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**Bio-intervention of naturally occurring silicate minerals for alternative source of potassium: Challenges and opportunities**

Biraj Bandhu Basak[1*], Binoy Sarkar[2], Dipak Ranjan Biswas[3], Subhas Sarkar[4], Peter Sanderson[5] and Ravi Naidu[5, 6]

[1]ICAR-Directorate of Medicinal and Aromatic Plants Research, Boriavi 387310, Anand, India

[2]Future Industries Institute, University of South Australia, Mawson Lakes Campus, SA 5095, Australia

[3]Division of Soil Science and Agricultural Chemistry, Indian Agricultural Research Institute (IARI), New Delhi 110012, India

[4]Central Institute for Fresh Water Aquaculture, RRC Anand, Anand 388001, India

[5]Global Centre for Environmental Remediation, and [6]Cooperative Research Centre for Contamination Assessment and Remediation of the Environment, ATC Building, University of Newcastle, Callaghan, NSW 2308, Australia.

[*]Corresponding author:

Dr Biraj Bandhu Basak; ICAR-Directorate of Medicinal and Aromatic Plants Research, Boriavi 387310, Anand, India; Telephone: +91 2692 271605; e-mail: biraj.ssac@gmail.com

## Abstract

Soil needs simultaneous replenishment of various nutrients to maintain its inherent fertility status under extensive cropping systems. Replenishing soil nutrients with commercial fertilizer is costly. Among various fertilizers, deposits of potassium (K) ore suitable for the production of commercial K fertilizer (KCl) are distributed in few northern hemisphere countries (Canada, Russia, Belarus and Germany) which control more than 70% of the world's potash market. Naturally occurring minerals, particularly silicate minerals, could be used as a source of K, but not as satisfactorily as commercial K fertilizers. In this context, bio-intervention (in combination with microorganisms and/or composting) of silicate minerals has been found quite promising to improve plant K availability and assimilation. This is an energy efficient and environmentally friendly approach. Here we present a critical review of existing literature on direct application of silicate minerals as a source of K for plant nutrition as well as soil fertility enhancement by underpinning the bio-intervention strategies and related K solubilization mechanisms. An advancement of knowledge in this field will not only contribute to a better understanding of the complex natural processes of soil K fertility, but also help to develop a new approach to utilize natural mineral resources for sustainable and environmental friendly agricultural practices.

**Key words:** Alternative K fertilizer, Silicate minerals, Bio-intervention, Plant nutrition, Sustainable 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. Modern intensive agriculture leads to a decline in soil nutrient levels due to mining through crop uptake and other losses. The issue of K is more pronounced in the developing countries as most of the farmers have mainly focused on the application of nitrogen and phosphorus for crop production neglecting K and micronutrients. Such an imbalanced nutrient management practice has badly impaired the productivity of soil. According to an estimate by the Food and Agriculture Organization of the United Nations (FAO), the global demand of potash fertilizer was likely to increase annually by 2.6% over 2014 and the supply would balance the demand. Of the overall increase in demand for 3400,000 tonnes of potash between 2014 and 2018, 56% would be in Asia, 27% in the America, 11% in Europe, 6% in Africa and0.4% in Oceania (FAO, 2015).Most of these have to be imported to respective continents (FAO, 2015). Most importantly, K fertilizers make up only 10% or less of the total fertilizer inputs despite the fact that K undergoes the highest nutrient depletion rates in developing countries, especially in African countries. These countries do not have any suitable K bearing mineral ores from which commercial K fertilizers can be produced. Potash ores have a rather limited distribution globally (Rittenhouse, 1979; Moores, 2009), with the bulk of the world's K mined in Canada, Europe and the Middle East (Figure 1). Most of the Kores suitable for commercial K fertilizer production are distributed in few countries in northern hemisphere (Canada, Russia, Belarus and Germany) and control more than 70% of the existing potash market. In terms of the consumption patterns, it is in the order of East Asia> Latin America> South Asia> Africa (Figure 1) where no significant K ore deposit is available for commercial K fertilizer production. Thus, there is a very little scope for many developing countries to be selfsufficient in K nutrition by using conventional fertilizers. On global basis the supply of K experiences an annual deficit of 20 kg K $ha^{-1}$ (Sheldrick et al. 2002). In African countries and China, the total annual K deficits reach up to 4.1 and 8.3 million tonnes respectively, which correspond to a respective estimate of (20 and 60 kg K $ha^{-1}$ $year^{-1}$) in these regions (FAO, 2015). The K deficit in East Asia is in excess of 9 million tonnes per year, mostly dominated by China (FAO, 2015). India and other developing countries are having almost a similar situation. The extent of K fertilizer deficit in these areas is increasing over the years. On the other hand, removal of K from soil in comparison to N and P is remarkably high in different copping systems particularly in those involving cereal and fodder crops. A huge gap between K removal and replenishment has been found in various cropping systems (Yadav et al.1998). For example, the gap between soil K removal and replenishment in India was estimated as high as 196, 170 and 255 kg $ha^{-1}$ in the rice-wheat, soybean-wheat and rice-wheat-green gram cropping systems, respectively (Yadav et al.1998).

Potassium bearing minerals are limited and finite resource in selected few counties. Therefore, to satisfy the K demand for world crop production, the amount of additional potash required is more than the current global production. The requirements of potash fertilizers in developing countries are so substantial that production must be more than double to sustain the soil K stocks (Manning, 2010). The cost of K-fertilizers increased tremendously throughout the world. The situation in Southeast Asia, Africa and Oceania are alarming because there is no reserve of K-bearing minerals. The whole consumption of K-fertilizers is imported in these regions. Thus, there is an urgent need to find alternative K sources to mitigate plant needs and thereby to reduce the dependency on costly K fertilizers. To address the problem it is necessary to consider the unconventional sources of K like naturally occurring rocks and minerals, particularly the silicate minerals.

Despite silicate minerals are not as effective as commercial K fertilizers, novel approaches may speed up K release from the mineral structures, which is appropriate in circumstances where farmers are presently deprived of the global K fertilizer market. This review aims to demonstrate the importance of alternative K sources for plant nutrition since commercial K fertilizers are under shortage, particularly in developing countries. Critically, the review focuses on the K dynamics in soil, K bearing minerals, approaches of K mobilization from different K bearing minerals, evidence of use of K bearing minerals as K fertilizers, and the effect of modification, especially microbial inoculation and composting, on K mobilization in soils. By critically analyzing the K nutrition results from existing published trials, this review also discusses whether K bearing minerals with suitable modification can be considered as an alternative to conventional K fertilizers for sustainable crop production.

