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Clay mineralogy and its relationship with potassium forms in some paddy and non-paddy soils of northern Iran

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Abstract

Forms of potassium in soils have been a key focus in soil-fertility studies. Clay minerals are the main source of plant nutrients in soil, as their specific surface characteristics determine the release pattern of some important nutrients, such as potassium. Three forms of K consist of unavailable, slowly available and readily available exist in equilibrium in the soil system. Relationships between soil potassium forms within the clay mineralogical suite were determined in twenty four soil samples in three pedons from paddy soils, two from kiwifruit and one from citrus land in the north of Iran. The results showed that, the characteristics of different forms of potassium in adjacent pedons under different land uses depended on their specific clay mineralogy. Mineralogical analyses showed that smectite, illite and vermiculite were the most abundant clay minerals in the studied soils. Mean soluble and exchangeable potassium in paddy soils were rather low compared to non-paddy soils due to potassium fertilization in non-paddy soils. Non-exchangeable potassium in the samples, which was dominated by smectite, was lower than that in samples dominated by vermiculite, hydroxy-interlayer vermiculite (HIV) and illite; this was related to the inability of smectite in potassium fixation. Therefore, taking into account both exchangeable and HNO_3-extractable K gives a better indication for K potential and soil-quality management.

Keywords: Exchangeable and non-exchangeable K; Kiwi fruit; Mineralogy; Smectite.

Abbreviations: Illi- Illite; HI- Hydroxy Interlayer Vermiculite; Smc- Smectite; Kao- Kaolinite; Ver- Vermiculite; Cl- Chlorite; Mix- Mixed mineral.

Introduction

Southern and southeastern Asia contains the world's most important paddy soils, comprising about 126 million ha of the worldwide total of 135 million ha (IRRI, 2002). Climate and landforms are the two determinants for this strongly biased distribution of paddy lands and their fertility (Kyuma, 2004). Rice is the staple food for billions of people worldwide (Akbar et al, 2011) and is one of the most important grains in the world (Rahimi Petroudi et al, 2011). Rice cultivation in paddy field is of great importance in the north of Iran, especially in Mazandaran and Guilan provinces with totally 78% of cultivation area and rice yield (Rahimi Petroudi et al, 2011). Potassium is an essential and major nutrient for crop production in paddy soils (Sparks and Huang, 1985). The exact function of K in plant growth has not been clearly defined, although its association with the movement of water, nutrients and carbohydrates in plant tissue has repeatedly been reported. Soils commonly contain over 20,000 ppm of total potassium (McLean and Watson, 1985). Nearly all soil K is in a structural form, and thus not available for plant growth. Plants can use only the exchangeable potassium on the surface of soil particles and potassium dissolved in the soil water (these often amount to less than 100 ppm) (Rehm and Schmitt, 2002). Soil potassium is classified in three forms according to availability: unavailable, slowly available and readily available or exchangeable (Sharpley, 1989; Bhonsle, 1992). Crystalline and insoluble soil K, which is in an unavailable form, comprises approximately 90-98% of total soil K (Sparks, 1987; Martin and Sparks, 1985). Slowly available potassium, which is fixed and non-exchangeable, is the form trapped between the layers or sheets of certain kinds of clay minerals; plants can use only very little of it during a single growing season (Sparks, 1987). The major sources of non-exchangeable K in soils are K-rich 2:1 clay minerals such as micas and vermiculite (Sparks, 1987; Moritsuka et al. 2004). Mica (illite) clays also fix K between their layers when they become dry, but do not release all of the fixed K when wet. This fixation without release causes problems in the paddy-soil regions for management of potash fertilizers in crop production. K release from the interlayer of these minerals is very slow, depending on their weathering stage (Rehm and Schmitt, 2002). The release of K from clay minerals is influenced by particle size and chemical composition (Huang, 2005). It is generally accepted that trioctahedral micas, such as biotite and phlogopite, release K more readily than dioctahedral ones, such as muscovite (Fanning et al., 1989). Readily available potassium is a dissolved form of K (water-soluble) or held on the surface of clay particles (exchangeable K). Different articles have reported that plants can take up both exchangeable and non-exchangeable forms of potassium. Bhonsel, et al. (1992) suggested that fixed or non-exchangeable forms of K can be the main source of potassium for plants. Minerals' K release to soluble and exchangeable forms and its adsorption by exchange sites

