

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/232923949>

Release Kinetics of Nonexchangeable Potassium by Different Extractants from Soils of Varying Mineralogy and Depth

Article in *Communications In Soil Science and Plant Analysis* · March 2006

DOI: 10.1080/00103620500449351

CITATIONS

70

READS

664

5 authors, including:



Srinivasrao Ch.

Indian Agricultural Research Institute

659 PUBLICATIONS 11,384 CITATIONS

[SEE PROFILE](#)



Thauhida Rupa

National Research and Education Network of India (ERNET)

18 PUBLICATIONS 610 CITATIONS

[SEE PROFILE](#)



Annangi Subba Rao

Indian Institute of Soil Science

186 PUBLICATIONS 6,094 CITATIONS

[SEE PROFILE](#)



G. Ramesh

JCT College of Engineering and Technology, Coimbatore, Tamilnadu

69 PUBLICATIONS 1,300 CITATIONS

[SEE PROFILE](#)

Release Kinetics of Nonexchangeable Potassium by Different Extractants from Soils of Varying Mineralogy and Depth

Ch. Srinivasarao

Central Research Institute for Dryland Agriculture, Hyderabad,
Andhra Pradesh, India

T. R. Rupa

Sugarcane Breeding Institute, Coimbatore, Tamil Nadu, India

A. Subba Rao

Indian Institute of Soil Science, Bhopal, Madhya Pradesh, India

G. Ramesh

Central Research Institute for Dryland Agriculture, Hyderabad,
Andhra Pradesh, India

S. K. Bansal

Potash Research Institute of India, Gurgaon, Haryana, India

Abstract: Nonexchangeable potassium (K) release kinetics of six major benchmark soil series of India as affected by mineralogy of clay and silt fractions, soil depth and extraction media was investigated. The cumulative release of nonexchangeable K was greater in smectitic soils (353 mg K kg^{-1} at 0- to 15-cm depth and 296 mg K kg^{-1} at 15- to 30-cm depth, averaged for 2 soils and 3 extractants) than in illitic (151 mg K kg^{-1} at 0- to 15-cm depth and 112 mg K kg^{-1} at 15- to 30-cm depth) and kaolinitic (194 mg K kg^{-1} at 0- to 15-cm depth and 167 mg K kg^{-1} at 15- to 30-cm depth) soils. Surface soils exhibited larger cumulative K release in smectitic and illitic soils, whereas subsurface soils had larger K release in kaolinitic

Received 24 September 2004, Accepted 2 September 2005

Address correspondence to Ch. Srinivasarao, Central Research Institute for Dryland Agriculture, Santoshnagar, Hyderabad, 500 059 Andhra Pradesh, India.
E-mail: cheruku65@rediffmail.com

soils. Among the extractants, 0.01 *M* citric acid extracted a larger amount of nonexchangeable K followed by 0.01 *M* CaCl₂ and 0.01 *M* HCl. The efficiency of citric acid extractant was greater in illitic soils than in smectitic and kaolinitic soils. Release kinetics of nonexchangeable K conformed fairly well to parabolic and first-order kinetic models. The curve pattern of parabolic diffusion model suggested diffusion controlled kinetics in all the soils, with a characteristic initial fast rate up to 7 h followed by a slower rate. Greater nonexchangeable K release rates in smectitic soils, calculated from the first-order equation ($b = 91.13 \times 10^{-4} \text{ h}^{-1}$), suggested that the layer edge and wedge zones and swelling nature of clay facilitated the easier exchange. In contrast to smectitic soils, higher release rate constants obtained from parabolic diffusion equation ($b = 39.23 \times 10^{-3} \text{ h}^{-1}$) in illitic soils revealed that the low amount of exchangeable K on clay surface and larger amount of interlayer K allowed greater diffusion gradients, thus justifying the better fit of first-order kinetic equation in smectitic soils and parabolic diffusion equation in illitic soils.

Keywords: Nonexchangeable K release, extractants, mineralogy, first order, soil depth

INTRODUCTION

It has been well established that a significant proportion of plant needs of potassium (K) are met from nonexchangeable fraction of soil K (Mengel 1985; Srinivasarao et al. 1999, 2000). Under intensive cropping, in the absence of K fertilization, initially exchangeable K in soil contributes to plant K nutrition, but with further cropping, exchangeable K attains a certain minimal level; afterward, plant K removal from soil and contribution of nonexchangeable K to K uptake are almost synonymous and accounts for up to 90–95% of the total plant K uptake (Srinivasarao and Khera 1994). Because of the larger contribution of nonexchangeable K to plant K needs, lack of crop responses to applied K have been reported even in soils with low exchangeable K (Mengel and Uhlenbecker 1993). The major sources of nonexchangeable K in soils are K-rich 2:1 clay minerals such as micas and vermiculite (Sparks et al. 1987; Moritsuka et al. 2004). However, the release of K from the interlayer of these minerals may be very slow, depending on the weathering stage of these minerals; therefore, whether the K release rates of soils under cropping are in tune with plant K needs becomes the most important aspect as far as K nutrition of crop plants is concerned.

Nonexchangeable K in soil is extracted by using several extractants such as dilute salt solutions (Lopez-Pineiro and Garcia-Navarro 1997), cation exchange resins (Martin and Sparks 1983), organic acids (Song and Huang 1988), sodium tetraphenyl boran (Cox and Joern 1997), nitric acid (Gil-Sotres and Rubio 1992). Electroultrafiltration (EUF) is also used (Rubio and Gil-Sotres 1996). Several kinetic equations have been used to study the release of nonexchangeable K. These include first-order (Srinivasarao et al. 1998), parabolic diffusion (Sharma and Swami 2000), zero-order

(Srinivasarao et al. 1998) and *Elovich* equation (Martin and Sparks 1983). However, different models have been found to fare better in explaining K release from soil particles or whole soils under particular condition because of the differences in release mechanisms (Carey and Metherell 2003). The performance of a particular model may be varying in relation to soil K status (Elkhatib and Hern 1988), K-depleted/undepleted soils (Srinivasarao et al. 1998), extraction media (Sharma and Swami 2000), and stage of extraction (early/late) (Burns and Barber 1961). Better performance of parabolic diffusion equation for light textured Chomu and Pali series compared with heavy textured Chambal series of India was reported by Sharma and Swami (2000) in explaining K release in CaCl_2 solution. Better performance of first-order equation for smectitic black soils was also reported earlier by Dhillon et al. (1989) in CaCl_2 medium over illitic alluvial and kaolinitic red soils. Nonexchangeable K release confirmed to first-order kinetics better in K-rich clay soils in 0.01 M CaCl_2 medium compared with light textured soils (Sharma and Swami 2000).

