of C atoms in the alkyl chain) was intercalated in layer silicates[14]. The step-increase in 001 spacing of the intercalated samples was measured using X-ray diffraction. The number of cations occurring in the interlayer was calculated from known size of the alkylammonium molecule whose intercalation resulted in transformation from mono-layer (1.36 nm) to bi-layer (1.77 nm) structures. Further, using Mering's method[17] and assuming random interstratifications of mono-layer (1.36 nm) and bi-layer (1.77 nm) structures, the gradual transition in spacing between 1.36 nm to 1.77 nm allowed calculation of layer charge heterogeneity.

Morphology and microanalyses by electron microscopy: The sand grains were hand-picked, mounted on carbon stub with a double sided adhesive tape and sputter coated with carbon. The silt was suspended in acetone, mounted as a drop of dilute suspension on a carbon stub and sputter coated with Au. Microprobe analysis of the sand and silt fractions was carried out on a Joel-35 scanning electron microscope (SEM) equipped with a microprobe. Morphology of the silt was examined with a Joel-T330 SEM operated at 20 kv at a working distance of 15 to 20 mm. A droplet of the clay suspension was placed on a 200 mesh copper grid covered with carbon film. The carbon films were prepared by vacuum evaporation of C on a freshly cleaved muscovite surface. The samples were viewed under a Zeiss 10C transmission electron microscope (TEM). For high resolution transmission electron microscopy (HRTEM), the clay was embedded in epoxy-arilddite and ultramicrotomed perpendi-cular to 001 plain and viewed under a Zeiss TEM.

Potassium quantity/intensity relation: Potassium adsorption isotherms were developed for each sample from top four horizons of each soil through batch experiments. Replicated 1 g < 2 mm soil was equilibrated with graded amount of KCl in aqueous solution of 0.002 M $CaCl_2$ for 24 h and centrifuged to separate suspended solids. Potassium, calcium and magnesium concentration in the supernatant was determined by atomic absorption spectroscopy. Activity (α) of various cations was calculated using Debye-Hückel equation from the concentration data. Activity of K^+ *vs.* activity of Ca^{2+} + Mg^{2+} (AR^K) was plotted against change in solution K (ΔK) where AR^K is $a_K/(a_{Ca} + a_{Mg})^{0.5}$ (mol $L^{-1})^{0.5}$ and ΔK, the concentration difference before and after equilibration with soil (mol_e kg^{-1}). Further, the following Q/I parameters were calculated from the adsorption isotherms: (1) PBCK, potential buffering capacity of K was the slope of linear portion of the curve ($cmol_c$ $kg^{-1}/(mol\ L^{-1})^{0.5}$); (2) AR^K_e, activity ratio of K at $\Delta K = 0$, (X1000 $(mol\ L^{-1})^{0.5}$); (3) ΔKiw, K adsorbed in interlayer spaces and wedge sites ($cmol_c$ kg^{-1}); (4) ExK_0, exchangeable K at $AR^K = 0$ ($cmol_c$ $kg^{-1})^2$.

RESULTS AND DISCUSSION

Mineral composition of various size-separates and the mineral characteristics are presented first followed by layer density and heterogeneity. Finally, the mineral composition and characteristics are correlated with K Q/I parameters.

Sand and silt mineral composition: The sand was composed of quartz, mica, feldspar and chlorite as indicated by X-ray diffraction (Fig. 1). The 3 pedons had similar sand mineral composition except that the shale derived pedon from Peshawar had stronger 1.42, 0.7 and 0.351 nm chlorite peaks than the alluvial Gujranwala and Lyallpur pedons which had stronger mica peaks. Mica increased with the pedons' depth in the Gujranwala and Lyallpur soils as suggested by increase in the intensity of both 1.0 and 0.5 nm peaks. The 2Bwb1 horizon of the Peshawar soil had the lowest mica peak intensity. The ratio of 1.0 to 0.5 nm peaks and occurrence of 0.168 nm peak in the randomly oriented powder mounts may suggest presence of both di- and trioctahedral micas[24]. The silt fraction was also composed of quartz, mica, chlorite and feldspar as determined by X-ray diffraction (Fig. 1).

The electron microprobe analyses further confirmed the presence of both di- and trioctahedral micas in the sand and silt fractions in all the 3 soils. Although microprobe analysis was carried out on a large number of sand and silt size grains, Fig. 2 presents only selected data. The microprobe analyses reinforced the X-ray identification of mineral phases such as chlorite (Fig. 2b) and various feldspars including Ca-, Na- and K-feldspar (Fig. 2d). The sand chlorite appeared to be trioctahedral as indicated by substitution of Fe and Mg for Al in the octahedral sheet (Fig. 2b). The sand size grains were mostly platy and subrounded with freshly cleaved surfaces as seen under SEM. The silt grains were mostly platy with smooth surfaces, some had particles with rounded corners (Fig. 3a), many particles had fractures or cleavage surfaces which were apparently products of physical weathering with little evidence of chemical etching (Fig. 3e & f). One exceptional particle was composed of thin plate with frayed and notched edges (Fig. 3d). A few particles were etched or deeply pitted (Fig. 3g & h, respectively).

