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Long-term influence of different production systems on potassium buffering capacity of *Typic Ustochrept* soil

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ABSTRACT

Imbalanced application of nutrients in the intensively cropped areas results in deterioration of soil fertility. Application of recommended dose of potassium (K) is essential for improving the use efficiency of other nutrients. To assess the buffering capacity of soil, three composite soil samples were collected from the surface soil (0–30 cm) during 2015 from 3 production systems *viz.*, organic, inorganic and integrated which was maintained from 2004 with basmati rice–wheat–*Sesbania* system under Network Project on Organic Farming at ICAR-Indian Institute of Farming Systems Research, Modipuram. Fractionation of potassium (K) was achieved by sequential extraction of soil samples with distilled water, ammonium acetate and nitric acid in the same order. The relationship between the adsorbed and equilibrium potassium concentration, quantity was determined by plotting Freundlich adsorption isotherms. This was used to determine the buffering capacity and the concentration levels of potassium adsorbed on un-specific sites in the soil. The suitability of the adsorption equation was determined by applying the least square regression analysis. The results revealed that available potassium in the soils ranged from 119.51 to 135.01 mg/kg with 126.02 ± 5.24 mg/kg as mean (ammonium acetate method) while water soluble and nitric acid extracted potassium ranged from 28.51 to 29.05 mg/kg and 2594.49 ± 19.33 mg/kg (mean) in various production systems. The mean free energy of replacement was found to be -1998.01 ± 28.38 cal/mol indicating that soils have comparatively higher potassium supply under organic system. The potassium buffering capacity of the soils was found to be 0.7462 ± 0.16 mg/kg, 0.6295 ± 0.20 mg/kg and 0.6774 ± 0.09 mg/kg in organic, integrated and inorganic systems, respectively. The amount of potassium adsorbed on un-specific sites of the organic, integrated and inorganic systems was found to be 7.4730 ± 1.81 , 15.11 ± 2.40 and 11.689 ± 3.58 mg/kg, respectively. It can be concluded that long-term organic production system improves K⁺ buffering capacity of *Typic Ustochrept* soil as compare to the integrated as well as inorganic production systems.

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buffering capacity; free
energy; potassium fractions

Introduction

Potassium is the most abundant macro plant-nutrient in most soils. It is crucial since it serves three important functions in plant i.e. enzyme activation, charge balance and osmotic regulation in higher plants (Mengel and Kirkby 2001). Different fractions of K in soils are essential for

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potassium management to determine long-term sustainability of a cropping system. It is generally assumed that our soils are not deficient in available potassium; therefore, farmers usually skip the application of potassium in many crops. But increased cropping intensity and introduction of hybrid varieties are resulting in a considerable drain of potassium reserves and crops are becoming responsive to potassium fertilizer application. A small proportion (0.1–0.2%) of the total soil K become directly available to plants (i.e. in soil solution) whereas water-soluble fraction and the exchangeable fraction comprise 1–2% became immediately available and the soil-unavailable fractions 96–99% (Wang et al. 2010; Britzke et al. 2012). K in soil can be differentiated to three pools of availability for uptake by roots. It is dissolved in soil water, adsorbed onto particles of clay and organic matter and held within the crystal structures of feldspar and mica. Based on the degree of availability to crops, soil potassium can be classified into four forms i.e. soil solution K, exchangeable K, non-exchangeable K and mineral K (Darunsontaya et al. 2012). The primary source of potassium absorbed by plant roots is that which is present in soil solution. The concentration of the readily available K forms are relatively small at any time and do not provide a good indication long-term ability of soils to supply K to plants (Jibrin 2010). The dynamics of potassium in soil depends on the magnitude of equilibrium among various forms and mainly governed by the physicochemical properties of soil. The bulk of soil potassium (about 98% of total K) usually exists in unavailable form in primary (micas and feldspars) and secondary (illite group) clay minerals. The available K and exchangeable K in general are readily available to plants. The distribution of K forms in the soil and the equilibrium between them determine the K status of the soil and the potential of K supply to plants (Pavlov 2007; Srinivasarao, Subba Rao, and Rupa 2000). More recently, new techniques that use adsorption isotherms and thermodynamic parameters such as ionic activity, activity coefficient, ionic strength and free energy of replacement to determine potassium levels and its availability for plant uptake have been reported (Al-Zubaidi et al. 2008). Long-term studies are the basic platform for examination and quantification of cultivation-based changes in agro-eco-systems and enables the evaluation of effects of continuous fertilizer application on different nutrient dynamics in soil (Merbach and Deubel 2008). The potassium release rates from soil under long-term cropping, fertilizer application and manuring helps to predict the fate of added K in soil as well as nature of K supply from soil to plant (Samra and Swarup 2001) i.e. potassium buffering capacity of soil. Therefore, this study aims to determine the buffering capacity of soil as well as the equilibrium concentration of different levels of potassium under basmati rice–wheat–*Sesbania* cropping systems in a long-term experiment.

