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REGULAR ARTICLE

Plants use alternative strategies to utilize nonexchangeable potassium in minerals

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Abstract Plant species differ in their capacity to use nonexchangeable potassium (NEK) in soils. In this study two typical plants with high K use efficiency, ryegrass and grain amaranth, were compared with regard to their capacity to use K from five K-bearing minerals. Biomass relative yield and K uptake data indicated that ryegrass was much more efficient than grain amaranth at using NEK in minerals. Root exudates of grain amaranth collected under hydroponic culture contained considerable amounts of oxalic and citric acids, while these acids were not detected in ryegrass root exudates. Compared with grain amaranth, the kinetic parameters of K uptake by ryegrass roots were characterized by a significantly higher K uptake rate (V_{max}) and a significantly lower C_{min}, the minimum external K concentration at which K is taken up. The dynamic release of NEK from minerals in various solutions showed that the release rate of NEK was largely K-concentration dependent and some thresholds of K concentration prevented further NEK release from minerals. The K thresholds were related to mineral type and increased in the presence of Ca^{2+} or Na^+ in solutions. The positive effect of H^+ (20 mmol L^{-1}) on NEK release was also mainly attributed to elevating the thresholds of K concentration, rather than to the effects of weathering. The results indicated that the main mechanism by which plant species efficiently use NEK in minerals was to the capacity of plants to absorb K at low concentrations. The lower the C_{min} for the root K uptake, the higher the expected NEK use efficiency of the plant.

Keywords Ryegrass · Grain amaranth · K efficiency · K threshold · Root exudates · Minerals

Introduction

Soil potassium reserves are generally large since K is the seventh most abundant element in the earth's crust (Schroeder 1978). Only a small portion of the soil K is in solution or exchangeable forms that can be easily used by plants, with the majority of soil K retained in minerals in nonexchangeable or structural forms that are slowly or less available to plants (Sparks 2000; Huang, 2005). In countries lacking K fertilizer resources, there is great potential to improve the use of soil K by plants. Nonexchangeable K (NEK) is the K held between adjacent tetrahedral layers of diocta-

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hedral and trioctahedral micas, vermiculites and intergrade clay minerals and not bonded covalently within the crystal structures of soil minerals particles (Martin and Sparks 1985). The NEK content of soils varies from 2% to 8% of total K as evaluated with the traditional boiling HNO_3 method (Xie et al. 2000). The total amount of soil NEK released in tetraphenylboron sodium solution can reach up to 20–55% of total K (Zhou and Wang 2008). This indicates that NEK reserves in soils are quite large, and the majority of the soil K not recovered by the boiling HNO_3 method but exploited by K efficient plants in many studies might initially be in the nonexchangeable form. Thus NEK plays a much more important role in soil K supply to plants than structural K.

Plant species or genotypes within species may differ in their capacity to use NEK in soils or minerals (Coroneos et al. 1996; Rengel and Damon 2008). Ryegrass could mobilize more K from gneiss than pak-choi, while alfalfa could not utilize K from gneiss (Wang et al. 2000a). Sugar beet was more effective in mobilization of low available K in the rhizosphere than wheat and barley (Dessougi et al. 2002). Different cultivars of many plant species such as amaranth (Tu et al. 2000), potato (Trehan et al. 2005), rice (Jia et al. 2008) and maize (Lv and Zhang 2010) differed in their K uptake efficiencies. However, breeding new K-uptake-efficient genotypes has so far been sporadic, because the exact or determinative mechanisms by which plants sequester K efficiently from soils were unknown. Differential exudation of organic compounds to facilitate release of NEK was considered as one of the mechanisms of differential K uptake efficiency (Rengel and Damon 2008). Organic acids such as oxalic acid for maize or grain amaranth (Krafffczyk et al. 1984; Tu et al. 1999), tartaric acid for pak-choi or radish (Chen et al. 1999; Zhang et al. 1997), malic acid for oilseed rape (Zhang et al. 1997) and citric acid for maize (Krafffczyk et al. 1984) could be released in root exudates under K sufficient or insufficient conditions. These acids facilitate release of NEK or mineral K to various extents according to data from batch or incubation experiments (Song and Huang 1988; Zhu and Luo 1993; Wang et al. 2000b; Li et al. 2006; Wang et al. 2007). In addition to mineral K activation by root exudates, both root morphology including root length, biomass and root hairs (Hogh-Jensen and Pedersen 2003; Li and Ma 2004) and root K uptake activity measured in terms of rates of K uptake or affinity of K uptake systems (Hinsinger and Jaillard 1993; Trehan and Sharma 2002) have been investigated with regard to plant K uptake efficiency (Rengel and Damon 2008). Most studies hypothesise possible mechanisms through morphological and physiological differences in K uptake efficiency, but very few make detailed assessments of the observed differences at a mechanistic level. Uncertainty of the key mechanism prevents us from taking a strategic approach towards breeding efficient K uptake genotypes through conventional breeding or genetic engineering.

