Potassium fertilization combined with crop straw incorporation alters soil potassium fractions and availability in northwest China: An incubation study

Xiushuang Li, Yafei Li, Tianqi Wu, Chunyan Qu, Peng Ning, Jianglan Shi, Xiaohong Tian

College of Natural Resources and Environment, Northwest A&F University/ Key Laboratory of Plant Nutrition and the Agri-environment in Northwest China, Ministry of Agriculture and Rural Affairs, Yangling, Shaanxi, China

Scientific Laboratory of Heyang Agricultural Environment and Farmland Cultivation, Ministry of Agriculture and Rural Affairs, Heyang, Shaanxi, China

* shij81@nwsuaf.edu.cn

Abstract

Potassium (K) input is essential for the improvement of soil fertility in agricultural systems. However, organic amendment may differ from mineral K fertilization with respect to modifying the soil K transformation among different fractions, affecting soil K availability. We conducted a 60-day lab incubation experiment to evaluate the response of soil K dynamics and availability in various fractions with a view to simulating crop residue return and chemical K fertilization in an Anthrosol of northwest China. The tested soil was divided into two main groups, no K fertilization (K0) and K fertilization (K1), each of which was subjected to four straw addition regimes: no straw addition (Control), wheat straw addition (WS), maize straw addition (MS), and both wheat straw and maize straw addition (WS+MS). Soil K levels in the available (AK) and non-exchangeable (NEK) fractions were both significantly increased after K addition, following the order of K > WS > MS. Fertilizer K was the most efficient K source, demonstrating a 72.9% efficiency in increasing soil AK, while wheat and maize straw exhibited efficiencies of 47.1% and 39.3%, respectively. Furthermore, K fertilization and wheat and maize straw addition increased the soil AK in a cumulative manner when used in combination. The mobility factor (MF) and reduced partition index (IR) of soil K were used to quantitate the comprehensive soil K mobility and stability, respectively. Positive relationships were observed between the MF and all relatively available fractions of soil K, whereas the IR value of soil K correlated negatively with both MF and all available fractions of soil K. In conclusion, straw amendment could be inferior to mineral K fertilization in improving soil K availability when they were almost equal in the net K input. Crop straw return coupled with K fertilization can be a promising strategy for improving both soil K availability and cycling in soil–plant systems.
Introduction

Potassium (K) is an essential macronutrient for plant growth, a large quantity of which is present in the soil within secondary clay minerals [1,2]. In the agricultural ecosystem, K plays a key nutritional role in determining crop yield [3–5]. Over recent decades, intensive agriculture has substantially increased crop production in both developed and developing countries [6–8], resulting in considerable depletion of soil K through crop removal. Soil K deficiency, especially in the fractions available to plants, is currently a worldwide problem [9–11].

In China, soil K deficiency is closely correlated with the excessive application of nitrogen (N) and phosphorus (P) [12,13]. In intensive agricultural systems, fertilizer recommendations and the subsequent application of N and P have increased annually over recent decades, whereas the application of K has not been increased accordingly [14]. Farmers are not aware of the economic benefit of K fertilizer application since it is more expensive than N and P fertilizer and does not increase crop yield as quickly [10,15]. However, results of soil fertility tests have shown that soil K content is declining nationwide, especially in originally infertile and intensive agricultural soils [5,10,12]; therefore, management aimed at mitigating the negative K budget is urgently required.

The return of crop residue is crucial for maintaining soil quality and increasing agricultural productivity since it is rich in soil organic matter and mineral nutrients [16–20]. Particularly in cereal crops such as maize and wheat, a large amount of K is present in crop straws with extremely low harvest indexes (12–18%). Moreover, the K content of plants is not linked to organic compounds and can therefore be easily released and available after straw return [21–22]. It has been well documented that both crop yield and soil K availability can be improved by long-term straw return [11,23,24]. In China, crop straw return is widely practiced in agricultural production [25,26]; however, relying only on internal circulation of the soil–plant system is not sufficient to relieve the soil K deficit. Crop straw return should be combined with K fertilization to not only offset soil K deficit, but also improve K cycling.

The fraction in which soil K resides determines its bioavailability [27,28]. Generally, soil K exists in water-soluble (WSK), exchangeable (EK), non-exchangeable (NEK), and structural (SK) fractions, among which WSK and EK are easily released into the soil and readily available to plants [2,27]. Soil EK is the dominant form of available K (AK), which is electrostatically retained on the outer surface of clay minerals and organic substances [29–31]. According to previous studies, soil EK can be further separated into non-specific adsorptive K (NSAK) and specific adsorptive K (SAK). Soil SAK is adsorbed around the edges and wedge zones of micaeous clay minerals and is more intensively held by soil minerals, with relatively lower mobility as compared with NSAK [27,32]; however, dynamic equilibrium reactions of soil K exist among different fractions [2,33]. For example, soil AK can be fixed as NEK, which reduces its bioavailability for the current crop since soil K$^+$ ions in soluble or adsorbed forms enter the adsorption sites in mineral matrixes of 2:1 type clay [2,27,31]. Therefore, the relative distribution of soil K among different fractions can be altered by variations in dynamic equilibrium, which affects soil K availability.

In turn, the redistribution of soil K among different fractions can also break the dynamic equilibrium, driving K transformation. Increased soil AK can simultaneously cause its fixation as NEK, reserving it as the major source of K for following cropping systems [2,34–36]. In some cases, the release of soil NEK to available fractions occurs when EK and WSK levels are decreased by crop removal and/or leaching [27,35]; thus, both soil AK and NEK characteristics must be considered when assessing soil K availability and exogenous K efficiency, particularly in long-term cropping systems. Moreover, soils differ in their tendency to fix applied K, with each soil having its own fixing capacity for K that is also affected by changes in soil solutions.
Theoretically, soils with a relatively higher content of organic matter provide a greater number of adsorption sites for EK, protecting soil AK against fixation. However, the addition of organic carbon (C) to soil may also lead to immobilization of available nutrients by altering physical, chemical, and biological factors in the soil [20,37,38]. As a result of concomitant organic C addition, it remains uncertain whether crop straw return differs from mineral K fertilization with respect to regulating the relative distribution of AK. Further, suitable methods to assess soil K bioavailability by simultaneously considering soil AK and NEK characterization are required for long-term cultivation.