Although a major portion of plant nutrients is absorbed by crop plants from the surface soil, subsoil contribution to nutrition is often substantial (Beringer 1985). A great majority of studies on K in soils have been solely concerned with samples collected from the surface soils (0–15 cm). Different forms of K in subsoil (15–30 cm) were evaluated in relation to those in surface soil (0–15 cm) in 22 benchmark soil series of India, which indicated that subsoil K contribution was up to 96% of the surface soils (Srinivasarao et al. 2001). The present study examines the nonexchangeable K release from different benchmark soils of India representing a wide area varying in their mineralogy and K status. Nonexchangeable K release from subsoils is important because many crops can obtain substantial amounts of K from lower layers especially in deep rooted crops. Therefore, the objectives of present study are 1) to evaluate the nonexchangeable K release from important benchmark soils varying in mineralogy, K status, and also in relation to soil depth and extraction media; 2) to evaluate different mathematical models for describing nonexchangeable K release and to find whether their performance varies with mineralogical composition of soils, soil K status, and extraction media; and 3) to examine the relationship of K release rates obtained in the kinetic studies with conventional soil test measures of K.

MATERIALS AND METHODS

Soil Analysis

Physicochemical and mineralogical properties of six benchmark surface (0–15 cm) and sub-surface (15–30 cm) soils that occur widely in intensively cultivated regions in six states of India sampled by Potash Research Institute

of India, Gurgaon, were used in the present study. Details on soil series, location, taxonomic classification, selected soil properties, and soil test K are given in Table 1. Soil pH was measured in a 1:2.5 (w/v) soil to water mixture by using a glass pH electrode (Elico pH analyzer model LI-612). Organic carbon (organic C) was determined by the wet oxidation method of Walkley and Black (1934), and calcium carbonate (CaCO_3) was estimated by using the method of Bundy and Bremner (1972). Cation exchange capacity (CEC) of the soils was determined by the sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2$) method (Richards 1954). Different extractable forms of K [e.g., water-soluble (Jackson 1973), 1 *N* NH_4OAc (Hanway and Heidel 1952), and sodium tetraphenyl boron (NaTPB) (Schulte and Corey, 1965)] were determined.

Mineralogical Analysis

The mineralogical composition of silt and clay fractions is given in Table 2. For mineralogical analysis, the soils were dispersed in 1% sodium hexametaphosphate with vigorous shaking (Sidhu and Gikes 1977). The sand fraction (0.05–2 mm) was separated by wet-sieving, and the silt fraction (0.002–0.05 mm) was separated by sedimentation. The clay (<0.002 mm) suspension was siphoned off after requisite settling time (Jackson 1973). The silt and clay samples were flocculated with excess KCl and MgCl_2 . The Mg-saturated silt and clay samples were X-rayed, glycolated, and X-rayed again with a Philips diffractometer. Potassium-saturated silt and clay samples were X-rayed after drying for 1 h and again after heating to 500°C for 1 h. Based on the peak area of different reflections, a semiquantitative analysis of different minerals in the silt and clay fractions was undertaken by following the procedure of Klages and Hopper (1982).

Kamliakheri and Noyyal soil series belong to Vertisol and Vertic subgroups, are alkaline in pH, calcareous in nature, fine textured, and are smectite dominant soils. Lukhi and Rarha series belong to Inceptisols with illite as dominant clay mineral. Kodad and Vijayapura series belong to Alfisols and are kaolinite dominant. Soils of Vijayapura series had a considerable amount of amorphous materials, which are mainly hydrous oxides of iron (Fe), aluminum (Al), manganese (Mn), and hydrated silico-aluminas. In each group, two series with wide variation in soil test nonexchangeable K were included in this study to understand the differences in K chemistry of soils with similar mineralogical composition.

Nonexchangeable Potassium Release Kinetics

Native exchangeable K was removed from surface and subsurface soils before initiating the kinetic studies (Martin and Sparks 1983). For this, soil samples were calcium (Ca) saturated by equilibrating 5 g soil with 0.25 *M* CaCl_2 three

Table 1. Soil properties, mineralogy, and K status

Soil series	Location	Classification	pH _w (1 : 2.5)	Org. C (g kg ⁻¹)	CaCO ₃ (g kg ⁻¹)	Clay (%)	CEC (Cmol (+) kg ⁻¹)	K concentration (mg kg ⁻¹)		
								WS	NH ₄ OAc	NaTPB
Kamliakheri	Indore (Madhya Pradesh) ^a	Vertic Ustochrept	7.8	4.8	65	40	39.8	9	151	630
Noyyal	Coimbatore (Tamil Nadu)	Ustothermic Chromustert	8.4	6.9	52	36.5	34	33	515	1440
Lukhi	Gurgaon (Haryana)	Udic Ustochrept	8.4	3.8	29	6.4	5.8	21	69	605
Rarha	Kanpur (Uttar Pradesh)	Udic Ustochrept	8.2	3.1	24	9.6	7.1	12	48	1865
Kodad	Nalgonda (Andhra Pradesh)	Typic Paleustalf	6.0	4.2	19	19	8.9	19	61	755
Vijayapura	Bangalore (Karnataka)	Oxic Haplustalf	5.7	4.0	11	14	6.3	12	19	340

^aName of the State in India; WS, water-soluble; Org. C, organic carbon.

