Research Findings

Soybean harvest in Brazil. Photo by ICL Brazil.

Introducing Polyhalite to Brazil: First Steps of a New Fertilizer

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Abstract

Being among the world's leading agricultural producers, Brazil imports and uses huge amounts of fertilizer, yearly. High soil acidity, adverse side-effects of liming and poor soil fertility challenge the efficacy of conventional fertilizers. Alternative options are required to overcome poor potassium (K) recovery in the soil, deprived calcium (Ca) and magnesium (Mg) mobility in the soil profile, and excess soil-chloride concentrations. Fertilizers also need to meet the crop demand for sulfate (SO_4^{2-}); soil levels of which gradually decline over time to below critical levels. An examination of polyhalite, an evaporate mineral comprised of S, Ca, Mg, and K, has revealed equivalent effectiveness in supporting the nutrient requirements of rice when compared to corresponding soluble salts. In a soybean field test, polyhalite showed enhanced Ca and Mg mobility in the soil profile, as well as equivalent effectiveness as a K-donor compared to potassium chloride (KCl). This report discusses the potential of polyhalite to contribute to the Brazilian agricultural production.

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Introduction

Due to continued population growth, worldwide demands for food, fibers, and energy are rapidly increasing. Therefore, agricultural resources, namely water and soil, must be rationally and carefully managed. In order to maintain or even increase the productivity of existing arable land, soil qualities should be preserved and enhanced through several elementary practices such as soil conservation management, soil amendment, crop rotation, use of crop varieties with high genetic potential, and efficient use of mineral fertilizers.

Brazil is among the leading producers of agricultural commodities (Table 1). In the recent decade (2006-2016), Brazilian agricultural production and export have displayed a consistent increasing trend, including for 'new' commodities such as wheat, potato, and peanut. This boost in production has resulted in increased fertilizer requirements. Consequently, the amount of fertilizer delivered to farmers in Brazil in 2015 reached 30.2 million tons, of which the share of potash fertilizer was considerably high at 29.2%. This figure indicates the significance of potassium (K) to crop production, but also raises questions regarding the efficacy of the common potash fertilizer, potassium chloride (KCl), when applied to most soils in Brazil.

KCl (or muriate of potash) dominates the Brazilian potash fertilizer market (ANDA, 2016) however, local KCl production comprises less than 6% of total consumption and the rest is imported. In 2015, the share of potash fertilizers other than KCl imported to Brazil was only 1%. Such alternative K sources include mainly potassium sulfate (K_2SO_4) and potassium magnesium sulfate (K-Mg-S) (SIACESP, 2016).

Potash fertilizers, other than KCl, are advantageous due to the absence of chlorine (Cl), which is suspected to negatively affect produce quality of important crops such as tobacco, potatoes, and pineapples. Furthermore, these alternative fertilizers provide additional nutrients such as sulfur (S), calcium (Ca), and magnesium (Mg) which are important to the nutritional balance of crops (Malavolta, 1980). Nevertheless, the production costs of most Cl-free potash alternatives are significantly higher than that of KCl, therefore increasing economic constraints.

Polyhalite is one of a number of evaporate minerals containing K. Polyhalite (dehydrate) is a single crystal complex, the chemical formula of which is $K_2Ca_2Mg(SO_4)_4{\bullet}2(H_2O)$, with a low impurity content (up to 5%), comprising mostly of sodium chloride. Polyhalite displays some slow-release characteristics, thus providing progressive nutrient availability to the soil. Evaluations carried out into soil columns by the University of Nottingham, UK, showed that 50-60% of polyhalite S was immediately available, while the remaining S was slowly released (Jiang *et al.*, 2016). Polyhalite mined and manufactured in the UK (Cleveland Potash Ltd.) typically consists of 14% potassium oxide (K_2O); 48% sulfur trioxide (SO_3); 6% magnesium oxide (MgO); and 17% calcium oxide (CaO). As a fertilizer comprising four key plant nutrients - S, K, Mg, and Ca - polyhalite provides a new solution to crop nutrition.

Table 1. Agricultural production in Brazil in recent years (Data extracted from: http://www.indexmundi.com/agriculture/).