Soils in the main agricultural areas of northern China are generally developed from K-rich parent materials; hence, the soil K content is not a major limiting factor in crop production [10,11,29]. The winter wheat (Triticum aestivum L.)–summer maize (Zea mays L.) rotation system is commonly practiced in these areas and is characterized by intensive agriculture with a high input of N and P but inadequate K addition [12,14,19,39]. Despite the original abundance of K in these regions, soil K has been in deficit for decades; it is estimated that approximately 4333 kg·ha⁻¹ net K has been removed from the soil over the past 20 years with no K replacement [40]. Soil K is gradually limiting crop production, particularly in the major grain-producing areas of northern China [1,3,10]; thus, increasing the addition of K is urgently required in these areas to maintain crop production and improve soil fertility.

On the other hand, the use of both the mobility factor (MF) and reduced partition index (IR) has already been confirmed as an efficient assessment of the redistribution and bioavailability of metals in soil [41,42]. The MF, which is dictated by the metal content of the soluble and exchangeable fractions, can be used to describe the metal mobility in soil. In contrast, IR expresses soil metal transformation in individual fractions and explains their redistribution. Both of these indexes are promising for the appropriate quantitation of K bioavailability of multiple fractions but reports regarding their use for this purpose are rare.

Considering this background information, we hypothesized that mineral K fertilization and straw (wheat and maize) return would differentially affect the relative distribution of soil K among various fractions, thus determining soil K availability dependent on variations in the MF and IR values. An incubation experiment was performed to monitor soil K dynamics in various fractions following simulated crop straw return, K fertilization, and a combination of both treatments. The objectives were: (i) to assess the responses of soil K in different fractions to K addition, including K fertilization and straw return; (ii) to examine how K fertilization and straw return influence soil K bioavailability when considering all K fractions, based on the observed changes in the MF and IR of soil K; and (iii) to develop the optimal management practice for the improvement of soil K availability and cycling in this intensive agricultural system.

**Materials and methods**

**Soil and crop straw**

An incubation experiment was carried out to determine the dynamics of soil K following straw incorporation and K fertilizer application. Soil samples (0–20 cm layer) were collected from the Northwest A&F University Experimental Station (34°17'44" N, 108°04'10" E, 524.7 m above sea level), Shaanxi Province, North China. Annual winter wheat–summer maize cropping rotation has long been the dominant system in this region. Summer maize (Zea mays L.) is grown from June to October every year, followed by winter wheat (Triticum aestivum L.) from October to the following June. There has been no potash fertilizer applied in this region for decades due to the inherently K-rich soil parent materials with a total K of more than 20g kg⁻¹. Soil was collected from a field without straw return to avoid the crop residue effect. The
soil was classified as an Earth-cumuli Orthic Anthrosol and had a pH of 8.08, SOC of 9.92 g kg\(^{-1}\), total N, P, and K of 1.17, 0.81, and 22.32 g kg\(^{-1}\), respectively, and an available N, P, and K of 20.26, 10.53, and 142 mg kg\(^{-1}\), respectively. The major minerals in the soil were illite and montmorillonite. Soil samples were air-dried, ground to particles <2-mm in size, and divided into two subsamples. Most of the soil was used for the incubation experiment and a small proportion was used to determine the basic physicochemical properties.

The winter wheat and summer maize straw was collected after each crop harvest in 2015, dried, and ground to <1 mm for subsequent incubation and total K analysis. The K concentrations in wheat and maize straws were 1.45% and 1.25%, respectively.

**Experimental design**

The tested soil was divided into two groups, no K fertilization (K0) and 200 mg K\(_2\)O kg\(^{-1}\) dry soil fertilization (K1), each of which were subjected to four simulated straw addition regimes: no straw addition (Control), wheat straw addition (WS, straw was applied at 12 g kg\(^{-1}\) dry soil), maize straw addition (MS, straw was applied at 12 g kg\(^{-1}\) dry soil), and both wheat and maize straw addition (WS+MS, both wheat and maize straw were applied at 12 g kg\(^{-1}\) dry soil). For the laboratory incubation experiment, the treatments were arranged using a completely random design and 12 replications were performed for each treatment. For the incubation, 250 g soil (dry weight) and the corresponding amount of straw and K fertilizer (K\(_2\)SO\(_4\)) were added to each 1-L jar (15 cm in height, 9 cm in diameter, with a perforated cover) and mixed thoroughly. A nutrient solution containing nitrogen (urea) and P\(_2\)O\(_5\) (superphosphate) was mixed with distilled water and applied to each jar to achieve 70% of the water-holding capacity of the soil. The N and P were applied at 200 mg kg\(^{-1}\) soil and 40 mg kg\(^{-1}\) soil, respectively, in all treated soils, to supply the metabolism of soil microorganisms. All jars were incubated in the dark for 60 days (d) at 25°C. Deionized water was added weekly, as required, to maintain a constant soil moisture by weight.

**Sampling and analyses**

Soil in each jar was sampled on incubation days 15, 30, 45, and 60 by removing three replicates from each treatment condition using a destructive sampling method. Soil samples were air-dried, ground, and sieved to particles <1 mm for WSK, AK, NASK, SAK, and NEK determination, and to 0.15 mm for total K determination.

