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Potassium dynamics in three alluvial soils differing in clay contents

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Abstract

Despite the presence of a huge amount of potassium (K^+) in the soil, most of the soils are deficient in plant available K^+. A large amount of the K^+ is fixed by clay minerals present in such soils and cannot be taken up by plants to achieve optimum plant growth. In such type of soils, large amount of K^+ fertilizers are required for optimum plant growth, as plants do not respond enough to a normally recommended K^+ fertilization. Vermiculite clay minerals can fix an enormous amount of applied K^+, which becomes slowly available to the plants. The K^+ dynamics in such soils are valuable to recommend K^+ fertilizer requirements for sustainable nutrient management. We analyzed the K^+ dynamics of three alluvial soils, i.e Kleinlinden, Giessen and Trebur, collected from Germany and found that the soils with vermiculite and smectite clay minerals have more K^+-fixing ability than soils dominated by illite clay minerals. However, as the K^+ concentration decreased in the soil solution, smectite-dominant soils may easily release fixed K^+ due to lower particle-charge, whereas vermiculite and illite dominant soils may not release fixed K^+ easily. Moreover, ammonium exchangeable K^+, non-exchangeable K^+, total K^+ and K^+-fixing capacity of these soils are directly proportional to the soil clay contents. While recommending K^+ fertilizers clay contents and the type of clay minerals is not considered and recommended K^+ fertilizers sometimes do not response plant growth enhancement. Therefore potassium fertilizer should be recommended by taking into consideration the type and amount of clay minerals present in the soil.

Key words: Alluvial soils, Clay, Electro-ultra-filtration, K^+-dynamics, K^+-fixing soils

Introduction

Potassium (K^+) is the most abundant macro plant-nutrient in most soils. It is crucial since it serves three important functions i.e. enzyme activation, charge balance and osmotic regulation in higher plants (Mengel, 2007). Its concentration in the earth's crust is 2.3%, but the greatest part of this K^+ is bound to primary and secondary clay minerals, and thus not readily available for plants. Its availability to plants depends upon the K^+ concentration in the soil solution and transfer of K^+ from exchangeable and fixed form to soil solution. The concentration of K^+ in soil solution is referred to as "intensity", whereas the soils "capacity" is the total amount of K^+ in the soil which can be taken up by plants. The transfer rate from "capacity" to "intensity" reflects the kinetic factor of renewal of potassium (Barber, 1984).

The major natural source of soil potassium is the weathering of K^+-containing minerals such as micas and alkali feldspars, which contain 6 - 9 and 3.5 - 12% K^+, respectively. During K^+ uptake, plants reduce its concentration in the immediate vicinity of roots which releases K^+-ions from the minerals (Kuchenbuch and Jungk, 1984). The release of K^+ converts micas to secondary 2:1 clay minerals illite and then vermiculite (Figure 1) (Havlin et al., 1999). Application of K^+ fertilizer to soils containing illite and vermiculite clay minerals often leads to fixation of some of its fraction by soil particles. This fraction then becomes unavailable or slowly available to the plants (Scott and Smith, 1987). The fixed K^+ can be made available to plants by its release from soil particles into soil solution when the concentration of K^+ is lowered in soil solution (Cox et al., 1999), but in many cases this release is too slow to meet the plants requirement.

Potassium sorption on exchange sites and its fixation depend on the physicochemical properties of the soil, as well as type and content of the clay minerals (von Braunschweig, 1980).

