

University of São Paulo
“Luiz de Queiroz” College of Agriculture

The potential of polyhalite as a multi-nutrient fertilizer for sugarcane

Wilfrand Ferney Bejarano Herrera

Thesis presented to obtain the degree of Doctor in
Science. Area: Soil and Plant Nutrition

Piracicaba
2019

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The potential of polyhalite as a multi-nutrient fertilizer for sugarcane

versão revisada de acordo com a resolução CoPGr 6018 de 2011

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DEDICATION

This work is dedicated to my parents,
Dora Herrera and Gonzalo Bejarano,
my mothers-in-love,
Luisa, Leonor and Bertilda,
my sister Marcela Bejarano and
my nieces Mariana and Salomé,
that all time have been source of
inspiration to achieve each goal in life.

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Countries can defend themselves in two ways:
with their army and their Science.
If there is no Science, the country
belongs to another.

Rodolfo Llinás

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RESUMO

Potencial da polihalita como fertilizante multi-nutriente para cana-de-açúcar

A cana-de-açúcar é uma das culturas com maior extração de macronutrientes do solo, tanto em cana-planta quanto em soca, sendo fundamental sua reposição por meio de fertilizantes. O fornecimento de elementos como potássio (K), cálcio (Ca), magnésio (Mg) e enxofre (S) para cana-de-açúcar é comumente realizado por fertilizantes, como o cloreto de potássio, e condicionadores do solo, como calcário e gesso agrícola, gerando altos custos por cada aplicação. Neste contexto, o estudo teve como objetivo determinar o potencial de polihalita (POLY) como fonte multi-nutriente de K, Ca, Mg e S e seus efeitos na produtividade e qualidade da cana-de-açúcar. Para isso, o estudo foi dividido em três etapas: i) avaliação em campo usando solo com baixo nível de K comparando doses de POLY com a aplicação combinada de KCl e gesso agrícola (GYP) para avaliar rendimento, qualidade, parâmetros químicos do solo, teor de macronutrientes de palha e colmo em duas variedades de cana-de-açúcar, CV7870 e RB867515. ii) caracterização elementar, mineralógica e de liberação do polihalita (POLY) e cloreto de potássio (KCl) pelo uso de espectrometria de micro fluorescência de raios X (μ XRF) e espectrometria de difração de raios-X; e (iii) avaliação em condições de casa de vegetação do efeito residual da aplicação de dosagens de POLY em contraste com a aplicação conjunta de KCl, GYP e kieserite (KIE) no teor de macronutrientes foliares, e produção de biomassa. Com base no experimento de campo, a aplicação de Ca, Mg, S e principalmente K, independentemente da fonte aplicada, afetou positivamente o rendimento em cana-de-açúcar. Em relação à dosagem, a aplicação de $105 \text{ kg K}_2\text{O ha}^{-1}$, que corresponde à dosagem recomendada, promoveu os maiores rendimentos de colmos para ambas as variedades, CV7870 e RB867515. Essa dosagem mantém o estado nutricional adequado da cana-soca e aumenta o teor de K no colmo, promovendo o acúmulo de sacarose na planta. Em relação aos parâmetros do solo, para a variedade RB867515, após o cultivo, a maior parte da concentração de nutrientes remanescente no solo não teve efeito significativo em relação ao controle, sugerindo que, quanto mais fertilizante for aplicado, essa variedade será capaz de absorver e exportar. Em contrapartida, a variedade CV7870 apresentou maiores valores remanescentes de Ca, Mg e S no solo em relação ao controle após o cultivo, indicando um efeito residual, independentemente do tratamento. Com base nos resultados laboratoriais, o grânulo de KCl em solo úmido com baixo teor de K promoveu rapidamente a dissolução dos nutrientes e liberou Cl^- e K^+ , sendo mais suscetível à lixiviação, enquanto que o grânulo POLY apresentou baixa solubilidade em comparação ao KCl, aumentando o efeito residual ao longo do tempo. Os resultados mostraram que a produção de biomassa e a absorção de nutrientes foram mais correlacionados às altas doses K (42 e 63 mg kg^{-1}) e fontes de K contendo Ca e S na formulação (POLY, KCl + GYP + KIE e $\frac{1}{2}\text{KCl } \frac{1}{2}\text{POLY}$), tanto para cana-planta quanto para soca. Entretanto, quando essas fontes foram fornecidas na dose mais baixa (21 mg kg^{-1}), foi observada eficiência agrônômica superior para todos os nutrientes adicionados, indicando que uma combinação de KCl e POLY seria mais eficiente como fonte de K para cana-de-açúcar. Numa avaliação geral, a polihalita foi adequada para fornecer K, Ca, Mg e S na dose recomendada de $105 \text{ kg K}_2\text{O ha}^{-1}$. Assim mesmo, a mistura de 50% de polihalita e 50% de KCl pode ser adotada para os agricultores reduzindo as perdas nutricionais para planta.

Palavras-chave: Fontes alternativas de potássio; Adubação da cana; Fluorescência de raios X; Liberação de nutrientes

ABSTRACT

The potential of polyhalite as a multi-nutrient fertilizer for sugarcane

Sugarcane is one of the crops with the highest extraction of macronutrients from the soil, both in cane-plant and ratoon crops, being critical its reposicion by means of fertilizers. In the Brazilian sugarcane agrosystem, the supply of elements, such as, potassium (K), calcium (Ca), magnesium (Mg) and sulfur (S) is commonly performed by fertilizers, like potassium chloride, and soil amendmets, such as, lime and phosphogypsum, producing high costs by sole application. In this context, the study aimed to determine the potential of polyhalite as a multi-nutrient source of K, Ca, Mg and S and its effects on yield and quality of sugarcane. In order to reach this objective, the study was divided into three stages: i) field evaluation in low K soil comparing doses of POLY with the combined application of KCl and GYP to evaluate yield, quality, soil chemical parameters, straw and stalk macronutrient content in two sugarcane varieties. ii) elemental, mineralogical and release characterization of the polyhalite (POLY) and potassium chloride (KCl) by the use of micro X-ray fluorescence spectrometry (μ XRF) and X-ray diffraction spectrometry; and (iii) evaluation under glasshouse conditions to evaluate the residual effect of the application of POLY dosages contrasted to the application of KCl, GYP and kieserite (KIE) in the leaf macronutrients content, and biomass production in an Oxisol with a low level of K. Based on the field experiment, the application of calcium (Ca), magnesium (Mg), sulfur (S) and mainly potassium (K), irrespective the source applied, affected positively the yield in sugarcane. Related to the dosage, application of $105 \text{ kg K}_2\text{O ha}^{-1}$, which corresponds to farmer's recommended dosage, promoted the highest stalk yields for both varieties, CV7870 and RB867515. This dosage keeps the adequate nutritional status of sugarcane ratoon and enhance the K content in stalk, promoting the accumulation of sucrose in this plant organ. In relation to the soil parameters, for the variety RB867515, after cultivation, most of the nutrient concentration remained in soil were not significant compared to control, suggesting that as much fertilizer is applied this variety will uptake and export. In contrast, the variety CV7870 showed higher remained values for soil Ca, Mg and S in the treatments compared to the control after cultivation, indicating a residual effect, irrespective the treatment. Based on the laboratory results, KCl granule in the moisture low-K sandy Oxisol has rapidly promoted dissolution of nutrients and then released Cl^- and K^+ , being susceptible for leaching, whereas POLY granule performed as a slow-release fertilizer due to its low solubility compared to KCl, enhancing residual effect over time. The results of the glasshouse showed that DM yield and nutrient uptake were more correlated to high K dosages applied (42 and 63 mg kg^{-1}) and K sources containing Ca and S in the formulation (POLY, KCl+GYP+KIE and $\frac{1}{2}\text{KCl } \frac{1}{2}\text{POLY}$), for both cane-plant and ratoon. However, when these sources were provided at the lowest dosage (21 mg kg^{-1}) it was observed superior agronomic efficiency for all added nutrients, indicating that a combination of KCl and POLY can be used more efficiently as K source for sugarcane. Taking together, both experiments, in the field and in the greenhouse, showed that polyhalite is suitable to supply K, Ca, Mg and S at the farmer's dosage recommendation. Furthermore, the blend of 50% polyhalite and 50% KCl could be adopted for farmers minimizing plant nutrient losses with a more balanced nutrition.

Keywords: Alternative sources of potassium; Fertilization in sugarcane; X-ray fluorescence; Nutrient release

1. GENERAL INTRODUCTION

Sugarcane is one of the world's most productive crops, producing the greatest crop yield and supporting the fourth highest amount of vegetal calories in the human diet (MOORE; BOTHA, 2014). Brazil is the largest producer of sugarcane, followed by India and China (FAO, 2014), which has 8,73 million hectares, producing 633 million tons (t), reaching an average yield of 72,5 t ha⁻¹ (CONAB, 2018). This productivity has a positive trend thanks to plant breeding programs and the use of machinery in crop practices, however, there is still a gap for improvement of genetic potential in national varieties. One of the main factors limiting the increase of sugarcane yield is the low availability of nutrients in soils. Thus, Brazilian sugarcane production is conditioned by the application of fertilizers, being the third crop with the greatest demand of fertilizers (13,6%) in the country (ANDA, 2017).

To overcome this constraint in the current idea of agricultural sustainability, research on the rational use of fertilizers is a critical factor for the success of sugarcane production, since it represents a high percentage of production costs. Besides, as mineral reserves have been depleted and prices of fertilizer raw materials rise up, it is important to identify new sources. One alternative is the use of multi-nutrient sources, such as polyhalite, since it can provide several macronutrients in a single application. Sugarcane as a high-yielding crop needs a large quantity of nutrients, being potassium (K) the essential element with the highest absorption and exportation, followed by nitrogen (N), calcium (Ca), magnesium (Mg), sulphur (S) and phosphorus (P) (Orlando Filho, 1993), which can be supplied by mineral fertilizers. Furthermore, K is involved in the transport of sugars (Cai et al., 2012), nitrogen metabolism, water absorption and transport, osmoregulation, enzyme activation and charge neutralization (Römheld and Kirkby, 2010). Hence, K is crucial to maintain ratoon sugarcane yields (Paneque et al., 1992).

Polyhalite is an evaporite mineral containing K, Ca, Mg and S in its composition, bearing a low water solubility and versatility to manufacture several fertilizer formulations. Given the relevance of these four macronutrients to crop production in tropical soils in Brazil, it may well suit polyhalite to sugarcane, however, there are no published scientific reports on this crop yet.

The use of polyhalite as a source of K is profitable in high leaching and low cation exchange capacity (CEC) soils, since the slow release of nutrients from the granule can minimize leaching and reduce the luxury consumption, increasing the percentage of bases in the soil and therefore improving the cost-benefit ratio. Polyhalite has some advantages over commercial use of potassium chloride (KCl), the key one is that it does not contain chloride in its chemical composition. Chloride is an essential element to plants; however, sugarcane is a glycophyte species, having moderate sensitivity to high concentrations of salt (KUMAR et al., 2014). Nevertheless, the use of KCl may have negative effects on other species of vegetables and fruit. Another benefit of polyhalite is its natural occurrence in mineral form, therefore it is a fertilizer that can be used in organic agriculture, being a promising market in Brazilian organic sugarcane production. Also, polyhalite has approximately 14% of K_2O , being able to be used in mixture with other potassium sources like KCl, in order to guarantee the demand of this element and to supply at the same time other nutrients like Ca, Mg and S.

We have tested the hypotheses that polyhalite can be an alternative fertilizer to supply K, Ca, Mg and S for sugarcane in a sandy low-K soil and due to its lower solubility, polyhalite can perform as a low release fertilizer. In this scenario, this study is needed to increase our knowledge about polyhalite performance on sugarcane production and its dynamics in a low-K tropical soil, by means of field, greenhouse and laboratory experiments.

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2 POLYHALITE AS A MULTI-NUTRIENT FERTILIZER FOR SUGARCANE. FIELD EXPERIMENT

Abstract

Currently, Brazilian sugarcane production is based on potassium chloride (KCl) as source of potassium (K), but KCl is also the most soluble K fertilizer being susceptible for expressive leaching losses from the soil. To overcome it, this study aimed to evaluate polyhalite (POLY) as a multi-nutrient source on sugarcane yield and soil K, Ca, Mg content compared to combined applications of a commercial K fertilizer (KCl) associated to Ca and S source (phosphogypsum – GYP). The experiment was conducted from 2013 to 2015 with two sugarcane varieties (*Saccharum* ssp. cultivar. CV7870 and RB867515) in their first ratoon stage on a Hapludox soil in Agudos-SP, Brazil, arranged in a randomized block design with three replications. The dosages of K were: 0, 70, 105 and 140 kg K₂O ha⁻¹ via POLY compared to a fixed dosage of 105 kg K₂O ha⁻¹ via KCl plus four dosages of Ca and S by means of GYP (80, 120 and 160 kg CaO ha⁻¹). The application of these four nutrients, regardless the source applied, reflected positively in the yield increase in sugarcane, depending on the variety cultivated. The variety RB867515 differentiated markedly from CV7870 in K content accumulated in stalk, suggesting a better performance in stalk yield and higher percentage of sucrose. Concerning to dosage, the application of 105 kg K₂O ha⁻¹, which corresponds to farmer's recommended dosage, promoted the highest stalk yields for both varieties, CV7870 and RB867515. This dosage kept an adequate nutritional status of sugarcane ratoon and enhanced the K content in stalk, promoting an adequate accumulation of sucrose. In relation to the soil parameters, for the variety RB867515, most of the nutrient concentration remained in soil were not significant compared to control, suggesting that the residual effect is null irrespective the source used. Conversely, the variety CV7870 showed higher values for Ca, Mg and S in fertilizer treatments compared to the control after cultivation, indicating an expressive residual effect of fertilizers. Thus, the use of polyhalite, as a multi-nutrient fertilizer, was as efficient as the standard K source for sugarcane.

Keywords: Potassium sources; Phosphogypsum; Calcium; Sulfur; Agronomic efficiency

2.1 Introduction

Brazil is currently the largest sugarcane producer, and the national sugar and ethanol sector is considered a global benchmark. This is due to the high efficiency of production and even the current increasing demand for biofuels and renewable energy sources. This change in the energy matrix is an opportunity for the Brazilian market, given the comparative advantage in the production and the generation of value and income by this crop (Hoofmann, 2006).

The supplement of nutrients to main crops is normally done by using fertilizers in mineral forms. Nitrogen, phosphate and potassium fertilizers assume the higher costs in

sugarcane production, directly affecting the crop quality and productivity. According to projections from the Food and Agriculture Organization of the United Nations (FAO, 2017), world consumption of K fertilizers in 2020 is estimated to reach 37 million tons. Furthermore, the demand of potash is expected to grow annually on average by 2.5%, positioning Brazil as the third largest consumer of fertilizer worldwide, with a demand of 35.5 million tons, and sugarcane as the third crop with the greatest demand of fertilizers (13,6%) in the country (ANDA, 2017).

In plants, potassium is related to transporting sugar in nitrogen metabolism; in the absorption, use and transportation of water; in addition to stomata opening and closing. It also acts as a water-holding mechanism and resistance to stress (Römheld and Kirkby, 2010). Under deficiency, classic symptoms include low productivity due to low-growing plants, reduced internodes due to the enzymatic activation of respiration, and low photosynthesis reactions (Krauss, 2005; Novais et al., 2007). In sugarcane K is the most absorbed and exported nutrient, connected to various structural and metabolic functions, such as stomatal aperture, enzyme activation and protein synthesis (Felipe, 2008).

Response of sugarcane to potash fertilizer application in low exchangeable K soil levels is significant and directly influences the productivity (Korndörfer and Oliveira, 2005). Moreover, the response of sugarcane to K fertilization is built upon the soil K availability (Kumawat et al., 2016; Korndorfer et al., 2018). According to Orlando Filho (1993), for the production of 100 t ha⁻¹ of sugarcane, is extracted around 210 kg ha⁻¹ of K₂O, 43 kg ha⁻¹ of P₂O₅ and 143 kg ha⁻¹ of N, thus observed that its largest export between macronutrients. According to Raij et al. (1997), the appropriate dose for sugarcane range from 0 to 200 kg ha⁻¹ of K₂O, depending on the soil type, texture and K content in the soil. Thus, choosing the most appropriate fertilizer, coupled with the appropriate dose, it becomes fundamental to the sustainable production of sugarcane, aimed at saving supplies and even better use by the plant.

The most widespread potassium fertilizer is potassium chloride (KCl), at the lowest cost because of its high percentage of K₂O (60%). The main national producer is Vale Company, but it represents only about 10% of the market. Brazilian consumption, presents a demand of approximately 5,2 million tons, and currently 91% of consumption is imported (ANDA, 2017). A potassium alternative source that is emerging in the world market is the polyhalite (K₂SO₄.MgSO₄. 2CaSO₄.2H₂O), being not widely used in Brazil yet. The potential of this alternative source is to provide nutrients not provided by other sources, in this case, sulfate,

calcium and magnesium, being an interesting source for crops with high requirements, including sugarcane.

Field studies on polyhalite are limited because it only recently emerged as a commercial fertilizer. Therefore, studies are needed to determine the crop response in different growing environments. Given the number of nutrients in balance in polyhalite, greater crop response should be expected due to the presence of K, S, Ca and Mg in its constitution. In this way, the objectives of the proposed studies here were to evaluate polyhalite as a source of K, S, and Ca compared to KCl as a K source and gypsum as a Ca and S source for sugarcane fields in a sandy soil of Sao Paulo State, Brazil.

2.2 Material and Methods

2.2.1 Site and Soil Characterization

The experiment was conducted from 2013 through 2015 under field conditions at the Glória Farm, located in Agudos, São Paulo State (SP), Brazil (22°33' S, 49°06' W, altitude 715 m above sea level). The area was selected according to the low levels of K, Ca, Mg and S in the soil (Table 1). The regional climate is classified as Aw (A: tropical; w: dry winter) (Rolim et al., 2007, CEPAGRI, 2015), with average annual precipitation of 1500 mm, during the dry winter precipitation is less than 60 mm (Fig. 1). The soil is a sandy Typic Hapludox (Soil Survey Staff, 2014), classified as Latossolo Vermelho-Amarelo distrófico from the Brazilian System of Soil Classification (EMBRAPA, 2013) and was chemically and granulometrically characterized as presented in Table 1. According to the characterization, the area is classified as cultivation environment class C2, due to low water availability potential, low CEC and base saturation less than 50% (Prado, 2005).

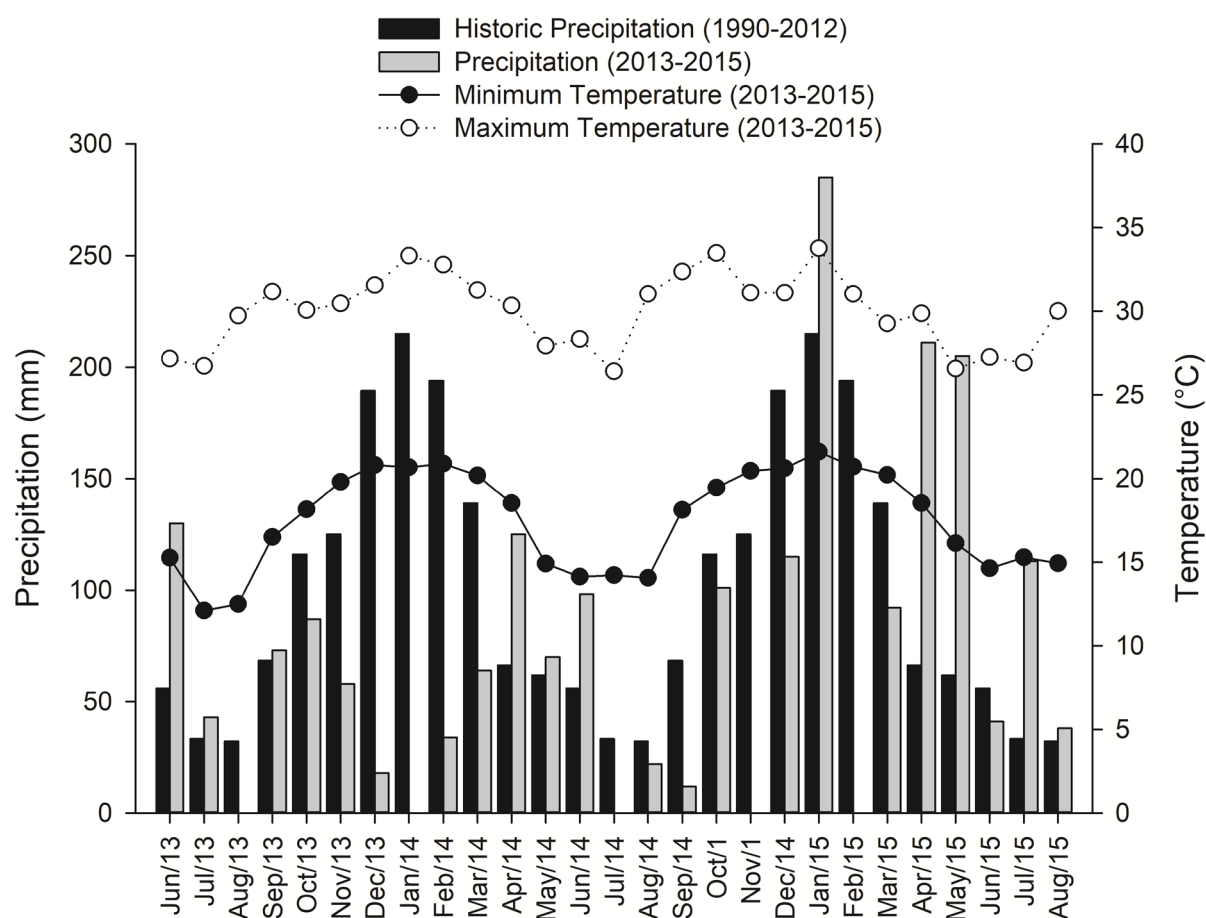


Figure 1. Average monthly temperatures (maximum and minimum) (°C) and precipitation distribution (mm) historically and during the period June-2013 to August-2015 in the experimental site. Sources: BPZ Group and CEPAGRI (2015)

Soil mineralogical characterization was based on X-ray diffraction (XRD) (Jackson, 1969), analyzed from a sample collected (0-20 cm) prior the experiment establishment (2013). All patterns were obtained using a Rigaku Miniflex II Desktop diffractometer (Tokyo, Japan), CuK α radiation, with a range of 5 to 30° (2 θ) for the specimen, operated at 30 kV and 15 mA. Interpretation of this pattern peak extraction was performed using Match! 3 software coupled with the international standard mineral database verifying that the XRD pattern displayed the major mineral phases, including, kaolinite and anatase, followed by gibbsite, hematite, and chlorite (Fig. 2).

