



Waste mineral powder supplies plant available potassium: Evaluation of chemical and biological interventions

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ABSTRACT

A study was conducted to evaluate a waste rock powder collected from the Seaham quarry in New South Wales, Australia, as a source of potassium (K) in soil. The K supplying capacity of different size fractions of the mineral powder was evaluated by employing five chemical extractants as well as growing maize and holy basil in sand culture experiments. The K release by chemical extractants increased with decreasing particle size of the mineral powder. The amount of K released by different extractants followed the order: water < 0.01 M calcium chloride < 0.01 M citric acid < 1 N ammonium acetate < 1 N boiling nitric acid. The cumulative K release from the mineral powder in successive extraction procedure was recorded higher with organic and mineral acids, which suggested that the material was a slow release K source. A significant positive correlation was observed between K release by different chemical extractants and the biomass yield ($r = 0.93$; $p < 0.05$) and K uptake ($r = 0.96$; $p < 0.05$) by plants. Among the different chemical extractants, 1 N ammonium acetate and 1 N boiling HNO₃ showed higher correlations ($r = 0.91$ and 0.96 , respectively) with plant K uptake values. Both the chemical and biological methods were able to extract only a portion (12–20%) of total K present in the mineral powder. The results indicated that the mineral powder could be used as a slow release K fertilizer in soils. Further studies in long term applications with exhaustive crops under field conditions are needed to assess its feasibility as a source of K in agriculture.

1. Introduction

Potassium (K) ranks third among the essential plant nutrients after nitrogen and phosphorus, and seventh among all the elements in the earth's crust (Manning, 2010). Potassium makes 2.6% of the earth's crust, and it is the third most mineral element used as nutrients by plants after iron and calcium (Sparks, 1987). Mineral K in rocks is found mainly in the silicates, which release into the soil through the process of continuous weathering (vonWilpert and Lukes, 2003). The reserves of K bearing minerals present in many countries are mostly of low-grade which are not suitable for production of commercial K fertilizers (Manning, 2010). In many parts of the world particularly South-East Asia, Africa and Latin America where agriculture contributes significantly to the overall economy of individual countries, the use of commercial K fertilizers is fully dependent on an import business which involves a huge foreign exchange (Basak et al., 2017).

Worldwide potassium chloride (KCl) is the key source K fertilizer accounting the present annual demand of 31.04 million tones potash as K₂O (FAO, 2015). The entire amount of commercial K fertilizer (KCl) is imported from overseas in the South-East Asian, African and Latin American countries. However, in certain cultivation systems, such as organic agriculture, the use of chemical fertilizers including KCl is not permitted (Codex Alimentarius Commission, 2007). Therefore, the supply of nutrients needs to come from alternative sources such as organic materials and rock mineral powders. Although the crushed rock materials which are mainly produced from mining industries still do not have definite uses, these products are becoming an alternative method of fertilization in various systems of agricultural production (Leonardos et al., 1987; Bolland and Baker, 2000; vanStraaten, 2002; Theodoro and Leonardos, 2006; Basak and Biswas, 2009, 2010; Silva et al., 2013; Madaras et al., 2013; Mohammed et al., 2014). Scientists have taken initiative of investigating silicate rock materials as a source of plant

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nutrients. Pot trials have been conducted with maize (*Zea mays* L.), Italian ryegrass (*Lolium multiflorum* L.), perennial ryegrass (*Lolium perenne* L.) and two alfalfa varieties (*Medicago sativa* L.) using gneiss as the source of K (Wang et al., 2000). A consistent set of trials were also carried out in Western Australia, where granite was used in field trials on wheat, and pot trials on wheat, clover and ryegrass (Coreonos et al., 1996; Hinsinger et al., 1996; Bolland and Baker, 2000). Feldspars have been used in field trials with okra (Abdel-Mouty and El-Greadly, 2008), legumes (Sanz-Scovino and Rowell, 1988) and tomatoes (Badr, 2006). The okra and tomato yields increased with feldspars application. Sanz-Scovino and Rowell (1988) opined that the application of K feldspar might be beneficial as an alternative to KCl in Colombia. Therefore, application of rock mineral powders in agriculture might be a promising alternative to the conventional source of K for plant nutrition.

