

Research Findings



Polyhalite solubility field experiment. Photo by the authors.

Solubility of Granular Polyhalite under Laboratory and Field Conditions

Yermiyahu, U.^{(1)*}, I. Zipori⁽¹⁾, C. Omer⁽¹⁾, and Y. Beer⁽²⁾

Abstract

The potential of polyhalite, a natural mineral consisting of K_2O , SO_3 , MgO , and CaO at 14%, 48%, 6%, and 17%, respectively, to become a slow-release multi-nutrient fertilizer was the focus of the present study. Fertilizer solubility, and hence the potential availability of its various constituent minerals, was investigated in both a laboratory test and a field experiment. In the laboratory test, the potassium (K) and magnesium (Mg) salts were completely dissolved, while the calcium (Ca) salts displayed significantly limited solubility. In the field experiment, under repeated cycles of wetting that simulate successive rainfall events, all polyhalite constituents were between 75-100% dissolved following 300 mm of accumulating water application, in the order of $K > Mg > S > Ca$.

Significant differences in solubility occurred with the rising amounts of water application up to 800 mm. While K and Mg displayed no or negligible residues, S dissolution was very gradual, and Ca residues remained constant. Supported by previous studies, the present study demonstrates that polyhalite dissolution in water takes longer and requires larger water volumes compared to other soluble fertilizers. This advantage reduces possible risks

⁽¹⁾Gilat Research Center for Arid and Semi-Arid Agricultural Research (GCASAR), Agricultural Research Organization, Mobile Post Negev 2, 85280, Israel

⁽²⁾ICL Specialty Fertilizers, Israel

*Corresponding author: uri4@volcani.agri.gov.il

of damage due to over-fertilization and enables the application of polyhalite as a slow-release substance.

Keywords: Calcium; fertilizer; magnesium; polyhalite; potassium; sulfur.

Introduction

Polyhalite gained strong interest during the early 1930's as a potassium (K) fertilizer or a source of sulfate of potash (SOP) (Mansfield and Lang, 1929; Fraps, 1932). However, the interest vanished after the discovery of muriate of potash (MOP) in vast quantities, making the industry move completely to MOP (Lazenby, 2012). Since then, polyhalite has not been commercially available as a fertilizer, and consequently there is little recent published information about its performance as a fertilizer for crop production. In recent years, there have been three major reasons why the potassium fertilizer industry is shifting back, while polyhalite is emerging as a potential fertilizer source. First, the dramatic price increase of MOP has resulted in significant economic incentives for alternative K fertilizers. The second reason is the emerging need for sulfur (S) fertilization to optimize crop yield and quality (Khan *et al.*, 2005; Haneklaus *et al.*, 2008), a consequence of the prompt decline in atmospheric S concentration due to changing regulations to reduce industrial pollution (Kovar and Grant, 2011). The recent development of significant minable deposits of high quality polyhalite in the United Kingdom is the third. ICL Fertilizers currently mines polyhalite from a portion of the Zechstein deposits in the UK and is marketing polyhalite fertilizer under the product name Polysulphate® with a published analysis of 14% K₂O, 48% SO₃, 6% MgO, and 17% CaO (Imas, 2017).

Solubility is an important fertilizer property, and it varies considerably between fertilizers. Solubility affects nutrient release rates and therefore nutrient availability to plants, potential for losses due to leaching, runoff, and volatilization, and their use in liquid fertilizers. The solubility threshold of MOP, 344 g L⁻¹, is approximately three times greater than for SOP (120 g L⁻¹) (IPNI, 2010a, b). Barbarick (1991) stated that polyhalite was less water soluble than more conventional fertilizer sources. That study suggests that the behavior of nutrients after polyhalite was applied to soil may be different from its behaviour in water, although polyhalite nutrient release rates in soil are relatively unknown. Barbier *et al.* (2017) characterized a polyhalite fertilizer (POLY4, Sirius) in terms of total elemental content, solubility in water, salt index, and mobility in soil compared with other potassium based fertilizers.

