

Chemical Extractors to Assess Potassium Availability in Glaucanitic Siltstone

Eliana Paula Fernandes Brasil¹, Wilson Mozena Leandro¹, Welldy Gonçalves Teixeira¹, Marcos Antônio Vieira²,
José Patrício Nunes de Souza² & Henrique Victor Vieira²

¹ Soil Sector, Federal University of Goiás, Goiânia, Goiás, Brazil

² Victor Vieira Consultoria Agronômica, Paraúna, Goiás, Brazil

Correspondence: Eliana Paula Fernandes Brasil, Campus Samambaia, Agronomy School, Federal University of Goiás, Goiânia, Goiás, Brazil. E-mail: elianafernandesufg@gmail.com; elianafernandes@ufg.br

Received: March 31, 2020

Accepted: July 12, 2020

Online Published: August 15, 2020

doi:10.5539/jas.v12n9p166

URL: <https://doi.org/10.5539/jas.v12n9p166>

Abstract

This paper aimed to evaluate the efficiency of chemical extractors to measure the availability of potassium (K) in glauconitic siltstone. An experiment with successive crops of beans and maize was installed under field conditions in Quirinópolis, Goiás State, Brazil, in a typical ortic Neossolo Quartzarênico. For both crops, the experimental design was a randomized block with four replications, resulting in a total of 24 experimental plots. Two sources and four doses of K₂O were used, in addition to a control treatment with any K fertilization. The sources used were glauconitic siltstone and potassium chloride (KCl), and the doses applied through glauconitic siltstone corresponded to 1, 2, 4 and 8 times the dose of K₂O applied via KCl as a reference. The following extractors were used: neutral ammonium citrate (NAC), citric acid 2% (CA), CA + ammonium fluoride 0.5% (NH₄F), tartaric acid 5% (TA) + sodium fluoride 0.5% (NaF) (1:100), TA + NaF 0.5% (1:500), hydrochloric acid (HCl), and the method for extracting potassium from silicatic materials (MAPA-8.2.4.2). Among the tested extractors, the best one regarding productivity was the MAPA-8.2.4.2. The NAC and CA extractors showed the lowest correlations and should not be used henceforth to quantify soluble K from glauconitic siltstone.

Keywords: potassium sources, glauconite, chemical extractors, plant nutrition

1. Introduction

Potassium chloride (KCl) is the main source of potassium (K) used worldwide, representing more than 95% of potassium fertilizers consumed (ANDA, 2016). Brazil is the world's second-largest K importer, behind China, and the third largest K products consumer, which represents 15% of the market worldwide. However, about 90% of the K consumed in the country is imported; mainly from Canada and Russia, which account for more than 60% of the world's K supply (Quaresma, 2009).

Because KCl contains about 63% K₂O, this fertilizer is economically competitive and has a good efficiency compared to other K sources (Martins et al., 2008). However, the low national production capacity of KCl (Brazil currently exploits one single K deposit) along with the high demand from agriculture makes the country vulnerable and extremely dependent on the import of K fertilizers. This scenario harms the Brazilian trade balance, thus justifying the need for research into other unconventional sources of K (Nicolini, 2009).

One unconventional source of K is glauconitic siltstone, a sedimentary rock founded in São Gotardo, located in Minas Gerais State, Brazil. This rock is about 70m thick and is highly homogeneous in texture, mineralogy, and K distribution. It is mostly composed of glauconite mineral (40-80%), K-feldspar (10-15%), quartz (10-60%), and muscovite (5%) (Moreira et al., 2016). Glauconitic siltstone is a promising K fertilizer, with about 10% K₂O (Violatti et al., 2019). The production process for glauconitic siltstone fertilizers is based on mechanical activation technology (Singla et al., 2019). This process requires size reduction, screening, and classification.

The advancement of studies on the use of new K sources with low solubility in water and high agronomic efficiency has highlighted the need for investigating new methods of K analysis in soluble forms. Several studies have shown positive responses with alternative sources of K to improve soil fertility, yield, and quality of plants, such as the ones using glauconite as a K source for crops including coffee (Dias et al., 2018) and sunflower

(Torqueti et al., 2018). Therefore, this paper seeks to identify the most suitable extractor to characterize the availability of K in soils fertilized with glauconitic siltstone.