## 2. Potassium dynamics in soil

Potassium exists in soil in different forms, which are in quasi-equilibrium with each other. Based on the availability to plants and microbes, forms of soil K are categorized into four groups, namely water-soluble (solution-K), exchangeable, non-exchangeable and structural or mineral-K. Exchangeable K or available K is held by negatively charged clay minerals and organic matter in soils, while non-exchangeable K is consisted predominantly of interlayer K of non-expandable clay minerals such as illite and lattice K in K-minerals such as K-feldspars (Sparks 1987). The major portion of the total soil K exists in the mineral fraction. Total soil K reserves are large in most of the soils, but the distribution of different K forms differs from soil to soil as a function of the dominant soil minerals present (Jiyun1993;Steingrobe and Claassen 2000; Shanwal and Dahiya, 2006). It is reported that about 92 to 98% of the total soil K exists as part of mineral or structural-K in a fixed or non-exchangeable form. The sum of solution and exchangeable forms of K is considered as the 'readily available form' which constitutes about 1 to 2% of the total K in soil. Further, the share of the readily available forms is 98% in exchangeable and 2% in solution. However, all these forms exist in dynamic equilibrium with each other (Subba Rao and Brar, 2002; Tripler et al. 2006). It is evident that non-exchangeable K (also called as 'slowly available K') is released and become available to plant uptake when solution and exchangeable K are depleted (Sharpley 1989).The various K forms in soils and their transformation into soil solution through various pools and pathways are represented schematically in Figure 2. The exchangeable K tends to attain equilibrium with solution K rapidly but only slowly with non-exchangeable K. Because of the crop removal, soil solution K gets depleted. The replacement of the K-depleted soil solution is then affected primarily by the release of exchangeable K from mineral K (clay minerals). As and when the exchangeable K-fraction is depleted substantially or exhausted by crop uptake, the non-exchangeable K replenishes the exchangeable form, thus the K supply is maintained.

## 3. Potassium bearing minerals in soil environment

Potassium in soil is mainly present as K-bearing minerals. The K-supplying power of a soil depends on the content and the nature of K-bearing minerals as well as on the rate at which structural and fixed-K become available to plants. More than 90% of the total K in soils is found in mineral form or as structural K. Mineral K is generally assumed to be only slowly available to plants; however, the availability is dependent on the level of K in other forms, and the degree of weathering of the mineral K fractions (Sparks and Huang 1985; Sparks 1987; Jiyun1993; Tripler et al. 2006). The major rock-forming minerals of almost all igneous and metamorphic rocks are silicates. Similarly, the dominant rock-forming minerals in sediments are also usually silicates. The mineralogy of sedimentary rocks is very important as many nutrients are associated with the layer silicate clay minerals. However, both igneous and metamorphic rocks consist of mixtures of the four major rock-forming mineral groups: quartz, feldspar, mica and ferromagnesian minerals (Steingrobe and Claassen 2000; Harley and Gilkes 2000; Manning 2010). The primary sources of K-bearing minerals in soils are feldspars, micas (e.g., muscovite - white micabiotite - black mica and phlogopite), zeolite, glauconite, potassium-taranakite, illite, vermiculite and chlorite. Mica-group minerals are of special interest for plant nutrition as they may be a major source of K, Mg, Zn and Mn. It may be either muscovite (white mica), biotite (black mica) or phlogopite. Muscovite is dioctahedral mica, while biotite and phlogopite are trioctahedral micas which exhibit greater repulsion, and thus weather more easily and release K. Another important mineral is glauconite which is essentially a hydrated-iron-magnesium-potassium-aluminium-silicate (hydrated-Fe-Mg-K-Al-silicate). It contains about 5-6% $K_2O$ and can be used as a source of K. Potassium is also present in the form of secondary or clay minerals like illite or hydrous mica, vermiculite, chlorite and interstratified minerals (Jiyun 1993; Mengel and Rahmatullah 1994). Due to advanced weathering process, the K in these secondary or clay minerals are relatively easily available to plants than primary minerals. The principle K fertilizer ore minerals together with the dominant rock-forming K silicate minerals are listed in Table 1.

### 3.1. Silicate minerals as a source of potassium

A number of studies have presented the ability of different K bearing silicate minerals to yield nutrients under laboratory, pot and field trial conditions (Table 2). These trials include pot (greenhouse) and field experiments using a range of crops, different time scales and under different climates. The most commonly trialed minerals include granite, glauconite, phlogopite, biotite, gneiss, feldspar, etc.

The agronomic effectiveness of K bearing minerals is largely determined by their mineralogy and chemical composition. A consistent set of trials were carried out in Western Australia, in which granite was used in pot trials on wheat, clover and ryegrass (Coroneos et al. 1996; Hinsinger et al. 1996; Bolland and Baker 2000).The application of granite (2.29% $K_2O$) significantly increased biomass yield (10%–20%) in wheat, whereas ground diorite (0.3% $K_2O$) did not show any significant response. Pot trials conducted with clover and ryegrass (Coroneos et al.1996; Wang et al.2000; Silva et al.2013) also showed that application of granite powder enhanced both yield and shoot K content significantly compared to the control.

Agronomic effectiveness is also greatly influenced by the plant species and soil types. Among several plant species investigated, the utilization of K from gneiss followed the order: maize > ryegrass > alfalfa and a greater uptake was possible from finer sized particles (Wang et al. 2000). So, type of plants and their root architecture played a vital role in releasing K from minerals. In another study, phlogopite mica and K-feldspars significantly improved the yield and K uptake by rice grown in a sandy soil having very low exchangeable K (Weerasuriya et al. 1993). These minerals might be effective K suppliers in highly weathered soils where use efficiency of chemical fertilizer is very low. For example, application of K-feldspar served as an alternative to KCl in Colombia, where economic and agricultural conditions, including the occurrence of Oxisol exerted problems with KCl use (Sanz-Scovino and Rowell 1988; Wang et al.2000).Initial soil K status also influenced the effectiveness of the minerals and their application is quite effective particularly in K deficient soil.

Few field trials were also conducted in order to work out the efficiency of the mineral as source of K for crop growth. For example, feldspar was tested as a source of K using okra (Abdel-Mouty and El-Greadly 2008), legumes (Sanz-Scovino and Rowell 1988) and tomato (Badr 2006) cultivation. These studies showed that okra and tomato yield increased by 39.3 and 40%, respectively, with feldspar application whereas legumes did not show any response. Application of K bearing minerals like biotite, microcline, orthoclase and waste mica increased plant biomass yield and K uptake in spring barley (Madaras et al. 2013) and leek (Mohammed et al. 2013) as well. The mineral source of K was effective in some long duration crops like grape, coffee and olive. Berry yield K content in grape increased when biotite was used as a source of K in vineyard (Stamford et al. 2011), while phonolite was as effective as KCl in increasing fruit yield in coffee (Mancuso et al. 2014).These studies indicatedthat plantspecies along with their growth pattern also could facilitate the release of K from K bearing minerals.

Although crushed rock materials were promoted as nutrient sources for some time, this was largely confined in alternative or organic farming sectors (Lisle 1994; Walters 1975). The use of K bearing minerals as such or silicate rock fertilizers in traditional agricultural practices was found poor because of low solubility of silicate rocks, subsequent low availability of nutrients to plants, and the practicality of applying large amounts of ground rock to agricultural land (Hinsinger et al. 1996; Bolland and Baker 2000; Harley and Gilkes 2000). So, only crushed rock materials as such were not sufficient to supply K to plant as compared with conventional soluble K sources. However, several biological means, particularly the use of K mobilizing microorganisms, can mobilize K from rocks and minerals and thus can increase K availability to plants. So, the use of rock powders in combination with some suitable biological modification can be an alternative source of K for crop production, especially with the gradual growth in popularity of organic farming.