Table 1. Soil attributes before establishment of the experiment – sandy soil, Agudos-SP, 2013.

Soil layer (cm)	pH CaCl_2	P -----mg dm ⁻³ -----	S-SO ₄	K* -----	Ca ‡	Mg †	H+Al‡	BS¶	CEC§	V#
Site CV7078										
0-10	4.8	4	9	1.0	17	5	15	23.0	38.0	61
10-20	4.5	3	11	0.8	14	3	15	17.8	32.8	54
20-40	4.1	3	20	0.6	8	3	18	11.6	29.6	39
Site RB867515										
0-10	5.0	6	15	2.6	17	7.5	14	27	41	66
10-20	4.6	4	16	1.6	16	7.2	17	25	41	59
20-40	4.1	4	15	1.2	8	4.7	21	14	36	40
Soil layer cm	Clay -----			Silt g kg ⁻¹ -----			Sand			
0-20	112			4			884			
20-40	138			27			835			

* Exchangeable potassium extracted by resin: low, between 0 to 1.5 mmol_c dm⁻³; medium, between 1.6 to 3.0 mmol_c dm⁻³; high, greater than 3.0 mmol_c dm⁻³

‡ Low calcium, between 0 and 4 mmol_c dm⁻³

† Low Magnesium, between 0 and 6 mmol_c dm⁻³

‡ Exchangeable acidity. ¶ Sum of bases. § Cation exchange capacity. # Bases saturation index.

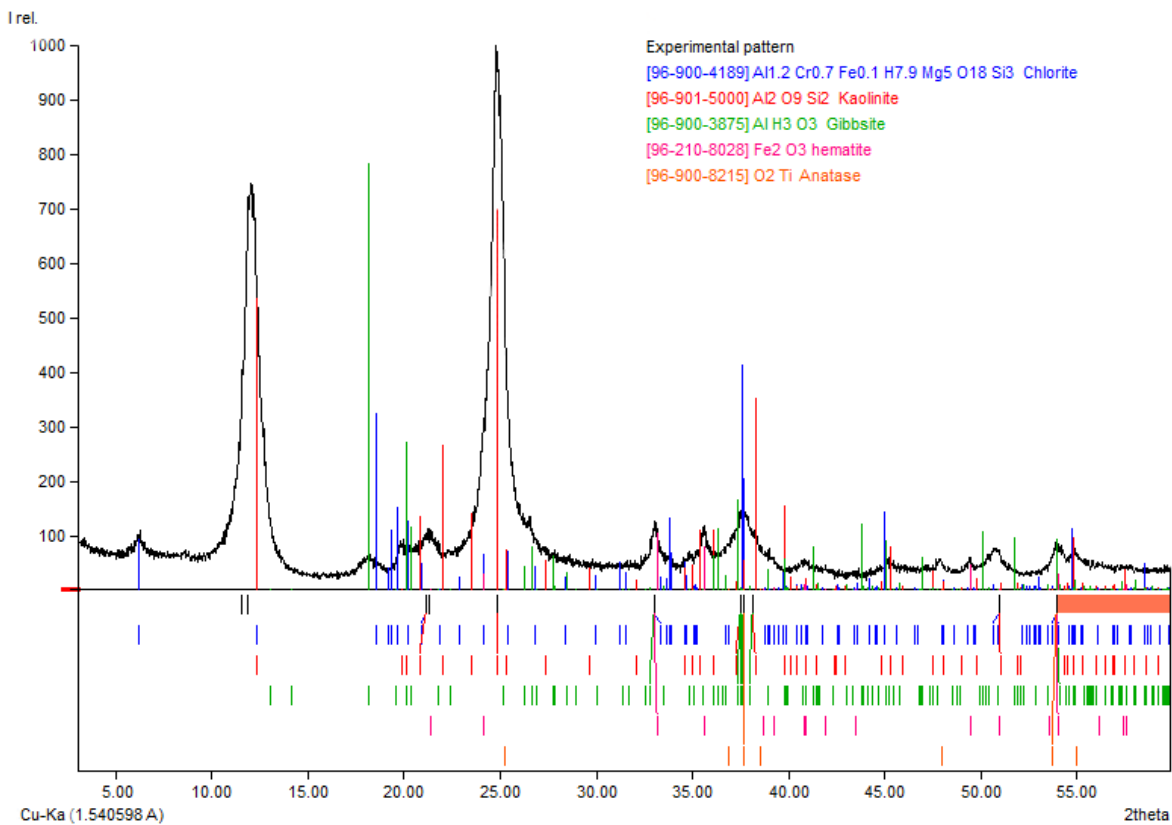


Figure 2. XRD of oriented clay fraction at 0-20 cm soil layer. CuK α radiation. Main minerals: Kt – Kaolinite, An – Anatase, Gb – Gibbsite, Hm – Hematite, Cl – Chlorite.

2.2.2 Experiment Set-Up

The experiments were carried-out in a randomized complete block design with two potassium sources, polyhalite (POLY) and potassium chloride (KCl) (60% K₂O and 45% Cl). Polyhalite is a single crystal sulfate mineral complexing K, Ca and Mg in its composition, corresponding to 14% K₂O, 19% S, 6% MgO and 16% CaO (Sirius Minerals PLC, Scarborough, United Kingdom). Four dosages of K₂O via POLY (0, 70, 105 and 140 kg ha⁻¹) were compared to a fixed dosage of 105 kg K₂O ha⁻¹ via KCl plus four dosages of Ca and S (0, 80, 120 and 160 kg CaO ha⁻¹) by means of phosphogypsum (GYP) (Table 2). These fertilizer dosages were based on prior soil analysis and sugarcane ratoon requirement, assuming 105 kg K₂O ha⁻¹ as the farmer's dosage. The supplement of Ca, and S in the treatments of KCl were based on the amount supplied in POLY treatments, however, the dosage of S was lower because of the GYP composition (15% S, 20% CaO). Treatments were replicated in three blocks and plot size was composed of six rows of 10 m length, spaced 1.5 m between rows, totaling 90 m². These

fertilizer dosages were based on expecting cane yield above 100 Mg stalk ha⁻¹, recommended by Raij et al. (1997).

Table 2. Treatments evaluated in a sugarcane ratoon in two varieties CV7870 and RB867515, corresponding to dosages of polyhalite (POLY) and commercial potassium source (KCl) combined with phosphogypsum (GYP), Agudos-SP, Brazil, 2014 to 2015.

Treatment	Applied nutrient kg ha ⁻¹								
	K ₂ O	K	MgO	Mg	S	CaO	Ca	N	P ₂ O ₅
Absolute control	0	0	0	0	0	0	0	0	0
Control	105	87	0	0	0	0	0	100	0
POLY 70	70	58	30	18	96	80	57	100	0
POLY 105	105	87	45	27	144	120	86	100	0
POLY 140	140	116	60	36	192	160	114	100	0
KCl 105+GYP 80	105	87	0	0	60	80	57	100	0
KCl 105+GYP 120	105	87	0	0	90	120	86	100	0
KCl 105+GYP 160	105	87	0	0	120	160	114	100	0

Prior to sugarcane establishment, this area was a degraded pasture for more than 20 years succeeding deforestation (Fig. S1a). Before sugarcane planting, the natural grasses were desiccated with an application of glyphosate at the rate of 4 L ha⁻¹ and the residual straw was incorporated into the soil by deep ploughing (0-50 cm). Later, the soil was limed with 3 Mg ha⁻¹ of lime (CaCO₃ + MgCO₃) and treated with 1.5 Mg ha⁻¹ of gypsum (CaSO₄). Both soil amendements were incorporated twice using a disc harrow to about 20 cm depth. The area was planted in July 2013 by disposing stalks in the planting furrow with 18 to 20 buds and covered with soil at 15 cm depth (Fig. S1b). The varieties used were CV7870 and RB867515. RB867515 is the most cultivated variety in the Central-Southern Brazilian region, accounting for about 24.5% of the cropping area, whereas CV7870 is cultivated in approximately 3% of the cropping area. These varieties are recommended in production environments C and D, with medium to low natural fertility and low water retention capacity, reaching high agroindustrial productivity (RIDESA, 2016).

The cane-plant management was performed by farmer's standards. This management consisted of a subsoiling at depth of 80 cm in the planting furrow. Then, phosphorus (P) was applied to the bottom of the furrow at the dosage of 180 kg P₂O₅ ha⁻¹ in the form of triple super phosphate (0-46-0). The nitrogen and potassium fertilization were applied in the dosage of

100 kg N ha⁻¹ via urea and 105 kg K₂O ha⁻¹ by KCl, respectively. The harvest of the first season (cane-plant) occurred in July 2014. Afterwards, the experiment was set-up (Fig. 3). The experimental period was from September 2014 to August 2015 (Fig. S1c), comprising ratoon 1 (2014/15). After cane-plant's harvest, 100 kg N ha⁻¹ as ammonium nitrate (30–2–0) was applied as a topdressing in September 2014, aiming to satisfy the requirement of this nutrient for the second season (ratoon 1). Phosphorus was only applied in at planting. Potassium, calcium and sulfur dosages, according to each treatment, were applied as a topdressing in the same time of N fertilizer application. Ratoon cane harvest was performed in August 2015.

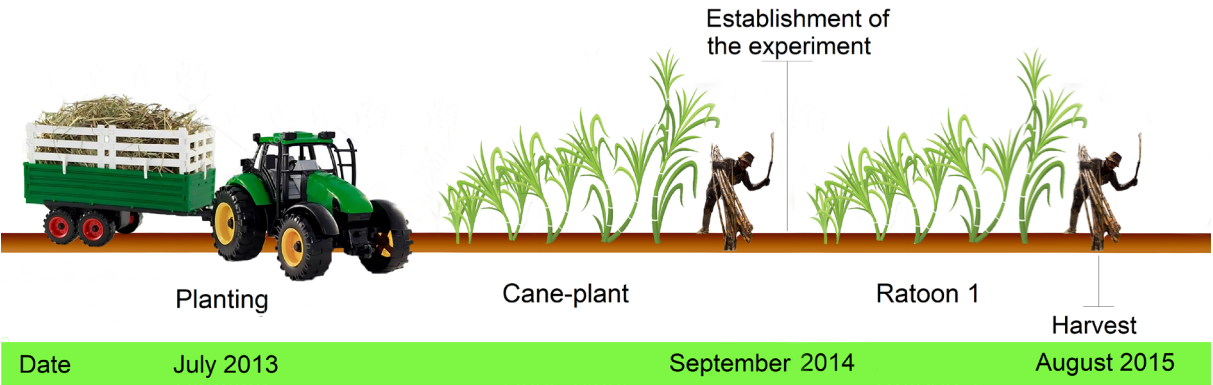


Figure 3. Timeline of the establishment of the experiment, application of treatments and harvests on sugarcane varieties CV7870 and RB867515 cropped in a sandy Oxisol.

2.2.3 Yield Assessments

Before harvest of both experiments, two central rows were selected to determine the number of cane stalks in 10 m and thus calculate the number of cane stalks per hectare. The biometric measurements were performed according to Sundara (1994) using 10 plants per plot, fractionated into cane stalk, dead leaves and top leaves (Fig. S2a). Top leaves contemplated all green leaves on the top and those green leaves adhere in upper nodes, while dead leaves were considered the senescent leaves, with beige and yellowish colors, adhere in the cane stalk and those accumulated on the ground. All plant fractions were weighed immediately after collected using a portable scale to acquire the fresh biomass yield. Then, all fractions were chopped separately using a forage chopper and tissue sub-samples were packed in polyethylene bags and stored for determination of moisture content (Fig. S2b), estimated by weighing before

and after drying in a forced air circulation oven for 72 h at 60 °C. In addition, macro-nutrients content (K, Ca, Mg and S) were analysed following the methodology described in Malavolta et al. (1997).

Cane yield was performed manually, based on four central rows of sugarcane in each plot (60 m² per plot) and measured by means of a digital dynamometer (Fig. S2c), coupled in a cane loading machine (Fig. S2d). Additionally, a sample composed of six stalks, collected in the biometry measurements but not chopped, were used for laboratory determination of technological quality (brix, apparent sucrose content, purity, fiber and total recoverable sugar) according to the methodology described by Consecana (2006).

The apparent sucrose content (Pol) produced per hectare was calculated using the equation (1):

$$\text{Pol (t ha}^{-1}\text{)} = \text{Pol (\%)} \times \text{cane yield (t ha}^{-1}\text{)} / 100 \quad (1)$$

The total recoverable sugar (TRS) was calculated according to equation (2):

$$\text{TRS (t ha}^{-1}\text{)} = \text{TRS (kg t grounded stalk}^{-1}\text{)} \times \text{cane yield (t ha}^{-1}\text{)} / 1000 \quad (2)$$

2.2.4 Soil analysis

Soil cores were collected in August 2015, immediately after each harvest to perform chemical analyses. Four sub-samples were collected right beside the four central rows to a depth of 40 cm segmented into 0-10, 10-20 and 20-40 cm. Soil samples were air dried, sieved through a 2.0 mm sieve, and then analyzed. Soil K, Ca, Mg and S were determined according to Raij et al (2001).

2.2.5 Data and statistical analysis

The effectiveness of each K source relative to the standard KCl was calculated from the yield response relationships using the Equation (3):

$$\text{RAE (\%)} = Y_i / Y_{\text{Control}} \times 100 \quad (3)$$

where, Y_i is cane yield in treatments with added K fertilizers (t ha⁻¹); Y_{Control} is the cane yield obtained by potassium chloride (Control, RAE = 100%) treatment.

Agronomic efficiency was calculated according to Equation (4):

$$AE \text{ (kg kg}^{-1}\text{)} = [(\text{stalk yield in added fertilizers (kg ha}^{-1}\text{)} - \text{stalk yield in absolute control) (kg ha}^{-1}\text{)}] / \text{nutrient applied via fertilizer (kg ha}^{-1}\text{)} \quad (4)$$

All data were tested for Shapiro-Wilk's normality test and Bartlett's homogeneity test, and suitable transformations used when these settings were not met, before to perform analysis of variance (ANOVA). The data was submitted to ANOVA using PROC-GLM, in case of significance in the effects of the K, Ca, S formulations on yield parameters and soil parameters they were compared using t test (LSD). Additionally, the dry matter fractionation and agronomic efficiency of K, Ca and S were compared using a Duncan's multiple range test. The relationship analyses between two variables were adjusted to a linear regression model in case of significance according to Pearson's correlation. Relative agronomic efficiency was compared using Dunnett's test. All statistical analyses were performed using SAS statistical software version 9.3 (SAS INSTITUTE, 2008) and the graphs and regressions by Sigma Plot (Systat Software, San Jose, CA). The determinations of statistical significance were based on a critical value of $p \leq 0.10$.

2.3 Results and discussion

2.3.1 Biomass Production and Cane Yield

The results of this study demonstrate clear differences in the stalk yield, pol (POL), total recoverable sugars (TRS) and biomass production among the experiments with both varieties and the treatments assessed (Table 3).

The variety CV7870 exhibited lower biomass production compared to RB867515 in all treatments assessed, with mean values of 34 and 43 Mg ha⁻¹, respectively. Considering a general view among these two varieties, plant DM production was distributed into about 20% of dead leaves, 13% top leaves and the 67% of stalks. Regarding to variety CV7870, applying POLY at 105 kg K₂O ha⁻¹ reached the highest DM production in all plant fractions, dead leaves (7.7 Mg ha⁻¹), top leaves (5.8 Mg ha⁻¹) and stalks (26.3 Mg ha⁻¹), resulting in one of the highest total DM production together with POLY applied at 140 kg K₂O ha⁻¹ (39.8 and 38.7 Mg ha⁻¹, respectively), whereas KCl at 105 kg K₂O ha⁻¹ (control) and absolute control obtained the lowest total DM productions, with mean values of 28 and 30 Mg ha⁻¹ respectively (Fig. 4a).

Concerning the variety RB867515, DM allocated into dead leaves was positively affected by the highest dosage of Ca applied via KCl+GYP (105 kg K₂O and 160 kg CaO), exhibiting the highest DM (9.7 Mg ha⁻¹), whereas when the same amount of Ca was applied via POLY, it was observed the lowest DM in this plant fraction (Fig. 4b). The largest increments in total DM production were observed when the formulation KCl105+GYP80 was applied, (105 kg K₂O ha⁻¹ and 80 kg CaO ha⁻¹), accounting the highest production (48.4 Mg ha⁻¹), however, when the formulations KCl sole at 105 kg K₂O and POLY at 70 kg K₂O ha⁻¹ were applied, total DM decreased approximately 25% compared to the highest production. No significant differences in the DM allocated to top leaves were observed ($p > 0.10$). Overall, due to the high proportion of DM allocated into stalks, this plant fraction was responsible for the differences among fertilization treatments in total DM production, for both sugarcane varieties.

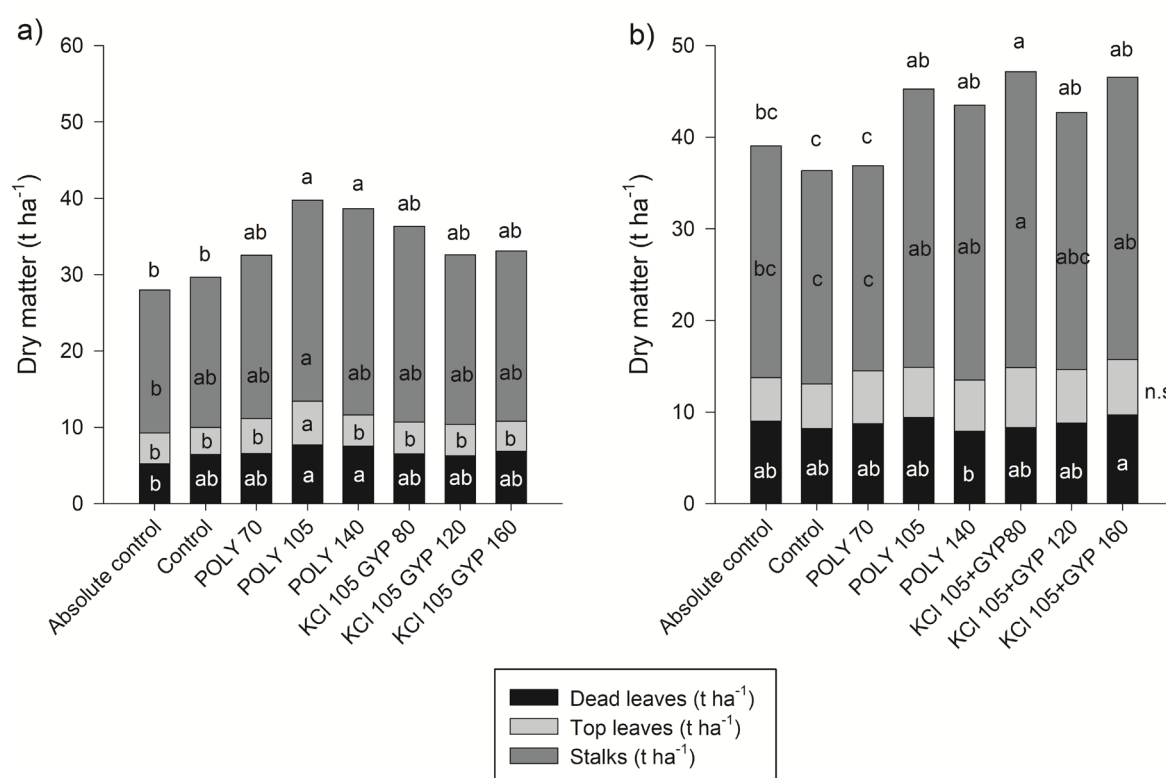


Figure 4. Plant dry matter (DM) fractionated into dead leaves, top leaves and stalks of two sugarcane varieties as affected by K, Ca and S dosages applied in ratoon 1. a) Variety CV7870 and b) Variety RB867515. Columns followed by the same lowercase letter within each plant fraction do not differ statistically by Duncan's multiple range test, ($p \leq 0.10$).

n.s: non-significant

In general, the application of K influenced the stalk yield, apparent sucrose content (Pol) and total recoverable sugar (TRS) in both varieties assessed ($p \leq 0.10$). The average sugarcane stalk yield, Pol and TRS were 107.3, 20.3 and 16.9 Mg ha⁻¹ for variety CV7870 and 136.4, 21.9 and 18.8 Mg ha⁻¹ for variety RB867515 (Table 3), indicating that the latter showed higher performance in stalk production and quality parameters under similar soil conditions.