Practical examinations of polyhalite in recent years have demonstrated significant advantages for a broad number of crops (PVFCCo, 2016a, b; Satisha and Ganeshamurthy, 2016; Tam *et al.*, 2016; Vale and Sérgio, 2017; Bernardi *et al.*, 2018; Melgar

et al., 2018; Tien *et al.*, 2018; Eryuce *et al.*, 2019). Nevertheless, there have been field observations that granules remain visible in the field for some time after application, raising doubts regarding nutrient availability following application of this fertilizer. The objective of the present study was therefore to characterize solubility under laboratory as well as field conditions, focusing on the different nutrients comprising this fertilizer.

Materials and methods

The work was divided into two stages: a laboratory observation and a field experiment.

Laboratory observation

Amounts of 9, 18 and 27 g of polyhalite were dissolved in beakers containing 1 liter of tap water, and stirred with a magnetic stirrer for 24 hours. Tap water, and not distilled water, was used as the field experiment also used tap water with similar qualities. The concentrations of Ca, Mg and K were measured in the solution.

Field experiment

In a field at the western Negev in Israel (sandy soil), 0.5 x 0.5 m agryl sheets were placed and fixed to the soil with hooks (Fig. 1). The sheets were covered with a layer (1-2 cm) of dry, sieved soil (<2 mm). A wooden 0.3 x 0.3 m frame was placed at the center of each sheet. Granular polyhalite was broadcast over the soil, within the outline of the wooden frame, at 9, 18 and 27 g sheet⁻¹ (equivalent to 1,000, 2,000 and 3,000 kg ha⁻¹), respectively (Fig. 2). The wooden frame was removed after application.

Two soil samples (<2 mm) were taken for analysis, to assess soil Ca, Mg, K and S contribution, without polyhalite application.

A pre-installed sprinkler irrigation system applied water every five days at rates of 10 mm h⁻¹, 35 mm per application, including rainfall events. This irrigation scheme was adopted in order to avoid runoff. Rainfall was monitored in a nearby (200 m) standard



Fig. 1. Agryl sheet installation, and soil application, in the field experiment. Source: Authors.