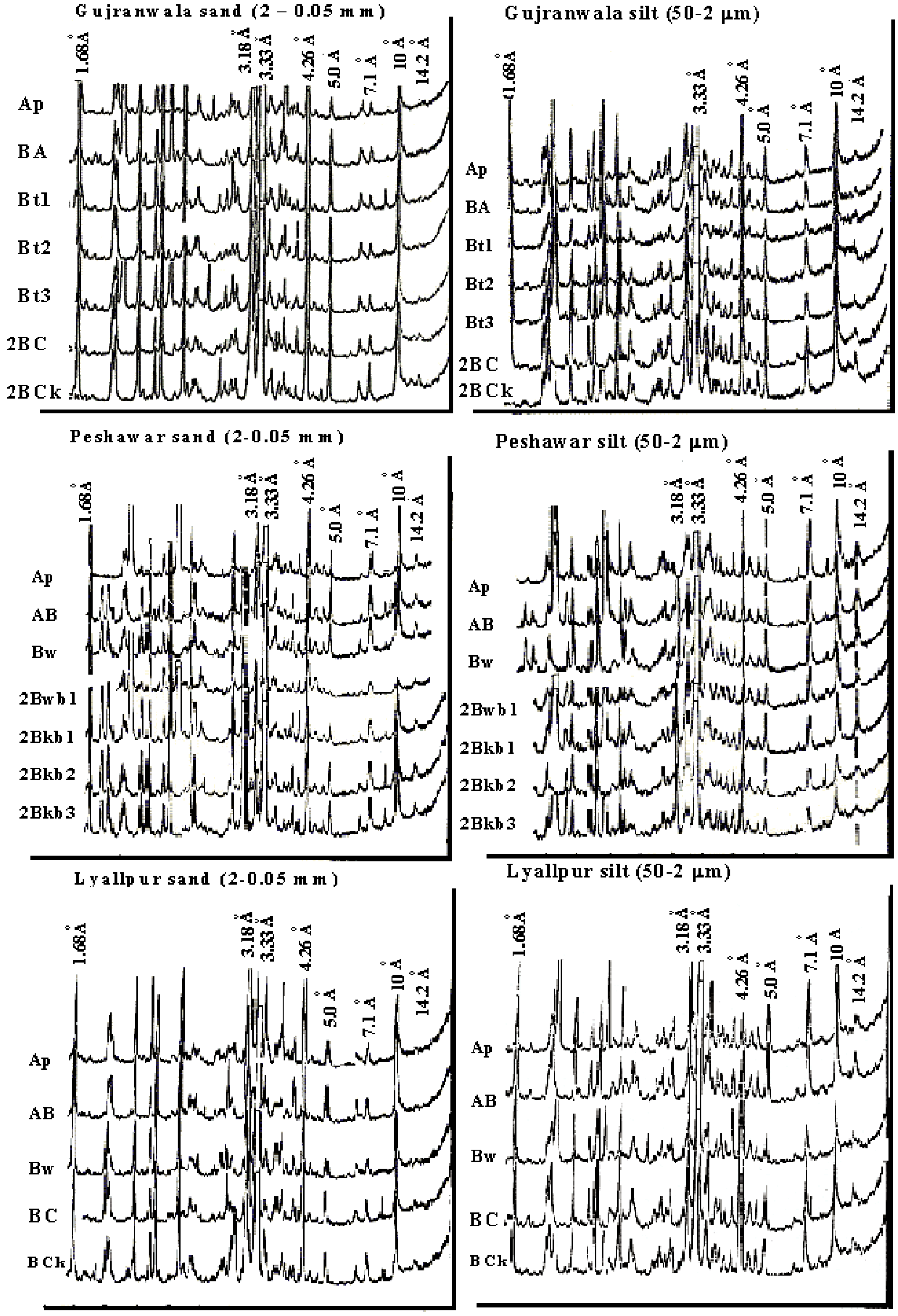

Fig. 1. X-ray diffraction pattern of the sand and silt fractions from the three soils