## 4. Bio-intervention of silicate minerals and K availability

Applications of silicate minerals as such are not as effective as commercial K fertilizers. So, some interventions are needed to speed up the K release rate. Release of K in soil from K bearing minerals is influenced by many factors, especially by the microbial activity in the rhizosphere region. Microbial activity releases K directly from the mineral structure as well as from the non-exchangeable reserve. Many microorganisms hold a primary catabolic role in the degradation of silicate mineral structure, which contributes to the release of K in soils. These microorganisms are able to solubilize the unavailable forms of K from K-bearing minerals, such as micas, illite and orthoclase, by excreting organic acids which either directly dissolves the rock K or chelates the silicon ions to bring the K into solution (Friedrich et al. 1991; Vandevivere et al. 1994; Ullman et al. 1996; Bennett et al. 1998; Biswas and Basak 2013). These microorganisms are commonly known as K solubilizing microorganisms (KSM). In China and South Korea the K dissolving bacteria are known as 'biological K fertilizer' (BPF) and used for bio-activation of soil K- reserves so as to alleviate the shortage of K-fertilizers (Lin et al. 2002; Sheng et al. 2002; Han and Lee 2005; Han et al. 2006). On the other hand, blending of K-bearing minerals during composting is an alternative and viable technology to release K from minerals (Badr 2006; Nishanth and Biswas 2008; Zhu et al. 2013). Therefore, biological modification or bio-intervention (microbial intervention and composting) can turn out to be an important and effective means to mobilize K from K-bearing minerals for plant nutrition. Such bio-intervention strategies (Figure 3) provide fewer chances for pollution and consume less energy in improving available K assimilation by plants.

## 5. Mechanisms of potassium mobilization from silicate minerals

### 5.1. Dissolution by organic acids

The principal mechanism of K solubilization from K-bearing minerals is the action of organic acids synthesized by the soil microorganisms (Table 3) (Huang and Keller 1972; Huang and Kiang 1972; Leyval and Berthelin1989). The protons associated with the organic acid molecules decrease the pH of the solution, and therefore, induce the releasing capacity of cations such as Fe, K and Mg. Microbial respiration and degradation of particulate and dissolved organic carbon can elevate the carbonic acid concentration at mineral surfaces, in soils and in ground water (Barker et al. 1998; Calvaruso et al. 2006), which can lead to an increase in the rates of mineral weathering by a proton-promoted dissolution mechanism. Experiments revealed that species of Bacillus increased the soluble K content in the culture medium (Sheng et al., 2002; Han et al. 2006). It was also proposed that Bacillus mucilaginosus increased the dissolution rate of silicate and aluminosilicate minerals and released the $K^+$ and $SiO_2$ from the crystal lattice primarily by generating organic acids like oxalic, citric, tartaric, fumaric, glycolic, etc. Among these acids, oxalic and citric acids were the most common and present in a relatively larger quantities. In addition to production of carboxylic acids (citric, tartaric and oxalic acids), microorganisms could also produce some intermediate and high molecular weight organic molecules like mannuronic and guluronic acids. Like the low molecular weight organic acids, the high molecular weight acids could also increase the extent of mineral weathering presumably by complexing with the ions in solution, thereby lowering the solution saturation state (Welch and

Vandevivere 1994; Welch et al. 2002).It was found that the exopolysaccharides produced by microorganisms strongly adsorbed to organic acids and thus assisted in their attachment to the mineral surface, resulting in an area of high concentration of organic acids near the mineral(Liu et al. 2006). The EPS adsorbed $SiO_2$and thus affected the equilibrium between the mineral and fluid phases and directed the reaction towards $SiO_2$and K solubilization. Bacteria might also increase the release rates by creating and maintaining microenvironments where metabolite concentrations, such as extracellular polymer, primarily proteins and polysaccharides, were higher than in the bulk solution (Malinovskaya et al. 1990; Ullman et al. 1996). Organic acid molecules have a triple action on mineral weathering: (i) they adhere to the mineral surface and extract nutrients from the mineral particles by electron transfer reaction; (ii) they break the oxygen links; and (iii) they chelate ions present in solution through their carboxyl and hydroxyl groups. The third mechanism indirectly accelerates the dissolution rate by creating gradient between cation and anion concentrations in the solution (Welch et al. 2002).

## 5.2. Metal complexing ligands

Another possible mechanism of K mobilization by microorganisms is the production of metal-complexing ligands. In addition to producing a variety of organic acids, microbes also produce high molecular weight polymers and organic ligands (mannuronic acid, guluronic acid and alginates). Ligands can complex with ions on the mineral surface and can weaken the metal–oxygen bonds. Alternatively, ligands in directly affect the reactions by forming complexes with ions in solution, thereby decreasing solution saturation state. The high molecular weight polymers can accelerate the ions diffusion away from the mineral surface by producing slime layer around the mineral surface, which increases the contact time between water and the mineral

(Banfield et al.1999). For example,the production of capsular polysaccharide or extracellular polysaccharides (EPS) and enzymes by K solubilizing microorganisms' viz., Bacillus mucilaginosus and Bacillus edaphicus (Richards and Bates1989; Lin et al. 2002; Banfield et al. 1999) may accelerate the dissolution of a variety of silicates. The capsular polysaccharide produced by Bacillus edaphicus contained functional groups (—COO—) that complexed with mineral ions, lowering solution saturation state, and thereby enhanced dissolution (Sheng et al. 2002).

In addition to many simple and complex organic acids, microbially produced organic ligands might include metabolic by-products, extracellular enzymes and chelates, which would help in the dissolution of K-minerals by decreasing the pH of the environment. Chelating molecules might increase the dissolution rates of cations by forming strong bonds with them or with mineral surfaces (Welch et al. 2002). Mixture of polymers and low molecular weight ligands produced by Bacillus mucilaginosus had a beneficial effect on silicate mineral (biotite and muscovite) weathering (Malinovskaya et al.1990). Bacteria might also increase the release rate of K by creating and maintaining microenvironments where metabolite concentrations are higher than in the bulk solution (Ullman et al.1996). Thus, the production and release of extracellular polymers, primarily proteins and polysaccharides into surrounding environment increase the release of K from silicate mineral structure.

### 5.3. Formation of biofilm

An additional hypothesized mechanism of mobilization of mineral K is by the formation of biofilm on the rhizospheric mineral surfaces by certain bacterial strains (Balogh-Brunstad et al. 2008). Biofilm was defined as a microbial community concentrated on the root-hypha-mineral interface and was protected by extracellular polymers produced by themselves utilizing plant and fungal exudates in soils (Banfield et al. 1999; Gadd 2007). These bacteria were remarkable for their tremendous phylogenetic and metabolic diversity and for their ability to adapt and colonize extreme environments which were not tolerated by other organisms. In such a microenvironment, bacteria extracted inorganic nutrients and energy directly from the mineral matrix and thereby helped in mineral weathering. Extracellular polymers, primarily proteins and polysaccharides produced by the microorganism served as catalyst and thereby induced the K release from silicate mineral structure.

It was also reported that ectomycorrhizal hyphal networks and root hairs of non-ectomycorrhizal trees could embed in biofilms and transfer nutrients to the host. It suggested that the presence of biofilms accelerated the weathering of biotite and anorthite, and thereby increased the mineral uptake by plants (Adey et al. 1993; Shi et al. 2014).