Table 3. Stalk yield, Pol and total recoverable sugar - TRS (Mg ha⁻¹) of two sugarcane varieties (CV7870 and RB867515) as affected by K, Ca and S dosages applied in ratoon 1

Treatment	K ₂ O	CaO	S	CV7870			RB867515		
				Stalk yield	Pol‡	TRS†	Stalk yield	Pol	TRS
				----- (Mg ha ⁻¹) -----			----- (Mg ha ⁻¹) -----		
	(kg ha ⁻¹)								
Absolute control	0	0	0	92.1	18.5	15.3	116.1	19.4	16.5
Control	105	0	0	97.6	18.4	15.4	137.5	22.1	19.1
POLY	70	80	96	105.8	20.3	16.8	136.4	21.9	18.8
POLY	105	120	144	120.5	21.8	18.3	148.3	23.9	20.4
POLY	140	160	192	111.2	20.8	17.2	131.3	19.6	16.9
KCl+GYP	105	80	60	104.7	19.8	16.3	140.3	22.2	19.1
KCl+GYP	105	120	90	115.7	22.2	18.4	139.4	24.2	20.4
KCl+GYP	105	160	120	111.1	20.5	17.1	141.9	22.3	19.5
Mean				107.3	20.3	16.9	136.4	21.9	18.8
SD ¢				6.8	1.7	1.4	3.9	0.7	0.5
LSD¶ (0.10)				16.6	3.3	2.7	16.7	3.6	2.7

‡ Apparent sucrose content; † Total Recoverable Sugar; ¢ Standard Desviation;

¶ Least Significant Difference

POLY dosages applied in the variety CV7870 increased the stalk yield, Pol and TRS compared to control, reaching the maximum yield of 120.5, 21.8 and 18.3 Mg ha⁻¹, respectively, when was applied 105 kg K₂O (Table 3). In contrast, control treatment presented the lowest values of stalk yield, Pol and TRS, with mean values of 97.6, 18.4 and 15.4 Mg ha⁻¹, respectively. KCl+GYP dosages also obtained higher stalk yield, Pol and TRS compared to control, resulting in average 16% more production when was applied KCl+GYP (105 kg K₂O and 120 kg CaO), which is the equivalent dosage of POLY105. In spite of K promotes the increase of stalk yield in sugarcane, high concentrations of this element in stalks can cause problems during sugar industrialization, mainly because K ions are not precipitated during the clarification process, remaining through the boiling house and becoming concentrated in the molasses.

Thus, K inhibit crystallisation of sucrose, raises the molasses purity and causes losses in the amount of sugar produced (James, 2004).

The stalk yield, Pol and TRS in the variety RB867515 was also affected by POLY and KCl+GYP when compared to absolute control, being between 16 to 18% more productive (Table 3). However, these two K sources did not show any difference when compared to the control (105 kg K₂O ha⁻¹ via KCl). The highest stalk yield, Pol and TRS was observed when applied 105 kg K₂O via POLY, achieving the highest yield of 148.3, 23.9 and 20.4 Mg ha⁻¹, respectively. Conversely, absolute control exhibited the lowest stalk yield, Pol and TRS, with mean values of 116.1, 19.4 and 16.5 Mg ha⁻¹. Furthermore, when KCl+GYP was applied at the dosage of 105 kg K₂O and 120 kg CaO it was obtained the highest Pol and TRS, similar to the results when POLY was used in its equivalent dosage. The average yield of sugarcane was greater than 125 Mg ha⁻¹, exception only to absolute control, showing higher responses than expected according to the fertilization recommendations (Raij et al., 1997; Vitti and Mazza, 2002). This outcome can be explained by previous land use, since the grassland previous present in the experimental area may have favored the increase of the organic matter and, consequently, the nutrient availability for sugarcane.

The relationship between total DM and stalk yield in response to the application of K, S and Ca formulations in both varieties, CV7870 and RB867515, is illustrated in Fig. 5. In general, a significant relationship was detected, showing a similar linear trend for both varieties, with r^2 values between 42 to 45%. As previously discussed in Fig. 4, it is noticed that most of the higher values observed in the relationship are related to the variety RB867515, whereas the lower values are related to the counterpart, variety CV7870. This indicates that the increase in stalk yield can be related with the increase of biomass production, as mentioned previously by Menandro et al. (2017). Moreover, these authors evaluating the biomass yield for second-generation ethanol production of several sugarcane varieties, including RB867515, found average ratios of dry straw/fresh stalk of 12%, similar to our results which accounted 10% for variety CV7870 and 11.5% for RB867515. However, these ratios are lower than the reported by Hassuani et al (2005), assessing potential varieties for sugar/ethanol production in Brazil, which average approximately 14%.

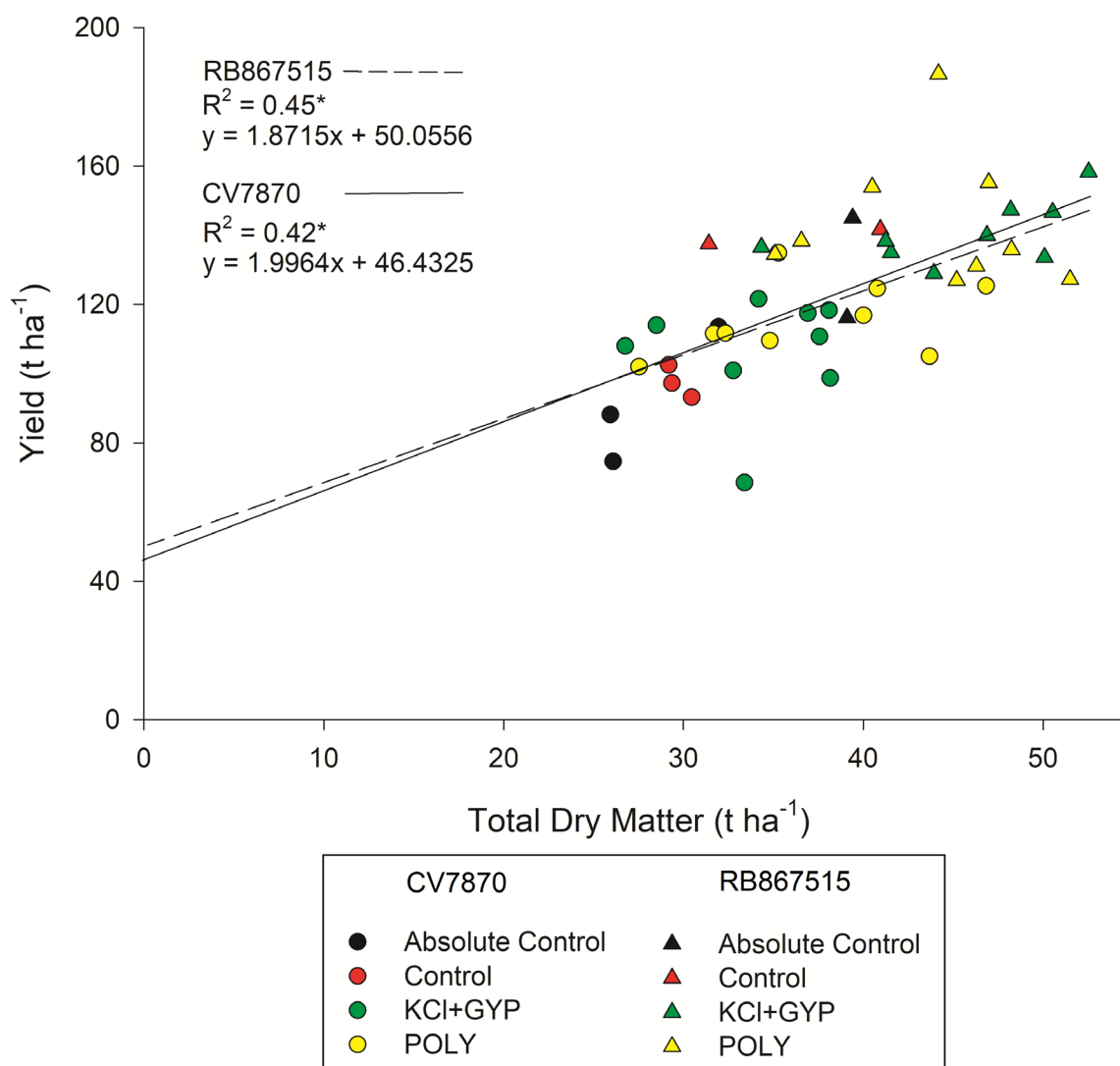


Figure 5. Relationship between total plant dry matter and stalk yield of two sugarcane varieties (CV7870 and RB867515) as affected by K, Ca and S dosages applied in ratoon 1.

The Fig. 6 shows the relationship between plant DM and nutrient content in each plant fraction. Although, there was not any significant effect among the treatments evaluated ($p > 0.10$), this relationship revealed that each sugarcane variety distributed the nutrients in its plant organs in a specific way. This characteristic can be associated to the differences observed in stalk and straw yield, and the performance in low fertility soils in both varieties, CV7870 and RB867515. For instance, K content in stalk was different in both varieties, ranging 10 to 27 g K kg⁻¹ in RB867515 and 5 to 15 g K kg⁻¹ in CV7870 (Fig. 6a). This difference in K content can suggest a marked performance in stalk yield because this nutrient enhanced translocation of sucrose from leaves to stalk, increasing the accumulation of sugar and higher percentage of sucrose

(Moore and Botha, 2014), as observed in the variety RB867515 (Fig. 6b). Furthermore, K content in top leaves also were higher in the variety RB867515 than CV7870, representing 70 and 75% of the total nutrient present in the straw, respectively. Thus, top leaves accumulated K more than 3 times compared to dead leaves. Overall, average leaf K contents in the two varieties evaluated varied between 10 and 20 g kg⁻¹, regardless the source applied (data not shown), which is adequate for sugarcane (Fageria et al., 2011).

Considering the layer 0-40 cm assessed, comparing the initial K soil availability for both varieties (Table 1) and total K uptake at the end of the ratoon (Fig. S3 and S4), the amount of K that was taken up by both sugarcane varieties were higher than the amount of initial K available summed to the amount of fertilizer applied by each treatment. Over the past three decades, several studies were conducted to assess the effect of non-exchangeable forms of K in plant nutrition and explain why the amount of K fertilizer recommended was lower the sum of crop K removal, K losses by leaching and K transformations in the soil (Sadusky et al., 1987; Wulff et al., 1998; Chiba et al., 2008). In general, they indicate that soils with low K availability caused by intensive use could promote the increase of K buffer power, releasing K from non-exchangeable K fractions. Furthermore, the sand and the silt fractions contain about 10% K-feldspar minerals, which accounts the total soil K of 26 Mg ha⁻¹ in a 0-30 cm soil. Although the low rate of weathering of these minerals could provoke K release affecting positively this nutrient uptake, indicating that the K content of silicate minerals in the sand and silt fraction may be an important source of K for plants.

It is important to highlight that sugarcane allocates high amount of K in the straw (dead leaves and tops), considered relevant for K recycling. Potassium is readily recycled, because it does not participate in any structural function in the cell and does not comprise organic compounds in plants (Römheld and Kirkby, 2010). Research found releases of approximately 90% of the K from sugarcane straw in a short-time, nearly a year (Menandro et al., 2017; Oliveira et al., 1999; Fortes et al., 2012).

Among all nutrients assessed, Ca was the element with less content in stalks compared to top and dead leaves, representing only 50% for CV7870 and 40% RB867515 of the total nutrient present in the straw. Overall, Ca content varied from 1 to 2 g kg⁻¹, irrespective the variety. However, comparing the 'straw fractions' (dead leaves and top leaves), Ca content in top leaves was lower in the variety CV7870 (Fig. 6c) and similar in the RB867515 (Fig. 6d). This dynamics is due to the low mobility of Ca in plants, accumulating in higher proportions in leaves,

promoting stabilizitation and strengthening of the cell walls and regulation of the membrane permeability (Hawkesford et al., 2012).

For Mg, CV7870 showed similiar content in the stalk and straw, showing values between 1 and 3 g kg⁻¹. On the other hand, RB867515 showed more content in the straw (2.8 to 4.9 g kg⁻¹) compared to the stalks (1 to 2 g kg⁻¹). The same trend was observed for S, CV7870 showed a huge range (0.5 to 2 g kg⁻¹) but the same S content between stalks and straws. For RB867515, S was more concentrated in the top leaves, while dead leaves and stalks presented a similar content (0.2 to 1 g kg⁻¹).

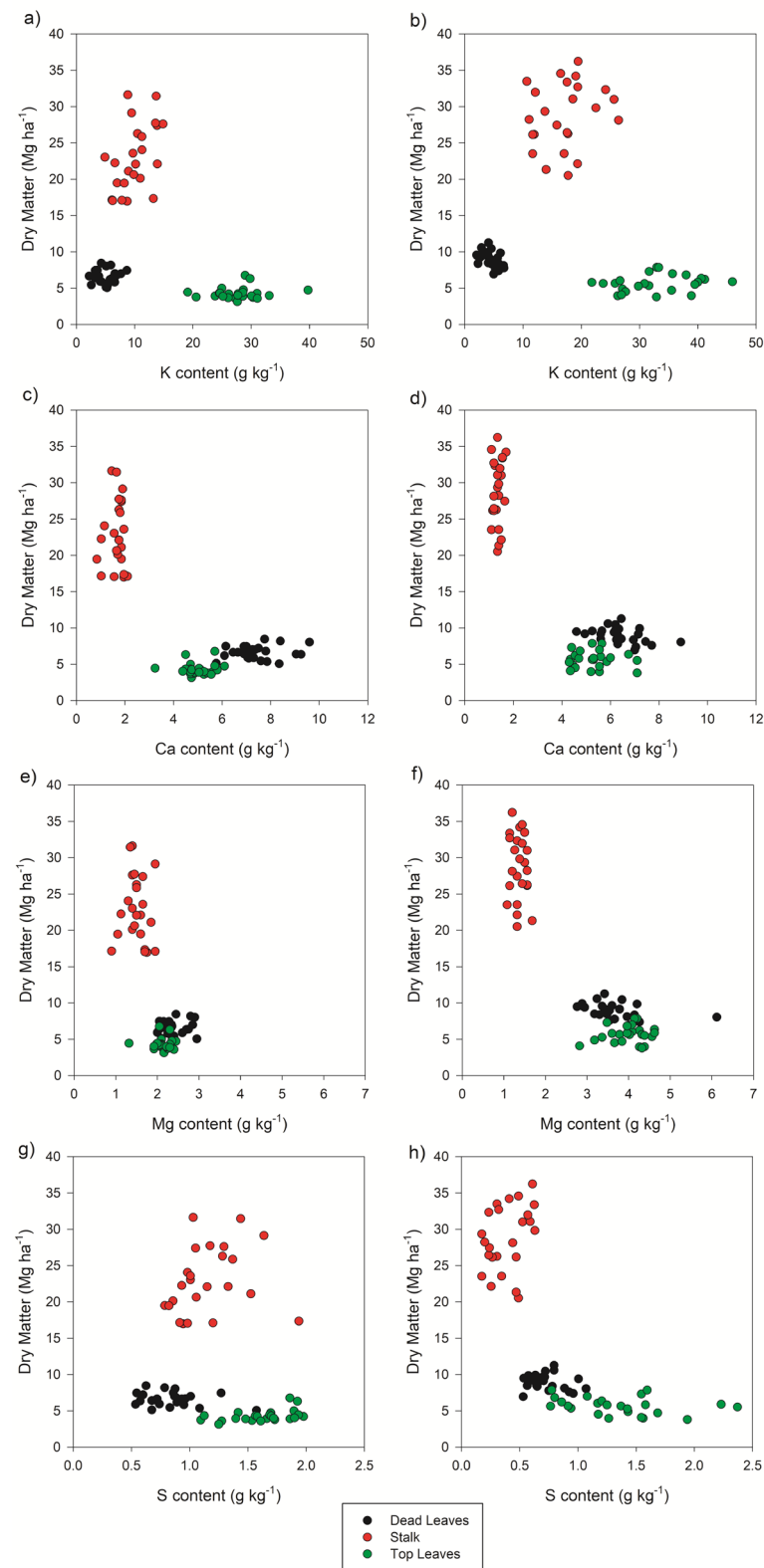


Figure 6. Relationship between plant dry matter and nutrient content fractionated into dead leaves, top leaves and stalks of two sugarcane varieties, CV7870: a) K, c) Ca, e) Mg and g) S, and RB867515: b) K, d) Ca, f) Mg, and h) S, as affected by K, Ca and S dosages applied in ratoon 1.

2.3.2 Relative Agronomic Effectiveness and Agronomic efficiency

The relative agronomic effectiveness (RAE) was significant depending on the K source and dosage applied (Fig. 7), indicating that POLY and KCl+GYP are more efficient than KCl applied sole as K source in both sugarcane varieties evaluated. In these sense, the highest RAE was achieved when POLY was applied at 105 kg K₂O ha⁻¹, being 23% and 27% more efficient than applying KCl at dosage of 105 kg K₂O ha⁻¹, for CV7870 and RB867515, respectively. In previous studies in other crops lower relative yield of rye and barley were observed while potato and sugarbeet responded to K application, which indicates that every crop specie has difference K use efficiency and thus to maintain yields in high-K demanding crops, such as potato and sugarbeet the quantity of K to supplied must be equivalent to the amount absorbed by the crop, as found in our results (Wulff et al., 1998).

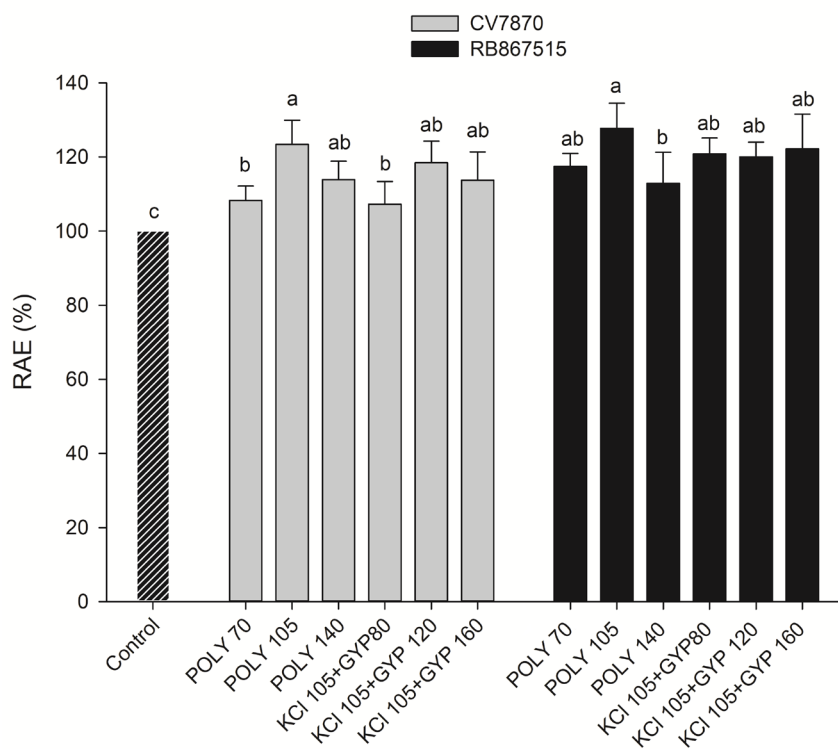


Figure 7. Relative agronomic effectiveness (RAE) of potassium fertilizers of two sugarcane varieties (CV7870 and RB867515) as affected by K, Ca and S dosages applied in ratoon 1. For the K reference fertilizer, the potassium chloride (Control), RAE=100% (cross hatched bars). Vertical bars (T) represent the standard error of the means (n = 3). ns: non-significant

There is a lack in literature for a suitable comparison among K formulations used in our research, mainly in sugarcane crop under field conditions, however, POLY is currently applied in other crops, which can be comparable. Bernardi et al (2018) has reported similar findings, when evaluating the efficiency of POLY relative to KCl+GYP and KCl combined with POLY under three dosages of K (50, 100 and 200 kg K₂O ha⁻¹) on alfafa (*Medicago sativa* L.) in a pot experiment, where POLY was more effective than KCl, indicating that POLY is a promising K fertilizer alternative for alfalfa in Brazilian acidic soils.

