RESEARCH ARTICLE

Quantity-to-intensity (Q/I) relationships can efficiently characterize intensively cultivated agricultural soils in Bangladesh for better potassium supplying capacity

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Abstract

Aim of study: Firstly, to evaluate the K dynamics of soils through a quantity-intensity isotherm study; and secondly, to characterize the soils on the basis of quantity-intensity (Q/I) parameters.

Area of study: Gazipur, Bangladesh

Material and methods: Eleven soils collected from major agro-ecological zones in Bangladesh were evaluated for their varying K dynamics parameters, and K supplying capacities of these soils were described.

Main results: The Q/I plot showed both linear and polynomial relationships for soils in the study. The eleven soils had labile K ranging from 0.022 in Palashbari clay loam to 1.35 cmol kg^{-1} in Barisal clay. The latter soil had the highest equilibrium K activity ratio (0.003 mol L^{-1})$^{1/2}$ and potential buffering capacity (PBC) (460.4 (cmol kg^{-1}) (mol L^{-1})$^{1/2}$). The PBC of soils for non-exchangeable pool (PBCne) was much higher than that of exchangeable pool (PBCe) in most soils. The largest amount of PBCne and PBCe occurred in Barisal clay, Gopalpur clay, Jhalokathi clay and Nachol loam which had a higher K desorption rate than all the other soils. The equilibrium exchangeable K, critical exchangeable K and equilibrium solution K of the soils varied widely (0.0006-0.035, 0.06-0.61 and 0.06-0.604 cmol kg^{-1}, respectively). The added K was converted almost equally for the respective soils, with specific reference to the respective exchangeable and non-exchangeable pool for Barisal clay and Nachol loam.

Research highlights: All the studied parameters revealed wide variations among the soils. The linear and polynomial relationships for soils can efficiently characterize intensively cultivated soils in Bangladesh.

Additional key words: inceptisols; intensive cropping system; K dynamics; K recommendations; Q/I isotherm study

Abbreviations used: AEZ (agro-ecological zone); AR^K (activity ratio for K); CK$_f$ (final solution K); CKi (initial solution K); CK$_0$ (equilibrium solution K); CK$_r$ (critical solution K); CR$_0$ (equilibrium K concentration ratio or activity ratio); EK (exchangeable K); EK$_f$ (final EK); EK$_0$ (equilibrium EK); EK$_r$ (critical EK); Emin (minimum EK); K^0 (labile K); NEK (non-EK); PBC (potential buffering capacity); PBCe (K buffering capacity for exchangeable pool); PBCne (K buffering capacity for non-exchangeable pool); PBCt (potential buffering capacity total); TK (total K); α (magnitude of the conversion of added K to exchangeable pool); β (magnitude of the conversion of added K to non-exchangeable pool); Φ (initial disequilibrium of soil solution, an initial constraint)

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Introduction

Crops take up abundant amounts of potassium (K) from soils, which is buffered by rapidly exchangeable forms of K. Bangladesh, India, China and other countries in South and South-East Asia are currently experiencing a lot of K depletion due to the incessant harvesting of crops and indiscriminate use of fertilizers (Dobermann *et al.*, 1998; Jiyun *et al.*, 1999; Hasan, 2002; Islam *et al.*, 2017). Submerged rice soils (Islam *et al.*, 2017), highly weathered and coarsely textured soils (Dobermann *et al.*, 1998), illitic soils in alluvial and micaceous soils (Tiwari, 1985; Jalali, 2007) and vermiculitic clay soils of central Luzon, Philippines (Oberthuer *et al.*, 1995) have major K deficiencies. The cultivation of hybrids and modern varieties with high yielding capacity is removing large amounts of K which sometimes dominates phosphorus (P) or even nitrogen (N) uptake from the soil (Liu *et al.*, 2009; Sharma *et al.*, 2013; Islam & Muttaleb, 2016). Furthermore, soils containing inherently small amounts of K and low supplying capacity, and soils cultivated with no or insufficient K fertilizer have shown K deficiency (Dobermann *et al.*, 2003; Zhu *et al.*, 2019). In Bangladesh, application of K amounts to only 27% of the total removal by rice-wheat cropping systems (Saunders, 1990). The general recommendation for rice − to apply on average 80 kg ha^{-1} of K (BARC, 2012) − seems to be low in many soils which obtain a negative balance of K. Farmers generally rely mostly on the application of nitrogen fertilizers. They remove crop residues from the field on the one hand and apply less K fertilizer on the other. Both degenerative practices deteriorate soil fertility and lead to potassium deficiency in soils.

There are four different forms of K (solution, exchangeable, non-exchangeable and mineral K), which remain in equilibrium with each other (Selim *et al.*, 1976; Johnston & Goulding, 1990). The intensity, capacity or quantity (Q) and renewal rate of K in the soil solution determine the availability of K to plants, while the renewal rate depends on, among other factors, the capacity/quantity of K (Claasen *et al.*, 1986; Jimenez & Parra, 1991). K concentration ratio (CR) explains the intensity of K in the presence of Ca and Mg. The ammonium acetate (NH$_4$OAc) extraction method of K which is undertaken in some countries including Bangladesh (Saleque *et al.*, 2009; Islam *et al.*, 2017), cannot generate enough K to satisfy crops, because this reagent may extract only exchangeable portion of K, which is mostly pH dependent. Furthermore this method may not properly determine the level of exhaustion of soil K involving crops, and consequently deficiency increases in soils under rice-based intensive cropping systems. Potential buffering capacity of K (PBCt) is the potentiality of a soil to supply labile K at a given energy level. Soils with low PBCt deplete K faster than those with higher PBCt and vice versa.

Saleque *et al.* (2009) reported that higher PBCt soils may supply K in soil solution for a longer period of time than lower ones. However, a soil with low PBCt might not respond to K fertilizer if the soil contains large quantities of K-bearing minerals that could release K to exchange sites and also to solution (Sparks & Huang, 1985). Cropping for several years without K application may change the PBCt and Q/I relationship of a soil (Bertsch & Thomas, 1985). In order to characterize K supplying power of soils under intensive cultivation, the PBCt of K could be an important indicator.

Accordingly, exchangeable/extractable K may not indicate a soil's capacity to supply K under intensive cropping conditions (Rupa *et al.*, 2001; Jalali, 2007). To better understand the K fertility status and its capacity to be supplied to agricultural soils in a wide context; it is imperative to study the ionic equilibrium relationships of the nutrient. Since a major role of exchangeable K is to replenish soil solution K which has been removed by cropping or lost by leaching, defining the relationship between exchangeable K (Q for quantity) and the activity of K in soil solution (I for intensity) is very important (Beckett, 1964a; Evangelou *et al.*, 1994; Saleque *et al.*, 2009). The equilibrium activity ratio (CR$_0$) in the soil solution can be used to measure K availability. The uptake of K$^+$ by plants from soil solution depends on cations like calcium (Ca^{2+}) and magnesium (Mg^{2+}) (Evangelou *et al.*, 1994), which rapidly exchange K$^+$ electrostatically to the clay micelle and humic substance surfaces (Sparks, 1987).

Predicting accurately the available K$^+$ supplied by the soils has been a problem over a long period of time (Islam *et al.*, 2017). Beckett (1964a) developed a tool for investigating the Q/I relationship with the intensity (K concentration in solution) *vs.* quantity (exchangeable K$^+$) function, based on Schofield's ratio law. The Q/I approach has been useful in understanding, characterizing and evaluating the K$^+$ fertility status of soils (Wang & Scott, 2001). The classical Q/I curves are related to the change in exchangeable K to ascertain the effect of quantity on intensity. The Q/I relationship quantitatively refers to the amount of adsorbed forms of an ion required for the chemical potential of that ion in the equilibrium solution. Since its first application to soil K by Beckett (1964b), the Q/I relationship has been studied by many scientists to evaluate the availability of K (Beckett & Nafday, 1967; Evangelou *et al.*, 1994; Wang *et al.*, 2004; Jalali & Kolahchi, 2007; Saleque *et al.*, 2009). However, our understanding of the application of K to the intensively cropped soils of Bangladesh is still very limited.

The Q/I curve is constructed by plotting the change of exchangeable K (ΔK), against the potassium CR. The Q/I relationship helps to predict the PBCt of soil, which is an important fact of crop nutrition (Wang *et al.*, 2004; Islam *et al.*, 2017). The quantity factor (ΔK) and the intensity factor (CR) provide a better understanding of the soil's

ability to supply K than either the available K or the ionic activity ratio of K. Sparks & Huang (1985) described the use of a Q/I plot for interpreting soil's K chemistry. Beckett (1964a) proposed a PBCt with respect to K by combining the quantity and intensity factors in one parameter. Incorporation of soil buffer properties into a soil-testing program enhances accuracy of soil tests in predicting K availability (Nair *et al.*, 1997).