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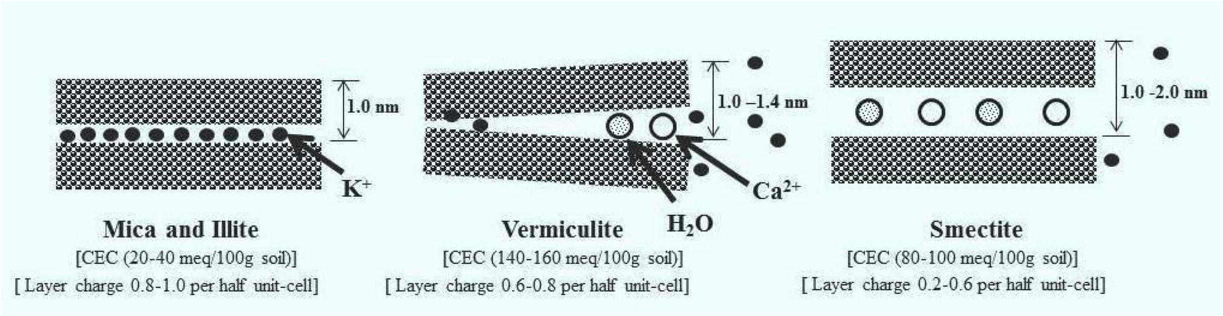

Figure 1. Properties of different types of clay minerals developed by weathering of Mica.
(modified after Wakeel et al., 2011).

The soils containing vermiculite clay minerals are able to fix huge amounts of K^+. Their cation exchange capacity (CEC) is 1.2 – 1.5 mol (+) kg^{-1} soil and the layer basel distance for such soils is 1.4 – 1.5 nm with a layer charge of 0.6 – 0.9 per half unit-cell. Other K^+-fixing clay minerals 'smectites' have CEC 0.8 – 1.2 mol (+) kg^{-1} soil, layer thickness 1.0 – 2.0 nm and layer charge 0.2 – 0.6 per half unit-cell (Bohn et al., 2001).

Sometimes plants do not respond to the application of generally recommended levels of K^+ fertilizer in the soils with expandable clay minerals (Mengel and Kirkby, 2001). Doll and Lucas (1973) reported from Michigan that in a sandy clay loam soil about 92% of the applied K^+ fertilizers were fixed and 1600 kg K^+ ha^{-1} were applied to make it responsive for tomato production. This soil was rich in illite and vermiculite clay minerals with high CEC and a major part of applied K^+ was fixed immediately and became unavailable to the plants. Similar results have been obtained in other parts of the USA (Mengel and Kirkby, 2001).

The fate of K^+ fertilizers applied to the soil depend upon the clay contents, clay minerals and fractions of K^+ already available in the soil. This study shows the K^+ fractions and its correlation with the clay contents of three different soils of Germany differing in clay contents. The aim of the proposed study was to extract the information for precise K^+ fertilizer recommendations may be helpful for research experiments to be conducted for optimal K^+ management in the soils differing in clay minerals for better plant growth and yield production for farmer community as well (Moyin-Jesu, 2008).

Materials and methods

Physicochemical properties of the soil

Three soils i.e. Kleinlinden, Giessen and Trebur, differing in clay contents, were selected for the study. The soils are named based on the location name. Kleinlinden is a subsoil while Giessen and Trebure are surface soils (up to 45 cm depth). The pysicochemical properties of these soils are enumerated in Table 1.

Analysis for inorganic cation (K^+, Na^+, Ca^{2+}, Mg^{2+})

Finely ground 10 g soil and 50 mL 1 M NH_4-acetate were shaken for 1 h on a mechanical shaker. After filtration from white-band 589 filter paper (Schleicher and Schuell Co., Dassel, Germany) cation concentrations of K^+, Na^+, Ca^{2+} and Mg^{2+} were determined by means of atomic absorption spectrophotometry (SpectrAA 220FS, Varian) (Igwe et al., 2005).

Determination of K^+-fixing capacity of soil

Fine ground 10 g soil was shaken for 1 h on a mechanical shaker with 50 mL 0.005 M KCl in Erlenmyer flask. The sample was oven-dried at 100°C and 50 mL 1 M NH_4-acetate solution were added followed by 1 h shaking on a mechanical shaker. After filtration through white-band 589 filter paper (Schleicher and Schuell Co., Dassel, Germany) the samples were analyzed for K^+ concentration using atomic absorption spectrophotometer (SpectrAA 220FS, Varian).