Commodity	World ranking	Production	Export	Harvested area	Year
		------------*1,000 MT*------------		---*1,000 ha*---	
Soybean oilseeds	1	102,000	58,400	33,800	2016
Green coffee	1	3,357	2,120	1,896	2017
Orange juice	1	885	885	480	2016
Sugarcane	1	739,300	24,350	9,080	2016
Corn	3	83,500	25,500	16,400	2016
Cotton	6	3,500	1,400	930	2016
Wheat	17	6,340	1,500	2,100	2016
Potato	21	3,935	-	131	2016
Peanut oilseeds	26	425	180	123	2016

Early studies confirmed polyhalite's efficiency as a fertilizer. Polyhalite was equivalent to or better than sulfate of potash magnesia, and consistently better than KCl with or without Mg (Boratyński and Turyna, 1971). In a study by Barbarick (1989), the continuous cropping of sorghum-sudangrass in a greenhouse showed that polyhalite was as effective, or superior to, equivalent rates of soluble sources of K, Ca, Mg and S. More recent field studies demonstrated that polyhalite was as effective or better than gypsum for a number of cruciferous crops, such as rape oilseed in France (Dugast, 2015) and mustard (Tiwari *et al.*, 2015), cabbage and cauliflower in India (Satisha and Ganeshamurthy, 2016). Sesame and peanut yield and quality were improved in India (Tiwari *et al.*, 2015) and Vietnam (Tam *et al.*, 2016), respectively. Tea (PVFCCo (a), 2016) and coffee (PVFCCo (b), 2016) crops grown on acid tropical soils in Vietnam were also found to benefit from the use of polyhalite as a slow-release, multi-nutrient donating fertilizer.

The potential of polyhalite fertilizer and its relevance to Brazilian agriculture have thus far been inadequately addressed. The objectives of the present study were to: 1) assess the agronomic effectiveness of polyhalite as a nutrient donor in potted rice plants grown on Oxisol; 2) evaluate Ca and Mg mobility in the soil profile with polyhalite as the K-donor for soybean growth on no-tillage Oxisol, and; 3) discuss the possible contribution of polyhalite to the nutritional solutions of important crops in Brazil.

Materials and methods

Potted rice experiment

The study was carried out in 2013 in a greenhouse located at São Paulo University in Piracicaba, Brazil. Oxisol soil, which has a very low clay content (88; 83; 829 g kg^{-1} of clay, silt and sand, respectively) and low organic matter and micronutrients content, was put into 4 dm^3 polyethylene pots. One month before fertilizer application, calcium carbonate ($CaCO_3$) and magnesium carbonate ($MgCO_3$) were added to raise soil base saturation (V%) to 50%. The trial was comprised of six treatments (Table 2) in four replications, in a completely randomized design.

Table 2. Description of the treatments used in the potted rice experiment (after Vitti and Vale, 2013).

Treatment	K_2O	S	Ca	Mg	N + P_2O_5 + micronutrients
	-------Doses equivalent to kg ha^{-1}-------				
1. Control	-	-	-	-	+
2. No K, S, Ca, Mg	-	-	-	-	+
3. Granular polyhalite (1 g pot^{-1})	70	96	60	18	+
4. Soluble K, S, Ca, Mg salts	70	96	60	18	+
5. Granular polyhalite (2 g pot^{-1})	140	192	120	36	+
6. Polyhalite powder (1 g pot^{-1})	70	96	60	18	+

Plants were harvested 78 days after fertilizer application, and the dry matter production and nutrient uptake were evaluated.

Evaluating nutrient mobility in the soil

The on-field trial was located in Sapezal, Mato Grosso state, Brazil, on Oxisol with a medium clay content (143; 72; 785 g kg^{-1} of clay, silt, and sand, respectively), and employed a completely randomized design comprising two fertilization treatments - KCl and polyhalite (Table 3). A month before soybean sowing, dolomitic limestone (2.5 Mg ha^{-1}) was applied and incorporated using a heavy harrow. On sowing, an onto furrow base fertilizer application of 200 kg ha^{-1} of mono-ammonium phosphate (MAP) was applied. KCl or polyhalite were then applied onto the top soil at V1 and V6 soybean developmental stages.

After harvest, the soil was sampled at the following depths: 0-5, 5-10, 10-15, 15-20, 20-30, and 30-40 cm, and analyzed for soil K, Ca, Mg and S contents.