Different soils show the same value of activity ratio for K (AR^K) and may not possess the same capacity for maintaining AR^K while K^+ is removed by plant roots (Beckett, 1964a). These findings brought about the classic Q/I curves where the ratio of $^aK/(^aCa + ^aMg)^{1/2}$ is linked to the change in exchangeable K^+ so that the effect of quantity (exchangeable K) on intensity can be documented. For Q/I relationships to be valid in indicating the amount of soil K available for plant uptake during the growing period, they must not be affected by the amount of K normally released, fixed or added during the growing season. These assumptions were proved by a number of scientists (Beckett *et al.*, 1966; Beckett & Nafady, 1967). For soils that were cropped for a long time without K fertilization (Beckett & Nafady, 1969; Islam *et al.*, 2017), the Q/I relationships were not greatly affected by K^+ removal. However, cropping for several uninterrupted years without K application may change the Q/I relationship of a soil (Bertsch & Thomas, 1985) and PBC may also be changed accordingly (Saleque *et al.*, 2009). These dynamics need to be explored in soils of intensively grown rice-upland cropping systems.

Various attempts have been made to characterize the relationship between intensity and capacity of soil K or soil K buffering characteristics (Evangelou *et al.*, 1994; Nair, 1996; Wang *et al.*, 2004; Jalali & Kolahchi, 2007; Saleque *et al.*, 2009; Uddin, 2009). The Q/I curve can be used to obtain the following K fertility indices: the equilibrium K concentration ratio (CR_0), amount of adsorbed or released (ΔK), labile K (absolute value of ΔK^0), equilibrium exchangeable K (EK_0), degree of conversion of solution K to exchangeable K (α), PBCt, minimum exchangeable K (Emin), and initial disequilibrium of soil solution (Φ), etc. (Saleque *et al.*, 2009). Such parameters for understanding the K dynamics of intensively cropped soils in the major agro-ecological zones of Bangladesh remain scarce.

For this reason, efforts have been made to document the K dynamics for a range of soils through Q/I isotherm studies. Attempts have also been made to characterize those soils on the basis of Q/I parameters for understanding K fertility management under intensive crop cultivation conditions. Therefore, the objectives of this experiment were to: (i) study the K dynamics of soils through quantity-intensity isotherm studies; and (ii) characterize the soils on the basis of Q/I parameters so that K fertility management under intensive crop cultivation is better understood.

Material and methods

Soils for the study

Eleven sites of Bangladesh were selected on the basis of initial K status (low, medium, optimum and high) during 2010-2011 (Fig. S1 [suppl.]). Floodplain and terrace soils were collected because crops are grown intensively in these soils. Calcareous, non-calcareous and tidal soils were collected from the floodplain zone, while both grey terrace and red terrace soils were collected from the terrace category. Five soil samples (0-15 cm) were collected from all selected eleven sites (Table 1) and mixed together thoroughly to make a composite sample. From each sampling site, the samples were collected maintaining the same topography mostly medium high land during fallow period (turnaround time to go for the next crop). Distance (roughly 100 to 400 m) from five individual samples maintained on the basis of topography and land size of the dominant cropping patterns of the locality making representative soil for certain location. The samples were collected (February, 2011) from intensively crop cultivated farmers' fields, which are considered as being representative of the particular location under certain agro-ecological zones (AEZ). Therefore, there were in total 55 soil samples for the chosen eleven locations, and these samples were composited to make 11, which is an ideal size for conducting comprehensive Q/I studies (Shil *et al.*, 2016). For isotherm Q/I studies in the laboratory, each sample was replicated in twice for making sure statistical analysis and interpretation.

Collected soil samples were air-dried, powdered with a wooden mallet and passed through a 2 mm sieve. The samples were then analyzed for texture, pH, organic carbon, cation exchange capacity (CEC), and exchangeable cations (K^+, Ca^{2+}, Mg^{2+}, Na^+). Particle size distribution was determined utilizing the hydrometer method (Bouyoucos, 1962) and the textural class was determined from Marshall's triangular coordinate following the USDA system. The pH level was ascertained by glass electrode meter using a soil:water ratio of 1:2.5 (Page *et al.*, 1982). CEC was determined by the Schollenberger (1980) method. Exchangeable bases were extracted with 1 M NH_4OAc solution as described by Thomas (1982). Name of the soil, location, geographical position, agro-ecological zones with soil taxonomy of the soils collected for this study are summarized in Table 1. The most relevant physical and chemical properties of the soils are documented in Table S1 [suppl.].

Soil sample preparation, analyses and determination of quantity/intensity (Q/I) relationships

Potassium Q/I isotherm studies were conducted according to the procedure devised by Beckett (1964b)

Table 1. Site description of the selected eleven soils (Bangladesh) under study

Soil No.	Name of the soil and abbreviation		Location	Geographical position	Agro-ecological zone (AEZ)	Soil taxonomy
1	Amnura loam	AL	Birgonj, Dinajpur	25.938 N 88.755 E	Old Himalayan Piedmont Plain (AEZ 1)	Albaquept
2	Palashbari clay loam	PCL	Sonatola, Bogura	25.1975 N 89.465 E	KaratoyaBangali Floodplain (AEZ 4)	Albaquept
3	Nachol loam	NL	Godagari, Rajshahi	24.7408 N 88.7583 E	High Barind Tract (AEZ 26)	Eutrochrepts
4	Sara loam Pabna	SLP	Ishurdi, Pabna	24.104 N 89.233 E	High Ganges River Floodplain (AEZ 11)	Eutrochrepts
5	Sara loam Kushtia	SLK	Bheramara, Kushtia	24.2425 N 89.1092 E	High Ganges River Floodplain (AEZ 11)	Eutrochrepts
6	Gopalpur clay loam	GCL	Ghop, Jashore	23.2939 N 89.48667 E	High Ganges River Floodplain (AEZ 11)	Haplaquepts
7	Barisal clay	BC	Benerpota, Satkhira	22.98 N 89.2003 E	Ganges Tidal Floodplain (AEZ 13)	Haplaquept
8	Jhalokathi clay	JC	Mirzagonj, Patuakhali	22.5803 N 90.3919 E	Ganges Tidal Floodplain (AEZ 13)	Haplaquept
9	Gopalpur clay	GC	Kanaipur, Faridpur	23.7311 N 90.0014 E	Low Ganges River Floodplain (AEZ 12)	Eutrochrepts
10	Chhiata loam	CL	Yugitola, Gazipur	24.2197 N 90.50778 E	Madhupur Tract (AEZ 28)	Aeric Haplaquepts
11	Silmondi clay loam	SCL	Madhupur, Tangail	24.63333 N 90.1903 E	Madhupur Tract (AEZ 28)	Haplaquepts

and later modified by Wang *et al.* (2004). There were 10 treatments representing 0, 2.5, 5, 7.5, 10, 15, 25, 50, 75 and 100 mg L^{-1} K. For the formulation of these treatments, 1000 mg L^{-1} K stock solution using KNO$_3$ was prepared. Then it was diluted with 0.01 M CaCl$_2$ solutions which were the required amounts for preparing the respective treatments.

For the adsorption study, 20 conical flasks (100 mL size) were used for duplication of each treatment. Then an equal amount (2.5 g) of soil sample was put into each conical flask. After that, 25 mL of K solution was added in each flask as per treatment. The prepared soil suspensions were shaken for 30 min using a mechanical shaker, allowed to equilibrate for 18 hours, and then centrifuged (10,000 rpm; 10 min). Subsequently, they were filtered using Whatman No.1 filter paper. The supernatant solutions were then analyzed for K, Ca, Mg and Na using Atomic Absorption Spectrophotometer (Chemito AA 203). The soil left in the centrifuge tube was transferred to the conical flask again carefully, making sure to not leave any trace of soil. For smooth removal of soil from the centrifuge tube, the required amount (25 mL for each sample) of 1 M NH$_4$OAc for the following desorption study was used. The suspensions were then shaken again for 30 min. Then they were filtered through Whatman No. 42 filter paper and analyzed for exchangeable K using the same instrument. All isotherm experiments were conducted at 15°C ± 2°C.

The final exchangeable K (EK$_f$) for each equilibrium point was calculated based on 1M NH$_4$OAc extraction at end of contact with CaCl$_2$ of each residue soil samples left after completion of isotherm study with different K treatments. Other parameters were estimated as follows:

$$\Delta K = (CK_i - CK_f)\left(\frac{v}{w}\right) \tag{1}$$

where CKi is the initial K concentration (added); CK$_f$ is the final equilibrium concentration of K in solution (CaCl$_2$ extracted); v and w are the solution volume (in mL) and soil mass (in g), respectively. Positive ΔK values indicate K adsorption by the soil solid phase, whereas negative values indicate K release from the solid phase into solution.

Potassium CR was used to describe the intensity of K in the presence of Ca and Mg as

$$CR = CK_f/(Ca_f + Mg_f)^{1/2} \tag{2}$$

where Ca$_f$ and Mg$_f$ are concentrations of Ca and Mg in final equilibrium solutions, respectively (Wang *et al.*, 1988). For the diluted solution (0.01 M CaCl$_2$), the activity coefficient was close to unity; therefore, the concentration of the equilibrium solution was assumed to be activity of these ions.

Following the procedure of Wang *et al.* (2004), the amount of total K adsorbed or released (ΔTK) during the isotherm experiment was partitioned into changes due to

exchangeable K (ΔEK) and non-exchangeable K (ΔNEK). Calculations of ΔEK and ΔNEK were:

$$\Delta EK = (EK_f - EK_0) \tag{3}$$

$$\Delta NEK = \Delta K - (EK_f - EK_0) \tag{4}$$

where EK_0 is the exchangeable K corresponding to ΔK=0, estimated from the linear regression equation of EK_f *vs* ΔK.