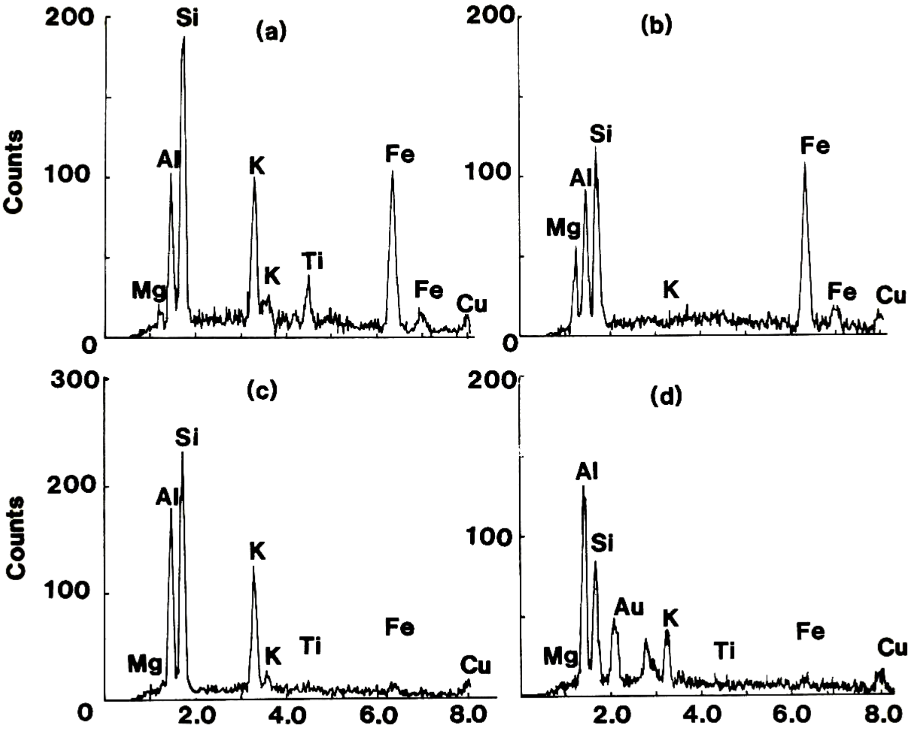

Fig. 2. Microprobe analyses of few selected sand and silt grains: (a) biotite, (b) chlorite, (c) muscovite and (d) K-feldspar. The first three particles (a, b, c) showed morphology resembling to layered silicates and (d) was a subrounded blocky silt size grain

Although all the sand and silt fractions contained mica, quartz, feldspars and chlorite the peak intensity of various minerals-which may relate to quantity of the relevant mineral-differed among the soils. In the Gujranwala and Lyallpur, the intensity of chlorite and mica peaks increased with profile depth suggesting greater weathering of these minerals at the surface. Both the Gujranwala and Lyallpur soils are from Pleistocene alluvial terraces and older than the Peshawar soil[21]. The upper three horizons of the Peshawar profile are part of the young lithological unit. Further, the decrease in mica and chlorite peaks' intensity toward the surface in the Gujranwala profile points to more *in situ* weathering compared to the Lyallpur profile: The Lyallpur occurs in dryer region. The Peshawar 2Bwb1 has the lowest amount of mica both on clay and on soil weight basis which exposed to the weathering in the paleoenvironment hence depletion of mica (and feldspar) has occurred. Therefore, the sand and silt mineral composition was related both to the source of parent material and climatic conditions.

Clay mineral composition: The coarse clay (2-0.2 μm) fraction in all 3 pedons contained mica, kaolinite and smectite as major minerals and chlorite, quartz and vermiculite as less abundant minerals. Fig. 4 presents only selected X-ray diffraction