## 6. Bio-approaches for K mobilization from silicate minerals

### 6.1. Microbial intervention

Potassium solubilizing microorganisms (KSM) include mainly bacteria and some fungi, but bacteria are the most dominant members. They are also known as potassium solubilizing bacteria (KSB) or potassium dissolving bacteria or silicate dissolving bacteria (SDB).A wide range of KSMs including bacteria (Bacillus mucilaginosus, Bacillus edaphicus, Bacillus circulans, Acidothiobacillus ferrooxidans,), fungi (Aspergillus niger, Aspergillus fumigatus, Aspergillus terreus) and some arbuscular mycorrhizal fungi (AMF) were reported to release K from K bearing minerals in plant available form (Lian et al. 2002;Wu et al. 2005; Sheng et al. 2008; GeetaSingh et al. 2010; Liu et al. 2011; Biswas and Basak 2013; Prajapati et al. 2012; Rajawat et al. 2012). Apart from the above mentioned microorganisms, some rhizospheric microorganisms were also reported as K solubilizers. These include Enterobacter hormaechei (KSB-8) (Prajapati et al. 2012), Arthrobacter sp. (Zarjani et al. 2013), Paenibacillus mucilaginosus (Liu et al. 2011; Hu et al. 2006), P. frequentans, Cladosporium (Argelis et al. 1993), Aminobacter, Sphingomonas, Burkholderia (Uroz et al. 2007),Paenibacillusglu-canolyticus (Sangeeth et al. 2012), etc. But the strains like B. mucilaginosus and B. Edaphicus were the most efficient in their action (Zhao et al.2008; Sheng 2005; Lian et al. 2002; Li et al. 2006; Li 2003). Table 4 summarizes several examples where K-release from minerals was augmented by bio-intervention (microbial and composting).

### 6.1.1. Potassium solubilizing bacteria

Potassium solubilizing bacteria, particularly the genus Bacillus, enhances K availability through solubilization of the insoluble K from silicate minerals during the process of biodegradation of silicate minerals (Han et al. 2006; Liu et al. 2006). The results of such activity involve both geochemical and structural changes in the rocks and silicate minerals. The metabolic diversity of Bacillus spp .i.e., the various types of Bacillus strains and their mutants, has led to the fact that many representatives of this group are being used as K biofertilizers (Sheng et al.2003; Sheng and He 2006). It was found in several experiments that species of K solubilizing bacteria increased the soluble $K^+$ content when cultured with media containing K bearing minerals under in-vitro laboratory conditions (Sheng et al. 2002; Han et al. 2006). The K solubilization capacity was also governed by the type of bacterial strains. For example, local bacterial strain (K-81) solubilized 2.6, 2.0 and 4.6 times more K from biotite, muscovite and hydromuscovite, respectively, than K-31 strain under same laboratory conditions (Mikhailouskaya and Tchernysh

2005). On the other hand, the amount of K solubilization was found to differ from mineral to mineral by the same bacterial strain (Liu et al. 2006; Sheng and He 2006). K released by Bacillus mucilaginosus was observed as 4.29 mg $L^{-1}$, 1.26 mg $L^{-1}$ and 0.85 mg $L^{-1}$ from mica, microcline and orthoclase, respectively (Sugumaran and Janarthanam 2007). Thus, both the types of silicate minerals and the associatedbacterial strains could play anequallysignificant role in K solubilization.

### 6.1.2. Potassium solubilizing fungi

Like KSB, some fungi (Aspergillusniger, A. fumigatus, A. awamori, Penicilliumsp) and yeast (Torulaspora globose) could release K from K bearing minerals (Lian et al. 2008; Prajapati et al. 2012; Song et al. 2014), and they are known as potassium solubilizing fungi (KSF). Among the KSFs, Aspergillus niger, A. fumigatus,and A. terreus were able to release significant amount of K from insoluble source of K under laboratory conditions within a short period of time (Lian et al. 2008; Prajapati et al. 2012). Penicillium purpurogenum and Torulaspora globose were able to release 30 and 38% of the total K, respectively, from a silicate rock powder within 15 days under laboratory conditions. So, KSF could be a potential bio-agent for improving K release from silicate minerals as well as a promising K biofertilizer.

### 6.1.3. Arbuscularmycorrhizal fungi

Arbuscular mycorrhizal fungi (AMF) could also release nutrient elements including K from the mineral structure by releasing protons, $CO_2$ and organic acids in surrounding environment (Jones et al.2009; Veresoglou et al.2011; Yousefi et al.2011). The AM fungi, which are well known to improve P nutrition of plants (Bolan 1991), were alsoable to solubilize K, Fe, Mg and Al from apatite, phlogopite,biotite, feldspars and other silicates rock powders, and promote plant growth under nutrient-limiting conditions (Leyval and Berthelin1989; 1991; Paris et al. 1995; Jongmans et al. 1997; Wallander and Wickman1999; Hoffland et al. 2003; Balogh-Brunstad et al. 2008). But the K release rate was very slow and only occurred when surrounding environment was deficient in K. So, the AM fungi could be a promising K biofertlizer for long duration crops (plantation and fruit) where slow but continuous supply of the nutrient is required.

### 6.2. Composting

Composting of organic matter with K-minerals can release K and improve the K availability in the system. The silicate structure of K-minerals could be disintegrated during the composting process because of the production of organic acids and $CO_2$, which rendered low pH environment in the system. Carbonic acid produced from $CO_2$ is assumed to play an important role in weathering of minerals through suppression of pH and the known impact of increased proton activity to accelerate the weathering of primary silicate minerals (Banwart and Berg 1999). This mode of action is similar to low molecular weight organic acid produced by the microorganisms. Similarly, vermicomposting (with the introduction of earth worms) accelerated the K release from silicate minerals due to the low pH, high microbial population and improved enzymatic action in the earthworm intestine (Liu et al.2011).There are only few evidences available in the literature which demonstrated enhanced K release from silicate minerals through composting process (Badr 2006; Nishanth and Biswas 2008; Biswas et al. 2009). For example, concentration of available K releasing from feldspar increased markedly through composting process and the maximum increase was observed with 40% feldspar addition in the total compost dry weight (w/w) (Badr 2006). In another study, a significant amount of K released from waste mica when composted with rice straw and cow dung slurry for 120 days (Nishanth and Biswas 2008). Addition of low-grade rock phosphate along with waste mica to crop residue during composting improved the quality of the compost in terms of its total N, P and K contents which helped to enhance the mobilization of unavailable K in waste mica into plant available forms (Biswas et al. 2009). Significant release of K was observed when K bearing mineral powder (PBMP) was composted in the presence of earthworm (Eisenia foetida), which increased the available and effective K content in the final compost (Zhu et al. 2013).The amount of acids which are produced during the composting process is presumably much higher than an individual microorganism because composting often involves a heterogeneous microbial strain. In case of vermicomposting, the K release from silicate minerals might be accelerated by both the chemical and physical actions of earthworms. These actions come from the enhanced enzymatic activities and the grinding of minerals within the earthworm's gut. Hence, composting process could significantly contribute to the K mobilization from rocks and minerals and become available option for the production of K-enriched organic fertilizer.

