Research Findings

Photo 1. Field experiment exploring the effects of potassium applied through either mineral fertilizer or rice straw. Photo by the authors.

Effects of Long-Term Application of K Fertilizer and Rice Straw on Yields, Crop K Uptake, and Soil K Supply Capacity in Double Rice Cropping Systems on Reddish Paddy Soils

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Abstract

The effect of potassium (K) application through mineral fertilizer or rice straw (RS) on rice yield, crop K uptake, and soil K supply capacity were studied in a long-term fertilization experiment (1981-2012) under an intensive double rice cropping system. The application of combined mineral K and soil-embedded RS significantly increased rice grain and straw yields. Potassium uptake significantly increased following consistent application of mineral K, RS, or both. The average annual amount of crop K uptake was in the order of: mineral NPK+RS > NPK > NP+RS > CK > NP. Long-term absence of K application led to a deficit in available, slowly-available, and total topsoil K. Long-term K application through mineral fertilizer and RS not only increased topsoil illite content, but also transformed poor-crystallized illite into well-crystallized illite. In-vitro K saturation treatments

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demonstrated the increased X-ray diffraction peak area of illite versus the declining vermiculite/chlorite peak. Soil K quantity/intensity (Q/I) parameters indicate an improved soil K capacity following long-term K application. It appears that two contradictory processes occurred in the reddish paddy soil, when applied with K releasing materials. The first is the enrichment of the soil solution with K^+ ions and its positive consequences on the clay composition and on K saturation of clay minerals, mostly illite. While mineral K application boosts the soil solution with K at the beginning of the crop cycle, the degrading RS provides a consistent K supply thereafter. The conflicting process is the declining soil pH, with its negative effect on clay mineral structure and its affinity to K and other cations. So far, the positive effects dominate, demonstrating significant influences on crop performance as well as soil fertility. However, the mechanisms involved in the long-term K status in paddy soils are very complex, with many interactive factors, most of which are still obscure. Apparently, RS can successfully replace much of the mineral fertilizer, however, the particular sensitivity of the paddy soil system to soil pH must be taken into account.

Keywords: Illite; long-term K application; potassium quantity/intensity; *Oryza sativa* L.; reddish paddy soil; rice straw.

Introduction

Potassium (K) is an essential nutrient for plants' metabolism and growth, and it has an irreplaceable role in agricultural production (Huang *et al.*, 1998; Liao *et al.*, 2008; Liao *et al.*, 2010). The shortage of K resources in China, and insufficient soil K supply, have severely restricted the development of agricultural production. Therefore, evaluating soil capacity for K supply and the effects of enduring fertilization is critical.

Soil K occurs in different forms: water soluble - free K^+ in the soil solution; exchangeable form - K^+ adhered to the surface of soil particles; non-exchangeable form - K adsorbed to the inner fractions of soil particles; and, mineral form - where K is intrinsic to the chemical structure of the soil minerals. Soil K supply capacity is attributed mostly to the former available forms - water soluble K and exchangeable K, nevertheless, on the long-term, the other two forms may also contribute to the soil K supply. The available K forms are the main source for the current crop's K requirements; therefore, they are considered as an important index characterizing the actual or immediate soil K status. The non-exchangeable K, including mineral lattice K (e.g., biotite) or fixed mineral K (such as in vermiculite and other 2:1 layered silicate minerals), may be converted under certain conditions into exchangeable K or even into soluble K. Different K pools are transformable, and the direction, extent, and rate are affected by various factors (Scherer and Zhang, 2002; Liao *et al.*, 2013a; Liao *et al.*, 2013b), among which mineral composition and quantity have important roles (Zheng *et al.*, 1989; Jin, 1994; Fan and Xie, 2005; Liao *et al.*, 2013b).

Plant response to K availability is often influenced by other soluble nutrients in a given soil. Therefore, methods of physical chemistry must be employed. Thus, thermodynamic parameters, such as relative K activity, K intensity, K-specific site, K strength, K capacity, and potential K-buffering capacity have been widely applied in the efforts to assess soil K supply capacity (Woodruff, 1955; Salmon, 1960; van Schouwenburg and Schuffelen, 1963; Beckett, 1964; le Roux and Sumner, 1968; Molina, 2016).

In earlier studies, basic mechanisms related to the variation and transformation of soil K forms, the interaction between crop root and soil K transformation, and to the interaction between organic and inorganic K fertilizer sources with soils under redox effects remained unclear, particularly under conditions of

Photos 2. Plots with different nutrients omitted (left); plots with and without K application (right) (at tillering stage). Photos by the authors.

continuous cropping systems. Therefore, it is important to further investigate the transformation characteristics of soil K in general, and especially of clay mineral K under long-term continuous cropping rice systems that are very common in China. Understanding these mechanisms will enable the design of improved fertilization management, which will consider the inherent soil K balance and its interactions with applied organic and inorganic K fertilizers, all together meeting crop K demands (Xie *et al*., 2000; Chen *et al*., 2000; Liao *et al*., 2009).

The objectives of the present study were to determine the influence of long-term application of K fertilizer and straw on rice yield and crop K uptake, and to evaluate and quantify the dynamics of soil K forms, including K-bearing clay minerals and K adsorption and desorption under continuous application of K fertilizer and straw. The study provides a theoretical basis for optimal K management of double-rice cropping systems on red soils.

