Research Findings

Photo 1. Polyhalite, mined at the Boulby mine, UK, is a natural mineral formed by evaporation from the seas, shown in its original composition. Photo: ICL, UK.

Fertilization Efficiency with Polyhalite Mineral: A Multi-Nutrient Fertilizer

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Abstract

As the world's population approaches eight billion people, there is an increasing demand for cereals, grains, vegetables, animal protein, as well as energy. At the same time, in the shadow of the COVID-19 pandemic, world hunger has increased. After remaining virtually unchanged for five years, the prevalence of malnutrition (PoU) increased from 8.4% to about 9.9% in just one year, further adding to the challenge of achieving the Zero Hunger target by 2030.

To sustainably increase agriculture productivity, the use of best plant nutrition practices is essential. The shortage of any one nutrient has the potential to limit the growth, productivity, and quality of crops,

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as stated in Justus von Liebig's "Law of the Minimum". In addition to nitrogen (N), phosphorus (P), and potassium (K), attention must be paid to other macronutrients including calcium (Ca), magnesium (Mg), and sulfur (S), and to the management of micronutrients as well. Balanced fertilization is essential to obtain the maximum potential for crop yield.

Since 2015 a new natural mineral fertilizer, polyhalite, has stood out as an alternative fertilizer. Polyhalite provides four macronutrients in a single granule: K, Ca, Mg, and S. Polyhalite has several differential characteristics, such as a low salt content and prolonged availability of nutrients. Polyhalite has a lower carbon footprint than similar fertilizers and can be used in organic production systems.

Reviewing the research into the use of polyhalite as a sustainable multi-nutrient fertilizer consistently reveals its potential to increase agricultural productivity, where it consistently and significantly improves the yield, health, and quality of a wide range of crops.

Keywords: polyhalite, fertilizer, balanced nutrition, multi-nutrient, macronutrient, micronutrient, organic

Introduction

The world population is expected to reach eight billion people later this year, increasing demand for food, including cereals, grains, vegetables, and animal protein, as well as increasing demand for energy. World hunger increased in 2020 under the shadow of the COVID-19 pandemic. After remaining virtually unchanged for five years, the prevalence of malnutrition (PoU) grew from 8.4% to about 9.9% in just one year, further increasing the challenge of achieving the Zero Hunger target by 2030 (FAO, 2021).

Food production is basically dependent on agriculture, so the need to adopt correct management within production systems is gaining in importance, as producers aim at increasing agricultural production, without threatening environmental sustainability. The challenge is to increase productivity, producing more food while only minimally altering with the size of the cultivated area. Within this scenario, the use of best practices aimed at adequate plant nutrition is essential for success, and care must be taken to ensure plants have access to adequate amounts of all the nutrients required by each cultivated species. Individual nutrient's requirements are related to each other, and the shortage of any one of them has the potential to limit the growth, productivity, and quality of crops, as stated in Justus von Liebig's "Law of the Minimum" (Browne, 1942). This means that, in addition to nitrogen (N), phosphorus (P), and potassium (K), attention should be paid to other macronutrients including calcium (Ca), magnesium (Mg), and sulfur (S), and to the management of micronutrients as well. Balanced fertilization is essential to obtain the maximum potential for crop yield.

Despite the existence of K in most rocks and soils, the economic sources of K are associated with sedimentary evaporitic deposits in chloride and sulfate forms. Few K minerals are used in the production of potassium fertilizers, with sylvinite and carnallite being the most common in the production of the most abundant source of the potassium, muriate of potash (KCl). Deposits of these minerals were formed millions of years ago by the evaporation of saline waters in restricted basins which generated minerals concentrated at depths ranging from 300 m to more than 2,500 m in some parts of the world. Fertilizers can also be extracted from deposits in lakes with high saline concentration. Israel and Jordan produce KCl through evaporation of water from the Dead Sea (Roberts, 2005).

In addition to KCl, other sources of the nutrient have been used in recent decades, mainly potassium sulfate (K_2SO_4), double potassium, and magnesium sulfate obtained from the mineral langbeinite ($K_2SO_4 \cdot 2MgSO_4$) and potassium nitrate (KNO_3) (Table 1, adapted from Agrolink, 2022).

Brazil is the fourth largest consumer of fertilizers in the world, accounting for 7% of the volume, behind China, USA, and India (Saab and Paula, 2008). It is estimated that Brazil's consumption of fertilizers exceeded 42 million tons in 2021, with more than 11 million tons being KCl making Brazil the second largest consumer of potassium, third of phosphorus and fourth of nitrogen (Oliveira *et al.*, 2019).

Since 2015 a new mineral, polyhalite, has stood out as an alternative and complementary source for potassium fertilization providing four macronutrients in a single granule: K, Ca, Mg, and S. Polyhalite has several differential characteristics, such as a low salt content and the nutrients' prolonged availability. It has proven to be a source with high potential for sustainable management of the main crops' nutritional balance, allowing higher yield, health, and quality (Vale and Sério, 2017).

Table 1. Potassium mineral fertilizers.

Fertilizer	N	K_2O	S	Mg	Cl
Muriate of potash		58-62%			47%
Potassium sulfate		48-53%	15-19%		
Langbeinite		21-22%	20-22%	10-11%	
Potassium nitrate	12%	44-46%			

Adapted from Agrolink, 2022

Photo 2. Boulby mine, located in Yorkshire, UK is the only commercial polyhalite mine currently in operation. Photo: ICL, UK.

Map 1. Location of the ICL mine at Boulby, UK. Source: Google Earth.

Formation and extraction of the polyhalite mineral

Polyhalite is a dihydrated potassium, calcium, and magnesium sulfate ($K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$). It is a natural mineral produced by successive marine evaporation events throughout history (Kemp *et al.*, 2016) and it has great potential as a potassium fertilizer with low chlorine (Cl) content, while being rich in K, Ca, Mg, and S (Ogorodova *et al.*, 2016; Albadarin *et al.*, 2017). Polyhalite is widely formed as a constituent of marine evaporates, associated with halite (NaCl) and anhydrite ($CaSO_4$) (Barbier *et al.*, 2017).

Polyhalite deposits exist in several places in the world, being initially found in Austria and described by Stromeyer (1818), and later found in other areas of Europe. The main deposits of the mineral were recorded decades later in Texas and New Mexico, USA (Schaller and Henderson, 1932), then in Russia (Kurnakov *et al.*, 1937), and finally in Zechstein Basin in Yorkshire, UK (Stewart, 1949).

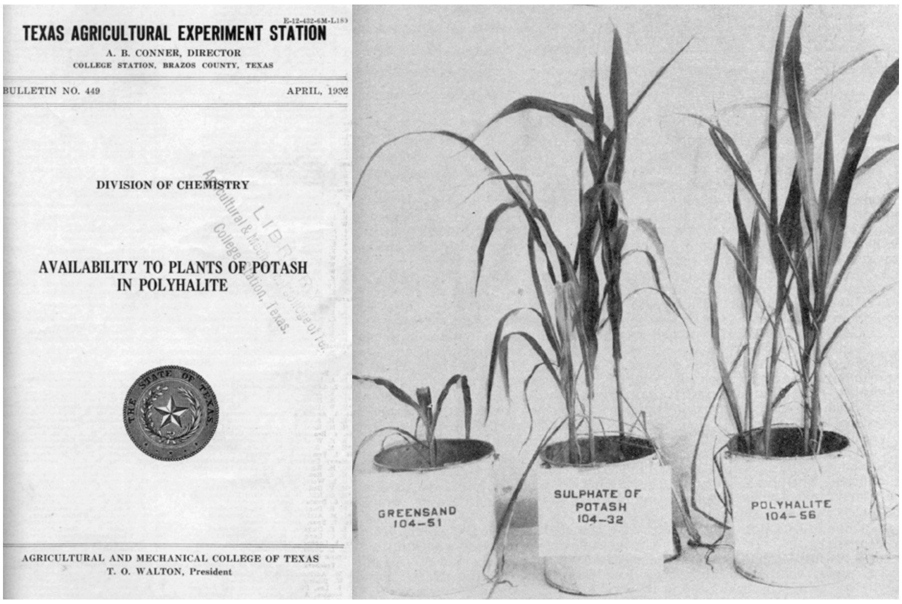
In the 1930s, the USA showed strong interest in this mineral due to its abundance in western Texas and New Mexico, about 106,800 km^2 of deposit (Mansfield and Lang, 1929). But with the discovery of KCl in large quantities in Saskatchewan, Canada, interest in polyhalite waned as the industry turned to this mining area instead.

Historically, the mineral has attracted reduced interest from companies due to its lower K content and prolonged availability compared to other sources. However, in recent years, polyhalite has increasingly been seen as a potential source of fertilizer due, in part, to the increase in the price of KCl which enabled incentives for the use of alternative potassium fertilizers. Polyhalite is also a source of S, helping meet crops' demand for S to optimize the productivity and quality of crops. It is currently extracted in small volumes, compared to other fertilizers, but this has increased significantly in recent years. The industry continues to evolve, with the UK subsidiary of Israel Chemicals Limited (ICL UK) currently extracting the mineral from a depth of 1,200 m at their Boulby Mine, in Yorkshire, UK (Map 1), distributing around 800,000 t/year of polyhalite worldwide, as a fertilizer for

Photo 3. Polyhalite extraction from 1,200 m below ground at Boulby Mine, Yorkshire, UK. Photo: ICL, UK.

direct application or to complement NPK blends (Imas, 2017) (Photos 2 and 3).