Results

Potted rice experiment

Rice plants lacking the macronutrients K, S, Ca, and Mg displayed very poor development (Fig. 1). Soluble sources of these nutrients and granular or powder polyhalite application, enabled normal plant development.

Both granular and powder polyhalite displayed a similar effectiveness in supplying plants with K_2O, S, Ca, and Mg, when compared to soluble sources (Fig. 2). No toxicity or salinity problems occurred following normal or doubled polyhalite application.

Examinations of K, S, Ca, and Mg uptake in potted rice plants showed that the recovery of polyhalite-supplied K, S, and Mg was equal to that occurring in plants fertilized with the equivalent soluble sources (Fig. 3). Ca uptake by rice was significantly better under the soluble fertilizer, however, the availability of this nutrient from polyhalite was high and sufficient for normal plant development. Doubling the polyhalite dose resulted in a consequent increase in K uptake, a slight decrease in Ca uptake, and no response in rice S or Mg uptake (Fig. 3). These results, collated under greenhouse conditions, demonstrate the principal effectiveness of polyhalite as a fertilizer, even on low fertility soils.

Evaluating nutrient mobility in the soil

Limestone, applied to reduce soil acidity, enriches the shallow soil layer into which it has been incorporated with Ca and Mg. In no-tillage systems, where limestone is broadcast onto the soil surface without incorporation into the soil, Ca and Mg are concentrated in the top soil. This restricts the root system to a shallow soil layer, increasing plant susceptibility to transient water shortages and to consequent yield reduction under unstable precipitation regimes. It was interesting to compare the distribution of K, S, Ca, and Mg in the

Table 3. Description of the soybean experiment evaluating nutrient mobility in the soil (after Vale, 2016).

Treatment		Liming	Base fertilizer	Additional fertilization	
	Timing	A month before sowing	On sowing	First trifoliate (V1)	First flower (V6)
		Heavy harrow	Onto furrow	Top soil	
KCl		Dolomite limestone (2.5 Mg ha^{-1})	MAP (200 kg ha^{-1})	KCl (70 kg K_2O ha^{-1})	KCl (70 kg K_2O ha^{-1})
Polyhalite				Polyhalite (eq. to 70 kg K_2O ha^{-1})	Polyhalite (eq. to 70 kg K_2O ha^{-1})

