

Polyhalite as a multi nutrient fertilizer – potassium, magnesium, calcium and sulfate

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ABSTRACT

Polyhalite is a hydrated sulfate of potassium (K), calcium (Ca) and magnesium (Mg) with the formula: $K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$. The main objective of the present study was to investigate and compare the efficiency of polyhalite as a fertilizer supplying K, Ca, Mg and sulfur (S) relative to equivalent soluble salts. The specific objectives were to investigate: 1. The release and transport of Ca, Mg, K and S in soil; 2. Uptake of these minerals by wheat plants and 3. Biomass production of wheat plants. To meet these objectives, two pot experiments (20 l pots filled with dune sand) were conducted in which the effects of four doses of polyhalite (0, 500, 1,500 and 2,500 kg/ha) and one dose of Ca, Mg and K sulfate salts (equivalent to the 1500 kg/ha polyhalite dose) were investigated. In a third experiment, residual effects of the fertilizers were studied using the pots from the first experiment. Different leaching fractions were used in the experiments (30% in the first one and 7–10% in the second and third experiments), to investigate the effect of water management on mineral transportation in the soil and plant uptake. Polyhalite was found to be a more efficient fertilizer for supplying K, Ca, Mg and S relative to equivalent soluble salts. To meet the plant required ratios for Ca, Mg and K, the polyhalite dose should be applied accordingly to provide sufficient Ca and Mg, and additional fertilizers should be used as a source of K. Transport and leaching of Ca, Mg, K and S in soil following polyhalite application was lower than following the application of the equivalent sulfate salts. The residual effect of polyhalite fertilizer on the subsequently grown crop was higher than the effect from the equivalent sulfate salts, especially regarding Ca, Mg and S. Irrigation management, as determined by the leaching fraction, has a strong impact on the efficiency of polyhalite as a source of K, Ca, Mg and S for plant nutrition.

KEYWORDS

fertilization; polyhalite; potassium; calcium; magnesium; sulfate

Introduction

Polysulphate fertilizer is the trade mark of the natural mineral polyhalite and is produced by ICL (North York Moors National Park, UK) at the Boulby mine in Cleveland, UK. The mineral is a hydrated sulfate of potassium (K), calcium (Ca) and magnesium (Mg) with the formula: $K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$ (Tiwari *et al.*, 2015). The mineral was identified in a number of locations including Cleveland (UK), Poland, Rajasthan (India), Texas (New Mexico) and Russia (Frafts, 1932; Lepeshkov & Shaposhnikova 1958; Tiwari *et al.*, 2015). The mine in Cleveland is the first operational polyhalite mine in the world. In this mine, the polyhalite mineral seam is at a depth of about 1,250 m, approximately 170 m below the potash seam. Polyhalite is a single complex crystal (triclinic, pseudo-orthorhombic). It usually appears as fibrous, massive pieces and rarely appears as tabular

crystals. It is water soluble with precipitation of gypsum and syngenite ($K_2Ca(SO_4)_2 \cdot 2H_2O$) which is also soluble, leaving behind a precipitate of gypsum.

The purity of the Polysulphate product is very high (95% polyhalite) with <5% sodium chloride (NaCl) and traces of boron (B) and iron (Fe) at 300 and 100 ppm, respectively. The declared minimum analysis of polyhalite for S, K, Mg and Ca is 48% sulfur trioxide (SO_3), 14% potassium oxide (K_2O), 6% magnesium oxide (MgO) and 17% calcium oxide (CaO), respectively. After mining, the material is treated to produce different granule sizes (ICL Fertilizers, Cleveland, UK).

Polyhalite, which may serve as a suitable fertilizer to supply four nutrients, is less water soluble than the more conventional sources and may conceivably provide a slower release of nutrients (Barbarick, 1991). A number of studies comparing polyhalite to other K and Mg fertilizers have shown that polyhalite is at least as effective as

potassium sulfate (K_2SO_4) as a source of K, and at least as effective as potassium chloride (KCl) plus magnesium sulfate ($MgSO_4$) as a source of K and Mg (Barbarick, 1991).

In pot experiments with corn (*Zea mays*, L.) and sorghum (*Sorghum bicolor*, L.), Fraps (1932) showed that polyhalite is suitable for use as a potash fertilizer when ground to pass through a 20 mesh sieve. He showed that polyhalite provided a 96% equivalency of K availability compared to KCl and K_2SO_4 fertilizers. Similar results were found for potato (*Solanum tuberosum*, L.), flax (*Linum usitatissimum*, L.) and beets (*Beta vulgaris*, L.) (Panitkin, 1967; Lepeshkov & Shoposhnikova, 1958). Barbarick (1991) was the first to compare polyhalite with the same rates of S, K, Ca and Mg sulfate salts.

Field and pot trials recently carried out in the UK on Cleveland polyhalite products (done by Cleveland Potash Ltd.) demonstrated that the K, Mg and S nutrients in polyhalite are as available and effective as those from established standard fertilizer sources (K_2SO_4 , KCl, $MgSO_4$ and $CaSO_4$) (Tiwari *et al.*, 2015). The molecular ratios of K : Ca : Mg : SO_4 are 2:2:1:4, respectively and the weight ratios of these nutrients are 3.2:3.3:1:5.3, respectively. The desired ratios in fertigation are 5:2:1:1.5, respectively. This means that if, for example, Mg is maintained at the optimal level, there will be a K deficiency and over-fertilization with Ca and SO_4 .

As polyhalite is not a mixture of salts but a single crystal, it would be expected that its constituents would be released into solution proportionally, and indeed this was found to be the case (Barbarick, 1991). This behavior is expected to be similar in polyhalite-soil systems. However, after solubilization, each constituent will interact with the soil differently and be affected by soil properties. For example, the adsorption strength of K^+ to mineral soil surfaces is lower than Ca^{2+} and Mg^{2+} and the total adsorption capacity increases as the clay mineral (e.g. montmorillonite) content in the soil increases (Feigenbaum *et al.*, 1991; Bar-Tal *et al.*, 1991a; Bar-Tal *et al.*, 1991b). Unlike the aforementioned cations, sulfate is an anion and has a relatively low interaction with mineral surfaces of the soil. Moreover, chemical interactions in the soil solution between the constituents themselves (Ca and SO_4) and with other soluble elements, affect the constituents' free concentrations. These processes affect nutrient mobility in the soil profile and thus, their availability to plants (Nye & Tinker, 1977; Addiscott & Wagenet, 1985; Barber, 1995; Bar-Tal *et al.*, 1991a; Bar-Tal *et al.*, 1991b; Kolahchi & Jalali, 2006).