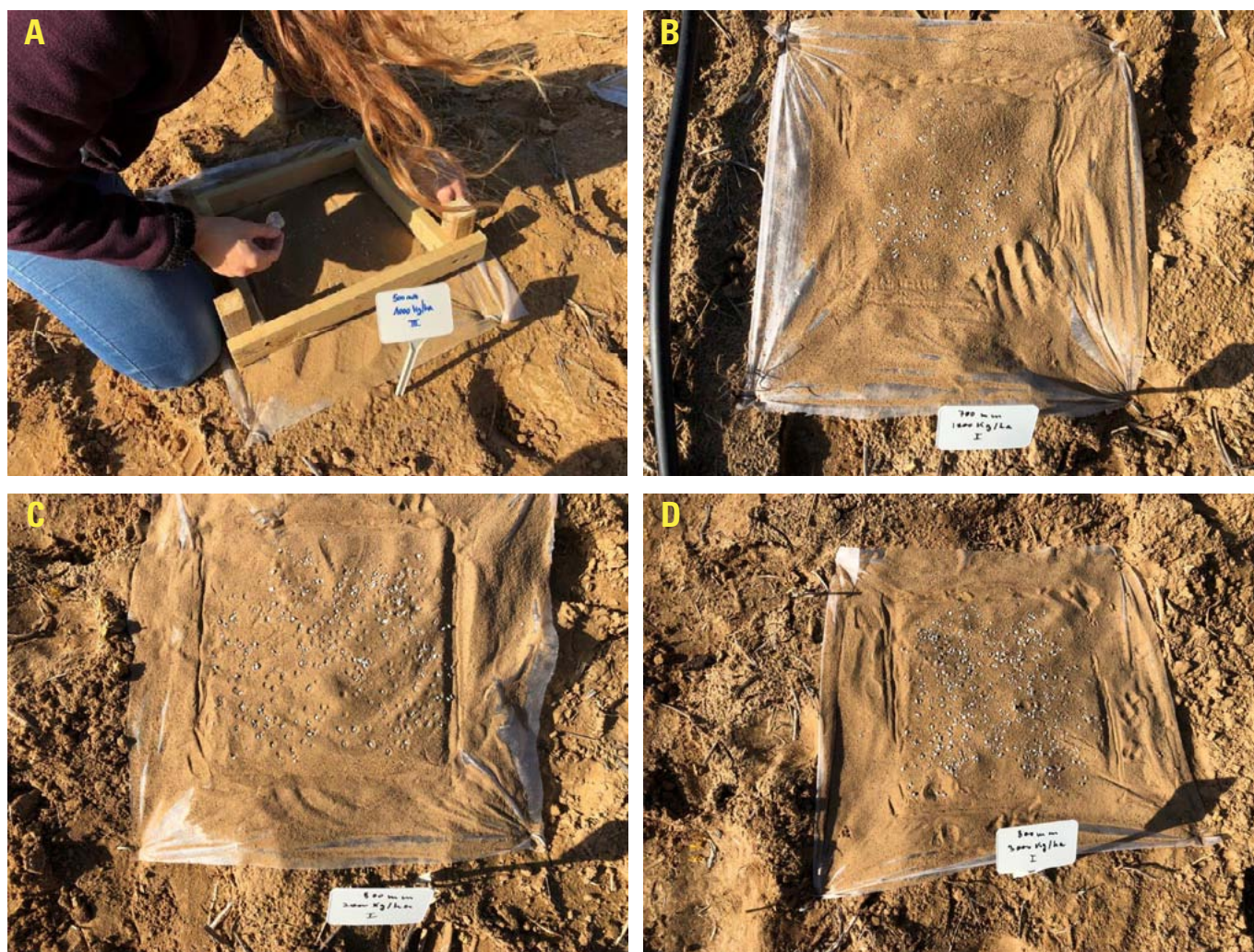


Fig. 2. Polyhalite application onto the agryl sheet, within the wooden frame (A); polyhalite application rates of 9 (B), 18 (C), and 27 (D) g per frame, equivalent to 1,000, 2,000, and 3,000 kg ha⁻¹, respectively. *Source:* Authors.

meteorological station. Weed control was carried out regularly using herbicides.

Following about 300 mm of accumulated water application, one set (three polyhalite application levels in four replicates) of agryl sheets were collected. The soil + residual polyhalite from each sheet was dried, weighed and homogenized using a soil grinder. A 25 g sample of soil homogenate was mixed with 500 ml distilled water (soil:water ratio 1:20) and shaken for 24 hours. The suspension was filtered and the concentrations of Ca, Mg, K, and S were determined, followed by calculation of their residual amounts and, subsequently, percentage of the initial application. This procedure was repeated following each interval of 100 mm water application, up to 800 mm (six sampling events).

The reference soil samples were analyzed using the same

methodology. The residual amounts of each element for each treatment were calculated, after subtracting the soil's contribution.

Statistical analysis

The field experiment was carried out in a randomized block design with four replicates. Each block comprised six replicates of three polyhalite application rates for the six accumulated water application rates. One-way ANOVA was practiced using JMP 13.0.

Results and discussion

Laboratory observations

The results of the laboratory observation are presented in Fig. 3, where the measured solubility values of Mg, Ca, and K were scattered against the assumed 100% hypothetical solubility of each element in polyhalite.