Efficient K uptake plant species or genotypes may have specific physiological mechanisms to promote NEK release in the rhizosphere. Release of NEK from soil or minerals is reliant on or influenced by factors including concentrations of ions and K in solution (Martin and Sparks 1985; Huang 2005). In plant-soil systems, root secretion of organic acids or depletion of solution K to a low level in the rhizosphere would be the main mechanisms that facilitate NEK release. However, the relative importance of NEK activation by organic acids in root exudates and the K-sequestration capacity of roots in facilitating NEK release and utilization by plants is still obscure.

The current study aimed to i) compare the K-sequestration capacity from various K-bearing minerals of the two plant species, ii) explain the differences between the K-sequestration capacity from various K-bearing minerals by the two plant species.

Materials and methods

Minerals

Five minerals (biotite, vermiculite, muscovite, phlogopite and feldspar) with varying K availabilities were used in this study. The mineral samples were collected from Linshou County, Hebei Province, and their mineral and chemical compositions showed some impurities (Table 1). The mineral samples were ground, passed through a 60 mesh screen, and washed three times with 0.5 mol L^{-1} $CaCl_2$ to remove labile K and with deionized water to remove free $CaCl_2$. The samples were then air-dried.

Table 1 Composition of K-bearing minerals used in the experiment

		Feldspar	Muscovite	Phlogopite	Vermiculite	Biotite
Mineral composition		Orthoclase 30–40% Plagioclase 35–45% Quartz 15–25% Mica littele	Muscovite 75–85% Quartz 10–20% Ferruginous matter little	Phlogopite 60–70% Orthoclase 15–25% Involving biotite <10%	Vermiculite 15–25% Quartz 35–45% Orthoclase 15–25% Achromaite <10% Dolomite little	Biotite 55–65% Magnesium amphibole 25–35% Quartz little
Chemical composition (%)	K_2O	5.76	10	10.71	3.87	3.72
	Na_2O	5.02	0.61	0.61	1.46	1.82
	Al_2O_3	14.86	28.94	31.06	14.02	12.52
	CaO	0.44	0.12	0.29	4.63	9.8
	MgO	0.25	1.15	1.18	5.05	6.9
	SiO_2	76.36	50.68	49.94	58.73	42.56
	Fe_2O_3	0.53	7.24	7.07	12.44	24.95
	P_2O_5	0.0268	0.0747	0.0474	0.4523	1.9827
	MnO	0.0045	0.0009	0.0034	0.1041	0.2141

Use of mineral K by plant species

Ryegrass (*Lolium perenne* L.) has a comparatively high capacity for K uptake from minerals (Hinsinger and Jaillard 1993). Grain amaranth (*Amaranthus sp.*) K12 is a K enrichment genotype selected by Li and Ma (2003) that is able to activate soil K (Li et al. 2006). Their capacities to sequester K were compared in a pot experiment. Each pot contained a mixture of 500 g quartz sand and 50 g mineral. Seven treatments were set up, comprising the five K-bearing minerals, quartz with enough K in nutrient solution, and quartz without K. Seeds of ryegrass or grain amaranth were sown on minerals, with three replicates of each. One hundred ml of half strength nutrient solution (Hoagland and Arnon 1950) omitting K was added to each pot every day, while a nutrient solution containing K was only added to the quartz with K treatment. The surplus nutrient solution was discharged from the bottom of the pot to prevent accumulation of salts, including K, released from the minerals, thus the K used by the plants was predominantly the newly released K from minerals. The experiment was carried out in a greenhouse with ambient light and a temperature ranging from 15°C to 30°C. After a growth period of 7 weeks, the above-ground part of the plants was harvested. Samples were oven-dried, weighed and digested using the H_2SO_4+H_2O_2 method (Lu 1999) for K concentration determination.

Kinetics of root K uptake and root exudate collection

Seedlings of ryegrass and grain amaranth were raised in quartz sand watered with deionized water daily and with nutrient solution once a week. After 20 days the seedlings were transferred to a hydroponic culture system. For each species, a 40 L PVC tank with a 50-hole cover was used. Two seedlings were supported with sponge in each hole. The nutrient solution was aired continuously, renewed once a week for the first 2 weeks and then every 3 days. The pH was adjusted daily to 6.0 with 0.1 mol L^{-1} HC1 or NaOH.