Material and methods

Site description

This study was conducted as a part of an ongoing Network Project on Organic Farming (NPOF) under basmati rice–wheat–*Sesbania* — (green manuring) cropping system in the Research Farm of the Indian Institute of Farming Systems Research (29.84°N, 77.46°E, Meerut, India, 237 m above sea level). The experimental site is comes under western Uttar Pradesh, part of Indo-Gangetic plain, having sandy loam texture soil of Gangetic alluvial origin, very deep (>20 m), well drained and with flat (~1% slope) topography. Data on initial soil characteristics (0–15 cm depth) measured at the onset of the experiment during 2004 revealed that the soil was mildly alkaline (pH 7.9) and non-saline (electrical conductivity (EC) 0.42 dS m⁻¹) and contained 5.1 g kg⁻¹ WBC, 16.4 kg ha⁻¹ available (0.05 M NaHCO₃-extractable) P, 96 kg ha⁻¹ available (1 M ammonium acetate-extractable) K. The soil of the experimental site was Typic Ustochrept and average monthly minimum and maximum temperatures in January (the coolest month) are 7.2 °C and 20.1 °C, respectively. The corresponding temperatures in May (the hottest month) are 24.2 °C and 39.8 °C, respectively. Average annual rainfall is 823 mm, and over 75% of this is

received through the south-west monsoon during July–September. The experiment was in strip plot design and 100% organic, 100% inorganic and integrated (50% organic + 50% inorganic) nutrient management was maintained by the use of vermicompost as an organic source of nutrient. Nutrients were applied as per recommended dose. The mean annual rainfall of this area is 2118.6 mm, mean annual relative humidity (RH) 70.68%, maximum and minimum temperature was 29.39 °C and 17.03 °C, respectively. This region belongs to sub-arid ecosystem characterized by hot air conditions.

Soil sampling and analysis

Soil samples were collected by boring at 4 random places with the help of post-hole auger from all the plots at 30 cm soil depths after the completion of cropping system basmati rice–wheat–*Sesbania* – (green manuring) in 2015. Soil core sampler (each core had an inner diameter of 7 cm and length of 4.5 cm) was used to take the sample. Soil samples were air dried in shade. Less than 2 mm size fraction of soil samples were used for determining different fractions of potassium and adsorption isotherm of potassium in soil.

The physical–chemical parameters of the soil were determined using standard procedures described below. All chemical analysis was done in triplicate. Soil pH and electrical conductivity (EC) of soil pastes (soil to water weight ratio of 1:2.5) were determined using electrical pH and conductivity meters, respectively. Total organic carbon was determined using the standard Walkley Black rapid titration method (Walkley 1947). The concentration levels of phosphorus content were determined using the Olsen method (Olsen et al. 1954). Nitrogen concentration levels were determined by the Kjeldal method (Kjeldahl, 1883). The concentration levels of potassium in the various forms were obtained by extracting with water, ammonium acetate and nitric acid as described in the literature (Samira et al. 2009) and measurements in extracts done using a flame photometer (Systronic).