2. Method

2.1 Site Selection and Soil Characterization

A field experiment was conducted in Quirinópolis, Goiás state, Brazil, in a successive crop system with common bean (*Phaseolus vulgaris* L.) and maize (*Zea mays* L.). The soil from the experimental site was classified as Entisol according to the USDA soil taxonomy (Soil Survey Staff, 2010), which correspond to a typical ortic Neossolo Quartzarênico (RQo) according to the Brazilian System of Soil Classification (SiBCS) (Santos et al., 2013). The physical and chemical characteristics of the soil are indicated in Tables 1.

Table 1. Physical analysis and chemical analysis of the soils used in the study in Quirinópolis, Goiás State, Brazil

Soil	Sand						Silt				Clay	
	----- g kg ⁻¹ -----											
RQo-typical ortic Neossolo Quartzarênico	650						75				275	
pH	P	K	Al ³⁺	Ca ²⁺	Mg ²⁺	SB	t	CTC	V	m	OM	
	--- mg dm ⁻³ ---			----- cmol _c dm ⁻³ -----				----- % -----		g kg ⁻¹		
5.1	5.6	30	0.4	1.2	0.7	1.98	2.38	7.30	27.12	16.81	10.1	

Note. Soil: Pipette Method. P, K: Mehlich-1 extractor; Al, Ca, Mg: extracted with 1.0 mol/L KCl; SB: sum of bases; t: CTC effective; CTC: cation exchange capacity at pH 7.0; V: base saturation; m: exchangeable acidity saturation; OM: organic matter (Walkley-Black).

2.2 Experimental Design and Treatments

A successive crop system was carried out with common bean (variety BRS Style) followed by maize (hybrid AS 1581 from Dow AgroSciences company). The experiment was laid out in a randomized complete block design with four replicates. The treatments consisted of two K sources, such as granular potassium chloride (KCl) and powder glauconitic siltstone, which were applied at the standard rate of K recommended for common bean (72 kg ha⁻¹ K₂O) and maize (150 kg ha⁻¹ K₂O) crops. The K sources were characterized in terms of total K concentration of K₂O (Table 2).

Table 2. Chemical characterization of KCl and glauconitic siltstone

Source	Total K ₂ O (% w/w)
KCl	60
Glauconitic siltstone	10

Note. KCl: water; Glauconitic siltstone: method for extracting silicatic minerals (MAPA-8.2.4.2).

The experimental plot consisted of 20 m². On the first treatment, the total rate of K₂O was applied to the first crop of the growing system, and on the other three it was applied at 222, 444, and 888 kg ha⁻¹ of K₂O, in the form of glauconitic siltstone. The highest rate of glauconitic siltstone applied was 1,776 kg ha⁻¹ of K₂O and a control treatment without K application was included. The treatments are described in Tables 3 and 4.

Table 3. Treatments applied to the common bean crop (first crop)

N.	Treatment	K ₂ O	Commercial fertilizer
		----- kg ha ⁻¹ -----	
1	Absolute control	0.00	0.00
2	Positive control (KCl)	72.00	120.00
3	Glauconitic siltstone 1x	222.00	2,220.00
4	Glauconitic siltstone 2x	444.00	4,440.00
5	Glauconitic siltstone 4x	888.00	8,880.00
6	Glauconitic siltstone 8x	1,776.00	17,760.00

Table 4. Treatments applied to the maize crop (second crop)

N.	Treatment	K ₂ O	Commercial fertilizer
			kg ha ⁻¹
1	Absolute control	0.00	0.00
2	Positive control (KCl)	150.00	250.00
3	Glaucanitic siltstone 1x	0.00	0.00
4	Glaucanitic siltstone 2x	0.00	0.00
5	Glaucanitic siltstone 4x	0.00	0.00
6	Glaucanitic siltstone 8x	0.00	0.00