Total K (TK) in the soil was digested in a nickel crucible with sodium hydroxide at 750°C [10]. Available K (AK) was extracted using 1 mol L\(^{-1}\) ammonium acetate [43]. Moreover, three solvents were used to extract the other K fractions. Water-soluble K (WSK) was extracted using distilled water. Soil exchangeable K (EK) was calculated by subtracting WSK from AK. According to previous research [27,32], soil non-specific adsorptive K (NSAK) was extracted using 0.5 mol L\(^{-1}\) magnesium acetate and calculated by subtracting WSK from the K extracted using 0.5 mol L\(^{-1}\) magnesium acetate. Subsequently, soil specific adsorptive K (SAK) was calculated by subtracting both WSK and NSAK from AK. Non-exchangeable K (NEK or slowly available K) was extracted using the hot nitric acid extraction method and calculated by subtracting AK from the K extracted using hot nitric acid [43]. Structural K (SK) was calculated by subtracting the K extracted using hot nitric acid from TK. Plant K in crop straw was digested using the H\(_2\)SO\(_4\)-H\(_2\)O\(_2\) method. K concentrations in all sample solutions were determined using an atomic absorption spectrophotometer (Analyst 400, PerkinElmer, U.S.).
Calculations and statistical analysis

The efficiency ratio of exogenous K was used to assess the apparent bioavailability after K addition to soil, which is defined as the ratio of the increase in AK relative to exogenous K addition, according to Eq 1 [11,29,31]:

\[
K \text{ efficiency ratio (\%)} = \left( \frac{\text{AK}_T - \text{AK}_C}{\text{K input}} \right) \times 100
\]  

(1)

where \( \text{AK}_T \) is the amount of available K in the soil after exogenous K addition; \( \text{AK}_C \) is the amount of available K in the soil without exogenous K addition; and K input is the net amount of K added.

Further, the mobility factor (\( M_f \)) was used to assess the relative K mobility and bioavailability in the soil, which is defined as the ratio of the K concentration in the mobile or available fraction relative to the sum of the K concentration in all fractions, according to Eq 2 [42,44]:

\[
M_f (\%) = \left( \frac{F_1 + F_2 + F_3}{F_1 + F_2 + F_3 + F_4 + F_5} \right) \times 100
\]  

(2)

where \( F_1 \)–\( F_5 \) are the soil levels of WSK, NSAK, SAK, NEK, and SK respectively. \( F_1 \)–\( F_3 \) are commonly considered mobile (available) fractions of soil K.

The partition index (\( I_R \)) of soil metal elements describes their relative binding intensity and is widely employed in research regarding the mobility of metals or microelements in soil [42,45]. Accordingly, in the present research, \( I_R \) was expressed to assess the relative binding intensity of soil K based on synthesizing various fractions using Eq 3:

\[
I_R = \sum_{i=1}^{k} \frac{F_i}{F_k^2}
\]  

(3)

where \( i \) is the index number of the K fraction, progressing from WSK for the \( F_1 \) fraction to SK for the \( F_5 \) fraction (dependent on our extraction method, \( k = 5 \)), \( F_i \) is the K percentage content of the considered K in the \( i \)th fraction. Soil K sequentially decreased its mobility as the fraction number increased.

Statistical analysis was performed using the SPSS v19.0 program (Chicago, U.S.). The soil K content of multiple fractions was analyzed using a two-way analysis of variance (ANOVA). Other indicators identified in the eight treatments were simply analyzed using one-way ANOVA. Differences between mean values were compared using the least significant difference (LSD) method at a significance threshold of 5%.

Simple nonlinear regression equations were also developed to evaluate the relationships among the response variables (K inputs and soil AK equilibrium). The experimental means were compared at the 95% probability level. Principal components analysis was performed using the Canoco 5.0 program for Windows to sort various indexes of soil K, including the K content of various fractions and the \( M_f \) and \( I_R \) values of soil K.

Results

Soil K content after a 60-d incubation

Soil AK, its sub-fractions (WSK, NSAK, and SAK), and NEK were all significantly influenced by K fertilization, straw addition, and a combination of the two (Table 1; \( P<0.05 \)). After the 60-d incubation, K fertilization alone, single wheat straw addition, and single maize straw addition increased soil AK and NEK by 85.2% and 18.7%, 57.7% and 20.2%, and 41.5% and 15.5%, respectively, relative to the control. A combination of K fertilization and straw addition
increased soil AK and NEK by 87.3–230% and 19.8–29.9%, respectively, relative to the control (Table 2; \(P<0.05\)). Moreover, soil AK was increased by interactions between K and WS and between K and WS+MS, whereas the interaction between K and MS decreased both the soil AK and NEK (Table 3; \(P<0.05\)). Additionally, soil SK was slightly decreased by K fertilization and straw addition (Table 2; \(P<0.05\)).

Dynamics of soil K in available fractions

K fertilization increased soil WSK, NSAK, and SAK by 111.6%, 97.5%, and 42.7%, respectively, during the 60-d incubation (Fig 1). Similarly, straw addition also followed the same trend in increasing these three K fractions: WS+MS>WS>MS>Control.

Table 1. ANOVA of the effects of K fertilization, straw return, and their interactions on soil K fractions after a 60-d incubation (P-values).

| Source of variation | AK | NEK | SK | TK |
|---------------------|----|-----|----|----|
|                     | WSK | NSAK | SAK | Total | NEK | SK | TK |
| K fertilization (K1) | \(<0.001\) | \(<0.001\) | \(<0.001\) | \(<0.001\) | \(<0.001\) | \(<0.001\) | 0.048 |
| Straw addition (S)  | \(<0.001\) | \(<0.001\) | \(<0.001\) | \(<0.001\) | \(<0.001\) | \(<0.001\) | ns |
| K1×S               | \(<0.001\) | \(<0.001\) | \(<0.001\) | \(<0.001\) | 0.028 | ns | ns |

AK, available K; NEK, non-exchangeable K; SK, structural K; TK, total K; WSK, water-soluble K; NSAK, non-specific adsorptive K; and SAK, specific adsorptive K. ns indicates a non-significant difference (\(P<0.05\)).