Table 1. Physicochemical properties of soils i.e. Giessen, Kleinlinden and Trebur.
Clay-mineral types are according to Paul, (1989).

Soils	pH	Clay	Silt	Sand	Soil textural class	Dominant clay minerals
			($g\ kg^{-1}$)			
Kleinlinden	5.8	207	338	455	loam	Illite
Giessen	5.2	303	631	47	silty clay loam	Vermiculite & smectite
Trebur	7.4	446	436	112	silty clay	Smectite

K^+ fixing capacity was calculated by using the formula (Wakeel, 2008);

K_{fix} (µg /g or mg kg^{-1}) = (9800 + K_a - K_r)/10

Where,

9800 = µg of K^+ in 50 mL of 0.005 M KCl solution

K_a = Exchangeable K^+

K_r = K^+ concentration in soil filtrate after fixation on soil particles

Note: Three replications for each soil were processed and mean values were compared.

Total cation concentration in the soil

Samples of finely ground soil (100 mg) were placed in a 30 mL platinum crucible. After addition of few drops of water, 5 mL of 48% hydrofluoric acid (HF) and 0.5 mL of 72% perchloric acid ($HClO_4$) were added. Soil acid mixture was heated on a hot plate until fumes of $HClO_4$ appeared. Crucibles were cooled, and then 5 mL of HF was added. The crucibles were placed in a sand bath covered about 9/10 of the crucible top with a Pt lid. Crucibles were heated to 200 to 225°C and the contents were evaporated to dryness. After cooling the crucibles, 2 mL of water were added followed by few drops of $HCLO_4$. Crucibles were placed again in the sand bath and the contents were evaporated to dryness. The crucibles were removed and 5 mL 6 N hydrochloric acid and 5 mL of double deionized water were added after allowing it to cool. The crucibles were then heated over a burner until the solution started boiling gently. When the residues were completely dissolved in HCl, the material was filtered into a 100 mL volumetric flask and cation concentration (K^+, Na^+, Ca^{2+} and Mg^{2+}) was measured in the filtrate by Atomic Absorption Spectrophotometery (SpectrAA 220FS, Varian) (Jackson, 1958).

Determination of interlayer K^+

Interlayer potassium was determined by means of electro-ultra-filtration (EUF) technique from the soils used for the various experiments (Schubert et al., 1989). The principle of EUF technique is presented in Figure 2. The soil suspension was exposed to an electric field and K^+ ions migrated to the cathode, where they were collected. Soil samples were extracted for 60 min at 20˚C and 200 V followed by extraction for 60 min at 80˚C and 400 V. Extraction was carried out at 10 min intervals so that 12 sub samples were obtained. Collected extracts were filled up to mark in 200 mL volumetric flasks and were analyzed for K^+ by Atomic Absorption Spectrophotometry (SpectrAA 220FS, Varian). The dynamics of available K^+ was considered for the six samples obtained in the first 60 min at 200 V and the dynamics of non-exchangeable K^+ release was obtained by considering the data obtained in following 60 min at 400 V. Extracted K^+ was plotted against time to characterize the desorption dynamics.

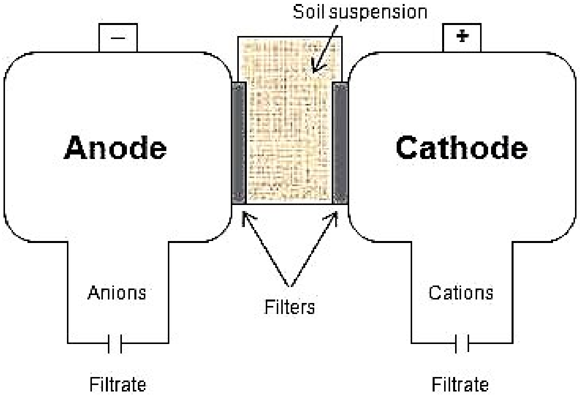

Figure 2. Scheme of the electrofiltration (EUF) apparatus. Migration of ions to electrodes results in dilution of ions in the solution and thus promotes the desorption of adsorbed ions
(Mengel and Uhlenbecker, 1993).