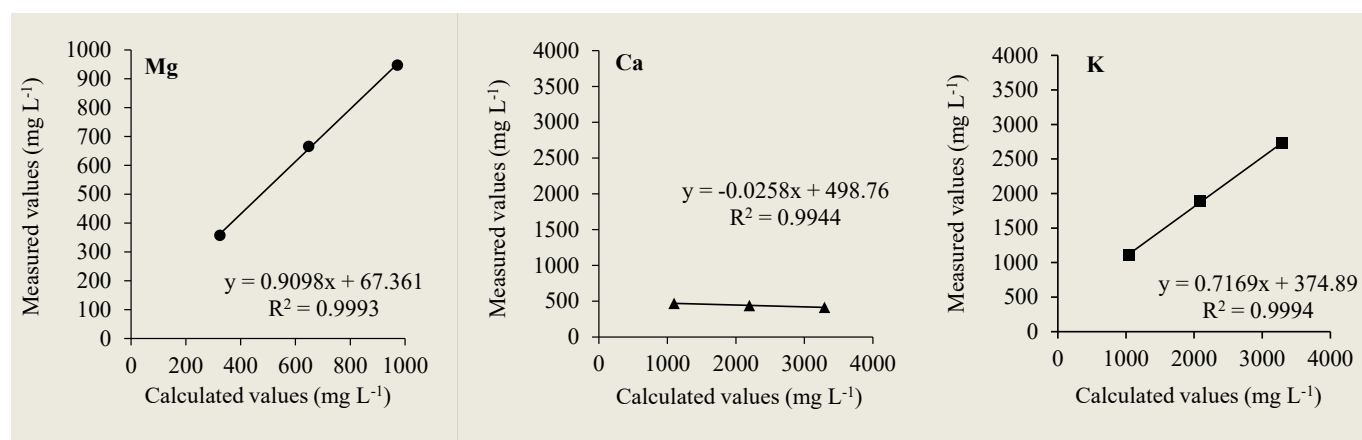


Fig. 3. Polyhalite's measured vs. expected (calculated) dissolution rates of Mg, Ca, and K in a laboratory observation. For a detailed description, please see the 'Materials and methods' section.

In agreement with earlier work (Barbarick, 1989), preliminary studies carried out within the framework of the CFPN in 2016 revealed a differential dissolution of polyhalite constituents. This differential dissolution was confirmed in the present laboratory test (Fig. 3). The Mg fraction of the fertilizer dissolved completely, even at the highest polyhalite concentration tested, 27 g L⁻¹. The K dissolved completely at the lowest fertilizer concentration (9 g L⁻¹), however the dissolution rate decreased with the rising concentration of polyhalite in the solution. Yet, most of the K in the fertilizer, about 72%, dissolved well. On the other hand, very little Ca dissolved at the lowest fertilizer application rate, and this decreased further from 470 to 415 mg L⁻¹ with the rising polyhalite concentration (Fig. 3). The Ca in polyhalite is in fact comprised mostly of gypsum (22.6%), a low-solubility salt with a saturation threshold of 1.5 g L⁻¹. Mixing 9 g of polyhalite in one liter of water yields 2.03 g L⁻¹ of CaSO₄ (gypsum), already above the maximum solubility threshold. Thus, adding more polyhalite to the solution will cause no further increase in Ca concentration, as it would immediately precipitate.

These results should be interpreted according to the methodology of the solubility test. In solubility tests where the draining water constantly removes the

dissolved Ca, more Ca is dissolved from the polyhalite crystals. Still, the CaSO₄ dissolution rate is much slower than K₂SO₄ and MgSO₄, the saturation thresholds of which are two orders of magnitude higher at 351 and 120 g L⁻¹, respectively.

In accordance with our results, Barbier *et al.* (2017) found that solubility of natural polyhalite, when determined using the "simple solubility" method, showed a solubility range at 25°C of 11.9-17.3 g L⁻¹ and a slightly higher solubility for calcined polyhalite, with a range of 18.3-21.8 g L⁻¹. It is worth mentioning that significant differences might emerge from differing methodologies. Nevertheless, all measurements show that the solubility of polyhalite is much lower than reported values for other K source fertilizers such as MOP and SOP (IPNI, 2010a, b).

Barbier *et al.* (2017) also concluded that while polyhalite has a lower solubility limit in water than other K source fertilizers, when it is applied at rates below its solubility limit, it should provide more than enough Ca, Mg, K and S for plant growth.

Field experiment

Mineral concentrations decreased with the increasing amounts of applied water (Fig. 4). For all polyhalite constituents, most of the dissolution occurred during

the initial 300 mm of water application. For Ca, a residual value of about 20-25% was measured after the initial 300 mm application, followed by a much slower decline during the 300-800 mm water application. At the two lower polyhalite application levels (1,000 and 2,000 kg ha⁻¹), the percentage of residual Ca remained more or less constant at about 20%, regardless of the amount of water applied, whereas it decreased a bit further at the highest polyhalite dose (3,000 kg ha⁻¹) (Fig. 4). A significantly large portion of the Mg in the applied polyhalite, 94.5%, dissolved during the first 300 mm application of water. The residual Mg percentage remained more or less constant afterwards, regardless of the amount of applied water (Fig. 4).

