



International Journal of **Soil Science**

ISSN 1816-4978



Academic
Journals Inc.

www.academicjournals.com

Effect of Different Factors on Diffusion Characteristics of Potassium in Alluvial Soils of Eastern Indo Gangetic Plain

Sourov Chatterjee and Debjani Ghosh

Department of Agricultural Chemistry and Soil Science, Bidhan Chandra Krishi Viswavidyalaya, Mohanpur, 741252, Nadia, West Bengal, India

Corresponding Author: Sourov Chatterjee, Department of Agricultural Chemistry and Soil Science, Bidhan Chandra Krishi Viswavidyalaya, Mohanpur, 741252, Nadia, West Bengal, India

ABSTRACT

To understand the transport behaviour of potassium as influenced by different factors, the tracer diffusion (D_a) and porous diffusion (D_p) coefficients of potassium were studied in three alluvial soils of varying potassium content and mineralogical composition. Diffusion coefficients were increased with increase in moisture content (θ), temperature (T), bulk density (d) and tracer:background ratio (R). The D_a and D_p values were significantly higher when NaCl was taken as background electrolyte than for CaCl_2 . Soil with higher exchangeable K and illite content recorded higher D_a and D_p values. The energy of activation (E_a) decreased significantly with increase in bulk density and the Arrhenius frequency factor (A) and entropy factor of diffusion (σ) were found to significantly decrease with increasing tracer component. Exchangeable K, nonexchangeable K and illitic fraction of the clay minerals was found most relevant factor predicting the diffusion coefficients of potassium in the alluvial soils.

Key words: Potassium, tracer diffusion, porous diffusion, clay mineralogy, alluvial soil, exchangeable K

INTRODUCTION

Management of potassium has become very important in sustaining or increasing crop yield. Proper potassium management requires thorough understanding of soil potassium behaviour and the various potassium inputs and outputs of cropping systems. It is well known that the availability of potassium to plants depends not only on the size of the available pool in soil but also on the transport of potassium from soil solution to the root zone and from the root zone into plant roots.

The rate of solute movement in soil has a direct relationship with the soil fertility status and diffusion coefficients of the nutrient ion provide the information for that solute movement (Olsen and Kemper, 1968). Diffusion accounts for more than 90% of potassium moving to the plant roots, depending on the initial potassium concentration in the soil solution (Nye, 1972) and can contribute from 72-96% of the total potassium uptake (Oliveira *et al.*, 2004). Such diffusion coefficient of potassium may be successfully utilized to predict the plant uptake of the same from soil. The tracer-diffusion may be defined as diffusion of a single component present in very small concentration, in a large excess of the other components; in others words, the tracer-component is subjected to a concentration gradient of its own (Sanyal, 1980).

This tracer diffusion coefficient is influenced by different factors like, tracer:background ratio (R), background electrolyte (E), volumetric soil-water content (θ), bulk density (d) and

temperature (T) (Mani and Sanyal, 1995; Dhar and Sanyal, 2002). The soil potassium mobility increases with soil moisture content and had a positive correlation with effective diffusion coefficient (D_e) (Zeng and Brown, 2000) which suggest that more K^+ can diffuse to plant roots at sufficient soil moisture. The diffusion coefficient is also related with the exchangeable form of potassium and soils with higher exchangeable potassium content having higher diffusion coefficients (Wani and Datta, 2007; Benipal *et al.*, 2006). Deb *et al.* (1983) obtained the highest diffusion coefficient of Zn at a particular bulk density, irrespective of the variations in soil characteristics. The temperature effect may be attributed to a higher probability of the diffusing entities, being more readily able to overcome the activation energy hill at a higher temperature due to concomitant larger kinetic energy content of the diffusing ions (Mani and Sanyal, 1995). However, there is lack of detail information on diffusion characteristics of potassium and its relation with different forms in a particular soil type viz., alluvial soils. Thus, the objective of this investigation was to study the effect of different factors like bulk density, temperature, moisture content background electrolyte, tracer:background ratio on apparent and porous tracer-diffusion coefficient of potassium in alluvial soils widely varying in characteristics with respect to potassium status and mineralogical composition. The relationship between the apparent self-diffusion coefficient of potassium and the corresponding energy of activation (E_a), Arrhenius frequency factor (A) and the entropy factor of diffusion (σ) was also studied to understand the mechanism of diffusion in terms of thermodynamic suitability. In addition to study the semi-quantitative assessment of the clay mineralogical make-up of the given soils to ascertain the latter's ability to release potassium towards supporting the diffusion process under study. Finally to develop a prediction relationship of diffusion of potassium with different forms and different compositions of clay minerals to probe the transport behaviour of potassium in a particular domain which may help for efficient management of added fertilizer for plant uptake.

MATERIALS AND METHODS

Soil samples (0-0.15 m) were collected from three sites namely Nonaghata Uttarpara (S_1), Telegacha (S_2) and Moratripur (S_3), where rice-wheat cropping system was followed from last 15 years located in the hot, humid subtropics at Nadia District of West Bengal, India (22° N and 88° E) which is located at Eastern Indo Gangetic Plain considering the wide variability in their potassium supplying capacity. Some important physicochemical characteristics of the soils were determined following the standard procedure and given in Table 1. Exchangeable K was determined by neutral 1M NH_4OAc extractant and nonexchangeable K was determined using boiling 1 M HNO_3 for a period of 10 min as stated by Pratt (1965). The clay fractions of the soils were fractionated by the method described by Jackson (1973) and for the interpretation of the minerals present, the clay samples were Ca-saturated, Ca-glycolated, K-saturated and heated to 300 and 550°C. For the semi-quantitative estimation of the clay minerals, the methodology proposed by Gjems (1967) was adopted.

Diffusion studies were conducted following the Browns' half-cell technique (Brown *et al.*, 1964). The soil samples were air dried, finely powdered and passed through a 2 mm sieve. Calcium and sodium were used as the background cation for diffusion of K in soils, all having limiting ionic conductance of the same order of magnitude. A bulk amount of soil (600 g) was equilibrated with calcium chloride and sodium chloride solutions separately leading to a cationic concentration in the homoionic soils of 3200 mg kg^{-1} with respect to each cation. The soil was mixed thoroughly with the appropriate aqueous salt solution in order to ensure a uniform distribution of Ca^{++} and Na^+ ions.