This natural mineral, with its unique characteristics, is used as a multi-nutrient fertilizer. In addition, it is one of the few sources of K suitable for chloride-sensitive crops. The first use of polyhalite as a fertilizer was reported when Fraps (1932) published results of experiments carried out in pots with corn and sorghum in Texas, USA, and showed that polyhalite would be suitable for use as a potassium fertilizer, providing equivalence of 96% K availability compared to KCl and K_2SO_4 fertilizers (Photo 4).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TEXAS AGRICULTURAL EXPERIMENT STATION
A. B. CONNER, DIRECTOR
COLLEGE STATION, BRAZOS COUNTY, TEXAS

BULLETIN NO. 449 APRIL, 1932

DIVISION OF CHEMISTRY

AVAILABILITY TO PLANTS OF POTASH
IN POLYHALITE

AGRICULTURAL AND MECHANICAL COLLEGE OF TEXAS
T. O. WALTON, President

Photo 4. First recorded work to evaluate plant nutrition with polyhalite. Cover of the publication and images of pots showing the comparison between corn grown with polyhalite and potassium sulfate. Fraps, 1932.

Several experiments have compared the use of polyhalite as a fertilizer to the use of equivalent commercial soluble salts. At the University of Colorado, USA, Barbarick (1991) found a better yield response of forage sorghum with increasing levels of polyhalite, when compared to soluble salts at the same application rate (Fig. 1) and associated this response with the slower solubility of polyhalite. Tiwari *et al.* (2015) found an advantage regarding oil production in mustard and sesame when applying polyhalite compared to using equivalent amounts of soluble fertilizers. In cabbage and cauliflower, higher quality and higher yields were obtained when polyhalite was used as a source of Ca, Mg, and S compared to fertilization with the equivalent soluble salts (Satisha and Ganeshamurthy, 2016).

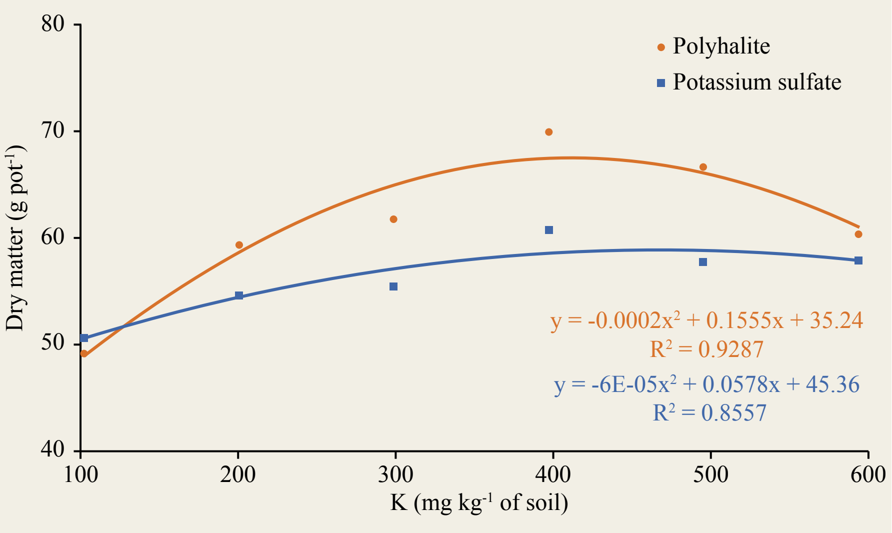


Fig. 1. Forage sorghum dry matter productivity as a function of K application through polyhalite and potassium sulfate. Barbick, 1991.

Polyhalite characteristics and properties

Polyhalite is a mineral with unique characteristics, making it a fertilizer with a high potential for main crops, bringing several benefits related to quality and yield.

Mineralogical composition

Polyhalite is an evaporitic mineral, hydrated sulfate of potassium, calcium, and magnesium. It crystallizes in the pseudo-orthorhombic triclinic system, although crystals are very rare. The normal habit is massive to fibrous. It is white to gray in color, like the mineral mined at the Boulby mine in the UK (Photo 1), although it can be red in some regions due to iron oxide inclusions. It is transparent, fluorescent, and non-magnetic in nature. Its fractures are brittle, similar to glass and non-metallic minerals (Bindi, 2005).

Chemical composition

Polyhalite is a naturally occurring mineral containing four macronutrients, K, Ca, Mg, and S. The mineral mined at the UK's Boulby mine has a very high purity (95% polyhalite) with a concentration of less than 5% sodium chloride (NaCl). There are traces of boron (B) and iron (Fe) at 300 and 100 mg kg^{-1}, respectively. Polyhalite has 48% SO_3 (19.2% S), 14% K_2O (11.6% K), 6% MgO (3.6% Mg) and 17% CaO (12.2% Ca), all available for plant uptake. Although it has a lower water solubility limit than other K sources,

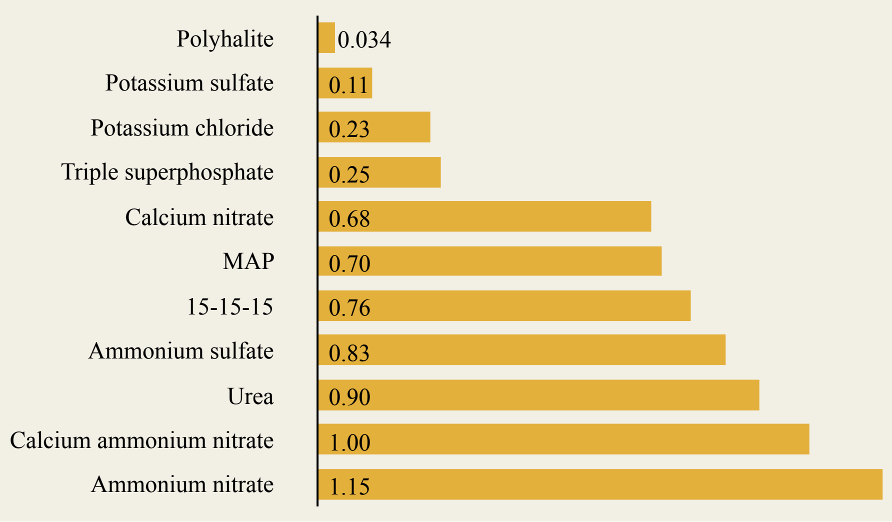


Fig. 2. Carbon footprint measurement of products used as fertilizers in agriculture. Source: ICL.

when applied at rates below its solubility limit, it provides more than enough K, Ca, Mg, and S for plant growth (Yermiyahu *et al.*, 2017).

Natural mineral for direct use in agriculture

As it is a mineral practically free of contaminants and with nutrients present in the form of soluble salts, polyhalite is simply extracted, crushed, and sieved, with no chemical processes in its production. Due to this simplified production, polyhalite fertilizer has a low carbon footprint (Fig. 2), which is an increasingly important factor for food producers and processors globally.

