Quantity-intensity relations of potassium in representative coastal soils of eastern India

Ranajit Panda[a],[*], S.K. Patra[b]

[a] IMD, GKMS, Majhian, Uttar Banga Krishi Viswavidyalaya, West Bengal 733133, India
[b] Bidhan Chandra Krishi Viswavidyalaya, Mohanpur, Nadia, West Bengal 741252, India

ARTICLE INFO

ABSTRACT

Quantity-intensity (Q/I) isotherms were used to evaluate the dynamics of K^+ in twelve coastal soils of eastern India. The activity ratio of K^+ (AR_e^K) and corresponding changes in labile K^+ ($\pm \Delta K$) at equilibrium increased with increasing K^+ concentrations. The equilibrium activity ratio of K^+ (AR_e^{0K}) varied between 0.09×10^{-3} and 7.50×10^{-3} $(mol\,L^{-1})^{1/2}$. The labile K^+ (K_L) ranged from 0.265 to 0.4 $cmol\,kg^{-1}$ constituting 43.8 to 204.5% of 1N NH_4OAc extractable K^+. The readily available (K_0) and fixed K^+ (K_X) varied from 0.082 to 0.290 and 0.041 to 0.278 $cmol\,kg^{-1}$ contributing 22.8 to 84.5 and 15.5 to 77.2% towards K_L, respectively. The potential buffering capacities for K^+ (PBC^K) fluctuated from 16.2 to 85.7 $cmol\,kg^{-1}(mol\,L^{-1})^{-1/2}$. The K^+ potential ranged from 2.38 to 10.76 $cmol\,kg^{-1}(mol\,L^{-1})^{-1/2}$. The free energy of K^+ exchange ($-\Delta G$) ranged from -5533 to -2906 $calories\,mol^{-1}$ indicating deficient to adequate in available K^+. The AR_e^{0K}, K_0, K_X and $-\Delta G$ had significant positive correlations with pH, CEC, available and reserves soil K^+, while there were inverse relationships between PBC^K and these soil parameters. A significant positive correlation was found between AR_e^{0K} and K_0, K^+ saturation, $-\Delta G$ and significant negative correlation with K_X and PBC^K. Significant positive correlations were observed between K_X and K_L and PBC^K and significant negative correlations with AR_e^{0K}, $-\Delta G$ and K^+ saturation. PBC^K had significant negative correlations with K_0, $-\Delta G$ and K^+ saturation. The study provided useful information for understanding K^+ dynamics in coastal soils and make significant contribution to operational K^+ management.

1. Introduction

Potassium (K^+) is one of the most important macronutrients in soils which are required relatively larger amounts for plant growth. There are four different fractions of K^+ viz., solution K^+, exchangeable K^+, non-exchangeable K^+ and mineral or structural K^+ exist in soil which are in a state of dynamic equilibrium with each other (Sparks, 1987; Johnston and Goulding, 1990). Plants absorb K^+ mainly from the soil solution which is buffered by the rapidly exchangeable forms (Idigbor et al., 2009). The availability of K^+ in the soil solution, and the capacity of soil to buffer this concentration are among the important parameters that determine the effective available K^+ for plant nutrition (Raheb and Heidari, 2012; Hamed and Amin, 2017). The amount of exchangeable K^+ measured with neutral 1N NH_4OAc is widely used as a way to characterize the soil K^+ status and to predict crop K^+ requirements. Several empirical methods have been attempted to find a suitable method for determining the availability of soil K^+ to evaluate the amount of K^+ fertilizers needed by a particular crop. Potassium

dynamics in relation to solution-exchange phase interactions of basic cations like K^+, Ca^{2+} and Mg^{2+} species have undergone rigorous testing for predicting the K^+ availability in different soil systems (Evangelou et al., 1994). The thermodynamic approach most often used in understanding, characterizing and evaluating the K^+ supplying capacity of soil is the quantity-intensity (Q/I) isotherm of K^+ (Beckett, 1964a, 1964b). This relationship implies that the ability of a soil system to maintain a certain concentration of a cation in solution is determined by the total amount of the cation present in readily available forms (exchangeable and soluble) and the intensity by which it is released into the soil solution (LeRoux and Summer, 1968). In the Q/I curve the equilibrium activity ratio of K^+ (AR_e^K) is a measure of availability or intensity of labile K^+ in soil. Different soil exhibiting the same value of AR_e^K values may not possess the same capacity for maintaining AR_e^K when soil K^+ is depleted by plant roots (Diatta et al., 2006). Higher values of labile K^+ indicated a greater K^+ release into soil solution resulting from a larger pool of soil K^+. A high value of the potential buffering capacity for K^+ (PBC^K) in soil is indicative of a good K^+
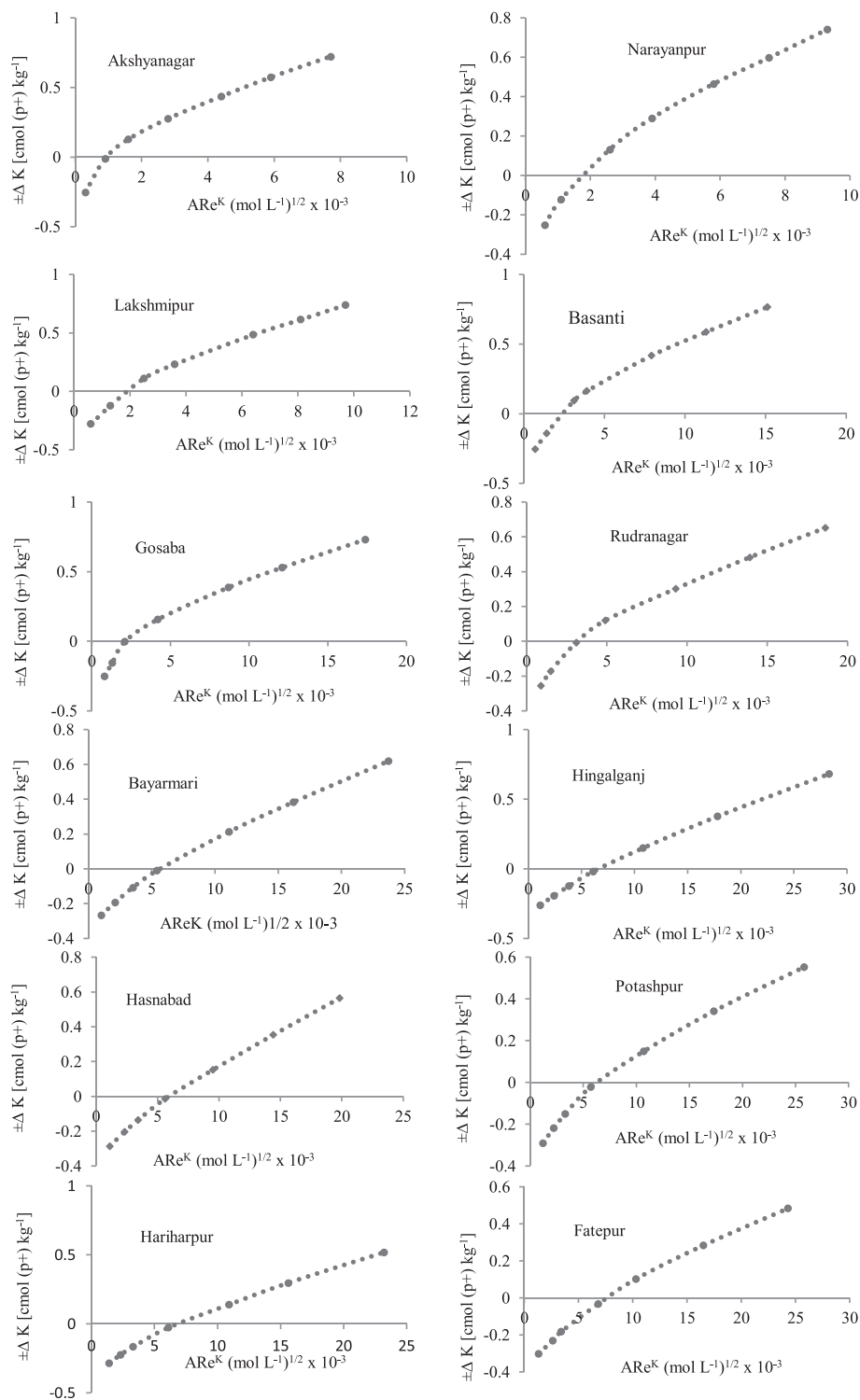
Fig. 1. Quantity-intensity curves of potassium for the selected coastal saline soils.