Materials and methods

Site description

Field experiments were conducted from 1981 until 2012 in Huangjin town, Wangcheng county, Hunan Province of China at the Scientific Observing and Experimental Station of Arable Land Conservation, Ministry of Agriculture, 28°37'N, 112°80'E, 100 m above sea level. The average annual rainfall was 1,393 mm, the annual mean temperature was 18°C, and the annual mean frost-free period was 300 days. Soil characteristics are given in Table 1.

Table 1. Experimental soil properties.

Soil type	Quaternary red soil
Soil texture	Silty light-clay
pH	6.6
Organic matter	34.7 g kg^{-1}
Total nitrogen (N)	2.05 g N kg^{-1}
Alkali-hydrolysable N	151.0 mg kg^{-1}
Total phosphorus (P)	0.66 g P_2O_5 kg^{-1}
Available P	10.2 mg kg^{-1}
Total potassium (K)	14.2 g K_2O kg^{-1}
Immediately available K	62.3 mg kg^{-1}
Slowly available K	173.8 mg kg^{-1}

Experimental design

The field experiment was laid out with five treatments (Table 2) in three replicates. Each plot area was 66.7 m^2, with 30 cm wide cement bunds between plots in order to avoid cross contamination. There were two rice crops each year, early (late April to mid July) and late (late July to late October), using regular and hybrid rice cultivars, respectively. Nitrogen (N), P and K mineral fertilizers used were urea, superphosphate and KCl, respectively.

Five treatments were: CK (no fertilizer); NP (mineral N and P fertilizer); NPK (mineral N, P, and K fertilizer); NP+RS (mineral N and P fertilizer, and rice straw); NPK+RS (mineral N, P, and K fertilizer, and rice straw). During the period from 1981 to 2012, N fertilizer was applied at 150 and 180 kg N ha^{-1} for early and late rice, respectively. Phosphate fertilizer was applied at a rate of 38.7 kg P_2O_5 ha^{-1} for the early as well as late crops. Potassium fertilizer rates were 99.6 kg K_2O ha^{-1} in early and late rice. Rice straw was incorporated into the soil at a rate of 2.1 Mg ha^{-1} (containing 21.4, 2.8, and 54.6 kg ha^{-1} of N, P_2O_5, and K_2O, respectively) in the early as well as in the late rice seasons. Phosphorus (P) and K fertilizer and straw were applied to the soil before transplanting, while N fertilizer was applied twice: 50% before transplanting, and the rest at tillering. The regular rice cultivar was planted for the early crop, and a hybrid rice for the late one. The early crop was planted in late April and harvested in mid-July. The late crop was planted in late July and harvested in late October. Seedlings at 30-35 days of age were transplanted into each plot; 4-5 per hole in the early rice, and 1-2 in the late rice. Plant spacing was 20 x 20 cm. Pest management and other routines were applied using local farmers' practices.

Sampling, measurements, and data analysis

Grain yield was determined from the whole plot of each replicate. Plant samples were collected from multiple points and mixed evenly. Plant K content was determined using a flame photometer (Lu, 2000).

Soil samples were collected from 0-15 cm topsoil (one week after the late crop harvest, 2 November 2012), using a tubular soil sampler. Soil was air dried, sieved and stored in a sealed jar. Soil K extraction and determination followed the methods described by Lu (2000), using a flame photometer. Total soil K was extracted with NaOH, slowly-available K was extracted with hot HNO_3 (1 mol L^{-1}), and available K was extracted with NH_4OAc (1 mol L^{-1}). Basic physical and chemical

Table 2. Detailed fertilization plan of the treatments.

Treatment	Mineral N		Mineral P_2O_5		Mineral K_2O		Straw N		Straw P		Straw K	
	Early	Late	Early	Late	Early	Late	Early	Late	Early	Late	Early	Late
	------	------	------	------	------	*kg ha^{-1}*	------	------	------	------	------	------
CK - no fertilizer	-	-	-	-	-	-	-	-	-	-	-	-
NP	150	180	38.7	38.7	-	-	-	-	-	-	-	-
NPK	150	180	38.7	38.7	99.6	99.6	-	-	-	-	-	-
NP+RS	150	180	38.7	38.7	-	-	21.4	21.4	2.8	2.8	54.6	54.6
NPK+RS	150	180	38.7	38.7	99.6	99.6	21.4	21.4	2.8	2.8	54.6	54.6

properties of the samples were conventionally determined according to Lu (2000). Clay mineral composition was determined using X-ray diffraction method (Moore and Reynolds, 1997), followed by numerical-graphic methods (Lanson, 1997), and the mineral diffraction peak areas were calculated using NEWMOD program (Reynolds, 1985). Potassium quantity/intensity (Q/I) parameters in soil samples were determined following Beckette (1964). Data analyses employed Microsoft Excel 2003 and 7.5 DPS data processing system.