Table 2. Percent minerals in clay and silt fraction of soils

Soil series	Illite	Vermiculite	Smectite	Chlorite	Kaolinite	Amorphous	Feldspar + Quartz
Clay fraction							
Kamliakheri	—	20	40	—	—	—	—
Noyyal	35	—	45	—	5	5	10
Lukhi	45	15	—	15	5	10	10
Rarha	60	5	—	20	5	—	10
Kodad	15	10	5	—	55	—	—
Vijayapura	15	5	—	—	40	25	10
Silt fraction							
Kamliakheri	—	—	—	—	—	—	100
Noyyal	20	—	—	—	—	—	70
Lukhi	40	5	—	—	—	—	55
Rarha	40	5	—	—	—	—	55
Kodad	4	3	—	—	—	—	93
Vijayapura	10	—	—	—	15	—	65

times and washing free of Cl^- with absolute alcohol, and then the samples were washed with deionized water until a negative test for Cl^- was obtained with AgNO_3 , and soils were oven dried at 60°C . One gram each of Ca-saturated soils, in duplicate, suspended in 20 mL of 0.01 M CaCl_2 , 0.01 M citric acid, and 0.01 M HCl media were equilibrated at 25°C for 1, 7, 19, 43, 67, 95, 115, 139, 163, 187, 211, 235, 259, 283, 307, 331, 355, 379, 403, and 427 h by shaking for 1 h before the suspensions were centrifuged for 10 min at $10,000 \times g$. The supernatant liquid was measured for K by flame photometer (Elico Model CL-360).

Nonexchangeable K released with time was fitted by using the different equations (Martin and Sparks 1983).

$$\text{First-order reaction: } \ln(K_0 - K_t) = a - bt$$

$$\text{Parabolic diffusion: } K_t/K_0 = a + bt^{1/2}$$

$$\text{Zero-order reaction: } (K_0 - K_t) = a - bt$$

$$\text{Elovich equation: } K_t = a + b \ln t$$

where K_t is the cumulative K released (mg/kg) at time t (hours), K_0 is the maximum cumulative K released (mg/kg), and a and b are constants. Four models were tested by the least-square regression analysis to determine which equation described better the nonexchangeable K release from the soils. Standard error of the estimate (SE) was calculated by $\text{SE} = [(q - q^*)^2 / (n - 2)]^{1/2}$, where q and q^* represent the measured and calculated amounts of nonexchangeable K in soil at time t , respectively, and n is the number of data points evaluated. The rate constants of K release from soils in different media of extraction were calculated on the basis of these models.

RESULTS AND DISCUSSION

Nonexchangeable Potassium Release

The pattern of successive extraction of nonexchangeable K from soils belonging to three mineralogically different soil series (i.e., smectitic Noyyal, illitic Rarha, and kaolinitic Vijayapura in different media of extraction) is presented in Figure 1. The amounts of K released during 427 h of extraction period was generally higher in smectite dominant soils followed by illite and kaolinite dominant soils (Table 3). However, there were deviations in the nonexchangeable K release in the citric acid medium where illitic Lukhi series (0–15 cm) and kaolinitic Kodad series (15–30 cm) showed larger K release than smectitic Kamliakheri series. The amount of K extracted was greater in the first 3–4 extractions, decreased in later extractions, and then remained nearly constant after 10–11 extractions (Carey and Metherell 2003; Pannu et al. 2003). Within each group, there was a wide variation in the cumulative K release between soils (Table 2). Kamliakheri

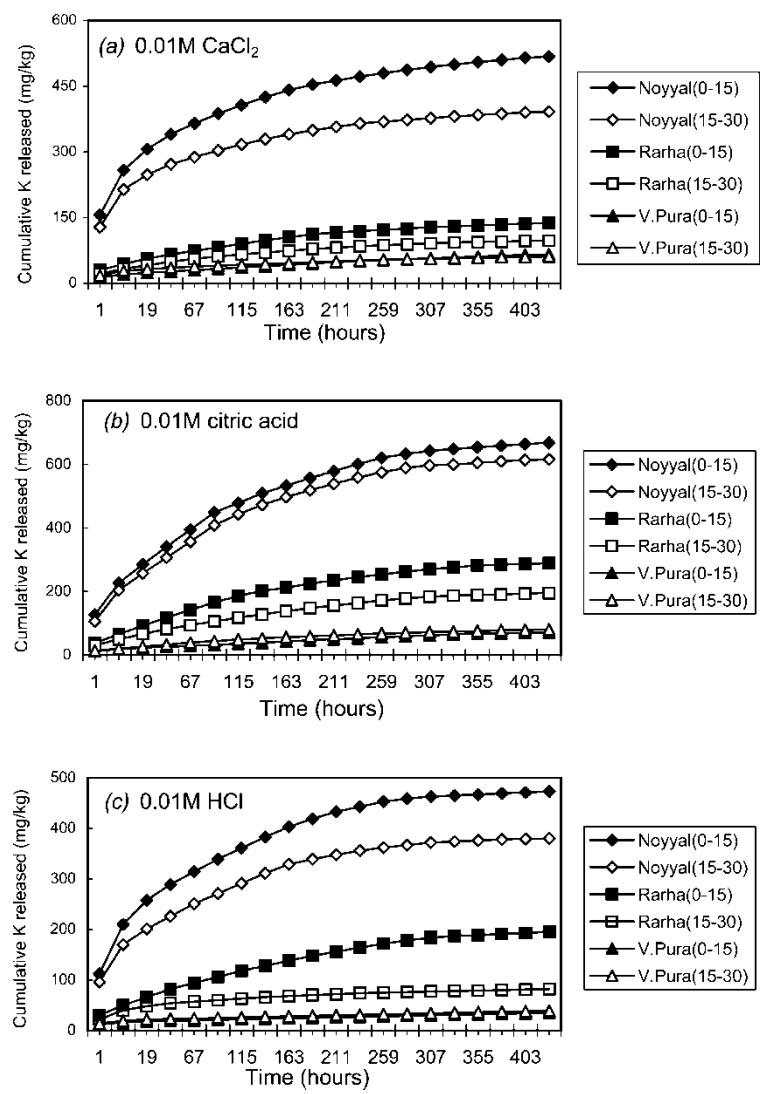


Figure 1. Cumulative amount of nonexchangeable K released by successive extractions with (a) 0.01 M CaCl₂, (b) 0.01 M citric acid, and (c) 0.01 M HCl media of extraction.