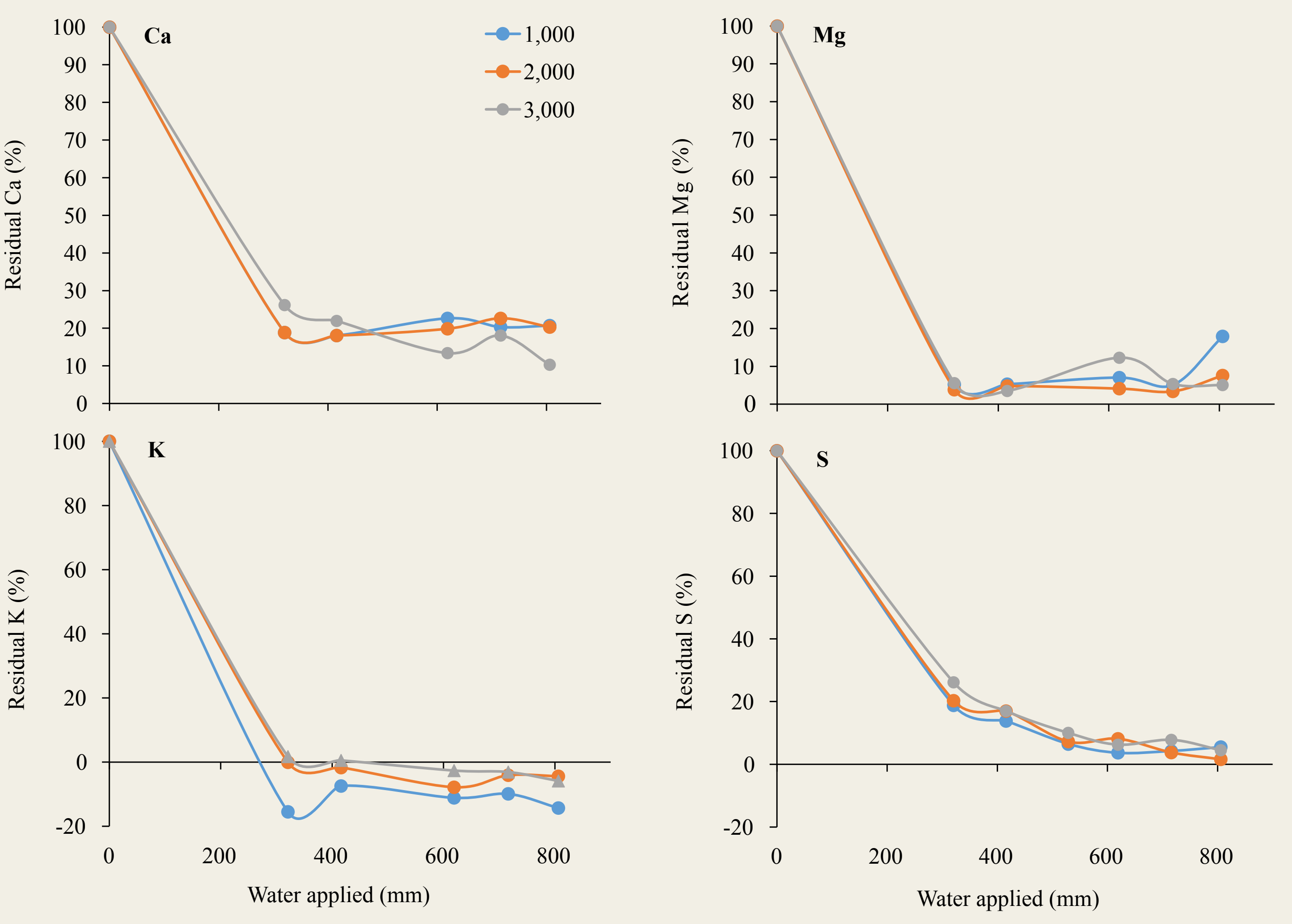


Fig. 3. Residual percentage of polyhalite elements Ca, Mg, K, and S from the field experiment. Polyhalite was applied at doses equivalent to 1,000, 2,000, and 3,000 kg ha^{-1}. The measurements took place at accumulated water applications of between 300 and 800 mm. Yermiyahu *et al.*, 2019.

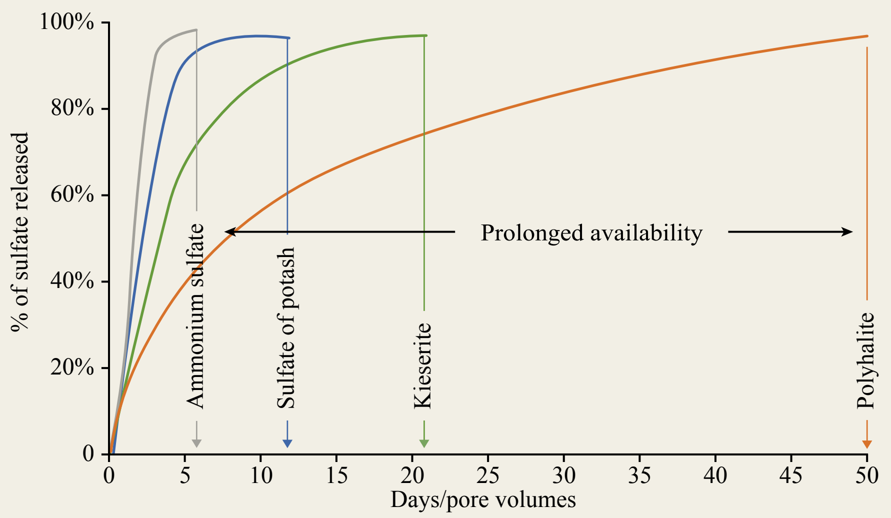


Fig. 4. Study in leach columns showing that polyhalite has prolonged availability (up to 50 days under laboratory conditions), in relation to other S sources. Jiang *et al.*, 2017.

Photo 5. Leach columns used in experiment at University of Nottingham.

Solubility with prolonged availability

Solubility is an important factor for fertilizers. Solubility varies considerably between sources affecting nutrient release rates and therefore their availability to plants, in addition to the potential for losses due to leaching, runoff and volatilization. Solubility also determines the potential for use in liquid fertilizer production. Barbarick (1991) stated that polyhalite was less soluble in water than conventional fertilizer sources and could provide a gradual release of nutrients. This prolonged availability of nutrients can guarantee nutrition at different stages of crop development, while also significantly reducing leaching losses.

Experiments evaluating the use of polyhalite have shown significant advantages for many crops (PVFCCo, 2016a, 2016b; Tam *et al.*, 2016; Melgar *et al.*, 2018; Tien *et al.*, 2018; Eryuce *et al.*, 2019). Polyhalite solubility and the potential availability of its various constituent minerals have been studied in both laboratory tests and field experiments (Yermiyahu *et al.*, 2019). In the laboratory test, the K and Mg salts were completely dissolved, while the Ca salts showed slower solubility. In the field experiment, carried out on a sandy soil in the Negev desert, Israel, under repeated wetting cycles that simulated successive rainfall events, all polyhalite constituents were dissolved between 75-100% after 300 mm of accumulated water application, in the order of K > Mg > S > Ca (Fig. 3). Significant differences in solubility occurred with application of increasing amounts of water, up to 800 mm. While K and Mg presented negligible or null residues, the dissolution of S was more gradual, and the Ca residues remained constant. Dissolving polyhalite in water takes longer and requires larger volumes of water compared to other soluble fertilizers. Any residual granules present on the surface after the evaluations did not show significant amounts of the nutrients. This indicates the safety of considering the guaranteed levels of the product, whilst reducing possible risks of fertilizer overuse and allowing the application of polyhalite as a fertilizer with slower release than most of soluble sources.

Research carried out in leach columns at the University of Nottingham, UK confirmed that polyhalite has a more prolonged release of S (Fig. 4) compared to other sources. Complete solubilization of S from polyhalite took 50 days, with about 50% of the nutrient already available after the first 10 days, which would allow adequate plant nutrition at that time. On the other hand, ammonium sulfate, the most soluble S source tested in the evaluation, made all S available within the first 5 days, indicating it was susceptible to leaching losses from the soil (Jiang *et al.*, 2017).

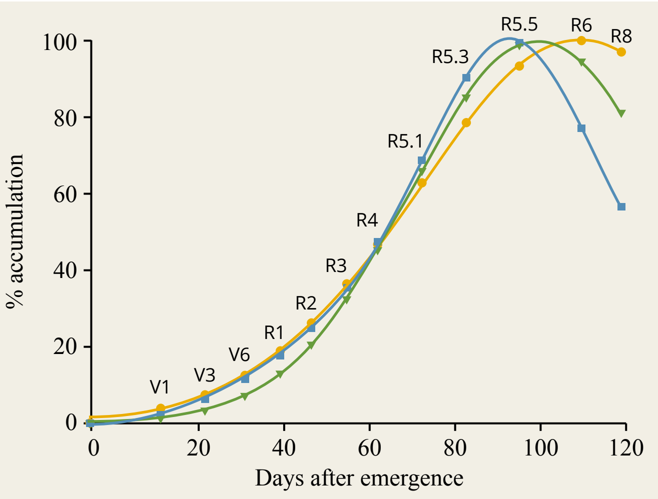


Fig. 5. Rate of sulfur absorption by different soybean cultivars: BRS 184, SYN 1059, DM 6563 - Intacta RR2 PRO. Oliveira Jr. *et al.*, 2016.

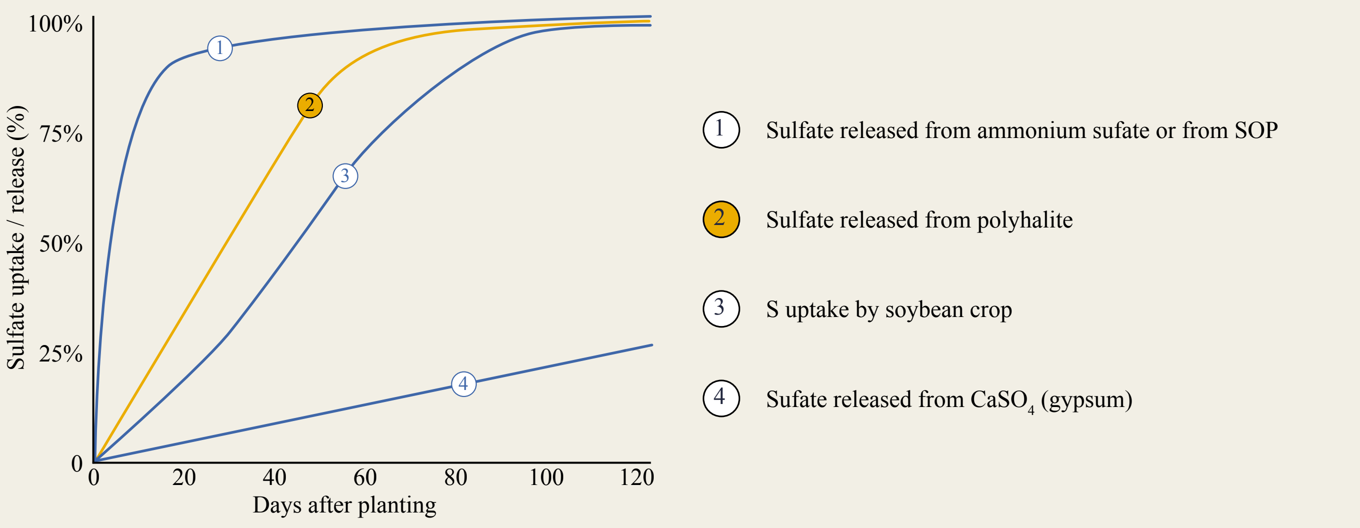


Fig. 6. Availability of sulfate from different sources and demand for sulfur by the soybean crop. Source: ICL.