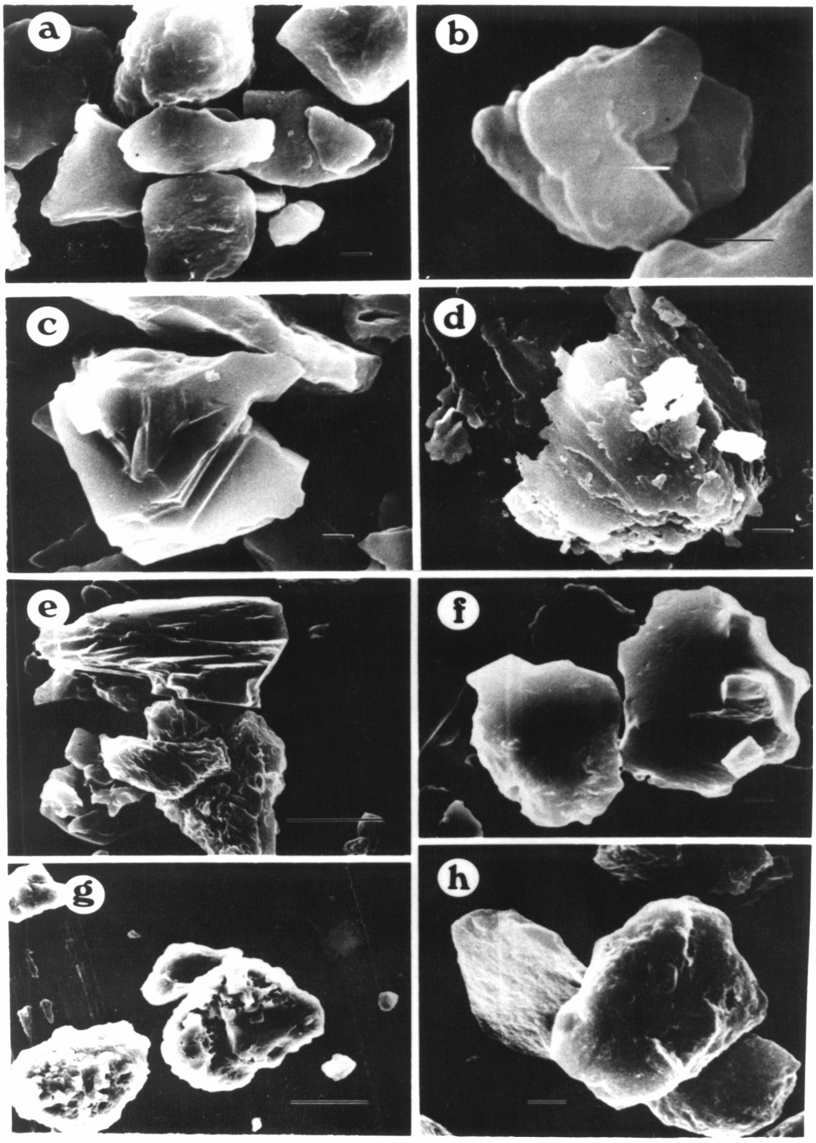

Fig. 3. Scanning electron micrographs of the silt fraction of the Gujranwala profile (a, b, c and d) and Peshawar profile (e, f, g and h): (a) subrounded layered particles (Gujranwala BA horizon; bar = 1 μm); (b) a rounded layered particle (Gujranwala BA horizon; bar = 0.5 μm); (c) subangular to angular layered particle (Gujranwala Bt1 horizon; bar = 1 μm); (d) thin layers exfoliating from a layered particle (Gujranwala Bt2 horizon; bar = 1 μm); (e) and (f) subrounded blocky particle showing freshly cleaved and deeply weathered surfaces (Peshawar BA horizon; bar = 5 μm) and (g and h; Peshawar 2Bwb1) subrounded particle, also some vermiform morphology visible in the middle right part of the micrograph; and (h) fractured and deep pitted surface of a subrounded particle (bar = 5 μm)

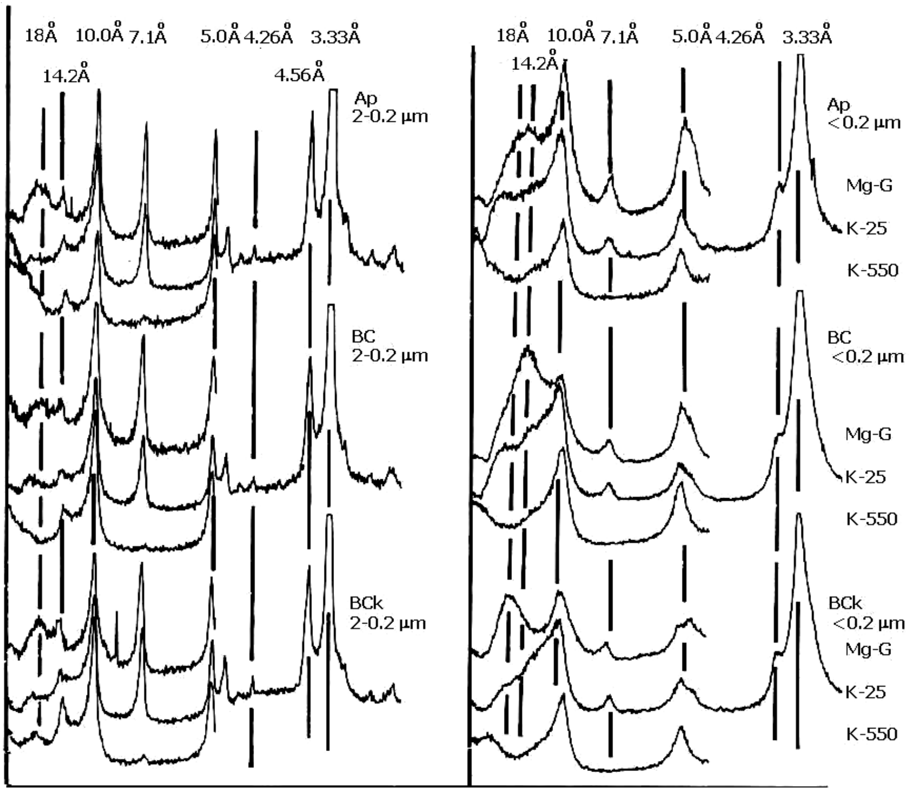

Fig. 4. X-ray diffraction pattern of the coarse clay (2-0.2 µm; left) and fine clay (< 0.2 µm) from selected horizons (Ap 0-10 cm; BC 62-114 cm and BCk 114-162 cm) of the Lyallpur profile: Mg-G, Mg-saturated and glycerated; K-25, K-saturated and dried at 25 ºC; K-550, K-saturated and heated for two h at 550 ºC. Note: all other clays had stronger diffraction line representative of smectite

data. The 155 °C heat treatment resulted in a discrete 1.42 nm peak only in case of Peshawar and Lyallpur coarse clays indicating the presence of chlorite. The intensity of this peak increased with the profile depth. In the Gujranwala coarse clay the same treatment resulted in a broad shoulder at 1.23 to 1.0 nm suggesting the presence of partially filled hydroxyl interlayered vermiculite (or smectite). The fine clay (< 0.2 µm) fraction had dominantly smectite and mica with small quantities of kaolinite and vermiculite. The sub-humid, Gujranwala pedon has interstratified chlorite-expansible (vermiculite, HIV or smectite, HIS) as indicated by a broad shoulder at the lower angle side of the 1.0 nm peak of the heat treated clay. The 1.8 nm peaks of Mg-saturated and glycerol solvated clays were broad and suggested presence of thin crystallites of the smectite. The other XRD peaks were sharp and symmetrical in the coarse clay and broad in the fine clay which suggested that the mineral particles were discrete and thick in the coarse clay and thin in the fine clay fraction.