It was also evaluated the agronomic efficiency of K (AEK) as illustrated in Fig. 8a. Supplying K at dosage of 105 kg K₂O ha⁻¹ via POLY resulted in higher AEK in both varieties. However, when POLY was applied in the highest dosage assessed (140 kg K₂O ha⁻¹) it showed the lowest values of AEK, 164 kg kg⁻¹ for CV7870 and 78 kg kg⁻¹ for RB867515. Focused on the variety CV7870, fertilization with KCl105+GYP80 also reached the lowest AEK, averaging 145 kg kg⁻¹, decreasing more than 2 times its efficiency compared to the maximum AEK achieved by POLY.

Considering Ca in fertilizer formulation (POLY and KCl+GYP), agronomic efficiency of calcium (AECa) was significantly affected by treatments applied (Fig. 8b), observing same dynamics to AE K. Regarding to variety CV7870, fertilization with POLY at dosage of 105 kg K₂O ha⁻¹ increased AECa by almost 3 times compared to the highest dosage of POLY and KCl+GYP applied. Likewise, when Ca was applied in the lowest dosage of Ca (80 kg CaO ha⁻¹) via POLY and KCl+GYP in the variety RB867515, the AECa achieved the highest values (355 and 423 kg kg⁻¹), increasing by 2.7 to 3.2 times the agronomic efficiency contrasted to the highest dosage of Ca applied (160 kg CaO ha⁻¹) via POLY.

Including the treatments with S in their formulation (POLY, KCl+GYP), agronomic efficiency of sulfur (AES) was significant due to the treatments used, in both sugarcane varieties (Fig. 8c). The lowest AES was found at applying 192 kg S ha⁻¹ via POLY, with average values of 99 and 78 kg kg⁻¹ in CV7870 and RB867515, respectively, while under lower S dosages the AES was higher, reaching the superior AES at 90 and 60 kg S ha⁻¹ via KCl+GYP, with mean values of 262 and 403 kg kg⁻¹ in CV7870 and RB867515, respectively.

Our findings on nutrient agronomic efficiency corroborate other studies in several crops, such as, rape oilseed (Dugast, 2015), mustard (Tiwari et al., 2015), cabbage (Satisha and Ganeshamurthy, 2016), cauliflower (Satisha and Ganeshamurthy, 2016), peanut (Hoang et al., 2016), coffee (PVFCCo, 2016), tea (PVFCCo, 2016), potato (da Costa et al.,

2018a, tomato (da Costa et al., 2018b), corn (Pavuluri et al., 2017), alfalfa (Bernardi et al., 2018). In general, these studies have indicated that POLY is as effective as the farmer's popular K sources, providing a slower release of nutrients to plant growth.

The south-central Brazilian region accounts about 90% of sugarcane production and the harvest period commonly ranges from April to December, including both weather seasons, dry (April to September) and wet seasons (October to January). The application of K treatments occurred during the end of the dry season (September 2014), resulting in a low solubilization rate of the fertilizer granules due to the water deficit but without any losses. However, in the subsequent weather seasons in 2015 were atypical with monthly precipitations above 200 mm in January (285 mm), April (211 mm) and May (205 mm) (Fig. 1), and resulting in different nutrient agronomic efficiency and may cause nutrient leaching. Additionally, other authors have indicated that in addition to soil available K, nutrient-use efficiency, site, cultivars, and years have a strong impact on yield increase to applied K fertilizer (Niu et al., 2011; Kuchenbuch and Buczko, 2011; Darunsontaya et al., 2012; Hussain et al., 2015).

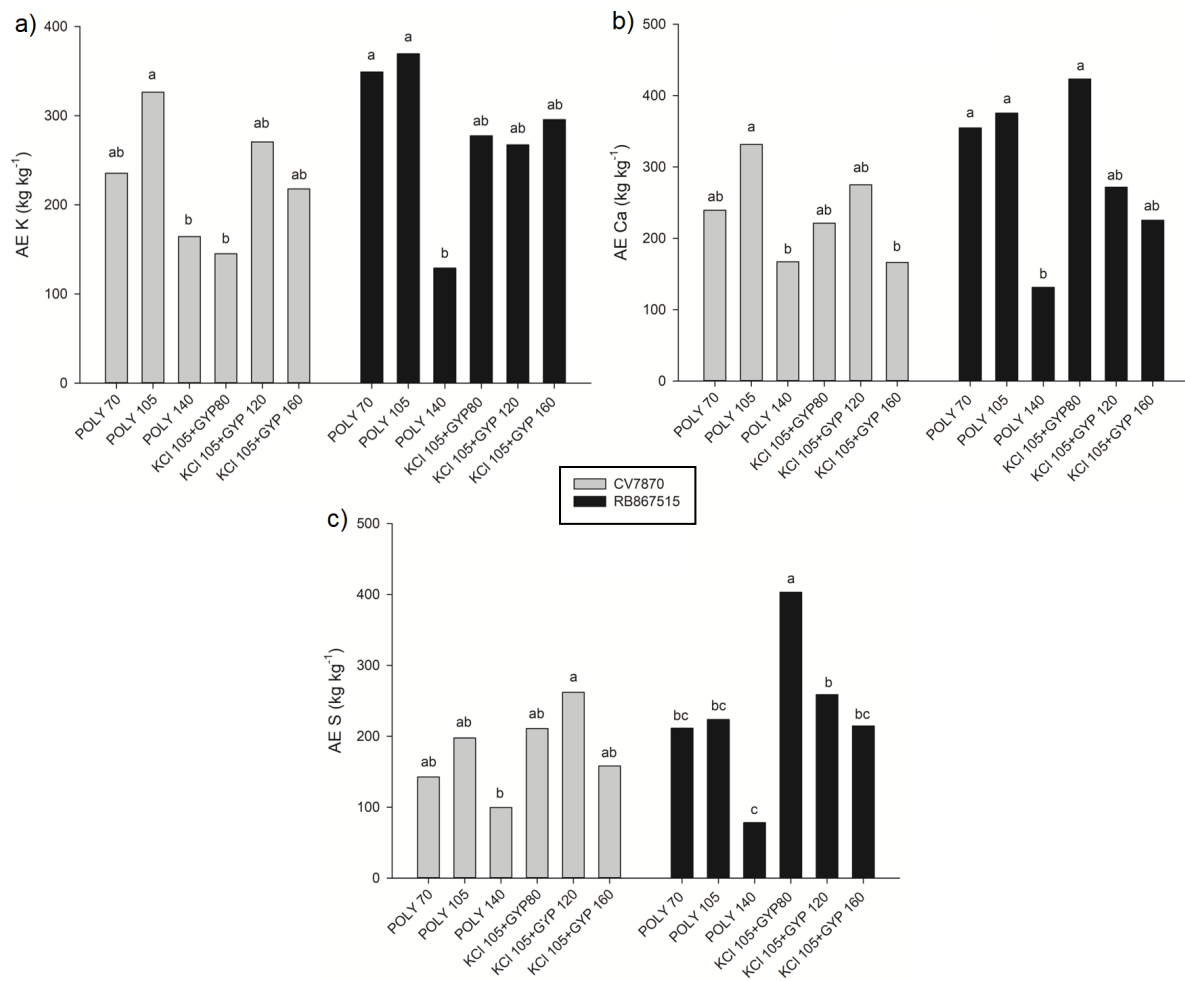


Figure 8. Agronomic efficiency of a) potassium (AEK), b) calcium (AECa) and c) sulfur (AES), considering six formulations of K, Ca and S applied in two sugarcane varieties (CV7870 and RB867515) cropped in ratoon 1. Columns followed by the same lowercase letter do not differ statistically by Duncan's multiple range test.

2.3.3 Soil nutrient concentration

For the variety CV7870, the results indicate that there is a difference ($p < 0.10$) in all the layers evaluated in soil profile (0-40 cm) for S-SO₄; Ca and Mg, however K did not show any difference across the profile. This suggest that providing a high K-demanding crop, such as sugarcane, with amounts of K equivalent to those needed for optimum yield which is about equal to those absorbed, can be observed adequate because K is sufficiently mobile in sandy

soils to be fully used by the crop (Wulff et al., 1998). Furthermore, available K at subsuperficial layers (10-20 cm and 20-40 cm) after harvest is considered low and very low according to Raij, 2011.

Even though Ca concentration was not statistically significant, the levels are greater than $7 \text{ mmol}_c \text{ dm}^{-3}$, which are considered as high according to Raij (2011). Concerning to S, in the upper 0-10 cm layer, the highest concentration was observed in POLY70. For Ca, KCl105+GYP120 and KCl105+GYP160 presented the highest values and for Mg POLY140 showed the highest concentration in the soil (Table 4). In the second soil layer, the highest S-SO₄ values were observed in the control and when POLY was applied in the doses of 70 and 105 kg K₂O ha⁻¹. Under KCl105+GYP80 a high S-SO₄ was also observed, otherwise the lowest Mg was observed in this same treatment. The lowest Ca concentration in the soil was observed in the POLY105 and the highest was observed in KCl105+GYP160 in the deepest layer assessed (20-40 cm) with all the treatments showing an increase in S-SO₄ compared to the control, except KCl105+GYP120, which also presented the lowest Mg. Our findings corroborate other studies showing that the release of SO₄²⁻ anion by phosphogypsum remains in the solution and could be leached, carrying with it Ca, Al, Mg or K cations. Chemical complexes are produced between sulfate and cations decreases the bioavailability of these ions, although they are not neutralized. Moreover, a high Ca concentration displaces Al³⁺ from negative charge colloids into the soil solution. Thus, phosphogypsum carries Ca to deeper soil layers, which results in the favor of ameliorate deeper soil environment, thereby improving high root growth (Morelli et al., 1987; Morelli et al., 1992; Spironello et al., 1996; Raij 2008; Barbosa, 2010).

On the other hand, the variety RB867515 did not show significant effect for S-SO₄, K and Ca across the soil profile and only Mg showed effect in all the layers assessed. According to Otto et al (2009), approximately 87% of the sugarcane roots are located within the 40 cm of the surface soil profile and 30 cm to the side of each plant furrow. In this sense, placing the K, Ca, and S fertilizers in the plant furrow which is nearby to the root system is an approach to guarantee high yields minimizing nutrient losses. S-SO₄ only showed effect in the deepest layer (20-40 cm). In this sense, when either formulations, POLY or KCl+GYP were applied, irrespective the dosage, the values of S-SO₄ were lower compared to the control. Potassium also had effect only in the layer 20-40 cm, where high values were observed in when POLY140 was applied, and KCl105+GYP80 and KCl105+GYP160 were applied. It is relevant to highlight that our study was carried out in a sandy Oxisol, which typically has low cation-exchange capacity (CEC)

containing clay minerals with pH-dependent charges, and therefore hold small amounts of cations promoting nutrient leaching (Raij, 2011). Furthermore, due to the predominance of negative charges in these soils, anions such as SO_4^{2-} are not adsorbed, being susceptible to be leached, but based on the electroneutrality principle this anion can carry equivalent quantities of cations such as Ca^{2+} , Mg^{2+} and K^+ . For Ca, an opposite situation was observed, and the treatments only presented effect in the upper layer, where the highest Ca was observed under KCl105+GYP160. For Mg, in the layers 0-10 and 10-20 cm, the highest values were observed in the absolute control, the control and the lowest POLY dosage (POLY70). In the deepest layer, 20-40 cm, the highest value was observed under absolute control, without any difference between the other treatments. According to Raij (2011), soil Mg availability is considered high when the levels are greater than $8 \text{ mmol}_c \text{ dm}^{-3}$, which did not occur in our study.

Table 4. Soil nutrient concentration in three soil layers: 0-10 cm; 10-20 cm; and 20-40 cm, submitted to six formulations of K, Ca and S applied in sugarcane ratoon variety CV7870.

Treatment	S-SO ₄ mg kg	K ----- mmol _c dm ⁻³ -----	Ca	Mg
Depth layer 0-10 cm				
Absolute control	5.5	1.1	10.5	4.7
Control	5.0	1.0	5.7	2.7
POLY 70	9.0	1.5	11.0	3.7
POLY 105	7.5	1.8	10.0	3.0
POLY 140	7.0	1.7	11.0	4.3
KCl 105+GYP 80	6.5	1.4	7.7	2.0
KCl 105+GYP 120	8.0	1.4	12.3	2.7
KCl 105+GYP 160	6.7	1.2	13.7	3.3
Mean	6.9	1.4	10.2	3.3
SD	1.2	0.2	2.4	0.8
LSD (0.10)	3.9	n.s	6.2	2.1
Depth layer 10-20 cm				
Absolute control	5.0	0.6	8.5	2.7
Control	9.0	0.5	7.0	1.7
POLY 70	8.7	0.7	8.0	2.3
POLY 105	9.3	0.9	6.0	1.7
POLY 140	7.3	0.7	9.3	2.0
KCl 105+GYP 80	8.3	0.9	6.7	1.0
KCl 105+GYP 120	7.5	0.7	9.7	1.7
KCl 105+GYP 160	7.5	0.6	11.0	2.0
Mean	7.8	0.7	8.3	1.9
SD	1.3	0.1	1.6	0.5
LSD (0.10)	3.3	n.s	3.8	1.4
Depth layer 20-40 cm				
Absolute control	7.7	0.3	5.5	2.7
Control	6.3	0.5	5.7	1.7
POLY 70	9.0	0.6	7.7	2.0
POLY 105	11.0	0.6	8.3	2.3
POLY 140	9.3	0.4	7.0	2.0
KCl 105+GYP 80	12.5	0.4	4.0	1.3
KCl 105+GYP 120	8.7	0.4	6.3	1.0
KCl 105+GYP 160	10.5	0.5	5.3	2.0
Mean	9.4	0.5	6.2	1.9
SD	1.8	0.1	1.3	0.5
LSD (0.10)	2.5	n.s	4	1.5

Table 5. Soil nutrient concentration in three soil layers: 0-10 cm; 10-20 cm; and 20-40 cm, submitted to six formulations of K, Ca and S applied in sugarcane ratoon variety RB867515

Treatment	S-SO ₄ mg kg	K ----- mmol _c dm ⁻³ -----	Ca	Mg
Depth layer 0-10 cm				
Absolute control	4.0	1.4	8.3	4.7
Control	5.3	1.7	9.7	5.3
POLY 70	4.0	1.4	10.0	4.0
POLY 105	5.0	1.6	9.3	3.3
POLY 140	4.0	2.2	7.0	2.0
KCl 105+GYP80	4.0	1.7	8.3	2.7
KCl 105+GYP 120	7.0	1.8	9.3	2.3
KCl 105+GYP 160	5.3	1.8	14.3	2.7
Mean	4.8	1.7	9.5	3.4
SD	0.9	0.2	1.9	1.0
LSD (0.10)	n.s	n.s	5.1	1.7
Depth layer 10-20 cm				
Absolute control	4.0	0.8	7.7	3.7
Control	4.0	1.1	6.3	2.7
POLY 70	4.3	1.0	7.7	3.0
POLY 105	7.7	0.8	7.3	2.3
POLY 140	8.7	1.4	4.5	1.5
KCl 105+GYP80	4.0	1.3	6.0	1.0
KCl 105+GYP 120	6.0	1.0	5.7	1.7
KCl 105+GYP 160	8.3	1.3	6.5	1.5
Mean	5.9	1.1	6.5	2.2
SD	1.8	0.2	1.0	0.8
LSD (0.10)	n.s	n.s	n.s	1.6
Depth layer 20-40 cm				
Absolute control	4.7	0.5	3.7	3.3
Control	6.5	0.8	3.7	2.7
POLY 70	4.0	0.6	5.0	2.7
POLY 105	4.0	0.6	3.7	2.0
POLY 140	4.0	1.3	4.0	2.0
KCl 105+GYP80	4.3	1.1	4.3	1.7
KCl 105+GYP 120	4.5	0.7	4.7	1.7
KCl 105+GYP 160	4.3	1.0	5.0	2.0
Mean	4.5	0.8	4.3	2.3
SD	0.7	0.2	0.5	0.5
LSD (0.10)	2.5	0.5	n.s	1.4

2.4 Conclusions

The application of K, Ca, Mg and S, regardless the source applied, reflected positively in the yield of sugarcane. Nowadays, the combination of fertilizers, such as, KCl and phosphogypsum guarantee the plant requirements are widely used. However, the use of polyhalite, as a multi-nutrient fertilizer, was as efficient as the standard source considering an agronomic viable fertilizer for sugarcane. Furthermore, each sugarcane variety has allocated nutrients in its plant organs in a particular way. The variety RB867515 differentiated markedly from CV7870 in K content accumulated in stalk, suggesting a better performance in stalk yield because this nutrient promotes translocation of sucrose from leaves to stalk, increasing the accumulation of sugar and higher percentage of sucrose.

Concerning to the dosage, the application of $105 \text{ kg K}_2\text{O ha}^{-1}$, which corresponds to farmer's recommended dosage, promoted the highest stalk yields for both varieties, CV7870 and RB867515. This dosage keeps the adequate nutritional status of sugarcane ratoon and enhanced K content in stalk, promoting adequate accumulation of sucrose in this plant organ.

In relation to the soil parameters after cultivation, for the variety RB867515 most of the nutrient content were not significant compared to control, suggesting that as much fertilizer is applied this variety will uptake and export or it is lost by leaching/runoff. On the other hand, the variety CV7870 showed higher values for Ca, Mg and S in the treatments compared to the control after cultivation, indicating this variety as promising for further studies of residual effect of fertilizers.

Long-term studies evaluating the cumulative effects of POLY for different soils of sugarcane areas should be encouraged with the objective of provide insights related to the best K management approaches.

One point to be considered is this study is that the dosage balance was performed based on Ca and K, whereas Mg and S were not balanced. The balance of these four elements are relevant for the fertilizer use efficiency and should be taken into account in further studies.

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Supplementary material

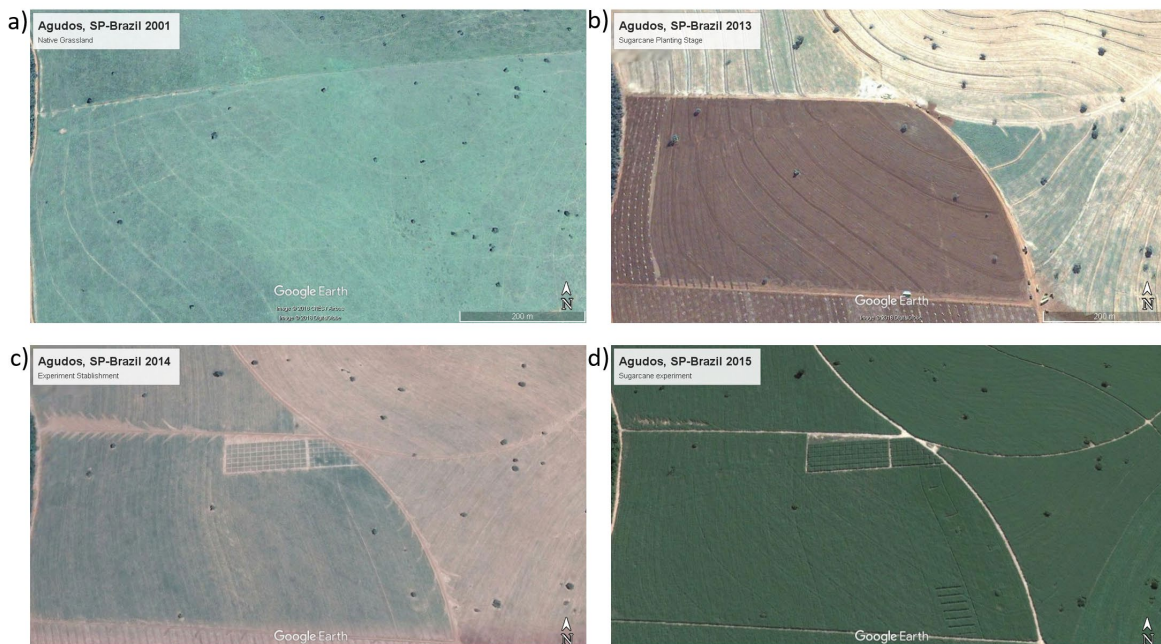


Figure S1. Satellite images of the experimental site. Agudos – SP, Brazil (22°33' S, 49°06' W).

a) View of native grassland before sugarcane establishment (12 December, 2001); b) View of sugarcane planting of two varieties CV7870 and RB867515 (10 July, 2013); c) View of sugarcane experiment establishment (21 September, 2014); and d) Sugarcane experiment view before harvest (3 April, 2015). Source: Google Earth Pro.