Results

Rice grain and straw yields increased significantly in response to long-term application of K, either through mineral K fertilizer, embedding of RS or both (Fig. 1). The order of grain yield in early and late rice was: NPK+RS > NPK > NP+RS > NP > CK. Compared with the non-fertilized control (CK), the application of NP fertilizer gave rise to 69.5% and 39.9% increase in early and late grain yields, respectively. Potassium supply, either through mineral NPK, organic K source (rice straw), or both, provided additional significant rise in grain yields, of 88-111% and 60-75% over CK, in the early and the late crop, respectively. When compared to the NP yield, K supply brought about 10.9%, 15.9%, and 24.7%, and 14.4%, 17.5%, and 25.2% increase in the grain yield of RS, NPK, and NPK+RS, of the early and late rice crops, respectively. Straw biomass tended to increase in response to application of NP fertilizer. However, this response was significant only following K supply, resulting in 41-58% and 38-62% increases in straw biomass of early and late rice crops, compared to CK (Fig. 1). No significant differences occurred between the K contributing treatments; however, when compared to NP, straw biomass increased by 9-21%, and 14-34%, in the early and late crops, respectively (Fig. 1).

Responding to application of NP fertilizer, K uptake by the grain yield increased significantly, by 99% and 56% in the early and late crop, respectively, compared to CK (Fig. 2). Mineral NPK

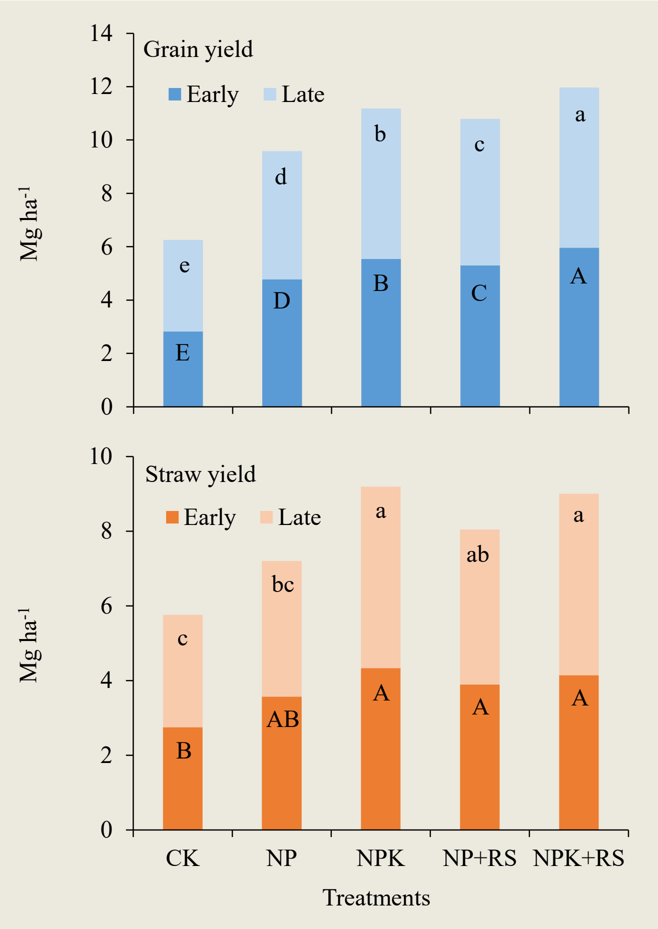

Fig. 1. Effects of K fertilization and rice straw (RS) application on grain yield and straw biomass of two successive rice crops, early and late, in 2017, following 32 years of the experiment. Similar lowercase and uppercase letters indicate no statistical differences at P = 0.01 within the early and the late crop, respectively.

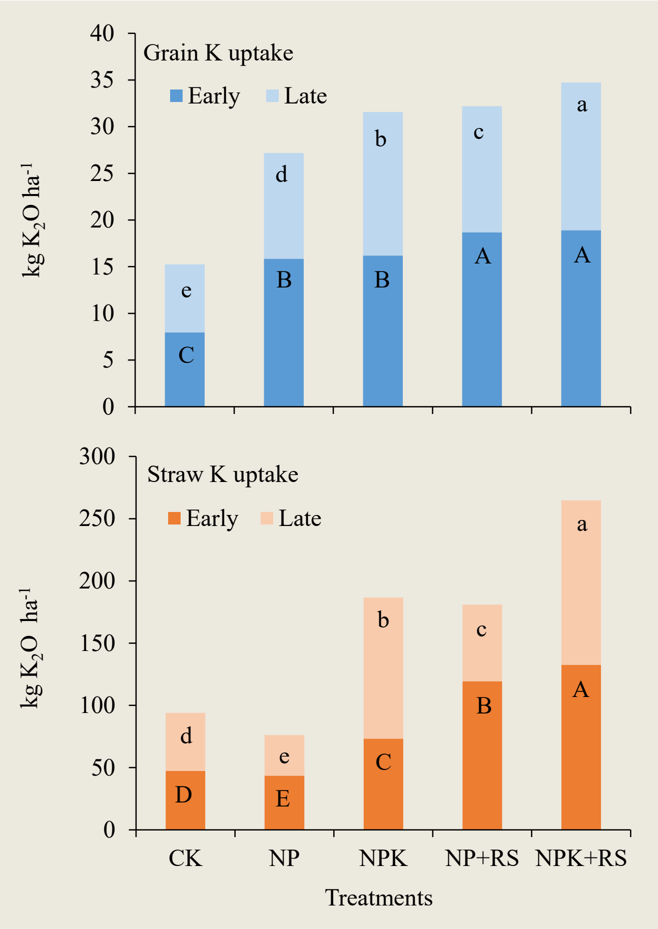

Fig. 2. Effects of K fertilization and RS application on K uptake by grain and straw biomass of two successive rice crops, early and late, in 2017. Similar lowercase and uppercase letters indicate no statistical differences at P = 0.01 within the early and the late crop, respectively.