2.3 Field Experiment

All K treatments were applied 30 days before sowing the common bean, incorporated into the soil and incubated. In addition, 270 kg ha⁻¹ of NP fertilizer on 7-34-00 formulation was added to the soil to supply nitrogen (N) and phosphorus (P₂O₅) in order to meet the crop nutrient requirements, corresponding to 18.9 kg ha⁻¹ N and 91.8 kg ha⁻¹ P₂O₅. Limestone was also added at different proportions to raise the percentage base saturation of soil to 70%. Gramoxone 3.0 L ha⁻¹ was used to desiccate the experimental area and invasive plants were controlled with specified products.

At the end of the common bean cultivation cycle, all plants were harvested, and soil samples were collected and analyzed. Before sowing the successive crop, the soil was again fertilized with N and P by applying 250 kg ha⁻¹ of 9-43-00 NP fertilizer, and a total of 250 kg ha⁻¹ of urea was applied at four different times during the experimental period to supply N to the crops.

The maize crop was then cultivated. Seeds were treated with Master root (2.0 mL kg⁻¹ seed), Maxim (2.0 mL kg⁻¹ seed), Premium (2.0 mL kg⁻¹ seed), and Fipronil (2.0 mL kg⁻¹ seed). In post-emergence weed control was performed using Atrazin (2.0 L ha⁻¹). At early growth stage (V2), 120 kg ha⁻¹ of ammonium sulfate was applied, and at stage V4, foliar fertilization was carried out using Equalizes 0.75 L ha⁻¹. At the stage R1, fungicide was applied using Native 0.6 L ha⁻¹ along with Mancozeb 1.5 L ha⁻¹.

2.4 Potassium Extractors

A total of eight methods were tested to extract K from glaucanitic siltstone. They are described below and can be accessed in more detail in the Brazilian manual of official analytical methods for fertilizers and correctives (MAPA, 2017).

2.4.1 Neutral Ammonium Citrate (NAC)

This extraction method consists of dissolving 370 g of pure crystallized citric acid monohydrate (C₆H₈O₇·H₂O) in 1.5 L of water and adding 345 mL of pure ammonium hydroxide (NH₄OH) containing 28-29% NH₃. If NH₃ concentration is less than 28%, add additional volume to compensate for the lower concentration and decrease the volume of water in which the citric acid will be dissolved. Allow the mixture to cool and then measure the pH. If needed, adjust the pH to 7.0±0.05 with solutions of aqueous ammonium hydroxide solution (1 + 7) and citric acid 10% w/v, or use more concentrated solutions of both reagents. Store the solution in a tightly closed bottle. Check the pH weekly, adjusting it when needed.

2.4.2 2% Citric Acid Solution

This extraction method consists of preparing a citric acid solution 20 g L⁻¹ as follows: weigh 10 g of pure crystallized citric acid monohydrate (C₆H₈O₇·H₂O) and dissolve in water, transfer to a 500 mL volumetric flask, and complete the volume. Use the freshly prepared extractor.

2.4.3 2% Citric Acid Solution + 0.5% Ammonium Fluoride

The methodology consists of preparing a citric acid solution with 20 g L⁻¹ and ammonium fluoride 5 g L⁻¹ as follows: weigh 10 g of pure crystallized citric acid monohydrate (C₆H₈O₇·H₂O) and 2.5 g of ammonium fluoride, dissolve in water, transfer to a 500 mL volumetric flask, and complete the volume. Use it freshly prepared.

2.4.4 5% Tartaric Acid Solution

This extraction method consists of preparing a solution of tartaric acid with 50 g L⁻¹ as follows: weigh 25 g of pure tartaric acid, dissolve in water, transfer to a 500 mL volumetric flask, and complete the volume. Use the freshly prepared extractor.

2.4.5 5% Tartaric Acid Solution + 0.5% Sodium Fluoride

This extraction method consists of preparing a solution of tartaric acid with 50 g L⁻¹ and sodium fluoride 5 g L⁻¹ as follows: weigh 25 g of pure tartaric acid and 2.5 g of pure sodium fluoride, dissolve in water, transfer to a 500 ml flask volumetric, and complete the volume with water. Use the freshly prepared extractor.