The use of polyhalite as a fertilizer in comparison to the equivalent soluble, commercial salts has been studied in a number of experiments. Barbarick (1991) found a better yield response of sorghum-sudangrass to increasing levels of polyhalite when compared to the same application rate of soluble salts. 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, increased quality and higher yields were obtained when polyhalite was used as a source for Ca, Mg and S compared to fertilization with the equivalent soluble salts (Satisha & Ganeshamurthy, 2016).

An important benefit of using polyhalite as a fertilizer, when compared to the equivalent salts, is the rate at which it releases minerals to the soil profile. The leaching of Ca, Mg, K and S from polyhalite appears to be slower than the leaching of these ions from the commonly used soluble salts (Barbarick, 1991; Vale, 2016). In this regard, polyhalite has the potential for longer-term effects compared to commercial fertilizers. The assumption was that uptake efficiency by wheat plants of Ca, K, Mg and SO_4 would be higher when the nutrients were applied as polyhalite than as their separate sulfate salts.

The main objective of the present study was to investigate the efficiency of polyhalite as a fertilizer supplying K, Ca, Mg and S relative to equivalent soluble salts. The specific objectives were to investigate the effect of fertilization with different doses of polyhalite relative to equivalent soluble salts on: 1. The release and transport of Ca, Mg, K and S in soil; 2. Uptake of these minerals by wheat plants and 3. Biomass production of wheat plants.

Materials and methods

2015 experiment

The experiment was carried out in 20 l pots filled with dune sand. At the bottom of each pot, a rockwool sleeve was fitted to ensure water suction and avoid water logging (Ben-Gal and Shani, 2002). Each pot was leached with 60 l (three pot volumes) of desalinated water to remove all salts, although low concentrations of some salts remained e.g. Ca and Mg, 10 and 1 mg/l, respectively. After leaching, the upper 5–7 cm layer of the soil in each pot was mixed with powder

Polysulphate (produced by ICL at Boulby mine in the UK) or the equivalent amounts of sulfate salts of K, Ca and Mg, which served as a fertilizer control. The application rates are detailed in Table 1. Each fertilization treatment had four replicates.

Wheat seeds (*Triticum aestivum* cv. Bar Nir) were planted on 18.6.15 and thinned out after germination to 20 plants/pot. Irrigation solutions were prepared with desalinated water in 60 l containers and contained 50 mg nitrogen (N)/l, 10 mg phosphorus (P)/l, 0.3 mg B/l, 1 mg Fe/l, 0.5 mg manganese (Mn)/l, 0.25 mg zinc (Zn)/l, 0.04 mg copper (Cu)/l, and 0.03 mg molybdenum (Mo)/l. The source materials for this solution were mono ammonium phosphate, ammonium nitrate and a mix of microelement chelates (Koratin, Chemicals and Fertilizers, Ltd, Israel). The irrigation system consisted of two 1 l/h drippers per pot. Irrigation was adjusted to plant water consumption. The leaching fraction was maintained at about 30%.

The plants were harvested after earing on 26.7.15 and the total fresh and dry matter (DM) yields per pot were determined. A subsample was taken for plant analysis of N, P, K, Ca, Mg, and S concentrations. The total duration of this experiment was 38 days. At the end of the experiment, soil samples were taken from the upper 5–7 cm of the soil and analyzed for K, Ca, Mg and S concentrations, using a 1:1 soil:water extraction.

2016 experiments

The 2016 experiment had two sets – the first set was an exact repetition of the 2015 experiment, referred to as the 2016 experiment hereafter. The other set repeated the experiment with the 2015 pots, without any additional application of polyhalite or equivalent sulfate salts to study the residual effect of polyhalite at different levels and its equivalent in sulfate salts. This set will be referred to as the 2015R experiment hereafter. The 2016 experiments started on 17.1.16 and ended on 7.3.16 – lasting a total of 49 days. The leaching fraction was maintained at 7–10% in both experiments. Leachate monitoring and analyses were conducted as in the 2015 experiment. On completion of both experiments, the plant and soil analyses were conducted as per the 2015 experiment.

Measurements

In all three experiments the leachate was collected and its volume and electrical conductivity (EC) were mea-

sured. An automated photometric analyzer (Gallery Plus, Thermo Scientific) was used to analyze the solutions for NO_3 and PO_4 whilst K, Ca and Mg were measured using an atomic absorption spectrophotometer (model AAnalyst 800, Perkin Elmer, Waltham, MA.). S concentrations were measured with inductively coupled plasma optical emission spectrometry (ICP-OES) (Spectro Arcox, Spectro, Germany).

All plant parts were washed with distilled water, dried in a ventilated oven at 60°C, weighed for DM, and ground and stored pending chemical analysis. Total N, P and K concentrations were determined following digestion with sulfuric acid and peroxide (Snell and Snell, 1949). N and P levels were measured using an automated photometric analyzer (Gallery Plus, Thermo Scientific), and K by an atomic absorption spectrophotometer (AAnalyst 800, Perkin Elmer, Waltham, MA). Total Ca and Mg concentrations were determined following digestion with nitric acid and perchlorate by the following procedure. 100 mg of dried and ground plant material digested with 4 ml of concentrated nitric acid (HNO_3) in tubes for one hour at 190°C until having a clear and non-colored solution. Then 2 ml of perchloric acid (HClO_4) were added and the tubes were heat at 230°C for one hour. After cooling the tubes to room temperature the digest was diluted with distilled water to final volume of 25 ml. Ca and Mg concentrations were measured using an atomic absorption spectrophotometer (AAnalyst 800, Perkin Elmer, Waltham, MA) and S by ICP-OES (Spectro Arcox, Spectro, Germany) following digestion with nitric acid and perchlorate.

Statistical analysis

Statistical analyses were carried out using JMP12 Software (SAS Institute Inc., NC, US). Following the randomized complete design, a one-way analysis of variance was carried out. The Tukey-Kramer HSD test was used to compare the paired means of the plant part weights, their nutrient concentrations and the various yield parameter values. Differences with a probability larger than 95% were deemed significant.