application brought about a significant increase in grain K uptake, 36% more than NP but only in the late crop, whereas no impact was observed for the early crop. Embedded RS, on the other hand, resulted in a significant rise in grain K uptake of both early and late crops, 18-20% more than NP. The combination of mineral NPK and RS application gave rise to the greatest grain K uptake, particularly in the late crop, 40% more than NP (Fig. 2). Nevertheless, K uptake by the straw biomass was far greater than that of the grains (Fig. 2). Under no fertilization (CK), K uptake by each crop was about 47 kg K_2O ha^{-1} and 7-8 kg K_2O ha^{-1}, in the straw and grains, respectively. Contrary to grain K uptake, straw K uptake declined significantly in response to NP fertilizer, especially in the late crop. Application of mineral NPK resulted in significant increases in straw K uptake, 70% and 250% more than NP, in the early and late crop, respectively. On the other hand, RS supported significant straw K uptake during the early crop, but a modest one in the late crop (174% and 88% more than NP, respectively). Yet, the most pronounced K uptake by straw biomass was in response to the combined treatment (NPK+RS), 180% more than CK in both crops, and 3- and 4-fold K uptake by NP straw in the early and late crop, respectively (Fig. 2).

The overall yearly K uptake of CK was 109 kg K_2O ha^{-1}, an amount which slightly decreased under mineral NP application to 103 kg K_2O ha^{-1}. Obviously, the origin of the K taken up in those two cases was the native soil (Fig. 3). Once mineral K was applied (NPK), crop K uptake surged to about 220 kg K_2O ha^{-1}, of which the soil K contribution was about 10%. Under application of mineral NP+RS (but no mineral K), crop K uptake was about 200 kg K_2O ha^{-1}, with an equal K contribution by RS and soil K. However, under combined application of mineral NPK+RS crop, K uptake increased to 300 kg K_2O ha^{-1}, 67% of which was supplied by the mineral fertilizer, and 33% by the embedded RS. Theoretically, under this practice, an excess yearly amount of about 9 kg K_2O ha^{-1} enriches the soil-K reserves (Fig. 3).

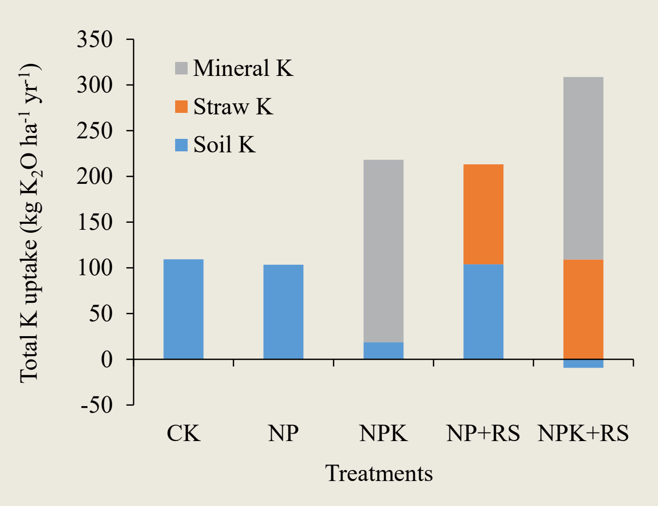

Fig. 3. The contribution of mineral fertilizer, RS, and soil K to total yearly K uptake by two rice crops following 32 years of experiment.

Compared to the initial soil properties, fertilization treatments - not including mineral K - brought about an obvious degradation in the soil exchangeable K content, which embedded RS alone did not prevent (Fig. 4). Application of mineral K fertilizer, alone or with RS, gave rise to significant increases of about 50% and 100% in exchangeable K content, respectively. A more or less similar pattern was observed with the non-exchangeable component of soil K; however, both degradation and repair rates were much smaller than in the exchangeable K fraction. During 32 years of the double rice cycle, total soil K content declined considerably in all fertilization treatments (Fig. 4). Total K loss from CK topsoil

Photos 3. Plots with different nutrients omitted (left) (mature stage); plots with and without K application (right) (just before mature stage). Photos by the authors.