Results and Discussion

Comparison of K^+ release from the soils

The soils were characterized according to potassium (K^+) release from the clay minerals of the soils. Figure 3 shows that K^+ release was almost similar in soils Kleinlinden and Giessen (10 to 20 mg K^+ kg^{-1}). However, K^+ dynamics were different in the soil Trebur i.e. 35 to 165 mg K^+ kg^{-1} (Wakeel et al., 2005).

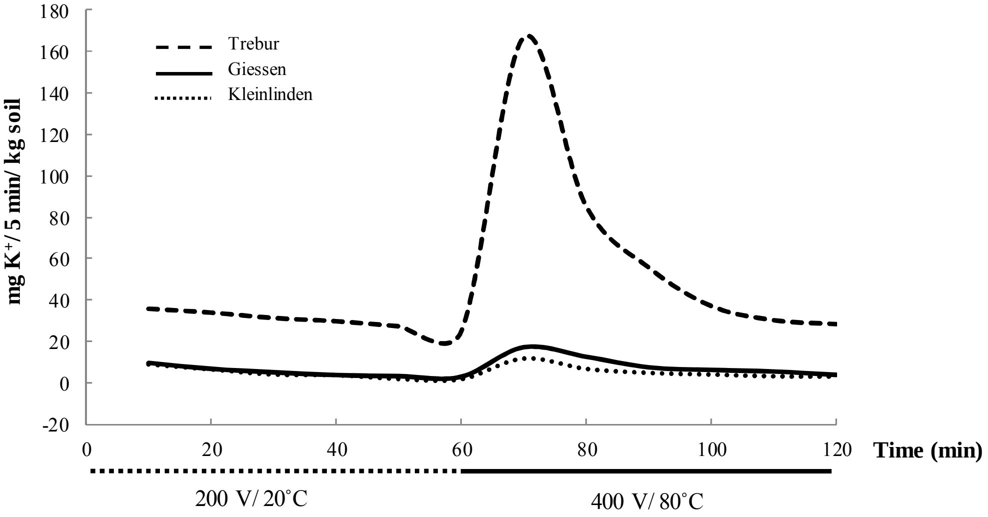

Figure 3. Potassium release from the soils (Kleinlinden, Giessen and Trebur) used for soil culture experiments. Potassium was extracted from the soils by electro-ultra-filtration (EUF) technique and K^+ concentration was measured with an atomic absorption spectrophotometer.

In the first 60 min, K^+ was extracted from all three soils at 200 V and this amount is known to be easily available for plants. If we compare this value obtained in soil Trebur with the other two soils, the easily available K^+ in soil Trebur was ~33 mg K^+ kg^{-1} soil, which was significantly higher (p = 0.05) than in soils Giessen and Kleinlinden (~10 mg K^+ kg^{-1}). Similarly, when the soils were exposed to 400 V from 60 - 120 min and K^+ release was measured from the filtrate. This was again almost similar for soil Giessen and Kleinlinden (~20 mg K^+ kg^{-1}), but the difference with soil Trebur was higher (p = 0.05), about 160 mg K^+ kg^{-1}, and afterwards this release was almost constant at the concentration of 40 mg K^+ kg^{-1} soil. Potassium extracted at 400 V is considered as slowly available K^+. Total amount of K^+ present in the soils, i.e. 14.5 - 16.5 g kg^{-1} do not show much variation between the soils, however the NH_4^+-exchangeable K^+ was much higher in the soil Trebur (Table 2). We can attribute higher K^+ values in first 60 min to higher exchangeable K^+, however higher values in the next 60 min show the characteristic of smectite clay minerals dominantly present in this soil (Paul, 1989). Such types of soils are able to release from total K^+ present in the soil when its concentration decreased in the soil (Schubert et al., 1989). Earlier in a field study no difference was found in plant growth and beet yield of sugar beet treated with 0, 400 and 1575 kg K^+ ha^{-1}, although the initial analysis of soil showed K^+ deficiency (Wakeel, 2008). We suggest that more interlayer space and the lower layer charge (Table 1) for smectite clay minerals was a factor for K^+ release on decreased K^+ concentration in the soil solution (Hinsiger and Jaillarr, 1993).