The change due to NEK was estimated from the difference between the total amount of K adsorbed and the amount of K re-extracted with 1 M NH₄OAC.

The changes in the amount of K adsorption or release by soil solids depend not only on the nature of soil solids, but also on the initial disequilibrium of soil solution K applied to the soil. The initial disequilibrium of soil solution applied to soil can be described by Φ, an initial constraint (Schneider, 1997 a, b, c), which is calculated as follows:

$$\Phi = (CK_i - CK_0)\left(\frac{v}{w}\right) \tag{5}$$

where CK_0 is the initial concentration corresponding to ΔK=0, and CK_i is the initial K concentration (added K).

Regression analysis was done to develop and understand the Q/I relationships. From Q/I studies, the following parameters were calculated for the characterization of K dynamics and soil's power to supply K (Fig. 1): (1) adsorbed K, (2) desorbed K, (3) percentage of applied K converted to exchangeable K, (4) percentage of applied K converted to non-exchangeable K, (5) equilibrium solution K, (6) critical solution K, (7) minimum exchangeable K, and (8) K buffering capacity (PBCt).

Statistical analysis

Least squares regression equations based on linear model (ΔK = α₁ + α₂CR) were used to develop the Q/I relationships between ΔK and CR (Wang *et al.*, 1988). Regression analysis was done with MS Excel software.

Results and discussion

Quantity-to-intensity (Q/I) relationships

The amount of total K adsorbed or released (ΔK) during the isotherm experiment was partitioned into
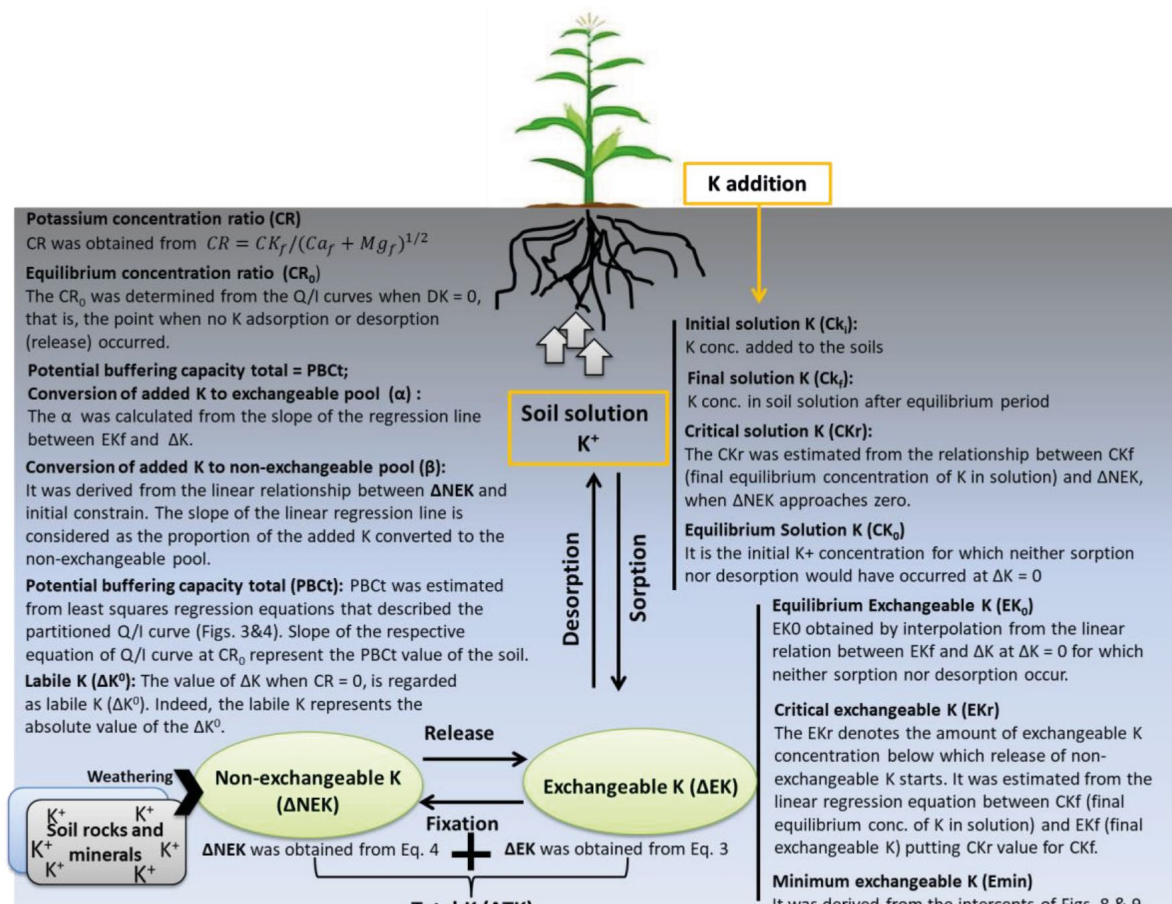

Figure 1. A graphic scheme showing all forms of potassium studied and how they were achieved

changes due to ΔEK and ΔNEK. The results of partitioned Q/I curves for the 11 studied soils at the 0-15 cm depth are presented in Figs. 2 and 3. The total quantity of K (ΔTK) was increased linearly with the increase in potassium CR for soils AL, PCL, SLP, CL and SCL, fitted well with the linear model having R^2>0.98, p<0.01 (Fig. 2). In contrary,

the rest of the six studied soils (NL, SLK, GCL, BC, JC and GC) showed quadratic relationship between ΔK and CR (Fig. 3). The relationship appeared to be highly significant (R^2>0.99, p<0.01) for all of the aforementioned soils. Positive significant relationship (R^2>0.98**) was also found between ΔEK and CR and also between ΔNEK
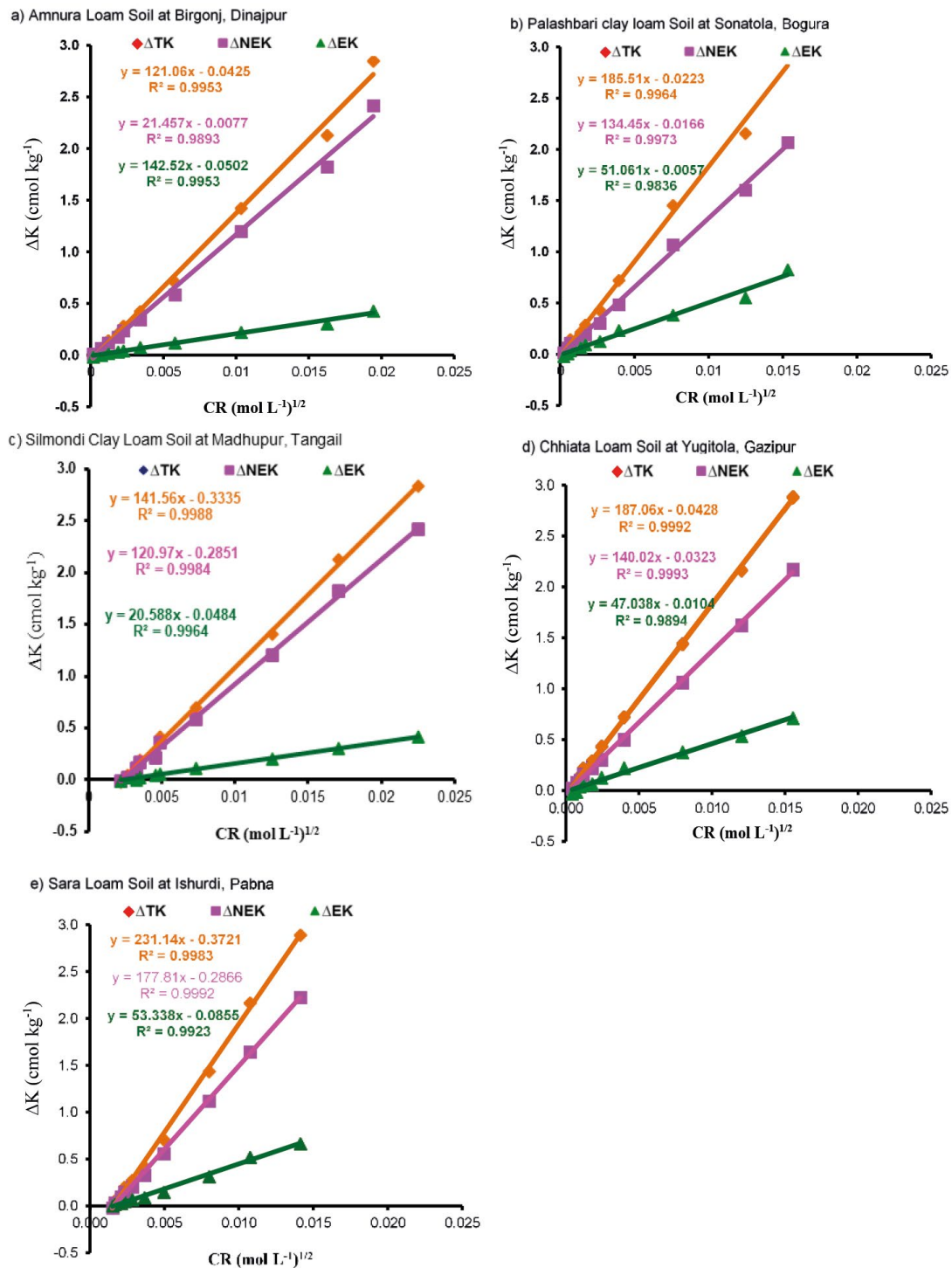