Results

Element composition in the leachate and soil

The EC values and K, Ca, Mg and S concentrations in the leachate during plant growth are presented in Fig. 1 for the three experiments. Similar trends in the

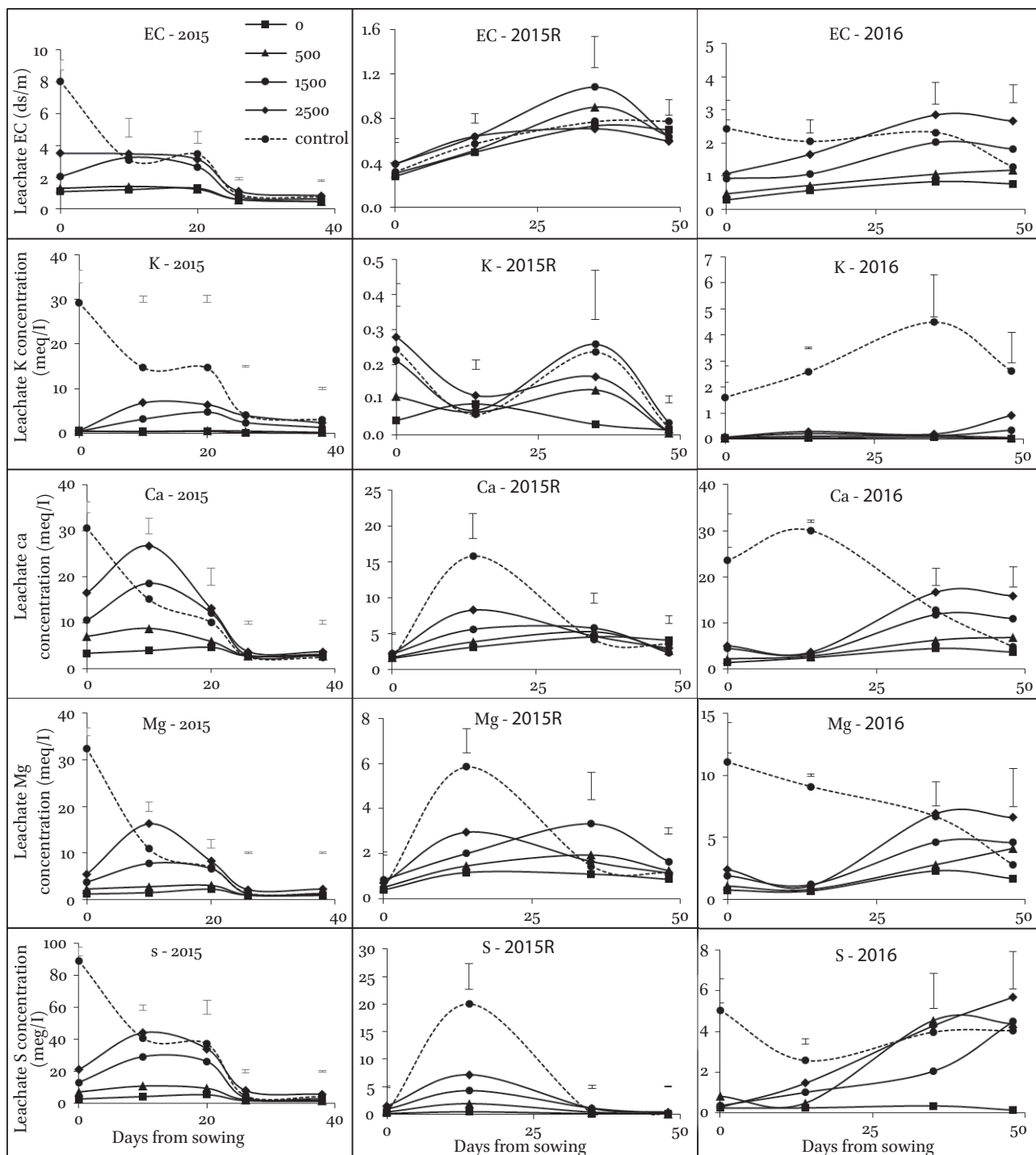


Figure 1. EC values and K, Ca, Mg and S concentrations in the leachate along the growth periods at different levels (kg/ha) of polyhalite application and control fertilizers equivalent to 1,500 kg/ha. The vertical bars represent the maximum SE value for each sampling date.

effects of the treatments on the change of EC and concentrations of these elements over time can be seen in each experiment. ECs and element concentrations increased as the dose of polyhalite increased. At the start of the 2015 and 2016 experiments, the ECs and mineral concentrations of the leachate in the control

fertilizer were higher than in the equivalent polyhalite dose, indicating its higher solubility over polyhalite. Higher EC and mineral concentration values were obtained in the leachates of the 2015 experiment than the 2016 experiment due to the higher leaching fraction (30% and 10% respectively). The use of different

leaching fractions led to varying ECs and mineral concentrations with time between the two experiments.

In the 2015 experiment, concentration changes over time differed for the three cations (K, Ca and Mg) in the leachate (Fig. 1). As sulfate was the only counter anion in both the polyhalite mineral and the control fertilizer, its concentration in the leachate was close to the sum of these cations and in general, its change with time was similar to that of the ECs. Concentration of the three cations from polyphosphate reached a peak during the second leachate sampling, then decreased reaching very low concentrations toward the end of the experiment.

In general, Ca concentrations from the polyhalite were much higher than K and Mg in accordance with its higher content in the mineral. However, in the control fertilizer, equivalent concentrations of K, Ca and Mg were obtained despite the differences in their application (Table 1). Thus, K concentration from the control fertilizer was much higher than from the equivalent polyhalite dose. In the first leachate sampling, Ca and Mg concentrations from the control fertilizer were much higher than from the equivalent polyhalite dose, however, later samples demonstrated similar concentrations of Ca and Mg from the two sources.

In the 2016 experiment, K concentrations in the leachate under all polyhalite doses were extremely low relative to the 2015 experiment, and much lower than the Ca and Mg concentrations in 2016. K concentrations in the leachate of the control fertilizer were much higher than that of the polyhalite treatments; the concentrations increased with time from 1.5 meq/l in the first sample to a peak of 4.5 meq/l in the third sample then decreased to 2.3 meq/l in the last sample. Unlike the 2015 experiment, Ca, Mg and S concentrations in the beginning of 2016 experiment were very low and increased gradually to maximum values in the end of the experiment. Thus a considerable gap in Ca, Mg and S concentrations between the treatments was observed in the last leachate sampling. The

concentrations of Ca, Mg and S in the leachate of the control fertilizer were much higher than that of the polyhalite treatments and the decrease in their concentrations over time was more moderate than in 2015 experiment (Fig. 1).