The key mechanism through which plants are expected to solubilise K from rock powders is by producing various organic acids (Basak et al., 2017). The plant rhizosphere itself is a sink of a complex mixture of various organic acids (Jones, 1998). Rock solubilizing organic molecules can also be produced by microorganisms including bacteria, fungi and mycorrhiza that are present in soils (Sheng et al., 2008; Yousefi et al., 2011; Song et al., 2014). The microorganisms can give rise to a biofilm which can create congenial micro-environment for rock dissolution (Balogh-Brunstad et al., 2008). Organic molecules either secreted by plants or microorganisms can form metal-organic complexes that promote dissolution of the rock powder. Organic acids also supply protons that decrease the pH of the system, which is needed for rock dissolution in soils (Basak et al., 2017). The dissolution reaction is expected to happen at a higher rate in the tropical climate (high temperature and rainfall) than the temperate region.

In Australia, particularly in mining areas, a lot of waste rock powders are generated as a by-product of mining activities. Recently these by-products in the major part of these regions are considered as an environmental liability if left uncleaned or unused. These rock mineral powders varied considerably in their composition and could be used as the sources of plant nutrients (Uren, 1976; Jenkins and Nethery, 1992). It would not only help the farmers in supplying plant nutrients at a very low investment, but also would be a valuable input in the organic farming sector (Codex Alimentarius Commission, 2007). However, only a limited information is available on K-supplying capacity of these indigenous minerals from agricultural point of view. The role of different size fractions on the K release pattern for meeting plant demands is not also fully known. Overall, there is a lack of systematic studies to evaluate these materials as the source of K for plant nutrition. So, the aim of this study is to evaluate a waste rock mineral powder collected from a quarry located in New South Wales (NSW), Australia, for predicting its agronomic potential as a source of K through various laboratory and pot culture methods.

2. Materials and methods

2.1. Rock mineral powder

A rock powder or mining by-product originates through different processes in different regions. The alkaline volcanic rock (with high $\text{Na}_2\text{O} + \text{K}_2\text{O}$ contents) is formed by fractional crystallization of a mafic parent magma (Jenkins and Nethery, 1992). Such a rock material was collected from the crushed waste of a mining quarry located at Seaham, New South Wales, Australia. The geographical location of the sampling site is $32^{\circ}79'S, 151^{\circ}63'E$. The exact mineralogical composition of the rock was not known, but a preliminary powder X-ray diffraction analysis indicated that the host rock was mainly composed of quartz, anorthite, albite, some K-feldspar, mica and chlorite (Supplementary Information; SI Fig. 1). The waste mineral sample from the Seaham quarry was selected for this study because it contained a significantly higher K than other near by quarry samples (Hunter: $32^{\circ}66'S, 151^{\circ}71'E$) (Table 1).

Table 1

Total elemental contents of rock mineral powder extracted by microwave assisted digestion in aqua-regia and analyzed by ICP-MS (mean \pm standard deviation, $n = 3$).

Element	Content (g kg ⁻¹)
Al	7.32 (\pm 0.201)
Ca	8.92 (\pm 0.233)
Cu	0.01 (\pm 0.003)
Fe	11.53 (\pm 0.457)
K	15.39 (\pm 0.080)
Mg	3.54 (\pm 0.096)
Mn	0.42 (\pm 0.016)
Na	1.29 (\pm 0.111)
P	0.18 (\pm 0.059)
Si	0.59 (\pm 0.102)
Zn	0.05 (\pm 0.007)

2.2. Sample preparation

The waste mineral powder was separated into four different size fractions: 10 ASTM (passed through 10 ASTM sieve but retained on 35 ASTM sieve), 35 ASTM (passed through 35 ASTM sieve but retained on 60 ASTM sieve), 60 ASTM (passed through 60 ASTM sieve but retained on 100 ASTM sieve) and 100 ASTM (passed through 100 ASTM sieve) by using a mechanical sieve shaker. The corresponding grain sizes of the four fractions were 2000, 500, 250 and 150 μm , respectively.

2.3. Total elemental analysis

Total elemental contents of the rock mineral powder (150 μm) was determined by microwave assisted digestion of the material in aqua-regia (EPA, 1996, Method 3050B). Mineral sample (0.1 g) was digested in a teflon tube with 10 mL mixture of concentrated nitric acid and hydrochloric acid (3:1). The mixture was digested in a microwave digester (750 W at 500 kPa for 30 min) (CEM5000, CEM Corporation USA). Elements of interest were analyzed in the aliquot following filtration through 0.45 μm nylon filter and appropriate dilution. An inductively coupled plasma-mass spectrometer (ICP-MS) (Agilent 7700 \times ICP-MS, Agilent Technologies Inc., USA) was used for the analysis.