This characteristic of prolonged availability of polyhalite nutrients, in addition to providing nutrition at the appropriate stages of crop development, also contributes to less leaching of the nutrients, especially S. Unlike other nutrient sources, polyhalite continues to supply sulfate to plants even after heavy rains, making it an adequate source for fertilization throughout the growing period. It also has the advantage of being recommended as the only source of S which requires just a single early dressing.

EMBRAPA studies with three soybean cultivars (Oliveira Jr. *et al.*, 2016) show that during the vegetative stage, S absorption remains low, accumulating less than 20% of the crop's needs, increasing during the reproductive stage when the accumulated values reached 20%, 50%, 70%, and 100% in stages R1, R4, R5.1, and R5.5, respectively (Fig. 5). Thus, it can be suggested that a single application of polyhalite as the source of S could meet the demand for the nutrient right from the initial vegetative stage to the beginning of the reproductive stage (Fig. 6).

Several studies carried out under laboratory and field conditions made it possible to define the average solubilization curves for polyhalite (Fig. 7). For K and Mg, complete solubilization is fastest, with nutrients completely available in the soil solution within 10 to 20 days. Within the first 15 days, between 70 and 80% of the S is solubilized with the remainder between 45 and 50 days after application. Ca has the slowest availability among the four guaranteed macronutrients, close to 60% at 10 days and finalizing complete dissolution after approximately 50 days. This shows the difference in solubility between the chemical forms present in the product: potassium sulfate and magnesium sulfate are more soluble, while calcium sulfate has a slightly slower solubility (Yermiyahu *et al.*, 2019).

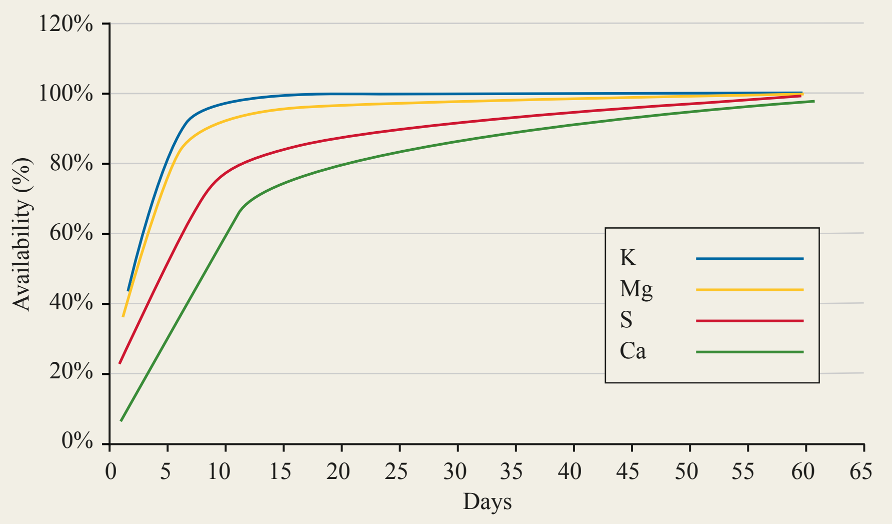


Fig. 7. Prolonged availability of polyhalite nutrients for 40-50 days under field conditions. *Source:* ICL.

Salt index

Fertilizer application is a pre-condition for sustainable agriculture, especially on weathered soils, such as those in tropical regions. When practiced correctly, fertilization must meet the nutritional demands of crops with minimal influence on the environment. Practically all fertilizing materials are salts; they dissolve in water, which transports nutrients through the soil, and is the medium where they are accessible to plant roots. However, increasing salt concentrations above certain levels can

Table 2. Salt index for different fertilizers (suppliers of K, Mg, Ca, or S) by calculation method (CPH, 2006) or by electrical conductivity determination (Jackson, 1958), at the IMI TAMI R&D Institute, Haifa, Israel. Fried *et al.* (2019).

Fertilizer	Salt index	
	CPH	Jackson
Polyhalite	32.3	52.0
KCl	116.2	138.0
Gypsum ($CaSO_4$)	8.1	42.0
K_2SO_4	42.6	100.0
$MgSO_4$	44.0	76.0
Langbeinite ($K_2SO_4{\cdot}MgSO_4$)	-	26.6
KNO_3	69.5	85.0

adversely affect the crop, usually described as salt stress. To avoid fertilizer-induced salinity problems, it is essential to recognize the chemical nature of the products in use, not only as nutrient providers but also as salts, and to establish rules and limits for reasonable application methods.

Salinity has two major impacts on plants: toxic and osmotic stress (Munns and Tester, 2008). Toxic effects occur when the concentration of sodium (Na) or Cl ions in the leaf cells' cytosol increases above a certain threshold, usually 150-200 µmol, damaging the enzymes and sensitive photosynthetic structures. Several plant species activate compartmentalization mechanisms, storing saline ions in vacuoles and organs, trying to avoid their harmful influence. However, as these abilities differ greatly between crop species, a toxicity test seems useless to assess and compare the effect of fertilizer salinity. In addition, most fertilizers do not contain Na, while fertilizers without Cl are gaining more and more value.

In contrast, the osmotic component of salt stress has similar effects on all plant species. As the ions, or soluble compound concentration in the liquid phase of the soil increases, the availability of water to the plant roots decreases. This phenomenon is expressed as the osmotic potential of the soil extract, whose strength also depends on the chemical properties of the soluble compounds. Consequently, fertilizers can differ significantly in their effect on soil osmotic potential. Thus, to evaluate the osmotic effect of fertilizers, the parameter known as salt index (SI) was established in the 1940s (Rader *et al.*, 1943). The salt index expresses the proportion of the increase in the osmotic pressure of the saline solution produced by a given fertilizer compared to the osmotic pressure of the same weight of sodium nitrate ($NaNO_3$). Sodium nitrate was selected as the standard to measure the salt content against because it is completely soluble in water ($NaNO_3$ SI is equal to 100). For example, the SI value for KCl considered by the authors was 116, that is the salinity of this fertilizer would be 16% higher than that of $NaNO_3$ when the products were applied at the same rate.

However, the Rader method often seemed impractical, and furthermore, their SI tables did not include many fertilizers developed later. Jackson (1958) published a simpler laboratory method, where the SI of the fertilizer was measured by the electrical conductivity in relation to $NaNO_3$. Several laboratories have used this method to evaluate new materials. More recently, many references, such as the Crop Protection Handbook (CPH, 2006), have adopted and published SI tables based on calculations that make use of values from both methods (Mortvedt, 2001). In comparison between four methods, Murray and Clapp (2004) showed that SI values obtained for different K fertilizers can differ significantly (Table 2) and therefore in fertilizer SI assessments more than one approach should be considered. For KCl, the authors presented an SI value close to 150 by the Jackson method, well above the standard defined in the initial research on the subject. When calculating by the CPH method they found a result similar to the Rader parameter, indicating the possibility of using the CPH method in practice. Barbier *et al.* (2017) also found considerable differences in SI values for the same fertilizer between laboratories, determining an SI value of 128 for KCl using the Jackson method.

Working at the IMI TAMI R&D Institute, Haifa, Israel, Fried *et al.* (2019) performed validations of the SI of polyhalite and other sources containing K, Ca, Mg and S, using both the calculated method described by CPH (2006) and the determined value according to Jackson (1958), with results shown in Table 2. The theoretical calculation of polyhalite's SI presented a value of 32.3 (Table 2), significantly lower than the standard 100 for $NaNO_3$. However, there were major differences between the theoretical calculation and the Jackson method, with the latter's values being much higher for all sources. Differences between fertilizers within each method, however, were consistent. Among K-supplying fertilizers, SI values decreased in the order of: KCl > K_2SO_4 > KNO_3 > polyhalite > langbeinite.