The residual effects of the polyhalite and control fertilizer on leachate composition were investigated in 2015R experiment (Fig. 1). In this experiment, ion concentrations from the polyhalite and control fertilizer were much lower than in the previous experiment. Therefore, the relative contribution of other added fertilizers and salts in the water to the EC was higher than in the 2015 and 2016 experiments. Consequently, the EC does not reflect the sum of the K, Ca and Mg concentrations from the polyhalite and control fertilizer treatments. The cations behaved differently with leachate K concentration extremely low throughout the experiment and under all treatments. Ca and Mg concentrations however were much higher than K concentrations, with both reaching peak values during the second leachate sampling. S concentration was similar to the sum of the Ca and Mg concentrations throughout the experiment. In the control fertilizer treatment the highest Ca, Mg and S concentrations (15, 6, and 20 meq/l) were obtained in the second leachate sampling and were much higher than under the equivalent dose of polyhalite.

The residual concentrations of K, Ca and Mg in a soil extract of the top 0–5 cm at the end of each experiment are presented in Table 2. In general, the residual concentrations of these elements increased with increasing polyhalite dose, however, the residual effect on Ca concentration was much higher than on Mg, K and S. For example in 2015 in the 1,500 kg/ha dose, the equivalent ratio between the elements Ca:Mg:K:S was 12.2:1.7:1.0:12.6, whilst the equivalent ratio in polyhalite is 2:1:1:4. No consistent differences between the residual effects of the control fertilizer and the equivalent polyhalite treatments on the different elements were obtained. In terms of the treatments residual effects

Table 1. Details of applied treatments: polyhalite and equivalent soluble salts (control fertilizer).

Treatment	Polyhalite kg/ha (meq/pot)	Equivalent salts	K	Ca	Mg	S
				kg/ha (meq/pot)		
PS0	–	–	–	–	–	–
PS500	500 (3.1)	–	58.5 (9.3)	61 (18.9)	18 (9.2)	100 (38.8)
PS1500	1,500 (9.3)	–	175.5 (27.9)	183 (56.7)	54 (27.6)	300 (116.4)
PS2500	2,500 (15.5)	–	292.5 (46.5)	305 (94.5)	90 (46)	500 (194)
Control fertilizer	–	K ₂ SO ₄ CaSO ₄ MgSO ₄	175.5 (27.9)	183 (56.7)	54 (27.6)	300 (116.4)

on element concentration, in general, no considerable differences were obtained between the 2015 and 2016 experiments – except for Ca in the 1,500 and 2,500 kg/ha treatments. In 2015R, the mineral concentrations dropped dramatically relative to the 2015 experiment.

Dry matter production and nutrient uptake by wheat

DM production by wheat plants during all three experiments is presented in Fig. 2. DM production levels were lowest during the 2015 experiment which is most likely due to the reduced period of time allowed for plant growth and the unfavorable environmental conditions. The 2015 experiment lasted only 38 days and was conducted during the summer season, which was very hot. Conversely, the 2015R and 2016 experiments lasted 49 days and were conducted during the moderate weather conditions of the winter. Hence, plant growth and DM production was greater during the 2015R and 2016 experiments.

DM production was significantly higher under all polyhalite doses than under nil polyhalite for the 2015R and 2016 experiments. A positive response of DM production by the plants to polyhalite application was observed in all three experiments, reaching a maximum of DM in 2015 and 2016 at 500 kg/ha, and at 1,500 kg/ha for the 2015R experiment. DM production

under the control fertilizer was significantly lower than the equivalent polyhalite treatment in 2015R, whereas no significant differences were obtained for the 2015 and 2016 experiments.

Shoot N and P concentrations were not affected by polyhalite application levels in all three experiments. Average shoot N concentration was 1.52, 1.53 and 1.30 mole/kg DM and average shoot P concentration was 0.08, 0.10 and 0.11 mole/kg DM for the 2015, 2015R and 2016 experiments, respectively. This result indicates that N and P supply were not limiting factors for biomass production in this series of experiments.

In the 2015 and 2016 experiments, shoot K concentration increased significantly with increasing application of the polyhalite fertilizer. However, following a saturation response at application level 1,500 kg/ha, no further uptake was recorded on elevating the dose to 2,500 kg/ha (Fig. 3). In the 2015R experiment, due to low residual K levels measured in the soil of the plant pots after the 2015 experiment (Table 2 and Fig. 1), no response to residual levels of polyhalite or the fertilizer control was observed.

K uptake increased with increasing polyhalite application up to 1,500 kg/ha in the three experiments (Fig. 3) and was highest in the 2016 experiment in which the highest DM production of all 3 experiments was obtained. K uptake was lower in the 2015 experiment than in the 2016 experiment due to lower DM

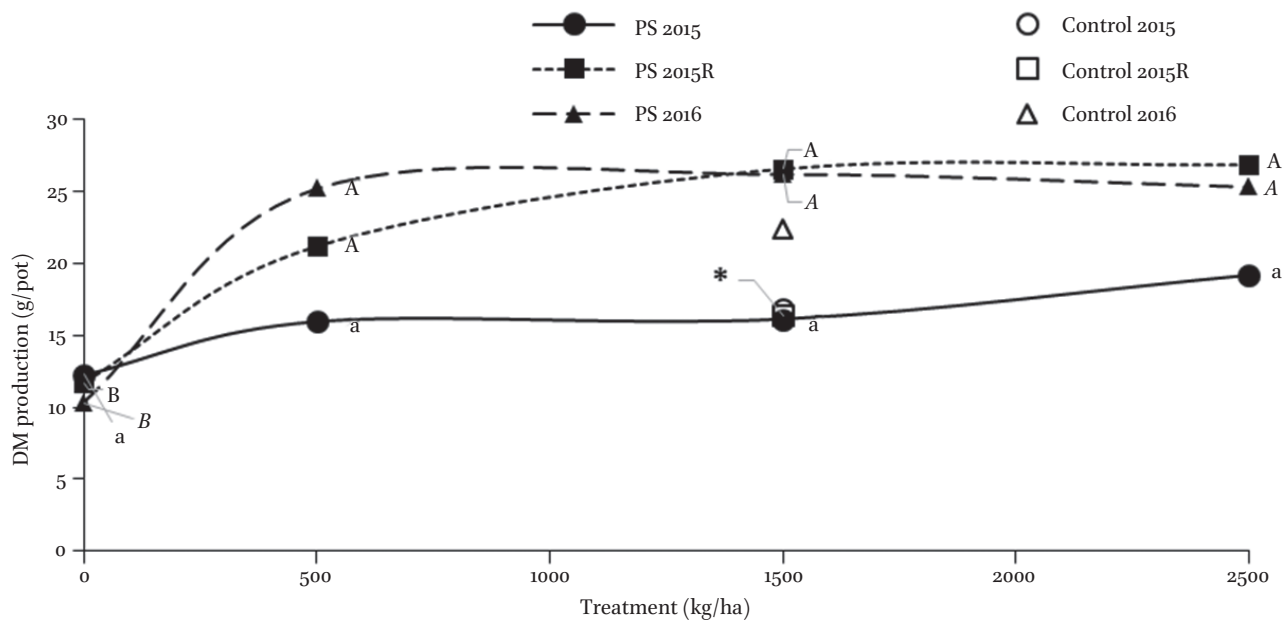


Figure 2. Response of above-ground DM production of wheat plants to different application levels of polyhalite (PS) or the fertilizer control (equivalent to 1,500 kg/ha polyhalite). Different letters indicate significant differences between treatments in each experiment, $p < 0.05$.