## 7. Structural changes of silicate minerals due to bio-intervention

Bio-intervention of silicate minerals leads to the release of K either by direct K dissolution from the mineral structure or by chelation of Si and Al ions with organic molecules. Both the processes might lead to some structural alternation of the mineral species. As the Si and Al ions are the main structural frame work of silicate minerals, there is a significant possibility of their structural change or breakdown. For example, soil microorganisms were able to transform biotite minerals following the release of K and other ions (Boyle and Voigt 1973). Microbial destruction of feldspar was evident due to an accelerated weathering by ligand excretion and release of limiting nutrient from the mineral structure (Bennett at al. 1998). The structural degradation of silicate minerals (e.g., mica and feldspar) by Bacillus mucilaginosus occurred as a result of the release of $K^+$ and $SiO_2$ under laboratory conditions (Liu et al. 2006). Significant changes of full-width at half maximum (FWHM) in the X-ray diffraction (XRD) reflection of mica was observed when inoculated with B. mucilaginosus under both the laboratory and pot culture conditions (Basak and Biswas 2009; Biswas and Basak 2014). The same bacterial strain was found to alter a montmorillonite structure under laboratory conditions (Yang et al.2016). These alterations also led to thestructural degradation of the mineral and reduced the water retention capacity of montmorillonite, which might raise a question about the long term sustainability of the technology (Yang et al. 2016). However, further research is needed in order to unravel the microstructural changes of minerals due to bio-intervention and its possible environmental impacts. Advanced instrumental techniques like scanning electron microscopy (SEM), transmission electron microscopy (TEM), XRD, neutron scattering, and also synchrotron based methods could be used to pin point the specific change or alteration of minerals occurred due to the microbial intervention.

## 8. Plant growth and K nutrition on bio-intervened silicate minerals

Application of silicate rocks alone as the source of K has yielded varying results, and sometimes was not very effective in increasing the crop growth and nutrition. But an integrated application of silicate minerals with K mobilizing microorganisms was found promising in increasing the crop growth and yield under both pot culture and field experiments using a range of K-bearing silicate minerals in combination with either different species of KSM or composting.

## 8.1 Pot trials

Reports on the bio-intervention of silicate minerals as a source of K under pot culture experiments are listed in Table 5. Significant amount of K uptake was reported from biotite and microcline by Pinus sylvestris colonized by two ectomycorrhizal fungi, Paxillus involutus and Suillus variegatus (Wallander and Wickman1999). Slime-forming bacteria (Bacillus mucilaginosus, Bacillus edaphicus and Bacillus cereus) isolated from soils, rock surface and earthworm intestine could dissolve silicate minerals. This helped in improving yield and K uptake in tomato, cotton, rape, mustard, groundnut, wheat, sorghum and sudan grass by supplying K to K-deficient soils (Lin et al. 2002; Sheng 2005; Sheng and He 2006; Badr et al. 2006; Sugumaran and Janarthanam2007; Basak and Biswas 2009). Inoculation of these bacterial strain could improve the yield by 21% in rape, 24% in cotton, 125% in tomato, 58% in sorghum and 125% in groundnut while K uptake increased by 31% in rape, 34% cotton and 71% in sorghum (Lin et al. 2002; Sheng 2005; Badr et al. 2006; Sugumaran and Janarthanam2007). Application of enriched vermicompost prepared from gneiss and steatite powder also resulted in a higher growth and yield than plants grown in Oxisol with non-enriched vermicompost. Further, vermicompost enriched with steatite powder increased the dry matter yield of maize by 21.5% in comparison to applying non-enriched vermicompost and steatite alone to the soil (de Souza et al. 2013). Apart from improving plant growth parameters, soil K content was also improved by inoculation of bacterial strain. The available K content increased from 3.63 mg $kg^{-1}$ in non-rhizosphere soil to 5.73 mg $kg^{-1}$ in rhizosphere soil when plant root was inoculated with Bacillus mucilaginosus strain (Lin et al. 2002).

Sometimes co-inoculation with other bacteria like plant growth promoting rhizobacteria (PGPR), phosphate solubilizing bacteria (PSB) and N-fixing bacteria may improve the performance of individual inoculants due to synergistic effects on each other. The use of PGPR including PSB and KSB as biofertilizers was suggested as a sustainable solution to improve plant nutrition and production (Alexander1977; Park et al.2003; Vessey2003). Synergistic effects of soil fertilization with rock P and K materials and co-inoculation with phosphate solubilizing bacteria (PSB) Bacillus megatherium and potassium solubilizing bacteria (KSB) Bacillus mucilaginosus KCTC 3870 on the improvement of P and K uptake by eggplant (Solanum torvum L. NIVOT) grown under limited P and K soil in greenhouse was reported (Han and Lee 2005).Although individual inoculation did not increase the yield and uptake of N, P and K by eggplant, co-inoculation with both bacteria and fertilized with rock P and K materials increased the yield as well as N, P and K uptake by shoot (14, 22 and 14%, respectively) and roots (11, 14 and 21%)(Han and Lee 2005). Similarly co-inoculation of biofertilizer containing N-fixer (Azotobacter chroococcum), P-solubilizer (Bacillus megatherium) and K-solubilizer (Bacillus mucilaginosus) and AM fungi (Glomus mosseae and G. intradices) had beneficial effect on soil properties and maize growth. The study also indicated that half the amount of biofertilizer applications had similar effects when compared with organic fertilizer or chemical fertilizer treatments. Microbial inoculums not only increased the nutritional assimilation total N, P and K in plants, but also improved soil properties (Wu et al. 2005). The potential of co-inoculation with phosphate solubilizing bacteria (PSB) Bacillus megatherium var. phosphaticum and potassium solubilizing bacteria (KSB) Bacillus mucilaginosus on mobilization of P and K from rock minerals and their effect on nutrient uptake and growth of pepper and cucumber was also studied in Korea (Han et al. 2006). The integrated use of co-inoculation with two bacterial strains and insoluble rock P and K materials resulted in higher yield and nutrient uptake by pepper and cucumber as well as 36 and 31% increase in P and K availability in soils, respectively, as compared to the control (Han et al.2006). Similarly waste mica (K source) co-inoculated with K solubilizing (Bacillus mucilaginosus) and nitrogen fixing (Azotobacter chroococcum A-41) bacteria was found to be effective in increasing the biomass yield and N and K uptake in Sudan grass grown under K limiting soil (Basak and Biswas 2010). Soil fertilization with apatite (P source), feldspar and illite powders in combination with P and K solubilizing bacteria (Bacillus megaterium var. phosphaticum) and KDB (Bacillus mucilaginosus and B. subtilis) significantly improved P and K uptake, P and K availability and growth of maize plant grown under P and K limited calcareous soil (Abou-el-Seoud and Abdel-Megeed 2012).

Therefore, bio-intervention of silicate mineral was found to be effective as a source of K and could be an alternative to commercial K fertilizer. These results of pot and green house studies are quite promising, but still need to be replicated the success under in field conditions for better acceptance of this technology in sustainable faming system.