and Noyyal series were dominantly smectitic, but there was three- to four-fold higher release in Noyyal series than in Kamliakheri series. The difference between nonexchangeable K release between two series could be due to variation in clay mineral composition in silt and clay fractions of soil (Table 2). In Kamliakheri soil series, smectite and vermiculite were the

Table 3. Cumulative nonexchangeable K released in different media of extraction (mg kg^{-1})

Soil series	0.01 M CaCl_2		0.01 M citric acid		0.01 M HCl	
	0–15 cm	15–30 cm	0–15 cm	15–30 cm	0–15 cm	15–30 cm
Smectitic soils						
Kamliakheri	165	131	152	135	142	120
Noyyal	518	392	668	616	473	380
Mean	342	262	410	376	308	250
Illitic soils						
Lukhi	105	84	163	135	94	77
Rarha	138	97	289	195	118	82
Mean	122	91	226	165	106	80
Kaolinitic soils						
Kodad	101	102	126	165	72	117
Vijayapura	66	62	71	80	35	39
Mean	83	82	99	123	54	78
Mean of six series	182	144	245	221	156	136

dominant minerals in clay fraction and in silt fraction, feldspars + quartz was the dominant mineral. In Noyyal soil series, smectite and illite were the dominant mineral followed by feldspars + quartz, and kaolinite in clay fraction, and feldspars + quartz and illite in silt fraction. Presence of considerable amounts of K-rich minerals, such as illite in silt and clay fractions of soils with fine texture, could result in larger K release as in Noyyal series.

Lukhi and Rarha series belonging to Inceptisols showed considerable differences in nonexchangeable K release. Rarha series showed higher K release than Lukhi series, irrespective of soil depth and extraction medium. In both cases, illite was the dominant mineral followed by chlorite, vermiculite, feldspars + quartz, and kaolinite in clay fraction. Illite was dominant in silt fraction of both Rarha and Lukhi series. Similarly, in kaolinitic soils, considerable quantities of illite in silt and clay fractions of Kodad series resulted in larger K release than Vijayapura series. Thus, fine texture, together with illite/mica dominance in silt and clay fractions of soils, are major factors for larger nonexchangeable K release in soils. Several authors reported earlier that soils of fine texture showed larger K release than coarse textured soils (Martin and Sparks 1983). On the basis of relationships established between K replenishment rates of soils and amount and nature of clay minerals in illitic alluvial soils (Srinivasarao and Khera 1994) and smectitic Vertisols (Srinivasarao et al. 1998) it was stated that the release of K from nonexchangeable source depends mainly on the composition of clay minerals in soils. Although soils having high clay are generally associated with high reserves of soil K, it is not essentially true for all the soils.

Surface soils (0–15 cm) showed larger cumulative K release in smectitic and illitic soils than subsurface (15–30 cm) soils, irrespective of the medium of extraction. In kaolinitic soils, surface soils showed either the same or lower K release than subsurface soils. This result could be due to downward movement of finer particles with leaching during rainy seasons. Therefore, subsoil K plays an important role in Alfisols soils, which are generally low in K because of lower levels of K-bearing minerals. Evaluating the subsoil K availability of 22 benchmark soil series of India, Srinivasarao et al. (2001) reported that light textured red and lateritic and acidic alluvial soils had larger K availability in subsurface soils than surface soils.

Cumulative K release varied significantly among the media of extraction. In all the soils, larger amount of K was extracted in 0.01 *M* citric acid followed by 0.01 *M* CaCl₂ and 0.01 *M* HCl. The differences in K release among the extraction media could be attributed to differences in their nature of reaction in soil. Larger amount of K released in citric acid is due to the dissociated H⁺ ions and complexing organic ligands in the organic acid medium. The low molecular weight organic acids with OH and COOH groups in the ortho-position tend to form metal-organic complexes in solution with some metal ions from mineral structures (Kononova et al. 1964), thus accelerating the mineral decomposition. Although the HCl medium also possesses proton source, the mechanism is restricted only to exchange of H⁺ ions with K⁺

ions of minerals. Once exchange positions are filled with H^+ , further exchange from highly selective sites of minerals is difficult with dilute acid solutions. In 0.01 *M* $CaCl_2$, the K^+ ions on the surface of mineral structure are exchanged by Ca^{2+} in the $CaCl_2$ solution. Because of larger size of Ca^{2+} ions and hydration energy (Rich 1968), it does not exchange easily with K further in the interlayer.

The efficiency of citric acid medium was greater than $CaCl_2$ solution in illitic soils than in smectitic and kaolinitic soils. The increase in extracted K was 20 (68 mg/kg) to 43% (114 mg/kg) in smectitic soils, 85 (104 mg/kg) to 81% (74 mg/kg) in illitic soils, and 19 (16 mg/kg) to 50% (41 mg/kg) in kaolinitic soils, respectively.