Adsorption studies

2.50 grams of the soil samples were put in 25 mL solutions of 0.01 M CaCl₂ that contained potassium concentrations of 0, 20, 30, 40, 50, 60, 70, 80, 90, and 100 mg L⁻¹ and shaken for 24 hours at 25 ± 1 °C to achieve equilibration (Table 1). The contents were filtered using Whatman filter papers No. 42. The concentration levels of potassium in the filtrate were measured using a flame photometer.

Thermodynamic data analysis

The amount of K adsorbed was obtained by subtracting the amount found in filtrate from the initial amount that was in solutions as shown in Eq. (1).

Table 1. Adsorbed potassium and the equilibrium potassium concentration (EKC) at various initial doses.

C _{ik} (mg/l)	Organic		Integrated		Inorganic	
	C _{rk} (mg/l)	Adsorbed K (mg/kg)	C _{rk} (mg/l)	Adsorbed K (mg/kg)	C _{rk} (mg/l)	Adsorbed K (mg/kg)
0	4.37	–43.70	5.87	–58.67	5.13	–51.33
20	19.10	8.97	16.37	36.30	17.55	24.49
30	25.10	48.97	24.84	51.60	25.44	45.64
40	31.90	80.97	32.82	71.80	32.52	74.85
50	45.17	88.30	41.15	88.50	38.53	114.69
60	55.03	102.64	47.85	121.50	47.97	120.33
70	64.23	116.64	57.77	122.33	56.57	134.32
80	72.30	141.97	65.68	143.21	65.42	145.79
90	81.30	151.97	72.21	177.86	74.24	157.65
100	90.73	157.64	80.12	198.76	84.04	159.65

C_{ik}: initial concentration of K in solution; C_{rk}: final concentration of K in solution/equilibrium potassium concentration.

$$\Delta K = (CK_i - CK_f) * (V/M) \quad (1)$$

ΔK is the amount adsorbed. A positive ΔK values indicate adsorption whereas negative values indicate desorption of potassium by the solid phase of soil. CK_i and CK_f are the initial K concentration added and final equilibrium concentrations of K in solution, respectively. V and M are the solution volume and mass of the soil used. Adsorption isotherms were constructed as per the method described by Omanga et al. (2013). The K adsorption data were fitted into the Freundlich adsorption equation as describe in Eq. (2). Freundlich isotherms assume unlimited sorption sites of heterogeneous medium and hence are expected to give better correlations for the mixed mineralogy contained in soils.

$$\log \left(\frac{X}{m} \right) = \log a + b \log C \quad (2)$$

where (X/m) is the adsorbed amount of K per unit mass of soil (mg kg^{-1}), C is the equilibrium K concentrations of solutions (mg L^{-1}), a and b are constants obtained from the intercept and slope, respectively.

The ionic strength in the soil was calculated by a formula proposed by Griffin and Jurinak (1973) as shown in Eq. (3).

$$\text{Ionic strength } (\mu) = 0.0129 \times EC \quad (3)$$

where C is the electrical conductivities of soil pastes in mmhos/cm .

Activities (a_i), of potassium, calcium and magnesium ions, in the water extracts were estimated as the product of their activity coefficients, (f_i), and their concentrations, (c_i), as shown in Eq. (4).

$$a_i = f_i \times c_i \quad (4)$$

The f_i of the ions were determined using the extended Debye–Huckel in Eq. (5)

$$\log(f_i) = -AZi^2 \frac{\sqrt{\mu}}{1 + Bdi\sqrt{\mu}} \quad (5)$$

where Z_i = valence of ion, $A = 0.508$ for water at 298 Kelvin, $B = 0.328 \times 10^8$ for water at 298 Kelvin, di = effective size of hydrated ions and μ = Ionic strength of cation.

The activity ratio of potassium ions was tabulated using Eq. (6)

$$\text{Activity ratio} = \frac{a_{Ca}}{\sqrt{a_{Ca} + a_{Mg}}} \quad (6)$$

The free energy of replacement was calculated by Woodruff (1955) proposed equation as shown in Eq. (7). It is an index of the amount of work that must be done to remove one mole of K from exchange complex or to fix it.

$$-\Delta F = 2.303 RT \log \frac{a_{Ca}}{\sqrt{a_{Ca} + a_{Mg}}} \quad (7)$$

where R = Gas constant = 1.987 Cal/K.Mol , T = Absolute temperature at $25^\circ\text{C} = 298 \text{ K}$ and a = activity of the metal ions.