Table 1: Some important properties of soil in West Bengal

Soil parameters	Nonaghata (S ₁)	Telegacha (S ₂)	Moratipur (S ₃)
Soil taxonomy (Typic Haplusteps)			
Sand (%)	20.80	17.70	17.40
Silt (%)	52.70	51.60	47.30
Clay (%)	26.50	30.70	35.30
Texture (Silty clay loam)			
pH (1:2.5 w/v)	7.17	6.90	6.84
EC (1:2.5) (dS m ⁻¹)	0.15	0.10	0.17
Organic C (g kg ⁻¹)	0.50	0.57	0.63
CEC [cmol (p ⁺) kg ⁻¹]	14.30	15.70	16.50
Maximum water holding capacity (%)	43.30	48.60	54.80
Available N (kg ha ⁻¹)	280.00	320.00	376.00
Available P ₂ O ₅ (kg ha ⁻¹)	57.30	43.80	71.40
Available K ₂ O (kg ha ⁻¹)	127.00	182.00	227.00
Exchangeable bases [cmol (p⁺) kg⁻¹]			
Ca+Mg	7.43	8.30	9.71
Na	0.14	0.13	0.15
K	0.40	0.48	0.53
Forms of soil potassium [cmol (p⁺) kg⁻¹]			
Water soluble K	0.05	0.07	0.08
Exchangeable K	0.09	0.13	0.17
Non-exchangeable K	5.20	5.82	6.07
Semi-quantitative composition of clay fraction (%)			
Kaolinite	5.21	3.30	2.44
Smectite	11.10	19.50	20.20
Mica/Illite	29.10	40.50	43.40
Chlorite	17.60	9.50	3.05
Vermiculite	13.20	7.70	5.70
Mixed minerals	23.80	19.50	25.30

This was followed by six cycles of alternate wetting and drying after which the water extractable Ca⁺⁺ and Na⁺ ion concentrations in the treated soils were found to attain constant values. The potassium chloride was added to one half of the calcium and sodium-equilibrated soils to have two different K levels of 100 and 200 mg kg⁻¹. Three additional cycles of wetting and drying processes were continued in each treated soil sample for ensuring a uniform distribution of the tracer. For measurement of diffusion coefficient of K, experiments were run marinating two different bulk densities of 0.99 and 1.08 Mg m⁻³ for the selected soils. The corresponding amounts of the oven dry soil to be packed in each half-cell (M) was obtained by using the equation:

$$M = V \cdot \rho$$

where, V is the inner volume (m³) of each half-cell and ρ is the required bulk density (Mg m⁻³). The inner volume V is given by:

$$V = \pi r^2 h$$

where, r is the inner radius of the half-cell and h is the length of each half-cell. The desired moisture level was maintained by adding water to the surface of the soil. One half of the diffusion cell was packed with only background electrolyte treated soil, while the other half with (background+tracer)-equilibrated soil at the desired bulk density and moisture content. The two half-cells were slowly brought together and were held in position by tightening the screws (at four corners) across the supporting pair of bakelite sheets. The cells were covered with polythene sheets and kept inside an incubator at the desired temperature for the requisite period of diffusion (Sanyal and Bhattacharya, 1986). A cellotape seal was used along the periphery where the two half-cells joined each other in order to ensure (water) leak-proof condition in course of diffusion. Potassium diffusion experiments were run maintaining two different temperatures, 25 and 35°C for all three soils, in an incubator which allowed temperature fluctuations within $\pm 1^\circ\text{C}$. On expiry of the diffusion period (six days in the present case), the two half-cells were carefully detached from each other and the soil from each half-cell was thoroughly mixed, from which 5 g soil was extracted with 50 mL of distilled water and the suspension was filtered. The K contents of the filtrates corresponding to soil extracts were determined flame photometrically.

The capacity factor (b) was determined by the method described by O'Connor *et al.* (1971, 1975). One, 2, 3, 4 and 5 g soil containing no extraneous K was taken. The 25 mL of 100 ppm KCl solution was added and was kept for two days to ensure equilibrium and maximum K adsorption by the soil. After shaking for 1 h, the suspensions were centrifuged and total K present in the supernatant was determined flame photometrically. The difference between the initial and the final K contents of the soil solution indicated the amount of K adsorbed by the soil. For each treatment, K adsorbed, expressed as percent of K adsorbed per cm^3 of soil, was plotted against percent of added K left per cm^3 of the filtrate. The slope of the curve gave the b factor.

To study the effect of different factors such as soil moisture content (θ), temperature (T), bulk-density (d), tracer:background cation concentration ratio (R) and background electrolyte (E) on diffusion, a set of $2 \times 2 \times 2 \times 2 \times 2$ factorial experiments were conducted. The experimental set consisted of a combination of 32 treatments.

The apparent tracer-diffusion coefficient (D_a) of K was obtained by using the relationship (Porter *et al.*, 1960):

$$D_a = \frac{\pi h^2 f^2}{t} \quad (1)$$

where, f is the fraction of the tagged ion (K^+) which diffuses in time t from the tagged to the untagged half-cell and ' h ' is the length of each half-cell, f is given by:

$$f = \frac{\text{Amount of K in the untagged portion in time } t}{\text{Sum of amount of K in the both tagged and untagged portion in time } t} \quad (2)$$

The D_p is related to D_a as:

$$D_p = D_a(b+\theta)$$

where, b is the capacity factor and θ is the volumetric moisture content. As θ is generally small in comparison with b ($0 < \theta < 1$) for the agricultural soils, the approximation was made that:

$$D_p = D_a \times b \quad (3)$$

By the method described by De Lopez-Gonzalez and Jenny (1959) and Brown *et al.* (1968), E_a (energy of activation) was calculated using the following Eq. 4:

$$D_a = A \exp\left(-\frac{E_a}{RT}\right) \quad (4)$$

where, D_a is the apparent tracer-diffusion coefficient, A is the Arrhenius frequency, R is the universal gas constant and T is the absolute temperature of the study, thus:

$$\log D_a = \log A - \left(\frac{E_a}{2.203} \times \frac{1}{T}\right) \quad (5)$$

By plotting $\log D_a$ against $1/T$, one obtains E_a and A from the slope and the intercept, respectively of the resulting linear plot.

Entropy factor of diffusion (σ) (De Lopez-Gonzalez and Jenny, 1959) was calculated from the Eyring's theory of absolute reaction rate (Atkins, 1982) by using the D_a values in the following Eq. 6:

$$D_a = \sigma d^2 \cdot \left(\frac{kt}{h}\right) \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{E_a}{RT}\right) \quad (6)$$

where, e is the base of natural logarithm, k is the Boltzman constant, T is the absolute temperature, h is the Planck's constant, d is the average distance between adjacent equilibrium positions during diffusion, ΔS^* is the entropy of activation, E_a is the energy of activation and R is the universal gas constant. The parameter $[d \exp(\Delta S^*/R)]^{1/2}$ is designated as the entropy factor of diffusion and has the dimension of length.

Statistical analysis: Effect of soil moisture content (θ), bulk density (d), temperature (T), tracer:background ratio (R) and background electrolytes (E) on apparent diffusion coefficient (D_a) and porous diffusion coefficient (D_p) of K were tested by a $2 \times 2 \times 2 \times 2 \times 2$ factorial ANOVA. F-test and mean comparison by Tukey test (5%) was performed using Proc GLM (SAS, 2013). Multiple regression analysis was determined by SPSS (Chicago, IL.; version 16.0).