Polyhalite has low salt index values compared to more common and equivalent fertilizers and this can be attributed to the dominant

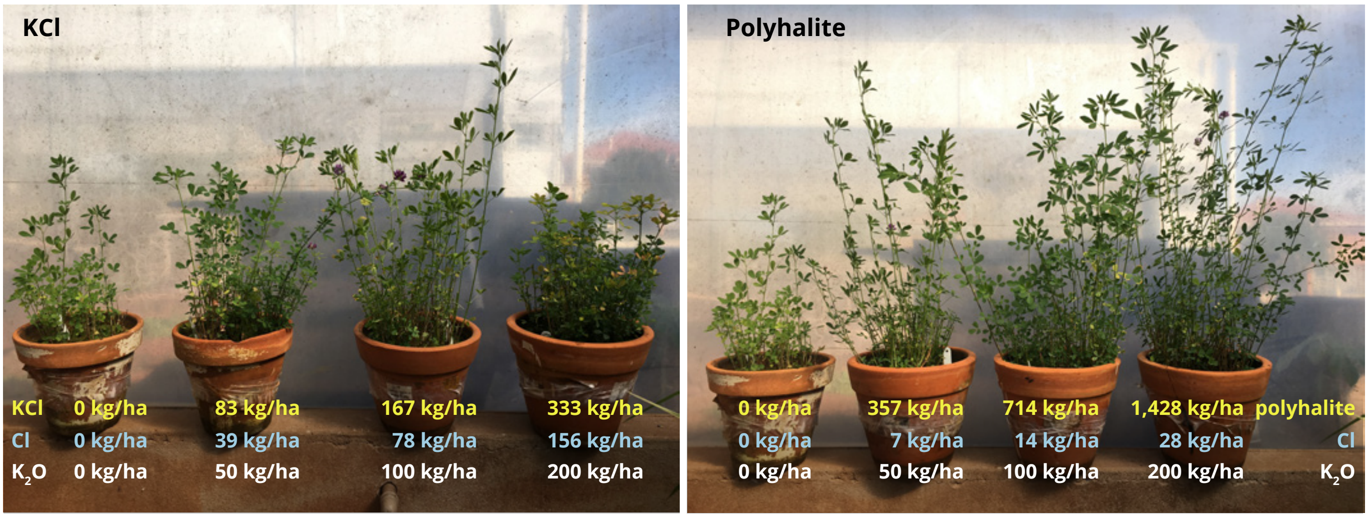


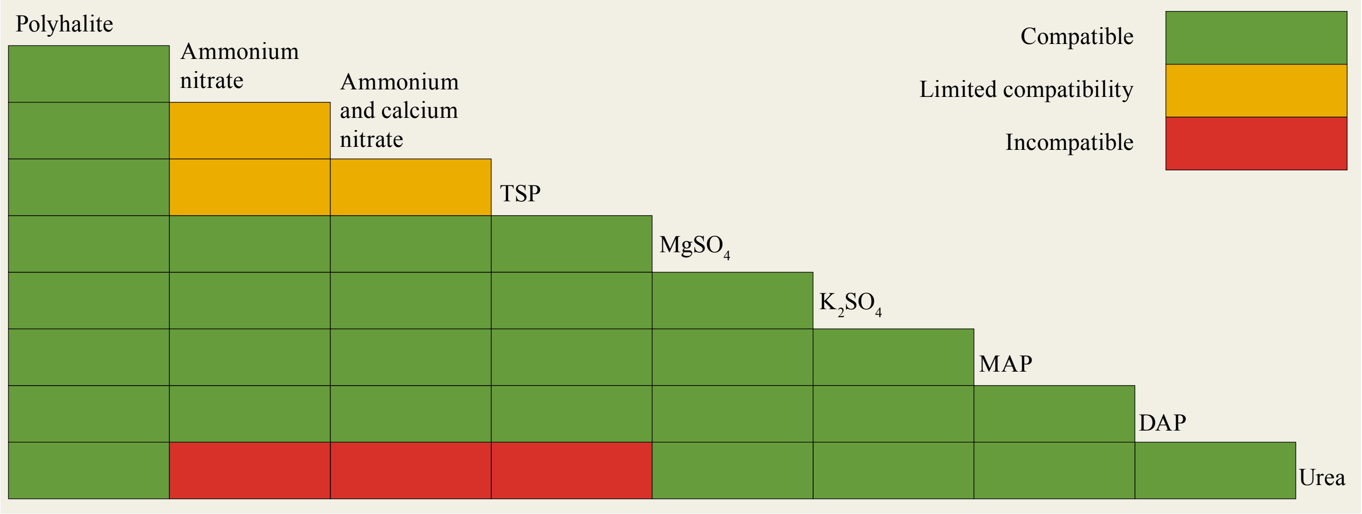
Photo 6. Performance of alfalfa grown in pots under four levels of K application (0, 50, 100, and 200 K_2O kg ha^{-1}) using KCl (left) and polyhalite (right). Photos: A.C.C. Bernardi.

portion of $CaSO_4$ in the fertilizer. This is one of polyhalite's significant advantages, reducing risk of salinity during the sensitive early stages of many crops (Havlin *et al.*, 1999). Another advantage of polyhalite, referring to the salt index, is related to the chloride levels, which are very low in the mineral, thus avoiding risks of ion accumulation at depth, and reducing impacts related to the root system development.

Bernardi *et al.* (2018) compared the supply of potassium fertilization from two sources, KCl and polyhalite for alfalfa crop (*Medicago sativa*) under controlled conditions. Fertilizer rates ranging from 0 to 200 kg K_2O ha^{-1} were evaluated, using single fertilizer sources or blends. The results showed the benefit of replacing KCl with polyhalite, which led to an increase in biomass, resulting in higher yield. Comparing the increasing rates of polyhalite and KCl, there is a greater risk when using KCl. Plants show less development due to the higher SI; at the same rate of K_2O, KCl applies approximately 5.5 times more Cl than polyhalite (Photo 6).

Ways of use and application

Another advantage of polyhalite relates to its versatility. Polyhalite can be used as a simple fertilizer or in NPK blends, providing S, K, Mg, and Ca with prolonged availability. In physical blends with other fertilizers available on the market, polyhalite is shown to be fully compatible, not affecting the chemical and physical-chemical characteristics of the formulations, thanks to its neutrality and low hygroscopicity characteristics (Fig. 8). Available in granular and powder forms, polyhalite can be applied to all crops, if it is managed according to nutritional demand, both in quantity and at the right time



	Polyhalite	Ammonium nitrate	Ammonium and calcium nitrate	TSP	$MgSO_4$	K_2SO_4	MAP	DAP
Ammonium nitrate	🟩							
Ammonium and calcium nitrate	🟩	🟨						
TSP	🟩	🟨	🟨					
$MgSO_4$	🟩	🟩	🟩	🟩				
K_2SO_4	🟩	🟩	🟩	🟩	🟩			
MAP	🟩	🟩	🟩	🟩	🟩	🟩		
DAP	🟩	🟩	🟩	🟩	🟩	🟩	🟩	
Urea	🟩	🟥	🟥	🟥	🟩	🟩	🟩	🟩

Compatible 🟩
Limited compatibility 🟨
Incompatible 🟥

Fig. 8. Compatibility between raw materials to produce formulated fertilizers, based on the IFDC method. Source: ICL.

Photo 7. Polyhalite fertilizer available in granular (left) and powder (right) forms. Photos: ICL.

due to its gradual release. It can be applied in the planting furrow or incorporated, because of its low salt content, or applied to the surface, meeting the application ranges of the most used fertilizers in agriculture (Fig. 8).

Mobile calcium and magnesium in the soil profile

Due to the increasing use of potassium fertilizers in Brazilian soils, Ca and Mg availability have become a challenge in arable areas. Thanks to the chemical characteristics of limestones, which have low mobility in the soil profile, it has been observed that the practice of liming alone cannot correct the levels of both nutrients. At greater depths the situation worsens, especially in no-tillage areas and also in those with perennial crops, where limestone is applied superficially and without incorporation leaving the nutrients concentrated in the surface layer (Freiria *et al.*, 2018; Martinez *et al.*, 2000). Thus, the management of Ca and Mg, also included in fertilization, becomes a tool to reach greater agricultural sustainability.

Calcium is responsible for the structural and physiological stability of plant tissue, generating phytates and pectates, which make it important for maintenance of the integrity of the cell wall. Calcium activates multiple growth regulatory enzyme systems, helps convert nitrate into forms necessary for protein formation, and contributes to improved disease resistance. Since calcium is immobile within the plant, deficiency symptoms appear on younger leaves. New leaves are usually smaller than normal, are distorted, curled or hook-shaped, and the growing tip may die (Marschner, 2012).

Magnesium has an important role in plant metabolism, including photosynthesis and carbon incorporation, being the central atom of the chlorophyll molecule (Marschner, 2012). It also plays a key role in defense mechanisms under abiotic stress conditions (Senbayram *et al.*, 2015), and light intensity has a strong influence on it. Plants grown in environments with intense light show a greater need for Mg than plants grown in conditions of lower intensity. As Mg is mobile within the plant, deficiency symptoms appear first on the lowest and oldest leaves. The first visible symptoms are pale leaves, which develop interveinal chlorosis. On some plants, reddish and/or purple spots will appear on the leaves. Several publications have shown the increasing extent of Mg deficiency in agricultural areas of different parts of the world. Plant Mg nutrition is often neglected, and scarcity negatively affects plant growth, with hidden hunger for this nutrient being one of the biggest nutritional problems of cultivated plants (Cakmak and Yazici, 2010; Guo *et al.*, 2016; Castro *et al.*, 2020).

In polyhalite, Ca and Mg are present in sulfate forms and so have greater mobility than when supplied as carbonates, causing them to occupy deeper layers of the soil allowing the root system to grow in depth and volume. Vale (2016) compared the effect of polyhalite with that of KCl as a source of K for soybean cultivation in Sapezal, Mato Grosso, an area that had received 2.5 Mg ha^{-1} of dolomitic limestone, incorporated with a harrow. At planting, 100 kg ha^{-1} of P_2O_5 was applied via MAP. Potassium sources were applied at a rate of 140 kg ha^{-1} of K_2O without incorporation, divided into two applications, 50% in V1 phase and the remainder in V6. The plots that received polyhalite showed a 10.2% increase in yield compared to KCl fertilization. After harvesting, soil samples were collected at depths 0-5, 5-10, 10-15, 15-20, 20-30, and 30-40 cm to determine levels of K, Ca, Mg, and S throughout the soil profile. Limestone application only influenced the availability of Ca and Mg in the 0-10 cm layer, proportional to its mechanical incorporation. The application of polyhalite increased the Ca and Mg contents throughout the profile, increasing Ca by 23% and 8%, respectively in the 0-20 and 20-40 cm layers. For Mg this increase was 25% and 17% for the same layers. This movement of the bases followed the sulfate movement, with an increase in the S content in the profile, mainly in the 20-40 cm layer (Fig. 9).