Mica based on total K content of the coarse clay varied from 40 to 50 % in the Gujranwala pedon, from 36 to 41 % in the Peshawar pedon with least mica in the 2Bwbl horizon and from 39 to 46 % in the Lyallpur pedon (Table-1). Generally, the surface horizons had more mica than the subsurface horizons in the canal irrigated soils. The coarse clay from Gujranwala pedon contained greater with vermiculite than the Peshawar and Lyallpur pedons. Smectite in the coarse clay fraction of the profiles varied between 13 to 18 %, except for the Gujranwala Bt2 horizon where it was 24 %. A small increase in smectite and vermiculite contents was evident in the Gujranwala coarse clay from Bt2 and Bt3 horizons (Table-1). Mica in the fine clay of Gujranwala was half of that of in the corresponding coarse clay while the fine clay of Lyallpur and Peshawar soils had only slightly lesser mica than the corresponding coarse clays again suggesting lesser weathering of the layered silicate in the Lyallpur and Peshawar soils. Smectite in the fine clay varied from 23 to 48 %.

TABLE-1
DISTRIBUTION OF LAYERED SILICATES IN THE SOIL CLAYS

Horizon	Depth (cm)	Mica		Vermiculite		Smectite	
		2-0.2 μm	< 0.2 μm	2-0.2 μm	< 0.2 μm	2-0.2 μm	< 0.2 μm
		%					
Gujranwala fine-loamy, mixed, hyperthermic Typic Haplustalf							
Ap	0-10	49	19	2	5	16	34
BA	10-24	44	21	8	2	18	46
Bt1	24-56	37	22	7	2	16	44
Bt2	56-86	43	22	12	4	24	42
Bt3	86-137	40	21	3	8	18	27
2BC	137-180	41	23	6	6	16	31
2BCk	180-205	42	24	3	10	15	31
Lyallpur fine-silty, mixed, hyperthermic Ustic Haplocambid							
Ap	0-10	46	38	1	3	15	35
AB	10-25	44	37	1	3	14	33
Bw	25-62	44	35	2	5	15	32
BC	62-114	43	31	1	3	16	39
BCk	114-162	39	27	-	-	-	48
Peshawar fine-silty, mixed, hyperthermic Haplocalcidic Haplustept							
Ap	0-10	39	34	2	13	14	23
BA	11-43	41	34	4	11	14	32
Bw	43-66	39	29	4	6	15	36
2Bwb1	66-98	36	28	4	-	16	-
2Bkb1	98-138	39	33	3	5	16	40
2Bkb2	138-188	39	34	4	9	13	35
2Bkb3	188-200	37	26	2	5	15	39

The observations of transmission electron micrographs (TEM) (Fig. 5) suggested that most of the clay particles had layered structure. The coarse clay particles had discrete boundaries (Fig. 5a, b, c and d) while the fine clay size particles had frayed edges showing signs of deep weathering. The thin particles associated with thicker ones in Fig. 5b and c may explain the broadening of smectite XRD peaks for the coarse clay. Ultramicrotomed reference mica (Fig. 5e) and the soil clays showed regular sequences of lattice fringes. In the Gujranwala clay several particles showed wedge formation as observed under TEM and HRTEM (Fig. 5f) suggesting partial opening of layers leaving unweathered mica core in the center. Fig. 5g shows one clay particle from the Lyallpur exhibiting layer-weathering where the lattice fringes were spaced repetitively at 1.4 and 1.0 nm. All of the electron micrographs collectively support the interpretation that these soils are slightly weathered as most of the platy mineral grains were smooth and showed few signs of alteration except for rounding at the corners.