Table 1. Land use, soil classification and some physico-chemical properties of the studied pedons

Horizon	Depth	Clay	Tex.	pH	EC	OC	CEC	K_{sol}	K_{ex}	K_{nonex}
	cm	%			µS m^{-1}	%	cmol$^+$ kg^{-1}	ppm		
(P1)Citrus: Oxiaquic Udipsamments										
Ap	0-13	15.6	SL	7.85	1022	1.97	15.18	17.94	120.9	641.9
AC	13-23	9.6	LS	8.08	557	0.4	7.91	4.29	35.1	335.4
C1	23-61	5.6	S	8.13	347	0.2	4.75	2.11	29.64	259.6
C2	61-100	3.6	S	8.38	336	0.2	4.9	2.53	26.13	284.3
(P2) Paddy: Typic Endoaqualfs										
Apg	0-12	49.9	C	7.85	1030	3.75	21.56	1.95	58.11	253.1
Bg	12-25	43.6	C	7.89	1022	3.75	25.15	1.95	65.52	276.9
Btg1	25-60	45.6	SiC	8.18	563	1.97	21.35	1.56	51.48	696.9
Btg2	60-100	43.6	SiC	8.12	524	0.6	18.03	1.56	52.26	188.6
(P3) Paddy: Typic Endoaquepts										
Apg	0-20	43.6	C	7.79	1095	0.79	21.04	2.73	54.6	189.9
2Bg1	20-40	15.6	SL	7.92	1119	0.2	9.65	1.95	24.57	198.3
2Bg2	40-75	27.6	CL	7.93	866	0.6	12.33	2.34	50.7	139.8
(P4) Paddy: Typic Endoaqualfs										
Apg	0-14	52.16	C	7.81	1055	2.57	24.83	2.34	82.29	299
Btg1	14-35	53.6	C	8.09	716	1.38	24.05	1.56	69.03	313.1
Btg2	35-50	43.6	C	8.22	501	0.99	18.81	2.73	59.67	229
2Bg1	50-75	17.6	SL	7.99	917	0.39	9.65	2.11	29.64	180.1
3Bg2	75-110	27.6	L	7.98	841	0.99	12.02	2.34	44.85	209
(P5) kiwi: Typic Endoaquepts										
Ap	0-12	42.16	C	7.73	1005	6.71	30.36	6.63	110.8	281
Bg1	12-27	35.6	CL	7.56	882	5.33	32.59	3.12	56.55	247.5
Bg2	27-45	29.6	CL	7.29	1459	5.92	36.22	3.12	41.34	175.5
2Cg	45-100	19.6	SL	7.28	2130	2.76	17.22	3.51	30.03	207.3
(P6) kiwi: Oxiaquic Hapludalfs										
Apg	0-20	62.5	C	7.56	1066	5.33	34.01	10.53	164.9	268.5
Bg	20-38	43.6	C	8.13	587	0.99	24.21	1.95	62.01	201.6
Btg1	38-45	43.6	SiC	8.28	494	0.99	23.25	1.56	49.92	218.5
Btg2	45-70	31.6	CL	8.26	578	0.6	18.19	2.34	54.99	216.7