2.4. Chemical extraction

Potassium released from the four size fractions of the mineral powder was determined by using different extractants, namely water, 0.01 M calcium chloride (CaCl_2), 0.01 M citric acid, neutral 1 N ammonium acetate (NH_4OAc) and boiling 1 N nitric acid (HNO_3) as per the standard procedure (Table 2). While mineral acids are well-known extractant of K from rock samples, several organic acids can also extract K efficiently (Song and Huang, 1988). The plant rhizosphere itself is a sink of a complex mixture of various organic acids. The K extraction with multiple extractants in this study also enabled to examine which extractant would provide a good correlation with plant K uptake. K was extracted from 5.0 g mineral powder sample by shaking in an incubated shaker (30 ± 0.5 $^{\circ}\text{C}$) by maintaining different mineral and extractant ratio and shaking time (Table 2). The successive K extraction was continued until K release from the mineral powder reached a certain minimum level, at which no further significant K release occurred. This level, was taken as the constant K release point. The K content in the solution was measured by a flame photometer (FP 6420, MesuLab, China). The summation of K release above the constant point in each extraction process was taken as the 'step K', whereas the summation of K release in the all the extraction processes was taken as the 'cumulative K'.

Table 2
Different extraction procedures for evaluating the release of potassium from rock mineral powder.

Extractants	Mineral-extractant ratio (w/v)	Equilibration time (min)	Reference
Distilled water	1:2.5	30	Jackson, 1979
0.01 M Calcium Chloride (CaCl ₂)	1:5	30	Woodruff and McIntosh, 1960
1 N Ammonium acetate (NH ₄ OAc)	1:5	5	Hanway and Heidel, 1952
0.01 M Citric acid	1:5	30	Zhu and Luo, 1993
Boiling 1 N Nitric acid (HNO ₃)	1:10	15	Wood and DeTruck, 1940

2.5. Potassium release kinetics

Potassium release kinetics from the four different size fractions of mineral powder was studied by equilibrating 2.5 g of the material in 25 mL of 1 N NH₄OAc solution shaking for 1 h and equilibrating for 24 h at room temperature. These mineral suspensions were then centrifuged (Sigma 4–16; Model:10490) at a speed of 10,000 rpm for 5 min. The K content in the clear supernatant was determined by a flame photometer (FP 6420, MesuLab, China). The sediment which was left in the centrifuge tube was again extracted with a fresh lot of 25 mL of 1 N NH₄OAc solution, and the whole process was repeated up to a total of 14 times. To compute the rate of release of K from the mineral powder as a function of time, the data were fitted into different mathematical models including zero-order, first-order, Elovich and parabolic diffusion equations (Supplementary Information; SI Table 1). The best-fitted kinetic model was selected from the correlation coefficient (r value; $p \leq 0.05$) and standard error of estimate (SE) value, which were computed for the four models in case of each of the materials. The release rate constant/slope and intercept values were calculated from the best fitted model. The constants of each model represented the intercept and slope of the curves which were calculated by plotting K release versus time.

2.6. Biological method

To examine K uptake from different size fractions of mineral powder, a sand culture experiment was conducted in plastic pots by growing maize (*Zea mays*) and holy basil (*Ocimum sanctum*) as the test crops under natural condition in a greenhouse of the University of Newcastle, Newcastle (32°53'39"S latitude and 151°42'59"E longitude) in Australia, at an altitude of 21 m above sea level. The experiment was conducted in late spring season (October–November 2015) with a monthly maximum and minimum temperature 30 °C and 18 °C, respectively, average relative humidity 74% and average rainfall of 90 mm. Five treatments (four size fractions of rock mineral powder (RMP) + control) were taken in acid washed sand by keeping the sand and mineral powder in the ratio of 2:1 (80 g sand + 40 g RMP) in 10 cm × 4 cm plastic pots. Maize and holy basil seeds from Bunnings Warehouse, garden store, Newcastle, Australia were sown in the pots, placed in completely randomized design and ultimately 5 plants were maintained in each pot. The K contents in maize and basil seeds were 0.51 and 0.44%, respectively. The plants were irrigated with K free Hoagland solution on each alternative day to maintain an optimum moisture level throughout the growth period. The whole plants were uprooted at the optimum vegetative growth stage (45 days after sowing) and the biomass yield (root + shoot) was recorded after drying the samples at 65 ± 1 °C in a hot air oven for 24 h. The plant samples were ground to powder using a Wiley mill (5-mm size), and digested using a di-acid mixture containing HNO₃ and HClO₄[9:4 (v/v)] (Piper, 1967). The concentration of K in the acid digest was determined by flame photometry (FP 6420, MesuLab, China), and micronutrients in the acid digest were determined by an atomic absorption spectrophotometer (AA 7000, Labindia Instruments Pvt. Ltd., India) against standard elemental solution provided by the National Institute of Standards and Technology (NIST) (purchased from Merck Millipore, Mumbai,