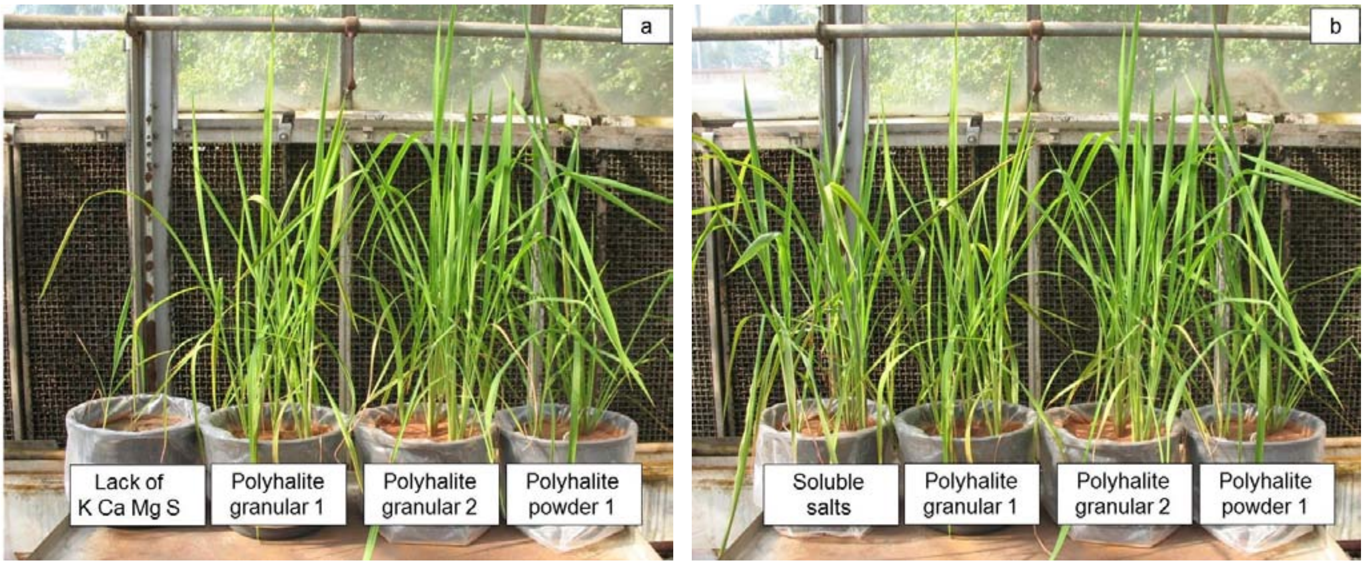

Fig. 1. Development of rice plants applied with polyhalite fertilizer in comparison with plants lacking K_2O, S, Ca and Mg (a), or with plants applied with soluble salts comprising equivalent nutrients (b).

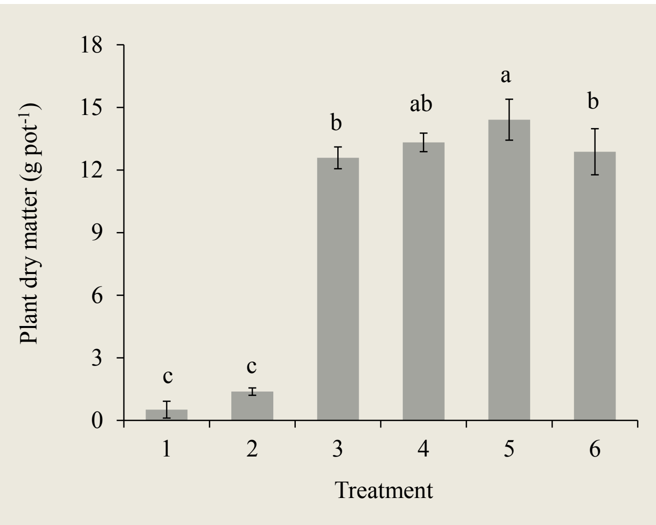

Fig. 2. Effect of fertilizer treatments on rice dry matter production. Treatments: 1. Control; 2. Lack of K, S, Ca, and Mg; 3. Granular polyhalite (1 g pot^{-1}); 4. Soluble K, S, Ca, and Mg salts; 5. Granular polyhalite (2 g pot^{-1}); 6. Powder polyhalite (1 g pot^{-1}). Different letters indicate statistically significant differences at P=0.05 (Duncan test). A detailed description of the treatments is available in Table 2.

soil profile of a soybean crop, following liming and fertilization treatments with KCl and polyhalite.

Limestone application increased Ca and Mg solely in the 0-10 cm layer, proportional to its mechanical incorporation. Compared to the KCl applied soil, polyhalite application resulted in a larger increase in Ca and Mg content throughout the soil profile; Ca content rose by 23% and 8% in the 0-20 and 20-40 cm layers, respectively, while the increments in Mg were of 25% and 17% for the same soil layers (Fig. 4).

Sulphate was the most mobile nutrient in the soil in both treatments, maintaining a narrow concentration range of 10-20 mg dm^{-3} throughout the examined soil layers (Fig. 4). While S contents were equal in the top soil layer, polyhalite significantly increased its concentrations in the deeper layers. In contrast, K content was significantly higher in the top soil, and markedly declined in soil layers deeper than 10 cm. No difference was observed in soil-K content between KCl and polyhalite applied soils (Fig. 4).

Discussion

Polyhalite potential for Brazilian agriculture

Added to the arsenal of available fertilizer, polyhalite may provide several alternative solutions to some chronic nutrition problems associated with Brazilian agriculture.