Mathematical Models

Different mathematical models (e.g., first-order, parabolic diffusion equation, zero-order, and Elovich) were tested for their suitability to describe the release of nonexchangeable K from six mineralogically different benchmark soils (i.e., Kamliakheri, Noyyal, Lukhi, Rarha, Kodad, and Vijayapura (Table 4). Results showed that parabolic diffusion equation described the reaction rates fairly well, as evidenced by the highest coefficient of determination values for 0.01 *M* $CaCl_2$ ($r^2 = 0.92-0.99$; mean = 0.98), 0.01 *M* citric acid ($r^2 = 0.94-0.99$; mean = 0.98), and 0.01 *M* HCl ($r^2 = 0.73-0.98$; mean = 0.93), respectively. The lowest standard error values ranged from 0.02 to 0.05 (mean = 0.03) for $CaCl_2$, from 0.03 to 0.05 (mean = 0.03) for citric acid, and from 0.03 to 0.08 (mean = 0.05) for HCl media. This result shows that rate of K release from nonexchangeable fraction is a function of the reciprocal of \sqrt{t} and is diffusion controlled exchange reaction from the mineral matrix or weathered periphery. The fit of K_t/K_0 and the \sqrt{t} for the three benchmark surface and subsurface soils with varied mineralogy and K status is shown in Figure 2. Successful description of K release by parabolic diffusion equation of K was reported by Martin and Sparks (1983) for Kalmia and Kennansville soils of the United States and by Dhillon et al. (1989) and Srinivasarao et al. (2000) for some Indian soils. However, there were some differences in r^2 and SE values of parabolic diffusion equation among soil series and extraction media. Relatively higher r^2 and lower SE values were observed for illitic and kaolinitic soils than for smectitic soils. Among the media, citric acid and $CaCl_2$ showed higher r^2 and lower SE values. Followed by parabolic diffusion equation, first-order kinetic equation also explained well the nonexchangeable K release from soils as indicated by higher mean r^2 values of 0.94 in all three extractants and lower SE ranging from 0.26 to 0.29 (Table 4). The performance of first-order equation holds good irrespective of extraction medium, but it explained better for smectitic soils ($r^2 = 0.95-0.96$) than for kaolinitic soils ($r^2 = 0.91-0.92$). Almost linear relationships between $\ln(K_0 - K_t)$ vs. time in different extraction media are presented in Figure 3. Successful description

Table 4. Coefficients of determination (r^2) and standard error of the estimate (SE) K of various kinetic equations for nonexchangeable release from six benchmark soils

Mathematical model	Extraction media					
	0.01 M CaCl ₂		0.01 M Citric acid		0.01 M HCl	
	r^2	SE (mg kg ⁻¹)	r^2	SE (mg kg ⁻¹)	r^2	SE (mg kg ⁻¹)
First-order						
Mean	0.94	0.29	0.94	0.31	0.94	0.26
Range	0.88–0.97	0.21–0.37	0.87–0.98	0.19–0.42	0.89–0.98	0.21–0.32
Parabolic diffusion						
Mean	0.98	0.03	0.98	0.03	0.93	0.05
Range	0.92–0.99	0.02–0.05	0.94–0.99	0.01–0.05	0.73–0.98	0.03–0.08
Zero-order						
Mean	0.88	12.6	0.9	19.34	0.79	12.9
Range	0.77–0.98	3.6–44.9	0.80–0.98	2.4–63.7	0.53–0.97	1.15–46.7
Elovich						
Mean	0.91	7.77	0.9	16.5	0.95	5.43
Range	0.81–0.99	3.76–14.6	0.85–0.97	4.9–38.8	0.81–0.99	1.7–19.2

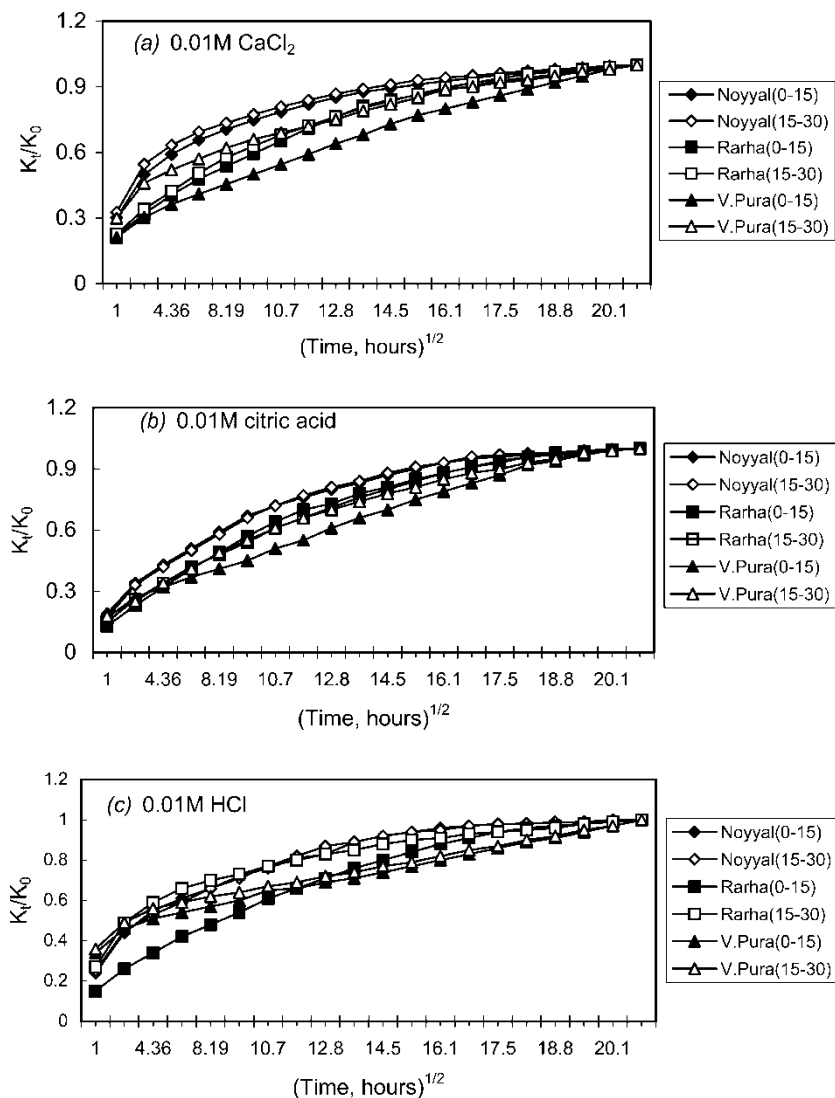


Figure 2. Parabolic diffusion kinetics of nonexchangeable K released by successive extractions with (a) 0.01 M CaCl_2 , (b) 0.01 M citric acid, and (c) 0.01 M HCl media of extraction.

of K release by first-order equation was earlier reported by several workers (Martin and Sparks 1983; Srinivasarao et al. 1999). Slightly lower SE values were observed for smectitic soils than for illitic soils. Zero-order and Elovich equations did not explain well the K release as indicated by lower r^2 and higher SE values.