availability while a low PBC^K value would suggest a need for K$^+$ fertilization (Wang et al., 2004).

Numerous studies have been conducted extensively to assess the availability of K$^+$ in soils using Q/I concept or soil K$^+$ buffering characteristics (Bandyopadhyay et al., 1985; Pal and Subba Rao, 1997; Dhillon and Parischa, 2000; Niranjana et al., 2000; Samadi, 2006; Patra et al., 2007; Abaslou and Abtahi, 2008; Yawson et al., 2011; Bahmni et al., 2013; Lalitha and Dhakshinamoorthy, 2015). Such information in the salt affected coastal soils of eastern India is limited. In this

perspective, the present investigation was carried out with the objectives of evaluating the potential capacity of selected coastal soils for K$^+$ supply and replenishment by characterizing the K$^+$ quantity-intensity (Q/I) concept and its relationship with some relevant soil properties.

2. Materials and methods

2.1. Study area and sample collection

Twelve representative surface soil (0–0.15 m) samples were collected from the agricultural lands of coastal region of West Bengal, India. The experimental area is located between latitudes 87° 25′ to 89° E and longitudes 21° 30′ to 23° 15′ N. Six samples were taken from the district of South 24 Parganas and three samples each were collected from the districts of North 24 Parganas and Medinipur East. The soils belonged to the order of Entisols and Inceptisols according to USDA soil taxonomy (Soil Survey Staff, 2006). The soil samples were air-dried, crushed and passed through a 2 mm sieve, prior to chemical analysis. Particle size distribution was determined by the hydrometer method (Bouyoucous, 1962). Soil pH and electrical conductivity (EC) were measured using 1:2.5 soil to water suspensions (Jackson, 1973). Organic carbon was determined by dichromate oxidation and the cation exchange capacity (CEC) of the soils was obtained by extracting the soil with neutral 1N NH_4OAc method (Jackson, 1973). Water soluble K^+ was determined by Grewal and Kanwar (1966). Available K^+ was extracted by 1N NH_4OAc buffered at pH 7.0 (Jackson, 1973). Exchangeable K^+ was deduced by subtracting water soluble K^+ from available K^+. Non-exchangeable K^+ was extracted by boiling the soil with 1N HNO_3 after removing available K^+ (Wood and DeTurk, 1940). Lattice K^+ was calculated from the difference between the total K^+ and the sum of NH_4OAc-K^+ and non-exchangeable-K^+ (Wiklander, 1954). Total K^+ was extracted by HF-$HClO_4$ digestion of the samples (Black, 1965). Potassium in all the extracts was estimated by flame photometer. K^+ saturation percentage of soils can be estimated from the following equation (Mutscher, 1995):

$$K^+ \text{ saturation}(\%) = \frac{K_{adsorbed}(\text{cmolkg}^{-1})}{CEC\ (\text{cmolkg}^{-1})} \times 100$$

2.2. Quantity-intensity (Q/I) relationship of potassium

The quantity-intensity of K^+ was determined according to the method of Beckett (1964a, 1964b) by adding 50 mL of 0.01 M $CaCl_2$ solutions containing 0, 0.1, 0.25, 0.50, 1.0, 2.0 and 3.0 mmol L^{-1}KCl concentrations to 5 g of the soil sample in bottles. The soil suspensions were shaken vigorously for 2 h, left for overnight (24 h) for equilibration and then centrifuged. The suspensions of soil samples were filtered and the supernatants were analyzed for K^+ by flame photometer and for Ca^{++} and Mg^{++} by versenate titration (Black, 1965).