Figure 2. Partitioned quantity-to-intensity (Q/I) relationship for different soils of Dinajpur (Amnuraloam), Bogura (Palashbari clay loam), Tangail (Silmondi clay loam), Gazipur (Chhiata loam) and Pabna (Sara loam Pabna). TK= total K; NEK= non-exchangeable K; EK=exchangeable K; CR=potassium concentration ratio.
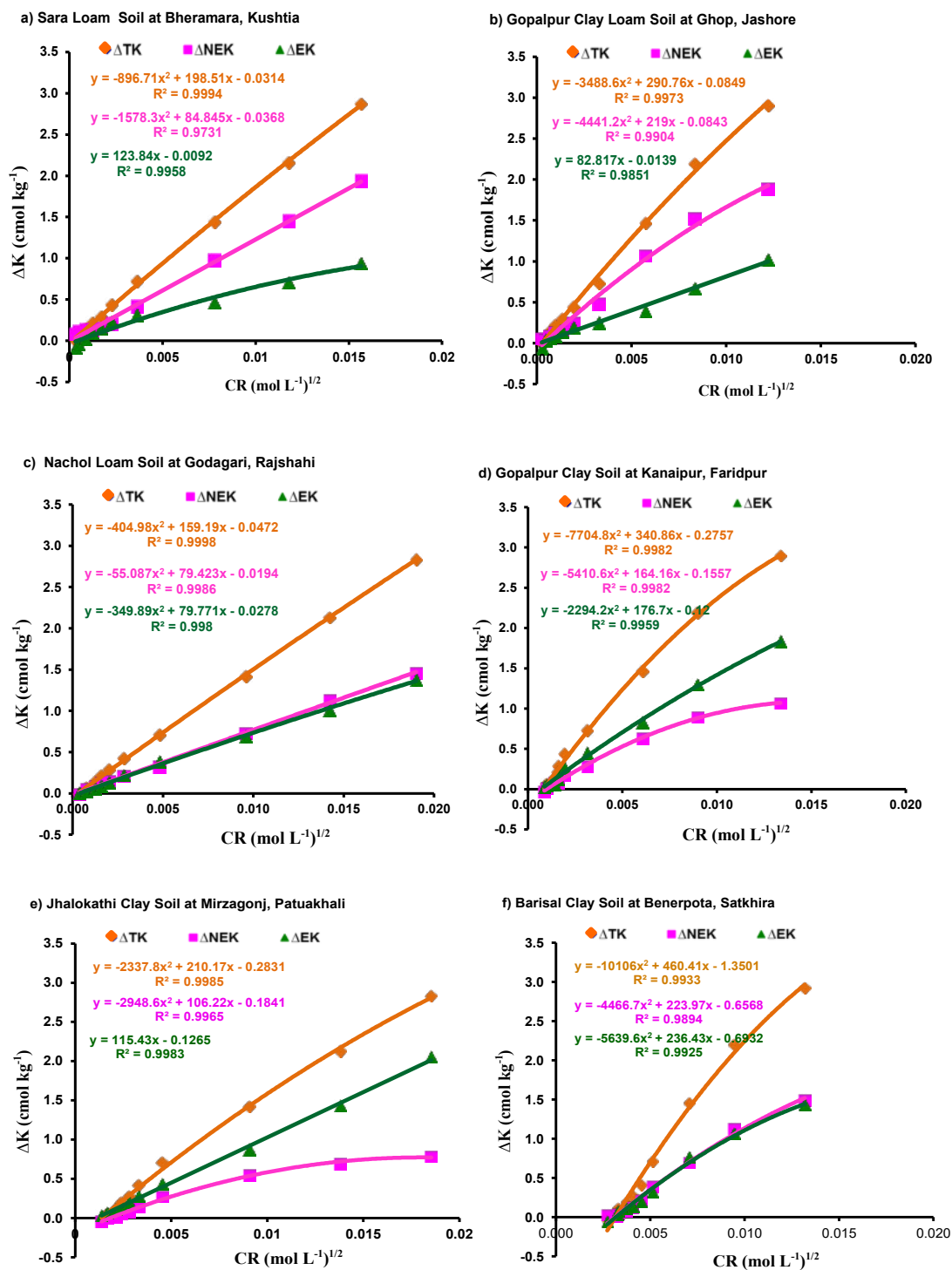
Figure 3. Partitioned Quantity-to-Intensity (Q/I) relationship for different soils of Kushtia (Sara loam), Jashore (Gopalpur clay loam), Rajshahi (Nachol loam), Faridpur (Gopalpur Clay), Patuakhali (Jhalokathi Clay) and Satkhira (Barisal Clay). TK= total K; NEK= non-exchangeable K; EK=exchangeable K; CR=potassium concentration ratio.

and CR. However, polynomial regression equation fitted well for all three pools of K (ΔTK, ΔEK and ΔNEK) for NL, BC and GC. The soils of GCL and JC showed a linear relationship between CR and ΔEK (R^2>0.99), again a linear relationship was also existed between CR and ΔNEK.

The quantity factor (ΔK) and the intensity factor (CR) provide a better understanding of the K supplying power of the studied soils than either the available K or the ionic activity ratio of K (Saleque *et al.*, 2009; Islam *et al.*, 2017). The diverse soils used in the present study indicated both linear and polynomial (quadratic) Q/I

relationships (R^2>0.98; *p*<0.01). Although the Q/I curve is a relatively unchangeable characteristic (Islam *et al.*, 2017), partitioning of the Q/I curve highlighted changes in soil K due to exchangeable pool (ΔEK) and non-exchangeable pool (ΔNEK) (R^2>0.98) (Wang *et al.*, 2004; Jalali & Kolahchi, 2007; Saleque *et al.*, 2009). A linear relationship was also discovered between ΔEK and CR and again between ΔNEK and CR (R^2>0.98). Soils of AL, PCL, SLP, CL and SCL showed increased ΔTK with the increase in CR. Saleque *et al.* (2009) and Islam *et al.* (2017) observed the existence of a linear relationship between ΔK and CR for Madhupur tract and Ganges floodplain soils, respectively, where they proposed the idea that the parameters of Q/I curve change with the depletion or replenishment of soil solution K, soil clay mineralogy, soil texture, CEC, cropping systems, etc. In contrast, the quadratic relationships as observed between ΔK and CR (R^2>0.99) for NL, SLK, GCL, BC, JC and GC were also found by Wang *et al.* (2004), Jalali & Kolahchi (2007) and Uddin (2009).

Potential buffering capacity of K (PBCt)

The slope of the Q/I curve indicates the potential buffering capacity (PBC) of soil. The soils exhibited different PBCt (Table 2), ranging from 142 to 460 (cmol kg^{-1}) (mol L^{-1})$^{1/2}$ with an average value of 232 (cmol kg^{-1}) (mol L^{-1})$^{1/2}$. The highest PBCt was obtained in BC, whereas the lowest PBCt was recorded in red terrace soil of Madhupur (SCL) which was similar to AL. The second highest PBCt, 341 (cmol kg^{-1}) (mol L^{-1})$^{1/2}$ was recorded in GC followed by GCL. The PBCne was much higher than that of PBCe except NL, BC, JC, and GC. The PBCne was 224, 164, 106 and 79.4 (cmol kg^{-1}) (mol L^{-1})$^{1/2}$ for BC, GC, JC and NL, respectively (Table 2). Similarly, PBCe accounted for 236 (cmol kg^{-1}) (mol L^{-1})$^{1/2}$ for BC, 176.7 (cmol kg^{-1}) (mol L^{-1})$^{1/2}$ for GC, 104 (cmol kg^{-1}) (mol L^{-1})$^{1/2}$ for JC, 84.9 (cmol kg^{-1}) (mol L^{-1})$^{1/2}$ for SLK and 79.8 (cmol kg^{-1}) (mol L^{-1})$^{1/2}$ for NL. As such the desorption rate of K regarding the aforementioned soils was higher than the rest of the soils being analyzed in this study.

The soil of BC has the highest PBCt, which is the potential of a soil to supply labile K at a given energy level. The second highest PBCt, 341 (cmol kg^{-1}) (mol L^{-1})$^{1/2}$ was recorded in GC followed by GCL, while the lowest PBCt was recorded in red terrace soil of Madhupur (SCL) and Dinajpur (AL). The results indicate that the PBCt was higher in the heavy textured soils than in the light textured soils, also suggesting that depletion of K by cropping will be faster in light textured soils than heavy textured ones (Sharma & Mishra, 1989). The high values of PBCt in clay textured soils of BC, GC and GCL are indicative of constant supply of K in the soil solution over a long period of time, whereas a low PBCt does suggest the need for frequent fertilizer application (Saleque *et al.*, 2009).