Figure S2. Yield assessment in sugarcane experiment, Agudos – SP, Brazil. a) Fractionation of the plant into cane stalks, dead leaves and top leaves for biometric evaluations; b) Chopping process of the plant fractions to obtain tissue samples for nutrient quantification and moisture content; c) Weighting process of cane stalks using a digital dynamometer; d) Yield weight process by means of cane loading machine.

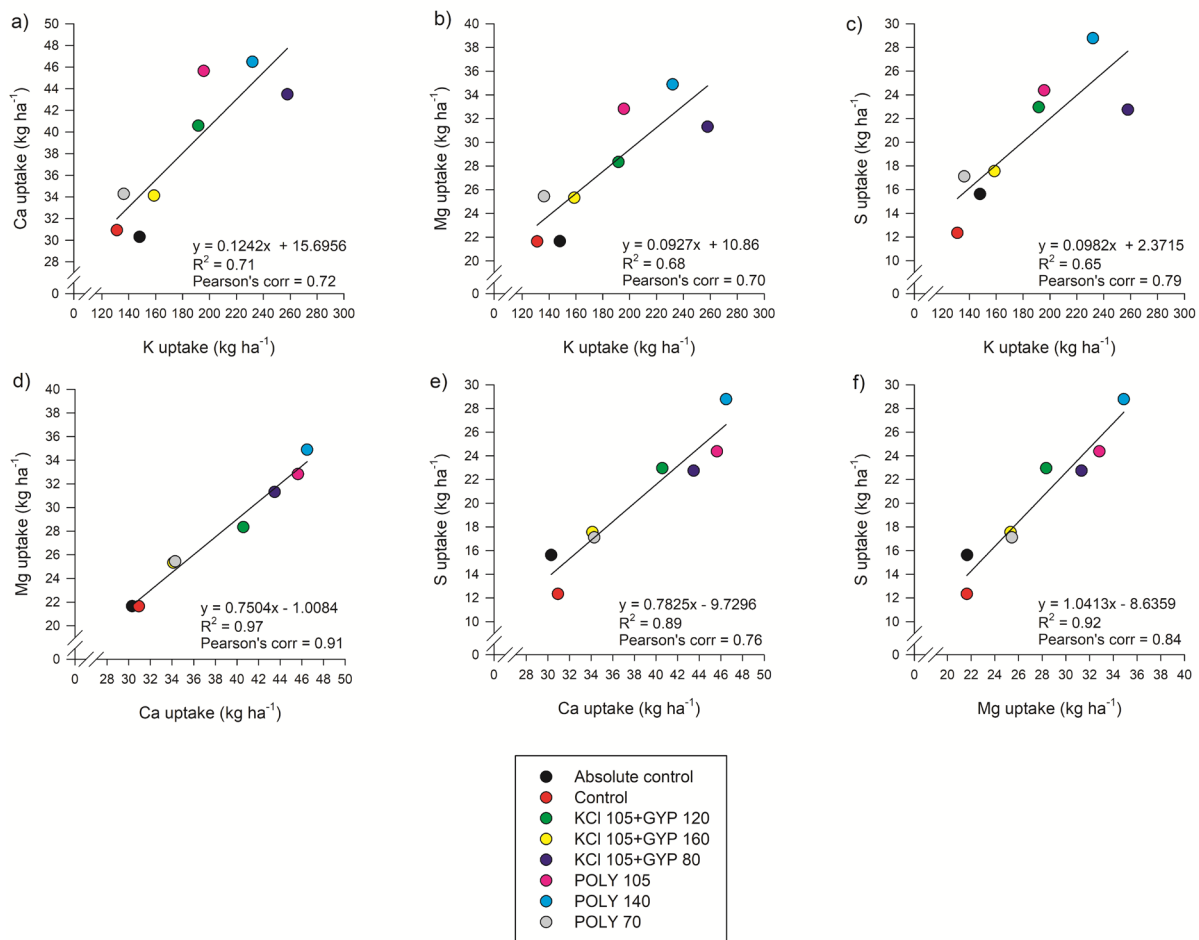


Figure S3. Relationship between nutrient uptake of sugarcane variety CV7870 as affected by K, Ca and S dosages applied in ratoon 1. a) K and Ca uptake; b) K and Mg uptake; c) K and S uptake; d) Ca and Mg uptake; e) Ca and S uptake; f) Mg and S uptake

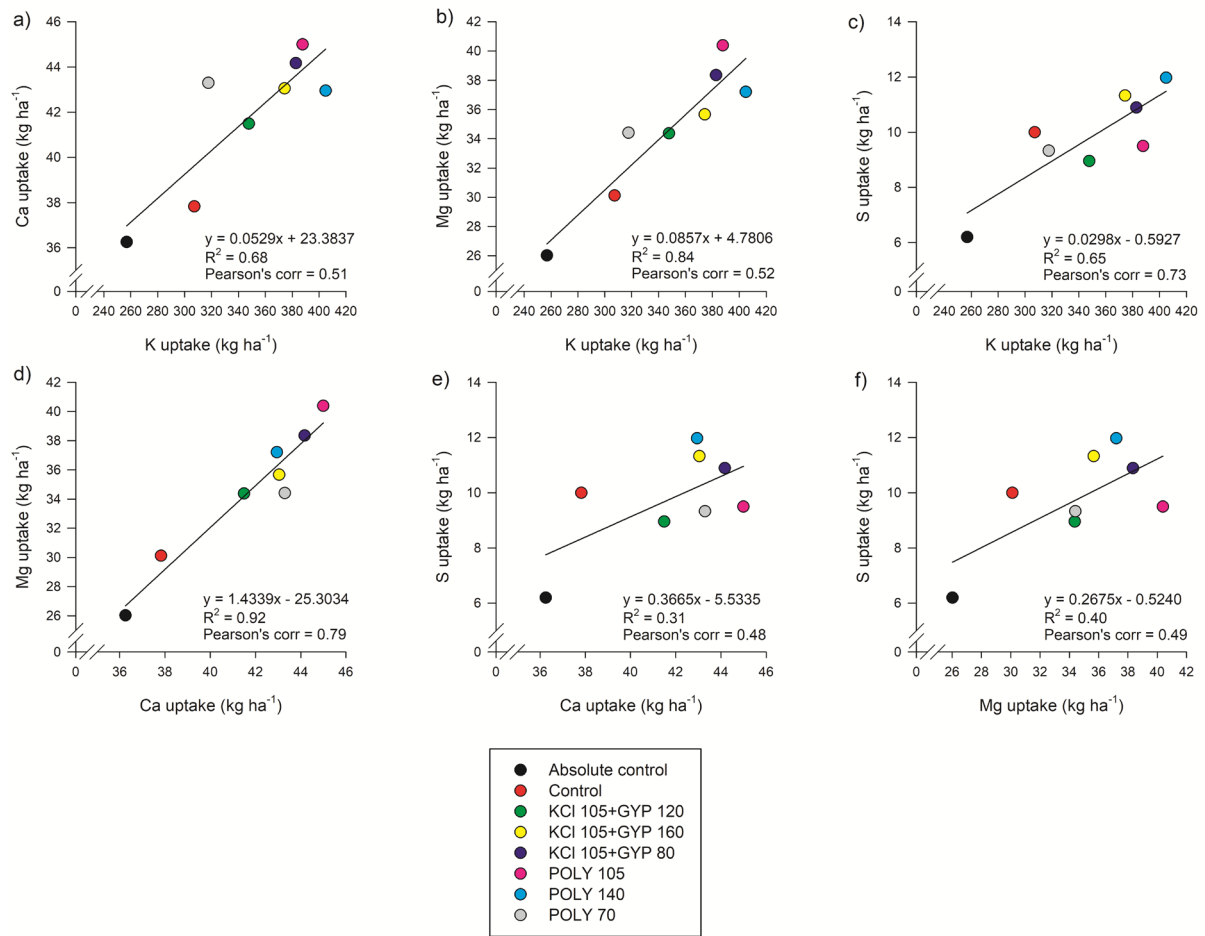


Figure S4. Relationship between nutrient uptake of sugarcane variety RB867515 as affected by K, Ca and S dosages applied in ratoon 1. a) K and Ca uptake; b) K and Mg uptake; c) K and S uptake; d) Ca and Mg uptake; e) Ca and S uptake; f) Mg and S uptake

3 POLYHALITE AS A MULTI-NUTRIENT SOURCE AFFECTING INITIAL DEVELOPMENT OF SUGARCANE IN BRAZIL. GLASSHOUSE STUDY

Abstract

Currently, Brazilian sugarcane (*Saccharum* spp.) fields use single nutrient fertilizer sources to meet potassium (K) requirement, which involves high production cost. To overcome this, our study aimed to evaluate the efficiency of polyhalite (POLY) as a multi-nutrient source for sugarcane compared to single sources of K (potassium chloride-KCl), Ca, Mg and S sources (phosphogypsum–GYP, kieserite–KIE). An experiment was carried with the cultivar CV7870 on a low-K Oxisol in greenhouse. A completely randomized design was followed with distinct management of K: four dosages of K (0, 21, 42 and 63 mg kg⁻¹) using as sources POLY (pure); KCl (pure); KCl+POLY in a ratio 1:1; and KCl combined with GYP and KIE, balancing Ca, Mg and S dosages supplied by POLY treatment. Two short growth cycles were evaluated; cane-plant harvested 131 days after transplanting and ratoon harvested at 253 days after transplanting. In general, shoot dry matter yield and nutrient uptake were more correlated to high K dosages applied and K sources containing Ca and S in the formulation, for both growth cycles, cane and ratoon crop. However, when these sources were provided at the lowest dosage were highly correlated with superior agronomic efficiency in all nutrients assessed, indicating that a mix of POLY and KCl can be used profitably as multi-nutrient fertilizer for sugarcane. Additionally, a laboratory study using μ -XRF spectroscopy was carried out on POLY and KCl to characterize the elemental distribution in the granule and to evaluate the release of K, Ca and S from POLY and KCl in a soil rhizobox. Results shown that water penetrates rapidly in KCl granule during the first hours, dissolving and releasing Cl⁻ and K⁺ fast, potentially leaching in the soil profile. Conversely, POLY granule performed as a slow-release fertilizer due to its slow solubility compared to KCl, enhancing residual effects over time.

Keywords: *Saccharum* spp.; Potassium; Calcium; Sulfur; Nutrient release; X-ray fluorescence; Agronomic efficiency

3.1 Introduction

One of the main factors limiting the increase of Brazilian sugarcane productivity is the low availability of potassium (K) in tropical soils (below 59 mg dm⁻³) (Santos et al., 2015). Thus, its supply is conditioned by means of fertilizers, becoming the world's second largest consumer of K, being potassium chloride (KCl) as the most widespread potassium-bearing fertilizer in sugarcane production due to the lower input cost in relation to K₂O (ANDA, 2017). To compensate its drawbacks in the context of agricultural sustainability, studies on rational use of fertilizers is a critical issue, as it represents a high percentage of production costs (Cortez,

2010). One alternative is the use of multi-nutrient sources, such as polyhalite (POLY), since this can provide several macronutrients in a single application.

In sugarcane, K is an essential element with the highest absorption and export (Orlando Filho, 1993), mainly by ratoon (Korndörfer and Oliveira, 2005), being involved in the transport of sugars (Cai et al., 2012), nitrogen metabolism, water absorption and transport, osmoregulation, enzyme activation and load neutralization (Römheld and Kirkby, 2010). Hence, K is crucial to maintain ratoon sugarcane yields (Paneque et al., 1992).

Additionally, in high weathering in tropical soils, K is one of the most limiting nutrients due to the low concentration of the element in parent material and the fixation in the structure of 2:1-layer silicate minerals (Conti et al., 2001).

An alternative K source emerging on the world fertilizer market is polyhalite, an evaporite mineral found in marine sedimentary deposits, described by the chemical formula $K_2Ca_2Mg(SO_4)_4 \cdot 2(H_2O)$ (Manning, 2017). The use polyhalite for agricultural purposes began when a deposit of commercial size was discovered in early 20th century in New Mexico and western Texas, United States (Hoots, 1925; Mansfield and Lang, 1929) and reported in some countries, such as, Austria (Stromeyer, 1820), Germany (Schober, 1868), France (Cloizeaux, 1867), Italy (Cortese, 1922), Russia (Kurnakov et al., 1937), Poland (Buyalov and Lepeshkov, 1937), India (Gohil et al., 1996). However, this commercial interest was abandoned after the discovery of a huge potash deposit in Saskatchewan, Canada. Few studies were conducted using polyhalite (POLY) as a K fertilizer in different crops, such as sorghum (Fraps and Schmidt, 1932), potato (Lepeshkov and Shoposhnikova, 1958; Panitkin, 1967), beet (Panitkin, 1967), maize (Fraps and Schmidt, 1932; Terelak, 1974; Barbarick, 1989), flax (Lepeshkov and Shoposhnikova, 1958), millet (Boratyński and Turyna, 1971) rye (Terelak, 1975), mustard (Boratyński and Turyna, 1971; Terelak, 1975), buckwheat (Boratyński and Turyna, 1971), oat (Terelak, 1975), barley (Mercik, 1981), ryegrass (Mercik, 1981) and sorghum-sudangrass (Barbarick, 1991).

Recently, since the discovery of Zechstein deposits located in North Yorkshire, United Kingdom, the world's largest highest grade deposit of polyhalite (Kemp et al., 2016), has again aroused interest in use this mineral as a fertilizer, promoting new research on crops, such as, rape oilseed (Dugast, 2015), mustard (Tiwari et al., 2015), cabbage (Satisha and Ganeshamurthy, 2016), cauliflower (Satisha and Ganeshamurthy, 2016), peanut (Hoang et al.,

2016), coffee (PVFCCo, 2016), tea (PVFCCo, 2016), potato (da Costa et al., 2018a), tomato (da Costa et al., 2018b), corn (Pavuluri et al., 2017), alfalfa (Bernardi et al., 2018).

Taken together, these studies indicate that POLY is as effective as KCl or K₂SO₄, providing a slower release of nutrients to plant growth, however, few of these studies balanced S, Ca and Mg concentrations similar to POLY treatments (Barbarick, 1991; da Costa et al., 2018a; da Costa et al., 2018b), avoiding negative plant responses derived to Ca, Mg or S not provided by nonPOLY treatments (Barbarick, 1991).

In the view of the above, research into K changes in weathered tropical soils under polyhalite fertilization regarding K uptake, and consequently in sugarcane is still restricted in literature. Therefore, this study aimed to evaluate the agronomic performance and residual effect of POLY as a multi-nutrient source for sugarcane on a low-potassium Oxisol contrasted to dosage of a commercial K fertilizer (potassium chloride) combined with Ca, Mg, S sources (gypsum and kieserite).

3.2 Material and Methods

3.2.1 Mineralogical, elemental and release characterization of polyhalite

This project was developed in partnership and partially supported by Sirius Minerals PLC. Samples of polyhalite (POLY) and kieserite (KIE) were supplied by Sirius Minerals PLC (Scarborough, UK) as granules with a size range of 2 to 3 mm in diameter and phosphogypsum and ammonium nitrate were obtained from local commercial companies (São Paulo, Brazil).

The mineralogical composition of polyhalite was based on X-ray diffraction (XRD) (Jackson, 1969) analyzed from a fertilizer sample collected in the shipped product. A powder slide was prepared from polyhalite sample grinded to a fine powder with a size particle less than 300 µm. Then, placed into a sample holder for diffractometry analysis. All patterns were obtained using a Rigaku Miniflex II Desktop diffractometer (Tokyo, Japan), CuKα radiation, with a range of 5 to 30° (2θ) for the specimen, operated at 30 kV and 15 mA. Interpretation of this pattern peak extraction was performed using Match! 3 software coupled with the international standard mineral database verifying that the XRD pattern displayed the major mineral phases, including polyhalite, gypsum, halite, magnesite and anhydrite (Fig. 1).

Elemental mapping of the POLY was performed by micro X-ray fluorescence spectroscopy (μ -XRF) (Jenkins, 1999). The fertilizer granules were cut crosswise using a stylet to obtain a flat surface. After, the samples were placed in a sample holder with a Kapton™ tape leaving the flat region exposed. Subsequently, the sample was loaded on the bench-top μ -XRF system (Orbis PC EDAX, USA), equipped with 30 mm² silicon drift detector (SDD) (140 eV fwhm at the 5.9 keV Mn-K α line) and a 30 μ m polycapillary optic. X-rays were produced by a Rh anode operating at 40 kV and 300 μ A. The distance between the sample and the X-ray source was 5 mm. Chemical maps were recorded using a matrix of 64 \times 50 pixels, dwell time per pixel of 2000 ms with a deadtime of nearly 5%, under vacuum conditions. The microanalysis shows high intensities of S located all over the region of interest (ROI), whereas K, and Ca are distributed in spots, possibly complexed by S (Fig. 2).

Elemental release from fertilizers was conducted in rhizoboxes using soil, and two K sources, POLY and KCl, in four replications. Rectangular rhizoboxes (67 mm wide, 98 mm height, and 20 mm thick) were built with perspex acrylic (2 mm thick) and the face exposed to the analysis was covered with polypropylene film (0.2 mm thick) to avoid spreading of soil particles by the air inside the bench-top μ -XRF system. The base of the rhizobox required holes to avoid water excess and 5 mm sponge sheet to avoid soil loss during drainage. Each rhizobox was filled up to 70 mm height (soil= 225 g). Soil was collected from the 0-20 cm layer of a native area nearby sugarcane farms in Agudos-SP, classified as sandy Typic Hapludox (Soil Survey Staff, 2014). Afterwards, the soil was air-dried and sieved in a 2-mm mesh, and chemical analysis was performed for initial characterization of nutrient contents and texture (table 1). The clay mineralogical characterization of this soil is predominantly anatase, kaolinite and gibbsite, and subordinate hematite, and chlorite (data not shown), typically found in Brazilian oxisols. After substrate placement in each rhizobox, a granule of POLY and/or KCl was added 20mm below surface facing the polypropylene film. Subsequently, the set rhizobox-substrate-fertilizer was placed in a petri dish contained deionized water to hydrate it by capillarity. This process is illustrated in Supplemental Figure S1. The microanalysis was performed by means of a benchtop μ -XRF spectrometer system operated with a Rh X-ray tube at 25 kV and 200 μ A and using a 25 μ m Al shutter filter. Line scans of 128 points were employed, analyzing on the granule and the surroundings region, every 178 μ m, to measure K, Ca and S intensities at 0.25, 6, 12, 24, 48 and 72 h after granule placement. The distance between the sample and the X-ray source

was 5mm, dwell time per pixel of 20000 ms per point, totalizing 45 min, with a deadtime of nearly 4%, under air conditions.