The K^+ intensity (I) or the activity ratio of K^+(AR^K) relative to Ca^{++}+ Mg^{++} species of each equilibrium solution was calculated using the formula:

$$AR^K = \frac{a_K}{(a_{Ca+Mg})^{1/2}} = \frac{C_K}{(C_{Ca+Mg})^{1/2}} \times \frac{f_K}{(f_{Ca+Mg})^{1/2}}$$

where, AR^K = activity ratio of K^+ to Ca^{++} + Mg^{++} after equilibration (mol L^{-1})$^{1/2}$,

a_K = activity of K^+ (mol L^{-1}), a_{Ca+Mg} = activity of Ca^{++} + Mg^{++}(mol L^{-1}),

f_K = activity coefficient of K^+ and f_{Ca+Mg} = activity coefficient of Ca^{++} + Mg^{++}.

For the dilute solution (0.01 M $CaCl_2$), the activity coefficient ratio of $f_K/(f_{Ca+Mg})^{1/2}$ is closer to unity, as the values vary little within the range of K^+ and Ca^{++} + Mg^{++}concentrations used in the equilibrium solutions (Beckett, 1965; Sinclair, 1979; Wang et al., 1988). Therefore, the concentrations of cations in the equilibrium solution were assumed as activity ratio of these ions i.e. $AR^K = C_K/(C_{Ca} + C_{Mg})^{1/2}$.

The quantity of K^+ gained or lost ($\pm \Delta K$) by the soil was calculated from the difference between the amounts of K^+ added and recovered in the final equilibrium solutions. The $\pm \Delta K$ (quantity factor) was plotted on the ordinate axis against the AR_e^K(intensity factor) on the abscissa axis to obtain the Q/I isotherm for each soil (Fig. 1). The intercept of the Q/I plot on the AR^K axis at zero level of $\pm \Delta K$ represented the equilibrium activity ratio for K^+ (ARe^{0K}), which denotes the soil solution K^+ activity relative to Ca^{++} + Mg^{++}at equilibrium. The linear portion of the curve was extrapolated to the ordinate by drawing a tangent from the point of abscissa where $\pm \Delta K = 0$; this represented the readily exchangeable K^+ held on non-specific edge or planar sites (K_0). The lower curvature at the low values of AR_e^K was due to the release of fixed K^+ from the soil particle. The intercept at the lower curved part of the Q/I plot represented the K^+ held on the specific sites with high K^+ affinity (K_X). The amount of ΔK at $AR_e^K = 0$ represented the total pool of labile K^+ (K_L) in a particular soil (K_0+ K_X). This parameter showed the amount of K^+ which is readily available and is capable of ion exchange during period of equilibrium between soil colloids and soil solution. The potential buffering capacity of K^+ (PBC^K) was calculated as the slope of $\Delta K/AR_e^K$ of the linear portion of the curve. It is a measure of soil ability to maintain the intensity of K^+ in soil solution. The K^+ potential of soil was determined by multiplying K_0 with PBC^K i.e. K potential = K_0 x PBC^K(Dutta and Joshi, 1990).The free energy of K^+ replenishment ($-\Delta G^0$) was computed from the following equation (Beckett, 1972).

$$\Delta G^O = 2.303\ RT\ \log\ ARe^{0K}$$

where, R and T are molar gas constant and absolute temperature, respectively.

The degree of association between the Q/I parameters and various soil variables and their interrelationship were worked out using correlation analysis (Panse and Sukhatme, 1961).

3. Results

3.1. Soil properties

The relevant physical and chemical characteristics of the soils are presented in Table 1. The soils belonged to the great group of Endoaquent, Fluvaquent and Endoaquept. The texture of soils was silty clay to clay with clay fractions ranging from 226 to 426 g kg^{-1}. Soil pH varied from 4.53 to 7.52. The electrical conductivity (EC) of soils ranged widely from 0.87 to 5.63 dSm^{-1}. Organic carbon contents (4.7 to 7.5 g kg^{-1}) were low to medium. The cation exchange capacity (CEC) of soils varied between 12.3 and 21.4 cmol kg^{-1}.

3.2. Different forms of soil potassium

The water soluble, exchangeable, available and non-exchangeable K^+ contents of the soils fluctuated from 10.16 to 52.27, 58.65 to 232.50, 68.81 to 284.77 and 534 to 1050 mg kg^{-1}, respectively (Table 2). Lattice K^+ and total K^+ content of the soils ranged between 0.93 to 2.60 and 1.00 to 2.74%, respectively. The soils contained moderate amounts of K^+ saturation percentage varying from 1.17 to 3.22. This value is used as the K^+ mobility parameter as well as assessment of K^+ status in soil (Mutscher, 1995; Yawson et al., 2011).

3.3. Potassium quantity-intensity (Q/I) relationship

The Q/I relationships of potassium for the coastal soils are illustrated in Fig. 1 and characterized by an upper linear portion at moderate to higher values of equilibrium activity ratio (AR_e^K) and a curved lower region at low values of AR_e^K. The amounts of different parameters of Q/I relations are presented in Table 3. The coefficients of correlation between Q/I parameters and soil properties and forms of soil K^+ and their interrelationships are given in Tables 4 and 5, respectively.

Table 1
Important physical and chemical characteristics of the selected coastal soils.

Soil no.	Location of soil	Great group	Clay	Silt	Sand	Texture	pH (1:2.5)	EC (dS m^{-1})	Organic C (g kg^{-1})	CEC (cmol kg^{-1})
			(mg kg^{-1})							
S1	Akshyanagar	Endoaquept	345	424	231	Clay loam	4.53	0.87	4.7	12.82
S2	Narayanpur	Fluvaquent	284	393	323	Loam	6.51	2.54	6.1	15.1
S3	Lakshmipur	Endoaquept	357	406	237	Clay loam	4.82	0.98	5.2	12.34
S4	Basanti	Endoaquept	403	328	269	Clay loam	6.42	3.28	5.4	16.5
S5	Gosaba	Endoaquent	226	479	295	Loam	6.12	1.09	6.6	18.2
S6	Rudranagar	Endoaquent	409	436	155	Clay loam	6.62	3.22	6.9	18.6
S7	Bayarmari	Endoaquent	366	193	441	Clay loam	6.82	3.73	6.8	19.6
S8	Hingalganj	Endoaquent	263	321	416	Loam	6.80	4.05	7.0	21.1
S9	Hasnabad	Endoaquent	423	455	122	Silty clay	6.75	4.61	7.5	21.4
S10	Potashpur	Fluvaquent	426	472	102	Silty clay	7.13	4.92	6.2	16.47
S11	Hariharpur	Endoaquept	385	492	123	Silty clay	7.52	5.31	6.2	17.12
S12	Fatepur	Endoaquept	402	524	74	Silty clay	7.34	5.63	5.3	18.52