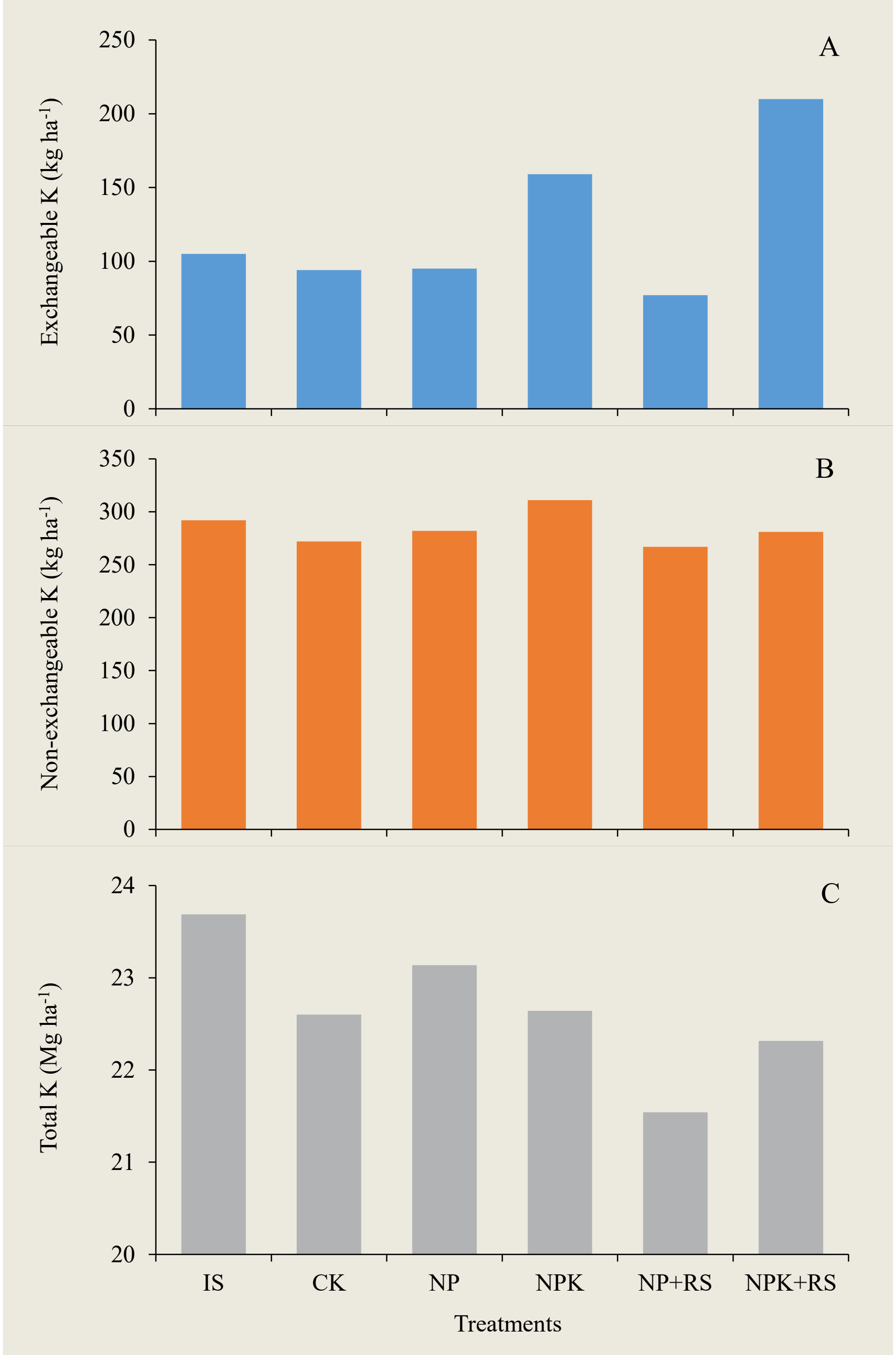

Fig. 4. Effects of long-term (32 years) treatments on the exchangeable (A), non-exchangeable (B), and total K (C) topsoil (depth 0-15 cm) contents. (IS: initial soil).

was about 1.1 Mg ha^{-1}, similar to that of NPK, and twice as high as NP treatments. Interestingly, the greatest total K loss, 2.15 Mg ha^{-1}, was recorded in NP+RS treatment, compared to about 1.37 Mg ha^{-1} in NPK+RS (Fig. 4).

X-ray diffraction patterns of the clay fraction (soil particles < 5 µm) treated with magnesium-saturated glycerin, ethylene-glycol, K$^+$ saturation, and 300°C or 550°C heat treatments, were used to determine the nature and distribution of the dominant clay minerals in the soil and to evaluate the influences of the different long-term fertilization treatments on clay mineral composition (Table 3).

Vermiculite/chlorite, the dominant clay fraction (36-40%), slightly increased from 38% (IS) to almost 40% under the absence of K fertilization, and decreased down to 36% under consistent K supply of mineral, as well as organic origin. Kaolinite proportion, 27.6% of the clay fraction, also increased in the absence of K supply, and declined to 25% where K was supplied. The mixed-layer mineral (comprising vermiculite/chlorite and illite) was stable at 18% under no K application, and dropped to 14-16% when K was supplied. An opposite response pattern was observed for illite and its two components - well- and poorly-crystalized illite; their portion decreased in the absence of K supply, and rose by 40-50% (from 16 to 24%) of the clay minerals in response to K application. All these changes were much more pronounced where mineral K was involved; however, the response to RS alone was obvious (Table 3).

Further in-depth X-ray diffraction analyses of the major K-responsive clay minerals (illite, vermiculite/chlorite, and the mixed-layered mineral of the two), before and after K$^+$ saturation, revealed the significance of illite fractions in the K$^+$ exchange processes. The profile of K-saturated illite in the X-ray diffraction tests was doubled, compared to the natural free illite (Fig. 5). In contrast, the vermiculite/chlorite profile tended to decrease in response to K-saturation treatments. As indicated from the various mixtures of clay minerals examined (data not shown), the greater the illite fraction in the clay mineral composition, the higher the soil K exchange capacity.