The residual K was very close to zero after the application of 300 mm water at both upper polyhalite application rates, 2,000 and 3,000 kg ha⁻¹, and decreased slowly but consistently to the negative range as accumulated water increased (Fig. 4). At the lowest polyhalite rate (1,000 kg ha⁻¹), negative residual values were obtained even earlier, at 300 mm of applied water. Negative values provide a strong indication that the soil contributed K to the samples, elevating the recovery above the applied amount. Percentage of residual S reached 20-26% after application of 300 mm water, and decreased steadily

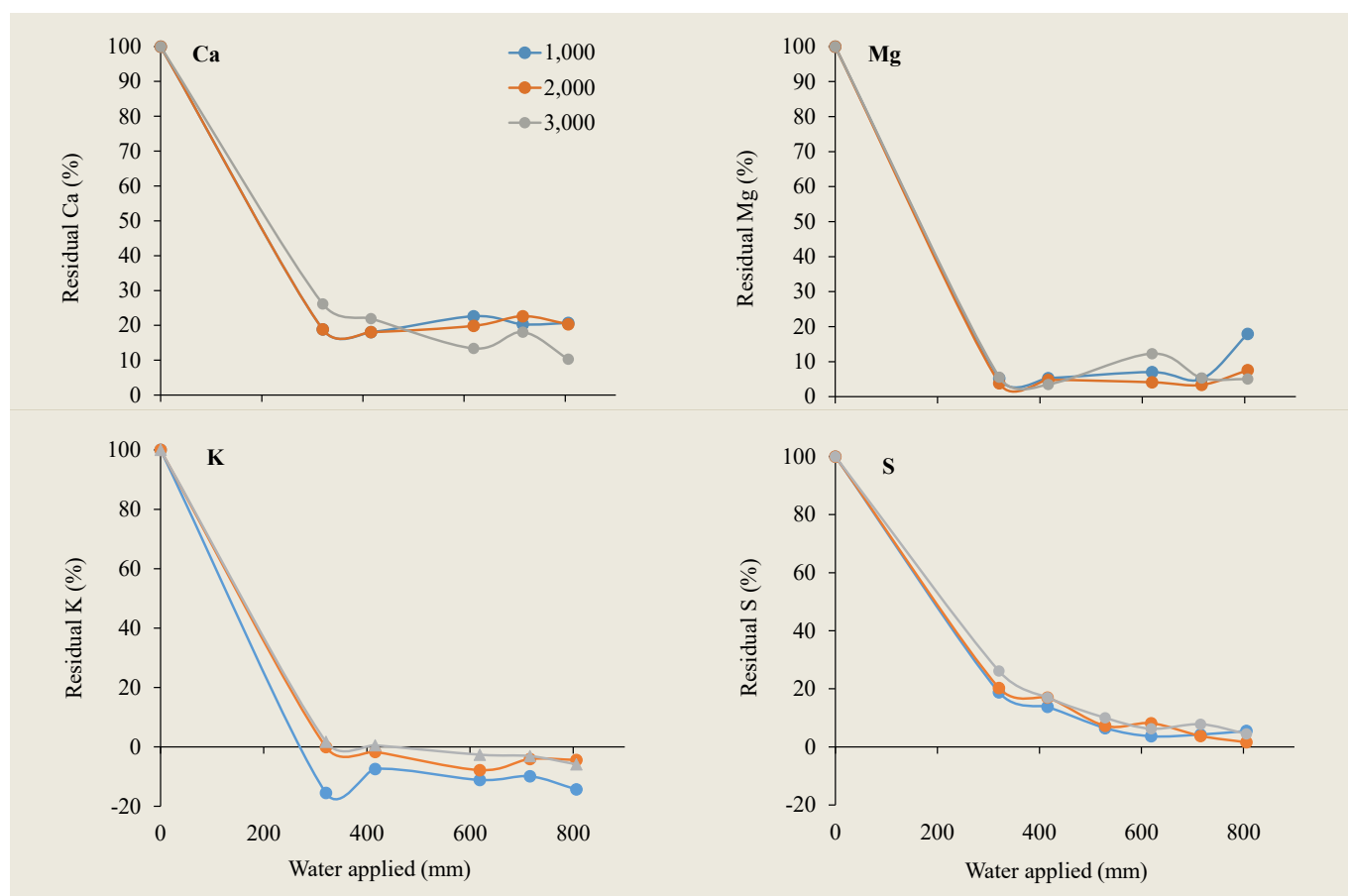


Fig. 4. Residual percentage of the polyhalite elements Ca, Mg, K, and S from the field experiment. Polyhalite was applied at rates equivalent to 1,000, 2,000, and 3,000 kg ha⁻¹. Measurements took place at accumulated water applications between 300 and 800 mm.

in all polyhalite treatments, reaching a value of 1.5-5.5% once 800 mm had been applied (Fig. 4).