3.3.1. Potassium intensity

The activity ratio of K$^+$ (AR$_e^K$) in equilibrium solutions is a measure of the intensity (I) of labile K$^+$ in the soil and represents the K$^+$ that is immediately available to crop roots. Fig. 1 shows that AR$_e^K$ values increased with increasing K$^+$ concentrations of the equilibrating solutions for all the soils. At zero level of applied K$^+$, the lowest AR$_e^K$ value was observed in soil number S1 and the highest by soil number S11. Similarly, at maximum level of applied K$^+$ (1.572 mol L^{-1}), the lowest AR$_e^K$ value was found in S1 whereas the highest in S8. The differences between the highest and the lowest values of AR$_e^K$ irrespective of soils was 1.1 and 20.6 (mol L^{-1})$^{1/2}$ × 10^{-3} at zero and maximum level of applied K$^+$, respectively. The increase in AR$_e^K$ values of soils ranged between 7.4 and 27.2 (mol L^{-1})$^{1/2}$ × 10^{-3} due to increasing K$^+$ application from 0 to 1.572 mol L^{-1}.

3.3.2. Potassium quantity

The quantity factor (Q) is indicative of the changes in labile pool of K$^+$ as represented by ± ΔK values increased with increasing K$^+$ concentrations of the equilibration solutions. The applied K$^+$ level up to which desorption of K$^+$ continued or beyond which adsorption of K$^+$ started varied from soil to soil. The desorption of K$^+$ was observed up to 0.052 mol L^{-1} of applied K$^+$ for soil number S1 to S4, 0.131 mol L^{-1} of applied K$^+$ for soil number S5 to S6 and 0.262 mol L^{-1} of applied K$^+$ for soil number S7 to S12. Even at the highest level of applied K$^+$ (1.572 mol L^{-1}), the adsorption of K$^+$ in the soils varied from 0.483 to 0.765 cmol kg^{-1} indicating low to moderate fixation of added K$^+$. The results are in agreement with the findings of Bandyopadhyay et al. (1985) for the coastal soils and Patra et al. (2007) for the foothill acidic soils.

3.3.3. Equilibrium potassium activity ratio (AR$_e^{OK}$)

The intercept of the curve with the activity ratio axis (ΔK = 0)

represents the value of the equilibrium activity ratio of K$^+$ in soils. The AR$_e^{OK}$ values varied widely ranging between 0.09 × 10^{-3} and 7.50 × 10^{-3} (mol L^{-1})$^{1/2}$ with an average value of 4.19 × 10^{-3} (mol L^{-1})$^{1/2}$. Soil number S12 and S1 exhibited the highest and lowest amount of AR$_e^{OK}$, respectively. Barring S1, all the soils showed the higher AR$_e^{OK}$ values, the more so in S7 to S12 than in S2 to S6.

AR$_e^{OK}$ had strong significant and positive correlation with soil pH and CEC. Similar relationship was reported by Niranjana et al. (2000) in some Alfisols and Inceptisol. AR$_e^{OK}$ showed highly significant positive correlation with water soluble K$^+$, exchangeable K$^+$ and available K$^+$. The results conform to the findings of close relation between AR$_e^{OK}$ and exchangeable K$^+$ (LeRoux and Summer, 1968) and NH$_4$OAc extractable K$^+$ (Samadi, 2006; Sharma et al., 2012) contents of soil. The correlation values between AR$_e^{OK}$ and non-exchangeable K$^+$, lattice K$^+$ and total K$^+$ were positive and highly significant, thereby indicating their significant contribution towards enrichment of AR$_e^{OK}$ in the soils. The AR$_e^{OK}$ had highly significant positive correlation with K$_0$, K$^+$ saturation percentage and −ΔG and strong significant negative correlation with K$_X$ and PBC^K. The results are in agreement with the report of Sharma et al. (2012) who found the significant positive correlation of AR$_e^{OK}$ with available K$^+$ and K$^+$ saturation percentage. Yawson et al. (2011) also found a similar observation between AR$_e^{OK}$ and −ΔG.

3.3.4. Labile potassium (K$_L$)

In the Q/I isotherms, the quantity of labile K$^+$ (K$_L$) that is readily available to plants ranged between 0.265 and 0.400 cmol kg^{-1}. Relatively maximum value was obtained in S5 soil, while minimum was recorded in S8 soil. The results are in agreement with the findings of Bandyopadhyay et al. (1985) who reported that the contents of K$_L$ in some coastal soils varied from 0.20 to 0.63 cmol kg^{-1}. Dhillon et al. (1986) observed that labile K$^+$ in some alluvial soils varied from 0.07

Table 2
Different forms of potassium (K$^+$) of the selected coastal soils.

Soil no.	Water soluble (mg kg^{-1})	Exchangeable (mg kg^{-1})	Available (mg kg^{-1})	Non-exchangeable (mg kg^{-1})	Lattice (%)	Total (%)
S1	10.16	58.65	68.81	534	1.12	1.18
S2	14.63	81.75	96.38	756	1.54	1.62
S3	11.84	72.4	84.24	631	0.93	1.00
S4	21.97	89.72	111.69	741	1.55	1.64
S5	28.93	124.53	153.46	794	1.70	1.79
S6	32.3	136.37	168.67	784	1.66	1.76
S7	36.02	158.17	194.19	896	1.85	1.96
S8	38.27	198.23	236.5	968	2.35	2.47
S9	42.3	206	248.3	949	1.92	2.04
S10	46.75	212	258.75	1050	2.60	2.74
S11	48.24	222.12	270.36	1022	2.40	2.53
S12	52.27	232.5	284.77	1008	2.43	2.55

Table 3
Potassium quantity-intensity (Q/I) parameters of the selected coastal soils.