depends on the equilibrium between different phases of soil K (McLean and Watson, 1985), which may be affected by such factors as root uptake, fertilizer K applied, soil moisture, soil pH and soil temperature (Sparks, 1987). The relationship between clay mineralogy composition and potassium forms has been demonstrated by several studies (Sharply, 1989; Bhonsle et al., 1992; Liu et al., 1997; Ghosh and Singh, 2001; Surapaneni et al., 2002; Srinivasarao et al., 2006). Knowledge of clay mineralogy is crucial to understanding soils' nutritional status and nutrient-supplying power. Mineralogical composition of soils may have a considerable influence on K dynamics (Surapaneni et al., 2002). Relationships between clay mineralogy and potassium forms can be used in evaluating potential soil K fertility, prediction of K cycling and plant uptake (Sharply, 1989). Information on the NH_4OAc-K form of potassium along with knowledge of clays' mineralogical composition can provide insights into the equilibrium and release of non-exchangeable K to plants and the need for K fertilizers (Bhonsle, 1992). Soils with high 2:1 clay minerals (micas, vermiculite and high-layer-charge smectite) contain larger amounts of HNO3-extractable K than kaolinite and other siliceous minerals (Martin and Sparks, 1985; Sharply, 1989; Ghosh and Singh, 2001). Bhonsle et al. (1992) stated that kaolinitic soils had low levels of NH4OAc-K, mixed and illitic soils had medium levels and smectitic soils had high levels; their estimates for HNO3-K, showed that kaolinitic, mixed and smectitic soils had low levels, and illitic soils had high. Their study set out the proportion of NH4OAc-K to HNO3-K in the sequence smectitic > kaolinitic > mixed > illitic. Sharpley (1989) stated that determining both exchangeable and HNO3-K could give a better indication of soil's potential K-supplying power. There is no report on the clay mineralogy and potassium status of the land used for different agricultural purposes in Iran (although in 1998 Towfighi estimated that available potassium in more than 100,000 ha of Iranian paddy soils varies between lower-than-critical to moderate). Therefore, the objectives of present study are: (1) to compare different forms of potassium (soluble K, exchangeable K and non-exchangeable K) in paddy soils and non-paddy soils, and (2) to compare the relationships between forms of K and clay mineralogy in paddy soils, and land uses under citrus and kiwi fruit cultivation.

Results and discussion

The paddy soils showed very distinct morphological, physical and chemical properties from those of non-paddy soils. Table 1 shows some physicochemical characteristics of the studied pedons, including pH, EC, CEC, OC, PSD and ammonium acetate and the forms of potassium that are extractable using nitric acid. pH values of saturated paste in the paddy and non-paddy pedons varied between 7.79 and 8.22 for paddy soils, and between 7.28 and 8.38 for non-paddy soils (Table 1). Electrical conductivity of saturated extracts (ECe) ranged between 336 and 2130 µS m^{-1}. Relatively strong differences (0.2 to 6.71 %) were observed in the horizontal (between pedons) and vertical (between horizons) distribution of soils' organic carbon. The largest amount of organic carbon was observed in the surface layer

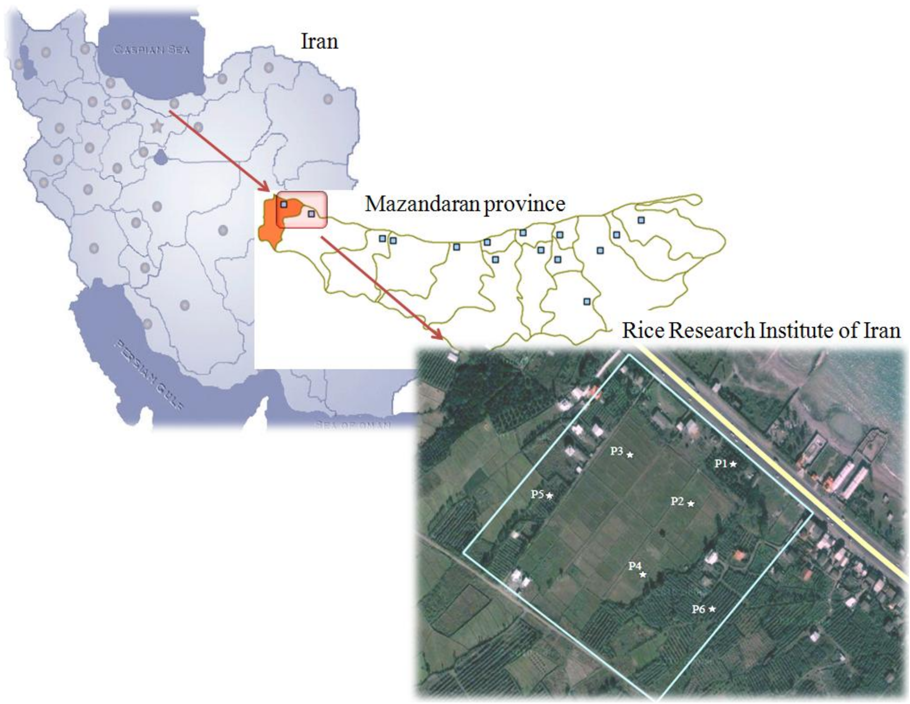

Fig 1. Map of studied region in Mazandaran province, Iran.