RESULTS

The important soil physicochemical properties, different forms of soil potassium and semi-quantitative composition of clay fraction of the experimental soil samples have been presented in Table 1. All three soils belong to silty clay loam, although, the clay content varied from 26.5-35.3%. The distribution of different forms of K in the three soils (Table 1) revealed that the exchangeable K, nonexchangeable K content was highest in Moratripur soil followed by

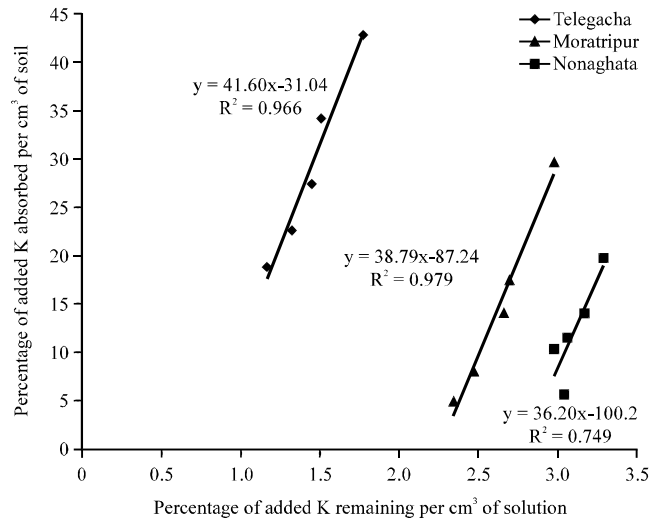


Fig. 1: Relationship between absorbed K and concentration of K in equilibrium solution of soils

Telegacha and Nonaghata soil. The distribution of different minerals in the clay fraction of the soils was presented in the Table 1 and X-ray diffractograms of the clay fraction of the soils was presented in Fig. 2. The result showed that all the soils were dominant in illite followed by smectite. Sekhon *et al.* (1992) also found that illite was the dominant clay mineral in the alluvial soils of West Bengal. The apparent tracer-diffusion coefficient of K (D_a) in Ca and Na-saturated background (E_1 and E_2) soils have been expressed as logarithmic functions of the inverse absolute temperatures of study (297 and 308°K) in Fig. 3 and 4, corresponding to two different bulk densities maintained. The corresponding porous diffusion coefficient (D_p) values were obtained by multiplying D_a values with the capacity factor of the soil (b), which was obtained from the slope of the plots (Fig. 1). The effect of different factors like soil moisture content (θ), bulk density (d), temperature (T), tracer:background ratio (R) and background electrolytes (E) on apparent diffusion coefficient (D_a) and porous diffusion coefficient (D_p) of K in the studied soils was presented in Table 2. The results reveals that with decrease in water content from 100% of water holding capacity to 85% water holding capacity, there was significant ($p < 0.05$) fall in D_a and D_p values (Table 2 and Fig. 3). Upon increasing the bulk density from 0.99-1.08 Mg m⁻³, the diffusion coefficient values significantly ($p < 0.05$) increased (Table 2 and Fig. 4). It has been observed that with increase of tracer: background ratio from 1:32 to 1:16, the D_a and D_p values (Table 2) significantly ($p < 0.05$) increased in all the soils. For all the soils, the D_p values (and also the D_a values) were significantly ($p < 0.05$) higher (Table 2) when NaCl was taken as background electrolyte than for CaCl₂. This increase may possibly be related to the difficulty of K⁺ to replace Ca⁺⁺ compared to Na⁺ in the exchange sites. The probability levels of 2×2×2×2 factorial ANOVA of different factors and their interaction effect on D_a and D_p of K in the studied soils were presented in Table 3. All the factors have significant effect ($p < 0.001$) on D_a and D_p of K in the studied soils. The interaction effects of different factors were significant ($p < 0.05$) for most of the cases except for the $d \times T \times E$ and $\theta \times d \times T \times E$.

The energy of activation (E_a) and Arrhenius frequency factor (A) under different treatments in all the three soils were computed from the slope and the intercept of the plots $\log D_a$ against T^{-1}

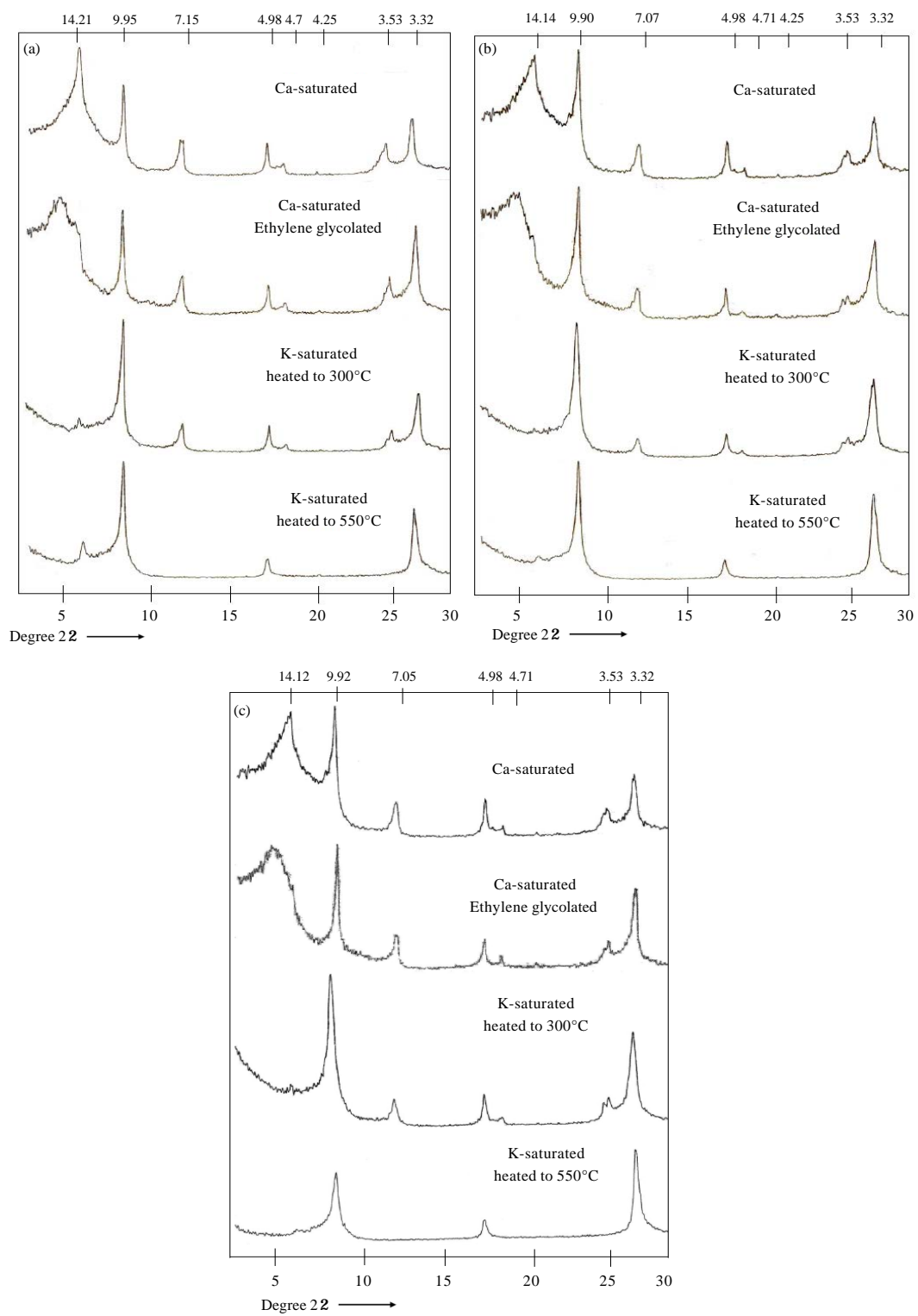


Fig. 2(a-c): X-ray diffractograms of the clay-fraction of the three soil, (a) Nonaghata (S₁), (b) Telegacha (S₂) and (c) Moratripur (S₃)