Soil no.	1N NH$_4$OAc-K$^+$	Q/I parameters							
		K$_0$	K$_X$	K$_L$	AR$_e^{OK}$ [(mol L^{-1})$^{1/2}$ × 10^{-3}]	PBC^K [cmol kg^{-1} (mol L^{-1})$^{-1/2}$]	K-potential [cmol kg^{-1}(mol L^{-1})$^{-1/2}$]	−ΔG (cal mol^{-1})	K saturation (%)
		← [cmol kg^{-1}] →							
S1	0.176	0.082 (22.8)	0.278 (77.2)	0.360	0.09	85.7	7.03	5533	1.17
S2	0.246	0.130 (33.1)	0.263 (66.9)	0.393	1.80	72.2	9.34	3754	1.38
S3	0.215	0.136 (36.8)	0.234 (63.2)	0.370	1.84	74.3	10.10	3741	1.50
S4	0.286	0.150 (39.5)	0.230 (60.5)	0.380	2.40	45.3	6.79	3583	1.39
S5	0.392	0.140 (35.0)	0.260 (65.0)	0.400	2.10	41.4	5.80	3662	1.75
S6	0.431	0.147 (38.7)	0.233 (61.3)	0.380	3.20	16.2	2.38	3412	1.88
S7	0.497	0.245 (71.0)	0.100 (29.0)	0.345	5.70	31.5	7.72	3069	2.06
S8	0.605	0.224 (84.5)	0.041 (15.5)	0.265	6.50	19.7	4.41	2991	2.40
S9	0.635	0.290 (80.6)	0.070 (19.4)	0.360	6.00	37.1	10.76	3038	2.46
S10	0.662	0.240 (63.2)	0.160 (36.8)	0.380	6.30	25.8	6.19	3010	3.29
S11	0.691	0.260 (68.4)	0.120 (31.6)	0.380	6.80	33.3	8.66	2964	3.32
S12	0.728	0.280 (75.7)	0.090 (24.3)	0.370	7.50	28.6	8.01	2906	3.21
Mean	0.464	0.194 (54.1)	0.173 (45.9)	0.365	4.19	42.6	7.27	3472	2.15

K$_0$: non-specific sites K$^+$, K$_X$: specific sites K$^+$, K$_L$: labile K$^+$, AR$_e^{OK}$: equilibrium activity ratio of K$^+$, PBC^K: potential buffering capacity of K$^+$; −ΔG: Gibb's free energy change; *figures in the parentheses indicate per cent contribution of K$_0$ and K$_X$ towards K$_L$.

to 0.85 cmol kg^{-1}. Comparatively a low K$_L$ value ranging from 0.052 to 0.320 cmol kg^{-1} was reported by Patra et al. (2007) in foothill acid Inceptisols. The labile K$^+$ for the seven soils (soil no. 6 to 12) constituted a fraction of 43.8 to 88.2% of NH$_4$OAc extractable K$^+$(exchangeable K$^+$ and water soluble K$^+$) while the remaining five soils (soil no. 1 to 5) accounted for 102.0 to 204.5% of NH$_4$OAc extractable K$^+$.

None of the soil parameters or forms of soil K$^+$ showed significant relations with K$_L$. However, there was significant positive correlation between K$_L$ and K$_X$.

3.3.5. Non-specific sites potassium (K$_0$)

The immediate available component of the labile K$^+$ (K$_0$) held on the non-specific planar sites of the soils varied from 0.082 to 0.290 cmol kg^{-1} with a mean value of 0.194 cmol kg^{-1}. Maximum value was obtained in S9 soil while minimum was recorded by S1 soil. Relatively higher values of K$_0$ were found in soil number S7 to S12 as compared with the soil number S1 to S6. The results conform to the findings of Dhillon et al. (1986) who observed that K$_0$ values in alluvial soils were within the range from 0.06 to 0.36 cmol kg^{-1}. The

contribution of K$_0$ towards K$_L$ varied from 22.8 to 84.5% (Table 3).

Non-specific planar sites K$^+$ (K$_0$) had highly significant and positive correlation with pH, CEC, available and reserve forms of soil K$^+$. There was highly significant positive correlation of K$_0$ with AR$_e^{OK}$, −ΔG and K$^+$ saturation percentage and highly significant negative correlations with K$_X$ and PBC^K.

3.3.6. Specific sites potassium (K$_X$)

The amount of fixed K$^+$ (K$_X$), the capacity of the edge and wedge sites of the soils which exhibit specific affinity for K$^+$, ranged from 0.041 to 0.278 cmol kg^{-1} with a mean value of 0.173 cmol kg^{-1}. Highest value of K$_X$ was observed in soil number S8, while lowest value was recorded in soil number S1. The soil number S1 to S6 contained relatively the higher values of K$_X$ as compared to the soil number S7 to S12. The results are in contrary to the observations of Patra et al. (2007) in the acidic Inceptisols and Dhillon et al. (1986) in the alluvial soils who reported comparatively the lower and higher values of K$_X$, respectively. The contribution of K$_X$ towards K$_L$ varied from 15.5 to 77.2% (Table 3).

The coefficients of correlation showed that K$_X$ had significant

Table 4
Coefficients of correlation between Q/I parameters and selected soil properties and forms of soil K$^+$.

Parameter	Clay	Silt	Sand	pH	CEC	Organic C	Water soluble K$^+$	Exchangeable K$^+$	Available K$^+$	NexK$^+$	Lattice K$^+$	Total K$^+$
AR$_e^{OK}$	0.353	0.094	−0.263	0.836***	0.689**	0.455	0.945***	0.968***	0.966***	0.953***	0.898***	0.902***
K$_0$	0.422	0.100	−0.305	0.786**	0.693**	0.480	0.908***	0.932***	0.930***	0.909***	0.806***	0.812***
K$_X$	−0.235	0.126	0.033	−0.649*	−0.750**	−0.504	−0.787**	−0.851***	−0.841***	−0.803***	−0.728**	−0.732**
K$_L$	0.215	0.474	−0.475	−0.055	−0.434	−0.276	−0.165	−0.272	−0.253	−0.215	−0.247	−0.246
PBC^K	−0.249	−0.009	0.143	−0.805***	−0.818***	−0.655*	−0.835***	−0.786**	−0.797**	−0.798**	−0.779**	−0.783**
K$^+$-potential	0.152	0.084	−0.147	−0.113	−0.249	−0.198	−0.102	−0.032	−0.045	−0.027	−0.186	−0.183
−ΔG	0.239	−0.002	−0.129	0.854***	0.691**	0.603*	0.792**	0.786**	0.789**	0.870***	0.736**	0.742**

*, ** and *** indicate significant at 5, 1 and 0.1% probability level, respectively; Nex: non-exchangeable.