Organic certification

Polyhalite mining does not involve chemical processes, so the mineral is available in its natural form. This makes it appropriate as a fertilizer for use in organic agriculture, meeting certification criteria worldwide. Polysulphate, the polyhalite fertilizer from ICL, has certification in countries such as the US, Canada, Italy, Brazil, the Netherlands, as well as the European Union and the UK.

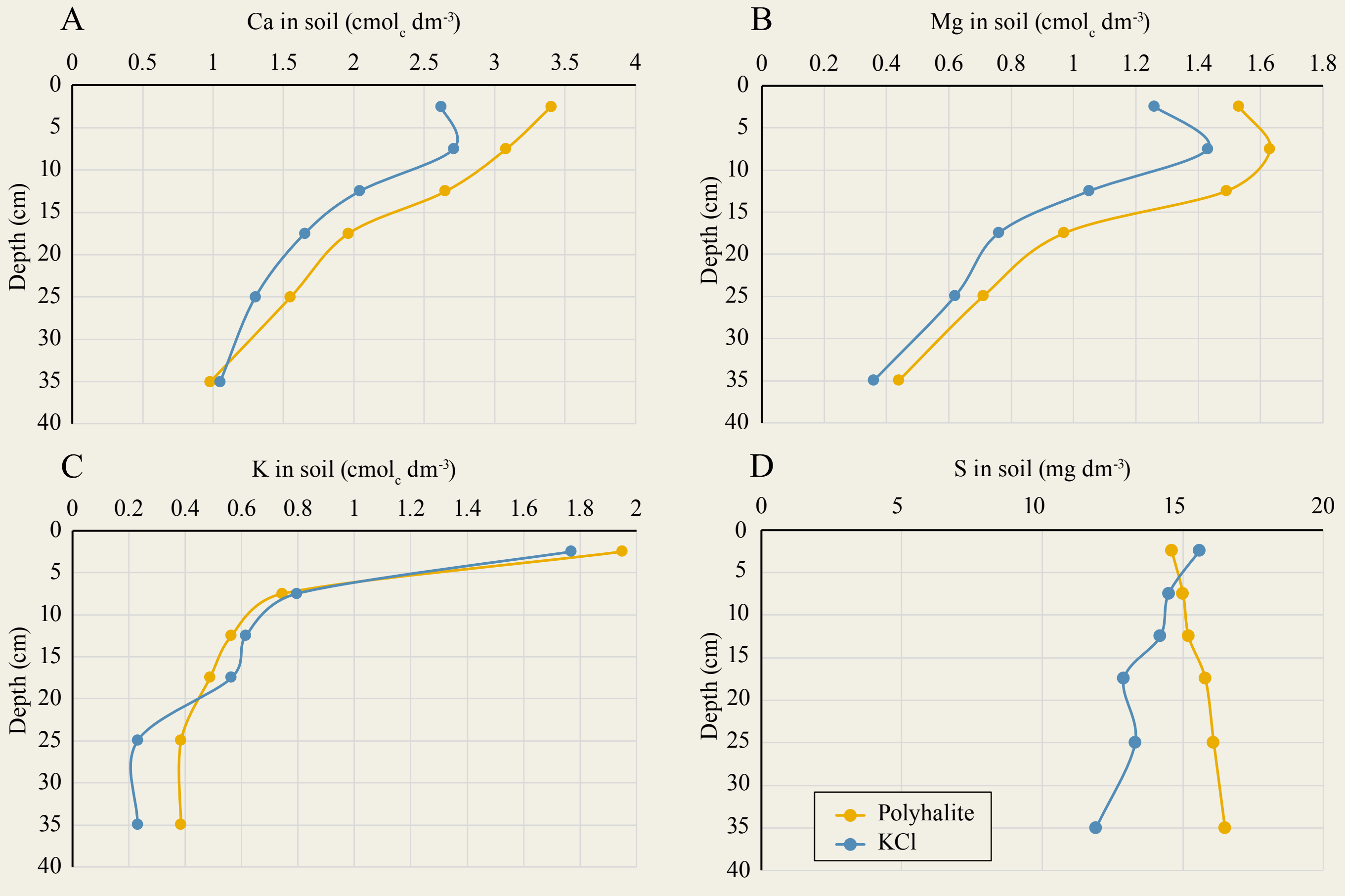


Fig. 9. Contents of Ca, Mg, K, and S in the soybean soil profile after treatments with liming and fertilization with KCl or polyhalite in Latosols. Vale, 2016.

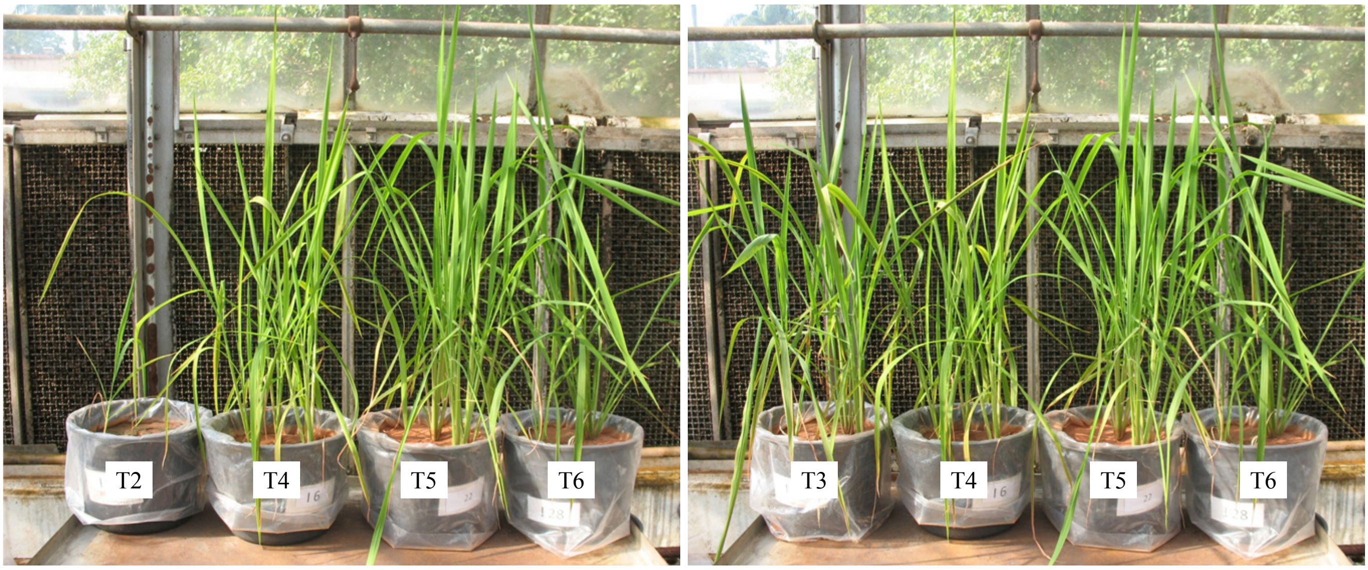


Photo 8. Rice grown in pots as part of the process to register polyhalite as a fertilizer in Brazil. Treatments: T2 control without K, Ca, Mg, or S; T3 Soluble salts of K, S, Ca, and Mg; T4 granular polyhalite; T5 granular polyhalite (double dose); T6 crushed polyhalite. Vitti (2013), referenced by Vale and Sério (2017).

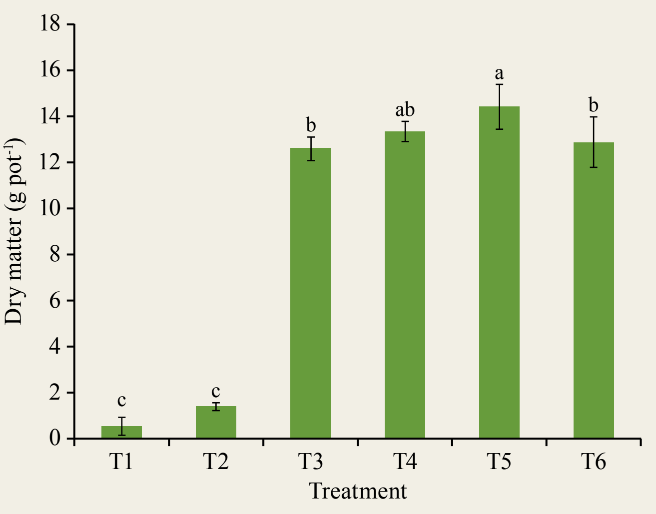


Fig. 10. Effect of fertilizer treatments on rice dry matter production. Treatments: T1. Absolute control; T2. No addition of K, S, Ca, and Mg; T3. Granular polyhalite; T4. Soluble salts of K, S, Ca, and Mg; T5. Granular polyhalite (double dose); T6. Crushed polyhalite. Different letters indicate statistically significant differences at P=0.05 (Duncan's test). Vale and Sério, 2017.