Potassium, calcium and magnesium concentration levels obtained from the water soluble soil extracts were used to calculate thermodynamic parameters such as free energy of replacement, potassium activity ratio and ionic strength of the soil solution. Furthermore, the K-potential is the product of amount of K adsorption on non specific with the buffering capacity and it is also an essential indicator of K availability in soil solution (Yawson et al. 2011).

Results and discussions

Water extracted potassium (soil solution K)

Water extracted potassium represent the potassium present in the soil solution and become readily available to the plants for uptake and relatively unbound by cation exchange forces and invariably subject to leaching losses in relation to soil properties. The amount of potassium in soil solution varies under different nutrient management systems of basmati rice–wheat–*Sesbania* cropping systems. The soil solution potassium is 1.68% and 1.89% higher in organic nutrient management systems as compare to the integrated and chemical nutrient management soil after completion of cropping cycle. The same trend was also reported by Mazumdar et al. (2014). Application of organic matter in the soil causes favorable changes in soil conditions for release of K in soil solution (Kher and Minhas 1991). Higher amount of soil solution K under organic nutrient management systems may be due to release of labile K from organic residues and addition of farmyard manure (Ranganathan and Satyanarayana 1980). The potassium content in the soil solution varies from 28.51 mg to 29.05 mg/kg of soil (Table 2). The soil solution potassium was 24.30, 21.16 and 23.07% of available potassium content (Ammonium Acetate extracted K) in the soil respectively under organic, integrated and chemically nutrient manage soil. Water soluble K being a readily available source of K may be subjected to change either under cropping or external K supply in the form of organic manures. This form of K is in dynamic equilibrium with exchangeable K and whatever change induced by crop removal of K, is compensated by the release of exchangeable K into solution (Srinivasarao, Satyanarayana, and Venkateswarlu 2011).

Ammonium acetate extracted potassium (exchangeable K)

The ammonium acetate extracted potassium represented the available potassium in soil that becomes available for plant uptake. The amount of available potassium in soil varies significantly under organic, integrated and inorganic nutrient management. The highest amount of available potassium was recorded (135.06 mg/kg) in the soil of integrated nutrient management under basmati rice–wheat–*Sesbania* cropping systems (Table 2). The value of available K comes under higher range of availability in integrated nutrient management practice. The critical level of potassium for basmati rice and wheat ranges from 113 to 117 ppm (Tandon, 1998) in soil. The available potassium in the soil under organic and inorganic nutrient management system was in the threshold level of critical K level in the soil. The low value (119.51 mg/kg) of available K in the organic nutrient managements systems may be due to non application of K through inorganic sources, where as higher amount of available K in the soils under integrated nutrient management may be due to judicious release of potassium from the binding site of soil. Application of inorganic source of potassium is positively correlated with the availability of potassium for plant uptake (Omanga et al. 2013). The form of K is in dynamic equilibrium with exchangeable K and whatever change induced by crop removal of K is compensated by the release of exchangeable K into solution (Mazumdar et al. 2014).

Table 2. Potassium adsorption pattern in the Freundlich model and specification of potassium forms in the soil under basmati rice–wheat–*sesbania* cropping systems.