Table 5
Coefficients of correlation between Q/I parameters and K^+ availability indices (K^+-saturation and NH_4OAc-K^+) and their interrelations.

Parameter	NH_4OAc- K^+	K_0	K_X	K_L	AR_e^{0K}	PBC^K	K^+-potential	$-\Delta G$
K_0	0.930***							
K_X	−0.841***	−0.911***						
K_L	−0.253	−0.267	0.635*					
AR_e^{0K}	0.966***	0.962***	−0.918***	−0.368				
PBC^K	−0.797**	−0.672*	0.648*	0.281	−0.768**			
K^+-potential	−0.045	0.237	−0.109	0.229	0.034	0.514		
$-\Delta G$	0.789**	0.817***	−0.723**	−0.169	0.842***	−0.800**	0.007	
K-saturation	0.952***	0.861***	−0.718**	−0.114	0.914***	−0.671*	0.026	0.717**

*, ** and *** indicate significant at 5, 1 and 0.1% probability level, respectively.

negative correlation with soil pH, CEC, available and reserve forms of soil K^+. There was a highly significant and positive correlation of K_X with K_L and PBC^K and highly significant and negative correlations with AR_e^{0K}, $-\Delta G$ and K^+ saturation percentage. Similar relations have been communicated by Patra et al. (2007) for K_X versus K_L; Jagadeesh et al. (2005) for K_X versus PBC^K and Diatta et al. (2006) for K_X versus soil K^+ fractions.

3.3.7. Potential buffering capacity of potassium (PBC^K)

The slope of the linear portion of the Q/I plots represents the PBC^K of the soils against the depletion of K^+ through crop removal and leaching losses. The PBC^K values fluctuated from 16.2 to 85.7 $cmol\,kg^{-1}\,(mol\,L^{-1})^{-1/2}$. Highest and lowest value of PBC^K was recorded in soil number S1 and S6, respectively. The soil number S6 and S8 contained less than 25 $cmol\,kg^{-1}\,(mol\,L^{-1})^{-1/2}$ of PBC^K values; soil number 4, 5, 7, 9, 10, 11, 12 possessed PBC^K values within limit of 26–50 $cmol\,kg^{-1}\,(mol\,L^{-1})^{-1/2}$ whereas soil number 1, 2, 3 recorded greater than 51 $cmol\,kg^{-1}\,(mol\,L^{-1})^{-1/2}$ of PBC^K values. The PBC^K values obtained were competitive with the values reported by Bandyopadhyay et al. (1985) in some selected coastal soils.

PBC^K had significant and negative correlation with soil variables like pH, CEC, organic C, available K^+ and reserves K^+ and Q/I parameters like K_0, AR_e^{0K}, $-\Delta G$, and percent K^+ saturation and significant positive correlation with K_X. Similar relations have been reported by Jagadeesh et al. (2005) for PBC^K versus K_X and AR_e^{0K}. There was no significant positive relationship between PBC^K with any of the soil parameters studied.

3.3.8. Potassium potential

The K^+ potential is the product of K_0 and PBC^K to define quantity and intensity in a single parameter. The values of K^+ potential ranged from 2.38 to 10.76 $cmol\,kg^{-1}\,(mol\,L^{-1})^{-1/2}$. Highest value was recorded by S9 soil and lowest value by S6 soil. None of the soil variables, different K^+ forms and Q/I parameters had significant relations with K^+ potential. This corroborated with the results of Dutta and Joshi (1990) who also did not find any correlation between K^+ potential and available forms of soil K^+.

3.3.9. Free energy of potassium exchange ($-\Delta G$)

The free energy of K^+-(Ca^{++}+Mg^{++}) exchange as expressed by $-\Delta G$ ranged from −5533 to −2906 $cal\,mol^{-1}$. Highest value of $-\Delta G$ was found in S1 soil, while lowest was recorded by S12 soil. The results are in line with the findings of Bandyopadhyay et al. (1985) for the coastal soils; Jagadeesh et al. (2005) for hill and coastal soils and Patra et al. (2007) for the acidic Inceptisols. According to the critical limit for $-\Delta G$ set by Woodruff (1955), five soil samples (soil no. 1–5) were likely be deficient in available K ($< -3500\,cal\,mol^{-1}$) and the plants are expected to respond to K^+ fertilization. The remaining seven soil samples (soil no. 6–12) were rated as optimum in respect of available K^+(-3000 and $-2500\,cal\,mol^{-1}$) and plants may not respond to K^+ fertilization.

The energy of K^+ exchange was significantly and positively

correlated with soil pH, CEC, organic C, available and reserve forms of soil K^+. There was significant positive correlation between $-\Delta G$ and pH. There were strongly significant and positive correlations of $-\Delta G$ with K_0, AR_e^{0K} and K^+ saturation percentage and significant and negative correlations with K_X and PBC^K. Abaslou and Abtahi (2008) also found a similar relationship of $-\Delta G$ with AR_e^K, K_0 and PBC^K.