2.4.6 Hydrochloric Acid (HCl)

This extraction method consists of weighing 0.5-2.5 g of the K source with an accuracy of 0.1 mg. Transfer the sample to a 150 mL beaker and add 10 mL of concentrated HCl. Cover the beaker with a watch glass and bring it to a moderate boil on a hot plate until dry, without letting the residue burn. For samples with contents above 5% by mass or less soluble raw materials, this step must be repeated with a new addition of concentrated HCl, heating again until close to dryness. Prepare a blank test in parallel. Add 20 mL of the aqueous HCl solution (1 + 5) to the residue, boil slightly for 10 min, allow it to cool and transfer to a 100 mL volumetric flask. Complete the volume with water and mix. Filter on medium or fine pore filter paper, if needed, collecting the filtrate in a dry container.

2.4.7 Method for Extracting Silicatic Minerals (MAPA-8.2.4.2)

This method is indicated for samples which contains fritted trace elements (FTEs) and another silicatic materials, insoluble in water (MAPA, 2017). This extraction method consists of weighing 0.5 to 1.0 g of the K source, with a precision of 0.1 mg, transferring it to a platinum crucible and adding 5 mL of HClO₄ and 5 mL of concentrated HF. Prepare a blank test in parallel. Place the crucible in a flat-bottomed porcelain dish and set on a hot plate. Heat until dense white HClO₄ vapors are released. Remove from the plate, allow to cool and transfer to a 150 mL beaker, adding water to a volume of about 50 mL. Heat until moderate boil for 10 min. Allow it to cool. Transfer to a 100 mL volumetric flask. Complete the volume with water and mix. Filter on medium or fine pore filter paper, if needed, receiving the filtrate in a dry container. If intermediate dilutions are needed to adjust the Ca concentration to the reading interval, use HCl solution (1 + 23), adding to the last dilution an adequate volume of the lanthanum solution, so that the reading solution contains 1% lanthanum w/v (10 mg L⁻¹ La).

2.4.8 Hot Plate Extraction (1:100 and 1:500)

This extraction method consists of weighing 0.5 g (1:100 ratio) and 0.1 g (1: 500 ratio) of the K source, quarter it with a smaller mesh size of 50 mesh and place it in a 100 mL beaker. Then, add 50 mL of the extraction solution to the container (to maintain a 1:100 or 1:500 ratio) and place it on the hot plate to heat to 95 °C. Keep this temperature for 15 min, without boiling. After heating, allow the solution to cool and transfer to a 100 mL volumetric flask, washing the beaker with small portions of distilled water until the volume is completed. Remove a 2 mL aliquot for 50 mL cup and add 18 mL of distilled water (10x dilution). For the K source, a new dilution of 10x was performed so that the readings would occur within the photometer curve.

2.5 Treatment Measurements

At the end of each cultivation cycle, all plants were harvested, and soil samples were collected using a hand auger, and analyzed.

For determining the levels of soluble K contained in the glauconitic siltstone, all samples were quartered (Jones riffles) until the final sample had the appropriate weight (about 250 g). The glauconitic siltstone was then crushed and sieved through a 100-mesh sieve to obtain the appropriate particle size (< 0.147 mm). Afterward, samples of glauconitic siltstone were submitted to chemical analyses by all eight extraction methods. For all methods, the concentration of K was determined by flame emission spectrophotometry. The concentration of total K₂O contained in the glauconitic siltstone solubilized by the extractor (Total Ks, kg ha⁻¹) were obtained by multiplying the rate of total K₂O applied by the average concentration K₂O extracted from each method, as follows:

$$\text{Total Ks} = \frac{K_2 \times K_1}{10} \quad (1)$$

2.6 Statistical Analysis

The different K concentration were subjected to analysis of variance by the F test, and the averages were compared by the Duncan test at 5% probability.