Table 2. Estimated potential buffering capacity of K (PBCt), labile K (ΔK$_0$), equilibrium exchangeable K (EK$_0$), equilibrium solution K (CK$_0$), and equilibrium K concentration ratio (CR$_0$) in major soils of Bangladesh

	Soil	PBCt (cmol kg^{-1}) (mol L^{-1})$^{1/2}$			Labile K (cmol kg^{-1})	CR$_0$ [4] (mol L^{-1})$^{1/2}$	EK$_0$ [5] (cmol kg^{-1})	CK$_0$ [6] (cmol L^{-1})
		ΔKt[1]	ΔKne[2]	ΔKe[3]				
1	AL	142.52	121.06	21.46	0.043	0.00035	0.06	0.0028
2	PCL	185.51	134.45	51.06	0.022	0.00012	0.109	0.00062
3	NL	159.19	79.42	79.77	0.047	0.00022	0.083	0.0024
4	SLP	231.14	177.81	53.34	0.37	0.0016	0.199	0.0179
5	SLK	198.51	123.80	84.84	0.031	0.00007	0.196	0.0006
6	GCL	290.80	219.00	71.80	0.085	0.00015	0.185	0.0005
7	BC	460.41	223.97	236.43	1.35	0.0029	0.604	0.035
8	JC	210.17	106.22	115.43	0.283	0.0011	0.232	0.0147
9	GC	340.86	164.16	176.7	0.276	0.0005	0.492	0.0055
10	CL	187.06	140.02	58.09	0.043	0.00023	0.081	0.0014
11	SCL	141.56	120.97	20.59	0.334	0.002	0.243	0.024
	SE (±)	29.35	13.88	19.87	0.117	0.00028	0.05222	0.00353
	STD	97.34	46.05	65.90	0.388	0.00095	0.17320	0.01172
	Mean	231.6	146.4	88.14	0.262	0.00084	0.22582	0.00958

[1] Total exchangeable K. [2] Non-exchangeable K. [3] Exchangeable K, [4] Equilibrium K concentration ratio. [5] Equilibrium exchangeable K. [6] Equilibrium solution K. SE (±): standard error. STD: standard deviation.

As per Beckett & Nafady (1968), the PBC of a soil depends on many factors, *e.g.*: surface area available for ion exchange and characteristics of the surface and charge density of the surface. The major exchange surfaces in soils include inorganic clays and organic humic substances. The contribution of organic matter to exchange sites may be nullified when the clay content increases. This explanation, however, may be applicable when the soil is K deficient. A soil with low PBCt would not respond to K fertilizer if the soil contains large quantities of K-bearing minerals that could release K to exchange sites and also to solution (Sparks & Huang, 1985). Nevertheless, the PBCt of soil is not a constant factor; it in fact changes when changes in intensity and capacity factors of soil K occur. Cropping for several years without K application may change the PBCt and Q/I relationship of a soil (Bertsch & Thomas, 1985).

The studied soils also differed widely in buffering capacities in respect to PBCne and PBCe. This might be due to pool sizes and degree of change from exchangeable pool to non-exchangeable pool and vice-versa in equilibrium system. The PBCne in studied soils was much higher than that of PBCe except for NL, BC, JC and GC. The values of PBCne and PBCe for Barisal clay, Jhalokathi clay, Gopalpur clay and Nachol loam soils indicate that the added K converted almost equally to both the exchangeable and non-exchangeable pools.

Labile K (ΔK^0)

The intercept of the Q/I relationship, *i.e.*, the value of ΔK when CR=0, is regarded as labile K (ΔK^0). Indeed, the labile K represents the absolute value of the ΔK^0. The results of ΔK^0 of 11 soils derived from Q/I curves are presented in Table 2. There was a large variation in ΔK^0 in the tested soils. The highest ΔK^0 (1.35 cmol kg^{-1}) was observed in BC, followed by 0.37, 0.33 cmol kg^{-1} for SL and SCL, respectively. JC and GC had the same ΔK^0 of 0.28 cmol kg^{-1}. The lowest ΔK^0 (0.02 cmol kg^{-1}) was recorded from PCL. Labile K values concerning AL, NL, SLK and CL varied from 0.031 to 0.085 cmol kg^{-1}.

The intercept of the Q/I relationship – the labile K (ΔK^0) – revealed a large variation in labile K in the tested soils because the soils studied are very heterogeneous in their characteristics. Their capacity to release K varies. In our study, BC, Satkhira had the highest labile K, while Uddin (2009) recorded the highest labile K (0.82 cmol kg^{-1}) for Madhupur (Tangail) soil under AEZ 28. A similar result for high labile K was also recorded by Saleque *et al.* (2009) with reference to Gopalpur soil of Tangail under AEZ 8.

Equilibrium concentration ratio (CR₀)

CR$_0$, which is a measure of K intensity in the soil CaCl2 system, was estimated from Q/I curves when

ΔK=0, *i.e.*, the point when no K adsorption or desorption occurred. The CR$_0$ presented in Table 3, elicited large variation among the studied soils. The highest CR$_0$ 0.003 (mol L^{-1})$^{1/2}$ was recorded from BC, followed by SCL, SLP and JC soils. The lowest CR$_0$ 0.00007 (mol L^{-1})$^{1/2}$ was recorded in SLK.

The greater CR$_0$ values indicate that the larger amount of plant available K and higher values are generally associated with K fertilization, or naturally high exchangeable K levels (Schindler *et al.*, 2005). Bahmani *et al.* (2013) stated that CR$_0$ depends on CEC and exchangeable K. They further observed that higher CR$_0$ is linked to lower CEC and higher exchangeable K.

The CR$_0$ showed a large variation among the studied soils: 0.003 (mol L^{-1})$^{1/2}$ with BC, followed by 0.002 (mol L^{-1})$^{1/2}$ with SCL to 0.00007 (mol L^{-1})$^{1/2}$ with SLK (Table 3). The magnitude of CR$_0$ indicates the type of exchange sites involved in the reaction (Barbayiannis *et al.*, 1996). Values of CR$_0$<0.001 (mol L^{-1})$^{1/2}$ suggest that K$^+$ is absorbed at high affinity (edge position) sites, and if the values are>0.01 (mol L^{-1})$^{1/2}$, K is adsorbed on planar sites (Sparks & Liebhardt, 1982). There may, however, be some questions regarding this interpretation due to adsorption sites on the organic matter (Jalali & Kolahchi, 2007). Nonetheless, Saleque *et al.* (2009) reported that CR$_0$ value of Ganges Floodplain soils varied from 0.007 to 0.021 (mmol L^{-1})$^{1/2}$. The critical CR$_0$ value of some of US soils varied from 0.0004 to 0.0008 (mmol L^{-1})$^{1/2}$

Table 3. Estimated critical solution potassium (CK$_r$), critical exchangeable potassium (EK$_r$) and minimum exchangeable potassium (Emin) in major soils of Bangladesh

	Soil	CK$_r$ (cmol L^{-1})	EK$_r$ (cmol kg^{-1})	Emin (cmol kg^{-1})
1	AL	0.0028	0.06	0.052
2	PCL	0.00065	0.109	0.103
3	NL	0.00242	0.083	0.0667
4	SLP	0.0179	0.199	0.0825
5	SLK	0.00075	0.197	0.193
6	GCL	0.0003	0.182	0.171
7	BC	0.035	0.61	0.168
8	JC	0.0139	0.223	0.106
9	GC	0.0051	0.484	0.421
10	CL	0.0015	0.0814	0.07
11	SCL	0.024	0.244	0.195
	SE (±)	0.0035	0.0523	0.0316
	STD	0.0117	0.1733	0.1047
	Mean	0.0095	0.2248	0.1480

CK$_r$: critical solution potassium. EK$_r$: critical exchangeable potassium. Emin: minimum exchangeable potassium. SE (±): standard error. STD: standard deviation

(Wang *et al.*, 2004). The CR_0 of BC, SCL, SLP, JC and GC appear to be better in this regard. The higher value of CR in soil may indicate that more K remains in soil solution. The above results suggest that the studied soils of BC, SCL, SLP, JC and GC districts might have sufficient amounts of solution K to meet crop demand.

Equilibrium exchangeable K (EK_0)

EK_0 is the exchangeable K corresponding to $\Delta K=0$, estimated from the linear regression equation of final exchangeable K (EK_f) of each equilibrium point against ΔK (Figs.4). The EK_0 denotes the exchangeable pool of K that a particular soil can maintain. However, the EK_0 of the studied soils varied widely from 0.06 to 0.604 cmol kg^{-1} (Table 3), where the highest result was observed in BC while the lowest was in AL. The second highest EK_0 (0.492 cmol kg^{-1}) was found in GC, which was followed by SCL (0.243 cmol kg^{-1}) and JC (0.232 cmol kg^{-1}). The EK_0 of AEZ 11 (SLP, SLK and GCL) was quite similar, recording 0.185 cmol kg^{-1} in GCL, 0.196 cmol kg^{-1} in SLK and 0.199 cmol kg^{-1} in SLP. The EK_0 of terrace soil of NL (AEZ 26) and CL (AEZ 28) was 0.083 and 0.081 cmol kg^{-1}, respectively. The Sonatola soil of Bogura retained 0.109 cmol kg^{-1} of EK_0.