Table 2. Effects of K fertilization and straw addition on soil Available K (AK), Non-Exchangeable K (NEK), and Structural K (SK) after a 60-d incubation.

| AK (mg kg\(^{-1}\)) | NEK (mg kg\(^{-1}\)) | SK (g kg\(^{-1}\)) |
|---------------------|----------------------|------------------|
| K0                  | K1                   | K0               | K1               | K0               | K1               |
| Control             | 142 g                | 263 d            | 1254 d           | 1488 bc          | 18.4 A’          | 17.9 AB          |
| WS                  | 224 e                | 383 b            | 1507 b           | 1531 b           | 18.2 A          | 17.9 AB          |
| MS                  | 201 f                | 286 c            | 1448 c           | 1550 ab          | 18.3 A          | 18.0 A           |
| WS+MS               | 266 d                | 469 a            | 1502 b           | 1629 a           | 17.5 B          | 17.7 B           |

Control, no straw addition; WS, wheat straw addition at 12 g straw-kg\(^{-1}\) dry soil; MS, maize straw addition at 12 g straw-kg\(^{-1}\) dry soil; WS+MS, wheat and maize straw addition, both at 12 g straw-kg\(^{-1}\) dry soil. K0, no K fertilization; K1, K fertilization at 200 mg K\(_2\)O-kg\(^{-1}\) dry soil. Significant differences are indicated by different case letters and ' (\(P<0.05\)). Lower-case letters correspond to the interaction between K fertilization and straw addition; upper-case letters correspond to the effects of the four straw addition regimes; and ' corresponds to the effect of the two K fertilization rates.

Table 3. Effects of the interaction between K fertilization and straw addition on soil Available K (AK), Non-Exchangeable K (NEK), and Structural K (SK).

| Type of interaction | AK (mg kg\(^{-1}\)) | NEK (mg kg\(^{-1}\)) | SK (g kg\(^{-1}\)) |
|---------------------|---------------------|---------------------|-------------------|
| K1×WS               | 19.0”’              | -105”              | ns                |
| K1×MS               | -18.1”’             | -66”              | ns                |
| K1×(WS+MS)          | 41.1”’              | ns                 | ns                |

WS, wheat straw addition at 12 g straw-kg\(^{-1}\) dry soil; MS, maize straw addition at 12 g straw-kg\(^{-1}\) dry soil; WS+MS, wheat and maize straw addition, both at 12 g straw-kg\(^{-1}\) dry soil. K1, K fertilization at 200 mg K\(_2\)O-kg\(^{-1}\) dry soil. “’ indicates an extremely significant difference (\(P<0.01\)). “’ indicates a significant difference (\(P<0.05\)). ns indicates a non-significant difference (\(P<0.05\)).
Soil AK content did not largely fluctuate during the 60-d incubation time (Fig 1). During the first few days (<15 d) after exogenous K addition, soil AK under each treatment condition remained relatively stable over time. Similar effects were seen with respect to soil WSK, NSAK, and SAK (Fig 1; \( P < 0.05 \)).

Efficiency of exogenous K addition

The efficiency ratio of exogenous K addition was calculated to estimate the amount of K retained in the soil, which was shown to be 38.3–72.9% across the different treatments (Table 4). The highest efficiency ratio of exogenous K was derived from the mineral K fertilizer (72.9%), which was markedly higher than that derived from wheat (47.1%) or maize (39.3%) straw (\( P < 0.05 \)). Additionally, treatment with combined K sources also resulted in neutralized K availability ratios.

Regression analysis showed that the AK increased exponentially with increasing net K addition to soils with or without chemical K (Fig 2; \( P < 0.05 \)). Moreover, the rate of increase in soil AK was markedly higher following treatment with mineral K fertilization (K1) as compared with that with no mineral K fertilization (K0) (186.3 > 148.0 in regression coefficient).
Changes in soil K mobility and stability

Soil SK made the largest contribution (89.4–93.0%) to total K as compared with the other fractions, whereas soil K in the WSK, NSAK, SAK, and NEK fractions centrally reflected the positive effects of exogenous K addition (Fig 3). In comparison with the control, the distributions of soil WSK, NSAK, SAK, and NEK, especially the K fractions with relatively higher mobility

Table 4. Effects of K fertilization and straw addition on the efficiency ratio of exogenous K after a 60-d incubation.

| Net K input (mg K kg⁻¹ soil) | Soil AK increase (mg kg⁻¹) | K efficiency ratio (%) |
|-----------------------------|-----------------------------|------------------------|
|                            | K0 | K1 | K0 | K1 | K0 | K1 |
| Control                    | 0  | 166| -  | 121d| -  | 72.9|
| WS                         | 174| 340| 82e| 241b| 47.1| 70.9|
| MS                         | 150| 316| 59f| 144c| 39.3| 45.6|
| WS+MS                      | 324| 490| 124d| 327a| 38.3| 66.7|

Control, no K addition; WS, wheat straw addition at 12 g straw-kg⁻¹ dry soil; MS, maize straw addition at 12 g straw-kg⁻¹ dry soil; WS+MS, wheat and maize straw addition, both at 12 g straw-kg⁻¹ dry soil. K0, no K fertilization; K1, K fertilization at 200 mg K₂O·kg⁻¹ dry soil. Lower-case letters indicate significant differences among the eight treatments (P<0.05).

https://doi.org/10.1371/journal.pone.0236634.t004

Fig 2. Nonlinear regression performance of soil available K according to K addition. K0, no K fertilization; K1, K fertilization at 200 mg K₂O·kg⁻¹ dry soil.

https://doi.org/10.1371/journal.pone.0236634.g002
(readily available to plants), increased following mineral K fertilization, straw addition, and their combination, at the expense of soil SK ($P < 0.05$).

Accordingly, the relative mobility factor ($M_F$) and reduced partition index ($I_R$) were calculated to comprehensively investigate the availability of soil K (Fig 4). In comparison with the control, both K fertilization and straw additions, as well as their combinations, increased the $M_F$ of soil K, whereas the $I_R$ value was decreased ($P < 0.05$). Moreover, different straw addition regimes showed the following trend with respect to affecting both the $M_F$ and $I_R$ values of soil K: WS+MS > WS > MS > Control. Further, the highest $M_F$ and lowest $I_R$ of soil K were both observed following K fertilization (K1) among the three treatments with a single K source (K1, WS, and MS).