The results of the field experiment are in agreement with the results of the laboratory observation, where most of the Ca, Mg, K, and S were released after 300 mm of accumulated water application, and the dissolution rate of Ca in polyhalite was slowest. The disintegration pattern of the polyhalite granule and its partial dissolution in the field trial are demonstrated in Fig. 5.

Nevertheless, due to the complex composition of polyhalite, there are plenty of potential chemical interactions with the solid and liquid soil phases, as well as with their interphase. Under field conditions, what occurs to the polyhalite constituents is determined by these interactions, not just by the solubility thresholds. A simplified qualitative demonstration of the complexity of the field experiment is shown in Table 1, with respect to each element in polyhalite.

It appears that the best indicator of polyhalite dissolution would

be S. Sulfur concentration in the irrigation water is negligible, it is not adsorbed to the solid soil phase, and its soluble amount in the soil solution is very low, hence the major contribution of S is from polyhalite. As mentioned above, the low solubility of gypsum (CaSO₄), an integral component of polyhalite, might explain the relatively high S residue following water application of 300 mm (Fig. 4). Calcium, in contrast, interacts strongly with calcareous soils, in addition to adhesion to soil particles. Thus, Ca adhesion to the thin soil layer might explain the relatively high and constant Ca residues found, in spite of considerably high precipitation rates on the agryl sheets. In a similar way, but to a considerably lesser extent, the weaker Mg interactions would explain its significantly smaller but constant residue under the field conditions in the present study (Fig. 4).

Potassium, however, is the most important nutrient in polyhalite, and the most soluble one as well. On the other hand, K⁺ cations interact with the soil's solid-liquid interphase, with significant dependence on soil texture (particle size) and pH. Furthermore, soluble K might be incorporated into certain clay particles on



Fig. 5. Polyhalite disintegration under field conditions at an application rate of 1,000 kg ha⁻¹ following accumulated water application of 530 mm (left); and at 3,000 kg ha⁻¹ following 400 mm of water (right). *Source:* Authors.

Table 1. Qualitative demonstration of the potential interactions between the soil and polyhalite constituents.

Element	Source				
	Irrigation water	CaCO ₃	Adsorbed	Soluble	Polyhalite
Ca	+	++++	++	++	+++
Mg	-	++	++	++	+
K	-	-	+++	++	+++
S	-	-	-	+	++++

Note: - no interaction; + very weak interaction; ++ weak interaction; +++ medium interaction; ++++ strong interaction.

K-poor soils, and vice versa; it might emerge from soil particles to the liquid soil phase (Zörb *et al.*, 2014). In the present study, K residues from the agryl sheets diminished after accumulating only 300 mm of water (Fig. 4). This may indicate that the K fraction in polyhalite is dissolved quite easily and rapidly. However, in terms of rain or irrigation in semiarid regions, 300 mm of water when applied gradually (as done here), can suffice an entire cropping season. Therefore, the starting point and resolution of sampling in the present field experiment did not allow for adequate discernment of the polyhalite K performance.

The interactions of the various constituent minerals in polyhalite with the local soil determine the ratio between leaching and retention, and hence, beyond solubility, define nutrient availability to the crop (Barbier *et al.*, 2017).

Conclusions

An optimal fertilizer should display a solubility level that would accurately match nutrient availability with current crop requirements and, at the same time, retain sufficient nutrient residues for as many subsequent opportunities as possible

(rainfall events or scheduled irrigations). Supported by previous studies (Barbarick, 1989; Barbier *et al.*, 2017), the present study demonstrated that polyhalite dissolution in water takes longer and requires larger volumes of water compared to other soluble fertilizers. This advantage reduces possible risks of damage due to over-fertilization and enables the application of polyhalite as a slow-release substance. Nevertheless, the slow-release impact would be largely

dependent on interactions with the local soil properties and on soil wetting regimes.

Acknowledgements

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The paper "Solubility of Granular Polyhalite under Laboratory and Field Conditions" also appears on the [IPI website](#).