## 8.1. Field trials

The effectiveness of integrated application of K-bearing mineralsandKSMs havealready been established, but through a fewer number of field trials (Table 6). Application of K bearing minerals (feldspar, illite, muscovite and biotite) inoculated with KSB strains (Bacillus cereus, Bacillus mucilaginosus and Bacillus pasteurii) significantly improvedthe yield and K uptake in wheat, tomato, hot pepper, peanut and sesame under field conditions (Mikhailouskaya and Tchernysh 2005; Badr 2006; Supanjani et al. 2006; Youssef et al. 2010). Soil inoculated with K solubilizing fungi (Pseudomonas putida) was found quite effective in plantation crops like tea and tobacco, and could supplement 25% of the chemical fertilizer (Bhagyalakshmi et al.2012; Subhashini 2015). Similarly, potassium enriched compost prepared from waste mica was quite effective as the source of K in potato-soybean cropping system (Biswas 2011). However, other mineral ions such as Si and Mg contained in the rock powder might have also contributed towards the yield. Application of enriched compost to the first crop resulted in a significant increase in soybean yield grown on residual fertility which could supplement 50% of the total K requirement of soybean crop (Meena and Biswas 2013).The application of bacterial strains (K-31 and K-81) with K mineral (hydromuscovite, muscovite and biotite) effectively improved the available K content in sandy loam soil (Luvisol) andindicated the effectiveness of K mobilizing bacteria in a K deficient situation (Mikhailouskaya and Tchernysh 2005). These results clearly indicated that both the microbes and composting process mobilized K from K bearing minerals which acted as a continuous source of K throughout the cropping system.

The result of field studies indicated that bio-intervention of silicate mineral could be a viable option of crop growth in place of costly commercial K fertilizer. In most of the cases, this technology performed better than control as well as application of silicate mineral alone. In some cases bio-intervention of silicate mineral was as effective as commercial K fertilizers or even better than that. So, more systematic study is needed to standardize this technology in large scale which can effectively supplement the costly K fertilizer while maintaining yield and quality of crops.

## 9. Conclusions and future prospect

This review highlighted the contribution of bio-intervention of naturally available K-bearing minerals as a possible alternative of K fertilizer for sustaining crop production and maintaining soil K level. Investigations on the possible use of silicate rocks for K supply through bio-intervention (K mobilizing microbes and composting) yielded promising results. The benefit of this approach was however confined mostly within laboratory or green house scale studies. The validity and possibility of sustaining agronomic performance and reduce the cost of cultivation through the use of cheap natural sources is highly important. Thus, combined application of different kind of bio-agent like KSB, KSF, AM fungi, yeast and earthworm in different combination could provide a faster and continuous supply of K from low cost mineral powder. Currently, there is a lack of consistency in terms of the design of individual trials, limiting comparison and extrapolation. Performance of this technology under different soil types and properties are rarely reported. The relative impact of this technology on the mineral-weathering process is still poorly understood. Further research is highly justified due to a continuously increasing price of conventional K fertilizers worldwide.

In further study, emphasis should be given to find out the best combination of different factors which can be suitable alternative of conventional potash fertilizers. There is a huge scope for careful selection of the silicate rock as K sources. On the basis of dissolution rate, priority should be given to rocks that are enriched with bioavailable K. It is appropriate to consider the use of commonly abundant K bearing minerals such as feldspars and mica (muscovite, biotite, etc.) for field crop trials. The best KSM strain can be selected on the basis of their ability to dissolve silicate minerals or release K from the minerals. There is also an opportunity to isolate indigenous KSM strains which may be more suitable in local argo-ecological conditions in comparison to an alien species. Composting process would enhance the dissolution of K from indigenous mineral which is very promising, but more systematic approaches are needed in order to explore their efficacy. It is essential that scientists from both biology and mineralogy disciplines effectively collaborate in conducting this research. Future studies should more concentrate to test this potential technology under field conditions.


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**Table 1** Chemical formula and potassium contents (expressed as element and oxide) for potash ore/ minerals and for common potassium silicate rock forming minerals

| Mineral | Formula | Weight % K | Weight % $K_2O$ |
|---|---|---|---|
| Potash ore/minerals | | | |
| Sylvite | $KCl$ | 52.35 | 63.09 |
| Carnallite | $MgCl_2,KCl,6H_2O$ | 14.05 | 16.94 |
| Kainite | $KMgSO_4Cl,3H_2O$ | 15.69 | 18.91 |
| Langbeinite | $2MgSO_4, K_2SO_4$ | 18.84 | 22.71 |
| Silicate minerals | | | |
| Potassium Feldspar | $KAlSi_3O_8$ | 14.03 | 16.91 |
| Leucite | $KAlSi_2O_6$ | 17.89 | 21.56 |
| Nepheline | $(Na,K)AlSiO_4$ | 13.00 | 15.67 |
| Kalsilite | $KAlSiO_2$ | 24.68 | 29.75 |
| Muscovite | $KAl_3Si_3O_{10}(OH)_2$ | 9.03 | 10.88 |
| Biotite | $K_2Fe_6Si_6Al_2O_{20}(OH)_2$ | 7.62 | 9.18 |
| Phlogopite | $K_2Mg_6Si_6Al_2O_{20}(OH)_4$ | 9.39 | 11.30 |

Source: Manning (2009)

845 **Table 2** Summary of crop trials with direct application of silicate minerals used as K fertilizer

| Crop | Minerals | Trial type | Agronomic benefit | Reference |
|---|---|---|---|---|
| Legume | Feldspar | Field | Insignificant | Sanz-Scovino and Rowell, 1988 |
| Rice | Phlogopite | Pot culture | Increased grain yield | Weerasuriya et al, 1993 |
| Wheat | Granite | Pot culture | Increased biomass and grain yield | Hinsinger et al, 1996 |
| Wheat | Diorite | Pot culture | Insignificant | Hinsinger et al, 1996 |
| Ryegrass | Granite | Pot culture | Increased in biomass yield and K uptake | Coroneos et al, 1996 |
| Pearl millet | Glauconitic sandstone | Sand culture | Dry matter yield K content significantly increased | Rao and Subba Rao, 1999 |
| Alfalfa | Gneiss | Pot culture | Insignificant | Wang et al, 2000 |
| Italian Ryegrass | Gneiss | Pot culture | Significant increase in K content in biomass | Wang et al, 2000 |
| Perennial Ryegrass | Gneiss | Pot culture | Significant increase in K content in biomass | Wang et al, 2000 |

| | | | | |
|---|---|---|---|---|
| Maize | Gneiss | Pot culture | Significant increase in K content in biomass | Wang et al, 2000 |
| Clover | Granite | Pot/Field | Insignificant | Bolland and Barker, 2000 |
| Chinese Cabbage | Fused potassium silicate | Sand and soil culture | Significant increase in K uptake | Yao el al, 2003 |
| Tomato | Feldspar | Field | Increased biomass and fruit yield | Badr, 2006 |
| Okra | Feldspar | Field | Increased pod yield | Abdel-Mouty and Greadily, 2008 |
| Grape | Biotite | Field | Increase berry yield and K content | Stamford et al. 2011 |
| Olive | Glauconitic sandstone | Hydroponics | Effect as slow release K fertlizer | Karimi et al. 2012 |
| Italian Ryegrass | Granite powder | Green house | Significant increase in plant biomass yield | Silva et al. 2013 |
| Spring Barley | Zinnwalidite, waste mica & orthoclase | Sand culture | Plant biomass and K uptake increased in the order of Zinnwalidite› waste mica › orthoclase | Madaras et al. 2013 |

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|---|---|---|---|---|
| Leek | Biotite, microcline and nephelinesynite | Pot culture | Biotite found most effective and readily available source of K | Mohammed et al. 2014 |
| Arabica coffee | Phonolite | Field | Increased fruit yield similar to KCl application | Mancuso et al. 2014 |