Clay contents and K^+ concentrations in the soils

The clay contents play an important role in K^+ availability to plants in the soils. Clay contents in the experimental soils were in the order, Trebur > Giessen > Kleinlinden. Total, fixed, and ammonium exchangeable K^+ concentration were directly proportional to the total clay contents of the soils. Figure 4A, 4B, and 4C show the correlation between clay contents and total potassium in the soil. The results revealed that more clay contents possessed more K^+ contents whether fixed or exchangeable (Jalali and Zarabi, 2006).

Table 2. Potassium dynamics in the soils and the K^+-fixing capacity of soil. The values are the mean of four replicates.
Means followed by the same letter in the same soil are not significantly different according to the LSD test at 5% level of probability.

	$K^+_{(Total)}$	Fixed K^+	$K^+_{(Exch.)}$	K^+-fixing cap. of soil
Soils	g kg^{-1}		mg kg^{-1}	
Kleinlinden	14.50 b	14.41 b	85 c	488 c
Giessen	14.90 b	14.80 b	98 b	526 b
Trebur	16.50 a	16.11 a	386 a	618 a

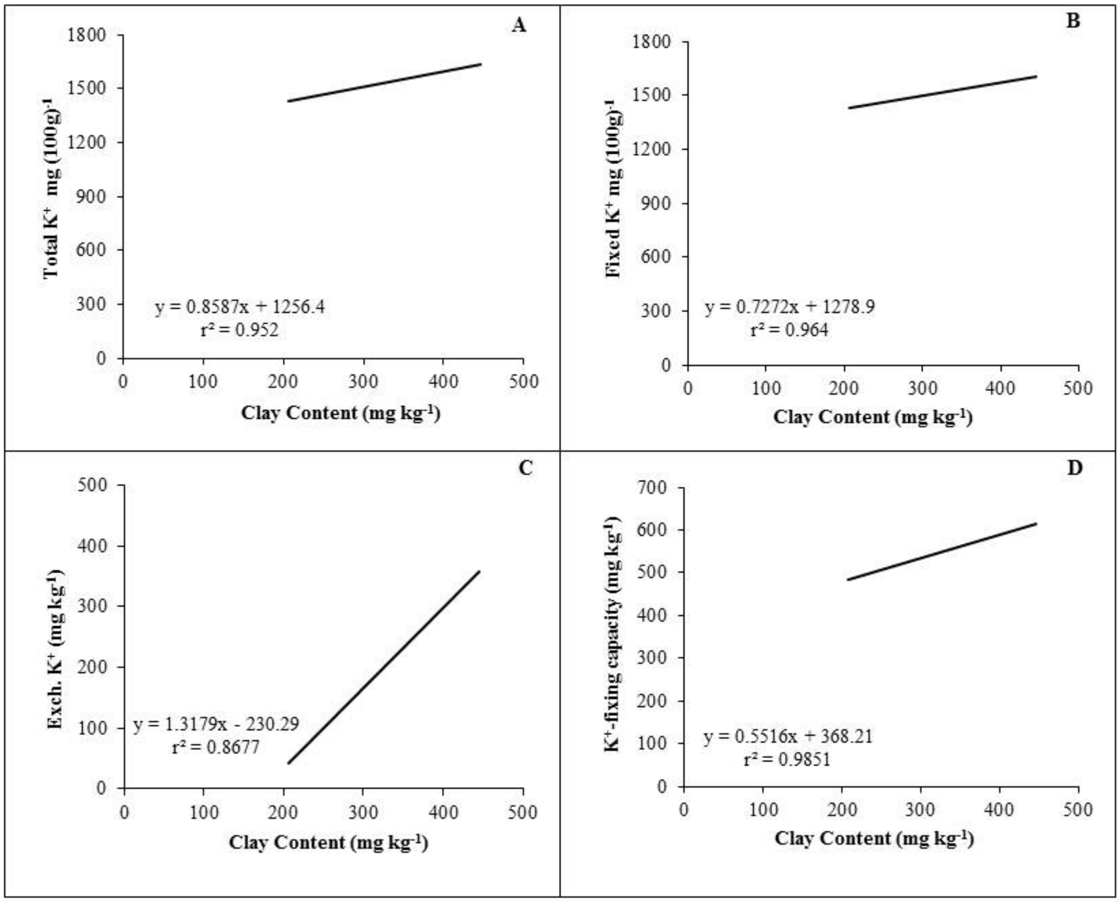

Figure 4. Correlation between soil clay contents and K^+ concentrations in the soils. A shows correlation between soil clay contents and ammonium exchangeable K^+, B shows correlation between soil clay contents and total K^+, C shows correlation between soil clay contents and fixed K^+ and D shows correlation between soil clay contents and K^+-fixing capacity of soil.

Possession of K^+ in different clay minerals was significantly different. The illites are contracted clay minerals with layer thickness of 1 nm. This is due to more interlayer K^+ ions than that in vermiculite and smectite. These all three clay minerals are developed from mica by its weathering. Mica is rich in interlayer potassium (Brady and Weil, 2001). Weathering occurs by release of interlayer K^+ and adsorption of other cations and water molecules.

Ammonium-exchangeable K^+ in all three soils is shown in the Table 2. Clay particles have -ve charge and have capacity to absorb K^+ ions. The soils with more clay contents (Trebur and Giessen) have more exchangeable K^+ as compared to soil with low clay contents (Blake et al., 1999). In Fig. 4C, a highly significant correlation (r^2= 0.87) between soil clay contents and exchangeable K^+ can