After 6 weeks in hydroponic culture, 42 plants of each species were moved to K-free nutrient solution for 48 h to induce K deficiency. After three rinses with 0.2 mmol L^{-1} $CaSO_4$, the plants were put into dark bottles (2 plants per bottle) containing 100 ml of 0.2 mmol L^{-1} $CaSO_4$ and various levels of KCl

(0.002, 0.005, 0.01, 0.1, 1.0, 5 or 10 mmol L^{-1}), with three replicates. The plants were harvested after six hours of K uptake, and their root length and fresh weight was measured. The length of the longest root was measured with a ruler. The K concentration and volume of solution in each bottle were measured to calculate the amount of K uptake by plants under the various K supply levels.

The remaining plants were cultured for another week in nutrient solution with the K level reduced to 0.125 mmol L^{-1}. After rinsing with deionized water, 18 plants of each species were put into 0.2 mmol L^{-1} $CaSO_4$ and 30 mg L^{-1} chloromycetin solutions for 120 and 30 min, respectively. Following this they were rinsed again with deionized water and then put into dark bottles containing 250 mL of deionized water (six plants per bottle) for 12 h to collect root exudates. For each bottle, the deionized water was renewed every 3 h, with four batches of root exudates being collected. These were combined and concentrated to 50 mL using a rotary-evaporator under vacuum at 40°C. The plants were harvested and the root fresh weights were recorded.

Activation of mineral K by citric and oxalic acid

Because the root exudates collected in the current study contained very high concentrations of K (data not shown) and were not suitable for a mineral K release experiment, 10 mL of deionized water or a solution containing 5 or 50 mmol L^{-1} of citric or oxalic acid was added to 5.00 g of minerals and incubated at 25°C for a week to investigate the effect of organic acids in root exudates on the release of mineral K. After incubation, the available K in the minerals was determined using the 1 mol L^{-1} NH_4OAc method (Lu 1999).

Release of NEK from minerals in various solutions

The release of NEK from the tested minerals was significantly influenced by various cations such as Ca^{2+}, Na^+, H^+ and NH_4^+ in solution (Shen et al. 2009). To investigate whether there is a threshold of K concentration for NEK release from minerals and how the threshold would be influenced by the presence of the various cations, the easily releasable NEK of the minerals was removed via a previous 60 d incubation. During the incubation, 50 mL of a solution of 0.01 mol L^{-1} $CaCl_2$, 0.02 mol L^{-1} NaCl or HCl, or water was added to 5 g of the minerals and was renewed daily (Shen et al. 2009). From the 61st day on, the solutions were not renewed and the minerals were incubated for another 50 d at 25°C. During the 50 d incubation period, 4.5 mL of solution was sampled periodically for K concentration, and 4.5 mL of the original solution was added to keep the solution volume constant in each tube. Three replicates were set up.

Analysis

The composition of K-bearing minerals was measured using an X'Pert-Pro X-ray diffractometer with Cu Ka radiation (40 kV, 40 mA) and a graphite filter, from 3.0° to 60.0° with a scan speed of 4.0°/min. The chemical composition of the minerals was determined by ICP-AES (IRIS-Advantage, Thermo Elemental, MA, USA) after melting by the lithium metaborate method (Lu 1999).

Determination of the potassium in solution was made using a flame photometer (Model HG-5, Beijing detection instrument Ltd.) using an internal standard procedure employing 3 mmol L^{-1} lithium chloride.

The organic acids in root exudates were detected by HPLC (LC-10AT VP, Shimadzu, Tokyo, Japan) equipped with a Shim-pack SCR-102 H column (8.0 mm i.d.×30 cm) according to Ma et al. (2002)

All data are means of three values. The differences among means was statistically evaluated with SPSS 10.0, using analyses of variance (ANOVA) taking a P value of <0.05 as significant. The parameters V_{max}, C_{min} and K_m of the Michaelis-Menten kinetics equation $V = (V_{max} \times (C - C_{min}))/(K_m + (C - C_{min}))$ were evaluated with the nonlinear regression procedure of SPSS 10.0.

Results

Growth of plant species with K supply from K-bearing minerals

Grain amaranth and ryegrass differed greatly in their ability to grow using the K supplied by the different minerals used in the current study. As indicated by the biomass accumulation (Fig. 1), grain amaranth only grew well in the full K treatment with K in nutrient