In Brazil, the current (2016/17) area of soybean, corn, wheat, and cotton crops is over 55 million hectares (CONAB, 2016). It is estimated that more than 75% of this area is cultivated under a no-tillage system in which limestone is applied superficially, without incorporation into the subsurface layers. The efficiency of surface limestone application onto no-tillage soil, particularly in the correction of soil acidity, is controversial. Studies of Brazilian soils indicate little or no limestone mobility deeper than the top soil layer (Gonzales-Erico *et al.*, 1979). Crops productivity under no-tillage systems is highly dependent on the fertility of a very shallow, 0-5 cm deep, soil layer, which is often characterized

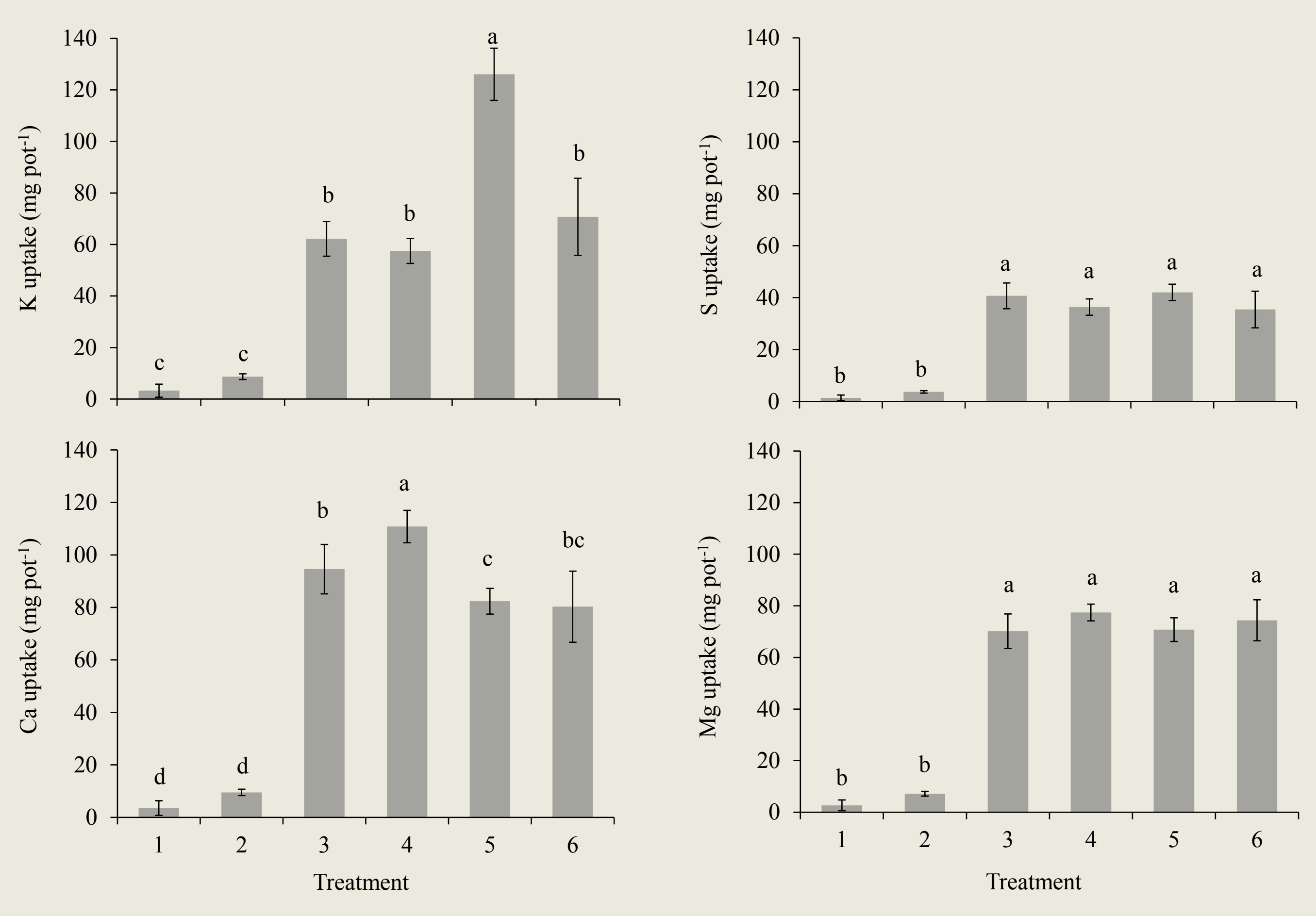

Fig. 3. K, S, Ca, and Mg uptake by potted rice plants in response to fertilization treatments on Oxisol. Treatments: 1. control; 2. lack of K, S, Ca, and Mg; 3. granular polyhalite (1 g pot^{-1}); 4. soluble K, S, Ca, and Mg salts; 5. granular polyhalite (2 g pot^{-1}); 6. powder polyhalite (1 g pot^{-1}). More details are provided in Table 2. Different letters indicate statistical significant differences at P=0.05 (Duncan test).