Management practice	Amount adsorbed (mg/kg)	Buffering Capacity (mg/kg)	Correlation coefficient (R^2)	Water soluble-K (mg/kg)	Am. acetate-K (mg/kg)	Nitric acid-K (mg/kg)
Organic	7.47	0.75	0.908	29.05	119.51	2406.64
Integrated	15.11	0.63	0.967	28.57	135.01	2598.53
Inorganic	11.69	0.68	0.942	28.51	123.54	2778.31

Nitric acid extracted potassium (non-exchangeable-K)

Narrow range of variability in Non-exchangeable-K content in the soil suggests that the soil may have similar mineralogy and parent rock. The highest amount (2778.31 mg/kg) of non-exchangeable K was recorded in the soil of inorganic nutrient management under basmati rice–wheat–*Sesbania* cropping systems, accounting 15.44% and 6.92% higher as compare to organic and inorganic nutrient management systems, respectively (Table 2). This may be due to the application of inorganic source of K in the soil that causes fixation to the binding site of the soil. This form of potassium in soil actually indicates the supply power of the potassium in long-term of cropping program (Jackson 1979, Srinivasarao, Subba Rao, and Rupa 2001). The soil of the experimental site is alluvial and showing higher non-exchangeable K under organic, integrated and inorganic nutrient management systems. Alluvial soils with higher contents of K rich mica with light texture showed medium in exchangeable K and high in non-exchangeable K content (Srinivasarao, Subba Rao, and Takka 1997). Non-exchangeable K is sensitive to detect the changes due to cropping systems, fertilization and manuring under long-term cropping and fertilization (Srinivasarao et al. 2001). Higher value of non-exchangeable K shows that the soil has good supplying power of K for long-term cropping systems.

Potassium adsorption isotherm and buffering capacity of soil

Potassium buffering capacity of soil is the ability of soil to resist changes of the K concentration in soil. Soils have the higher value of Potassium buffering capacity suggested that soil has the capacity to supply available K for long period of cropping systems (Sparks and Liebhardt 1982). The slope of the sorption isotherm indicates the K buffering capacity of soil (Backett 1964).

A plot of log concentration of adsorbed potassium against log equilibrium potassium concentration (EqK) gave linear graphs as shown on Figures 1–3. The adsorb data were significantly fitted in the adsorption isotherm, which was ascertained by looking at the values of r^2 which ranged between 0.908 and 0.967 and gave a mean value of 0.937. This indicated high conformity of the adsorption data to Freundlich model, thus the Freundlich isotherm gave a better fit to the adsorption data of the soils. Freundlich isotherms assume unlimited sorption sites of

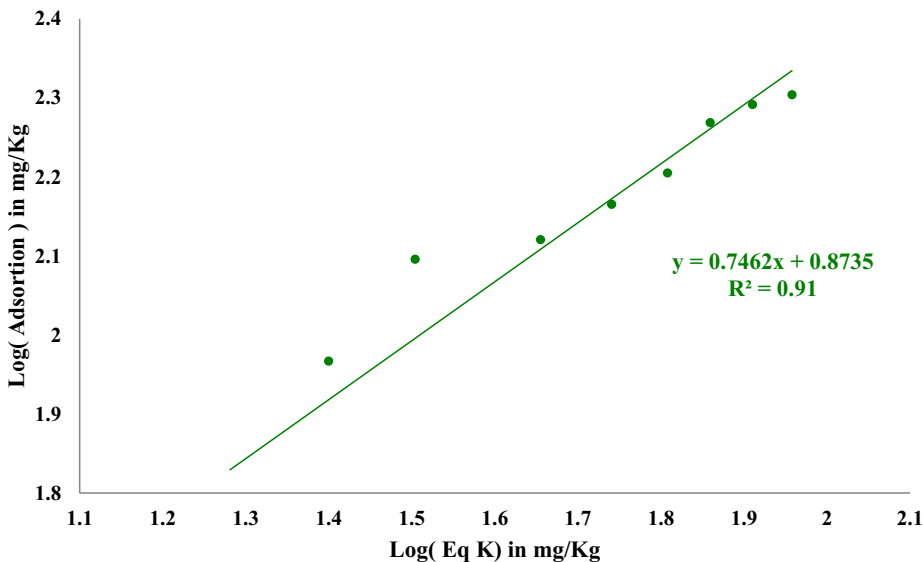


Figure 1. Freundlich adsorption isotherm for potassium under organic management of basmati rice–wheat–sesbania systems.