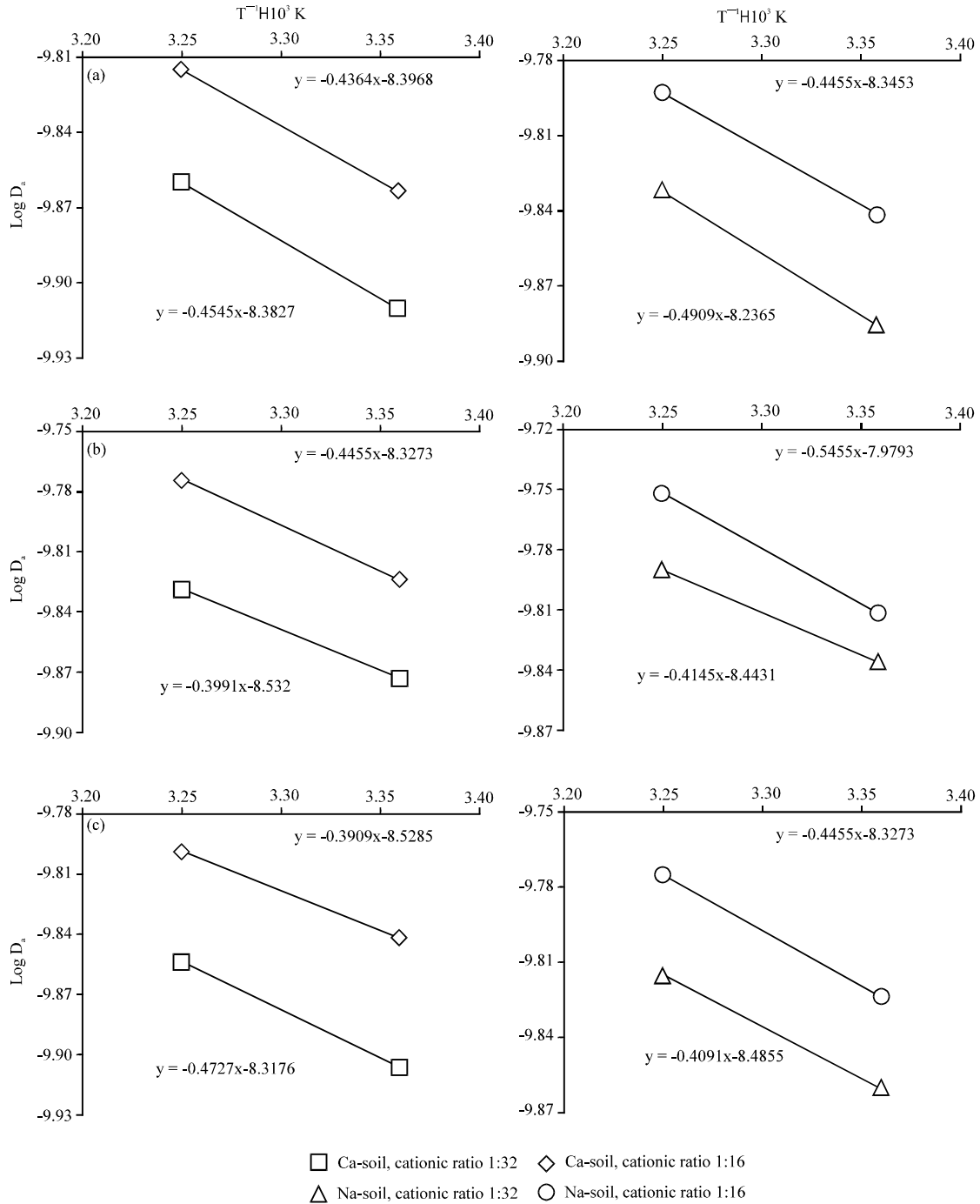


Fig. 3(a-c): Relationship between logarithm of apparent tracer-diffusion coefficient (D_a) of potassium and reciprocal of absolute temperature (T^{-1}) at 100% water holding capacity moisture content and at a bulk density of 0.99 Mg m^{-3} , (a) Nonaghata Uttarpara (S_1), (b) Telegacha (S_2) and (c) Moratripur (S_3)

and presented in Table 4. The entropy factor of diffusion (θ) for the given treatments was computed from D_a and E_a values by using the Eq. 6. The energy of activation (E_a) decreased