of the kiwi fruit soil (pedons 5 and 6) due to higher decay of the surface litter and rotting of roots caused by very poor drainage. Cation exchange capacities (CEC) varied between 4.75 (pedon 1) to 36.22 (pedon 5) cmol$^+$ kg^{-1}. Kyuma (1984) also found an average CEC for some paddy soils from tropical Asia of 18.6 cmol$^+$ kg^{-1}. The lowest CEC was obtained in the deeper horizons of the citrus pedon, due to its lower clay and organic-matter contents. In all studied pedons, the highest CEC values were found in the surface layers as a result of their higher organic carbon contents. The paddy soils had the highest clay content among the studied pedons.

The highest water-soluble K content was observed in the citrus pedons, followed by kiwifruit and paddy. In contrast, the highest NH_4OAc-K was observed in the kiwi fruit pedons, followed by citrus and paddy. For HNO_3-K, the citrus pedon had the highest value, followed by paddy and kiwi fruit (Table 1). The mineral composition of studied soils shows by the X-ray diffractograms of the clay fraction (Fig.2 and Table 2). Clay mineralogical composition was determined using the intensity and position of the X-ray diffractogram peaks, considering clay apparent CEC (CEC/Clay %). The high intensity of 1.43 and 0.71 nm peaks in Mg-saturated and Mg-saturated, glycerol-solvated treatments, and the collapse of the peaks in K-saturated and K550 treatments demonstrate the presence of vermiculite (Fig.2A). Also, 1.0, 0.5 and 0.33 nm peaks in Mg-saturated diffractograms indicate the presence of illite. Kaolinite was detected based on the presence of 0.71 and 3.56 nm peaks in Mg-saturated treatment that collapsed in K550 treatment. A shifting 1.43 nm peak in the Mg-saturated treatment toward 1.8 nm in Mg saturated-glycerol solvated treatment also indicated the presence of some expandable clay minerals (smectites). A shifting 1.43 nm peak toward 1.1-1.3 nm in K550 treatment showed the presence of hydroxy-interlayered minerals. Vermiculite, smectite-illite and vermiculite, hydroxy-interlayered vermiculite were the most prevailing clay minerals in citrus, paddy and kiwi fruit pedons, respectively (Table 2). Differences in clay mineralogical suites were most probably related to land management, different parent materials and soil-drainage conditions. Figure 3 shows the relationship between dominant clay minerals with exchangeable and non-exchangeable potassium in different horizons for some soil pedons. The exchangeable and non-exchangeable potassium in the surface layers of the citrus pedons were higher than that of the subsurface layers due to more suitable thermal and moisture status preconditioned for mica and feldspar weathering (Fig.3A). Potassium does not leach out from clayey and silty soils, but the sandy soil used for citrus is not able to hold high amounts of exchangeable and non-exchangeable potassium. Sinha and Biswas (2003) stated that water soluble, available and nonexchangeable potassium showed a positive and significant correlation with clay content and cation exchange capacity for soils of West Bangal, India. Further, Nabiollahy et al. (2006) reported that mineral K, HNO3-extractable K and the clay content of the soils containing lesser illite (10-30%) were significantly different from those with more illite (30-50%). Besides the clay content, K-bearing minerals and clay mineralogy may play a more important role in determining a soil's extractable K status. For example, the clay contents in pedon 1 were relatively low, and their dominant clay mineral was vermiculite, whereas the measured exchangeable and non-exchangeable K was medium and high, respectively (Table 1). Wedge zones or specific K-adsorption sites in vermiculite may have caused these results (Rich, 1972; Sparks and Liebhardt, 1982). Plant-available potassium (soluble K) and exchangeable potassium in the studied soils were very low (Table 1). Mean soluble and exchangeable potassium in paddy soil samples were lower than in kiwi fruit and citrus soil samples. Smectite was the most prevalent mineral in the paddy soils; this may be the main reason for their lower K forms compared to other land