India). The total K uptake was computed on plant dry matter yield basis.

2.7. Data analysis

The laboratory and pot experiments were carried out with three replications for each treatment. The data were subjected to analysis of variance (ANOVA) appropriate to the experimental design (Completely Randomized Design). The least square difference (LSD at $P = 0.05$) was computed and Duncan's multiple range test (Duncan, 1955) was used to compare the treatment means in the pot experiment. For data calculation, tabulation and graphical representations, the SPSS 20.0 and Microsoft Excel software packages were used.

3. Results and discussion

3.1. Potassium release by different extractants

The studied rock mineral powder contained about 15 g kg⁻¹ of total K as obtained in the microwave assisted aqua-regia digestion method (Table 1). The K content in the mineral sample was also confirmed by the mineralogical composition (e.g., mica, K-feldspar) of the sample (Supplementary Information; SI Fig. 1). The amount of K released by the different extractants from four different size fractions of the mineral powder is presented in Table 3. The data revealed that K release increased with the increase in the fineness of the material while the magnitude of such increase differed among the extractants. The lowest K release (5.03 to 7.06 mg kg⁻¹) was recorded by distilled water, while the highest K release (118.2 to 310.7 mg kg⁻¹) was recorded by boiling 1 N HNO₃ solution irrespective of particle sizes. The amount of K release by different extractants followed the order: water < 0.01 M calcium chloride < 0.01 M citric acid < 1 N ammonium acetate (NH₄OAc) < 1 N boiling nitric acid. A portion of the readily available form of K, which was present on the mineral surface, was extracted in water. The salt solution (CaCl₂ and NH₄OAc) was able to release the remaining portion of the available K by exchanging with cations present at the surface and wedge zone of the mineral. Citric acid having –OH and –COOH functional groups in ortho-position was liable to form

Table 3
Amount of potassium released (mg kg⁻¹) by different extractants from the rock mineral powder (n = 3).

Extractable K	Particle size (ASTM)			
	10	35	60	100
Water soluble K	5.03 (0.32)*	5.97 (0.36)	6.30 (0.35)	7.06 (0.32)
0.01 M Calcium chloride K	7.94 (1.18)	8.41 (1.17)	12.79 (2.10)	16.84 (1.88)
1 N Ammonium acetate K	18.70 (2.44)	22.67 (3.93)	28.43 (2.94)	40.39 (3.04)
0.01 M Citric acid K	15.66 (2.20)	16.97 (2.56)	23.68 (2.48)	29.93 (3.04)
Boiling 1 N Nitric acid K	118.20 (5.27)	150.8 (6.64)	214.7 (5.98)	310.7 (6.89)

*Values in the parentheses indicate standard deviation (SD).