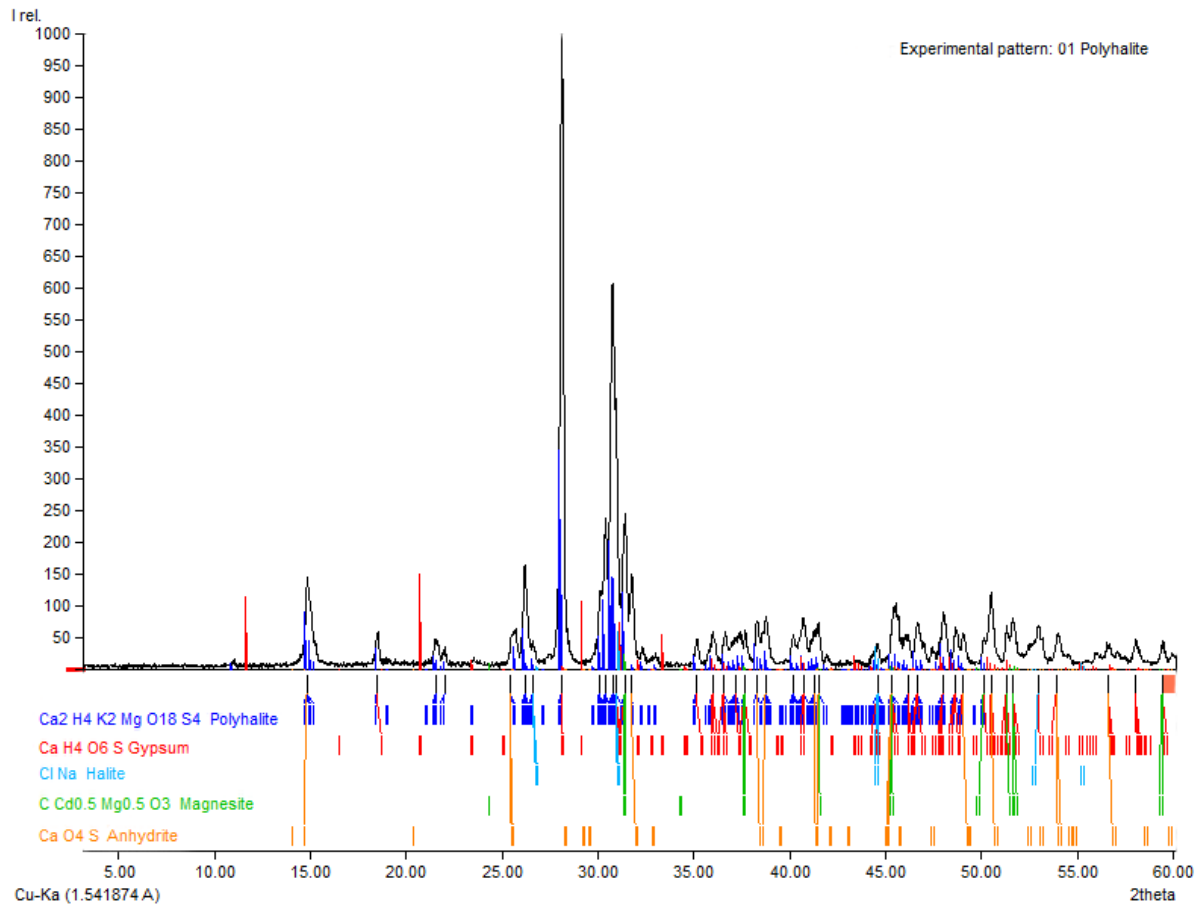


Figure 1. X-ray diffraction pattern of a powder sample from polyhalite (black) with peak information and identified mineral phases shown as stick patterns below. CuK α radiation.

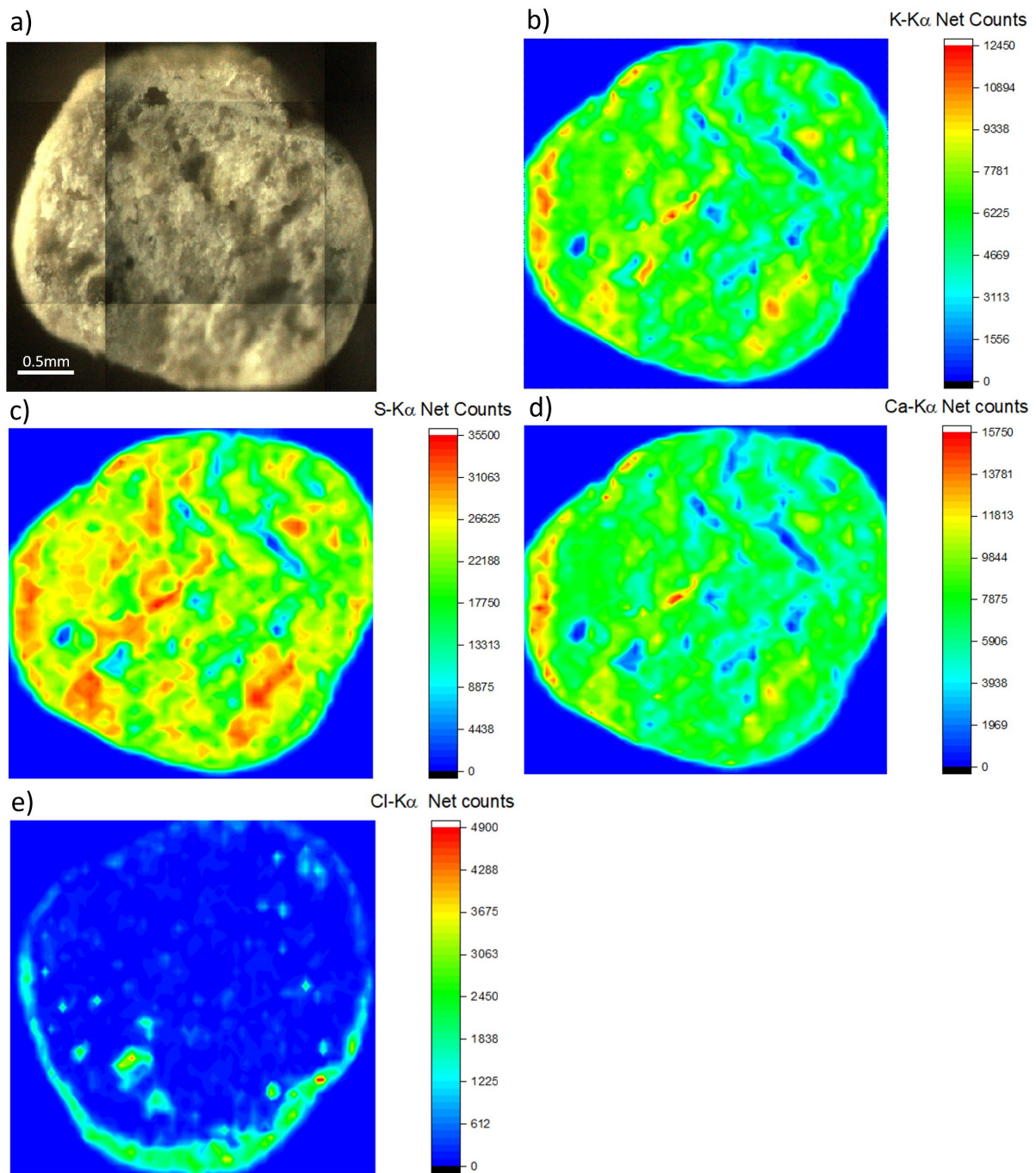


Figure 2. a) cross-section of a polyhalite granule followed by μ -XRF maps showing the spatial distribution of: b) potassium, c) sulfur, d) calcium and e) chloride

Table 1. Initial soil chemical and physical properties for a Typic Hapludox from the experimental site in Agudos-SP, Brazil.

Soil layer	P	OM‡	pH	H+Al‡	Al	K†	Ca	Mg	BS¶	CEC§	V#	m‡‡
cm	mg dm ⁻³	g dm ⁻³	CaCl ₂	-----			mg dm ⁻³	-----			-----%----	
0-20	6	8	4.4	235	18	55	120	48	223	459	48	15
Soil layer	Clay			Silt			Sand					
cm	-----			g kg ⁻¹ -----			-----					
0-20	38			17			945					

† Potassium extracted by resin. ‡ Organic matter. § Exchangeable acidity. ¶ Sum of bases.

§Cation exchange capacity. # Bases saturation index. ‡‡Aluminum saturation index.

3.2.2 Greenhouse experiment

3.2.2.1 Experiment Set-Up

The experiment was conducted in a greenhouse at the College of Agriculture Luiz de Queiroz, ESALQ/USP, Piracicaba-Brazil, with an average air temperature of 30/18°C (day/night) and the relative humidity between 50 and 90%. The soil was a sandy Typic Hapludox (Soil Survey Staff, 2014) collected from the 0-20 cm layer of a native area nearby sugarcane farms in Agudos-SP (table 1). The soil was air-dried and sieved in a 2-mm mesh for experiment. Homogenous stalks of sugarcane variety CV7870 were collected from 6 to 8-month-old plants from an experimental field. Stalks were cut in stem-node segments for propagation in washed sand for 25 days. After, uniform seedlings were chosen for transplanting into pots.

The experiment was set up in a completely randomized design with four replicates, in a factorial scheme: two potassium sources: KCl and POLY; and four doses: 0, 21, 42 and 63 mg kg⁻¹ K (table 2). The experimental unit was PVC pot of 6 kg containing one seedling. The treatments were applied in each experimental unit right before transplanting. Plants were watered daily with deionized water to maintain soil moisture in 70% of the maximum soil water-holding capacity during the experimental period.

Previous to establishment, the individual soil of each pot was mixed with powdered phosphate fertilizer at total rate of 150 mg kg⁻¹ P₂O₅ and homogenized in plastic bags. Nitrogen (N) was supplied in three applications: 30 mg kg⁻¹ of N at transplanting and two topdressing applications of 15 mg kg⁻¹ of N at 15 and 50 days after transplanting (dat). For the supply of Ca, Mg and S, these nutrients were balanced in the treatments of KCl, based on the quantity supplied in the POLY treatments, through the use of phosphogypsum and kieserite. However,

the dosage of Ca was still lower in the treatments where KCl was combined with phosphogypsum and kieserite than POLY alone. Micronutrients were also provided at transplanting in the following amounts (mg kg^{-1}): 5.0 Fe; 5.0 Zn; 4.5 Mn; 1.5 Cu; 0.3 B and 0.3 Mo.

In the sequence, after harvest the first cycle (131 d), the second cycle was fertilized with top-dressing application of N at the dosage of 30 mg kg^{-1} distributed in two applications at 15 and 30 days after harvest. Potassium treatments were not re-applied in order to evaluate its initial residual effect.

Table 2. Treatments to determine the effect of polyhalite as a multi-nutrient source of K on sugarcane variety CV7870 in an acid oxisol of sandy texture.

Treatment	Applied nutrient (mg kg^{-1})								
	K	Mg*	MgO	S*	Ca*	CaO	N	P ₂ O ₅	Cl
Absolute control	0	0	0	0	0	0	0	0	0
Control (N+P)	0	0	0	0	0	0	120	150	0
KCl 21	21	0	0	0	0	0	120	150	19
KCl 42	42	0	0	0	0	0	120	150	38
KCl 63	63	0	0	0	0	0	120	150	57
POLY 21	21	6.5	11	34	21.5	30	120	150	0
POLY 42	42	13	22	68	42	60	120	150	0
POLY 63	63	20	33	102	63	90	120	150	0
KCl 21 GYP KIE	21	6.5	11	34	17.5	24.5	120	150	19
KCl 42 GYP KIE	42	13	22	68	35	49	120	150	38
KCl 63 GYP KIE	63	20	33	102	52.5	73.5	120	150	57
½KCl ½POLY 21	21	3.3	5.5	17.5	10.5	15	120	150	9.5
½KCl ½POLY 42	42	6.6	11	34	21	30	120	150	19
½KCl ½POLY 63	63	9.9	16.5	51.5	32	45	120	150	28.5

* Ca, Mg and S in KCl treatments are applied by kieserite and phosphogypsum

POLY: Polyhalite KCl: Chloride of potassium GYP: phosphogypsum KIE: kieserite

3.2.2.2 Dry matter XRF and analyses

After 131 d after transplanting, sugarcane plants were harvested by cutting all shoot part at the soil surface. Afterwards, the shoot was oven dried at 60°C for 72 hours (constant weight) and weighed for dry matter (DM) production. The root system was left to allow regrowth simulating a ratoon. The DM production of the second cycle was evaluated at 122 d after regrowth. Before harvest in both cycles, leaf nutrient content (potassium – K, calcium –

Ca, sulfur – S and chloride – Cl) was carried out by cutting the middle portion of the Top Visible Dewlap (TDV) at 131 d after transplanting and 122 d after regrowth. Immediately after cutting, the leaf sample was washed with deionized water and dried with a clean paper right before analysis. Then, the sample was placed into a hand-held X-ray fluorescence spectrometer DELTA Professional model (Olympus, USA) equipped with a Rh target X-ray tube and a 10 mm² silicon drift detector (SDD), operated at 15 kV and 200 μ A. The dwell time was 90000 ms. A docking station and a lead enclosure radiation shield were used. A randomly selected sampling spot in the interveinal region on the adaxial side of the TDV was analyzed in triplicate.

3.2.3 Data and statistical analysis

The effectiveness of each K source relative to the standard KCl was calculated from the yield response relationships using the Equation (1):

$$\text{RAE (\%)} = [(Y_i - Y_0) / (Y_{\text{KCl}} - Y_0)] \times 100, \quad (1)$$

where, Y_i is shoot DM yield in treatments with added K fertilizers (g pot^{-1}); Y_{KCl} is the shoot DM yield with potassium chloride (reference fertilizer, RAE = 100%) treatment; Y_0 is the shoot DM yield without K fertilizer (absolute control).

The K, Ca and S uptake were calculated as the product of K, Ca and S concentration and shoot DM yield, applying a Equation (2):

$$\text{K, Ca or S uptake (mg pot}^{-1}\text{)} = \text{K, Ca or S content (mg g}^{-1}\text{)} \times \text{DM yield (g pot}^{-1}\text{)} \quad (2)$$

Agronomic efficiency (AE) was calculated according to Equation (3):

$$\text{AE (mg mg}^{-1}\text{)} = [(\text{shoot DM yield with added nutrient fertilizers (mg pot}^{-1}\text{)} - \text{Shoot DM yield in absolute control (mg pot}^{-1}\text{)}) / \text{nutrient applied via fertilizer (mg pot}^{-1}\text{)}] \quad (3)$$

All data were tested for Shapiro-Wilk's normality test and Bartlett's homogeneity test, and suitable transformations used when these settings were not met, before to analysis of variance (ANOVA). The data was submitted to a two-way ANOVA, in case of significance in the interaction between the K source within each dosage, and the effects of K dosages within each K source were compared using a Duncan's multiple range test, respectively. In the absence of interaction, the t test (LSD) was used to evaluate the isolated effect of sources and dosages effect was adjusted to a linear or quadratic regression model. Relative agronomic efficiency (RAE) was compared using Dunnett's test. Principal component analysis (PCA) was performed and visualized using PAST version 3.21 (University of Oslo, Norway). All statistical analyses were

performed using PROC-GLM and PROC-MIXED in SAS statistical software version 9.3 (SAS INSTITUTE, 2008) and the graphs and regressions by Sigma Plot (Systat Software, San Jose, CA). The determinations of statistical significance were based on a critical value of $\alpha = 0.10$.

3.3 Results and discussion

3.3.1 Elemental release

The rhizobox experiment illustrated strong differences in K, Ca, S and Cl net counts between the sources KCl and POLY in granules over the time (Fig. 3). The KCl treatment revealed that K and Cl was more concentrated in the first 0.25 h of placement (Fig. 3a), mainly concentrated in the granule area, approximately 2 mm, corresponding to the granule diameter. It presented in average 1600 net counts of potassium and 800 net counts of chloride, supporting the elemental composition of the source (50 % K and 45 % Cl). However, it is noticeable some peaks of sulfur (~200 net counts) which can be related to S-mineral contaminants derived from the K mine. After 6 h, the KCl fertilizer granule dissolved, showing high K net counts in the vicinity of the granule followed by a decline in the application area. As the element moves further away from the granule area, peaks of K of ~400 net counts appeared near to the soil surface and below the application zone, validating the high mobility of K in soils (Sparks and Huang, 1985) and the negative clay-influence of ion mobility (Basumatary and Bordoloi, 1992). In our soil only accounted 38 g kg⁻¹ of clay (Table 1), enhancing its easy movement throughout the profile.

Chloride did not display any signal after 6 h and also the next time points evaluated (Figure 3), suggesting it has moved distant from the selected rhizobox segment. The following time points evaluated presented similar dynamics (Fig. 3c, 3d, 3e, 3f) explaining how KCl has dissolved almost all after 72 h, releasing K and Cl to the soil phase. This dynamic can be also validated in Fig. S2a and S2b, which shows how KCl granule was disintegrated after 72 h of soil-water interaction. Sandy soils have generally low cation-exchange capacity and frequently are deficient in native K, and when soluble fertilizers are applied can be lost easily by leaching (Tiltsdale and Nelson, 2016), promoting potassium deficiencies in plants (Marschner, 2012). Potassium release rates of marketable fertilizers have been widely documented (Baligar, 1985; Kochba; Ayalon and Avnimelech, 1994; Notario et al., 1995; Dua and Shaviv, 2006; Broschat and Moore, 2007; Huett and Gogel, 2010; Jamnongkan; Kaewpirom, 2010; Adams et al., 2013).

Shavit et al. (1997) studying the processes that governed the release of nutrients by fertilizers, noted that the rate of wetting and the magnitude of water penetration into the granule called by them as “burst effect” increase with the fertilizer solubility, resulting in an increase in the rate of the nutrient release, as found in our study. It confirms that after placing the KCl granule in a moisture soil, during the first hours the water penetrates rapidly dissolving the nutrients and subsequently leaving of Cl^- and K^+ as recorded by our time intervals.

Polyhalite granule exhibited the highest net counts of K, Ca and S after 0.25 h of its placement (600, 250, 1500 net counts, respectively) (Fig. 3g). This result is consistent with the nutrient content of POLY, which is 12% K, 11% Ca, and 19% S, and Kemp et al. (2016), who reported polyhalite derived from deposits in North Yorkshire (United Kingdom), which is in the same region where POLY was mined and produced. However, a reduction of K counts of approximately 40% was observed in the granule zone after 6 h of application (Fig. 3h). After 12 h, POLY released away from the place of granule application about 75% of K, exposing some peaks in the surroundings (~8 mm distance) and the subsequent time intervals indicating that POLY released 100% of its K in the selected segment of the line scan analysis. Conversely, S and Ca were maintained constant nearby the granule zone during all the time points evaluated, confirming that POLY is less water soluble than KCl. These results can be confirmed in Fig. S2c and S2d, which illustrated that the integrity of the POLY granule remained unbroken after 72 h of exposure to the soil-water system.

Few studies on nutrients release from polyhalite have been conducted. Barbier et al. (2017) found similar nutrient dynamics evaluating the solubility and leaching of POLY, showing POLY as slow-release fertilizer due to its low solubility (17 g L^{-1}), compared to KCl (344 g L^{-1}) reported by IPNI (2010). Barbier et al. (2017) also observed that even though POLY has a lower solubility in water than KCl, it provides sufficient amounts of K, Ca and S for plant growth, more synchronized with the plant demand. However, Barbarick (1991) reported, from a leaching columns study, that higher concentrations of K and Ca were leached from POLY than the equivalents soluble fertilizers (K_2SO_4 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), but S had the opposite behavior. Yermiyahu et al. (2017) also observed, from a more realistic scenario for field condition using soil leaching columns with wheat growing plants, that lower concentrations of Ca and S leached below the root zone of wheat from POLY than soluble sulfate salts and contrary effect with K leach-out. Thus, as POLY is considered a single crystal mineral (Weck et al., 2014), hypothetically the nutrients should be released in equal proportions into soil solution. However, we did not

find this dynamics in our study because the net counts of S were higher in the granule zone over time (Fig. 3g, 3h, 3i, 3j, 3k, 3l), suggesting a subsequent interaction of SO_4^{2-} with cations, which promotes *in-situ* precipitation of sulfur salts and sequential dissolution, whereas K and Ca moved distant from the granule. Overall, expecting a congruent dissolution of POLY crystal in the soil system is questionable because each nutrient from the mineral owned different chemical properties and cation-affinities, interacting individually with the solid phase in an unpredictable way (Krishna, 2002).