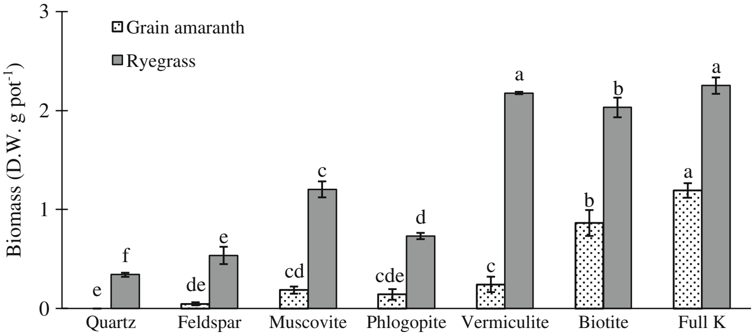

Fig. 1 Biomass accumulation of two species grown on K-bearing mierals. For each species, the same letter indicates no significant difference between treatments ($P<0.05$) by LSD

solution, followed by biotite as the second K-sufficient resource. With K supplied by vermiculite, phlogopite or muscovite, growth of grain amaranth was seriously stunted, ranking at the same level for the three minerals. Grain amaranth could not survive without external K when it grew on quartz or feldspar. Ryegrass showed better adaptability than grain amaranth to grow on K-bearing minerals, as indicated by biomass or relative biomass in Fig. 1. The most significant difference was found in the vermiculite treatment, where ryegrass had a relative biomass of 97%, while grain amaranth had only 20%, showing that ryegrass could grow well with K supplied by vermiculite but grain amaranth could not. The data in Fig. 1 also indicated that the biomass of ryegrass responded sensitively and proportionally to different K-bearing minerals; thus ryegrass was much more suitable than grain amaranth for use as an indicator species distinguishing the NEK availability of K-bearing minerals.

Grain amaranth was proposed as a K-enriched species because of its higher K concentration in tissue (Li and Ma 2003). With K supplied by biotite or nutrient solution, K content in grain amaranth reached >5%, reducing to about 1.5% in K insufficient treatments (Table 2). Grain amaranth had higher K contents than ryegrass under both K sufficient and insufficient conditions, except in the vermiculite treatment. Under K insufficient conditions, the higher tissue K content and lower relative biomass of grain amaranth (Fig. 1, Table 2) indicated that grain amaranth need higher tissue K content for normal growth. Thus grain amaranth could be termed as K-enriched, but compared with ryegrass was neither K-use efficient (related to tissue K concentration (Rengel and Damon 2008)) nor K-uptake efficient (Table 2). With K supplied by vermiculite, the K content in ryegrass was 50% higher than that in grain amaranth, and the difference between the K uptakes of the two species was evident (Table 2). The data demonstrate that ryegrass was more K-uptake efficient than grain amaranth. An adequate supply of K is very important to distinguish the K-uptake efficiencies of species. A very high K supply level, such as that supplied by biotite containing K in very high availability, or a very low K supply level, such as that supplied by phlogopite, muscovite or feldspar containing K in very low availability, were not suitable for distinguishing K-uptake efficiencies of species. However, a medium or adequate level of K supply, such as the K supplied by vermiculite, was much better to distinguish K-uptake efficiency among plant species or genotypes.

Root exudates and morphology

The weight and length of roots of the plants grown under hydroponic culture are compared in Fig. 2. The root weight of grain amaranth was 21.9% higher than that of ryegrass, while the root length of ryegrass was 13.5% higher than that of grain amaranth. By mass, the root morphology of the two species did not differ much. Data obtained under hydroponic culture may not represent what happens in pot culture, but could be compared with data also collected under hydroponic culture.

Significant amounts of citric (0.249 mmol kg^{-1} root h^{-1}) and oxalic acids (0.145 mmol kg^{-1} root h^{-1}) were detected in the root exudates of grain amaranth, but were not found in the root exudates of ryegrass. Research has previously shown that grain amaranth releases root exudates containing organic acids which activate mineral K and facilitate plant K uptake (Tu et al. 1999; Li et al. 2006). In the current study, grain

Table 2 Potassium content and uptake by two species with K supplied by K-bearing minerals

	K content (%)		K uptake (mg pot^{-1})	
Treat.	Grain amaranth	Ryegrass	Grain amaranth	Ryegrass
Quatz	0.00 d	0.45 d	0.0 (0%)[a] e	1.5 (1.6%) e
Feldspar	1.42 c	0.43 d	0.7 (1.1%) e	2.3 (2.5%) e
Muscovite	1.53 c	0.61 d	2.9 (4.4%) d	7.4 (8.0%) c
Phlogopite	1.77 bc	0.55 d	2.5 (3.8%) d	4.0 (4.3%) d
Vermiculite	2.05 b	3.00 c	5.1 (7.8%) c	65.2 (71%) b
Biotite	5.14 a	4.72 a	44.7 (68%) b	95.8 (104%) a
Full K	5.50 a	4.09 b	65.7 (100%) a	92.0 (100%) a

[a] The number in parentheses is the relative K-uptake taking the value of full K treatment as 100%. In each column, the same letter indicates no significant difference between treatments ($P<0.05$) by LSD.

amaranth was not as efficient as ryegrass at using the NEK in minerals even if organic acids were released by the roots of grain amaranth. The effect of organic acids on NEK release from minerals was largely dependent on the dose of organic acids. At low levels (5 mmol L^{-1}), the increase in available K caused by the addition of organic acids in biotite, vermiculite and feldspar was small (Fig. 3). Activation of NEK by organic acids could be significant when high levels of organic acids were added, and the effects were also related to the types of organic acids and minerals involved (Fig. 3). For ryegrass, organic acids in root exudates seemed to be unrelated to its higher K-uptake efficiency.