Agronomic efficiency of polyhalite use in Brazil

Agronomic research has proven the efficiency of polyhalite as a fertilizer. Polyhalite is registered with the Ministry of Agriculture (MAPA) and is included in Annex I of Normative Instruction No. 39 (Brasil, 2018).

The first study proving the availability of nutrients in comparison with supply from other recognized nutrient sources was carried out by Vitti (2013), referenced by Vale and Sério (2017), with rice grown in pots in greenhouse conditions. Polyhalite was applied in two physical forms, granular and powder. Two control treatments were used, the first one without the addition of any nutrients, and the second without the addition of the four macronutrients present in polyhalite (K, Ca, Mg, and S). One treatment received all nutrients in the form of recognized soluble fertilizers salts (calcium sulfate, magnesium sulfate, potassium sulfate, and KCl) at an equivalent level to the polyhalite treatment. To evaluate any possible toxicity of the product, one treatment was conducted with a double dose of polyhalite. Results found that rice plants lacking the macronutrients K, Ca, Mg, and S showed much lower development, while soluble

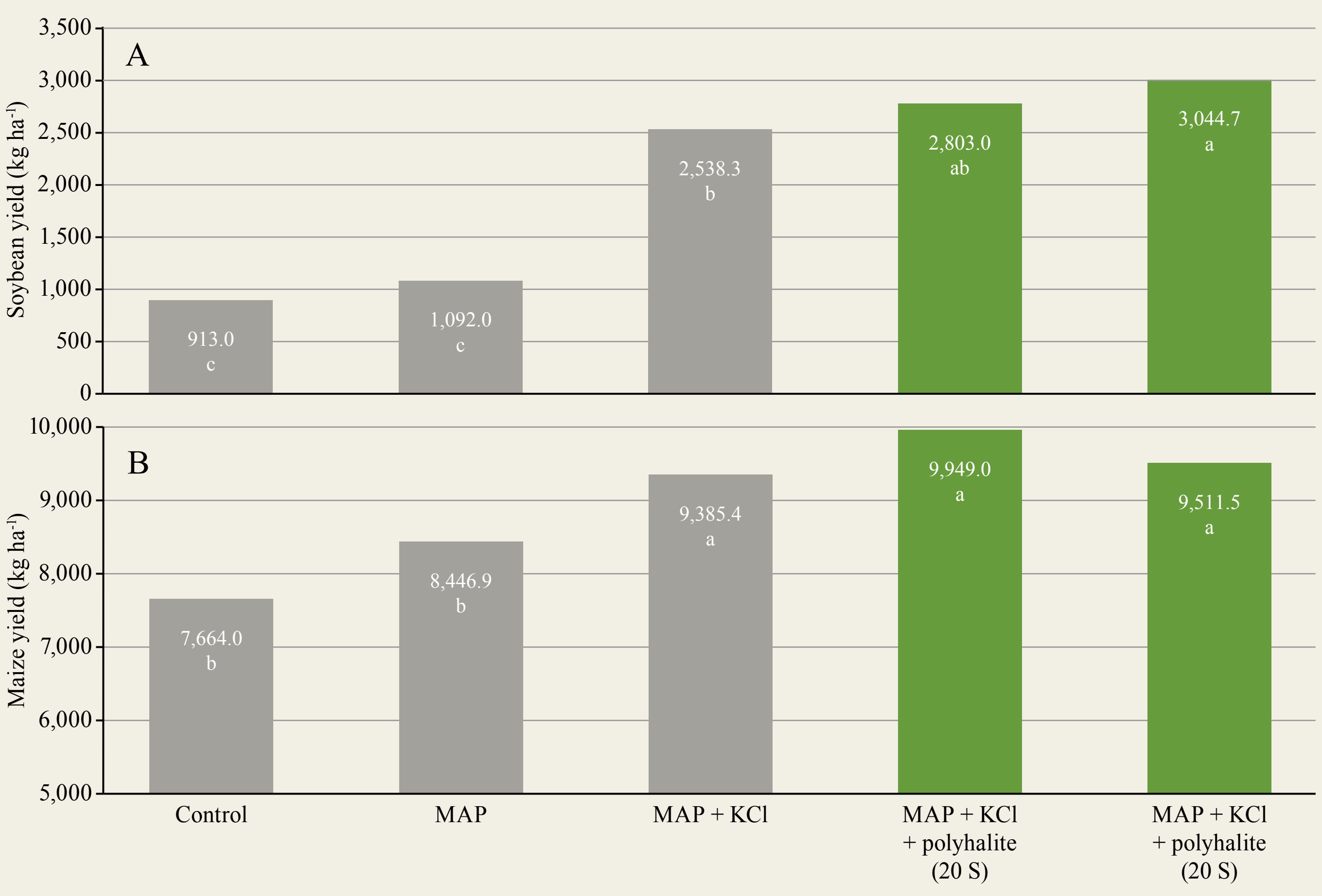


Fig. 11. Soybean yield as a function of partial replacement of KCl by polyhalite (A), and residual effect on corn (B), in Luis Eduardo Magalhães, Bahia state. Vale and Dowich, 2017.

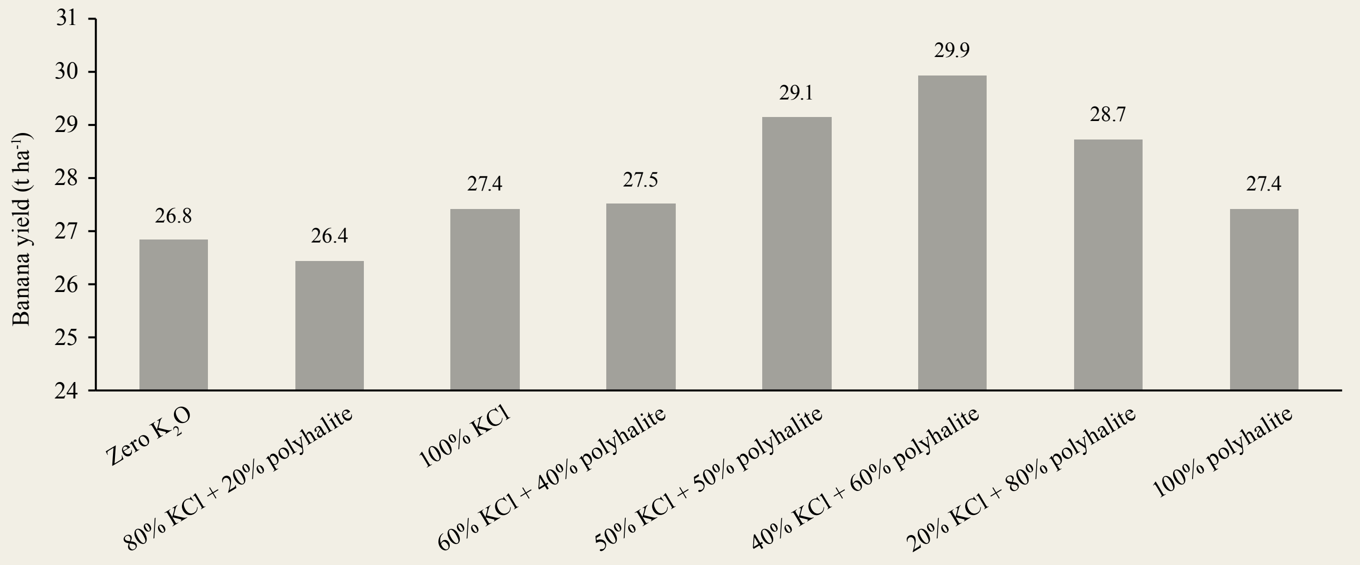


Fig. 12. Yield of banana in response to fertilization with different K sources, at a dose of 360 kg ha^{-1} of K_2O in Juquiá, Sao Paulo state. Silva *et al.*, 2018.

sources, including the application of granular or powdered polyhalite, allowed for normal plant development (Photo 8). Both granular and powdered polyhalite showed similar efficacy when compared to soluble sources (Fig. 10). There were no toxicity or salinity problems after applying the double dose of polyhalite.

Since 2016 polyhalite research in Brazil has continued, seeking to adjust the fertilization recommendations for the region's main crops. Several areas with soybean, corn, coffee, vegetables, sugarcane, cotton, among others, have already been fertilized with polyhalite, demonstrating its productive potential and superior quality compared to conventional nutrient sources.

The use of polyhalite in soybean fertilization, and its residual effect in the subsequent cultivation of corn was evaluated in an experiment in the Luis Eduardo Magalhaes region, west of Bahia (Vale and Dowich, 2017). Although soybean cultivation was influenced by the El Niño weather phenomenon that occurred in the 2015-16 season, with prolonged droughts and late rains, potassium fertilization had a high influence due to the reduction in rainfall. Combining MAP and KCl increased production by 36% in relation to fertilization with MAP alone. Introducing polyhalite to the MAP and KCl fertilizer strategy increased the yield by up to 19.9% compared to KCl treatment (Fig. 11A). After the soybean harvest and subsequent fallow period, corn was sown in October 2016, and all treatments received the same fertilization of 150 kg ha^{-1} N as urea, 100 kg ha^{-1} P_2O_5 as MAP and 60 kg ha^{-1} K_2O as KCl, to evaluate the residual effect of the sources applied in the previous soybean fertilization. Corn yield was 6% higher due to the residual effect of polyhalite compared to KCl fertilization, showing the importance of S, Ca, and Mg and the viability of polyhalite in the management of these crops (Fig. 11B).