by a highly exchangeable Ca content base saturation, but also by high exchangeable toxic aluminum ions (Caires *et al.*, 2000). An evaluation of soybean plant development in several regions of Brazil has revealed that high grain yields, above 4.5 Mg ha^{-1}, are associated with prosperous root systems at depths below 40 cm. A thriving root system provides the plant with significantly greater access to deeper soil water and nutrient resources, thus supporting enhanced crop development and improved resistance to unfavorable weather conditions. However, such subsurface rooting is only possible with high soil fertility at a depth of 40-100 cm.

Calcium plays an important role in root growth and development. Deficiency in Ca supply at the root tip causes almost immediate disruption of its growth, followed by tissue blackening and cell death (Mengel and Kirkby, 2001). In addition, Ca is a virtually immobile element in the phloem (Marschner and Richter, 1974). Therefore, sufficient Ca availability at the root apex is crucial for crop development. Sako *et al.* (2015) found that an in-depth minimum threshold of 8 $mmol_c$ Ca dm^{-3} was required to allow the expression of high soybean productivity. The application of calcium sulfate ($CaSO_4$), suggested as the solution for the fixation of limestone to the upper soil layer, has improved Ca movement to deeper layers (Ritchie *et al.*, 1980). The soybean field trial presented here indicates that polyhalite has an adequate solubility to reach and promote the active crop rhizosphere when applied to the top soil (Fig. 4). Thus, polyhalite is a fertilizer with considerable potential to improve productivity of no-tillage systems, where soils exhibit significant Ca deficiency in the subsurface layers.

Sulfur has essential functions in plant development and crop quality, from participation in amino acid and protein formation to hormonal control, photosynthesis and plant defense mechanisms against pathogens (Vitti *et al.*, 2015). An evaluation of 8,500 soil samples in Brazil showed that 75% had low or very low S. The