Principal components analysis (PCA) was performed to investigate the correlation between the $M_F$, $I_R$, and various fractions of soil K (Fig 5). The PC1 explained 94.31% of the composition variations in soil K across various exogenous K additions. The cluster containing all relatively available K fractions (AK, WSK, NSAK, SAK, and NEK) was well-loaded on the left axis of PC1 with the $M_F$ of soil K. In contrast, the other clusters containing relatively unavailable...
SK and TK were well-loaded on the right axis with the $I_R$ of soil K. The WSK, NSAK, SAK, and AK were all highly positively correlated with the $M_F$ of soil K, as was the NEK.

In addition, the treatments with a high net K input, especially WS+MS+K1 and WS+K1, were greatly responsible for the increases in both soil K in available fractions and $M_F$. On the contrary, the treatments with a relatively low net K (Control, WS, and MS) were responsible for an increase in the soil K stability and reserve (Fig 5).

Discussion

Effects of K addition on soil AK and NEK statuses

In comparison with K fertilization alone and single straw addition, a combination of K fertilization and straw addition resulted in larger increases in soil AK and NEK (Table 2 and Fig 3), implying that a greater net K addition can lead to greater increases in both soil AK and NEK. As mentioned previously, multiple factors including soil properties can affect soil AK levels and its fixation as NEK, with exogenous K addition and NEK release ultimately being the major sources of soil AK. In turn, fluctuating soil AK is also a primary factor that influences soil NEK through mineral fixation or release [29,33,46,47]. As is known, both mineral fertilizer K and crop straw K are released into the soil in a soluble form; therefore, irrespective of the K source, soil AK can be increased by increasing net K addition. As a result, soil AK was the most sensitive to K addition across the various fractions, responding more strongly to a combination of K fertilization and straw addition than to a single K source. Increased soil AK was also associated with increased exogenous K addition (Fig 2), which is consistent with previous studies [10,11,29]. However, our incubation experiment simulated practical K fertilization and straw return, and both were equivalent to almost triple the conventional application rates in field practices. The greatly increased soil AK cannot remain stable over time; instead, it is easily transformed into NEK with lower availability through soil K fixation [2,33,48]. With the exception of initial soil properties, soil K fixation capacity and rate are greatly associated with net K addition [2,29,46,49]. Soil K fixation capacity has been documented to increase with increasing net K addition, whereas the K fixation rate decreases [11,29]. That is, a relatively
higher K addition easily results in a larger soil K fixation capacity but retains a higher efficiency in increasing soil AK [46,49,50]. In the present study, a combination of K fertilization and straw addition with relatively higher K inputs generally resulted in larger increases in soil NEK, which closely responded to fluctuating soil AK (Table 2).

Concomitantly, lower efficiencies in increasing soil AK were observed after crop straw (especially maize straw) addition as compared with those after K fertilization (Table 4), which may be partially due to the lower amount of K derived from crop straw (especially maize straw) than from K fertilizer. However, relatively smaller differences in net K addition among the three K sources (K fertilizer, wheat straw, and maize straw) led to relatively larger differences in efficiency in increasing soil AK (Table 4). This indicates that, with the exception of K fixation in soil minerals, soil AK reduction can be caused by other factors, such as changes in the physical and biological properties of soil, which require further exploration [29,51,52].

In contrast, soil SK decreased slightly after exogenous K addition, especially following treatment with a high amount of K (Table 2). Similar results have rarely been reported. We speculate that the incubation conditions in the present study may be the main factor driving SK release due to its relatively high soil moisture and stable temperature, which are beneficial to
soil mineral weathering without crop growing. Thus, in addition to the external factors influencing soil K availability, further research is required to reveal the internal mechanisms of soil K transformation among different fractions.

**Effects of crop straw decomposition on soil AK status**

Straw addition was not as efficient as K fertilization in increasing the available K level in the soil (Table 3), which has not been well documented in previous studies. Typically, K exists in an ionic form in plants and can be easily released from decaying crop residue, becoming available for subsequent crops [21]; however, crop residue decomposition is certainly an important biochemical process dominated by soil microorganisms. Recent research has reported that the addition of organic material can trigger microbial activity and extracellular enzyme production, causing the decomposition of both newly added organic material and certain fractions of native SOC [53]. The increased number of microorganisms absorb soil available nutrients for metabolism and form microbial byproducts, implying reduced soil available nutrients, including extractable metals, with regard to microbial immobilization [37,51,52,54,55]. Moreover, the increased active SOC, with a lower degree of decomposition and a rich source of polar functional groups, can drive the formation of organo-mineral complexes, thus improving soil aggregate stability [38,56,57]. Soil aggregation can also help to protect soil available nutrients through physical occlusion [38,52,55]. Therefore, we speculated that although the increased SOC may be associated with increased adsorptive sites to protect AK against fixation, soil AK may also be reduced by microbial immobilization and aggregate occlusion. Maybe that’s why straw addition had a markedly lower efficiency in increasing soil AK than K fertilization in the present study (Table 3).

In addition, wheat straw differed from maize straw in efficiency in increasing soil AK (Table 3), which may be attributed to the different chemical compositions of the two types of straw. In the present research, the relatively higher efficiency of wheat straw in increasing soil AK may result from its higher C/N ratio (80:1) and higher lignin content (20%) than that of maize straw (57:1 C/N ratio and 14% lignin content). According to the microbial stoichiometry and metabolism theory, microbial activity is higher when the low C/N ratio (or high N availability) of substrates matches the microbial demand or when the compounds are easily decomposed by microorganisms, increasing both the enzyme production and organic C degradation [58–61]. Therefore, the relatively appropriate composition of maize straw may alleviate the metabolic constraint in the soil and improve the microbial activity and soil quality, but which can cause available K immobilization, leading to a lower efficiency in increasing soil AK than that of wheat straw. In addition, the results showed that the increases in soil AK and its sub-fractions (WSK, NSAK, and SAK) were stable during the first 15 days following straw addition and K fertilization (Fig 1). This suggests that the increased SOC may not be sufficient to overcome the multiple AK reduction forces, including microbial utilization, aggregate occlusion, and mineral fixation [22,29,31]. Moreover, the results also indicate that crop straw K can be easily released from decaying straw due to the commonly ionic form of K being present in plants. Straw decomposition did not slow the straw K release rate, whereas it greatly caused AK reduction through microbial and aggregation pathways. However, further studies regarding the relationship between soil K dynamics and straw decomposition, in addition to soil microbial activity, are required to verify our inferences.