Years of different fertilization regimes had only a slight influence on the topsoil organic matter content, which gradually increased from 33.14 g kg^{-1} to 38.55 g kg^{-1},

Table 3. Clay mineral distribution (%) in paddy soils after 32 years of consistent fertilization treatments compared to that of the initial soil (IS).

Treatment	V/CH	ML	KL	IL	WCI	PCI
IS	38.09	18.21	27.60	16.10	4.20	11.90
CK	39.23	17.32	28.75	14.70	3.08	11.62
NP	39.61	18.45	27.57	14.37	2.82	11.55
NPK	36.17	15.57	25.12	23.14	6.64	16.50
NP+RS	37.30	15.26	25.98	21.46	6.62	14.84
NPK+RS	35.99	14.41	25.31	24.29	6.88	17.41

Note: V/CH: vermiculite-chlorite; IL: illite; ML: a mixed-layer mineral of V/CH and IL; KL: kaolinite; WCI: well-crystallized IL; PCI: poorly-crystallized IL.

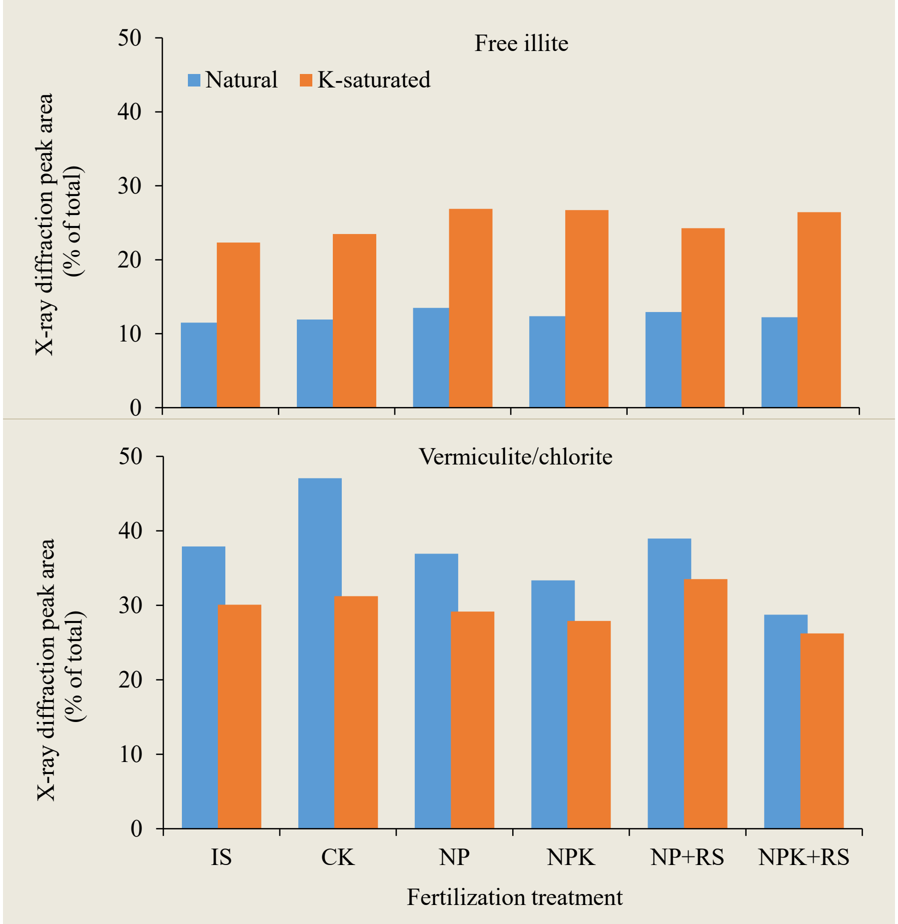

Fig. 5. Effects of long-term K fertilization regimes on the relative X-ray diffraction peak area of free illite and vermiculite/chlorite in the natural or K-saturated states.

from CK to NPK+RS (Table 4). This was in spite of the considerably large straw biomass quantities added to the RS treatments. Exchangeable K, measured using the NH_4OAc method, increased slightly at NP+RS, was higher at NPK, and much higher at NPK+RS.

Cation exchange capacity (CEC), also measured using the NH_4OAc method, was somewhat higher at NP+RS only, displaying no significant changes in the other treatments. Soil pH declined from 5.8 at CK, to 5.2-4.4 in the fertilized treatments (Table 4).

The long-term impact of the different fertilization treatments was further examined evaluating several K quantity/intensity (Q/I) parameters in the reddish paddy soil. Soil content of labile K ($-\Delta K^o$) in CK and NP was low, indicating poor levels of soluble K. While embedded straw (NP+RS) brought about a slight increase of labile K, mineral K application (NPK) caused a more considerable rise of this parameter (about 50%). Nevertheless, the most significant increase, about 100%, occurred in the combined NPK+RS treatment (Table 5).