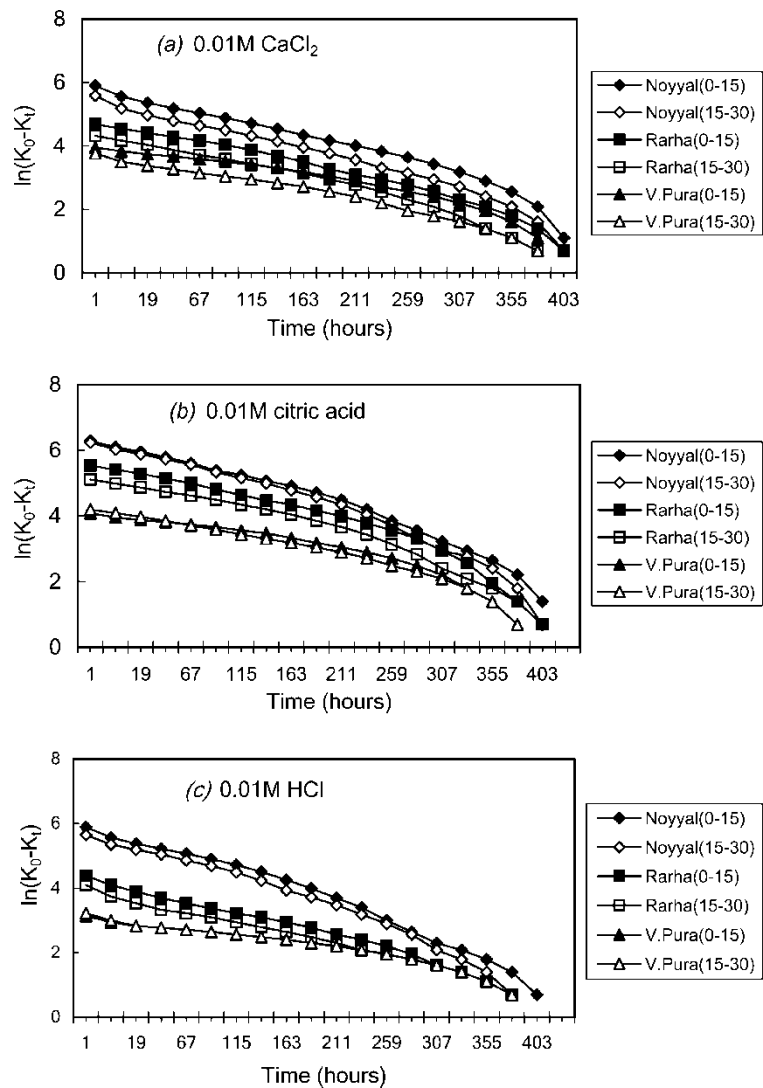


Figure 3. First-order release kinetics of nonexchangeable K released by successive extractions with (a) 0.01 M CaCl₂, (b) 0.01 M citric acid, and (c) 0.01 M HCl media of extraction.

Nonexchangeable Potassium Release Rate Constants

Release rate constants (b) and intercept (a) of nonexchangeable K for first-order and parabolic diffusion for different soils (Table 5) showed the variations in rate constants with respect to mineralogical composition, extraction

Table 5. Nonexchangeable K release rate constant (b) (h^{-1}) and intercept (a) for mineralogically different soils (average of 4 soils in each case)

Mathematical model/Soil group	Extraction medium					
	0.01 M CaCl_2		0.01 M Citric acid		0.01 M HCl	
<i>First-order equation</i>	$b \times 10^{-4}$	a	$b \times 10^{-4}$	a	$b \times 10^{-4}$	a
Smectitic	91.13	5.09	101.55	5.47	99.59	4.81
Illitic	87.49	4.52	91.38	5.20	81.02	3.91
Kaolinitic	74.75	4.13	81.26	4.61	63.81	3.53
Mean	84.45	4.58	91.40	5.09	81.47	4.08
<i>Parabolic diffusion</i>	$b \times 10^{-3}$	a	$b \times 10^{-3}$	a	$b \times 10^{-3}$	a
Smectitic	30.85	0.41	36.08	0.32	28.03	0.48
Illitic	39.23	0.23	41.25	0.19	28.84	0.46
Kaolinitic	34.40	0.25	40.78	0.17	27.30	0.42
Mean	34.83	0.30	39.37	0.23	28.05	0.45

media, and mathematical models tested. There were considerable differences in rate constants between surface and subsurface soils.