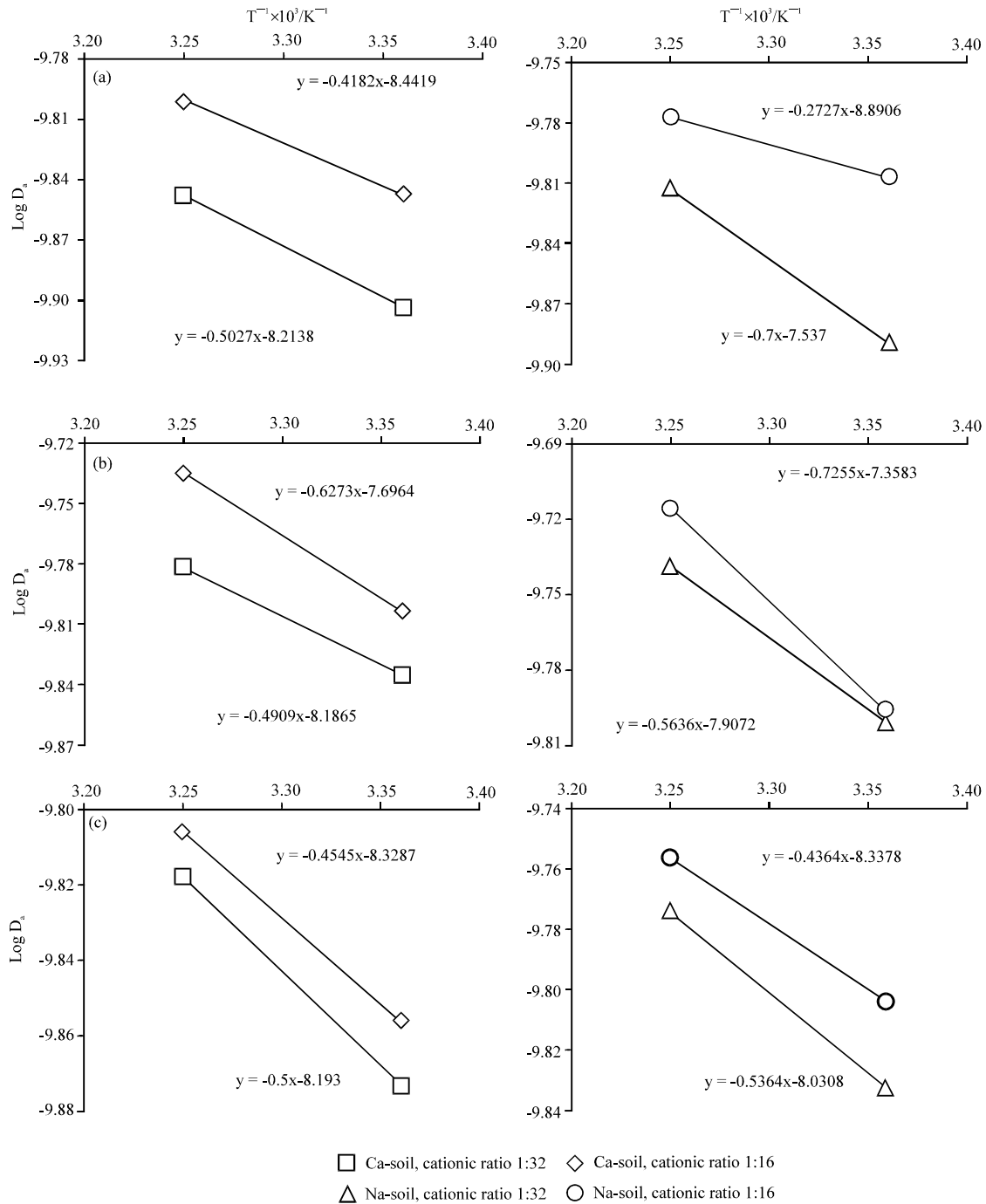


Fig. 4(a-c): Relationship between logarithm of apparent tracer-diffusion coefficient (D_a) of potassium and reciprocal of absolute temperature (T^{-1}) at 100% water holding capacity, moisture content and at a bulk of 1.08 Mg m^{-3} , (a) Nonaghta Uttarpara (S_1), (b) Telegacha (S_2) and (c) Moratripur (S_3)

significantly ($p < 0.05$) with increase in bulk density (Table 4). The Arrhenius frequency factor (A) and entropy factor of diffusion (θ) were found to significantly decrease in the given soils with

Table 2: Effect of soil moisture content (θ), bulk density (d), temperature (T), tracer:background ratio (R) and background electrolytes (E) on apparent diffusion coefficient (D_a) and porous diffusion coefficient (D_p) of K in Nonaghata Uttarpara (S_1), Telegacha (S_2) and Moratripur soil (S_3)

Factors	S_1		S_2		S_3	
	$D_a \times 10^{10}/$ [m ² sec ⁻¹]	$D_p \times 10^{10}/$ [m ² sec ⁻¹]	$D_a \times 10^{10}/$ [m ² sec ⁻¹]	$D_p \times 10^{10}/$ [m ² sec ⁻¹]	$D_a \times 10^{10}/$ [m ² sec ⁻¹]	$D_p \times 10^{10}/$ [m ² sec ⁻¹]
Soil moisture content (θ)						
100 % (θ_1)	1.44 ^a	52.1 ^a	1.50 ^a	58.4 ^a	1.62 ^a	67.3 ^a
85% (θ_2)	1.32 ^b	47.7 ^b	1.41 ^b	54.8 ^b	1.52 ^b	63.1 ^b
Bulk density (d)						
0.99 Mg. m ⁻³ (d_1)	1.34 ^b	48.6 ^b	1.42 ^b	54.9 ^b	1.49 ^b	62.2 ^b
1.08 Mg. m ⁻³ (d_2)	1.42 ^a	51.2 ^a	1.51 ^a	58.3 ^a	1.64 ^a	68.2 ^a
Temperature (T)						
297 (± 1)°K (T_1)	1.30 ^a	46.9 ^a	1.37 ^a	53.3 ^a	1.47 ^a	61.3 ^a
308 (± 1)°K (T_2)	1.46 ^b	52.9 ^b	1.55 ^b	59.9 ^b	1.66 ^b	69.1 ^b
Tracer:background ratio (R)						
1:32 (R_1)	1.31 ^b	47.3 ^b	1.41 ^b	54.8 ^b	1.51 ^b	62.9 ^b
1:16 (R_2)	1.46 ^a	52.6 ^a	1.51 ^a	58.5 ^a	1.62 ^a	67.6 ^a
Background electrolytes (E)						
Ca-saturated (E_1)	1.35 ^a	48.6 ^a	1.31 ^a	54.1 ^a	1.51 ^a	62.7 ^a
Na saturated (E_2)	1.42 ^b	51.2 ^b	1.52 ^b	59.2 ^b	1.63 ^b	67.7 ^b

Means followed by same lowercase letters in columns do not differ by Tukey's Studentized Range (HSD) test for diffusion at ($p < 0.05$, $n = 96$), θ_1 and θ_2 : 100 and 85% moisture content of the water holding capacity of the soil, d_1 and d_2 : Bulk density of the soil maintained at 0.99 and 1.08 Mg m³, respectively, T_1 and T_2 : Temperature of 297 (± 1) and 308 (± 1)°K maintained during the corresponding diffusion experiment, R_1 and R_2 : Tracer:background electrolyte of 1:32 and 1:16, respectively, E_1 and E_2 : Ca-saturated and Na-saturated background electrolyte, respectively

Table 3: Probability levels of 2⁶ factorial ANOVA using soil moisture content (θ), bulk density (d), temperature (T), tracer:background ratio (R) and background electrolytes (E) as independent factor and their interaction on apparent diffusion coefficient (D_a) and porous diffusion coefficient (D_p) of K in Nonaghata Uttarpara (S_1), Telegacha (S_2) and Moratripur (S_3) soil