Higher EK_0 values indicate greater capacity of soil to supply K to the growing plants for a longer period of time than soils with lower EK_0. A higher EK_0 value may be very significant in arable soils because it would help maintain the balance between the solution K and exchangeable K. The property of a soil with higher EK_0 would control the release of adsorbed K from the exchange sites and would subsequently result in lower K in solution, thus indirectly protecting the loss of K through leaching. Moreover, because K fertilizers are applied to K deficient soils, higher EK_0 would result in higher solution K (Saleque *et al.*, 2009).

Equilibrium solution K (CK_0)

CK_0 is the solution K corresponding to $\Delta K=0$, and it was calculated from the relationship between final equilibrium concentration of K in solution (CK_f) and ΔK (Figures not shown). The highest CK_0 (0.035 cmol L^{-1}) was estimated for BC, followed by SCL, SLP and JC soils (Table 3). The CK_0 value of GC soil was lower than expectations despite the fact that initial exchangeable K and EK_0 were much higher in GC. The lowest CK_0 (0.0006 cmol L^{-1}) was derived from SL and PCL.

The BC soil had the highest CK_0 (0.035 cmol L^{-1}), followed by SCL, SLP and JC soils. The CK_0 value of GC soil was lower than expected even though the initial exchangeable K and EK_0 was much higher in the soil. The SLK and PCL soils had poor CK_0 (0.0006 cmol L^{-1}). These results revealed that the retention of CK_0 for most of the studied

soils was low even though their background exchangeable K level was high. The higher CK_0 of soil is expected to make K instantly available for uptake by plants. Islam *et al.* (2017) found that rising concentrations of Fe, Mn and other cations in submerged phases of rice-upland cropping systems are triggered by declining conditions, causing K to be turned over from the exchange site to the soil solution (Dobermann & Fairhurst, 2000). The increase of K in the soil solution might lead K to leach to lower depths with irrigation or rain water if it is not absorbed by plants (Patrick *et al.*, 1986; Wells *et al.*, 1993). When initial K concentration (CK_i) equals CK_0, there is no exchange, release or fixation of K^+. This is consistent with the existence of equilibrium between solution K^+, EK and fixed K^+ (Mortland, 1961; Schneider, 1997b). When the exchange sites of a soil become saturated with K, the site is unable to hold more K on this site. In this situation, K originates from the upper soil layer by leaching and then it remains in the soil solution (Islam *et al.*, 2016).

Critical solution K (CK_r)

CK_r was estimated from the relationship between CK_f (final equilibrium concentration of K in solution) and ΔNEK, when ΔNEK approaches zero (graphics not presented). CK_r values of BC, SCL, SLP and JC were greater than those of other soils (Table 4). The critical solution K (CK_r) was highest (0.035 cmol L^{-1}) in BC, followed by SCL (0.024 cmol L^{-1}) and SLP (0.0179 cmol L^{-1}). However, the lowest CK_r (0.0003 cmol L^{-1}) was detected in GCL, which was closer to PCL (0.00065 cmol L^{-1}) and SLK (0.00075 cmol L^{-1}). The relationship between CR_0 and CK_r was highly significant ($R^2=0.996$) (Fig. 5a).

CK_r denotes the concentration of solution K at which the release of non-exchangeable K starts. According to Datta & Sastry (1988), CK_r is the critical value at which $\Delta NEK=0$, below which the release of NEK may be initiated. CK_r values of BC, SCL, SLP and JC were greater than those of the other soils. It may well mean that a smaller depletion of solution K is needed by these soils than other soils for commencing NEK release. It was observed that the estimated CK_r was almost the same or very close to the estimated CK_0 (similarly for EK_r and EK_0). Thus, the results cannot be used to assess the significance of the threshold concentration of K^+ release as pointed out by Datta & Sastry (1988). Moreover, Schneider (1997a) observed that the release of K occurs as soon as the K^+ concentration in solution is below CK_0.

Critical exchangeable K (EK_r)

EK_r values varied widely from 0.06 to 0.61 cmol kg^{-1} where the highest amount was reported in BC followed by

Table 4. Conversion of added potassium to exchangeable (α) and non-exchangeable (β) pool in major soils of Bangladesh

	Soil	Exchangeable pool (α) (%)	Non-exchangeable pool (β) (%)
1	AL	15.03	78.66
2	PCL	27.66	68.1
3	NL	48.36	47.7
4	SLP	23.12	72.68
5	SLK	33.23	62.4
6	GCL	32.87	63.66
7	BC	49.08	49.03
8	JC	69.12	28.61
9	GC	61.02	36.94
10	CL	25.81	70.21
11	SCL	14.53	79.48
	SE (±)	5.480	5.104
	STD	18.174	16.928
	Mean	36.35	59.77

SE (±): standard error. STD: standard deviation

GC and the lowest in AL (Table 4). The EK_r was higher than exchangeable K (EK) for PCL, SLK, SCL, GCL and AL soils where the amounts were 82%, 64%, 63%, 30% and 20%, respectively, but it was 36% lower for NL and 26% for CL soil. The EK_r value increased significantly (R^2=0.726) with the increase in CEC (Fig. 5b). Clay content also significantly (R^2=0.867) influenced the EK_r value of soils (Fig. 5c).

EK_r indicates the amount of exchangeable K concentration below which the release of non-exchangeable K starts. If the EK_r value is nearly that of EK, then the NEK pool mostly contributes to plant nutrition (Jalali & Kolahchi, 2007). In this regard, SLP, GC, BC and JC soils showed EK_r values that were closer to EK. It is well-established that some readily dissolved amounts of K of the soil applied with fertilizer K are fixed by soil clays and become non-exchangeable and not immediately available to uptake by plants (Scott & Smith, 1987).

Minimum exchangeable K (Emin)

Emin was found from the linear relationship between CR and EK_f when CR approached to zero (Fig. 6). In that case, EK_f remained >0. Thus, EK_f tended to a non-zero value which was defined as the minimum exchangeable K⁺ (Emin). The Emin was highest (0.421 cmol kg⁻¹) in GC and lowest (0.052 cmol kg⁻¹) in AL. Emin for SCL was 0.195 cmol kg⁻¹, which was closely followed by SLK, GCL and BC (Table 4). Emin for JC soil was 0.106 cmol kg⁻¹, which

was almost equal to that of PCL (0.103 cmol kg⁻¹). Emin for the terrace soil CL, and NL was low (0.07 cmol kg⁻¹).

When final exchangeable K⁺ tends to non-zero, it is defined as minimum exchangeable K⁺ (Emin). In this study, on average, Emin amounted to 68.1% of EK. Soil properties like CEC and clay content revealed a weak relationship with Emin because Emin can be explained by CEC and clay content only by 36% and 43%, respectively (figures not shown here). The lowest value recorded in AL, CL and NL corresponded to the most depleted soils containing less K⁺. In these soils, EK was close to Emin and subsequently EK is said to contribute only a small portion of K⁺ supply compared with NEK. The closer the Emin is to the EK of a soil, the more NEK pool could contribute to plant nutrition (Schneider, 1997a). In this scenario, EK would be meaningless as a soil fertility indicator. Therefore, EK_r and Emin can be used when interpreting EK as a fertility indicator.

The Emin does not exchange with Ca^{2+}, despite extraction by NH_4OAc (Schneider, 1997a) and may represent the amount of K⁺ fixed on some clay interlayer sites. Emin is a fraction of EK, which is virtually unavailable to plants. If EK could reach this point, the K⁺ concentration in solution would reach zero (Schneider, 1997b). The soil may reach the Emin stage only after extensive cropping (Tabatabai & Hanway, 1969; Schneider, 1997c; Jalali & Kolahchi, 2007). In soils where EK is much lower than Emin, EK contributes a large portion of the K⁺ supply.

Conversion of added potassium to exchangeable pool (α)

The slope (α) of the linear regression equation of final exchangeable K (EK_f) for each equilibrium point *vs* the change in solution K (ΔK) was used to measure the magnitude of conversion from solution K⁺ to exchangeable K⁺ in each soil (Fig. 4). The values α for the studied soils varied from 0.145 to 0.69 where the largest was observed in JC and the lowest was in SCL (Table 4). The second highest α (0.61) was estimated for GC, which was followed by BC (0.49) and NL (0.48). The α value for AL was the second lowest (0.15), while it was 0.23, 0.26 and 0.28, for SLP, CL, and PCL, respectively.