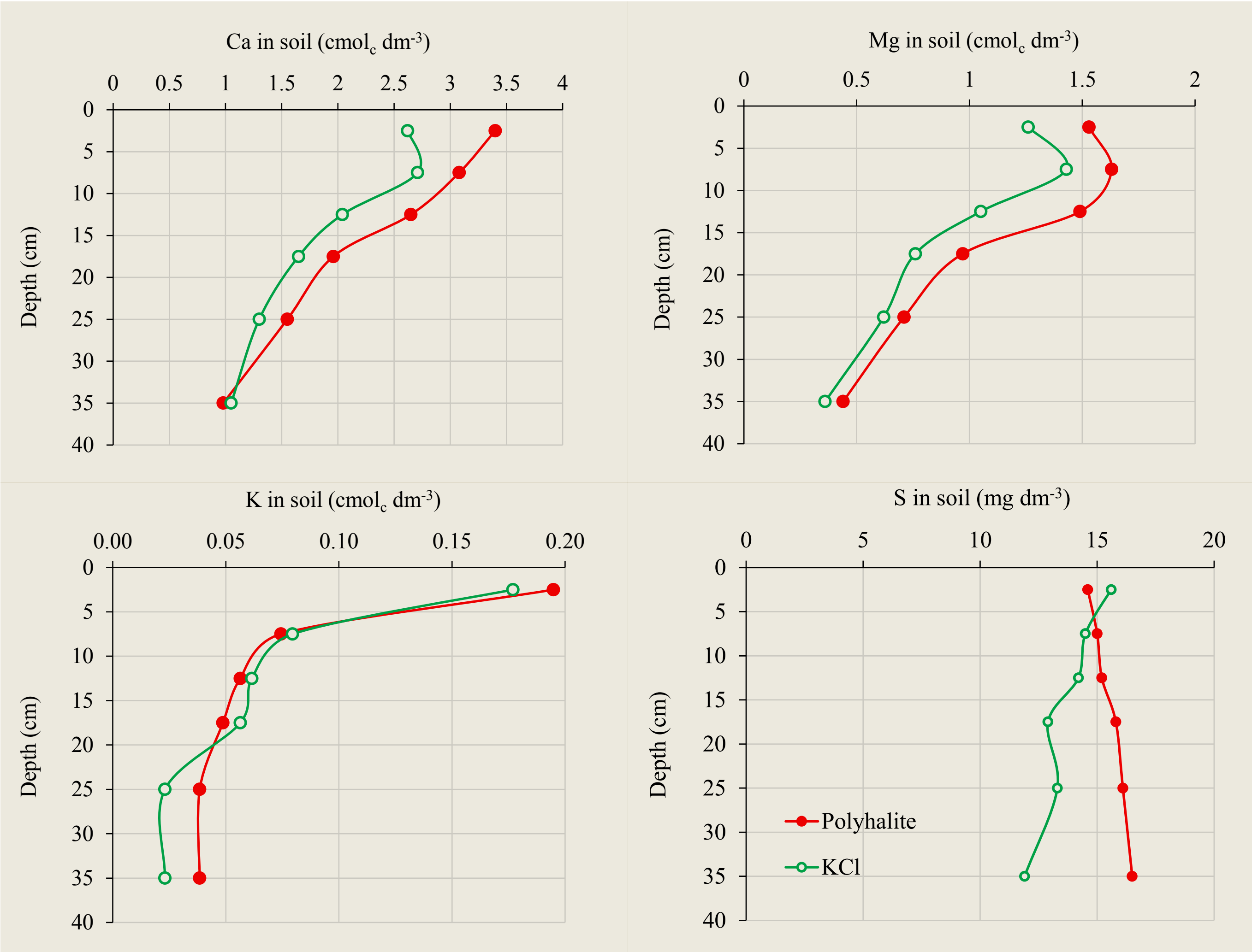

Fig. 4. Soybean soil profile contents of Ca, Mg, K, and S following liming and fertilization treatments with KCl or polyhalite on Oxisol soil.

main causes of S deficiency in tropical soils are associated with the high mobility of the sulfate ion in the soil, and the low amounts of S often found in the soil profile explored by the roots when compared to the temperate regions (Vitti, 1989). There are several reasons for the recent decline in available soil S. After more than a century of heavy-polluting industries and transportation, worldwide awareness has enforced a significant decline in sulfur dioxide emissions. Subsequently, the phenomenon of acid rain has almost vanished and S supply to the vegetation through foliar or root absorption has rapidly declined (Scherer, 2001). In addition, the considerable increase in the use of S-free pesticides and fertilizer has contributed to S deficiency in soils. Soil amendment practices that are very common in tropical acid soils, such as liming and phosphating, alter the chemical interactions between soil particles, resulting in increased leaching of the sulfate ion (SO_4^{2-}) and consequent soil S depletion (Kamprath and Till, 1983; Vitti *et al.*, 2015). Thus, crop S requirements that were fully met

Soybean crop in Brazil. Photo by ICL Brazil.

Sugarcane crop in Brazil. Photo by F. Vale.

A cotton field towards harvest in Brazil. Photo by ICL Brazil.

in the past by undesired resources (pollution) are now, not being met. Among S fertilizers, polyhalite provides a potential solution to meet this demand.

Magnesium is frequently overlooked in plant nutrition and shortages adversely impact plant growth. Adequate Mg supplies are required for many essential plant functions, the most noticeable of which are root formation, chlorophyll build up, and photosynthesis. Also, many less observable biochemical reactions are dependent on an adequate supply of Mg (Cakmak and Yazici, 2010). In no-tillage systems, this nutrient tends to concentrate in the top soil, fixed in various forms of $MgCO_3$, most of which are insoluble and immobile in the soil (Ritchey *et al.*, 1980). Low Mg availability throughout the soil has become a problem in the nutrition of perennial crops, such as coffee and citrus. As a result of superficial limestone application, Mg concentrates in the shallow top soil layer, and its subsequent availability throughout the soil is very low. Under these conditions the soil's content of exchangeable Mg is sufficient, but its concentration in the soil solution - the fraction absorbed by plant roots - is too low (Juo and Uzu, 1977). The application of sulfate of potash magnesia showed promising effects on orange productivity and fruit quality; favoring greater Mg uptake, the plant nutritional balance was improved and resulted in larger fruit with higher juice content and improved sugar to acid ratio (Vale, 2010). As shown above, polyhalite also provides a soluble Mg source, and should therefore be considered as an alternative fertilizer for perennial crops in Brazil.