Source of variation	df	S_1		S_2		S_3	
		$D_a \times 10^{10}/$ [m ² sec ⁻¹]	$D_p \times 10^{10}/$ [m ² sec ⁻¹]	$D_a \times 10^{10}/$ [m ² sec ⁻¹]	$D_p \times 10^{10}/$ [m ² sec ⁻¹]	$D_a \times 10^{10}/$ [m ² sec ⁻¹]	$D_p \times 10^{10}/$ [m ² sec ⁻¹]
Rep	2	<.0001**	<.0001**	<.0001**	<.0001**	<.0001**	<.0001**
θ	1	<.0001**	<.0001**	<.0001**	<.0001**	<.0001**	<.0001**
d	1	<.0001**	<.0001**	<.0001**	<.0001**	<.0001**	<.0001**
$\theta \times d$	1	<.0001**	<.0001**	<.0001**	<.0001**	<.0001**	0.002*
T	1	<.0001**	<.0001**	<.0001**	<.0001**	<.0001**	<.0001**
$\theta \times T$	1	0.12 ^{NS}	0.041*	0.036*	0.008*	<.0001**	<.0001**
$d \times T$	1	0.28 ^{NS}	0.21 ^{NS}	0.0001*	0.038*	<.0001**	<.0001**
$\theta \times d \times T$	1	<.0001**	<.0001**	0.0001*	<.0001**	<.0001**	<.0001**
R	1	<.0001**	<.0001**	<.0001**	<.0001**	<.0001**	<.0001**
$\theta \times R$	1	<.0001**	<.0001**	<.0001**	<.0001**	<.0001**	<.0001**
$d \times R$	1	<.0001**	<.0001**	<.0001**	<.0001**	<.0001**	<.0001**
$\theta \times d \times R$	1	<.0001**	<.0001**	<.0001**	<.0001**	0.17 ^{NS}	0.042*
$T \times R$	1	0.002*	<.0001**	0.21 ^{NS}	0.64 ^{NS}	<.0001**	<.0001**
$\theta \times T \times R$	1	<.0001**	<.0001**	0.53 ^{NS}	0.91 ^{NS}	<.0001**	0.001*
$d \times T \times R$	1	<.0001**	<.0001**	0.35 ^{NS}	0.47 ^{NS}	<.0001**	<.0001**
$\theta \times d \times T \times R$	1	<.0001**	<.0001**	0.53 ^{NS}	0.008*	<.0001**	<.0001**
E	1	<.0001**	<.0001**	<.0001**	<.0001**	<.0001**	<.0001**

Table 3: Countinue

Source of variation	df	S ₁		S ₂		S ₃	
		D _a × 10 ¹⁰ / [m ² sec ⁻¹]	D _p × 10 ¹⁰ / [m ² sec ⁻¹]	D _a × 10 ¹⁰ / [m ² sec ⁻¹]	D _p × 10 ¹⁰ / [m ² sec ⁻¹]	D _a × 10 ¹⁰ / [m ² sec ⁻¹]	D _p × 10 ¹⁰ / [m ² sec ⁻¹]
W×E	1	<.0001**	<.0001**	0.043*	0.034*	<.0001**	<.0001**
d×E	1	0.008*	0.003*	<.0001**	<.0001**	0.46 ^{NS}	0.67 ^{NS}
θ×d×E	1	0.07 ^{NS}	0.009*	<.0001**	0.011*	<.0001**	<.0001**
T×E	1	<.0001**	<.0001**	0.01*	0.038*	<.0001**	<.0001**
θ×T×E	1	0.28 ^{NS}	0.24 ^{NS}	0.88 ^{NS}	0.001*	<.0001**	<.0001**
d×T×E	1	0.55 ^{NS}	0.71 ^{NS}	<.0001**	0.13 ^{NS}	0.92 ^{NS}	0.125*
θ×d×T×E	1	0.55 ^{NS}	0.71 ^{NS}	0.44 ^{NS}	0.17 ^{NS}	0.75 ^{NS}	0.963 ^{NS}
R×E	1	<.0001**	<.0001**	<.0001**	0.001*	<.0001**	<.0001**
θ×R×E	1	0.008*	0.012*	<.0001**	<.0001**	<.0001**	<.0001**
d×R×E	1	0.008*	0.001*	<.0001**	<.0001**	<.0001**	<.0001**
θ×d×R×E	1	0.08 ^{NS}	0.041*	0.004*	<.0001**	<.0001**	<.0001**
T×R×E	1	<.0001**	0.001	0.16 ^{NS}	0.36 ^{NS}	<.0001**	<.0001**
θ×T×R×E	1	<.0001**	<.0001**	0.01*	0.061 ^{NS}	0.46 ^{NS}	0.057*
d×T×R×E	1	<.0001**	<.0001**	0.62 ^{NS}	0.20 ^{NS}	0.24 ^{NS}	0.74 ^{NS}
θ×d×T×R×E	1	<.0001**	<.0001**	0.28 ^{NS}	0.002*	<.0001**	<.0001**
CV(%)	--	0.61	0.55	0.65	0.68	0.89	0.71

** , *Significant at 0.01 and 0.05 probability levels, respectively, CV: Coefficient of variation, df: Degrees of freedom, Rep: Replication, θ: Soil moisture content, d: Bulk density of the soil, T: Temperature maintained during the corresponding diffusion experiment, R: Tracer:background ratio, E: Background electrolytes, NS: Non significant

Table 4: Effect of bulk density (d), temperature (T), tracer:background ratio (R) and background electrolytes (E) on Energy of activation (E_a), Arrhenius frequency factor (A) and Entropy factor of diffusion (θ) at 100% water holding capacity; probability levels of 2³ factorial ANOVA using bulk density (d), tracer : background ratio (R) and background electrolytes (E) as independent factor and their interaction on Apparent Diffusion Coefficient (D_a) of K in Nonaghata Uttarpara (S₁), Telegacha (S₂) and Moratripur soil (S₃)

Factors	Energy of activation (E _a) (KJ mol ⁻¹)			Arrhenius frequency factor (A) × 10 ⁹			Entropy factor of diffusion (θ) × 10 ¹¹ m		
	S ₁	S ₂	S ₃	S ₁	S ₂	S ₃	S ₁	S ₂	S ₃
Bulk density (d)									
0.99 Mg m ⁻³ (d ₁)	24.8 ^a	22.6 ^a	29.5 ^a	4.70 ^a	3.94 ^a	3.09 ^a	1.65 ^a	1.52 ^a	1.31 ^a
1.08 Mg m ⁻³ (d ₂)	23.9 ^b	19.8 ^a	23.6 ^a	3.48 ^a	6.26 ^a	2.77 ^a	1.39 ^a	1.91 ^a	1.20 ^a
Tracer:Background ratio (R)									
1:32 (R ₁)	28.1 ^a	25.2 ^a	24.5 ^a	4.83 ^a	5.96 ^a	3.58 ^a	1.66 ^a	1.85 ^a	1.40 ^a
1:16 (R ₂)	20.6 ^a	17.2 ^a	28.6 ^a	3.35 ^a	4.24 ^a	2.27 ^a	1.39 ^a	1.58 ^a	1.11 ^a
Background electrolytes (E)									
Ca-saturated (E ₁)	25.0 ^a	23.9 ^a	27.4 ^a	4.56 ^a	4.72 ^a	4.05 ^a	1.56 ^a	1.79 ^a	1.46 ^a
Na saturated (E ₂)	23.8 ^a	18.5 ^a	25.7 ^a	3.63 ^a	5.56 ^a	1.81 ^a	1.48 ^a	1.65 ^a	1.01 ^a
Interaction									
Rep	<.0001**	<.0001**	<.0001**	<.0001**	<.0001**	0.001**	0.014*	<.0001**	<.0001**
d	0.001*	<.0001**	<.0001**	<.0001**	<.0001**	0.0001*	0.001*	<.0001**	0.001*
R	<.0001**	<.0001**	<.0001**	<.0001**	<.0001**	<.0001**	<.0001**	<.0001**	<.0001**
d×R	<.0001**	<.0001**	<.0001**	<.0001**	<.0001**	<.0001**	0.008*	<.0001**	<.0001**
E	<.0001**	<.0001**	0.45 ^{NS}	<.0001**	<.0001**	<.0001**	0.006*	<.0001**	<.0001**
d×E	0.5809*	<.0001**	0.08 ^{NS}	<.0001**	<.0001**	<.0001**	<.0001**	<.0001**	<.0001**
R×E	<.0001**	<.0001**	0.001*	0.28 ^{NS}	0.19 ^{NS}	0.38 ^{NS}	0.55 ^{NS}	0.002*	0.04*
d×R×E	<.0001**	<.0001**	<.0001**	<.0001**	<.0001**	<.0001**	0.18 ^{NS}	<.0001**	<.0001**
CV(%)	2.22	3.83	1.69	2.75	3.46	5.08	2.39	2.34	4.07