The present study revealed that SCL could convert 14.5% of the added K to exchangeable pool, while it was as high as 69% for JC. The increased conversion of added K to exchangeable K pool (α) indicates that K remains available without being fixed in the fixation sites of soils. These results agree with what other studies have reported (Wang *et al.*, 2004; Jalali & Kolahchi, 2007; Saleque *et al.*, 2009). However, judging by the relationships between CEC and clay content and α, it was found that 36% and 44% of variability in α could be explained by CEC and clay content, respectively.
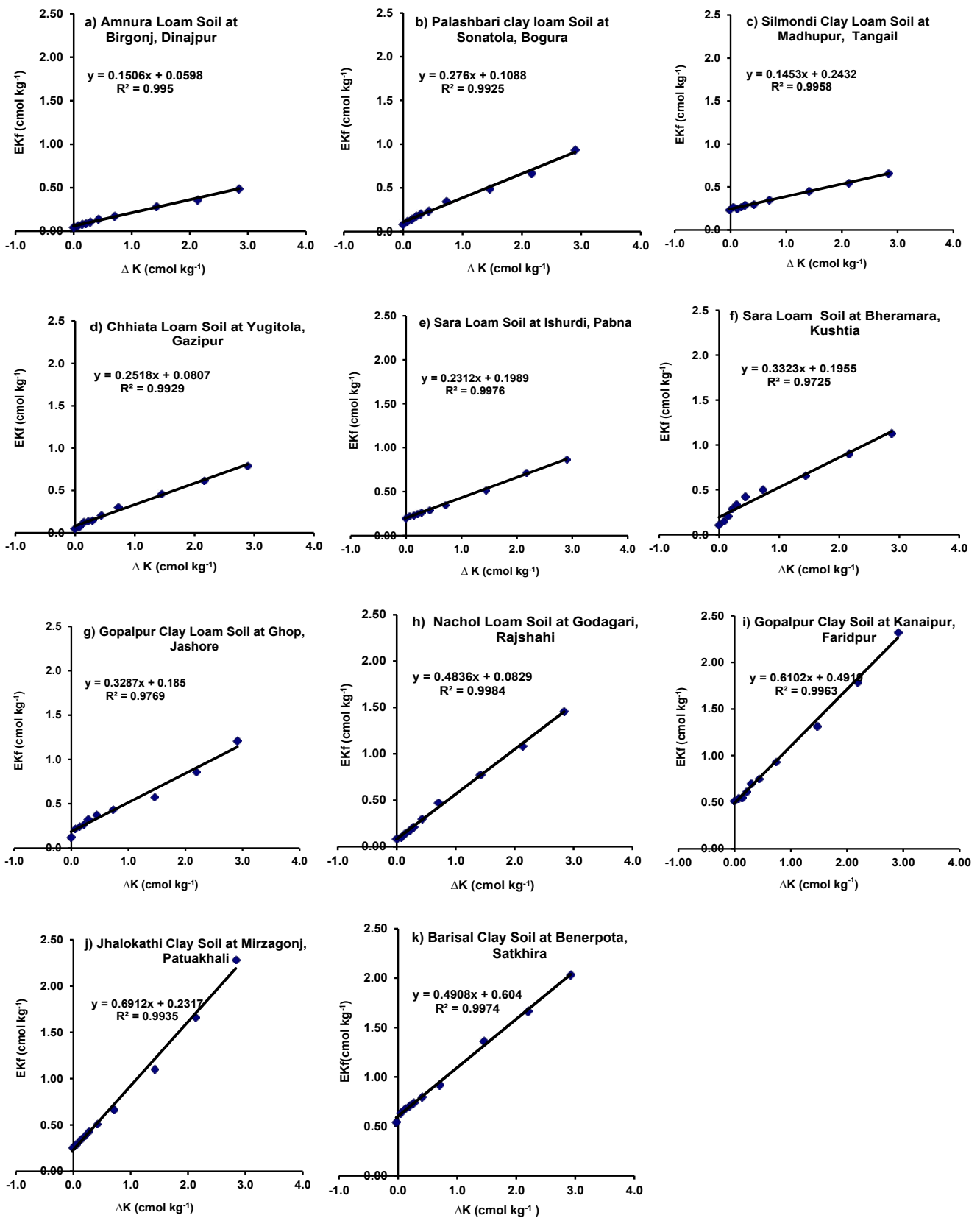
Figure 4. Relationship between exchangeable K (ΔK) and final exchangeable K (EKf) for Danajpur (Amnura loam), Borga (Polashbar clay loam), Tangail (Silmondi clay loam), Gazipur (Chhiata loam) and Pabna (Sara loam), Kushtia (Sara loam), Jashore (Gopalpur clay loam), Rajshahi (Nachol loam), Faridpur (Gopalpur Clay), Patuakhali (Jhalokathi Clay) and Satkhira (Barisal Clay) soils. Here, EK$_f$=final exchangeable K; ΔK=exchangeable K
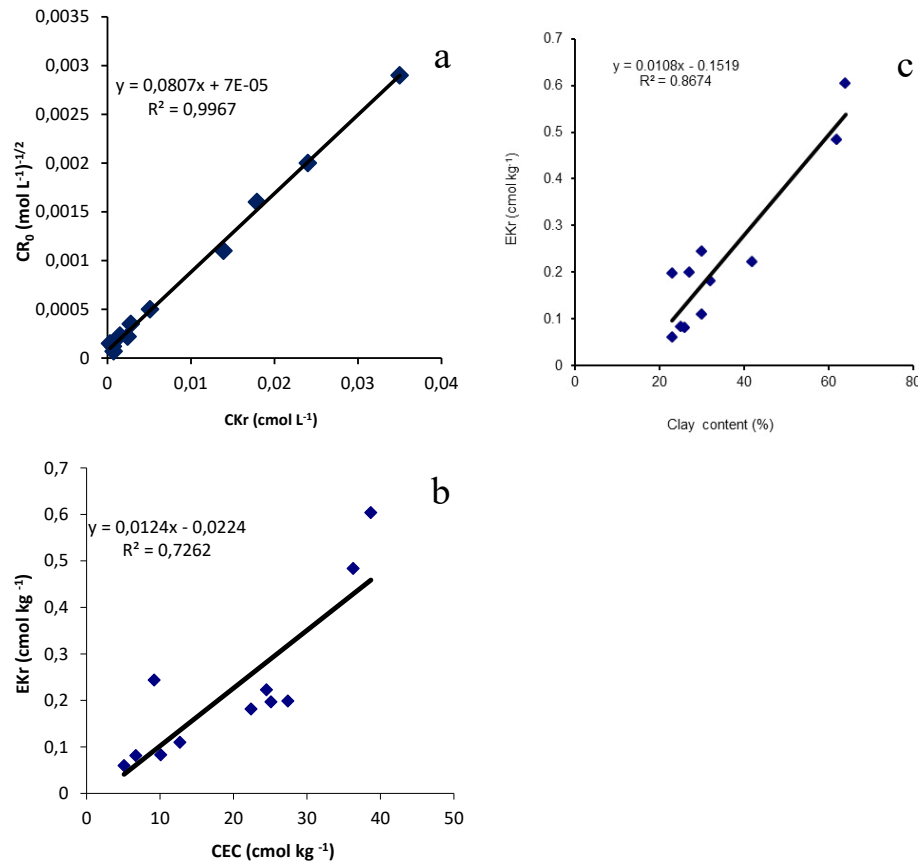
Figure 5. Relationships between critical solution K (CK_r (cmol L^{-1}) and equilibrium concentration ratio (CR_0 (mol L^{-1})$^{-1/2}$) (a), between cation exchange capacity (CEC) and critical exchangeable K (EK_r) (b) and between clay content and critical exchangeable K (EK_r) (c) in different soils.

Conversion of added potassium to non-exchangeable pool (β)

There was a linear relationship between initial constraint (Φ) and ΔNEK (Fig. 7). The slope of the linear regression equation indicates β, which implies the conversion of added K to non-exchangeable pool. The value of β (soils' ability for K^+ release or fixation) varied from 0.286 to 0.795 with a mean of 0.598 (Table 4), where the highest result was observed in SCL soil and the lowest occurred in JC soil. The second highest β was estimated from SLP (0.727) followed by CL (0.702).

The slope (β) of the linear trend line between initial constraint (Φ) and ΔNEK measures the impact of β on K dynamics in the soil-solution system (Schneider, 1997a,-b,c). The larger the β, then the greater the portion of added K converted to non-exchangeable K (fixed) at positive Φ, or the more fixed K released at negative initial disequilibrium of soil solution (Φ) (Wang *et al.*, 2004). The values of β (soils' ability for K^+ release or fixation) in this study attributed that 28.6% to 79.5% of added K might be converted to NEK for JC and SCL soils, respectively.

When fertilizer K is applied to a soil characterized with a large α and a small β, much of the fertilizer K is expec-

ted to be held at exchangeable sites and would stay available without being fixed during the growing season (Wang *et al.*, 2004; Saleque *et al.*, 2009; Islam *et al.*, 2017). This could be a favorable situation for crops that require large amounts of persistent available K during the growing period, and especially for an exhaustive crop like maize (Saleque *et al.*, 2009; Islam *et al.*, 2017). In this context, JC, GC and BC soils will have the potential to supply the desired amount of K for crops.