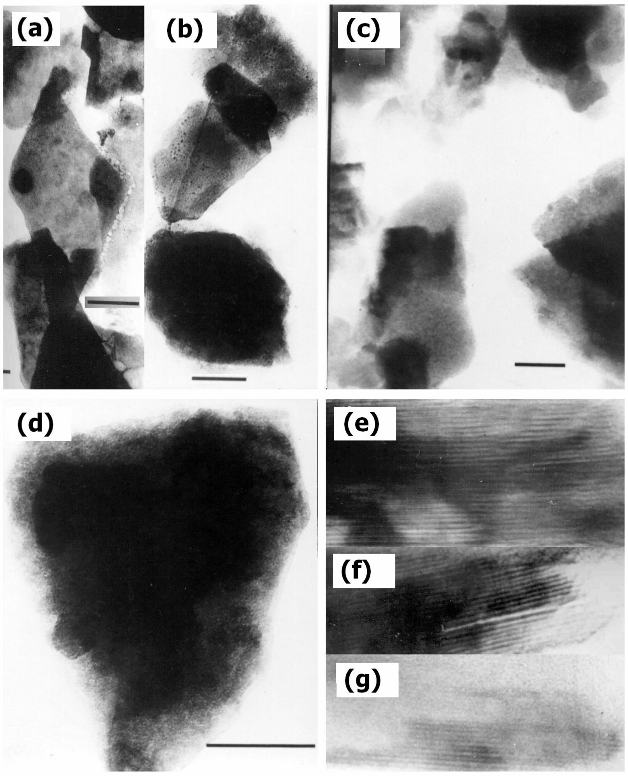

Fig. 5. Representative transmission electron micrograph of the clay fraction: (a, b, c and d) layered particle showing discrete boundaries with edge weathering and exfoliation of layers (bar 0.2 μm); and (e, f and g) HRTEM micrographs of a reference mica (e) and the soil clays showing wedges (f, Gujranwala clay) and regular sequences of lattice fringes spaced at 1.4 and 1.0 nm (g, Lyallpur clay)

The mica in the clay fractions was detritus as indicated by its distribution in the different size fractions. Sources of smectite appeared to be *in situ* weathering of biotite and chlorite, at least in the Gujranwala profile, as well as the detritus parent material. The chlorite mineral present in sand and silt size fractions is also inherited from the parent rocks. The interstratified chlorite-expansible (smectite or vermiculite) in the fine clay appeared to be a degradation product of chlorite rather than a consequence of deposition of hydroxy material in expansible layered silicates. A soil pH around 7.5 precludes formation of Al/Mg oxyhydroxide[25] and also the EM and XRD indicated presence of chlorite in sand and silt. An increasing intensity of chlorite peaks with depth in Gujranwala and Lyallpur profiles also suggested weathering of this mineral. The overall occurrence of weatherable minerals such as feldspars and biotite as coarse grains (> 2 μm) points towards an early stage of mineral weathering in the soils studied.

Layer charge characteristics: Selected X-ray diffraction data of the fine clays after intercalation with alkylammonium are presented in Fig. 6 comprising of 14 patterns one each for 5 to 18 carbons in the alkyl chain. The transition between a mono-layer (1.36 nm) to a bi-layer (1.77 nm) structure was gradual for most of the soil clays. The gradual transition from mono- to bi-layer structure is depicted for Camargo bentonite in Fig. 7. It is apparent that the particles with high charge density completed their bi-layer structure at lower nc than those with low charge. The gradual transition is indicative charge heterogeneity. The broad diffraction lines (sometimes the lines covered more than 2º 2θ) are also associated with thin flaky particles of the fine soil clays and presence of chlorite/HIS did confound the interpretation of the mono- to bi-layer transition.

Nevertheless, the Gujranwala clay samples attained bi-layer (1.77 nm) structure with an alkylammonium cation of smaller chain length (n = 8) compared to the clay sample from Lyallpur and Peshawar soils (n = 9 or more) as shown in Fig. 6. Average charge on reference hectorite, nontronite and Camargo bentonite was 0.23, 0.32 and 0.39, $mol_e/(O_{10}(OH)_2)$, respectively, which is inline with previous studies[26]. Further, the hectorite had uniformly charged layers (0.21) while 70 % layers of the nontronite had 0.28 charge, 15 % had 0.25 and the other 15 % had 0.30. The Camargo bentonite also charge heterogeneity, *i.e.*, 40 % layers had 0.28 charge, 40 % had 0.38 charge, 10 % had 0.27 and remaining 10 % 0.32 charge per formula unit.

The Gujranwala fine clay had greater average layer-charge density compared to Lyallpur and Peshawar clays (Table-2). The fine clay from the Peshawar profile had 0.35 to 0.38 $mol_e/(O_{10}(OH)_2)$ average charge density and the lowest in case of the fine from 2Bwb1 horizon. The fine clay from Lyallpur profile had 0.32 to 0.35 charge per formula unit. Further, the soil fine clays also exhibited charge heterogeneity - a mix of low and high charge layers. Peshawar fine clay from Ap, AB and Bw horizons had 60 to 80 % layers with charge density of 0.39 $mol_e/(O_{10}(OH)_2)$ and 2Bwb1 horizon had 75 % layers with charge density of 0.33 $mol_e/(O_{10}(OH)_2)$.