To evaluate the efficiency of each extractor, simple linear regression equations were adjusted to estimate the K levels recovered by the extractors and the plants as a function of the K rates applied via glauconitic siltstone.

Also, Pearson's correlation analyses were performed between the K concentration recovered by the extractors and the plants as a function of the K rates applied via glauconitic siltstone.

3. Results and Discussion

Data of common bean production showed that the 4x and 8x glauconitic siltstone were better than all other treatments the 1x and 2x glauconitic were statistically equivalent to positive control (KCl). For maize production, with glauconitic siltstone 2x, 4x and 8x, the highest yields were obtained; production of 1x glauconitic siltstone did not differ statistically from both absolute control and positive control (KCl) (Table 6). The results emphasize both the efficiency of glauconitic siltstone, and at the same time, the importance of the appropriate rate to be applied.

Table 6. Yield of common bean and maize crops as a function of different sources and rates of K₂O

Treatments	K ₂ O	Common bean	Maize	Accumulated
		----- kg ha ⁻¹ -----		
Absolute control	0.00	2,824.50 c	6,994.00 b	9,818.50
Positive control (KCl)	222.00	2,983.50 bc	7,286.00 b	10,269.50
Glauconitic siltstone 1x	222.00	3,035.25 bc	7,192.00 b	10,227.25
Glauconitic siltstone 2x	444.00	3,017.25 bc	7,488.00 ab	10,505.25
Glauconitic siltstone 4x	888.00	3,573.00 a	7,439.00 ab	11,012.00
Glauconitic siltstone 8x	1,776.00	3,233.25 b	7,854.00 a	11,087.25

Note. The means followed by the same letters in columns are not significantly different by Duncan's test ($p \leq 0.05$).

A simple linear correlation was built with these results and the accumulated yield of common bean and maize crops (Table 7). Figure 1 contains data related to the total level of K₂O contained in the extraction solution (kg ha⁻¹) and accumulate yield of beans and maize crops.

The best correlation between extracted K and accumulated yield was obtained using the MAPA-8.2.4.2 ($r = 0.76945$), revealing that it is the most appropriate method for extracting total levels of K₂O in soils fertilized with glauconitic siltstone.

Both MAPA-8.2.4.2 and tartaric acid 5% + 0.5% NaF (1:500 ($r = 0.76725$)) extractors greatly exceeded the others when correlated to the accumulated yield of common bean and maize crops. Further, they showed correlation coefficients values very close to each other.

The correlations between accumulated yield with K extracted by either neutral ammonium citrate ($r = -0.03655$) or citric acid 2% ($r = -0.03353$) were the lowest. However, the use of fluorides (citric acid 2% + NH₄F 0.5%) promoted a slight correlation increase ($r = 0.42948$), which increased a bit more when using tartaric acid 5% + NaF 0.5% at the ratios of 1:100 ($r = 0.63214$) and 1:500 ($r = 0.76725$). The increasing availability of K induced by fluorides reveals that K could be released from these sources over time in a slow-release.

The TA + NaF 0.5% (1:100), HCl, NAC, CA, and CA + NH₄F extractors presented a very poor correlation with an accumulated yield of the crops, indicating that they should not be used in the measurement of total K₂O.

Table 7. Pearson's correlation coefficients and probability between different extractors used in glauconitic siltstone and the accumulated productivity of common bean and maize

Variable	Pearson correlation coefficients (r), n = 24	Probability
NAC ¹	-0.03655	0.8654
CA ²	-0.03353	0.8764
CA + NH ₄ F ³	0.42948	0.0362
TA ⁴ + NaF ⁵ (1:100)	0.63214	0.0009
TA + NaF (1:500)	0.76725	< 0.0001
HCl ⁶	0.57318	0.0034
MAPA-8.2.4.2 ⁷	0.76945	< 0.0001

Note. ¹ NAC: neutral ammonium citrate; ² CA: 2% citric acid; ³ NH₄F: 0.5% ammonium fluoride; ⁴ TA: 5% tartaric acid; ⁵ NaF: 0.5% sodium fluoride; ⁶ HCl: hydrochloric acid; ⁷ Method for extracting silicatic minerals (MAPA-8.2.4.2).