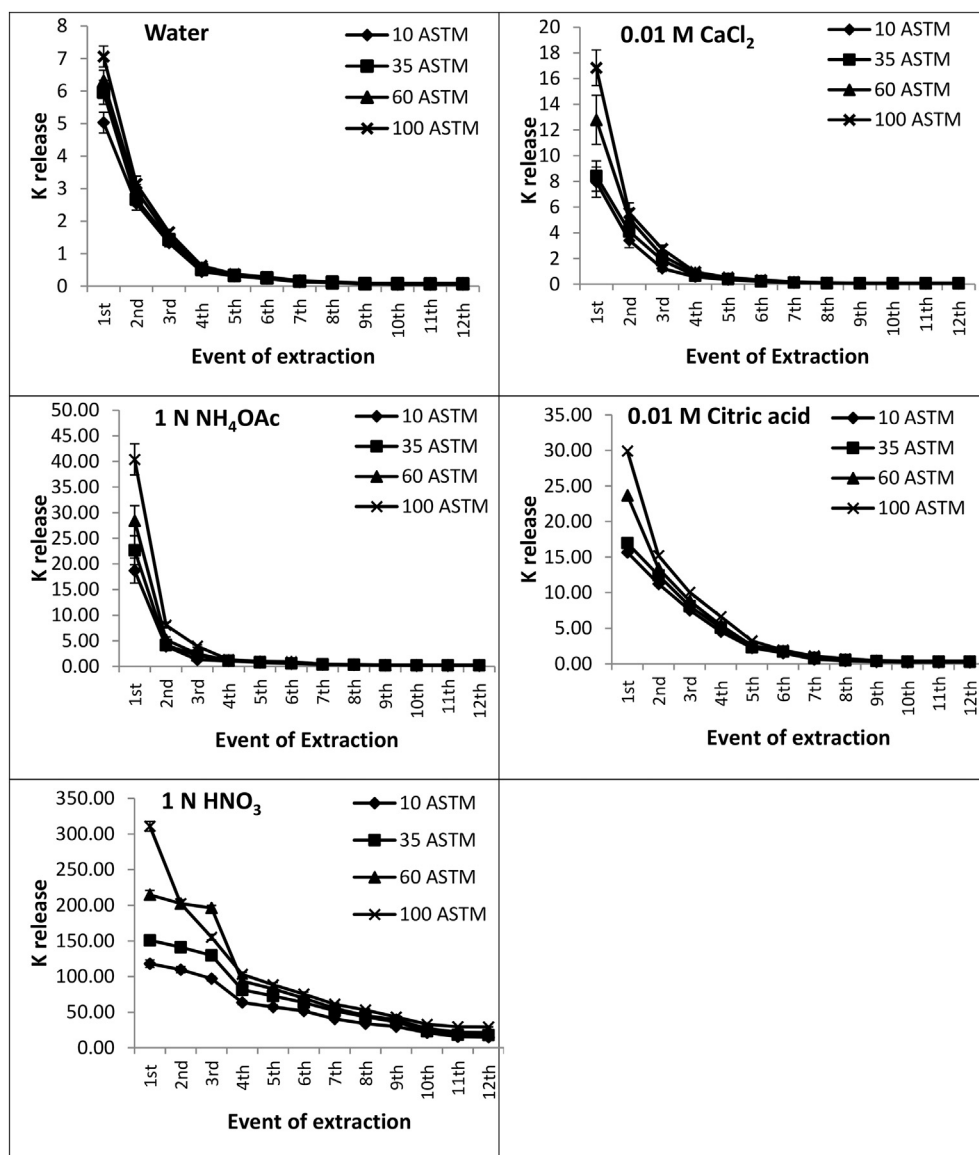


Fig. 1. Potassium released (mg kg^{-1}) from waste mineral powder in 12 consecutive extractions in water, 0.01 M CaCl_2 , 1 N NH_4OAc , 0.01 M citric acid and 1 N HNO_3 .

metal-organic complexes in the solution with the metal ions present in the mineral structure (Kononova et al., 1964; Manley and Evans, 1986; Banfield et al., 1999; Zhu et al., 2014), and thus induced dissolution of the mineral (Huang and Kiang, 1972; Wang et al., 2000; Li et al., 2006). The formation of inner sphere surface complexes with organic acids would be responsible for weakening the metal-O bonds by the protonation of surface $-\text{OH}$ groups. A higher release of K by the organic acid with increasing fineness of mineral particles might be due to an enhanced activity of the complexation process. A further larger amount of K release by a stronger mineral acid (HNO_3) indicated a significant mineral dissolution induced by the mineral acid. A higher K solubility from the finer fraction of the mineral powder was due to the larger surface area of the material exposed for the dissolution reaction.