**Soil K redistribution and bioavailability**

Soil metal elements present in each fraction dictate their specific mobility. The content of the extractable and exchangeable fractions of a metal may be described by the mobility factor (M_F)
Historically, WSK and EK (NSAK+SAK) with high mobility are also considered available to plants [1,2,31]. In agricultural practice, increased crop production is associated with increased soil AK (WSA+EK) [10,11,23,24]. Our results show that soil AK and its sub-fractions (WSK, NSAK, and SAK) increased following increases in exogenous K addition (Table 2 and Figs 1–3), thereby driving an increase in the soil K storage value (Fig 4). Although no crop was planted in the present incubation in response to the increased soil AK level, the soil K bioavailability was undoubtedly increased [41,42,45].

Nevertheless, the simultaneously increased soil NEK with lower mobility (relative to AK) should be equally considered when assessing soil K availability in long-term cropping (Table 2). As mentioned previously, metal transformation in all individual fractions concerns redistribution and can be expressed by the reduced partition index ($I_R$), which was introduced to quantitatively describe the relative binding intensities of soil metals. In contrast to $M_F$, $I_R$ not only includes metal transformation among labile fractions but also among those that are stable [41,42,45]. Since the binding intensity of soil K, in turn, decreases from the F1 to F5 fractions, it is reasonable to suggest that this index ($I_R$) is appropriate for assessing soil K redistribution. The calculated $I_R$ of soil K ranged from 0.04 to 1; a high value indicates soil K stability resulting from its occurrence in non-exchangeable (F4, NEK) and structural (F5, SK) fractions, and a low value represents a distribution pattern with a high proportion of exchangeable (F2 and F3, NSAK and SAK) and soluble (F1, WSK) fractions. In the present study, the $I_R$ of soil K was reliably decreased following increases in K addition, implying that increasing K input successfully increased the soil K bioavailability (Fig 4).

Moreover, the soil K $M_F$ value was positively correlated with the K in all relatively available fractions (AK and its sub-fractions, as well as NEK), whereas the soil K $I_R$ value was negatively correlated with all relatively available fractions of soil K (Fig 5). This implies that the use of both the $M_F$ and $I_R$ values of soil K is feasible to quantitatively assess soil K mobility, and thus determine soil K bioavailability [10,31,41,42]. The present results indicate that crop straw addition, specifically maize straw, was less efficient in increasing soil K bioavailability than K fertilization. However, the soil K bioavailability increased the most following the highest net K addition, which was a combination of straw addition and K fertilization (Fig 5). Therefore, when considering the K uptake by crops in agricultural practice, specifically in intensive agricultural systems in China with commonly practiced straw return [25,26], straw return should be combined with K fertilization to improve both soil K bioavailability and K cycling in soil–plant systems.

Conclusions

The present study suggests that K fertilization and crop straw addition were efficient in rapidly increasing soil K in fractions available to plants. Different K sources showed the following trend in increasing soil K availability: K fertilizer > wheat straw > maize straw. However, soil AK generally increased with an increase in net K addition, and the three K sources resulted in larger increases in both soil AK and NEK when used in combination as compared with being applied individually. Positive correlations existed between the $M_F$ value and each relatively available fraction of soil K, including WSK, NSAK, SAK, and NEK; and negative correlations existed between the $I_R$ value and each relatively available fraction of soil K. Therefore, the $M_F$ and $I_R$ values of soil K can be used to assess the comprehensive availability of soil K. K fertilization in combination with crop straw return appears to be the optimal method for improving soil K availability and K cycling in soil–plant systems.
Supporting information

S1 Dataset.
(ZIP)

Author Contributions

Conceptualization: Xiushuang Li, Jianglan Shi, Xiaohong Tian.
Data curation: Xiushuang Li.
Formal analysis: Xiushuang Li, Yafei Li, Tianqi Wu, Chunyan Qu.
Funding acquisition: Xiushuang Li, Jianglan Shi, Xiaohong Tian.
Investigation: Xiushuang Li, Peng Ning, Jianglan Shi, Xiaohong Tian.
Methodology: Xiushuang Li, Yafei Li, Tianqi Wu, Chunyan Qu.
Project administration: Xiushuang Li, Jianglan Shi, Xiaohong Tian.
Resources: Xiushuang Li, Yafei Li, Tianqi Wu, Chunyan Qu, Peng Ning.
Software: Xiushuang Li, Yafei Li, Tianqi Wu, Chunyan Qu.
Supervision: Xiushuang Li, Jianglan Shi.
Validation: Xiushuang Li.
Visualization: Xiushuang Li.
Writing – original draft: Xiushuang Li, Jianglan Shi, Xiaohong Tian.
Writing – review & editing: Xiushuang Li, Peng Ning, Jianglan Shi, Xiaohong Tian.

References

1. Huang SW, Jin JY, Tan DS. Crop response to long-term potassium application as affected by potassium-supplying power of the selected soils in Northern China. Communications in Soil Science and Plant Analysis. 2009; 40: 2833–2854.

2. Shakeri S, Abtahi SA. Potassium forms in calcareous soils as affected by clay minerals and soil development in Kohgiluyeh and Boyer-Ahmad Province, Southwest Iran. Journal of Arid Land. 2018; 10: 217–232.

3. Lin Z, Zoebisch MA, Chen GB, Feng ZM. Sustainability of farmers’ soil fertility management practices: a case study in the North China Plain. Journal of Environmental Management. 2006; 79(4): 409–419. https://doi.org/10.1016/j.jenvman.2005.08.009 PMID: 16337082

4. Zhao YC, Xu XH, Darilek JL, Huang B, Sun WX, Shi XZ. Spatial variability assessment of soil nutrients in an intense agricultural area, a case study of Rugao County in Yangtze River Delta Region, China. Environmental geology. 2008; 57(5): 1089–1102.