Table 2. Clay mineralogical suite of the studied soil samples

Horizon	Mineralogy
	(P2) Paddy
Apg	Illi. » HIV. › Smc. »Kao. › Ver.
Bg	Smc. › Ver. » HIV. › Illi. » Kao.
Btg1	Illi. » HIV. › Ver. »Kao. › Smc.
Btg2	Illi. » HIV. › Ver. »Kao. › Smc.
	(P3) Paddy
Apg	Smc. » Illi.› Kao. » HIV. › Ver.
2Bg1	Smc. › Ver. » Illi. › Kao. › HIV.
2Bg2	Smc. › Illi. › Kao. › HIV. › Ver.
	(P4) Paddy
Apg	Ver. » Illi. › HIV. » Kao › Smc.
Btg1	HIV. » Kao. › Illi. » Ver. › Smc.
Btg2	Smc. › HIV. › Ver. » Illi. » Kao.
2Bg1	Smc. › HIV. » Ver. › Illi. » Kao.
3Bg2	Smc. › Illi. » Ver. » Kao. › HIV.

Horizon	Mineralogy
	(P5) kiwi
Ap	Smc. › Ver. » Illi. › Kao. » HIV.
Bg1	HIV. › Smc. › Ver. › Illi. › Kao.
Bg2	HIV. › Smc. › Ver. › Illi. › Kao.
2Cg	HIV. › Smc. › Ver. › Illi. › Kao.
	(P6) kiwi
Apg	Smc. › HIV. ›Ver. » Illi. » Kao.
Bg	Ver. › HIV-Cl. » Kao. › Illi. » Smc.
Btg1	Ver. › HIV-Cl. » Kao. › Illi. » Smc.
Btg2	Ver. › Smc. » HIV-Cl. » Kao. » Illi.
	(P1)Citrus
Ap	Ver. › Smc. › Mix. » HIV. › Illi. » Kao.
AC	Ver. » Smc. › HIV. » Kao » Illi.
C1	Ver. › Illi. › HIV. › Kao. » Smc.
C2	Ver. › Illi. › HIV. › Kao. » Smc.

* Illi.: Illite, HI.: Hydroxy-Interlayer Vermiculite, Smc.: Smectite, Kao.: Kaolinite, Ver.: Vermiculite, Cl.: Chlorite, Mix.: Mixed mineral.

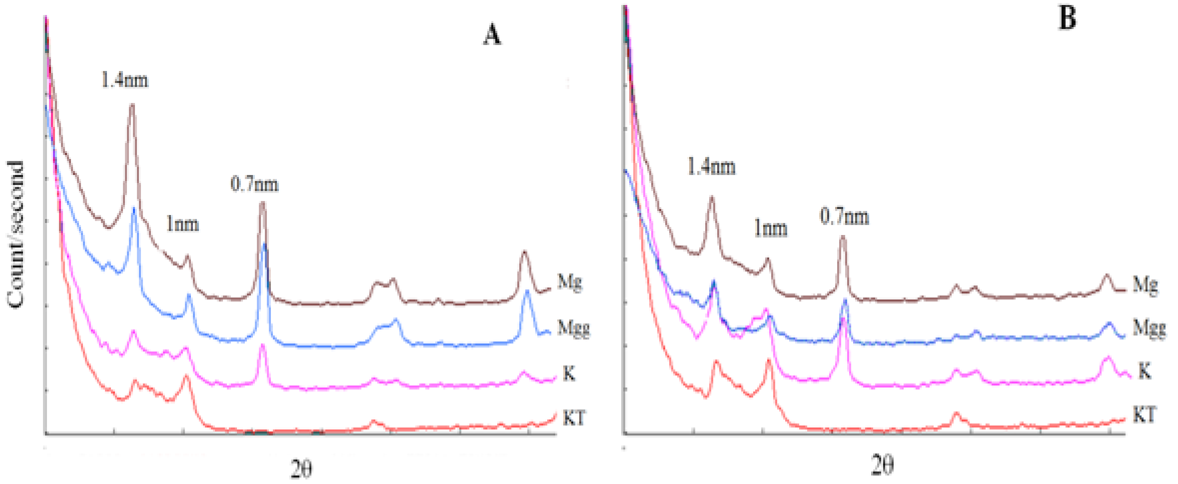

Fig 2. Representative X-ray diffractograms: A: Btg1 horizon, pedon no. 2 and B: Bg1 horizon, pedon no. 5.