** , *Significant at 0.01 and 0.05 probability levels, respectively. CV: Coefficient of variation. Means followed by same lowercase letters in columns do not differ by Tukey's Studentized Range (HSD) Test for Diffusion at (p<0.05, n = 9 6), d₁ and d₂: Bulk density of the soil maintained at 0.99 and 1.08 Mg m³, R₁ and R₂: Tracer:background electrolyte of 1:32 and 1:16, respectively; E₁ and E₂: Ca-saturated and Na-saturated background electrolyte, respectively

Table 5: Regression equation relating apparent diffusion coefficient (D_a) and porous diffusion coefficient (D_p) of K with different forms of potassium and different fractions of clay minerals

Parameters	Regression equation	R ²	SE	Standardized coefficient of beta maximum
Equation with forms of K/cmole(p⁺)kg⁻¹ WSK (X₁) EXK (X₂), NEK (X₃)				
D _a	0.680-2.632 X ₁ +2.188 X ₂ +0.120 X ₃	0.914**	0.038	X ₂ = 0.749
D _p	1.516+164.6 X ₁ +55.14 X ₂ +6.60 X ₃	0.899**	2.97	X ₃ = 0.396
Equation with different composition of clay fraction of the soils/Kaolinite (Y ₁), Smectite (Y ₂), Mica/Illite (Y ₃), Chlorite (Y ₄), Vermiculite (Y ₅), Mixed minerals (Y ₆)				
D _a	0.910-0.068 Y ₁ +0.011 Y ₂ +0.017 Y ₃ +0.012 Y ₄ +0.011 Y ₅ Excluded variables, Y ₆ (Beta ln = 61.832)	0.957*	0.035	Y ₃ = 1.079
D _p	-85.036+2.554 Y ₁ - 2.151 Y ₂ +3.610 Y ₃ - 0.592 Y ₄ +0.601 Y ₅ Excluded variables, Y ₆ (Beta ln = 55.68)	0.939*	2.99	Y ₃ = 3.27

**, *Significant at the 0.01 and 0.05 probability levels, respectively, SE: Standard error of estimate, R²: Regression coefficients for the fitted data

increasing tracer component (Table 4). Results of multiple regression equations for the apparent (D_a) and tracer diffusion coefficient (D_p) drawn with different forms of K and different fractions of clay are presented in Table 5. The regression equations revealed that exchangeable K (denoted by X₂) and illite (denoted by Y₃) fraction of the clay contributed significantly toward variability in diffusion coefficient of K (both D_a and D_p) as evidenced from the magnitude of coefficient of X₂ and Y₃ than other coefficients. However, the standardized coefficient of beta values was highest in X₂ (i.e., exchangeable K) for D_a and X₃ (i.e., nonexchangeable K) for D_p .

DISCUSSION

The data presented in Table 1 revealed that the soil of Moratripur has showed highest clay content (35.3%) and hence the highest cation exchange capacity as well as exchangeable bases. The clay fraction of Moratripur soil was dominated by micaceous minerals for which the exchangeable and nonexchangeable K content was highest of the above said soil (Table 1).

The decrease of D_a and D_p values due to decrease in soil moisture may be due to the fact that as the soil water content decreases, the cross-sectional area available for diffusion becomes smaller and the path length increases with the viscosity and negative adsorption becoming more important as the water films decrease in thickness (Paul *et al.*, 1998). The results are in satisfactory agreement with the observations made by Mani and Sanyal (1996) and Dhar and Sanyal (2002) on K. It may be mentioned here that b, the capacity factor values at different moisture levels, were taken to be same as the present method did not permit the determination of b value at different moisture levels, notwithstanding though the observation of Olsen and Kemper (1968) that with increasing soil moisture content, b value increases. The higher bulk-density causes the diffusion path to become less tortuous. Such decrease in tortuosity at higher compaction or higher bulk-density is resulted from effective destruction of air pockets by which the crumbs get pressed more readily into contact, thereby, reducing the tortuosity of the diffusion path (Meisheri and Deb, 1986).

A higher concentration of the background electrolyte may have hindered the effective passage of K from the tagged to the untagged soil (Phillips and Brown, 1964) for which with the increase

of tracer:background ratio the D_a and D_p values increased significantly. The Moratripur soil which had greater exchangeable K, nonexchangeable K and illite content than other two soils was found to possess higher D_a and D_p values.

The decrease of E_a due to increase of bulk density (Table 4) may be attributed due to the facilitated K diffusion at a higher bulk density as discussed earlier. While with increasing the tracer:background ratio, the E_a values decreased significantly ($p < 0.05$) for Nonaghata and Telegacha soil in contrast with Moratripur soil where, higher background concentration made the diffusion of potassium thermodynamically unfavourable as evidenced with the increase in E_a values. Significantly ($p < 0.05$) lower E_a values were observed when Na was taken as background electrolyte which again reflecting the fact of ease of replacement of Na from the exchange site as compared to Ca^{+2} ion by K. The Arrhenius frequency factor (A) defines the probability of ion interaction which includes the frequency of oscillations that an ion undergoes at a given exchange site (Brown *et al.*, 1968). The lower values of 'A' may be explained by lower probability of ion-exchange preceding diffusion (Mani and Sanyal, 1995).

The multiple regression equations for D_a and D_p with different forms of K suggested that exchangeable K appeared to be the most relevant form for apparent tracer diffusion coefficient (D_a) of K in alluvial soils while, nonexchangeable K is most relevant for porous diffusion coefficient (D_p) of K. For both the D_a and D_p , standardized coefficient of beta values were found maximum for illite fraction of the clay minerals. In illite mineral, the most of the exchangeable ions are in interlayer positions. However, when ion like potassium diffusing into the illite dominant soil, it may diffuse preferentially on the external surfaces rather the interlayer positions. Indeed, the main factor influencing the diffusion coefficient is the interlayer spacing of the clay mineral (Nye, 1980). In the present study, the alluvial soils having dominance of weathered illitic type of minerals characterized by sufficiently fast release of potassium from wedge zones of (2:1) type of minerals and thus appeared to be the most relevant for describing the diffusion coefficient.