3.2. Potassium release characteristics

The release of K from the four size fractions of the mineral powder continued in 14 successive extractions with water, 0.01 M CaCl_2 , 1 N NH_4OAc , 0.01 M citric acid and 1 N boiling HNO_3 (Fig. 1), but in last two extractions there was no significant change in K release. The water soluble K release decreased gradually from 7.06 to 0.09 mg kg^{-1} in the finest size fraction (100 ASTM) and from 5.03 to 0.05 mg kg^{-1} in the

largest size fraction (10 ASTM). The readily available K release by 0.01 M CaCl_2 was slightly higher than water and decreased gradually from the finer fraction to the coarser fraction. Similarly, 1 N NH_4OAc was a stronger extractant than 0.01 M CaCl_2 , and the former also represented the exchangeable K. As a result, the K release by 1 N NH_4OAc was significantly higher (49.5%) than that by 0.01 M CaCl_2 . There was a sharp decrease in the K release by water, 0.01 M CaCl_2 and 1 N NH_4OAc until the third extraction event and there after it decreased gradually. The K released by 0.01 M citric acid was slightly lower than 1 N NH_4OAc . However, unlike 1 N NH_4OAc , the release by citric acid was gradually decreased over the successive extraction events. The K release from mineral fractions by the strong mineral acid (i.e., 1 N boiling HNO_3) was found much greater than the other extractants. The gradual decrease in K release in 1 N boiling HNO_3 might be due to the continuous dissolution of minerals with successive extraction. The mineral structure is liable to get attacked by strong mineral acids by the substitution of K^+ with H^+ in the partially opened layers, thereby releasing K from the interlayer position (Datta and Sastry, 1995; Moritsuka et al., 2004).

The step K (reserve K) and cumulative K amounts were computed from the data obtained in consecutive K extraction events by different extractants (Table 4). The step K varied from 9.9 to 13.15 mg kg^{-1} in

Table 4
Step K and cumulative K from four size fractions of rock mineral powder under different chemical extractions (n = 3).

Size fraction (ASTM)	Step K (mg kg ⁻¹)	Cumulative K (mg kg ⁻¹)
	Water	
10	9.90 (0.91) ^a	10.38 (0.96)
35	11.15 (1.15)	12.35 (1.12)
60	11.88 (1.43)	12.42 (1.66)
100	13.15 (2.15)	13.81 (2.23)
	0.01 M CaCl ₂	
10	13.72 (1.23)	14.10 (1.33)
35	15.69 (1.81)	16.23 (2.11)
60	21.70 (2.55)	22.29 (2.41)
100	26.95 (2.89)	27.60 (2.93)
	1 N NH ₄ OAc	
10	26.35 (2.85)	27.76 (2.72)
35	31.43 (3.27)	32.99 (3.25)
60	39.06 (3.61)	40.83 (3.81)
100	55.63 (4.18)	57.56 (4.33)
	0.01 M citric acid	
10	42.77 (3.54)	44.76 (3.52)
35	46.66 (4.12)	49.31 (4.42)
60	55.77 (4.87)	58.74 (5.77)
100	67.01 (5.32)	70.46 (6.31)
	1 N boiling HNO ₃	
10	497.9 (26.3)	654.20 (36.3)
35	639.80 (42.6)	830.70 (45.70)
60	859.90 (43.9)	1070.70 (57.30)
100	935.60 (52.7)	1185.40 (62.40)

^a Values in the parentheses indicate standard deviation (SD).

Table 5
Potassium release rate constants (slope) and intercept values for different size fractions of rock mineral powder fitted in to first-order eq. (1 N NH₄OAc medium).

Size of the mineral fraction	First-order equation parameters	
	Slope × 10 ⁻² (h ⁻¹)	Intercept (mg kg ⁻¹)
10 ASTM	8.91	2.83
35 ASTM	8.93	2.92
60 ASTM	8.97	3.12
100 ASTM	9.11	3.43

water, from 13.72 to 26.95 mg kg⁻¹ in 0.01 M CaCl₂, from 26.35 to 55.63 mg kg⁻¹ in 1 N NH₄OAc, from 42.77 to 67.01 mg kg⁻¹ in 0.01 M citric acid and from 497.9 to 935.6 mg kg⁻¹ in 1 N boiling HNO₃. In all the cases, the step K level increased with an increase in the fineness of the particles. The highest cumulative K release by the mineral acid was recorded as 654.2 to 1185.4 mg kg⁻¹ which was many fold higher than other extractants. The considerably higher extraction of K by the mineral acid might be due to the reaction of the acid with the aluminosilicate network and possible dissolution of K into the solution (Badraoui et al., 1992; Srinivasarao et al., 2006).

Table 6
Biomass yield, K content and uptake by maize and holy basil plants as influenced by different size fractions of rock mineral powder in sand culture experiments.