First-order release rate constants showed larger values for smectitic soils followed by illitic and kaolinitic soils. For all soils, 0.01 *M* citric acid medium showed greater release rate constants followed by 0.01 *M* CaCl₂ and 0.01 *M* HCl. The rate constants for smectitic soils varied from 99.99 to $101.55 \times 10^{-4}/\text{h}$, for illitic soils from 81.02 to $91.38 \times 10^{-4}/\text{h}$, and for kaolinitic soils from 63.81 to $81.26 \times 10^{-4}/\text{h}$. The mean rate constants for all the soils were $91.40 \times 10^{-4}/\text{h}$ in citric acid, $84.45 \times 10^{-4}/\text{h}$ in CaCl₂ and $81.47 \times 10^{-4}/\text{h}$ in HCl media. The rate constants observed in the present study were comparable with those reported by Munn et al. (1976) for K release from soil separates ($22.8\text{--}56.2 \times 10^{-4}/\text{h}$) and Srinivasarao et al. (1998) for some smectitic soils of central India ($126\text{--}153 \times 10^{-4}/\text{h}$) in 0.01 *M* CaCl₂. In all the soils 20–50% of K release occurred within 7 h of extraction period. Thereafter, the release was a slow and continuing process. The rapid initial release may be from the easily accessible sites on the external planar surfaces and peripheral edge sites, whereas the later slow release may be from the interlayer sites of the clay complex (Bolt et al. 1963). In all the soil groups, the finer the soil texture, the higher were the rate constants. Smectitic soils with higher clay content and larger edge and wedge sites showed greater release rate constants. Higher K release rates in citric acid medium compared with CaCl₂ and HCl indicates greater mobilization of K by citric acid, especially during the later stages of K release by complexing organic ligands (Song and Huang 1988). This trend was very much pronounced in illitic soil series (Table 3). This finding was in accordance with Sposito's hypothesis that the surface bearing charged siloxane ditrigonal cavities in soils reacts with dissolved organic matter and forms complexes through exchangeable cations (Sposito 1984). Lower K release rate constants in CaCl₂ could be due to larger size of hydrated Ca²⁺ (4.3 Å) than hydrated K⁺ (3.3 Å); therefore, wedge zones would selectively screen out the Ca²⁺ ion because of its larger size (Martin and Sparks 1983).

Greater K release rate constants in smectitic soils could be due to fine texture and larger wedge zones, and its swelling clay where the exchange is relatively easier, whereas K⁺ in illitic soils is held tightly and exchange is slower. This may be the reason for better performance of first-order equation for smectitic soils irrespective of medium. Kaolinitic soils with light texture and lower amounts of K mica/illitic and vermiculite showed lower K release rates. Although illite-dominant alluvial soils possess large amount of nonexchangeable K reserves (NaTPB-K) as shown in Table 1, its release is slower. Furthermore, the correlation coefficient values between soil test non-exchangeable K extracted in NaTPB and cumulative K release in different extraction media were lower ($r^2 = 0.58\text{--}0.72$). Once the illitic soils were excluded, including smectitic and kaolinitic soils, r^2 values improved substantially ($r^2 = 0.94\text{--}0.95$). Because of this reason, illite-rich alluvial soils, even

though with high nonexchangeable K status, may suffer from K deficiency under intensive cropping because the rate of K release from nonexchangeable to exchangeable/solution phase is not sufficient to meet the plant K uptake.

Rate constants of parabolic diffusion equation in different media ranged from 28.03 to $36.08 \times 10^{-3}/\text{h}$ for smectitic soils, 28.84 to $41.25 \times 10^{-3}/\text{h}$ for illitic soils, and 27.30 to $40.78 \times 10^{-3}/\text{h}$ for kaolinitic soils. Unlike those of first-order equation, smectitic soils showed lower release rate constants than illitic and kaolinitic soils in all the three media of extraction. Release rate constants of parabolic diffusion equation depend on diffusion gradient between interlayer (source) and exchange surfaces (sink) in the clay structure because it assumes that the rate-limiting step is the diffusion of K ions from the interior of the particle to surface. Lower exchangeable K on clay surface and larger interlayer K in illite clay structure resulted in larger diffusion gradients in illitic soils, hence the higher release rate constants than smectitic and kaolinitic soils. This finding may be the most probable reason for better performance of parabolic diffusion equation in illitic soils. The lowest magnitude of parabolic rate constants in case of smectitic black soils could be attributed to higher clay content.

Similarly intercept (a) values of the first-order and parabolic models were higher for smectitic soils followed by illitic and kaolinitic soils (Table 5). The positive and highly significant correlation ($r^2 = 0.94$) between nonexchangeable K extracted in NaTPB and intercept values of the first-order equation as the extrapolated intercept is assumed to be proportional to the initial concentration in soil solution at time = 0. Therefore, the higher the intercept values, the greater was the initial soil test K (Elkhatib and Hern 1988).

CONCLUSIONS

For assessing K fertilizer needs, the information on nonexchangeable K release from smectitic, illitic soils, and kaolinitic soils should be taken into consideration. The study further indicated that the 0.01 M citric acid extracted more K than did 0.01 M CaCl_2 and 0.01 M HCl in these soils. Furthermore, citric acid medium was found to be superior in extracting nonexchangeable K from illitic soils compared with smectitic and kaolinitic soils. The better fit of the first-order model to the data for smectitic soils than for illitic soils and also the relatively better fit of the parabolic model to the data for illitic soils than for smectitic soils would suggest that the rate-limiting step is either film diffusion or exchange reaction for smectites (due to their swelling nature) and intraparticle diffusion for illites (the interlayer space being more closed). Thus, the information generated from the different kinetic models can help to explain the release mechanisms in mineralogically dissimilar soils.