Quite similar response patterns to the fertilization treatments were displayed by the K-specific adsorption sites parameter (K_X). Here, NPK and NP+RS had an equal impact, increasing K_X by about 30%, but NPK+RS yielded a 50% rise, compared to CK (Table 5). AR_e^k is another indicator of the intensity of easily released K. AR_e^k values in non-fertilized (CK) and NP treatments were significantly lower than those obtained by NPK and NPK+RS treatments, although NP+RS did not lag far behind (Table 5). PBC^K is a measure of soil potential K-buffering capacity - the ability to maintain K strength in the soil solution. High PBC^K values, such as displayed by CK and NP, indicate that large K^+ quantities are required to obtain a given soluble K concentration in the soil solution. In other words, the soil particles absorb most of the added K from the soil solution. The lower values observed in the K fertilized treatments indicate the smaller K amount required for the same purpose in those soils (Table 5). Gibbs free energy ($-\Delta G$) measures the energy required to exchange adsorbed K with an equivalent amount of Ca and Mg ions, and is an additional indicator of soil K availability. The high values observed for CK and NP indicate the considerably high energy needed to release K from the soil particles and a higher risk of crop K deficiency. $-\Delta G$ values slightly decrease in the NP+RS soil, but significantly drop in the NPK, and decrease even further in the NPK+RS soils (Table 5).

Table 4. Soil organic matter, pH, and cation exchange capacity (CEC) of reddish paddy soil samples representing long-term application of fertilizers and rice straw.

Treatment	Organic matter	Exchangeable K	CEC	pH
	g kg^{-1}	-----------------*cmol kg^{-1}*-----------------		*H_2O*
CK	33.14	0.17	12.9	5.8
NP	33.96	0.14	13.2	5.2
NPK	36.02	0.28	13.2	5.3
NP+RS	37.03	0.20	15.0	5.4
NPK+RS	38.55	0.37	13.5	5.4

Discussion

In the recent decades, Chinese agriculture has undergone tremendous changes in order to increase efficiency and productivity. Nevertheless, traditional farming is still the livelihood source for millions of farmers. Double-rice cropping on paddy soils is the basis of traditional farming in many regions. Improving the productivity as well as securing the sustainability of this system is essential. The maintenance of long-term soil fertility is pivotal; while N and P application is commonly practiced by most farmers, dissemination of the need to restore and maintain an appropriate soil K status requires further approval and demonstration. Rice crops produce significant straw biomass, which must be taken care of between cycles. Rice straw is commonly used as a biofuel; however, significant amounts of nutrition elements, including K, are withdrawn from the field that way. Another practice is on-field straw burning, so the ash returns to the soil. Nevertheless, this practice impedes the opportunity to enrich the soil with organic matter, which might affect soil structure and texture. The contribution of embedded RS to soil fertility, structure, and K status can be evaluated in the long-term - over many years - as the processes involved are very slow. The present study, ending 32 years and 64 cycles of rice crops, provides a comprehensive as well as an in-depth insight into the long-term impact of mineral NPK, with and without embedded RS application, on the system productivity, soil clay composition, and K status, compared to the necessary controls.

Unequivocally, mineral NP application brought about a significant primary boost in grain and straw biomass, about 40% more than the non-fertilized (CK) treatment (Fig. 1). NP application drew the limited K available from straw to grains (Fig. 2), and consequently significantly increased the harvest index from 52% to 57% (Fig. 6). The addition of K to the mineral NP application significantly increased crop K uptake (Fig. 2) and released the pressure from soil K (Fig. 3). It also increased crop biomass, especially that of straw (Fig. 1), thus reducing the harvest index (Fig. 6). Nevertheless, mineral NPK gave rise to a further significant increase in grain yields (Fig. 1). Interestingly, crop K uptake - where K supply was solely through RS (NP+RS) - was similar to that of mineral NPK (Fig. 2). Embedded RS contributed 50% of K uptake (Fig. 3). Grain and straw biomass were slightly (though statistically significant) lower than those of mineral NPK treatment (Fig. 1). The highest grain yields were obtained by the NPK+RS treatment which, together with the mineral NPK treatment, also had the highest straw biomass (Fig. 1). NPK+RS also displayed the highest K uptake, which was especially pronounced in the straw (Fig. 2). Noteworthy is the full dependency of the crop on supplied K and, moreover, the considerable support to soil K status in this treatment (Fig. 3). In both NP+RS and NPK+RS, the high harvest index of 57% was restored and maintained (Fig. 6). These results may suggest that mineral K has more impact on the vegetative biomass, while embedded RS supports the grains. An explanation may also be provided by the different nature of the two K origins. Mineral K is soluble and mobile in the soil, and its impact is therefore short-term and may be limited to the earlier crop phase, closer to its application. On the other hand, K release from organic matter, such as embedded RS, is much slower but consistent, and hence available during the grain-filling period.

As shown in Figs. 1-3, relying solely on soil K resources (CK and NP) certainly restricts crop performance and, furthermore, it might significantly

Table 5. Effect of long-term application of K fertilizer and rice straw on Q/I parameters in reddish paddy soil.