Root K uptake kinetics

The K uptake capacity of the two species was also compared under a hydroponic culture system. K uptake rates of the two species increased correspondingly as the K levels in solution increased from 0.078 to 390 mg L^{-1} (Fig. 4). At the same K supply level, K uptake rates of ryegrass were significantly much higher than that of grain amaranth (Fig. 4). The curves in Fig. 4 were well fitted by the widely accepted Michaelis-Menten kinetics. Kinetics parameters including V_{max}, K_m and C_{min} were computed and are listed in Table 3. V_{max} is the maximum root K-uptake rate when the K supply level in solution is very high and is not limiting root K uptake. K_m represents K-affinity of the roots. C_{min} is the minimum K concentration in solution at which net K-uptake could occur. With enough external K, the K uptake of ryegrass was much faster than that of grain amaranth as indicated by a V_{max} value six times higher than that of grain amaranth (Table 3). The higher K_m value of ryegrass meant it had a lower root K-affinity than grain amaranth. However, the value of K_m equals the external K concentration at which K-uptake rates reach up to half of V_{max}. The large difference between the V_{max} values of ryegrass and grain amaranth made K_m a less important parameter in the current study. The C_{min} of ryegrass was much lower than that of grain amaranth, suggesting a strong K-uptake capacity of ryegrass at low external K concentrations (Table 3). The K-uptake efficiency of plants was mostly considered when plants were grown in K insufficient conditions, thus C_{min} is the most important parameter to distinguish the K-uptake efficiency of the plants.

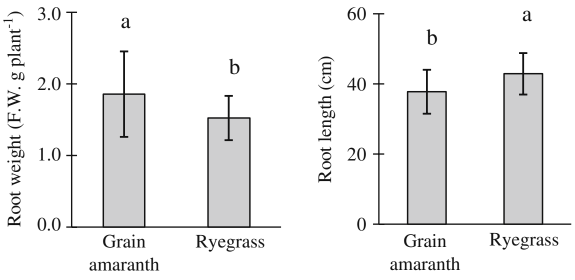

Fig. 2 Root weight and root length of two species after 6 weeks in hydroponic culture. Vertical bars represent standard deviation (n=21)

Discussion

The capacity of a plant to exploit soil NEK depends not only on the plant itself, but also relates to NEK release from soil or minerals. The mechanism for high plant K uptake-efficiency should facilitate soil NEK

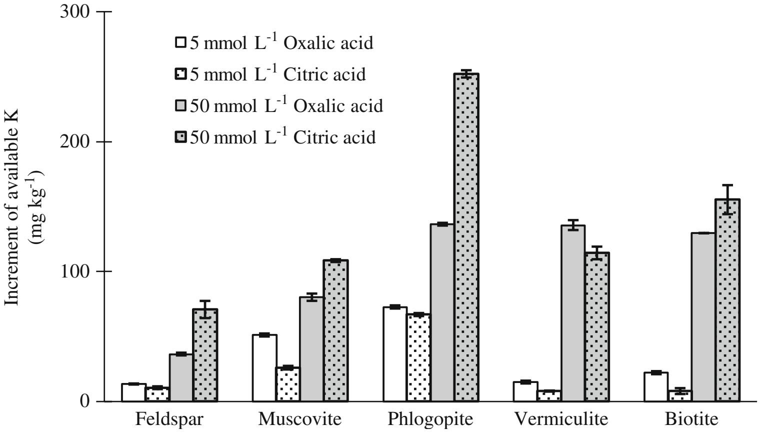

Fig. 3 Increment of NH_4OAc-extractable K in minerals after incubation with orgainc acids for 1 week (calculated as the difference between the measured values obtained for each acid-mineral extraction and the corresponding water-mineral extraction). Vertical bars represent standard deviation (n=3)

release, and thus closely link to the mechanism of NEK release. Ionic factors and K concentration are the main factors that determine NEK release from soil or minerals (Martin and Sparks 1985; Huang 2005).