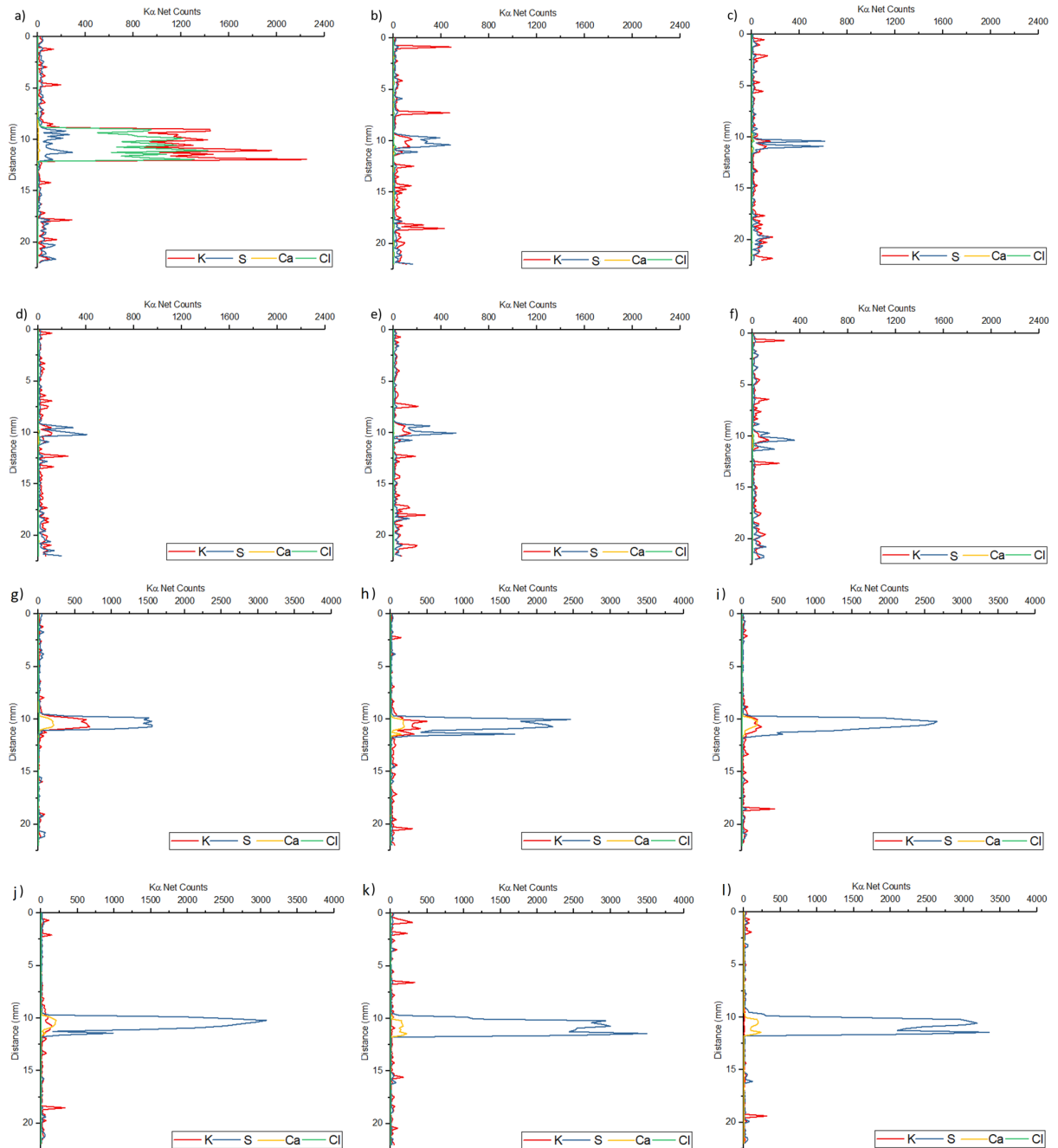


Figure 3. Linear u-XRF net counts of K, S, Ca and Cl at a) 0.25, b) 6, c) 12, d) 24, e) 48, and f) 72 hours after KCl granule placement; and at g) 0.25, h) 6, i) 12, j) 24, k) 48, and l) 72 hours after POLY granule placement in rhizobox containing a sandy low-K oxisol.

3.3.2 Plant response

The shoot DM yield was significantly influenced by K dosages, regardless of the source/formulation applied (Table 3). The average coefficient of variation was between 2 to 13% showing low variability between replicates within each treatment. There was no significant interaction between K sources/formulations and dosages on shoot DM yield and the

treatments were compared within each to outline the effect of K application in dosages. The first cycle of growth (cane-plant) resulted in the highest DM in all treatments (38.3 g pot^{-1}) compared to the ratoon crop (33.5 g pot^{-1}). Furthermore, significant increases in DM were observed when K was applied at 42 and 63 mg kg^{-1} compared to 21 mg kg^{-1} and control. For the second growth cycle (ratoon), the residual of supplying K resulted in 16% higher DM yield compared to control. Regarding the accumulated DM in both cycles, plants from pots receiving no K fertilizer (absolute control and control) produced 50 and 9 g pot^{-1} less than those receiving K fertilizer, respectively. Additionally, accumulated yield increased according to the dosage of K application relative to control (5, 11 and 19% with 21, 42 and 63 mg K kg^{-1} , respectively). The differences in plant response to K dosage can be explained by the genetic potential of the sugarcane because the variety CV7870 is adapted to more fertile soils (Table 1), being very responsive to K application.

Table 3. Shoot dry matter yield (g pot^{-1}) of sugarcane as affected by K dosages applied at transplanting from two consecutive harvests (cane-plant and ratoon).

Treatment	K applied (mg kg^{-1})	Cane-plant	Ratoon	Accumulated
Absolute control	0	11.7 ± 0.9	14.3 ± 1.7	26.0 ± 2.0
Control (N+P)	0	36.7 ± 2.1	30.5 ± 2.7	67.2 ± 4.3
KCl	21	37.3 ± 3.3	36.5 ± 0.8	73.8 ± 2.7
KCl	42	38.3 ± 1.3	34.2 ± 1.8	72.5 ± 1.5
KCl	63	44.0 ± 4.4	37.0 ± 1.0	81.0 ± 5.2
POLY	21	37.7 ± 3.9	33.5 ± 2.9	71.2 ± 6.7
POLY	42	42.8 ± 3.8	33.7 ± 2.1	76.5 ± 5.6
POLY	63	44.5 ± 4.7	35.0 ± 0.8	79.5 ± 5.9
KCl+GYP+KIE	21	36.0 ± 3.5	34.0 ± 2.1	70.0 ± 2.9
KCl+GYP+KIE	42	41.5 ± 5.0	36.0 ± 1.4	77.5 ± 5.0
KCl+GYP+KIE	63	43.3 ± 3.2	37.3 ± 0.8	80.6 ± 3.0
$\frac{1}{2}$ KCl $\frac{1}{2}$ POLY	21	36.0 ± 3.6	33.5 ± 2.6	69.5 ± 5.7
$\frac{1}{2}$ KCl $\frac{1}{2}$ POLY	42	41.8 ± 4.0	35.8 ± 1.9	77.6 ± 4.5
$\frac{1}{2}$ KCl $\frac{1}{2}$ POLY	63	45.0 ± 6.1	37.3 ± 1.8	82.3 ± 5.5
LSD (0.10)		6.9	3.2	8.6

The relationship between shoot DM yield and leaf nutrient concentration in response to the application of K formulations in both cycles, cane plant and ratoon, is presented in Fig. 4. In general, no significant relationship between DM and K, S, Ca and Cl concentration in leaves were detected, however, it is noticed that most of the plants with leaf content below the critical level (McCray et al., 2013) are linked to ratoon cycle, probably experienced a hidden hunger

scenario. Additionally, despite the fact that sugarcane in cane-plant absorbs more K when KCl+GYP+KIE is applied than when POLY is used, because of the solubility differences, this gap does not translate into higher productivity, suggesting that plants had K higher content than the sufficient. These findings support the hypothesis that sugarcane have the ability to absorb more K than is required for the growth cycle, a scenario that is typically referred to as luxury consumption.

Shoot DM oscillated between 25 and 50 g, except to absolute control (13 g). In these sense, plants derived from cane bud propagation exhibited sufficient concentrations of K, Ca and S for an initial development. However, when higher dosages of K formulations were applied led to luxury consumption suggesting that K, Ca and S were not limiting production, irrespective of the type of K fertilizer applied.

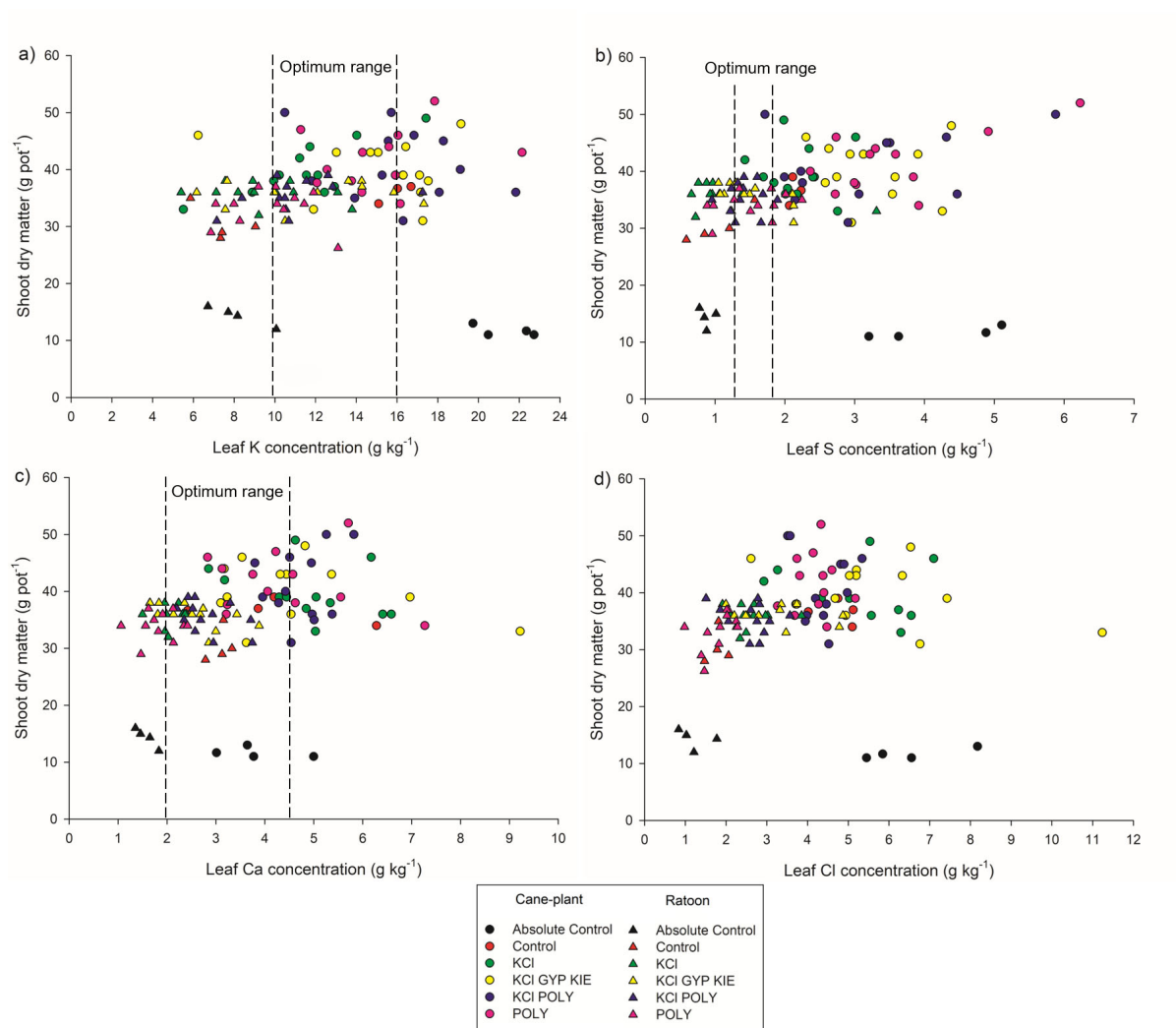


Figure 4. Relationship between shoot DM yield and leaf a) K, b) S, c) Ca and d) Cl concentration for all individual pots in each growth cycle, cane plant and ratoon. The optimum range for each nutrient is indicated by the vertical cutted lines.

In general, all nutrients analyzed (K, Ca, S and Cl) were affected by K dosages and sources in both growth cycles, however, the latter showed a decline in uptake irrespective the source and dosage supplied (Fig. 5), explained by a small effectivity of residual fertilizer over the time. Consistent with our findings, Körndorfer et al (2018) evaluated the residual effect of thermopotash fertilizer in sugarcane under similar K dosages applied in our study and observed higher leaf K levels in the first harvest than the second harvest. These differences suggest lower K availability in the soil due to the absence of subsequent K fertilizer applications.

For K, the uptake was influenced by sources in cane-plant, with higher results under $\frac{1}{2}$ KCl $\frac{1}{2}$ POLY, KCl+GYP+KIE and POLY than KCl, with mean values of 656, 607 and 630 mg pot⁻¹,

respectively (Fig. 5a), representing an average of 36% higher uptake compared to KCl treatment. However, in ratoon, KCl together with $\frac{1}{2}$ KCl $\frac{1}{2}$ POLY, KCl+GYP+KIE and POLY achieved in average 60% higher K uptake compared to control. Dosage also influenced K uptake with a quadratic adjustment in the first growth cycle (Fig. 5a). It was noticed variation in K uptake under dosage compared to control in cane-plant. Also, in ratoon the highest dosage (63 mg K kg⁻¹) had promoted a significant increment in K uptake, with a mean value of 457 mg pot⁻¹, approximately 202% higher than those observed in the control.

Sulfur uptake was affected by K dosage and sources, mainly in the cane-plant (Fig. 5b). Thus, POLY exhibited the highest S uptake (150 mg pot⁻¹), whereas KCl did not have any variation compared to control (87 and 77 mg pot⁻¹, respectively). Concerning dosage, higher amounts of K fertilizer imply increments in S uptake in sugarcane. Based on this parameter, the following ranking was obtained: K63 > K42 > K21 > K0. No variation in the S uptake in ratoon crop was found for K sources and dosage.

Calcium uptake was 400% lower under absolute control compared to the average of K dosages and sources in the cane-plant (Fig. 5c). In the second growth cycle, POLY and KCl had lower Ca uptake compared to the formulations $\frac{1}{2}$ KCl $\frac{1}{2}$ POLY and KCl+GYP+KIE. Non-significant interactions ($p > 0.10$) between sources were found in the cane-plant crop and between K dosages in the ratoon.

Chloride uptake was affected by K formulations and dosage. The largest increments in Cl uptake was observed under KCl+GYP+KIE in both growth cycles, plant-cane and ratoon, approximately 235 and 116 mg Cl pot⁻¹, respectively (Fig 5d). In general, Cl uptake under POLY and $\frac{1}{2}$ KCl $\frac{1}{2}$ POLY were less expressive than KCl sole, achieving similar values to control in the cane-plant, however, in ratoon only POLY reached similar Cl uptake compared to control. Additionally, all dosage applied significantly outperformed control treatment, exhibiting the residual effect of K fertilizer on the chloride uptake by sugarcane.

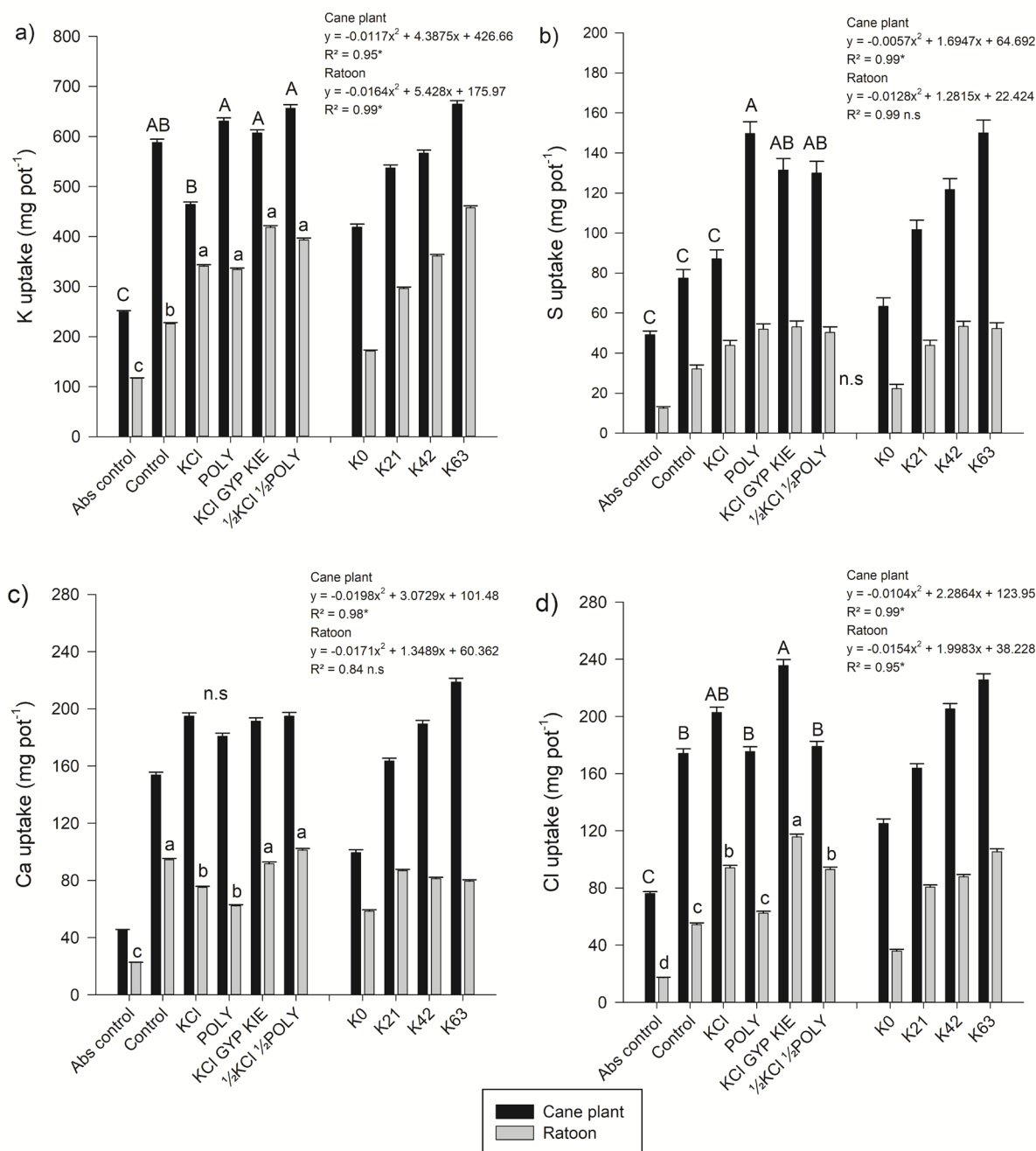


Figure 5. Uptake of a) potassium, b) sulfur, c) calcium and d) chloride as affected by potassium fertilizers in cane and ratoon crop of sugarcane. Source comparison: columns followed by the same uppercase letter do not differ statistically by Duncan's multiple range test ($p < 0.10$) in the cane plant crop, and columns followed by the same lowercase letter do not differ statistically by Duncan's multiple range test in the ratoon crop. Dosage comparison: regression analysis, the * in the R^2 indicates differences between dosage at level of significance of 10 %. ns: non-significant. Error bars (T) represent the standard error of the means ($n = 4$). Abs control: Absolute control K0 = non-K application; K21 = application of 21 mg K kg⁻¹; K42 = application of 42 mg K kg⁻¹; K63 = application of 63 mg K kg⁻¹

3.3.3 Relative agronomic effectiveness

The relative agronomic effectiveness (RAE) was not significant depending on the source of K applied (Fig. 6), indicating that POLY is efficient as KCl as a potassium source. Moreover, RAE varied between 92 and 106%, which means that K formulations evaluated here were as efficient as the reference fertilizer irrespective of the growth cycle. The adequate contrast between K formulations of our study are limited in literature and none of them included sugarcane, but POLY is widely spread in the fertilizer market for other crops. Barbarick (1991), assessing continuous cropping of sorghum-Sudan grass comparing POLY and other soluble sources of K, Ca, Mg and S in greenhouse, noted that POLY was as effective or superior to soluble fertilizers, as found in our study. Likewise, Yermiyahu et al. (2017) has reported similar findings, when evaluating the efficiency of POLY relative to equivalent soluble salts on wheat in a pot experiment, where POLY was at least as good as the reference fertilizers, indicating that POLY is a good alternative K source for agriculture.

Agronomic efficiency of K (AEK) is presented in Fig. 7a. Supplying K in lower dosage resulted in higher AEK in both growth cycles, cane-plant and ratoon, regardless the K sources used. The dosage 63 mg K kg⁻¹ reduced AEK by 2.3 times compared to the lowest dosage used (21 mg K kg⁻¹) in cane-plant and approximately 2.6 times in ratoon. The AEK varied between 87 to 201 mg mg⁻¹ in cane-plant and 59 to 160 mg mg⁻¹ in ratoon, averaging 135 mg mg⁻¹ and 101 mg mg⁻¹, respectively. No effect of source/formulation was detected here.

Considering the sources with S in their formulation (POLY, KCl+GYP+KIE and ½KCl ½ POLY), agronomic efficiency of sulfur (AES) varied significantly due to the dosage used, irrespective of sources, in both growth cycles (Fig. 7b), indicating similar dynamics to AEK. The lowest AES was found at applying 63 mg K kg⁻¹, with average values of 53 and 36 mg mg⁻¹ in cane-plant and ratoon, respectively, while under lower K dosages the AES increased progressively, obtaining the superior AES at 21 mg K kg⁻¹, with mean values of 122 and 95 mg mg⁻¹ in cane-plant and ratoon, respectively.