5. Zhang HM, Xu MG, Shi XJ, Li ZZ, Huang QH, Wang XJ. Rice yield, potassium uptake and apparent balance under long-term fertilization in rice-based cropping systems in southern China. Nutrient Cycling in Agroecosystems. 2010; 88(3): 341–349.

6. Matson PA, Naylor R, Ortiz-Monasterio I. Integration of environmental, agronomic, and economic aspects of fertilizer management. Science. 1998; 280: 112–115. https://doi.org/10.1126/science.280.5360.112 PMID: 9525856

7. Cassman KG, Dobermann A, Walters D. Agroecosystems, nitrogen-use efficiency, and nitrogen management. Ambio. 2002; 31: 132–140. https://doi.org/10.1579/0044-7447-31.2.132 PMID: 12078002

8. Niu JF, Zhang WF, Ru SH, Chen XP, Xiao K, Zhang XY, et al. Effects of potassium fertilization on winter wheat under different production practices in the North China Plain. Field Crops Research. 2013; 40: 69–76.

9. Malo DD, Schumacher TE, Doolittle JJ. Long-term cultivation impacts on selected soil properties in the northern Great Plains. Soil and Tillage Research. 2005; 81: 277–291.
10. Tan DS, Jin JY, Jiang LH, Huang SW, Liu ZH. Potassium assessment of grain producing soils in North China. Agriculture Ecosystems and Environment. 2012; 14: 65–71.

11. Tan DS, Liu ZH, Jiang LH, Luo JF, Li J. Long-term potash application and wheat straw return reduced soil potassium fixation and affected crop yields in North China. Nutrient Cycling in Agroecosystems. 2017; 108: 121–133.

12. Wang HJ, Huang B, Shi XZ, Darilek JL, Yu DS, Sun WX, et al. Major nutrient balances in small-scale vegetable farming systems in peri-urban areas in China. Nutrient Cycling in Agroecosystems. 2008; 81(3): 203–218.

13. Liu XM, Zhang WW, Zhang MH, Ficklin DL, Wang F. Spatio-temporal variations of soil nutrients by an altered land tenure system in China. Geoderma. 2009; 152: 23–34.

14. Gao C, Sun B, Zhang TL. Sustainable nutrient management in Chinese agriculture: challenges and perspective. Pedosphere. 2006; 16(2): 253–263.

15. Chipondi W, Syers JK, Lingard J. Soil nutrient audits for China to estimate nutrient balances and output/input relationships. Agriculture Ecosystems & Environment. 2003; 94: 341–345.

16. Chatterjee A. Annual crop residue production and nutrient replacement costs for bioenergy feedstock production in United States. Agronomy Journal. 2013; 105(3): 685–692.

17. Chen B, Liu E, Tian Q, Yan C, Zhang Y. Soil nitrogen dynamics and crop residues. A review. Agronomy for Sustainable Development. 2014; 34(2): 429–442.

18. Liu C, Lu M, Cui J, Li B, Fang C. Changes in soil organic carbon and nitrogen as affected by tillage and residue management under wheat–maize cropping system in the North China Plain. Soil and Tillage Research. 2014; 144: 110–118.

19. Zhao BZ, Zhang JB, Yu YY, Karlen DL, Hao XY. Crop residue management and fertilization effects on soil organic matter and associated biological properties. Environmental Science and Pollution Research. 2016; 23: 17581–17591. https://doi.org/10.1007/s11356-016-6927-3 PMID: 27234834

20. Sui N, Zhou ZG, Yu CR, Liu RX, Yang CQ, Zhang F, et al. Yield and potassium use efficiency of cotton with wheat straw incorporation and potassium fertilization on soils with various conditions in the wheat–cotton rotation system. Field Crops Research. 2015; 172: 132–144.

21. Kimetu JM, Lehmann J. Stability and stabilization of biochar and green manure in soil with different organic carbon contents. Australian Journal of Soil Research. 2010; 48(7): 577–585.

22. Yu CJ, Qin JG, Xu J, Nie H, Luo ZY, Cen KF. Straw combustion in circulating fluidized bed at low-temperature: transformation and distribution of potassium. Canadian Journal of Chemical Engineering. 2010; 88(5): 874–880.

23. Holland J, Conyers M, Orchard B, Poile G. Soil potassium relationships, uptake efficiency and availability for six distinctive soils in central and southern New South Wales, Australia. Soil Research. 2014; 52(2): 129–139.

24. Zhang HM, Xu MG, Zhang WJ, He XH. Factors affecting potassium fixation in seven soils under 15-year long-term fertilization. Chinese Science Bulletin. 2009; 54(10): 1773–1780.

25. Liao YL, Zheng SX, Nie J, Xie J, Lu YH, Qin XB. Long-term effect of fertilizer and rice straw on mineral composition and potassium adsorption in a reddish paddy soil. Journal of Integrative Agriculture. 2013; 12(4): 694–710.

26. Li N, Guo CL, Wang Y, Gao TY, Yang JF, Han XR. Effects of long-term fertilization on potassium fixation capacity in brown soil. IOP Conference Series: Earth and Environmental Science. 2018; 108: 032036. https://doi.org/10.1088/1755-1315/108/3/032036.