4. Discussion

4.1. Potassium fertility of soil

The soils examined were acidic to mildly alkaline in reaction. The high electrical conductivity of the soils might be due to the high contents of chlorides and sulfates salts of Na^+, K^+, Ca^{++} and Mg^{++}. The soils were low to high in available K^+ (Dutta et al., 1966) and medium to high in non-exchangeable K^+(Subba Rao et al., 1993) with substantial quantities of lattice K^+ and total K^+. The variability of labile and non-labile K^+ and fixed K^+ contents in the soils was probably due to the variations in the physical and chemical environment, differences in K^+-bearing minerals, presence of K^+ containing salts like KCl and K_2SO_4 and cropping history. Fairly high values of non-labile non-exchangeable K^+, fixed K^+ and total K^+ reserves in the soils were ascribed to the abundance of potash-bearing primary silicate minerals such as feldspar and muscovite in light and heavy fractions of sand and illitic minerals in clay particles (Ghosh and Datta, 1974; Adhikari et al., 1987; Bandyopadhyay et al., 2003). The low values of different fractions of K^+ in soil S1 and S3 indicate that the soil clay minerals were likely to be depleted in varying magnitudes.

4.2. Potassium quantity and intensity in soil

The quantity factor (Q) indicates the soil K^+ reserves of non-exchangeable K^+. There were distinct differences in the adsorption and desorption of applied K^+ indicating the magnitude of variations in K^+ retention capacity of the soils. The early curtailment of desorption of K^+ in soils S1 to S6 with applied K^+ as compared with soils S7 to S12 implies that the former groups of soils have more adsorptive capacity for K^+ than the latter, presumably due to low contents of labile and non-labile K^+ reserves. With maximum level of applied K^+ the variable adsorption of K^+ in the soils indicates low to moderate fixation of added K^+. The moderate to heavier soil texture, higher CEC, variability of easily and moderately replaceable K^+ forms and higher K^+ saturation percentage are likely to maintain the desorption and adsorption phenomenon in the equilibrium solutions in the soils provided with various K^+ concentrations.

The activity ratio of K^+ (AR_e^K) in equilibrium solutions provides a satisfactory estimate of K^+ availability in soil. These differences in activity ratio of K^+ (AR_e^K) in soils could be attributed to the differences in the K^+ concentrations of equilibrating solutions, period of equilibration, the Ca^{++} and/or Mg^{++} contents, and probably due to the differences in the mineralogical make up of the soils (Yawson et al., 2011).

4.3. Equilibrium potassium activity ratio

The AR_e^{OK} is a measure of the immediate available K^+ to plants. Higher AR_e^{OK} values are associated with higher ionic strength of K^+ in solution and thus higher availability of K^+ to plants relative to Ca^{++} and Mg^{++} cations (Beckett, 1964a, 1964b). In general the AR_e^{OK} value was relatively higher in soils with higher amounts of exchangeable and non-exchangeable K^+ and lower in the case of soils with lower amounts of exchangeable and non-exchangeable K^+ (Jagadeesh et al., 2005). Since these coastal soils are dominant with illitic clay minerals (Ghosh and Datta, 1974; Bandyopadhyay et al., 1985; Adhikari et al., 1987; Sanyal, 2000), the comparatively lower amounts of AR_e^{OK} in some soils could be attributable to a greater number of specific K^+ sites, which could fix K^+ (Abaslou and Abtahi, 2008). The high values in most of the soils suggest that adsorbed K^+ was primarily held at planar positions and thus have greater K^+ supply intensity and so more K^+ may be absorbed by plants instantaneously. However, there is a possibility of K^+ leaching as the study area is under high rainfall zone. As the soils were adequately enriched with labile K^+ and non-labile pool of K^+ with high AR_e^{OK} values, no immediate crop response to K^+ fertilization is expected unless intensive cropping and leaching deplete the readily available K^+ (Patra et al., 2007). On the other hand, the S1 soil with low amounts of labile K^+ and non-labile K^+ with low AR_e^{OK} may respond to K^+ fertilization even for the current crops. In such cases, frequent application of K^+ fertilizer at lower dose in the K^+-depleted soils could be advocated.

Highly significant and positive correlation of AR_e^{OK} with soil pH and CEC suggests that increase in pH and CEC resulted in increased amount of AR_e^{OK} in the soils. The highly significant positive correlation between AR_e^{OK} and non-exchangeable K^+, lattice K^+ and total K^+ indicate their significant contribution towards enrichment of AR_e^{OK} in the soils. Besides, there were significant positive correlation of AR_e^{OK} with K_0 and K^+ saturation percentage and significant negative correlation with K_X which indicates that AR_e^{OK} values depend upon the K_0 and K^+ saturation percentage status of the soils. Lower number of specific sites for K^+ adsorption with less ability of the soils to supply K^+ over an extended period of time might have encouraged the higher values of AR_e^{OK} in the soils for adequate plant K^+ nutrition.

4.4. Labile potassium

This high value of labile K^+ (K_L) in the soils may be attributed to the higher amounts of clay, CEC, non-exchangeable K^+ and amount of loosely bound K^+ ions in exchangeable site (Samadi, 2006; Jagadeesh et al., 2005). This thereby indicates the dependence of K_L on these soil attributes and K^+-forms. High values of labile K^+ due to a greater K^+ release in the soil solution resulted in an increase in availability of K^+ to plants.

The higher values of K_L than the NH_4OAc extractable K^+ indicates that K^+ in some of these soils should be released basically via solubility or diffusion processes than exchange (Abaslou and Abtahi, 2008). This also implies that any addition of K^+ through K^+ fertilization practices in these soils could result a significant partition of K^+ to the soil exchangeable portion. On the other hand, the higher values of NH_4OAc extractable K^+ than the labile K^+ (K_L) was probably due to the fact that part of the exchangeable K^+ was not subjected to the ion exchange equilibrium as described by immediate Q/I relations (Beckett and Nafady, 1967; Subba Rao et al., 1984). These soils have a strong capacity to adsorp K^+ on the clay colloids (Nash, 1971). This was likely since the clay contents of these soils are relatively high and being dominated by illite minerals (Ghosh and Datta, 1974; Sanyal, 2000). The number of specific K^+ sites in clay colloids as measured by K_X was also appreciable. In these categories of soils, K^+ should be released basically via exchange than solubility or diffusion processes (Diatta et al., 2006). Such soil reaction with K^+ was unexpected, since soils were characterized by relatively high K^+ saturation. This implies that

most soil retention sites were predominantly occupied and any additional K^+ (from fertilization practices) input in these soils could result in a significant partition of K^+ to the soil solution, i.e. a strengthened K^+ availability for plants.