Two trials were carried out at the Fundação Rio Verde experimental station, in Lucas do Rio Verde, Mato Grosso state, Brazil. A soybean trial compared polyhalite with simple superphosphate and pastilled elemental sulfur as sources of S, in both broadcast and furrow application. Polyhalite proved to be a viable soybean fertilizer using either application method, producing superior yields to the other treatments. The application of polyhalite in the furrow increased yield by 16.7% compared to KCl, 14.1% compared to elemental S, and 9.7% compared to simple superphosphate. The second trial, with cotton, compared polyhalite and ammonium sulfate as sources of S in broadcast application, when applied at different stages. Better yields were achieved with ammonium sulfate applied 20 days after sowing, polyhalite applied 5 days after sowing, and when polyhalite was applied at 5 and 20 days after sowing. This third way to apply the product was interesting as it produced the greatest average yield of cotton bolls per plant, which may be indicative of the effect of applying fertilizer with Mg (Pittelkow *et al.*, 2018).

Several experiments were carried out in fruit crops, including evaluation of the use of polyhalite for banana fertilization in Juquia, Sao Paulo state (Silva *et al.*, 2018). Typical crop management involves high doses of KCl, leaving soils with a high concentration of K and generally with high salinity. This can influence plant development and nutrition, mainly due to competitive inhibition from Ca and Mg. The treatments were blends of KCl and polyhalite tailored to provide 360 kg ha^{-1} of K_2O, and a control treatment with no nutrient application. As the soil had a high saturation of K, there was no significant effect of the application of KCl in relation to the control, with a 1.5% reduction in fruit production due to fertilization with K_2O alone. The best result was obtained with the 60:40 polyhalite:KCl blend, which increased the yield by 13.2% in relation to fertilization with KCl (Fig. 12). The plots that received polyhalite

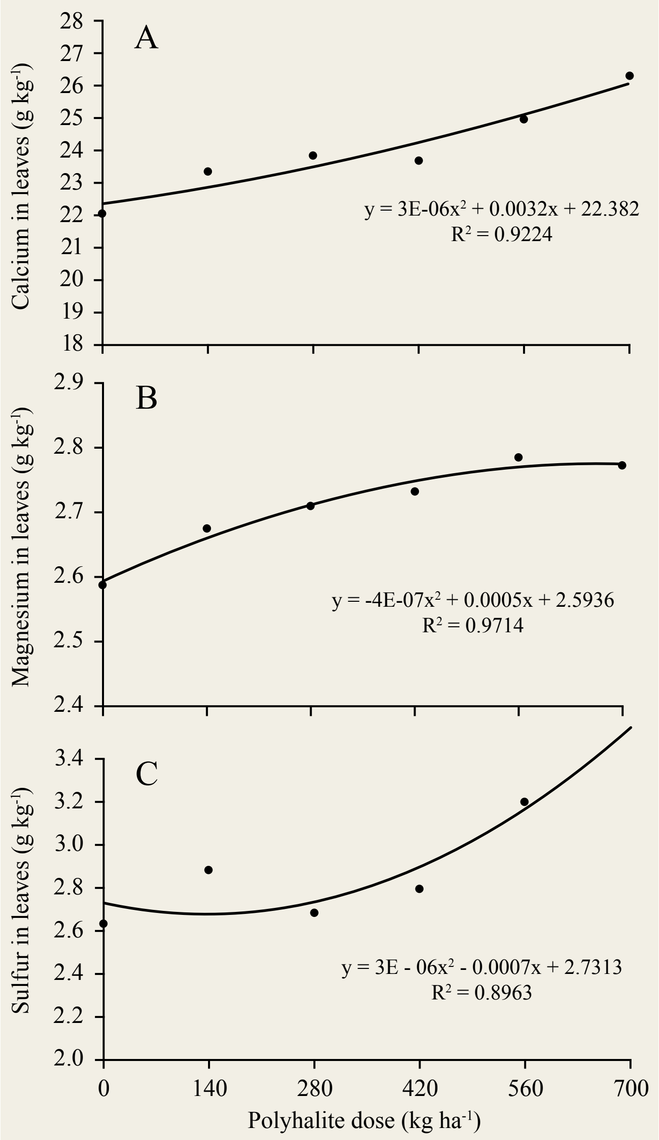


Fig. 13. Effects of polyhalite dose on foliar calcium (A), magnesium (B), and sulfur (C) concentration in Natal orange trees, expressed through binomial regression curves. * and ** indicate significance of the regression curve at $P < 0.05$ and $P < 0.01$, respectively. Silva and Vale, 2021.

showed bunches with greater vigor, and the plants with the largest stem diameter. Polyhalite is a viable alternative for use in banana fertilization, as it improves the nutritional balance with the supply of Ca, Mg, and S, in addition to reducing salinity and increasing yield potential.

In order to evaluate the effect of polyhalite on orange crops in Brazil, an experiment was conducted in 2017-2018 in Mogi Guaçu, Sao Paulo state (Silva and Vale, 2021). The treatments included fertilizer blends to partially replace KCl with polyhalite to maintain a constant dose of 300 kg ha^{-1} of K_2O. The foliar concentrations of Ca, Mg, and S significantly increased with the increasing polyhalite dose (Fig. 13). The treatment with the greatest proportion of polyhalite in the fertilizer blend (68% polyhalite) produced an increase in total soluble solid yield of 42% compared to the KCl control. Overall, the research indicated the optimal polyhalite application rate was close to 400 kg ha^{-1} (Fig. 14). This partial replacement of KCl with polyhalite presented significant advantages for the commercial orange production under tropical conditions.

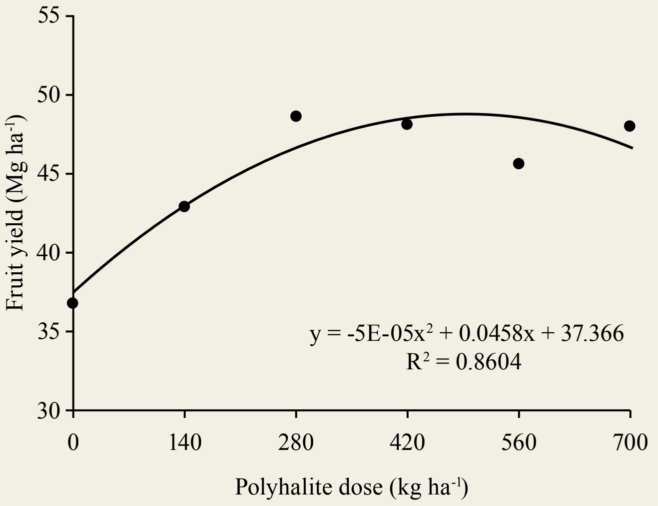


Fig. 14. Effects of polyhalite dose on fruit yield in Natal orange trees, expressed through binomial regression curves. * and ** indicate significance of the regression curve at $P < 0.05$ and $P < 0.01$, respectively. Silva and Vale, 2021.

Vegetables are usually grown in soils with high fertility, excessively corrected and fertilized, thus a low response to the use of nutrients in fertilization is expected. These soils usually have a high amount of chloride and sodium, and the use of less saline sources, such as polyhalite, can be an alternative for greater yield, health, and product quality. In the region of Piedade, state of São Paulo, a study evaluating potassium fertilization for cabbages showed that the partial replacement of KCl by polyhalite increased the yield by up to 12.4%, and the proportions between 40 and 80% of polyhalite in blends with KCl were the most suitable, even in high fertility soils. Plants that received polyhalite were less susceptible to leaf spot caused by *Xanthomonas campestris* (Vale and Silva, 2017). Using the same methodology in an experiment with potato, Vale *et al.* (2019) concluded that there was a positive effect on tuber production with the partial replacement of 50 to 75% of KCl by polyhalite. They also observed a reduction in the number of stems attacked with the bacterium *Pectobacterium carotovorum*, which causes blackleg.

Sugarcane production in Brazil is largely carried out in areas with Oxisols and Dystrophic Ultisols, which are poor in nutrients. Despite the corrections made at planting, S deficiency in ratoons is common. Vale and Sério (2019) evaluated the use of polyhalite compared to phosphogypsum and ammonium sulfate in the management of ratoon sulfur fertilization in the Catanduva region, state of São Paulo. The supply of S through blends of polyhalite with KCl presented the best result in relation to the yield of stalks and sugar. In this way, polyhalite is a viable source of S for sugarcane ratoons, being able to replace agricultural phosphogypsum.

Final considerations

Polyhalite is a natural fertilizer containing four macronutrients: K, Ca, Mg, and S. Polyhalite has a low salinity, which allows it to be used in various types of management and with a wide range of crops in general. The prolonged availability of nutrients is a significant characteristic, making it an interesting source for adjusting the nutritional balance of crops.

Photo 9. Continuous mining machine used to extract the polyhalite mineral from 1,200 m below ground in the polyhalite mine at Boulby, Yorkshire, UK. Photo: ICL, UK.

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