Previous research has shown that the presence of other cations can increase K release not only from exchangeable sites but also from nonexchangeable sites (Rich and Black 1963; Martin and Sparks 1985; Shen et al. 2009). In the current study, the effects of various ions on NEK release were investigated after the exchangeable and easily releasable NEK of minerals was removed via a previous 60 d incubation in the same solution. The data in Fig. 5 shows that the promotive effect of ions on NEK release followed the order of H^+ >> Na^+, Ca^{2+} > H_2O (except that Na^+ and Ca^{2+} had no significant effect on K release from feldspar) (Fig. 5). The effect of Na^+ and Ca^{2+} on the release of NEK was related to mineral type. Although Na^+ promoted a greater release of NEK from phlogopite and muscovite than Ca^{2+}, Ca^{2+} promoted a greater release of NEK from biotite than Na^+. For vermiculite, Ca^{2+} increased the release of NEK more than Na^+ during the previous 60 d extraction (Shen et al. 2009), and Na^+ increased the release of NEK more than Ca^{2+} at a later stage than that reported in this paper. All the results demonstrated that Na^+ has a more positive effect on the release of initially recalcitrant NEK than Ca^{2+}, while Ca^{2+} is stronger than Na^+ at promoting the release of easily releasable NEK from minerals. The relative effectiveness of Na^+ on the release of initially recalcitrant NEK may be due to the small diameter of its hydrated ion (0.45 nm) which facilitates access to the interlayer K that cannot be reached by Ca^{2+} (0.6 nm) (Bolt et al. 1963). For easily releasable NEK in swelling biotite, no access hindrance existed, so the higher valence of the Ca^{2+} ion led to more NEK release as compared to Na^+ (Rich 1964; Scott and Smith 1966).

As the contact time increased, the NEK release to all solutions was initially quick, but then slowed down and eventually almost stopped as the solution K concentration reached a certain level (Fig. 5). The results could be explained as NEK release from most minerals being a diffusion controlled process (Mortland and Ellis 1959;

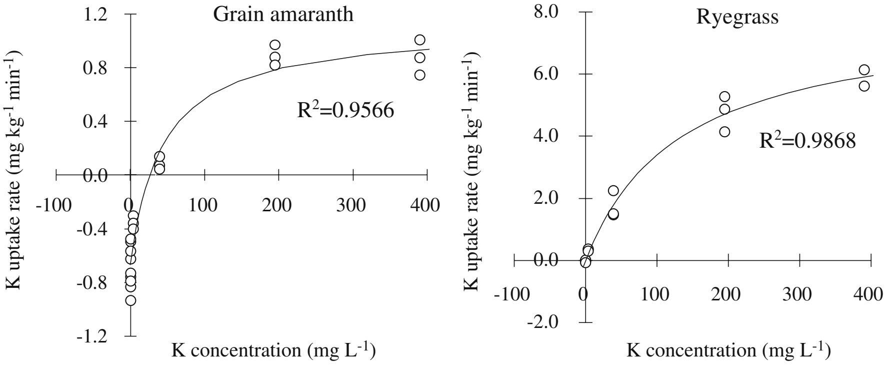

Fig. 4 Root K uptake rates of the two species as influenced by K concentration in solutions

Table 3 Kinetics parameters of K uptake by the two species used in the experiment

	V_{max} (mg kg^{-1} root F.W. min^{-1})	K_m (mg L^{-1})	C_{min} (mg L^{-1})
Grain amaranth	1.11±0.11	71.0±17.2	26.3±5.0
Ryegrass	7.94±0.43	133.3±23.6	0.20±1.36

Mortland 1961; Feigenbaum et al. 1981), and the K concentration in solution being a key factor in determining NEK release from minerals (Scott and Smith 1966; Martin and Sparks 1985; Huang 2005). The final K concentration in the solutions (Fig. 5) could be considered as the K thresholds for NEK release from the minerals, and are listed in Table 4. The data showed that K thresholds not only depended on mineral type, but were also significantly increased by the presence of Ca^{2+} or Na^+. The existence of K concentration thresholds for NEK release has been previously reported by many researchers (Datta and Sastry 1988; Adhikari and Ghosh 1993; Hinsinger and Jaillard 1993; Schneider 1997; Huang 2005), and indicates that the promotive effect of other cations on NEK release through ion exchange can only happen when the K concentration in solution is below the threshold. In real soil-plant systems, some researchers reported that the presence of Ca^{2+}, Mg^{2+} or Na^+ in irrigation water or the rhizosphere could increase soil NEK availability to plants (Rahmatullah et al. 1994; Moritsuka et al. 2004). The results obtained in the current study suggest that Ca^{2+}, Na^+ and some other metal ions not tested in this study may increase soil K availability not only through their exchange effect on initial exchangeable K, but also through their positive effect on the release of initial NEK via elevating the thresholds of K concentration for NEK release.