Size fraction	Maize				Holy basil			
	Biomass yield (g pot ⁻¹)	K content (%)	K uptake (mg pot ⁻¹)	% K release	Biomass yield (g pot ⁻¹)	K content (%)	K uptake (mg pot ⁻¹)	% K release
Control	5.12	0.91	46.4	–	1.53	0.89	13.6	–
10 ASTM	5.97	1.42	85.1	11.62	1.77	1.12	20.1	2.74
35 ASTM	6.77	1.66	112.3	15.34	1.79	1.23	21.8	2.97
60 ASTM	7.15	1.73	123.6	16.89	2.66	1.42	37.8	5.16
100 ASTM	7.89	1.84	146.9	20.02	2.93	1.63	47.7	6.52
CD ^a	0.25	0.17	11.4	–	0.17	0.09	4.4	–

^a CD: critical difference.

3.3. Potassium release kinetics

The cumulative K release from the rock mineral powder in 1 N NH₄OAc solution was fitted into different mathematical expressions including zero-order, first-order, Elovich and parabolic diffusion models (Supplementary Information; SI Table 1). The highest value of correlation coefficient (r) and lowest value of standard error of estimate (SE) considered as the best fitted model. The first order kinetic equation was found to be the best for explaining K release data as evidenced by higher correlation coefficients ($r = 0.97$; $p \leq 0.05$) and lower standard error of estimate (SE = 0.07) (Supplementary Information; SI Table 2). The fitting of the first order kinetic equation indicated that the release of K from the mineral powder was dependent on the concentration gradient of K. The K release rate constants and intercept values, which were calculated for the first order kinetic model, are presented in Table 5. Both the intercept and slope values showed an increasing trend with the increase in the fineness of the mineral particles possibly due to the higher exchange sites present in the finer fraction material. The rate of K release from mineral fractions decreased with continuous release of interlayer K due to increasing distance for subsequent K diffusion (Rahmatullah and Mengel, 2000). This result is in good agreement with the finding of Song and Huang (1988) and Basak and Biswas (2009) in case of K bearing minerals. However, diffusion of inos can be influenced by many factors such as distance, tortuosity, water content and changes in reactive mineral surfaces with time. In contrast to laboratory experiments, continuous stirring or flashing might not be present in the natural environment, but all other conditions are expected to exist in the plant rhizosphere both in laboratory and field experiments (Zhu et al., 2014).

3.4. Potassium release by plant intervention

Application of different size fractions of the mineral powder was found effective in increasing the biomass yield and K uptake by both the maize and holy basil plants under sand culture experiments (Table 6). The response of mineral powder application on the biomass yield was significantly higher with the finer fraction of the material than the coarser one. The K content in the plants increased from 0.89 to 1.63% and 0.91 to 1.84% in holy basil and maize, respectively, due to the application of the mineral powder. The total K uptake by maize increased from 46.42 to 85.09 mg kg⁻¹ in case of the coarser fraction material (10 ASTM) and to 146.85 mg kg⁻¹ in case of the finer fraction material (100 ASTM). Similar results were observed in holy basil plants also, but K recovery from the mineral powder was more with maize (20%) than holy basil (6.5%). The content of other elements including trace elements increased significantly in both the plants when grown in finer fraction of the mineral powder (Table 7). However, the micronutrient contents were within the permissible limits of these elements in agricultural crops (Gough et al., 1979; Nagajyoti et al., 2010), and thus did not pose any risk of heavy metal toxicity. The improvement in biomass yields, plant K contents and uptake indicated that the rock

Table 7

Silicon (Si), aluminium (Al) and micronutrient (Zn, Cu, Fe and Mn) contents in maize and holy basil plants as influenced by different size fraction of the rock mineral powder in sand culture experiments.