REFERENCES

- Beringer, H. (1985) Adequacy of soil testing for predicting fertilizer requirements. *Plant and Soil*, 83: 21–37.
- Bolt, G.H., Sumner, M.E., and Kamphorst, A. (1963) A study of the equilibria between three categories of potassium in an illitic soil. *Soil Sci. Soc. Am. Proc.*, 27: 294–299.
- Bundy, L.G. and Bremner, J.M. (1972) A single titrimetric method for determination of inorganic carbon in soils. *Soil Sci. Soc. Am. Proc.*, 36: 273–275.
- Burns, A.F. and Barber, S.A. (1961) Effect of temperature and moisture on exchangeable potassium. *Soil Sci. Soc. Am. Proc.*, 25: 349–352.
- Carey, P.L. and Metherell, A.K. (2003) Rates of release of nonexchangeable potassium in New Zealand soils measured by a modified sodium tetraphenyl boron method. *N Z J. Agric. Res.*, 46: 185–197.
- Cox, A.E. and Joern, B.C. (1997) Release kinetics of nonexchangeable potassium in soil using sodium tetraphenylboron. *Soil Sci.*, 162: 588–598.
- Dhillon, S.K., Sidhu, P.S., and Bansal, R.C. (1989) Release of potassium from some benchmark soils of India. *J. Soil Sci.*, 40: 783–797.
- Elkhatib, E.A. and Hern, J.H. (1988) Kinetics of potassium desorption from Appalachian soils. *Soil Sci.*, 145: 11–19.
- Gil-Sotres, F. and Rubio, B. (1992) Kinetics and structural effects of the extraction of nonexchangeable potassium from the clay fractions of soils of Galicia (N. W. Spain). *Commun. Soil Sci. Plant Anal.*, 23: 143–156.
- Hanway, J.J. and Heidel, H. (1952) Soil analysis methods as used in Iowa State college soil testing laboratory. *Iowa Agric.*, 27: 1–13.
- Jackson, M.L. (1973) *Soil Chemical Analysis*; Prentice Hall of India Private Limited.: New Delhi, India.
- Klages, M.G. and Hopper, R.W. (1982) Clay minerals in northern plain coal overburden as measured by X-ray diffraction. *Soil Sci. Soc. Am. J.*, 46: 415–419.
- Kononova, M.M., Aleksandrova, I.V., and Titova, N.A. (1964) Decomposition of silicates by organic substances in the soil. *Soviet Soil Sci.*, 9: 1005–1014 (English Translation).
- Lopez-Pineiro, A. and Garcia-Navarro, A. (1997) Potassium release kinetics and availability in unfertilized Vertisols of Southwestern Spain. *Soil Sci.*, 162: 912–918.
- Martin, H.W. and Sparks, D.L. (1983) Kinetics of nonexchangeable potassium release from two coastal plain soils. *Soil Sci. Soc. Am. J.*, 47: 883–887.
- Mengel, K. (1985) Dynamics and availability of major nutrients in soils. *Adv. Soil Sci.*, 2: 65–115.
- Mengel, K. and Uhlenbecker, K. (1993) Determination of available interlayer potassium and its uptake by ryegrass. *Soil Sci. Soc. Am. J.*, 57: 761–766.
- Moritsuka, N., Yanai, J., and Kosaki, T. (2004) Possible processes releasing nonexchangeable potassium from the rhizosphere of maize. *Plant Soil*, 258: 261–268.
- Munn, D.A., Wilding, L.P., and McLean, E.O. (1976) Potassium release from sand, silt and clay soil separates. *Soil Sci. Soc. Am. J.*, 40: 364–366.
- Pannu, R.P.S., Singh, Y., and Singh, B. (2003) Effect of long-term application of organic materials and inorganic N fertilizers on potassium fixation and release characteristics of soil under rice-wheat cropping system. *J. Potassium Res.*, 19: 1–10.
- Rich, C.I. (1968) Mineralogy of soil potassium. In *The Role of Potassium in Agriculture*; Kilmer, V.J., Younts, S.E. and Brady, N.C., eds.; American Society of Agronomy.: Madison, Wisconsin, 79–96.

- Richards, L.A. (1954) *Diagnosis and Improvement of Saline and Alkali Soils*; USDA Agricultural Handbook No. 60. U.S. Government Printing Office: Washington, D.C..
- Rubio, B. and Gil-Sotres, F. (1996) Determination of K forms in K fertilized soils by electroultrafiltration. *Plant Soil*, 180: 303–310.
- Schulte, E.E. and Corey, R.B. (1965) Extraction of potassium from soil with sodium tetraphenylboron. *Soil Sci. Soc. Am. Proc.*, 29: 33–35.
- Sharma, R.R. and Swami, B.N. (2000) Studies on kinetics of potassium release in surface horizons of three soil series of Rajasthan. *J. Indian Soc. Soil Sci.*, 48: 472–477.
- Sidhu, P.S. and Gikes, R.J. (1977) Mineralogy of soils developed in alluvium in the Indo-Gangetic plain (India). *Soil Sci. Soc. Am. J.*, 41: 1194–1201.
- Song, S.K. and Huang, P.M. (1988) Dynamics of potassium release from potassium bearing minerals as influenced by oxalic and citric acids. *Soil Sci. Soc. Am. J.*, 52: 383–390.
- Sparks, D.L. (1987) Potassium dynamics in soils. *Adv. Soil Sci.*, 6: 1–63.
- Sposito, G. (1984) *The Surface Chemistry of Soils*; Oxford University Press.: New York.
- Srinivasarao, Ch. and Khera, M.S. (1994) Potassium replenishment capacity of illitic soils at their minimal exchangeable K in relation to clay mineralogy. *J. Plant Nutri. Soil Sci.*, 157: 467–470.
- Srinivasarao, Ch., Pal, D.K., and Takkar, P.N. (1998) Mathematical models to study the kinetics of potassium release from swell-shrink soils of central India in relation to their mineralogy. *J. Plant Nutri. Soil Sci.*, 161: 67–71.
- Srinivasarao, Ch., Swarup, A., Subba Rao, A., and Rajagopal (1999) V. Kinetics of nonexchangeable potassium release from a Tropaeupis as influenced by long-term cropping, fertilisation and manuring. *Aust. J. Soil Res.*, 37: 317–328.
- Srinivasarao, Ch., Subba Rao, A., and Rupa, T.R. (2000) Plant mobilization of soil reserve potassium from fifteen smectitic soils in relation to soil test potassium and mineralogy. *Soil Sci.*, 165: 578–586.
- Srinivasarao, Ch., Rupa, T.R., Subba Rao, A., and Bansal, S.K. (2001) Subsoil potassium availability in twenty-two benchmark soil series of India. *Commun. Soil Sci. and Plant Anal.*, 32: 863–876.
- Walkley, A. and Black, I.A. (1934) An examination of the Degitjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method. *Soil Sci.*, 37: 29–38.