be seen. In fact on the clay minerals, there are three types of K^+ sites. The first is planar (p) which is not specific for K^+ binding, second is edge (e) positions which are more selective to K^+ and third is inter lattice (i) with highest K^+ selectivity (Rao et al., 1999). Potassium ions present on position (p) and (e) are exchanged by NH_4^+ but K^+ present at position (i) are out of NH_4^+ reach. Higher concentration of exchangeable K^+ in Trebur soil may be due to the presence of smectite clay minerals. Low layer charge leads to less contraction and more interlayer spaces, which keep the K^+ ion reachable to be replaced by NH_4^+.

Relation between clay contents and K^+-fixing capacity of soil is also positively correlated (r^2=0.98). Clay contents have the ability to fix more K^+. Instead of positive correlation, the critical analysis of this data showed that K^+-fixing capacity was not only a function of clay contents. The clay contents in Trebur, Giessen and Kleinlinden soil were 207, 303 and 446 g kg^{-1}, respectively and K^+-fixing capacity was 488, 526 and 618 mg K^+ kg^{-1}

soil, which was 2.4, 1.7 and 1.3 mg K^+ g^{-1} clay, respectively. The lower K^+-fixing capacity (=1.3 mg K^+ g^{-1} clay) of Trebur soil owing to lower CEC (80-100 meq/100g), lower layer charge (0.2-0.4) and lower K^+ selectivity of smectite clay minerals . Moreover, soil Trebur was dominant in smectite (50%) (Paul, 1989), which had less K^+ fixation due to its less attraction for K^+ ions. Instead of showing K^+-fixing capacity by conventional methods, such soils may release K^+ to fulfill the plant requirements (Wakeel, 2010, 2011).

Therefore it is concluded that the clay minerals present in the soils should be considered while conducting research experiments and recommending K^+ fertilizers. In most part of the developing world, K^+ fertilizers are recommended generally without considering clay minerals present in the soil and recommended fertilization do not give appropriate results discouraging the farmers to use K^+ fertilizers for crop production. We suggest the K^+ fertilizer recommendation considering soil clay minerals and also suggest that EUF may be a good tool to determine K^+-dynamics in the soils varying in clay contents.

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