In summary, studying with diversified soils on K adsorption isotherm revealed that critical exchangeable K and minimum exchangeable K can interpret exchangeable K (K fertility) of soils under rice-based intensive cropping system. Even though soils were K fertilized, most of the studied soils were K deficient and will require frequent applications of K due to their lower PBCt. However, soils of AL, CL, and NL may release K from non-exchangeable pool faster than other soils for their lower EK_0, CK_r and Emin. Thus, the parameters reported in the present study are good for understanding K availability in diversified soils and can be used for recommendation of potassic fertilizer. However, understanding the K availability in soils under saline/acid sulphate/sodic/drought prone soils may require further study.
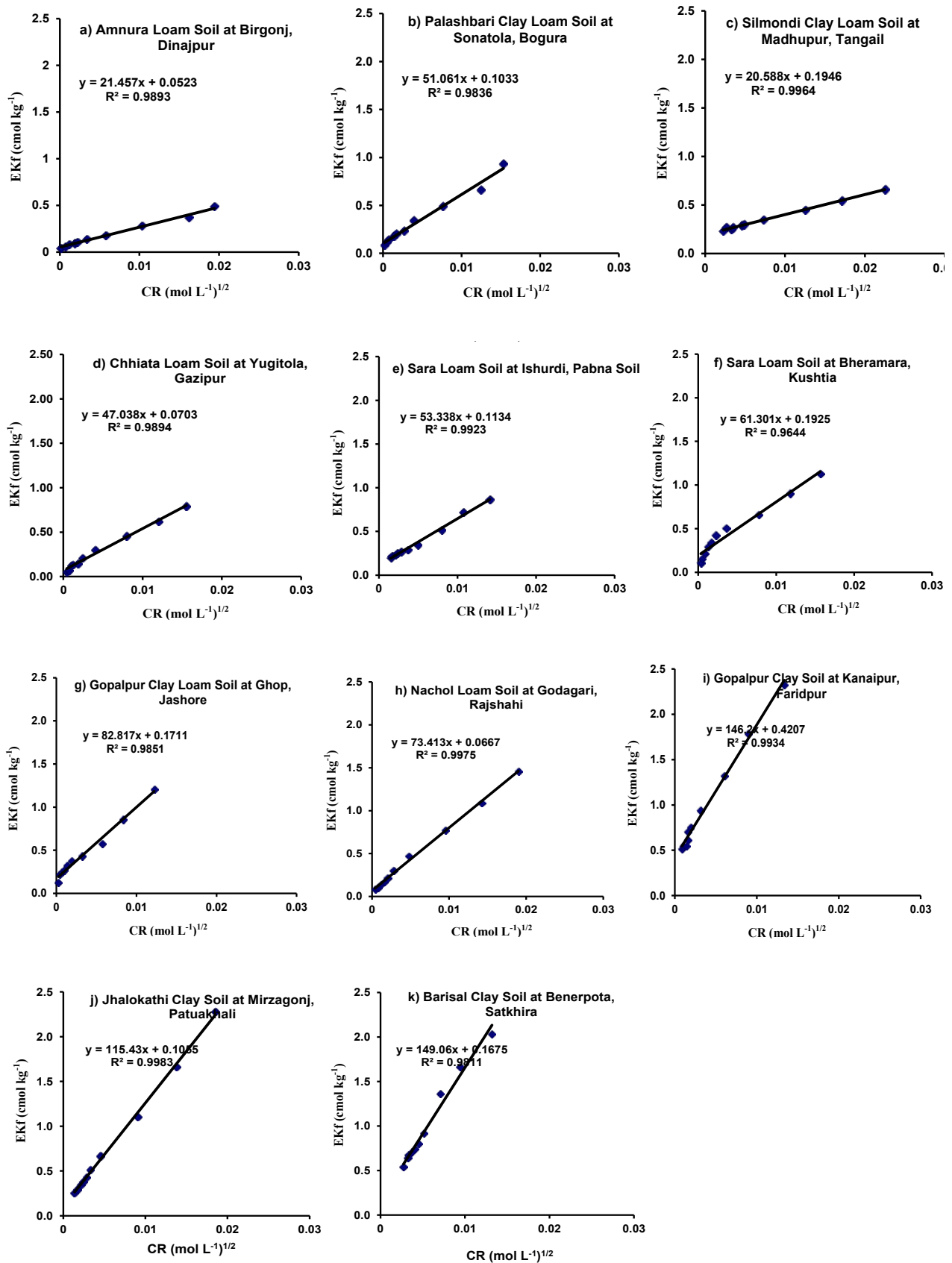
Figure 6. Relationship between K concentration ratio (CR) and final exchangeable K (EKf) for Amnura loam soil at Dinajpur (AL), Polashbari clay loam soil at Bogura (PCL), Silmondi clay loam soil atTangail (SCL), CL, Chhiata loam soil at Gazipur, Sara loam soil at Pabna, Sara loam soil at Kushtia, Gopalpur clay loam soil at Jashore, Nachol loam soil at Rajshahi, Gopalpur Clay soil at Faridpur, Jhalokathi Clay soil at Patuakhali and Barisal Clay soil at Satkhira.
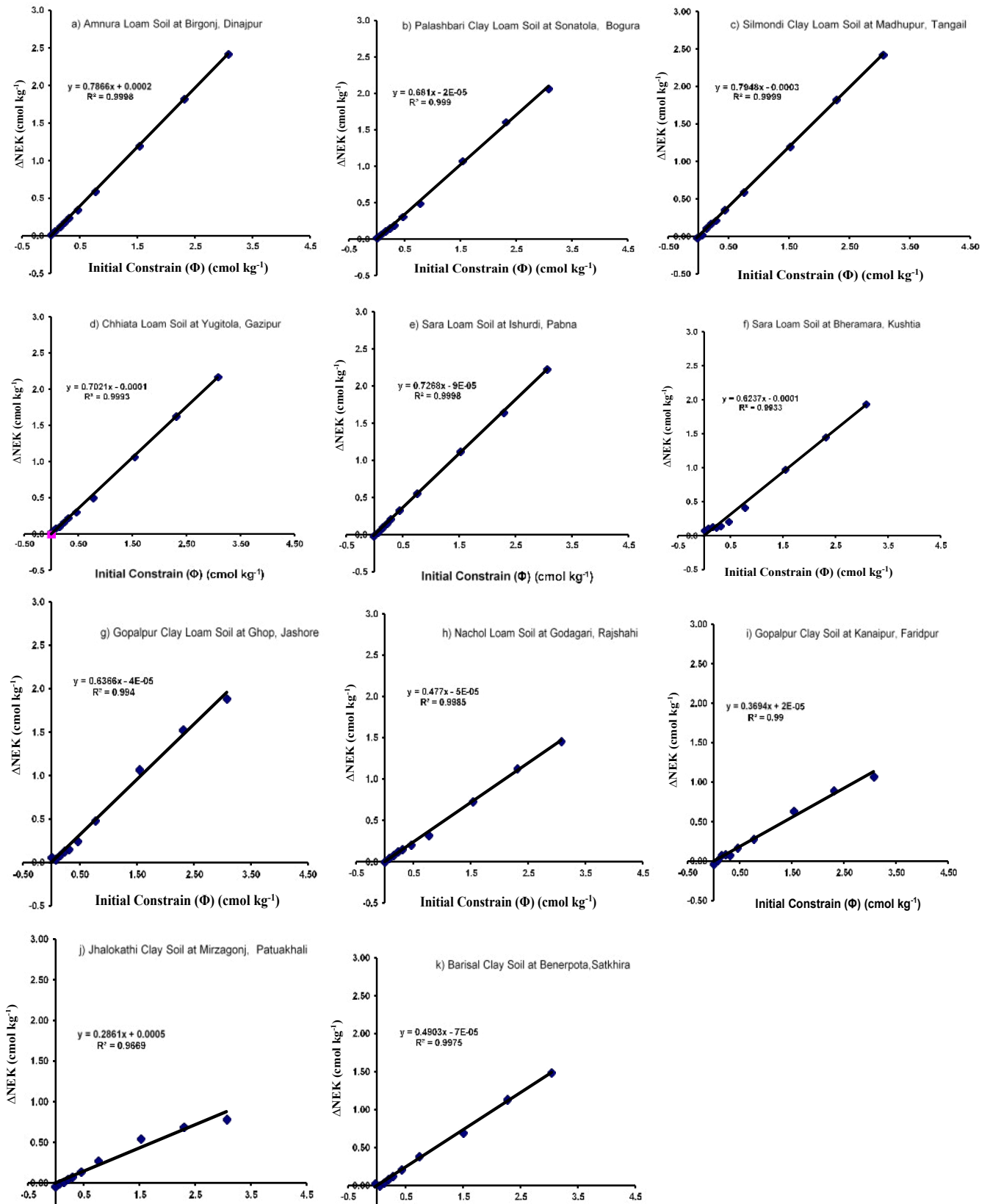
Figure 7. Relationship between Initial Constrain (Φ) and non-exchangeable K (ΔNEK) for Amnura loam soil at Dinajpur, Polashbari clay loam soil at Bogura, Silmondi clay loam atTangail, Chhiata loam soil atGazipur, Sara loam soil at Pabna, Kushtia (Sara loam), Jashore (Gopalpur clay loam), Rajshahi (Nachol loam), Faridpur (Gopalpur Clay), Patuakhali (Jhalokathi Clay) and Satkhira (Barisal Clay) Soil

Finally, further research is suggested to be conducted for other intensive crop cultivated soils, because it is important to characterize the K dynamics in order to do two things: maintain K fertility in soils and ensure K nutrition in plants.

Acknowledgements

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