The effect of H^+ on NEK release was traditionally explained as being due to its weathering effect on

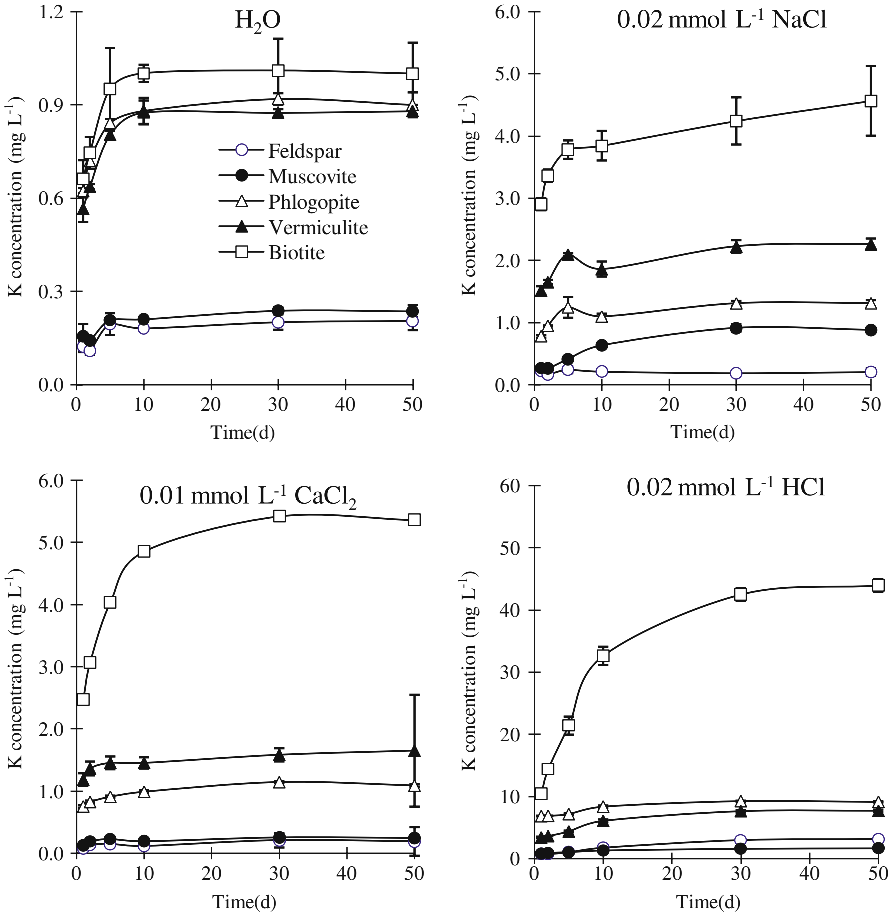

Fig. 5 K concentrations in solutions during a 50 d period of NEK release from K-bearing minerals. Vertical bars represent standard deviation (*n*=3)

Table 4 Thresholds of K concentrations in solutions for NEK release from K-bearing minerals (mg L^{-1})

Solutions	Feldspar	Muscovite	Phlogopite	Vermiculite	Biotite
H_2O	0.21±0.03	0.24±0.02	0.90±0.04	0.88±0.01	1.00±0.10
0.02 mmol L^{-1} NaCl	0.20±0.06	0.88±0.03	1.31±0.05	2.26±0.09	4.56±0.56
0.01 mmol L^{-1} $CaCl_2$	0.19±0.23	0.25±0.01	1.09±0.02	1.65±0.90	5.36±0.07
0.02 mmol L^{-1} HCl	3.10±0.14	1.66±0.10	9.09±0.09	7.66±0.20	43.90±0.01

minerals (Huang 2005). However, Norrish (1973) proposed that in concentrations lower than 1 mmol, the H^+ ion behaves as other cations do in replacing interlayer-K and that only with higher concentrations of acid is the octahedral sheet attacked and its structure destroyed (Martin and Sparks 1985). With 20 mmol L^{-1} HCl in the current study, the easy-dissoluble components of the minerals were removed during a prior 60 d incubation in the same solution, and the NEK released from minerals did not further increase after 30 d contact time (Fig. 5). Clear K thresholds were also obtained for NEK release from minerals in 20 mmol L^{-1} HCl, and the thresholds in HCl solution were much higher than in salts (Table 4). These results demonstrate that H^+ behaved like a metal cation in replacing NEK because under the weathering effect the release of NEK would not stop and no clear threshold of K concentration could be found, unlike in the present study.