Elements	Treatments (size fractions)					LSD (= 0.01)
	Control	10 ASTM	35 ASTM	60 ASTM	100 ASTM	
<i>Maize</i>						
Si (%)	0.44	0.45	0.47	0.48	0.53	0.011
Al (mg kg ⁻¹)	49.1	57.6	63.5	66.2	68.3	1.41
Zn (mg kg ⁻¹)	22.8	24.5	25.1	26.3	28.1	1.21
Cu (mg kg ⁻¹)	3.1	4.1	4.4	4.6	5.0	0.33
Fe (mg kg ⁻¹)	162.0	187.3	193.1	212.7	228.1	5.52
Mn (mg kg ⁻¹)	30.4	31.0	31.4	32.1	32.9	3.14
<i>Holy basil</i>						
Si (%)	0.14	0.13	0.17	0.18	0.21	0.007
Al (mg kg ⁻¹)	28.7	31.2	36.4	37.5	39.6	1.59
Zn (mg kg ⁻¹)	25.9	28.6	36.8	42.2	44.3	2.28
Cu (mg kg ⁻¹)	13.1	13.7	15.6	16.9	18.9	1.71
Fe (mg kg ⁻¹)	202.9	205.1	213.7	227.5	233.1	7.67
Mn (mg kg ⁻¹)	71.7	73.2	74.4	77.5	78.5	4.63

Table 8

Correlation coefficients (r value; $p \leq 0.05$) between different forms of K and biomass yield and K uptake by plants (average of maize and holy basil) ($n = 12$).

K extractant	Biomass yield	K uptake
Water soluble	0.87	0.89
0.01 M calcium chloride	0.84	0.87
1 N ammonium acetate	0.90	0.91
0.01 M citric acid	0.66	0.73
1 N boiling nitric acid	0.93	0.96

mineral powder acted as a source of K. The K utilization from different size fractions of the mineral powder could be attributed to the prevalence of the acidic environment in the rhizosphere (pH = 6.1 and 6.3 in case of maize and holy basil, respectively, in 1:2.5 soil:water ratio at plant harvest), which was created by the release of organic acids during the plant growth. Root exudation of sugar, amino acids and organic acids by maize and holy basil plants grown under nutrient deficient conditions (Carvalho et al., 2011; Shukla et al., 2013) might have played an important role in nutrient release from the rock mineral powder. Experiments conducted with other plants and silicate minerals (Hinsinger et al., 1996; Bolland and Baker, 2000; Harley and Gilkes, 2000) also support the outcome of the present study. The remarkable difference in K uptake between the smallest and largest particle size fractions may be due to the complex interactions of mineral surfaces occurring within the biogeochemical zone of plant rhizosphere (Wang et al., 2011). Plants might have more access of K from the smaller mineral particles due to a higher surface area exposed to the biogeochemical zone of the rhizosphere (Harley and Gilkes, 2000).

Data on Pearson's correlation matrix, indicated that K release by different extractants was significantly and positively correlated ($r = 0.73$ – 0.96 ; $p \leq 0.05$) with plant biomass yield and K uptake (average of maize and holy basil) in the sand culture experiment (Table 8). Potassium released by 1 N NH₄OAc and 1 N boiling HNO₃ showed higher correlation coefficients (r value) as compared to other extractants. Initially the K demand of plants would meet up with the readily available K and then the non-exchangeable K in later stage, which could be the reason of the higher r value with these two K forms (Hinsinger and Jaillard, 1993; Hinsinger et al., 1993; Wang et al., 2011). Highly significant r values were also obtained between the K uptake in plants and the extractable K in various extractants. The magnitude of r values between K uptake and different forms of K was higher as compared to that of the dry matter yield, which indicated that the forms of K present in the mineral fractions determined the K uptake by plants. The present results corroborate the findings of other workers

(Hinsinger et al., 1996; Harley and Gilkes, 2000) where mineral materials contained a higher amount of available K (water soluble and exchangeable) and resulted in a greater plant uptake.

4. Conclusions

This study indicates that only a fraction of the total K in the rock mineral powder was released by chemical extraction processes which are commonly used for soil K estimation. However, the amount of K release was significantly higher with organic and mineral acid extractants suggesting that the mineral powder could act as a slow release K source. The K uptake values in sand culture experiments also indicated a partial mobilization of K from the mineral powder by maize and holy basil plants. A significant positive correlation between K uptake by plants and K release by different chemical extractants indicated that the rhizosphere might accelerate the K release from mineral powder for an increased plant uptake. Both the chemical and biological methods were able to extract about 12–20% of total K present in the mineral powder. A further understanding of the underlying biogeochemical processes is needed so that mineral materials and conditions can be modified to achieve desired agronomic effectiveness. Further greenhouse trials with K exhaustive crops as well as long-term cropping studies under field conditions are needed to assess the quantitative K supply behaviors of the rock mineral powder in order to support sustainable agricultural production.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.gexplo.2017.11.023>.

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