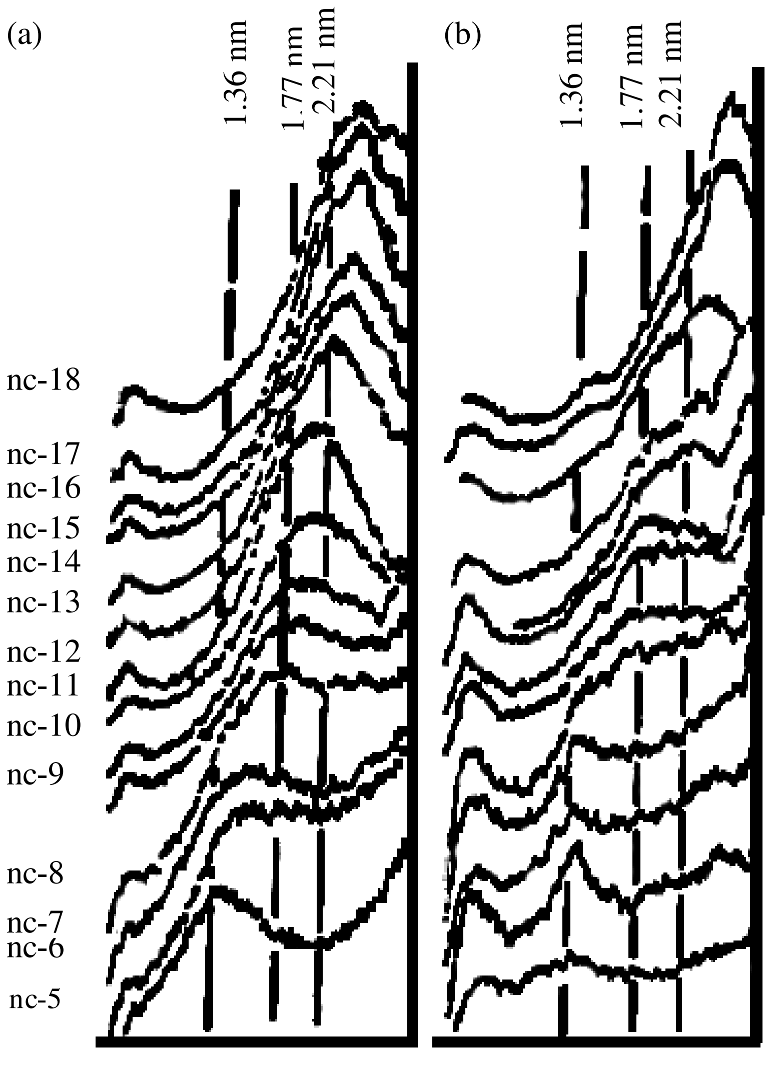

Fig. 6. X-ray diffraction pattern of *n*-alkyammonium intercalated fine clay: (a) Gujranwala Ap (0-12 cm), showing completion of bi-layer with n = 8; and (b) Lyallpur BC (64-114 cm), showing completion of bi-layer with n = 10

In the Lyallpur Ap horizon 85 % of the clay layers had charge density 0.36 and BA 60 % layer had charge density 0.39. The Lyallpur Bw and BC horizons clay was mixture of layers with charge density 0.33 to 0.44 per formula unit. The fine clay smectite from the Gujranwala Ap horizon had equal proportion of layers with charge densities 0.41, 0.45 and 0.50 per formula unit. Similarly, the Gujranwala BA, Bt1 and Bt2 horizon's fine clay had smectite with 20 to 30 % layers having charge in the range of 0.45 to 50, which qualify to be called as high charge smectite[27].

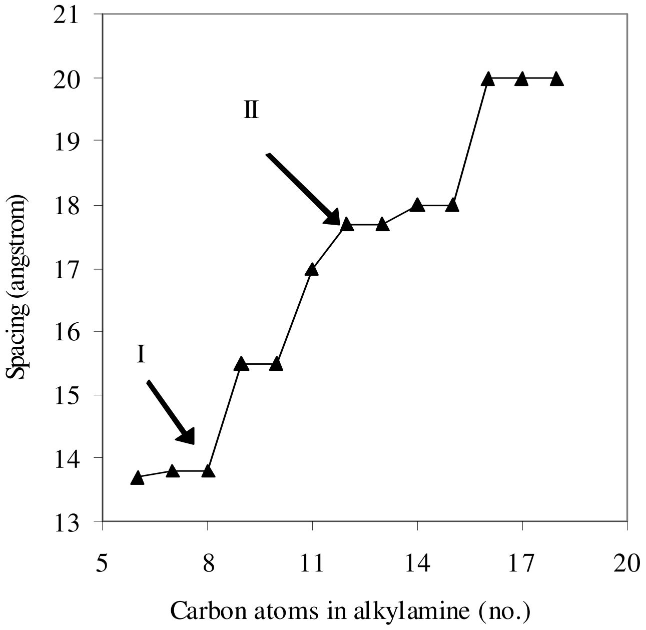

Fig. 7. Gradual transition from mono- to bi-layer structure of Camargo bentonite as determined by X-ray diffraction after intercalation with *n*-alkyammonium cation (n, the number of C atom the alkylamine)

The layer-charge density of the soil clays can be related to soil moisture conditions and parent material. The soils developed in the low soil moisture regime (Lyallpur and Peshawar) had lower charge density clays than the Gujranwala which is developed in a higher moisture regime. Overall, the clays had medium charge smectite as opposed to vermiculite reported for the soil under forest which had layer charge between 0.60 and 0.86 $mol_e/(O_{10}(OH)_2)$[16]. Under neutral and alkaline conditions the oxidation of octahedral Fe^{2+} in layer silicates is accompanied by a greater loss in the total surface charge than under acidic condition[28].