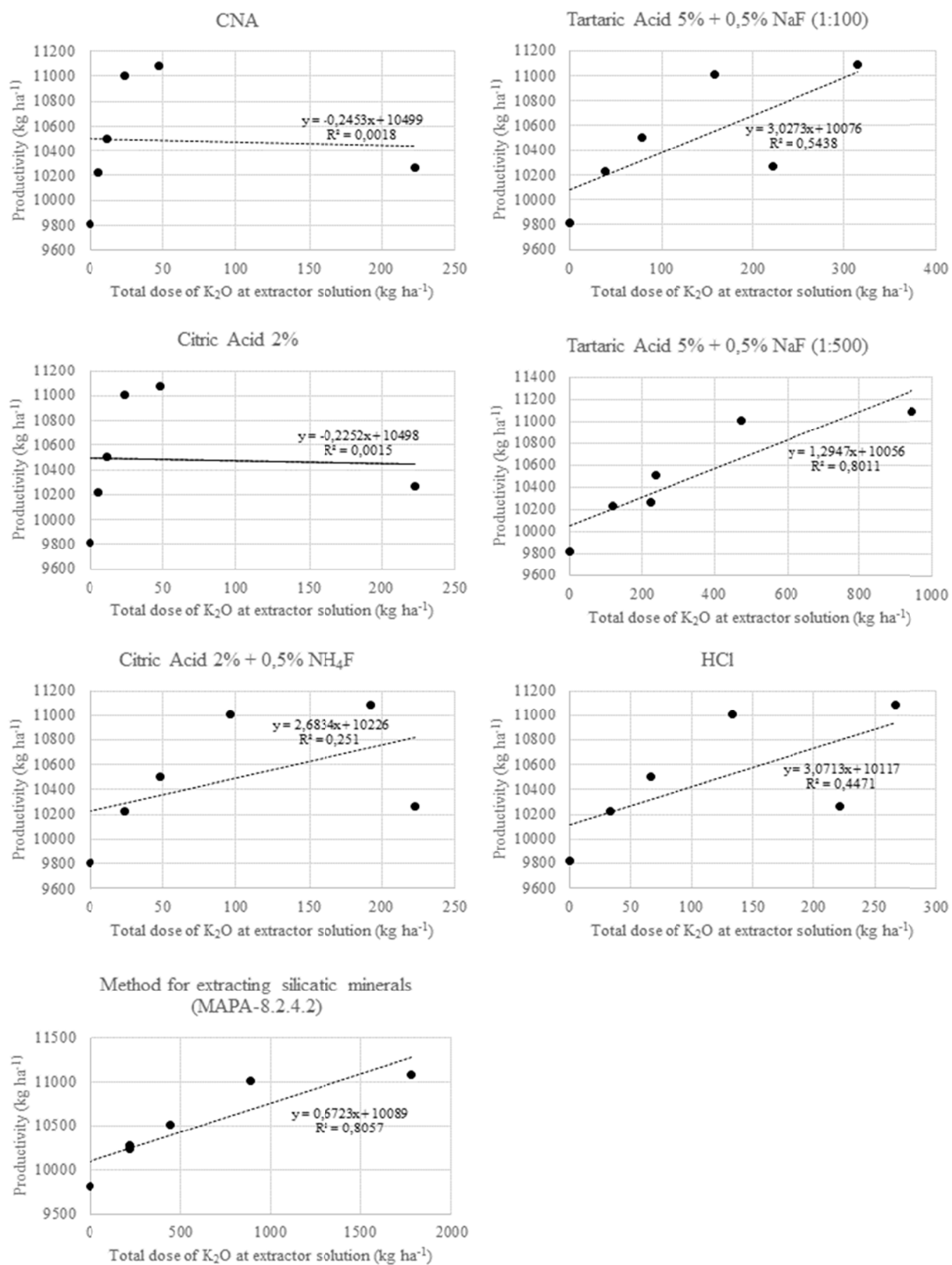


Figure 1. Total K_2O concentration contained in the extraction solution (kg ha⁻¹) and accumulates the yield of beans and maize crops

4. Conclusions

The results show that method for extracting silicatic minerals (MAPA-8.2.4.2) provided the best correlation between soluble K and accumulated yield of common bean and maize crops, demonstrating the high agronomic efficiency of glauconitic siltstone.