uses. Suitable soil aeration and high oxygen levels are necessary for K uptake by plants. K uptake decreases as soil moisture content increases to saturation. Shahbazi and Towfighi (2006) showed that exchangeable K decreases with increasing soil-saturation time. Results in this study showed that in soil samples in which smectite predominated, non-exchangeable potassium was about 200-300 ppm, while in vermiculitic and hydroxy-interlayered vermiculite and illite-dominanted soil samples, non-exchangeable potassium was about 300-600 ppm (Fig.3). Illitic soils, due to the higher fixed potassium in their interlayer positions, and vermiculitc soils, due to their more-negative layer charge, are among the most important factors in controlling soils' potassium status. Sparks (1987) and Moritsuka et al. (2004) reported that the major sources of non-exchangeable K in soils are K-rich 2:1 clay minerals such as micas and vermiculite. In general, paddy soils' mean non-exchangeable potassium, extracted by boiling nitric acid, was between moderately low and low. This may be attributed to the prevalence of smectite, which can cause these soils to be rich in ammonium acetate extractable potassium, yet moderately poor in HNO_3-K concentration. Years of cultivation without the use of potassium fertilizers have led to a drastic decrease in exchangeable potassium, followed by a decrease in non-exchangeable potassium, in paddy soils. So, for better understanding of the relationship between clay mineralogy and different forms of potassium, studying the processes and mechanisms of potassium absorption and release is essential to achieve sustainable agriculture and increase the efficiency of crop production.

Materials and methods

Study Area

This study examined paddy and non-paddy soils (about 10 ha) obtained from the Rice Research Institute of Iran (36º51´53´´ to 36º51´48´´ northern latitudes and 50º46´56´´ to 50º46´44´´ eastern longitudes, 20 m below sea level) (Fig.1). Mean annual precipitation in this region is 1253 mm,