Concentration of divalent cations (Fe^{2+} and Mg^{2+}) in the clays is presented in Table-2 as an indicator of tri-octahedral character of crystal structure. Lyallpur soil clay had the highest concentration of the divalent cations followed by the Peshawer. Both the coarse clay and fine clay from the Gujranwala profile had 2 to 3 times less Mg(II) + Fe(II) content suggesting that it had lesser quantity of trioctahedral clay minerals (Table-2). But as indicated by the X-ray diffraction, these clays are mixture of mineral species including mica and chlorite (or HIV). The source of the divalent cations could be octahedrally charged smectite as well as unweathered biotite, at least, in the coarse clays. However, whether the higher Mg(II) + Fe(II) content was due to trioctahedral nature of smectite or high amount of unweathered biotite. The soil with such a clay should support higher K-activity in solution than if it were dioctahedral[10].

TABLE-2
CLAY LAYER CHARGE DENSITY AND Mg + Fe(II) CONCENTRATION (AN INDICATOR OF TRIOCTAHEDRAL NATURE OF THE CLAYS) AND K QUANTITY/INTENSITY PARAMETERS

Horizon	Depth (cm)	Layer charge properties			Potassium Q/I parameters			
		Charge	C-trioct$^{\$}$	F-tricot	AR^K_e	ΔKiw	PBC^K	ExK0
		---@---	------#------		----¶----	---$$---	---##---	--@@--
Gujranwala soil is fine-loamy, mixed, hyperthermic Udic Haplustalf								
Ap	0-10	0.41	990	640	1.90	0.90	30	0.60
BA	10-24	0.41	1030	480	1.20	1.25	85	0.30
Bt1	24-56	0.38	1000	500	1.00	1.05	80	0.45
Bt2	56-86	0.38	860	440	0.50	1.60	110	1.00
Lyallpur fine-sillty, mixed, hyperthermic Ustic Haplocambid								
Ap	0-11	0.35	4100	1740	8.10	-0.10	40	-0.40
AB	11-25	0.32	2610	1360	2.80	0.10	50	0
Bw	25-62	0.35	2150	2180	1.80	0.20	35	0.05
BC	62-114	0.35	2220	2130	1.55	0.45	70	0.15
Peshawar fine-silty, mixed, hyperthermic Haplocalcidic Haplustept								
Ap	11-43	0.35	2780	1660	3.00	0.55	30	0.15
BA	43-66	0.38	2230	1680	2.20	0.95	100	0.45
Bw	66-98	0.38	2020	2100	0.90	1.30	75	0.50
2Bwb1	66-98	0.32	2180	1480	0.90	0.95	80	0.50

$ C-trioct. & F-trioct., sum of Mg + Fe(II) in the coarse clay (2-0.2 μm) and fine clay (< 0.2 μm), respectively; #, mmole kg^{-1}; @, layer charge density ($mol_e/(O_{10}(OH)_2)$) as by determined *n*-alkylammonium (Lagaly 1981); ¶, AR^K_e, Activity ratio of K at ΔK = 0, X1000 (mol L^{-1})$^{0.5}$; $$, ΔKiw, Potassium adsorbed in interlayer spaces and wedge sites, mol$_e$ kg^{-1}; ##, PBC^K, Potential buffering capacity of K, cmol$_c$ kg^{-1}/(mol L^{-1})$^{0.5}$; @@, ExK0, Exchangeable K at AR^K_e= 0, cmol$_c$ kg^{-1}.

Potassium quantity/intensity relations: Lyallpur soil samples had greater AR^K_e than the samples from corresponding horizons of Peshawar and Gujranwala soils (Table-2). Equilibrium activity ratio of K (AR^K_e) in all the surface soils was higher than the subsoil samples and progressively decreased with depth. The intensity of K appeared to correlate positively with divalent cations concentration of the soil clays, *i.e.*, trioctahedral nature of the crystallites. Lyallpur soil samples also had negative values of ΔKiw (adsorption on interlayer spaces and wedge sites) and ExK_0 (exchangeable K at $AR^K = 0$) which indicated that K was released from the soil minerals into the equilibrium solution (Table-2). Since, the Gujranwala had mostly dioctahderal minerals (had the lowest concentration of divalent cations), had high charge clay indicated by alkylammonium test and had particles partially opened (wedges), the release of K was less and adsorption was higher, consequently, it had the lower activity of K compared to Lyallpur. Gujranwala and Peshawar soils had almost similar and greater buffering capacity against change in solution K compared to Lyallpur soil samples. Soil buffering capacity for K is related to the clay content[29]. Gujranwala had mainly curvilinear isotherms which also showed greater adsorption on interlayer and wedge sites compared to Lyallpur soils and Peshawar soils samples.

Conclusion

Mineral composition and characteristics of the 3 alluvial soil profiles of Pakistan correlated well with the parameters of K Q/I relation as indicators of K availability. All the three profiles had mix mineral suite with abundant mica in all size fractions. Most of the particles showed only slight evidence of weathering. However, the clay from semi-arid alluvial soil (Lyallpur) had greater mica, greater concentration of divalent cations in the clays and lesser charge density smectite compared to its counter part occurring in the subhumid region (Gujranwala). Layllpur soil also maintained greater K activity in equilibrium solution but had lower buffering capacity than Gujranwala and Peshawer soils, which was attributed to the differences in clay contents. This soil may maintain critical K activity in soil solution over a crop growth period without K addition but the hypothesis needs to be tested in field conditions.

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