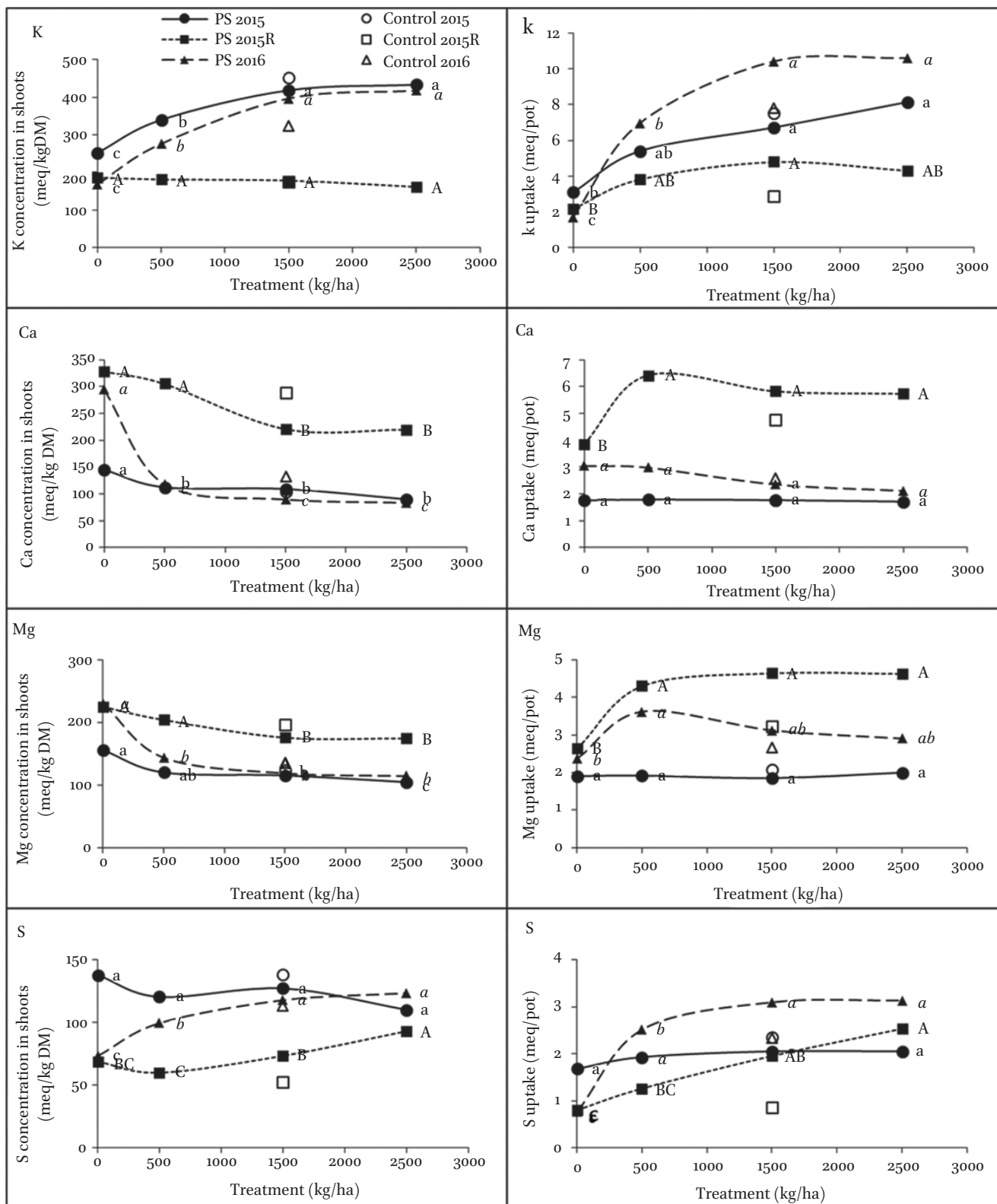


Figure 3. K, Ca, Mg and S concentrations in the DM of the aboveground wheat and the uptake of these nutrients in response to application levels of polyhalite or fertilizer control (equivalent to 1,500 kg/ha). Different letters indicate significant differences between polyhalite dose in each experiment, $p < 0.05$.

production. Extremely low K concentrations in the DM and low K uptake were observed in 2015R experiment (Fig. 3), probably due to the low residual K concentration in the soil in the end of 2015 experiment (Table 2 and Fig. 1).

In the 2015 and 2016 experiments, shoot Ca and Mg concentrations decreased with increasing polyhalite application levels, whereas their uptake increased suggesting that Ca and Mg levels are not limiting factors for biomass production. In all three experiments, the highest Ca and Mg concentrations were measured in the non-fertilized treatments. In contrast to the concentrations of Ca and Mg in plant shoots, their concentrations in the soil solution increased with increasing polyhalite application (Fig 1 and Table 2). Moreover, the highest Ca and Mg shoot concentrations were measured in the 2015R experiment, where soil Ca and Mg concentrations were lowest compared with the other two experiments (Fig. 1 and Table 2). The total amount of Ca and Mg taken up by the plants were not affected by the fertilization level in the 2015 and 2016 experiments, whereas lower uptake of both elements were obtained in the nil treatment in 2015R experiment (Fig. 3).

Sulfur concentrations in the shoots were not significantly affected by fertilization levels in the 2015 experiment, whereas a significant increase with fertilizer dose was obtained in the 2015R and 2016 experiments with maximum at 1,500 kg/ha (Fig. 3). High shoot S concentrations above 100 meq/kg were obtained in 2015 and similar values were obtained in the 2016 experiment at 1,500 and 2,500 kg/ha treatments. In the 2015R experiment, significantly lower shoot S concentrations were observed than in the other experiments, and only at the highest fertilizer dose the gap between the treatments became insignificant. No differences in shoot S concentrations were found between the fertilizer control and the equivalent polyhalite dose in all three experiments. S uptake varied in the three experiments as a response to polyhalite application. No response was

observed in the 2015 experiment; a linear response was recorded for the 2015R experiment and a saturation response was observed in the 2016 experiment. Under no fertilizer application, the S uptake in the 2015 experiment was higher than for the other experiments, whereas under all doses of polyhalite the highest uptake values were recorded in the 2016 experiment. For the 2015R and 2016 experiments, S uptakes were significantly lower under the fertilizer control than under the equivalent polyhalite dose.