The non-significant correlations of K_L with the soil parameters or forms of soil K^+ indicate that the selected soil variables and K^+-forms did not play any role in the contribution of K_L, rather K^+ dynamics in these soils might be controlled by soil mineral constituents (Diatta et al., 2006; Abaslou and Abtahi, 2008).

4.5. Non-specific and specific sites potassium

The higher values of non-specific sites K^+ (K_0) in the soil number S7 to S12 compared with the soil number S1 to S6 might be due to the predominance of exchangeable K^+ and non-exchangeable K^+ contents in these soils. The appreciable variations in the contribution of K_0 towards K_L (22.8–84.5%) could be attributed more to the available forms of K^+ and thus any change in the amounts of available K^+ due to intensive cropping or leaching loss should induce significant changes in the non-specific sites K^+. On the contrary, the higher values of K_X obtained in soil number S1 to S6 as compared with soil number S7 to S12 suggest that K_X in the soils was preferably associated with K_0 and AR_e^{OK} values and any change of the quantum of these parameters might have reflection of the adsorption of K^+ on the high energy specific sites instantaneously. The variability in the specific or selective adsorption of K^+ on the exchange sites of soil colloids was probably due to the variation in the specific surface area of the soil colloids and the type and composition of the K^+-bearing minerals.

Highly significant and positive correlation of K_0 with pH, CEC, available and reserves K^+ implies that each soil variable and soil K^+ form had a contributory role in determining the magnitude of K_0 values in the soils. The correlation values indicates that the soils with high K^+ intensity (AR_e^{OK}) and high PBC^K values and relatively higher clay, silt and organic carbon contents resulted in selective preference for K^+ adsorption to non-specific planar sites of these soil constituents, thereby leading to possible losses of K^+ through leaching and crop removal. The significant negative correlation of K_X with soil reserves K^+ indicates that specific type of clay minerals might have a significant bearing on the magnitudes of K_X in these soils.

4.6. Potential buffering capacity of potassium

PBC^K is a measure of the ability of soil to maintain the intensity of K^+ in the soil solution. The differences in PBC^K values in soils could be attributed to the differences in past cropping and management practices (Yawson et al., 2011) and clay mineralogical characteristics (Diatta et al., 2006). High PBC^K values are a measure of constant availability of K^+ in the soil solution over a long period. Conversely, low PBC^K values suggest the need for frequent K^+ fertilization practices (LeRoux and Summer, 1968). Removal of adsorbed K^+ from non-specific planar surface sites by cropping increases the potential buffer capacities, indicating that higher energy sites become involved as the number cropping increased (Abaslou and Abtahi, 2008). The soils with high PBC^K values were associated with lower K^+ saturation and low soil pH which is indicative of higher potential to replenish K^+ concentration in soil solution (Arnold, 1978). Conversely, low PBC^K values may be attributed to higher content of mica (illite) and high K^+ saturation (Munn and Mclean, 1975), indicating the low K^+ supplying capacity of these soils and may fail to mitigate crop K^+ requirement even when a single crop is considered. There is a need of K^+ fertilization practices at regular interval in these soils to sustain crop K^+ nutrition (Idigbor et al., 2009).

The lack of significant positive relationship between PBC^K with soil parameters may be attributed to the relatively high variations in the physicochemical properties of the soils studied, which resulted in inconsistent PBC^K values.

4.7. Potassium potential

It is an essential indicator of K$^+$ availability in soil solution. In general, the soils which have the higher K$^+$ potential, K$_0$ have the lower preference for specific adsorption of K$^+$. This means, on equilibration, more K$^+$ is released from non-specific planar sites, leading to higher PBC^K values. Conversely, high K$^+$ saturation can lead to lower PBC^K (Munn and Mclean, 1975; Diatta et al., 2006; Abaslou and Abtahi, 2008). The non-significant relationships of K$^+$ potential with the soil variables, different K$^+$ forms and Q/I parameters may be due to the fact that the content of K$^+$ associated with K$_0$ and PBC^K is the function of nature and amount of clay minerals.

4.8. Free energy of potassium exchange

In general, the higher free energy change of K$^+$ exchange ($-\Delta G$) in soils was found to be associated with lower K$^+$ saturation and less availability of easily extractable K$^+$. The significant positively correlation of $-\Delta G$ with soil pH, CEC, organic C, available and K$^+$ reserves indicates that increase in these physicochemical and soil K$^+$ parameters resulted in increase in $-\Delta G$ values in the soils. The significant positive correlation between $-\Delta G$ and pH implies that less energy is needed to remove 1 mol of K$^+$ from solution as pH increases (Yawson et al., 2011). This could also suggest that lower concentrations of K$^+$ in equilibrium solution are easily displaced than higher concentrations whereas much energy is required to release K$^+$ from K$^+$ reserves as PBC^K decreases.

5. Conclusions

The selected salt affected soil samples showed wide variation in the physicochemical properties, particularly texture, pH, EC, CEC, organic carbon, exchangeable and reserves K$^+$. The quantity-intensity (Q/I) approach for evaluating K dynamics in these coastal soils has provided a tool to predict K$^+$ availability to plants. The Q/I components such as labile K$^+$ (K$_L$), equilibrium activity ratio for K$^+$ (AR$_e^{0K}$) and potential buffering capacity of K$^+$ (PBC^K) could serve as better indices of K$^+$ availability in the soils. However, in some of the soils, part of the exchangeable K$^+$ was not subjected to the ion exchange equilibrium. About half of the studied samples enriched with higher solution K$^+$ activity, K$^+$ saturation percentage in the adsorbed phase and lower PBC^K values along with labile and non-labile K$^+$ reserves might sufficiently support cropping for a long period without any threat of K$^+$ shortage. The remaining samples with relatively lower pool of labile and non-labile K$^+$, less solution K$^+$ activity and K$^+$ saturation percentage will require frequent K$^+$ fertilization to moderate the further drop of soil available K$^+$. However, such an approach will ease the assessment of K$^+$ dynamics in saline soils and make significant practical contribution to operational K$^+$ management.

Acknowledgements

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