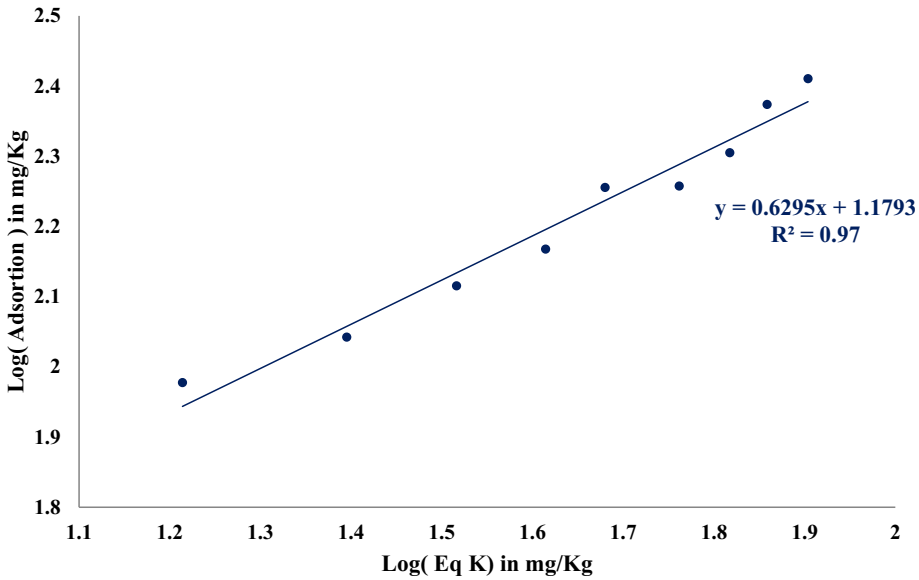


Figure 2. Freundlich adsorption isotherm for potassium under integrated management of basmati rice–wheat–*sesbania* systems.

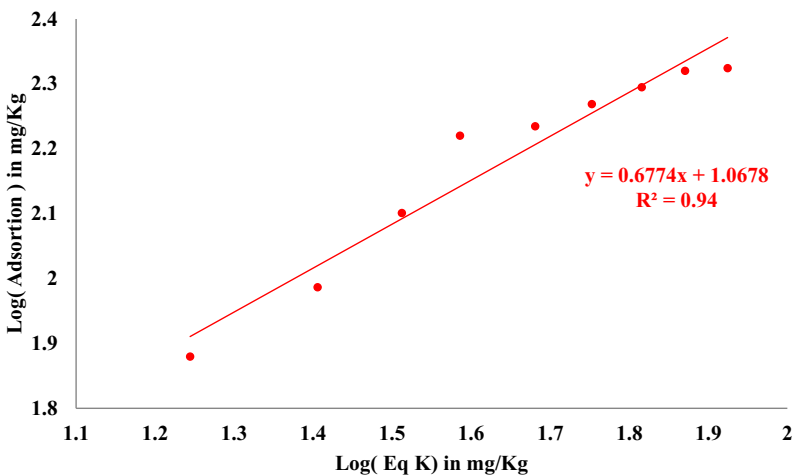


Figure 3. Freundlich adsorption isotherm for potassium under inorganic management of basmati rice–wheat–*sesbania* systems.

heterogeneous medium and hence are expected to give better correlations for the mixed mineralogy contained in soils. The K adsorption on soil depends upon the initial concentration of K in soil solution (Hussain et al. 2006).

The buffering capacity of soil under different nutrient management varies from 0.62 to 0.75 mg/kg of soil. Adsorption capacity of soil ranges from 7.47 mg/kg to 15.11 mg/kg soil (Table 2). The soil under long-term integrated nutrient management system adsorb 50.5% and 22.64% higher K adsorption potential as compare to organic and inorganic nutrient management systems respectively. Un-specific sites of the integrated nutrient managed soil adsorb higher amount of K (1.18 mg/kg) and this form of K become readily available for uptake by plants during a cropping season (Table 3). This form of adsorb K were very low as compare to the available K, irrespective of nutrient management practice, indicating that part of exchangeable potassium is held on exchange sites by high bonding energy (Omanga et al. 2013).

Table 3. Freundlich equation model for the studied soils.