Experiments were carried out in a well monitored system, which enabled the total amount of K, Ca, Mg and S to be calculated in two measured pools: leachate and plant uptake. The fraction of each nutrient in each pool was also calculated as a function of the applied element (Fig. 4 and Appendix 1). Consequently, the recoveries of an element in the different pools can be higher than 100%. These calculated values can be used as indicators of the efficiency of polyhalite at different doses as a source of K, Ca, Mg and S for crop nutrition and for the risk of environmental pollution (Fig. 4 and Appendix 1). Although the experiment was irrigated with desalinated water, certain amounts of nutrients were found in the non-fertilized treatment, both in the leachate and the plants (Figs. 1 and 3). This value is referred to as the potential soil contribution (PSC), above the applied polyhalite application and was taken into consideration as an input of the nutrient into the system. The residual amounts of each nutrient were calculated according to the following balanced equation:

$$RN = NA + PSC - RL - AP \quad (1)$$

Where:

RN = residual amount in the soil at the end of the experiment, meq/pot

NA = amount of nutrient applied, meq/pot

PSC = potential soil contribution, meq/pot

RL = amount recovered in the leachate, meq/pot

AP = amount taken up by the plants, meq/pot

Table 2. The residual concentrations (meq/l) of K, Ca, Mg and S in the soil extract (1:1) from the top layer (0–5 cm) at the end of each experiment. Different letters in a column indicate significant differences between treatments, $p < 0.05$.

Treatment	Ca			Mg			K			S		
	2015	2015R	2016	2015	2015R	2016	2015	2015R	2016	2015	2015R	2016
PS0	1.90b	0.93a	0.87b	0.32b	0.15a	0.12c	0.10a	0.05ab	0.05c	0.89b	0.06b	0.11a
PS500	1.96b	0.81a	1.81b	0.28b	0.12a	0.59ab	0.09a	0.05b	0.35bc	1.65b	0.12b	1.82ab
PS1500	6.95a	1.29a	3.04b	0.98a	0.15a	0.96a	0.57a	0.07a	0.68ab	7.18a	0.70a	4.31b
PS2500	6.55a	1.01a	3.34b	1.00a	0.12a	1.03a	0.61a	0.05ab	0.90a	6.89a	0.62a	5.08b
Control fertilizer	4.56ab	0.69a	4.64a	0.63ab	0.12a	0.18bc	0.87a	0.06ab	0.12c	4.95ab	0.08b	4.32b

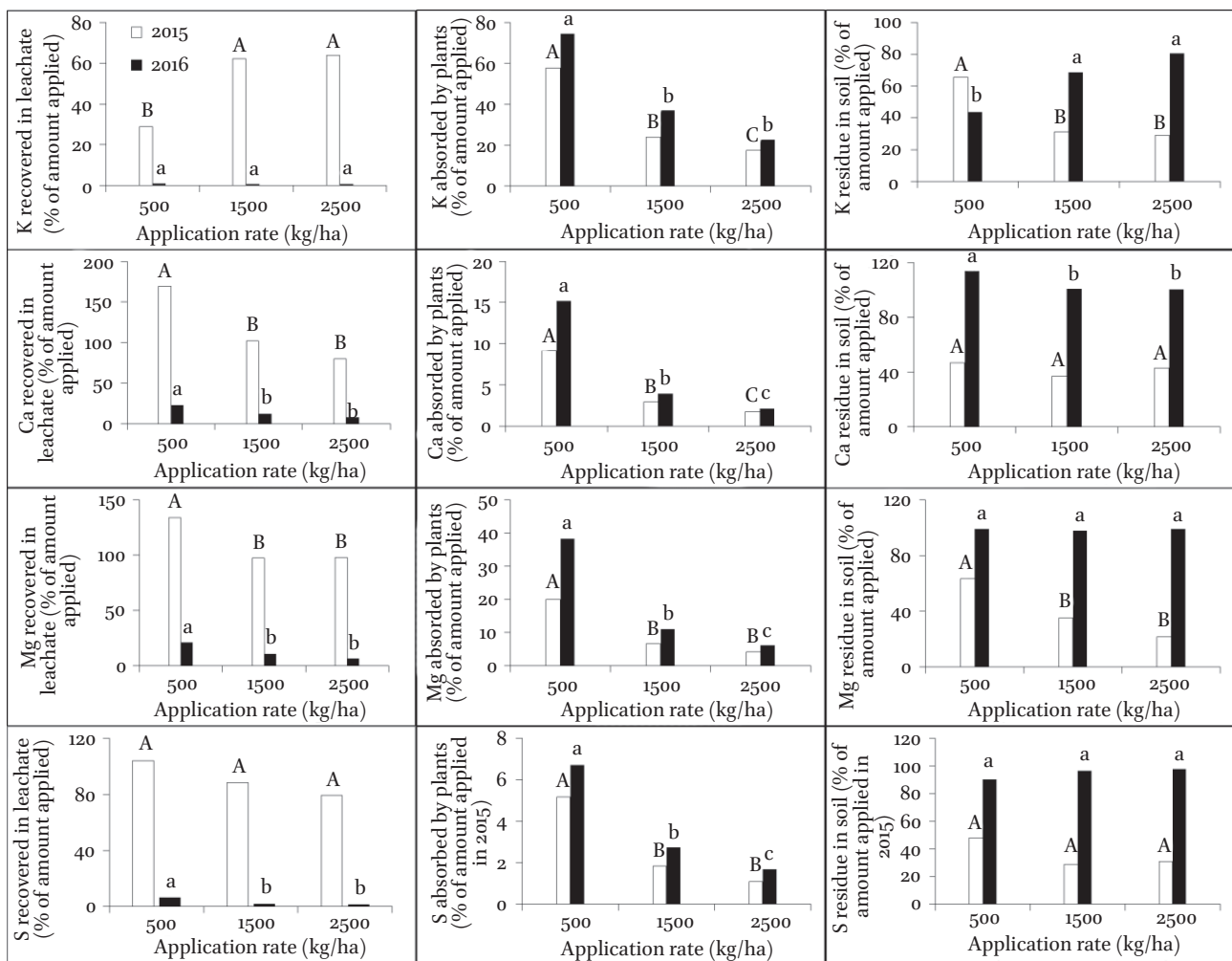


Figure 4. Recoveries of K, Ca, Mg and S in the leachate, plant uptake and soil in 2015 and 2016 experiments as affected by the applied polyhalite dose. Different letters indicate significant differences between polyhalite dose in each experiment, $p < 0.05$.