Treatment	Labile K; $-\Delta K°$	K-specific sites; Kx	Labile K intensity; AR_e^K	Potential K buffering capacity; PBC^K	Gibbs free energy; $-\Delta G$
	---------------------*cmol kg^{-1}*---------------------		*cmol kg$^{-1\ 0.5}$*	*cmol kg^{-1}/cmol kg$^{-1\ 0.5}$*	*kJ mol^{-1}*
CK	0.1498	0.1532	0.0078	19.67	15.34
NP	0.1608	0.1624	0.0082	19.85	14.87
NPK	0.2181	0.2194	0.0145	15.11	10.50
NP+RS	0.1868	0.2099	0.0136	15.48	13.80
NPK+RS	0.2970	0.2400	0.0168	14.29	9.79

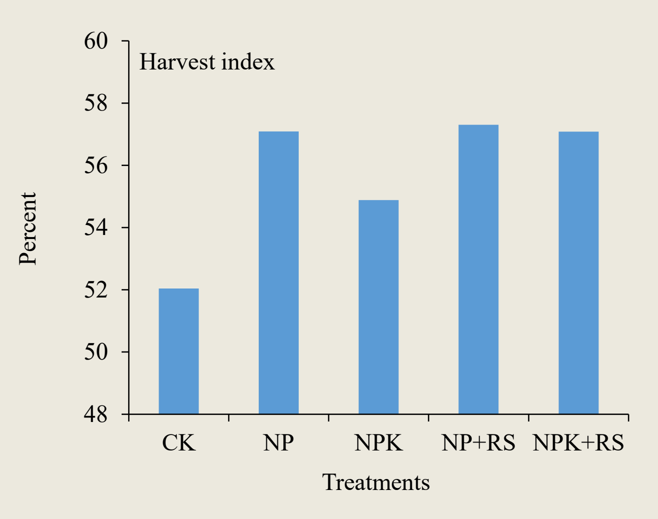

Fig. 6. Effect of long-term fertilization treatments on the harvest index of double rice crop in 2012, following 32 years of experiment.

degrade soil fertility. In fact, after 32 years of rice crops, the total topsoil K content declined in all treatments (Fig. 4). It was particularly reduced in the NP+RS treatment, where the enhancement of crop performance relied on the organic K from RS. Any expectation for higher yields must be accompanied by sufficient external K supply. Accounting for NP+RS, the amounts of RS should be increased in order to meet crop performance under mineral NPK. The NPK+RS combination, at the doses tested in the present study, seem to meet crop K requirements and provide the desired yield.

In intensive agricultural systems, K application is also essential for the maintenance of soil fertility. The type and rate of K application affect the exchangeable and non-exchangeable fractions of soil K. Excluding the NPK treatment, the non-exchangeable K declined in all treatments. Topsoil exchangeable K, however, increased significantly in the NPK and NPK+RS treatments, but decreased in the others (Fig. 4).

A long-term fertilization regime, 32 years, has significant influences on the composition of soil clay minerals (Table 3). While decreasing under regimes with no K application (CK and NP), illite fraction substantially increased under consistent K supply. These results support earlier evidence of gradual transformation of one clay mineral to the other as a result of long-term fertilization regime (Tributh *et al.*, 1987). The increasing fractions of poor- and well-crystallized illite under K fertilization, relative to the total illite fraction, clearly indicate an active development of new illite minerals at the expense of vermiculite/chlorite. This dynamic is absent, or even opposite where no K was applied (Table 3). Results of K-saturation treatments applied on the different clay minerals may demonstrate the process through which long-term K application can transform vermiculite to illite (Fig. 5).

Soil organic matter content is known to have a direct effect on soil CEC (Thomas and Hargrove, 1983). Nevertheless, the differences in soil organic matter content between treatments were very small in the present study, although substantial quantities of RS were applied to two of them. Possibly, the degradation rates of organic matter were very rapid under the typically high moisture and temperature conditions of the region. Fermenting organic matter might have contributed to the pH decline (Table 4) which might, in turn, negatively affect CEC (Helling *et al.*, 1964; Blum and Bride, 1979; Thomas and Hargrove, 1983).

It appears that two contradictory processes occurred in the reddish paddy soil when applied with K releasing materials. The first is the enrichment of the soil solution with K^+ ions and its positive consequences on the clay composition and on the penetration and saturation of clay mineral, mostly illite, with K, as reflected in the changes in Q/I parameters of soil K status (Table 5). While mineral K application boosts the soil solution with K at the beginning of the crop cycle, close to the application time, the degrading RS provides a consistent K supply thereafter. The higher affinity of soil particles vs. organic matter (Salmon, 1960) derive K from RS to illite. Thus, -ΔG values in CK and NP treatments were far below the K deficiency threshold (Woodruff, 1955), equal to this threshold in NP+RS, and considerably higher, with sufficient K in the NPK and NPK+RS treatments, although calcium (Ca) deficiency might be induced (Woodruff, 1955). The conflicting process is the negative effect of too lowered pH on clay minerals and their affinity to K and other cations (Prett *et al.*, 1962).

So far, the positive effects seem to dominate, demonstrating significant influences on crop performance as well as soil fertility. However, the mechanisms involved in long-term K availability in paddy soils are very complex, with many interactive factors, the full understanding of which still requires further substantial research efforts. The paddy soil system is extremely sensitive to many factors, including soil pH which must be taken into account.

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The paper "Effects of Long-Term Application of K Fertilizer and Rice Straw on Yields, Crop K Uptake, and Soil K Supply Capacity in Double Rice Cropping Systems on Reddish Paddy Soils" also appears on the IPI website at:

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