Soil sample	Model form	Linear form
Organic	$x/m = 7.473C^{0.7462}$	$y = 0.7462x + 0.8735$
Integrated	$x/m = 15.111C^{0.6295}$	$y = 0.6295x + 1.1793$
Inorganic	$x/m = 11.689C^{0.6774}$	$y = 0.6774x + 1.0678$

Table 4. Thermodynamic properties and free energy of replacement of the soil under basmati rice–wheat–*sesbania* cropping systems.

Management practice	Electrical conductivity (mmhos/cm)	Ionic strength (mmol/L)	K activity coefficient	K activity in (mmol/L)	Ca + Mg activity (mmol/L)	Activity ratio	Free energy (Cal.mol ⁻¹)
Organic	0.1841 ± 0.009	2.37 ± 0.17	0.947 ± 0.01	0.705 ± 0.02	0.4239 ± 0.04	0.03426 ± 0.001	-1998.01 ± 30.24
Integrated	0.1241 ± 0.001	1.60 ± 0.14	0.955 ± 0.12	0.700 ± 0.03	0.4286 ± 0.012	0.03383 ± 0.004	-2005.59 ± 51.20
Inorganic	0.1399 ± 0.002	1.80 ± 0.012	0.953 ± 0.01	0.697 ± 0.09	0.4291 ± 0.018	0.03365 ± 0.002	-2008.76 ± 21.36

Thermodynamics parameters in relation to K adsorption in soil

The thermodynamic parameters such as free energy of replacement, activity ratio and ionic activity were used to evaluate the dynamics behavior of potassium in soils (Table 4). These parameters give an indication about the rate at which potassium adsorbed on the soil and can replenish the soil solution potassium (Rasnaek and Thomas 1976). This method can be used to determine fertilizer dosage required to maintain optimum concentration levels of K in soil solution for better uptake.

The ionic strength (μ)

This ionic strength of K in soil solution indicates the availability of active form of K to meet out the demand of potassium for obtaining potential crop yields (Al-Zubaidi et al. 2008). The ionic strength of K in studied soils 1.6 to 2.37 mmol/L as shown in Table 4. Higher value of ionic strength (2.37 mmol/L) was recorded in the soil under organic manage soil and the value is 24.05% and 32.49% higher compare to the integrated and inorganic nutrient management practices. The higher value of ionic strength may be due to the presence of higher amount of organic matter in the soil as compare to the other nutrient management practice in basmati rice–wheat–*sesbania* cropping systems.

The activity ratio

The activity ratios normally reflect the chemical potential of the soil for making more potassium available for plant uptake. Higher the value of activity ratio, higher will be the K availability for absorption by the crop plant. The activity ratio ions in the studied soil 0.034 to 0.033 which was not significant under different types of nutrient managements (Table 4). This may be due to the alluvial soils properties of the studied soil.

The free energy of replacement (ΔF)

The free energy of replacement indicates the supply power capacity of soil. These values are used to classify the supplying power of potassium in soils.

According to the Woodruff free energy classification, soils with lower than (ΔF) – 3500 cal mol⁻¹ have poor supplying power of potassium and those with –3500 to –2000 cal mol⁻¹ have medium supplying power of potassium. Finally, soils with greater than –2000 cal mol⁻¹ are high in supplying power of potassium. The values obtained from our study ranged from –1998.01 to