In general, soil contribution was relatively high under a low dose of polyhalite and therefore, when calculating the recovery of the nutrients relative to the amount applied, a value of over 100% was obtained in some pools and some elements (Fig. 4 and Appendix 1). The recovery percentage of nutrients in the leachate was much higher in 2015 than in 2016, whereas the opposite was obtained in the recovery percentage in plant uptake and the residual amount in soil except K in soil at 500 kg/ha. In the 2015 experiment, K recovery in the leachate increased with application dose, however the opposite response was obtained in plant and soil uptake. In the 2016 experiment, K recovery in plant uptake decreased with application dose, the opposite response was obtained in soil, and negligible recovery was obtained in the leachate for all treatments. The effect of the polyhalite dose on the recovery of Ca, Mg and S in the three pools were similar in

the 2015 and 2016 experiments. The recovery of these elements in the leachate and plant uptake decreased with polyhalite dose. Conversely, the recovery of these elements in soil was not generally affected by the polyhalite dose – excluding Mg recovery in the 2015 experiment. The order of nutrient recovery in plants was: $K > Mg > Ca > S$.

Discussion

The main assumption tested in this work was that polyhalite can serve as an alternative fertilizer for K, Ca, Mg and S. The comparison of wheat biomass production supplied with 1,500 kg/ha polyhalite with that of the equivalent fertilizers in the three experiments presented above, showed that polyhalite was at least as good as the fertilizer control in two experiments (2015 and 2015R) and better than the control in a third

experiment (2016) (Fig. 2). This result is in agreement with published results on various crops including corn, sorghum, potato, flax, beets, cauliflower, oilseed crops and wheat (Fraps, 1932; Lepeshkov and Shoposhnikova, 1958; Panitkin, 1967; Barbarick, 1991; Dugast, 2015; Tiwari *et al.*, 2015; Satisha and Ganeshamurthy, 2016). A comparison of nutrient uptake by wheat plants supplied with polyhalite and the fertilizer control, shows that polyhalite was more efficient at providing K, Mg and S in two experiments (2015R and 2016) and Ca in one experiment (2015R). This is in agreement with the assumption on the availability of these nutrients from polyhalite and previous findings that polyhalite was efficient source for K and S (Barbarick, 1991). However, in most of the above cited publications except this of Barbarick (1991), the control treatment included just one or some of the elements, e.g. K (Fraps, 1932), K and S (Satisha and Ganeshamurthy, 2016), K and S (Tiwari *et al.*, 2015), or Mg and S (Dugast, 2015) whereas in the current research, polyhalite was tested as an alternative source for all four nutrients (K, Ca, Mg and S) compared with the equivalent sulfate salts.

The higher uptake of the four nutrients in the 2015R experiment supports the assumption that polyhalite is a more sustainable fertilizer with better residual effects. This assumption was based on the slower solubility of polyhalite than the sulfate salts of K, Ca and Mg. The lower leaching of all four nutrients in the polyhalite than in the fertilizer control (Fig. 1) further supports this theory. In a previous study by Barbarick (1991), downward leaching of the four elements from soil columns without plants was monitored and only the Mg and S leach-outs were higher from the free salts than from polyhalite, whereas the opposite finding was observed for K (1991). In another publication by Vale (2016), only Ca and Mg were monitored with similar results to the current study.

The unique aspect of the current study is that the leached elements were obtained below the root zone of growing plants, whereas in the paper by Barbarick (1991), soil columns without plants were used and in the study by Vale (2016), only Ca and Mg were monitored. The results of the higher uptake of the four nutrients from the polyhalite source in the 2015R residual experiment (Fig. 3) is in agreement with the leaching data from the 2015 experiment (Fig. 1). The Ca, Mg and S contents in the top soil layer (0–5 cm) at the end of the 2015 experiment, further supports the notion that polyhalite represents a more sustainable fertilizer with

longer term residual effects. The high leaching fraction in 2015 experiment combined with the high mobility of K led to very low residual K in the top soil layer (0–5 cm) with no differences between treatments. In the 2016 experiment where a lower leaching fraction was maintained, there was a significantly higher residual K content in the top soil layer under the polyhalite treatment than under the fertilizer control. This result is again in line with our assumption on polyhalite's residual effects.

Another potential advantage of using polyhalite is the simultaneous release of the four major nutrients through the dissolution of the mineral. However, it was assumed that ion (Ca^{+2} , Mg^{+2} , K^{+} and SO_4^{-2}) transport in the soil was controlled by their adsorptive affinity to soil particle surfaces. Leaching results are controlled by three factors – dissolution, transport and uptake by plants, therefore there is no direct relationship between the concentration of the ions in the leachate and their relative rate of movement in soil. However, the recovery rates were lower for all elements in the plants as the dose of polyhalite increased. The leaching fraction also appeared to have an impact on element recovery rates which were higher in the 2015 experiment when the fraction was at ~30%, than in the 2016 experiment when the leaching fraction was at 10% (Fig. 4). Therefore, the greatest difference in element content for the leachate and soil residue was obtained in the 1,500 and 2,500 kg/ha treatments of the 2015 experiment. Although the ratios of the ion concentrations (K^{+} , Ca^{+2} and Mg^{+2}) in the fertilizer were 1:2:1 respectively, the ratio in the first sampling leachates of the control fertilizer (1,500 kg/ha) was close to 1:1:1 (Fig. 1), indicating a relatively higher transport rate of K and Mg relative to Ca. However, in the highest doses of polyhalite, the ratio is closer to that in the fertilizer due to the slower dissolution of polyhalite than the control fertilizer. There was a much higher residual content of Ca than K and Mg in the top soil of the high dose treatments (1,500 and 2,500 kg/ha) in the 2015 experiment (Table 2); this result also indicates the slow transport of Ca relative to K and Mg.