27. Delahay P, Kelsh DJ. Calculation of the amount of specifically adsorbed ions. Application to potassium iodide in the $10^{-2}$–$10^{-3}$ M range. Journal of Electroanalytical Chemistry. 1968; 18(1): 194–197.
33. Moody PW, Bell MJ. Availability of soil potassium and diagnostic soil tests. Australian Journal of Soil Research. 2006; 44(3): 265–275.
34. Barre P, Montagnier C, Chenu C, Abbade L, Velde B. Clay minerals as a soil potassium reservoir: observation and quantification through X-ray diffraction. Plant and Soil. 2008; 302(1–2): 213–220.
35. Raheb A, Heidari A. Effects of clay mineralogy and physico-chemical properties on potassium availability under soil aquic conditions. Journal of Soil Science and Plant Nutrition. 2012; 12(4): 747–761.
36. Sarkar GK, Debnath A, Chattopadhayay AP, Sanyal SK. Depletion of soil potassium under exhaustive cropping in Inceptisol and Alfisol. Communications in Soil Science and Plant Analysis. 2014; 45(1): 61–72.
37. Smith SR. A critical review of the bioavailability and impacts of heavy metals in municipal solid waste comports compared to sewage sludge. Environment International. 2009; 35: 142–156. https://doi.org/10.1016/j.envint.2008.06.009 PMID: 18691760
38. Zhang XF, Xin XL, Zhu AN, Zhang JB, Yang WL. Effects of tillage and residue managements on organic C accumulation and soil aggregation in a sandy loam soil of the North China Plain. Catena. 2017; 156: 176–183.
39. Li S, Li YB, Li XS, Tian XH, Zhao AQ, Wang SJ, et al. Effect of straw management on carbon sequestration and grain production in a maize–wheat cropping system in Anhrosol of the Guanzhong Plain. Soil and Tillage Research. 2016; 157: 43–51.
40. Ge WJ, Chang YL, Liu JM, Zhang SL, Sun BH, Yang XY. Potassium balance and pool as influenced by long-term fertilization under continuous winter wheat-summer maize cropping system in a manural loess soil. Plant Nutrition and Fertility Science. 2012; 18(3): 629–636 (in Chinese). https://doi.org/10.11674/zwyf.2012.11347.
41. Miretzky P, Avendano MR, Munoz C, Carrillo-Chavez A. Use of partition and redistribution indexes for heavy metal soil distribution after contamination with a multi-element solution. Journal of Soils and Sediments. 2011; 11: 619–627.
42. Zygmunt MG, Dorota K. Influence of compost maturation time on Cu and Zn mobility (MF) and redistribution (IR) in highly contaminated soil. Environmental Earth Sciences. 2015; 74(7): 6233–6246.
43. Helmke PA, Sparks DL. Lithium, sodium, potassium, rubidium, and cesium. In: Sparks, D.L., et al. (Eds.), Methods of Soil Analysis, Part 3. ASA and SSSA, Madison, WI, pp 1996: 551–574.
44. Rodriguez L, Ruiz E, Alonso-Azcarrate J, Rincon J. Heavy metal distribution and chemical speciation in tailings and soils around a Pb-Zn mine in Spain. Journal of Environmental Science and Management. 2009; 90: 106–116.
45. Han FX, Banin A, Kiringry WL, Triplett GB, Zhou LX, Zheng SJ, et al. New approach to studies of heavy metal redistribution in soil. Advances in Environmental Research. 2003; 8: 113–120.
46. Schneider A. Release and fixation of potassium by a loamy soil as affected by initial water content and potassium status of soil samples. European Journal of Soil Science. 2010; 48(2): 263–271.
47. Blanchet G, Libohova Z, Joost S, Rossier N, Schneider A, Jeangros B, et al. Spatial variability of potassium in agricultural soils of the canton of Fribourg, Switzerland. Geoderma. 2017; 290: 107–121.
48. Ogaard AF, Krogstad T. Release of interlayer potassium in Norwegian grassland soils. Journal of Plant Nutrition and Soil Science. 2005; 168(1): 80–88.
49. Okl DC, Cassman KG. Reduction of potassium fixation by two humic acid fractions in vermiculitic soils. Soil Science Society of America Journal. 1995; 59(5): 1250–1258.
50. Chen JS, Mackenzie AF. Fixed ammonium and potassium as affected by added nitrogen and potassium in three Quebec soils. Communications in Soil Science and Plant Analysis. 1992; 23(11–12): 1145–1159.
51. Hassink J, Whitmore AP. A model of the physical protection of organic matter in soils. Soil Science Society of America Journal. 1997; 61(1): 131–139.
52. Balesdent J, Chenu C, Balabané M. Relationship of soil organic matter dynamics to physical protection and tillage. Soil and Tillage Research. 2000; 53: 215–230.
53. Fontaine S, Barot S. Size and functional diversity of microbe populations control plant persistence and long-term soil carbon accumulation. Ecology Letters. 2005; 8: 1075–1087.
54. Manzoni S, Taylor P, Richter A, Porporato A, Agren GI. Environmental and stoichiometric controls on microbial carbon-use efficiency in soils. New Phytologist. 2012; 196: 79–91. https://doi.org/10.1111/j.1469-8137.2012.04225.x PMID: 22924405
55. Mazzilli SR, Kemanian AR, Ernst OR, Jackson RB, Piñeiro G. Priming of soil organic carbon decomposition induced by corn compared to soybean crops. Soil Biology and Biochemistry. 2014; 75: 273–281.
56. Mulumba LN, Lal R. Mulching effects on selected soil physical properties. Soil and Tillage Research. 2008; 98: 106–111.
57. Xu MG, Lou YL, Sun XL, Wang W, Baniyamuddin M, Zhao K. Soil organic carbon active fractions as early indicators for total carbon change under straw incorporation. Biology and Fertility of Soils. 2011; 47: 745–752.
58. Craine JM, Morrow C, Fierer N. Microbial nitrogen limitation increases decomposition. Ecology. 2007; 88: 2105–2113. https://doi.org/10.1890/06-1847.1 PMID: 17824441
59. Drake JE, Darby BA, Giasson MA, Kramer MA, Phillips RP, Finzi AC. Stoichiometry constrains microbial response to root exudation- insights from a model and a field experiment in a temperate forest. Biogeosciences. 2013; 10: 821–838.
60. Chen RR, Senbayram M, Blagodatsky S, Myachina O, Dittert K, Lin XG, et al. Soil C and N availability determine the priming effect: microbial N mining and stoichiometric decomposition theories. Global Change Biology. 2014; 20: 2356–2367. https://doi.org/10.1111/gcb.12475 PMID: 24273056
61. Rousk K, Michelsen A, Rousk J. Microbial control of soil organic matter mineralization responses to labile carbon in subarctic climate change treatments. Global Change Biology. 2016; 22: 4150–4161. https://doi.org/10.1111/gcb.13296 PMID: 27010358