**Table 3** Potassium solubilizing microbes (KSMs) involve in solubilization K from minerals

| Microbes | Predominant acid produce | Reference |
|---|---|---|
| Bacteria | | |
| Bacillus mucilaginsus | Oxalic and Citric | Liu et al.2006 |
| Bacillus edaphicus | Oxalic and Tartaric | Sheng and He 2006 |
| Bacillus globiospora | Gluconic, Acetic and Tartaric | Sheng et al. 2008 |
| Paenibacillusmucilaginosus | Tartaric, Citric, Oxalic | Liu et al. 2012; Hu et al. 2006 |
| Fungi | | |
| Aspergillusniger | Citric, Glycolic and Succinic | Sperberg1958 |
| Torulasporaglobosa | Acetic acid | Vora and Shelat1998 |
| Aspergillusterreus | Itaconic | Magnuson and Lasure2004 |
| Aspergillusfumigatus | Succinic and Acetic | Song et al. 2014 |
| Penicilliumperpurogenum | Oxalic | Song et al. 2014 |
| AMF | | |
| Glomusmosseae | Citric, Malic and Oxalic | Yousefi et al. 2011 |
| Glomusintraradices | Citric, Malic and Oxalic | Yousefi et al. 2011 |

851 **Table 4** Summary of experiment of mobilization of K from silicate minerals through bio-intervention

| Type of experiment/condition | mineral | Microbial strain/bioagent | Outcome | Reference |
|---|---|---|---|---|
| Laboratory study/In vitro | Muscovite and Biotite | Local rhizobacterial strain (K-31, K-81) | Significantly improved K release from minerals | MikhailouskayaTchernysh 2005 |
| Laboratory study | Feldspar | Bacillus cereus | Increased K release from feldspar | Badr et al. 2006 |
| Composting | Feldspar | Bacillus cereus | Significant K mobilization from feldspar | Badr 2006 |
| Laboratory study | Mica and Feldspar | Bacillus mucilaginsus | K release increased by 66% from mica | Liu et al. 2006 |
| Laboratory study | Muscovite mica, Microcline and Orthoclase | Bacillus mucilaginsus | Significant amount of potassium released from different minerals | Sugumaran and Janarthanam 2007 |

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|---|---|---|---|---|
| Laboratory study | Mica and Feldspar | Bacillus strain | Increased soluble K content | Girgis et al. 2008 |
| Laboratory study | Feldspar and Illite | Aspergillusfumigatus | Drastically increased K release from the K minerals | Lian et al. 2008 |
| Composting | Waste mica | Aspergillusawamori | Sharp increase in water soluble K after 120 days | Nishanth and Biswas 2008 |
| Laboratory study | Feldspar and Potas-sium aluminum silicate | Aspergillusterreus and Aspergillusnigerwere | Higher K released by A. terreus from both the mineral | Prajapati et al. 2012 |
| Composting | Quartz powder | Earthworm (Eiseniafoetida) | Significantly increased available K content | Zhu et al. 2013 |
| Laboratory study | Alkaline ultramafic rock powder | Yeast (Torulasporaglobose) | 38% of total K released from rock powder | Rosa-Magri et al. 2012 |

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|---|---|---|---|---|
| Laboratory study | Waste mica | Bacillus mucilaginsus | About 34% increase in available K content after 28 days | Biswas and Basak 2014 |
| Laboratory study | Muscovite | Penicilliumpurpurogenum | 30% K dissolved from muscovite | Song et al. 2015 |

**Table 5** Summary of the pot experiment: Improved plant nutrition through bio intervention of silicate minerals

| Rock/mineral | Bio intervention (KSMs and composting) | Crop/plant | Salient outcomes | Reference |
|---|---|---|---|---|
| Biotite and Microcline | Paxillusinvolutus&Suillusvariegatus | Pine | Mycorrhizal fungi improved K uptake by releasing K from mineral structure | Wallander and Wickman 1999 |
| Illite powder | Bacillus edaphicusNBT | Cotton and Rape | Dry matter yield and K content increased | Sheng 2005 |
| Illite and rock phosphate power | Co-inoculation of Bacillus mucilaginsus (KSB) and Bacillus megatherium (PSB) | Eggplant | Enhanced plant growth and NPK uptake as well as soil availability of P & K | Han and Lee 2005 |
| Feldspar | Bacillus cereus | Sorghum | Yield and K uptake | Badr et al. 2006 |

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|---|---|---|---|---|
| | | | increased while K status in soil improved | |
| Feldspar and Illite | Bacillus edaphicuswild strain (MPs series) | Wheat | Crop growth and K content increased | Sheng and He 2006 |
| Illite and rock phosphate powder | Co-inoculation of Bacillus mucilaginsus (KSB) and Bacillus megatheriumvarphosphaticum (PSB) | Pepper and Cucumber | Increased availability of P & K in soil and uptake by plants | Han et al. 2006 |
| Microcline, Orthoclase and Muscovite mica | Bacillus mucilaginsus | Groundnut | Yield and oil content increased while K status in soil improved. | Sugumaran and Janarthanam 2007 |
| Waste Mica | Bacillus mucilaginsus | Sudan grass | Improved biomass yield and K uptake | Basak and Biswas 2009 |

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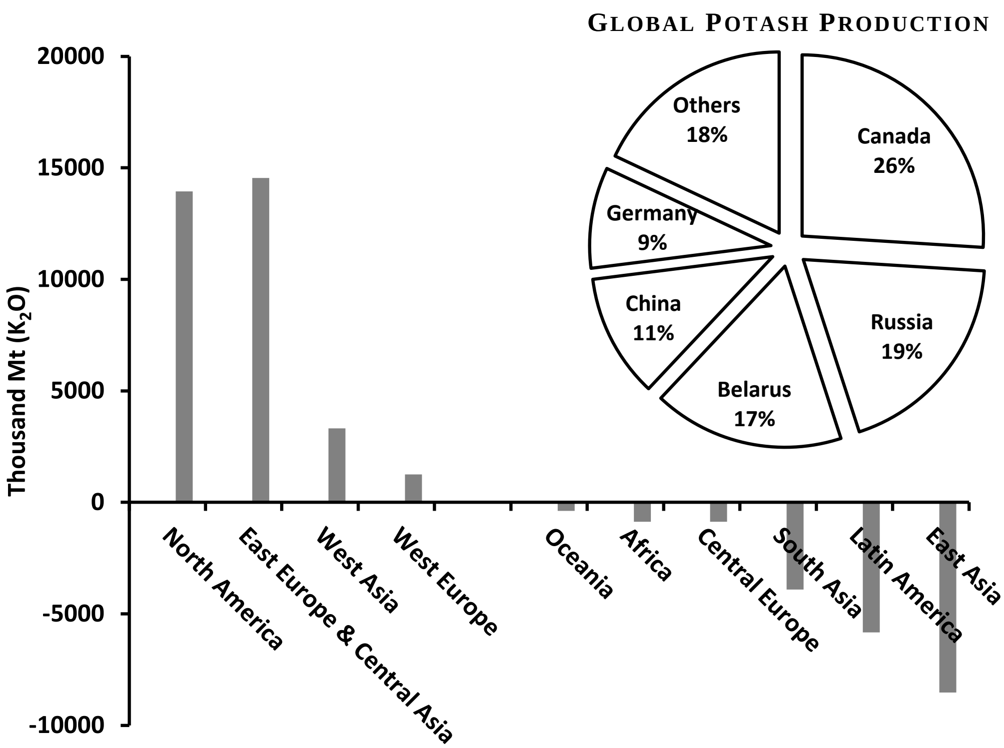
|---|---|---|---|---|
| | | | by Sudan grass as well as soil K status | |
| Waste Mica | Co-inoculation of Bacillus mucilaginsus (KSB) and Azotobacterchrooccum (N-fixer) | Sudan grass | Biomass yield, K and N uptake increased | Basak and Biswas 2010 |
| Feldspar | Bacillus mucilaginsus | Maize | Plant growth and K uptake increased | Abou-el-Seoud and Abdel-Megeed 2012 |
| Gneiss and steatite | Earthworms (Eiseniaandrei) | Maize | Steatite charged vermicompost increased 21.5 % dry matter yield over non-enriched vermicompost | de Souza et al. 2013 |