The very low polyhalite Cl content makes it a suitable fertilizer choice for many fruit and vegetable crops that require high K doses on the one hand, and suffer from excess Cl in the rhizosphere on the other. Chloride is often related to a deprived rooting of annual plants such as corn, wheat, cotton, and soybeans, as well as to a reduced nodulation capacity in legumes where the biological N fixation is hampered. Chloride toxicity to soybean crops increases when it is accompanied by K^+ (derived from KCl fertilizer), which particularly affects the reproductive phase and yield formation (Malavolta *et al.*, 1980). The high salinity index value of KCl (116.3) indicates possible germination delays, slow emergence or even reduced crop stand resulting from the high KCl doses applied in the roots' vicinity (Malavolta and Usherwood, 1982). Soybean crops cultivated on soils that frequently receive high KCl doses might exhibit severe toxicity symptoms due to accumulation of Cl and manganese, especially when droughts occur before flowering (Borkert *et al.*, 1994).

Potato, a rising crop in Brazil, demands high K doses during tuber development. Potassium is essential for supporting carbohydrate production and translocation to the starchy tubers (Zörb *et al.*, 2014), thus increasing their dry matter content. High dry matter content is a desired tuber quality trait, particularly when tubers are destined for processing (Reis Junior and Monnerat, 2001); it increases the palatability of French fries (potato chips), as they become crisper, tastier, and less oily (Zehler *et al.*, 1981). Excessive KCl use rapidly supplies the potato crop with available K, however the substantial chloride amounts added to the system might reduce tuber dry matter content, especially where salinity problems develop (Imas and Bansal, 1999). Replacing KCl with Cl-free potash fertilizers such as K_2SO_4 or sulfate of potash magnesia, seemed a viable alternative for potato crop nutrition management, as it improves both productivity and tuber quality (Vale and Silva, 2009). In a similar way, replacing KCl with sulfate of potash magnesia improves the produce quality of coffee due to a significant decrease in the concentration of reducing sugars in the beans (Silva *et al.*, 1999). Thus, polyhalite should be considered for crop nutrition where KCl or other Cl-rich fertilizers are unfavorable.

Concluding remarks

The results of the potted rice experiment provide convincing evidence that polyhalite, a natural complex mineral, is an effective fertilizer in supplying Ca, Mg, S, and K on Oxisol - a low nutrient sandy soil. Polyhalite was equal in supporting plant growth, development and nutrient uptake to the corresponding soluble salts (Figs. 1-3). Consequently, the Brazilian Ministry of Agriculture authorized the use of polyhalite as an agricultural fertilizer in 2015.

The soybean field trial presented here suggests that polyhalite has adequate solubility to reach and promote an active crop rhizosphere when applied to the top soil layer (Fig. 4). Thus, polyhalite is a fertilizer with considerable potential to improve production within no-tillage systems, where soils exhibit significant Ca and Mg deficiency in the subsurface layers. Moreover, polyhalite emerges as a relevant K fertilizer, with equal efficiency to KCl and without the adverse effects of chloride, making it more suitable for use on certain soils and for certain crop species. Yet, the major advantage of polyhalite is in the delivery of S, an essential nutrient which until recently, has often been overlooked. Brazil's leading crops - sugarcane (Oliveira, 2011), soybean (Gutierrez Boem *et al.*, 2007), corn (Ciampitti *et al.*, 2013), and cotton (Reiter, 2013) - require significant S inputs, as do other important crops including wheat (Zhao *et al.*, 1999) and peanut (Tam *et al.*, 2016). In accordance, new field trials have recently been launched in Brazil for soybean, corn, cotton, sugarcane, coffee, orange, banana, onion, cabbage, and potato crops, with the purpose of consolidating the potential of polyhalite as an important fertilizer for Brazilian crops.

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The paper "Introdrucing Polyhalite to Brazil: First Steps of a New Fertilizer" also appears on the IPI website at:

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