The behaviour of H^+ as a metal cation in replacing NEK would also be an important mechanism in the rhizosphere, where organic acids are secreted by roots. Song and Huang (1988) reported that these organic acids can facilitate the weathering of minerals and rocks through the formation of metal-organic complexes, but showed that the weathering of the K-minerals by organic acids resulted in a higher proportion of K loss than of Si loss, which was attributed to partial K release by H^+ exchange. The ability of organic acids to facilitate release of NEK or mineral K was also proved by many researchers (Zhu and Luo 1993; Wang et al. 2000b; Li et al. 2006; Wang et al. 2007), although the data could not clearly identify whether the NEK release was promoted by H^+ exchange or by weathering of the K-minerals. However, the dissolving effect of organic acids on K-minerals would be very slow, but the exchange of K^+ by H^+ would be much faster (Feigenbaum et al. 1981). Thus, the promotive effect of most organic acids on NEK release in the rhizosphere may also occur mainly through exchange of K^+ by H^+ and by elevating the thresholds of K concentration for NEK release.

H^+ acts as a metal cation and does better than other cations in replacing NEK from minerals. This conclusion has significant meaning in distinguishing what form of K could be activated or mobilized by acidification in real plant-soil system. Acidification of soils in cropland is a common phenomenon that may be resulted from high rate application of nitrogen fertilizer, acid rain, or H^+ secretion by plant roots etc. (Romheld et al. 1984; Barak et al. 1997; Liu et al. 2010). Presence of H^+ could activate K release in soils, but the soil K activated by H^+ is mainly from the nonexchangeable part but not from the structural part according to the results got in current study. It confirmed that NEK plays a much more important role in soil K supply to plants than structural K. Thus the soil NEK reserve, but not the total K reserve determines soil K fertility. Since the total amount of soil NEK can reach up to 20–55% of total K (Zhou and Wang 2008), how to evaluate the availability of soil NEK reserve and to exploit soil NEK reserve are substantial important for cropland K management in future.

Attributing the positive effect of H^+ (at a concentration of 20 mmol L^{-1}) on NEK release to ion exchange makes K concentration a much more important factor in determining NEK release in soils (Table 4). A very low concentration of K in solution could lead to a very quick NEK release from many kinds of K-minerals; this phenomenon could be easily proved by the high release rate of NEK during sodium tetraphenylboron extraction (Cox et al. 1999). In a plant-soil system, the ability of roots to reduce the K concentration in the rhizosphere would surely affect soil NEK release. The NEK in mineral can only be exploited by plant root when the C_{min}, the minimum external K concentration at which K is taken up by the plant root is lower than the K threshold for NEK release from the K-bearing mineral. Thus the C_{min}, a parameter reflecting the K-uptake capacity of roots at low K concentrations, would probably be a key parameter in determining plant NEK uptake efficiency. While the capacity to secrete organic acids into the rhizosphere is a secondary or minor mechanism for plant NEK uptake efficiency, since the release of organic acids to the rhizosphere is a common phenomenon for most plants, but does not inevitably result in a high NEK uptake efficiency in most plants.

Neither root exudates nor root morphology, but K-uptake capacity of roots at low K concentration determined plant NEK uptake capacity. This concept was physiologically consistent to recent discoveries of many transporters and channels involved in plant K uptake from the soil (Lebaudy et al. 2007; Chen et al. 2008; Lan et al. 2010). It was reported that K uptake and fluxes within the plant are mediated by several families of transporters and channels differing in their affinity for K (Markus and Pascal 2007; Lebaudy et al. 2007). To improve the plant NEK uptake capacity, transporters controlling K uptake at low concentration are extremely important according to the results got in current study. Discovery and regulation of such transporters through conventional breeding or genetic engineering might help to breed genotypes with high NEK uptake capacity in future.

Conclusions

Ryegrass showed a stronger capacity to use NEK from five K-bearing minerals than grain amaranth. Neither root morphology nor organic acids in root exudates could explain the different K-uptake efficiencies of the two species. The kinetics parameters of root K uptake of ryegrass were characterized by a very high V_{max} and a very low C_{min} in comparison with grain amaranth.

The K concentration in solution is a key factor determining the release of NEK from minerals. There were thresholds of K concentration in solution that prevented further NEK release from minerals. The K thresholds were related to mineral type and were increased by the presence of Ca^{2+} or Na^+ in solution. The positive effect of H^+ (at a concentration of 20 mmol L^{-1}) on NEK release was also possibly through exchange of K^+ for H^+ and elevating the threshold of K concentration for NEK release.

A low concentration of K in solution could inevitably facilitate NEK release from K-minerals, thus the low C_{min} of root K uptake of ryegrass would probably be a key parameter in determining plant NEK uptake efficiency. The capacity to secrete organic acids into the rhizosphere is a secondary or minor mechanism for plant NEK uptake efficiency.

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