**Table 6** Summary of the field experiments: Improved plant nutrition through bio intervention of silicate minerals

| Rock/mineral | Bio intervention (KSMs and composting) | Crop/plant | Salient outcomes | Reference |
|---|---|---|---|---|
| Muscovite and Biotite | Local rhizobacterial strain (K-31, K-81) | Wheat | Improved grain yield and K status of soil | Mikhailouskaya and Tchernysh 2005 |
| Feldspar | Bacillus cereus | Tomato | More fruit yield and potassium use efficiency (KUE) as compared to $K_2SO_4$ | Badr 2006 |
| Potassium rock (Illite) powder | Bacillus mucilaginosusstrain (KCTC3870) | Hot pepper | Improved biomass and fruit yield as well as K availability in soil | Supanjani et al. 2006 |
| Waste mica | Composting with Aspergillusawamori | Potato-Soybean | Mica enriched compost significantly increased yield K uptake by both the | Biswas 2011 |

| | | | | |
|---|---|---|---|---|
| | | | crops | |
| Feldspar | Bacillus pasteurii (Biopotash) | Peanut and Sesame | Increased K uptake by maize and wheat | Youssef et al. 2010 |
| Muriate of potash | Pseudomonas putida | Tea | Improved leaf yield and quality as well as nutrient uptake | Bhagyalakshmi et al.2012 |
| Waste mica | Composting with Aspergillusawamori | Soybean | Mica charged compost improved Soybean yield and K uptake as compared to ordinary compost | Meena and Biswas 2013 |
| Sulphate of potash | Frateuriaaurantia | Tobacco | Potassium content in tobacco leaf increased 39% when soil inoculated with bacterial strain | Subhashini 2015 |

## Figures




Source: World fertilizer outlook (FAO, 2015)

Figure 1: Projection of regional potash balance according to FAO for 2018 in thousand metric tonnes $K_2O$ equivalent

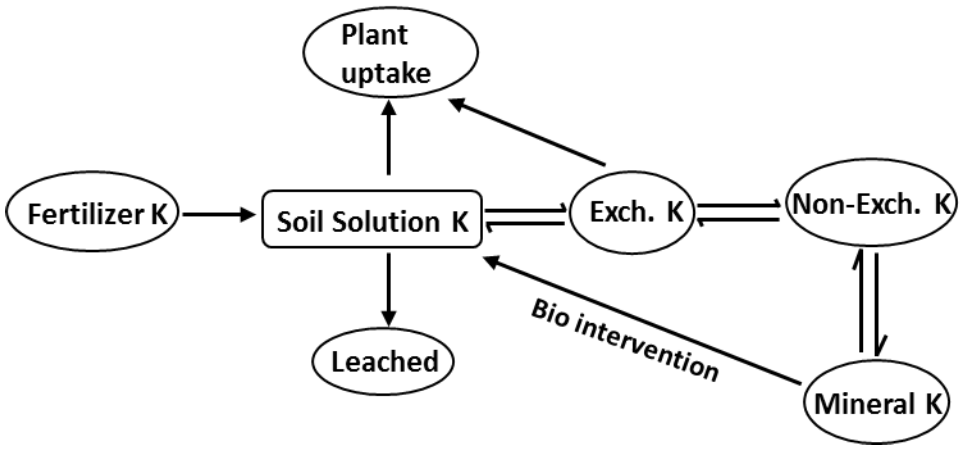



Figure 2: Scope of bio intervention for direct mobilization of potassium from mineral under dynamic pools of soil potassium

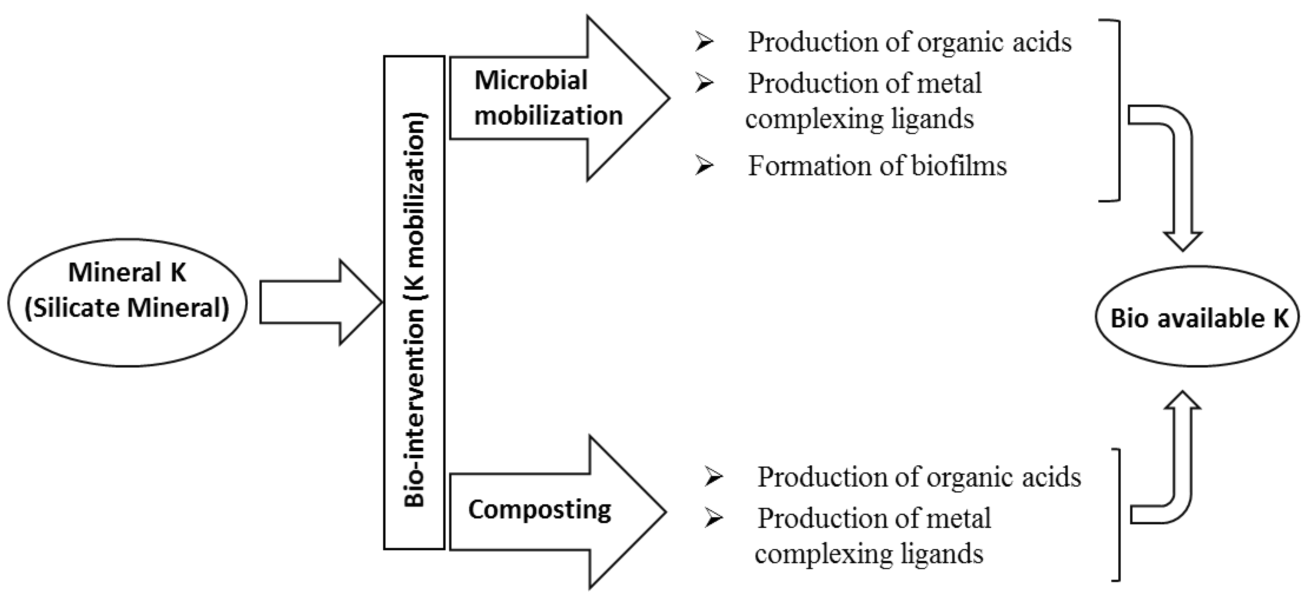



Figure 3: Brief mechanisms of potassium mobilization from silicate minerals through bio-interventions