The element ratio of polyhalite does not match plant requirements, therefore it was assumed that fertilization according to one of them will lead to deficiency or surplus supply of other elements. This assumption was validated in the current research through the application of a wide range of polyhalite doses. The different effects of the polyhalite doses

on nutrient concentrations in the plant shoots for the 2015 and 2016 experiments, indicate that K was a limiting factor up to a dose of 1,500 kg/ha, whereas sufficient Ca, Mg and S were supplied at the 500 kg/ha dose. The decrease in shoot Ca and Mg concentrations as the polyhalite dose increased (Fig. 3), indicates that K is in competition with Ca and Mg in ion uptake by plants. Additional cause to this reduction is probably the dilution effect as the biomass increased with the dose of polyhalite in response to the increased K supply. In the nil treatment, the source of Ca and Mg was probably the irrigation water which contained 10 and 1 mg/l, respectively. On the other hand, the high concentrations of Ca and Mg and uptake by plants in the 2015R experiment (Fig. 3) and the high accumulation of Ca and Mg in the soil at the end of 2015 and 2016 experiments (Table 2 and Fig. 4), indicates that polyhalite application which meets K plant requirements, leads to a surplus supply of Ca, Mg and S.

The differences in the leaching patterns between the 2015 and 2016 experiments are, most probably, the result of the differences in leaching fractions. In 2015, with a 30% leaching fraction, solute movement was relatively fast and the leachate's EC reached low values towards the end of the experiment. In 2016, with a 10% leaching fraction, solute movement was slower than in 2015 and the leachate's EC remained stable until the end of the experiment. The strong impact of the leaching fraction on the efficiency and sustainability of the polyhalite fertilizer is shown by the element recovery from the three pools: leachate, plants and soil (Fig. 4 and Appendix 1). In general, the lower leaching fraction in 2016 dramatically decreased element recovery in the leachate, but significantly increased the recovery in plants and soil, demonstrating the importance of polyhalite application management for its efficiency and sustainability.

Conclusions

Polyhalite is a more efficient fertilizer as broadcast application for supplying K, Ca, Mg and S relative to equivalent soluble salts. To meet the plant required ratios for Ca, Mg and K, the polyhalite dose should be applied accordingly to provide sufficient Ca and Mg, and additional fertilizers should be used as a source of K.

Transport and leaching of Ca, Mg, K and S in soil following polyhalite application is lower than following

the application of the equivalent sulfate salts. The residual effect of polyhalite fertilizer on the subsequently grown crop is higher than the effect from the equivalent sulfate salts, especially regarding Ca, Mg and S.

Irrigation management, as determined by the leaching fraction, has a strong impact on the efficiency of polyhalite as a source of K, Ca, Mg and S for plant nutrition.

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Appendix 1. Balance of K, Ca, Mg and S in the 2015 and 2016 experiments. Different letters indicate significant differences between treatments, $p < 0.05$.

Nutrient	Nutrient distribution	2015				2016			
		Treatment (kg/ha)				Treatment (kg/ha)			
		0	500	1500	2500	0	500	1500	2500
K	Potential soil contribution (meq/pot)	4.86	4.86	4.86	4.86	1.79	1.79	1.79	1.79
	Applied (meq/pot)	0.00	9.36	28.08	46.80	0.00	9.36	28.08	46.80
	Found in leachate (meq/pot)	1.74	2.71	17.52	29.87	0.08	0.10	0.24	0.34
	Absorbed by plants (meq/pot)	3.12	5.40	6.73	8.16	1.71	6.96	10.41	10.59
	Residue in soil (meq/pot)		6.11	8.70	13.63		4.09	19.23	37.67
	Found in leachate (% of applied)	–	29.0 B	62.4 A	63.8 A	–	1.1 a	0.8 a	0.7 a
	Residue in soil (% of applied)		65.3 A	31.0 B	29.1 B		43.7 b	68.5 a	80.5 a
Ca	Absorbed by plants (% of applied)	–	57.7 A	24.0 B	17.4 C	–	74.3 a	37.1 b	22.6 b
	Potential soil contribution (meq/pot)	24.65	24.85	24.65	24.65	10.18	10.18	10.18	10.18
	Applied (meq/pot)	0.00	19.66	58.98	98.30	0.00	19.66	58.98	93.30
	Found in leachate (meq/pot)	22.90	33.33	59.98	78.79	7.14	4.51	7.39	7.63
	Absorbed by plants (meq/pot)	1.75	1.80	1.75	1.70	3.04	2.99	2.35	2.10
	Residue in soil (meq/pot)		9.18	21.91	42.47		22.34	59.43	98.75
	Found in leachate (% of applied)	–	169.5 S	101.7 B	80.2 B	–	22.9 a	12.5 b	7.8 b
Mg	Residue in soil (% of applied)		46.7 A	37.1 A	43.2 A		113.6 a	100.8 b	100.5 b
	Absorbed by plants (% of applied)	–	9.1 A	3.0 B	1.7 C	–	15.2 a	4.0 b	2.1 c
	Potential soil contribution (meq/pot)	11.10	11.10	11.10	11.10	5.51	5.51	5.51	5.51
	Applied (meq/pot)	0.00	9.46	28.37	47.29	0.00	9.46	28.37	47.29
	Found in leachate (meq/pot)	9.21	12.66	27.63	46.22	3.13	1.97	2.96	2.96
	Absorbed by plants (meq/pot)	1.89	1.89	1.89	1.97	2.38	3.62	3.13	2.88
	Residue in soil (meq/pot)		6.00	9.95	10.20		9.38	27.80	46.96
S	Found in leachate (% of applied)	–	133.9 A	97.4 B	97.7 B	–	20.9 a	10.4 b	6.3 b
	Residue in soil (% of applied)		63.5 A	35.1 B	21.6 B		99.1 a	98.0 a	99.3 a
	Absorbed by plants (% of applied)	–	20.0 A	6.7 B	4.2 B	–	38.3 a	11.0 b	6.1 c
	Potential soil contribution (meq/pot)	21.39	21.39	21.39	21.39	1.23	1.23	1.23	1.23
	Applied (meq/pot)	0.00	37.49	112.46	187.44	0.00	37.49	112.46	187.44
	Found in leachate (meq/pot)	19.71	39.05	99.30	148.64	0.47	2.35	2.16	2.47
	Absorbed by plants (meq/pot)	1.68	1.93	2.06	2.06	0.76	2.51	3.09	3.13
	Residue in soil (meq/pot)		17.90	32.50	58.13		33.86	108.43	183.07
	Found in leachate (% of applied)	–	104.2 A	88.3 A	79.3 A	–	6.3 A	1.9 B	1.3 B
	Residue in soil (% of applied)		47.8 A	28.9 A	31.0 A		90.3 A	96.4 A	97.7 A
	Absorbed by plants (% of applied)	–	5.2 A	1.8 B	1.1 B	–	6.7 A	2.8 B	1.7 C