CONCLUSION

The different factors studied for their role in K diffusion have significant influence on diffusion of K in soil. It was evidenced that with the increase in moisture content, temperature, bulk density and tracer:background ratio there was a significant increase in both apparent and tracer diffusion coefficient. The interaction effects of different factors of K diffusion was found significant ($p < 0.05$) in most of the cases except for the interaction of bulk density, temperature and electrolyte together ($d \times T \times E$) and moisture content with the earlier ones ($\theta \times d \times T \times E$). It can be concluded that the diffusion coefficients of potassium in these alluvial soils can be predicted in terms of exchangeable K and nonexchangeable K (for D_a and D_p , respectively) and also in terms of the proportion of illitic minerals of the clay. Prediction of such diffusion coefficients of K may be successfully utilized to estimate the plant uptake of K from soil and also to understand the transport behaviour of K from bulk soil phase to crop root and hence its dynamics.

ACKNOWLEDGMENT

The authors are thankful to Prof. S. K. Sanyal, The Ex-Vice Chancellor, Bidhan Chandra Krishi Viswavidyalaya, Kalyani, West Bengal for his guidance and valuable suggestions received during this study. The authors also thankfully acknowledge the National Bureau of Soil Survey and Land Use Planning, Nagpur, India for providing the instrument facilities to obtain x-ray diffractograms of clay minerals.

REFERENCES

- Atkins, P.W., 1982. Physical Chemistry. 2nd Edn., Oxford University Press, Oxford, UK.
- Benipal, D.S., N.S. Pasricha and R. Singh, 2006. Potassium release to proton saturated resin and its diffusion characteristics in some alluvial soils. *Geoderma*, 132: 464-470.
- Brown, D. A., B.E. Fulton and R.E. Phillips, 1964. Ion diffusion: I. A quick-freeze method for the measurement of ion diffusion in soil and clay systems. *Soil Sci. Soc. Am. J.*, 28: 628-632.
- Brown, D.A., R.E. Phillips, L.O. Ashlock and B.D. Fuqua, 1968. Effect of Al^{3+} and H^+ upon the simultaneous diffusion of ^{85}Sr and ^{86}Rb in kaolinite clay. *Clays Clay Miner.*, 16: 137-146.
- De Lopez-Gonzalez, J. and H. Jenny, 1959. Diffusion of strontium in ion-exchange membranes. *J. Colloid Sci.*, 14: 533-542.
- Deb, D.L., A. Sen, R.K. Rattan, M.B. Meisheri, G.N. Gupta and K.N. Sharma, 1983. Diffusion of zinc as influenced by physical and chemical properties of soils. *Zeitschrift Pflanzenernahrung Bodenkunde*, 146: 494-503.
- Dhar, A. and S.K. Sanyal, 2002. Tracer diffusion of potassium and related parameters in three soils of West Bengal. *J. Indian Chem. Soc.*, 79: 159-162.
- Gjems, O., 1967. Studies on clay-mineral formation in soil profiles in Scandinavia. *Meddelelser fra Det Norske Skogforsoksvesen*, 21: 299-415.
- Jackson, M.L., 1973. Soil Chemical Analysis. Prentice Hall of India Pvt. Ltd., New Delhi, India.
- Mani, P.K. and S.K. Sanyal, 1995. Tracer diffusion of potassium in four soils of West Bengal. *J. Indian Soc. Soil Sci.*, 43: 166-172.
- Mani, P.K. and S.K. Sanyal, 1996. Tracer diffusion of potassium in some alfisols, inceptisols and entisols. *J. Indian Soc. Soil Sci.*, 44: 201-205.
- Meisheri, M.B. and D.L. Deb, 1986. Effect of bulk-density and moisture tension on transmission factor of three light textured soils. *J. Indian Soc. Soil Sci.*, 34: 458-463.
- Nye, P. H., 1972. Localized movement of potassium ions in soils. Proceedings of the 9th Colloquium of the International Potash Institute, July 1972, Landshut, Germany, pp: 147-155.
- Nye, P.H., 1980. Diffusion of Ions and Uncharged Solutes in Soils and Soil Clays. In: *Advances in Agronomy*, Brady, N.C. (Ed.). Vol. 31, Academic Press, New York, USA., ISBN-13: 9780120007318, pp: 225-272.
- O'Connor, G.A., W.L. Lindsay and S.R. Olsen, 1971. Diffusion of iron and iron chelates in soil. *Soil Sci. Soc. Am. Proc.*, 35: 407-410.
- O'Connor, G.A., W.L. Lindsay and S.R. Olsen, 1975. Iron diffusion to plant roots. *Soil Sci.*, 119: 285-289.
- Oliveira, R.H., C.A., Rosolem and R.M. Trigueiro, 2004. Importance of mass flow and diffusion on the potassium supply to cotton plants as affected by soil water and potassium. *Revista Brasileira Ciencia Solo*, 28: 439-445.
- Olsen, S.R. and W.D. Kemper, 1968. Movement of Nutrients to Plant Roots. In: *Advances in Agronomy*, Norman, A.G. (Ed.). Vol. 20, Academic Press, New York, ISBN-13: 9780080563336, pp: 91-151.
- Paul, B., D.L. Deb, M.S. Sachdev and P. Sachdev, 1998. Diffusion of ^{137}Cs and ^{65}Zn in different soils. *J. Indian Soc. Soil Sci.*, 46: 589-592.
- Phillips, R.E. and D.A. Brown, 1964. Ion diffusion: II. Comparison of apparent self and counter diffusion coefficients. *Soil Sci. Soc. Am. J.*, 28: 758-763.
- Porter, L.K., W.D. Kemper, R.D. Jackson and B.A. Stewart, 1960. Chloride diffusion in soils as influenced by moisture content. *Soil Sci. Soc. Am. J.*, 24: 460-463.

- Pratt, P.F., 1965. Digestion with Hydrofluoric and Perchloric Acids for Total Potassium and Sodium. In: Method of Soil Analysis, Part 2, Chemical and Microbiological Properties, Black, C.A. (Ed.). American Society of Agronomy Inc., Madison, WI., USA., pp: 1019-1020.
- SAS, 2013. SAS/STAT User's Guide. Version 9.3, SAS Institute, Cary, NC., USA.
- Sanyal, S.K. and U.S. Bhattacharya, 1986. A critical examination of diffusion studies in soil in relation to periods of diffusion. *J. Indian Soc. Soil Sci.*, 34: 720-727.
- Sanyal, S.K., 1980. Validity of simple form of Fick's first Law in self and tracer diffusion. *J. Indian Soc. Soil Sci.*, 28: 417-422.
- Sekhon, G.S., M.S. Brar and A. Subba Rao, 1992. Potassium in Some Benchmark Soils of India. Potash Research Institute of Harayana, Gurgaon, India, Pages: 82.
- Wani, M.A. and S.C. Datta, 2007. Nonexchangeable potassium release to H⁺-saturated resin and its diffusion characteristics in some soils of lesser Himalayas. *Soil Sci.*, 172: 546-552.
- Zeng, Q. and P.H. Brown, 2000. Soil potassium mobility and uptake by corn under differential soil moisture regimes. *Plant Soil*, 221: 121-134.