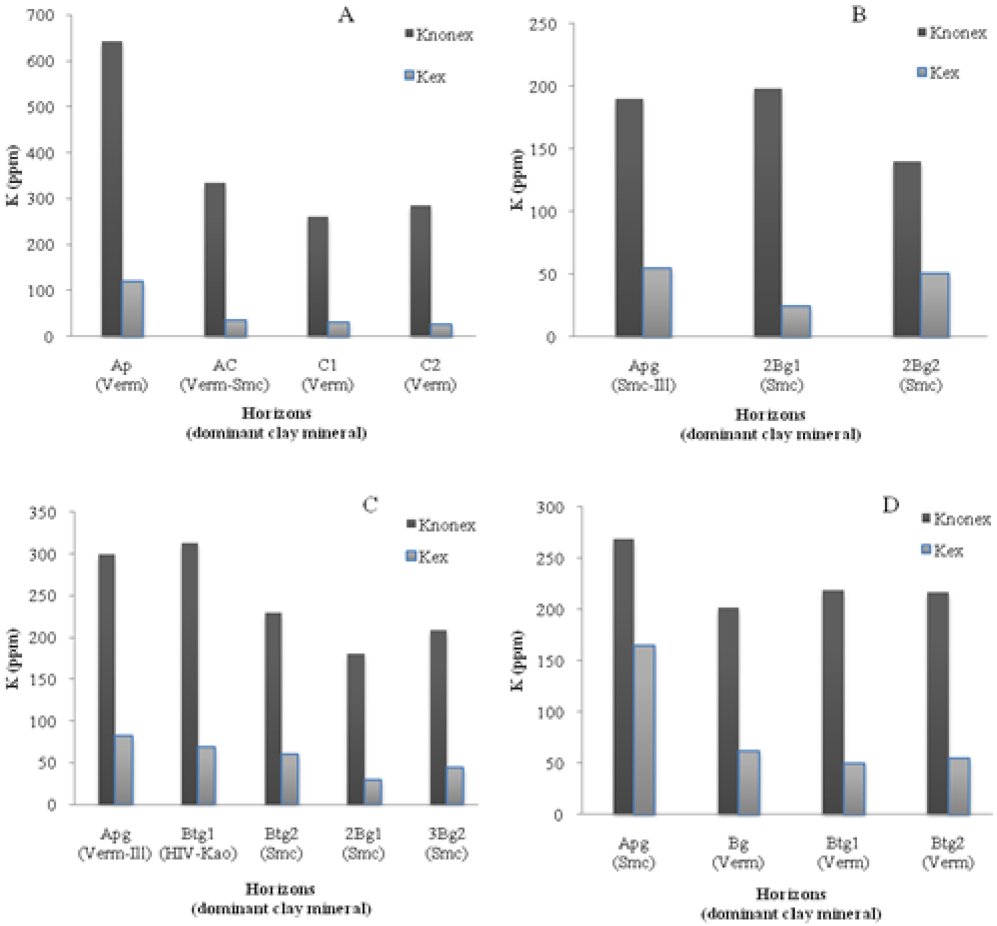

Fig 3. Relationship between dominant clay minerals with exchangeable and non-exchangeable potassium in different horizons, A: pedon no.1, B: pedon no.3, C: pedon no.4, D: pedon no.6.

and mean annual air temperature is 15.8 ºC. Soil moisture and temperature regimes, calculated according to the Newhall Simulation Model (Newhall and Berdanier, 1996), were udic and thermic, respectively.

Field Sampling

Three adjacent land uses, including paddy, kiwifruit and citrus, were selected. Ten pedons were dug, described and sampled according to the field book for describing and sampling soils, and were classified according to the Soil Taxonomy (Soil Survey Staff, 2010). From the pedon samples, six were included for comprehensive analysis in this study (three pedons from paddy soils, two pedons from kiwifruit and one pedon from citrus).

Physico-Chemical Analysis

All analyses were performed on air-dried soil samples passed through a 2 mm sieve (Pansu and Gautheyrou, 2006). The samples' physicochemical and mineralogical characteristics were analyzed according to standard methods (Kunze and Dixon, 1986). pH_{sp} was determined using a pH meter applied to soil saturated to a paste using deionised water. Electrical conductivity (EC_{se}) was also measured in the saturated extracts (Carter and Gregorich, 2008). Particle-size distribution was measured by the hydrometer method (Carter and Gregorich, 2008). Organic carbon was determined using wet oxidation (Pansu and Gautheyrou, 2006). Cation exchange capacity (CEC) was measured by the ammonium acetate method (pH=7) (Carter and Gregorich, 2008). Exchangeable potassium was determined using shaking of 2.5 g air-dried soil with 50 ml of 1 M NH_4OAc solution (pH=7) (Knudsen et al., 1996). Non-exchangeable potassium was determined by heating 10 g of soil with 25 ml of 1 M HNO3 solution in an oil bath (113 ºC) for 25 minutes (Pratt, 1965). The extracts' K concentrations were determined by flame photometry.

Mineralogical Analysis

Clay mineralogical studies were performed by removing soluble salts and gypsum by washing out (Konse and Rich, 1959), carbonates by neutralization with sodium acetate (pH=5) (Grossman and Millet, 1961), organic materials by oxidation with H_2O_2 (Konse and Rich, 1959) and ferrous oxides by citrate dithionate bicarbonate (CDB) (Mehra and Jackson, 1960). Clay fraction was separated by sedimentation and saturated with Mg^{2+} and K^+ ions using 1 N $Mgcl_2$ and KCl solutions. Mineralogical composition was determined by X-ray diffraction using a Siemens D5000 diffractometer via CuKα (λ=1.5409 Aº) and 30 kV voltage and 30 mA (Fig. 2, Table 2).

Conclusion

NH_4OAc-K is used as an indicator for the availability of potassium in soils, but it does not give similar trends in all mineralogical suites. A combination of both NH_4OAc-K and HNO_3-K gives a more applicable index for smectitic, illitic and vermiculitic soils. This study found that while smectitic soils are rich in NH_4OAc-K, they have modest amounts of HNO_3-K, with moderate K release rates. On the other hand, illitic soils have only modest amounts of NH_4OAc-K with high amounts of HNO_3-K, and high rates of K release. Accordingly, shallow smectitic soils could experience K exhaustion and the need for K fertilization more than illitic soils. Non-exchangeable K plays a significant role in supplying available K, particularly in soils containing K-bearing minerals. Therefore determination of both exchangeable and HNO_3-extractable K gives a better indication of the K potential and management for rice production in paddy soils. Hence, clay mineralogy should be considered as a main determinant in paddy soils' nutrient status. To improve rice production and potassium reserves in these paddy soils requires precise potassium management.

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