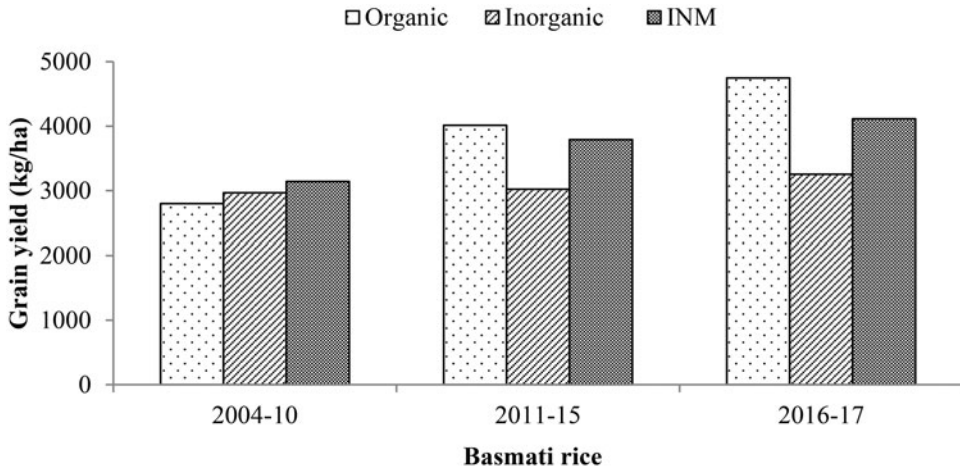


Figure 4. Effect of different crop management on grain yield of basmati rice.

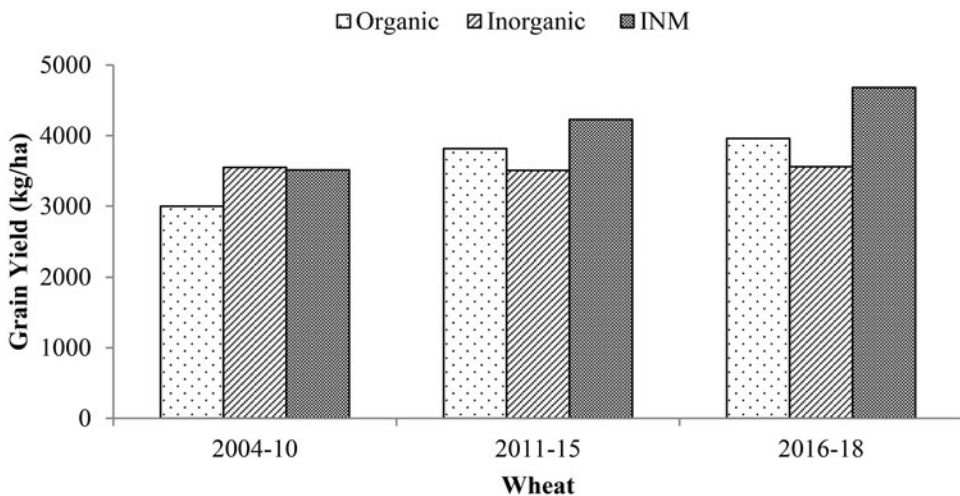


Figure 5. Effect of different crop management on grain yield of wheat.

–2008.76 cal mol⁻¹ (Table 4). The value of free energy of replacement of organic nutrient management soil come under the range of medium K supplying power as compare to the integrated and inorganic nutrient manage soil. The lower value of free energy of replacement may be due to non-application of inorganic source of K for a long time in the soil under intensive cropping systems.

Productivity

Grain yield of basmati rice and wheat was significantly affected by long term nutrient management practices. During the initial years of investigation (2004–10), average grain yields of basmati rice and wheat were lower under organic management as compared to integrated and inorganic management systems (Figures 4 and 5). However, over the period of time, grain yields of both the crops tended to increase under organic and integrated management systems. Higher yields under organic and integrated management might be due to balanced availability of macro and micronutrients through continuous green manuring and application of other organic manures

(Dhar et al. 2014). Long term application of organic matter in the soil improves the nutrient availability through improved soil health. Higher K buffering capacity under organic management might have contributed to better availability nutrient that ultimately led to higher yield under organic and integrated management over the period of time.

Conclusion

From the result, it can be concluded that the soils of the alluvial region under intensive cropping systems have the K supplying capacity is in the threshold level higher K availability to the plant nutrient uptake. We have to take different strategies for improving the K nutrient supplying capacity under organic nutrient management systems for the optimization of systems yield. Therefore, the assumptions that potassium is a non-limited nutrient in alluvial region are inaccurate. This implies that the application of balance amounts of potassium to the soils is required to avoid the nutrient mining from the soil as well as betterment of soil quality.

Disclosure statement

No potential conflict of interest was reported by the authors.

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