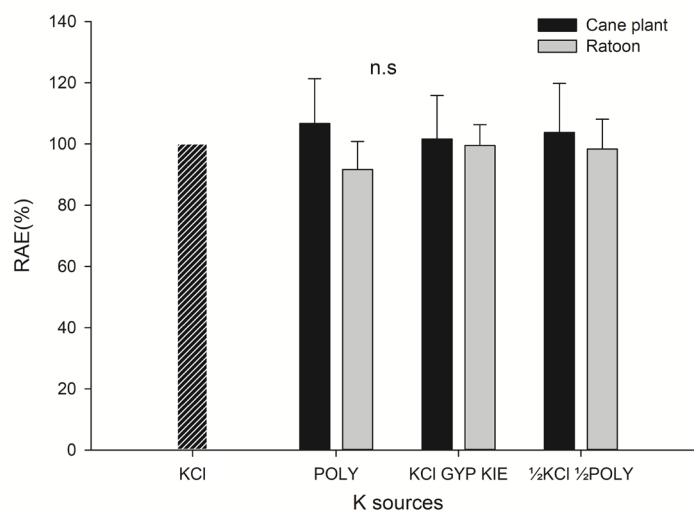


Figure 6. Relative agronomic effectiveness (RAE) of potassium fertilizers in cane and ratoon crop of sugarcane. For the K reference fertilizer, the potassium chloride (KCl), RAE=100% (cross hatched bars). Vertical bars (T) represent the standard error of the means ($n = 4$). ns: non-significant

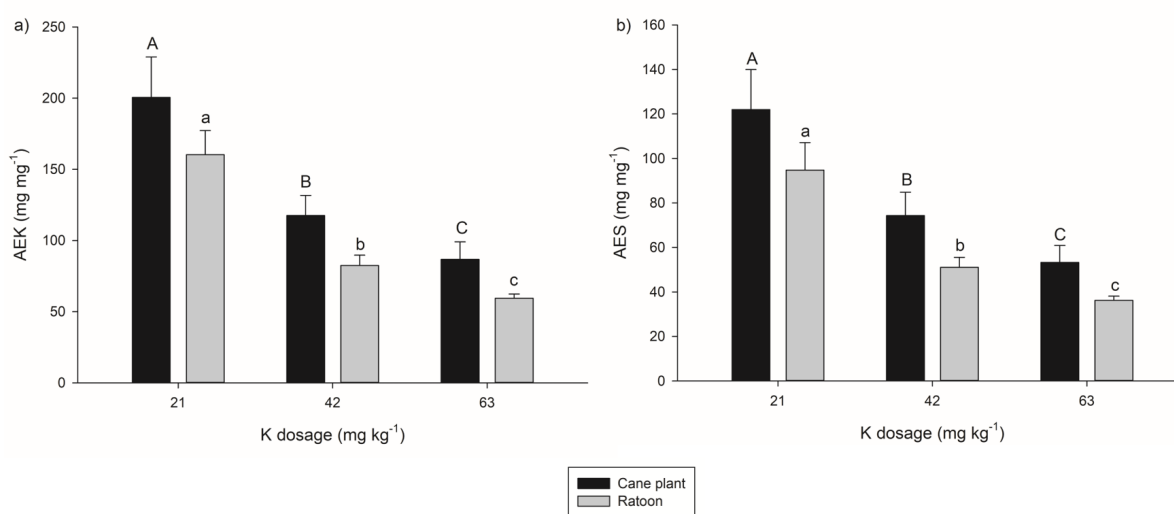


Figure 7. Agronomic efficiency of a) potassium (AEK) and b) sulfur (AES), considering three dosages of K fertilizers (KCl, POLY, KCl+GYP+KIE and 1/2KCl 1/2 POLY) in cane and ratoon crop of sugarcane. Columns followed by the same uppercase letter do not differ statistically by Duncan's multiple range test ($p < 0.10$) in the cane plant crop, and columns followed by the same lowercase letter do not differ statistically by Duncan's multiple range test in the ratoon crop. Error bars (T) represent the standard error of the means ($n = 4$).

Regarding to Ca in fertilizer formulation (POLY, KCl+GYP+KIE and $\frac{1}{2}$ KCl $\frac{1}{2}$ POLY), agronomic efficiency of calcium (AECa) was significantly affected by source and dosage but without any interaction (Fig. 8). Fertilization with $\frac{1}{2}$ KCl $\frac{1}{2}$ POLY increased AECa in the three dosages evaluated for both cane-plant and ratoon. In contrast, when Ca was applied via POLY or KCl+GYP+KIE, the AECa was similar in both cane-plant and ratoon regardless the dosage used. Furthermore, AECa increased as a result of K fertilization at the lowest dosage of K assessed. For instance, in cane-plant under application of 21 mg K kg⁻¹ the AECa was two times higher than in the highest K dosage applied (Fig. 8a), and in ratoon this efficiency had the same performance as cane-plant but in lower proportions, (Fig. 8b).

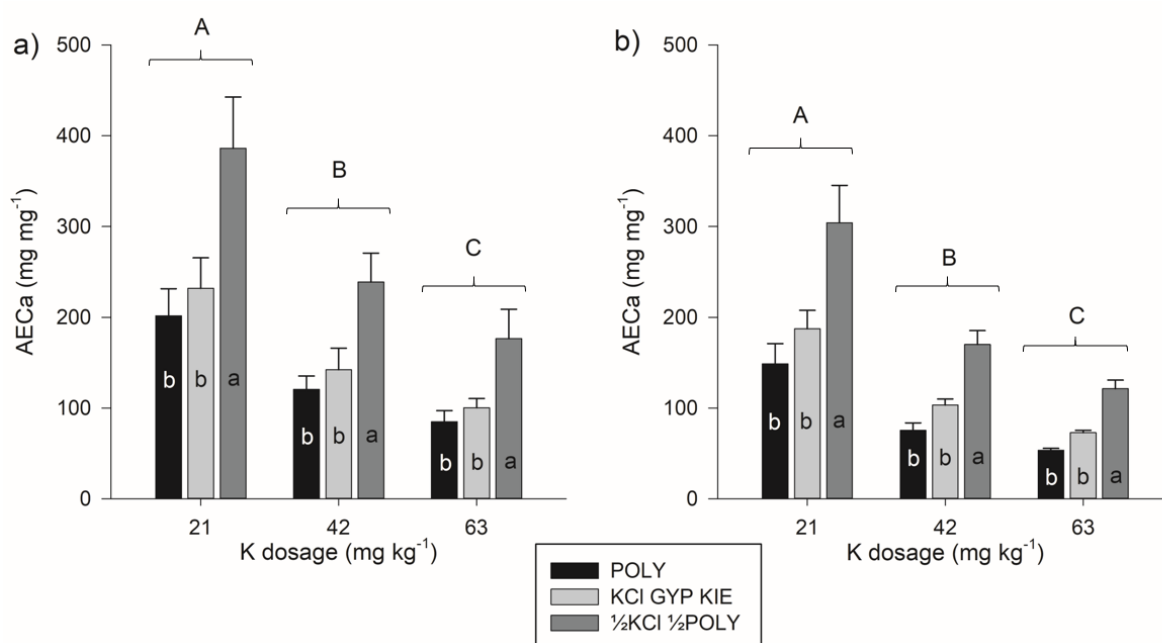


Figure 8. Agronomic efficiency (AECa) of calcium considering three dosages of formulations containing this nutrient (POLY, KCl+GYP+KIE and $\frac{1}{2}$ KCl $\frac{1}{2}$ POLY), evaluated in a) cane plant and b) ratoon crop of sugarcane. Dosage comparison: columns followed by the same uppercase letter do not differ statistically by Duncan's multiple range test ($p < 0.10$); source comparison: columns followed by the same lowercase letter do not differ statistically by Duncan's multiple range test. Error bars (T) represent the standard error of the means ($n = 4$).

Considering a general view among K dosage and sources/formulations, both cane-plant and ratoon biomass production (DM) and accumulated nutrient uptake were correlated to high dosages applied and K sources containing Ca and S in the formulation (Fig. 9). However, when

these sources were provided at the lowest dosage the highest correlation was observed with superior agronomic efficiency for all nutrients assessed (Fig. 9). The two-component analysis explained 81.3% of the total variation among traits. Using the K dosage, the PCA grouped into two main clusters (Fig. 9). POLY, KCl in combination with GYP and KIE; and POLY combined with KCl, applied at 42 and 63 mg K kg⁻¹ were located in quadrant II and are characterized with high S, K, Ca and Cl uptake and consequently in high accumulated shoot DM. In contrast, these sources supplied at the dosage of 21 mg K kg⁻¹ appearing in quadrant IV, which gave the highest agronomic efficiency for K, Ca and S, in both cane-plant and ratoon. In the quadrant I is clustered KCl regardless the dosage and the control, indicating similarity among them. Finally, the absolute control is located isolated in the quadrant III, showing that non-application of these nutrients resulted in low uptake and poor shoot DM yield, being agronomically inefficient.

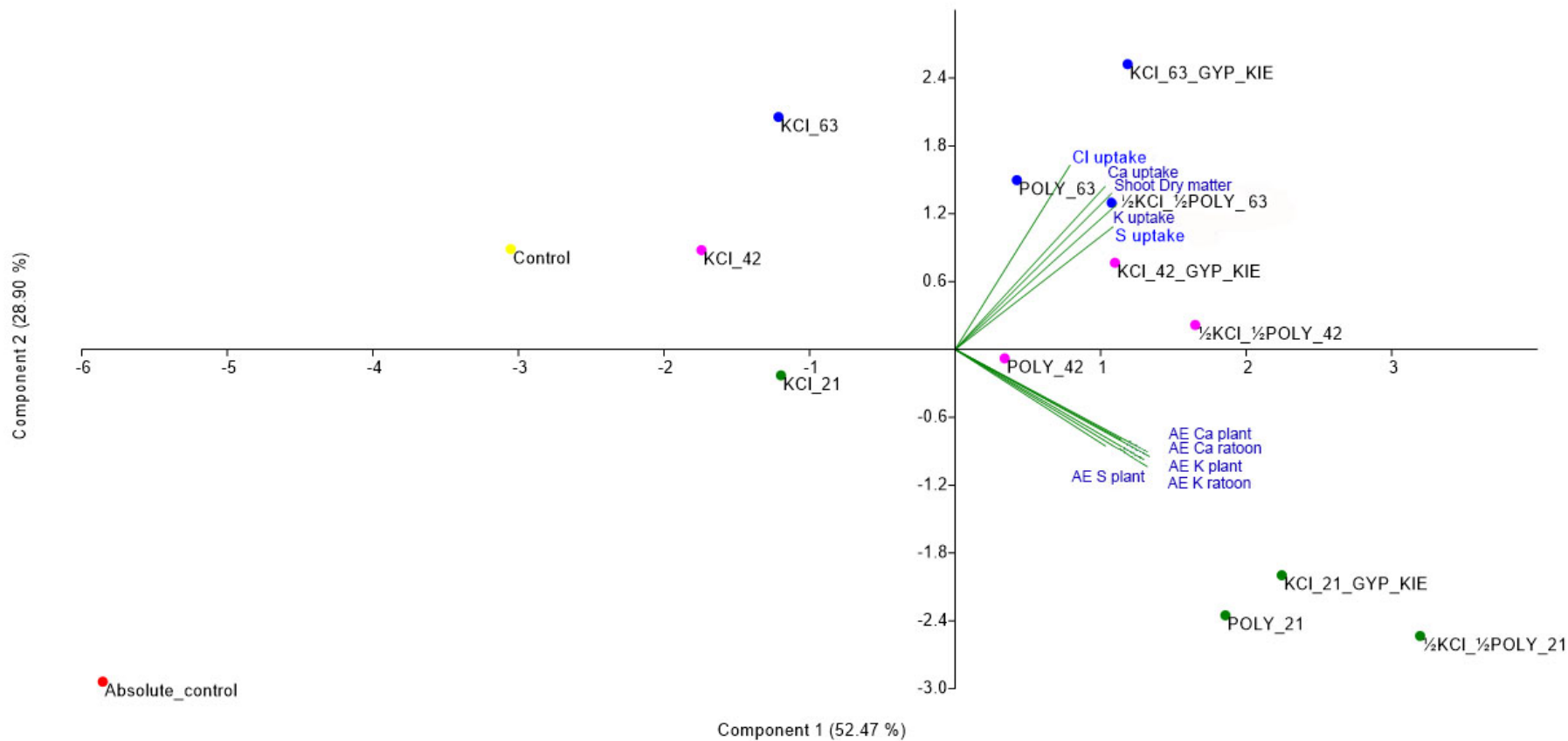


Figure 9. Principal component analysis (PCA) of accumulated K, S, Ca and Cl uptake, accumulated shoot dry matter and agronomic efficiency of K, Ca and S in sugarcane treated with three K dosages (21, 42 and 63 mg K kg⁻¹). AE = Agronomic efficiency; acc = accumulated

3.4 Conclusions

Application of KCl in the moisture low-K sandy Oxisol has rapidly promoted dissolution of nutrients and then released Cl^- and K^+ , being susceptible for leaching, whereas POLY granule performed as a slow-release fertilizer due to its low solubility compared to KCl, enhancing residual effect over time.

Shoot DM yield and nutrient uptake were more correlated to high K dosages applied (42 and 63 mg kg^{-1}) and K sources containing Ca and S in the formulation (POLY, KCl+GYP+KIE and $\frac{1}{2}\text{KCl } \frac{1}{2} \text{POLY}$), for both cane-plant and ratoon. However, when these sources were provided at the lowest dosage (21 mg kg^{-1}) it was observed superior agronomic efficiency for all added nutrients, indicating that a combination of KCl and POLY can be used more efficiently as K source for sugarcane.

Microchemical imaging measurements using XRF technique provides good results of fertilizer dynamics in the soil matrix in real time, helping to understand the nutrient release process and improving fertilizer application planning on the field. In addition, the direct multi-elemental quantitative plant leaf analysis using hand-held XRF is a quick and user-friendly tool for evaluating nutritional status without producing any chemical waste.

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Supplementary material

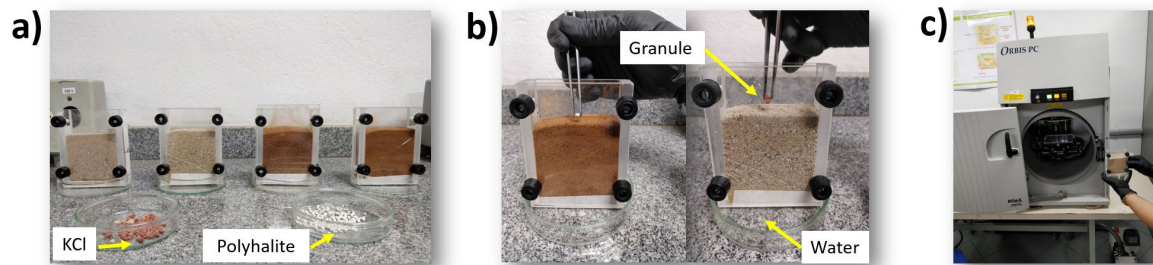


Figure 1S. μ -XRF experimental setup to determine K, Ca, S and Cl release from POLY and KCl granules on sand and a sandy oxisol. a) Rhizobox containing sand or a sandy oxisol and the fertilizer granules; b) Placement of KCl and POLY granules on soil and sand; c) Placement of rhizobox on μ -XRF spectrometer (Orbis PC, USA)

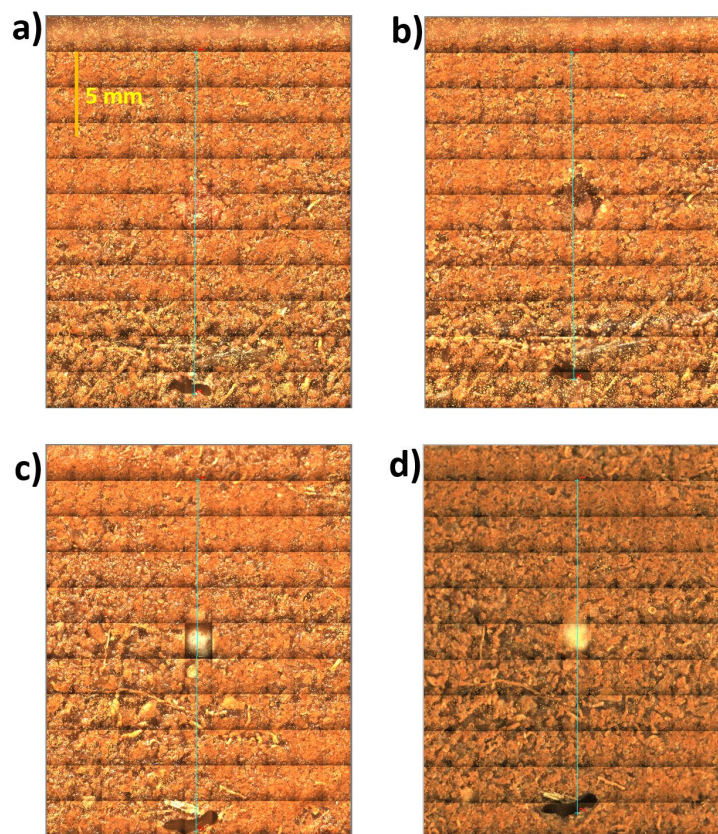


Figure 2S. Pictures of the selected segment for the line scan after 0.25 and 72 h of granule placement into the rhizobox. a) Picture of KCl granule after 0.25 h of placement; b) Picture of KCl granule after 72 h of placement; c) Picture of POLY granule after 0.25 h of placement; and d) Picture of POLY granule after 72 h of placement

4 FINAL REMARKS

Based on the field experiment, the application of calcium (Ca), magnesium (Mg), sulfur (S) and mainly potassium (K), irrespective the source applied, affected positively the yield in sugarcane. K, Ca and S sources, such as, KCl and phosphogypsum are the farmer's option to achieve the crop needs, widely used nowadays. However, the application of polyhalite, as a multi-nutrient fertilizer, proved being as efficient as the popular K, Ca and S sources, which may be an alternative to meet the plant requirements.

Regarding to the dosage, application of $105 \text{ kg K}_2\text{O ha}^{-1}$, which corresponds to farmer's recommended dosage, promoted the highest stalk yields for both varieties, CV7870 and RB867515. This dosage keeps the adequate nutritional status of sugarcane ratoon and enhance the K content in stalk, promoting the accumulation of sucrose in this plant organ.

In relation to the soil parameters, the cultivation environment studied was classified as C2, due to low water availability potential, low CEC and base saturation less than 50%. For the variety RB867515, after cultivation, most of the nutrient concentration remained in soil were not significantly altered when compared to control, suggesting that as much fertilizer is applied this variety will uptake and export. On the other hand, the variety CV7870 showed higher remained values for soil Ca, Mg and S in the treatments compared to the control after cultivation, indicating a residual effect, irrespective the treatment.

Based on the soil results, a study regarding to the release of nutrients by KCl and polyhalite was needed. In order to solve this enquire, a laboratory experiment was set up. Microchemical imaging measurements were performed using XRF technique providing good results of fertilizer dynamics in the soil matrix in real time, helping to understand the nutrient release process and improving fertilizer application planning on the field. As a result, KCl granule in the moisture low-K sandy Oxisol has rapidly promoted dissolution of nutrients and then released Cl^- and K^+ , being susceptible for leaching, whereas POLY granule performed as a slow-release fertilizer due to its low solubility compared to KCl, enhancing residual effect over time.

Furthermore, based on the field experiment a necessity of balance in the nutrients K, Ca, Mg and S was noticed, as well as the possibility of use blend between polyhalite and KCl. In order to solve these concerns, a glasshouse experiment was proposed. As the sugarcane varieties used in the field experiment performed differently in the same environment of

production, indicating a genetic dependency linked to the growth conditions. In this sense, the variety CV7870 was selected for the glasshouse experiment, which showed in the field a promising dynamics for further studies of residual effect of fertilizers.

The results of the glasshouse showed that DM yield and nutrient uptake were more correlated to high K dosages applied (42 and 63 mg kg⁻¹) and K sources containing Ca and S in the formulation (POLY, KCl+GYP+KIE and ½KCl ½ POLY), for both cane-plant and ratoon. However, when these sources were provided at the lowest dosage (21 mg kg⁻¹) it was observed superior agronomic efficiency for all added nutrients. It has indicated that a combination of KCl and POLY can be used more efficiently as K source for sugarcane.

Taking altogether, both experiments, in the field and in the greenhouse, is possible to conclude that polyhalite is suitable to supply K, Ca, Mg and S. Furthermore, the blend of 50% polyhalite and 50% KCl could be adopted for farmers minimizing plant nutrient losses with a more balanced nutrition.