The extractors tartaric acid 5% + NaF 0.5% (1:100), HCl, NAC, citric acid 2%, and citric acid 2% + NH₄F 0.5% (1:100) presented correlation coefficients values close to zero and, therefore, should not be used to quantify soluble K from glauconitic siltstone.

References

- ANDA (Associação Nacional para Difusão de Adubos). (2016). *Anuário estatístico do setor de fertilizantes*. São Paulo, Brazil. Retrieved from <http://anda.org.br/arquivos>
- Dias, K. G. L., Guimarães, P. T. G., Carmo, D. L., Reis, T. H. P. R., & Lacerda, J. J. J. (2018). Alternative sources of potassium in coffee plants for better soil fertility, productivity, and beverage quality. *Pesquisa Agropecuária Brasileira*, 53(12), 1355-1362. <https://doi.org/10.1590/s0100-204x2018001200008>
- Korndörfer, G. H., Pereira, H. S., & Nolla, A. (2004). *Análise de silício: solo, planta e fertilizante*. Uberlândia, MG: Instituto de Ciências Agrárias, Universidade Federal de Uberlândia. Retrieved from https://www.researchgate.net/publication/312454775_Analise_de_silicio_solo_planta_e_fertilizante
- MAPA (Ministério da Agricultura, Pecuária e Abastecimento). (2017). *Manual de Métodos Analíticos Oficiais para Fertilizantes e Corretivos* (p. 230). MAPA, Brasília.
- Martins, E. S., Oliveira, C. G., Resende, A. V., & Matos, M. S. F. (2008). Agrominerais—Rochas silicáticas como fontes minerais alternativas de potássio para a agricultura. In A. B. Luz, & F. A. F. Lins (Eds.), *Rochas e minerais industriais no Brasil: Usos e especificações* (2nd ed., p. 9). Rio de Janeiro: CETEM/MCT.
- Nicolini, K. P. (2009). *Produção de fertilizantes de liberação lenta a partir da torta de mamona (Ricinus communis) e de uréia intercalada em caulins* (Doctorate's thesis, Universidade Federal do Paraná, Programa de Pós-Graduação em Química, Setor de Ciências Exatas, Curitiba, Paraná, Brazil).
- Quaresma, L. F. (2009). *Desenvolvimento de estudos para elaboração do plano duodecenal (2010-2030) de geologia, mineração e transformação mineral*. Brasília: Ministério de Minas e Energia, Secretaria de Geologia, Mineração e Transformação Mineral. Retrieved from http://www.mme.gov.br/sgm/galerias/arquivos/plano_duo_decenal/a_mineracao_brasileira/P19_RT28_Perfil_do_Ouro.pdf
- Santos, H. G., Jacomine P. K. T., Anjos, L. H. C., Oliveira, V. A., Lumbreras, J. F., Coelho, M. R., ... Oliveira, J. B. (2013). *Sistema Brasileiro de Classificação de Solos* (3rd ed.). Brasília: Embrapa.
- Singla, R., Alex, T. C., & Kumar, R. (2019). On mechanical activation of glauconite: physicochemical changes, alterations in cation exchange capacity and mechanisms, *Powder Technology*, 360(15). <https://doi.org/10.1016/j.powtec.2019.10.035>
- Soil Survey Staff. (2010). *Keys to Soil Taxonomy* (11th ed.). USDA, National Resources Conservation Service, National Soil Survey Center, Lincoln, NE.
- Torqueti, S. T. S., Boldrin, K. V. F., Nascimento, A. M. P., Paiva, P. D. O., Furtini Neto, A. E., & Luz, I. C. A. (2016). Fonte alternativa de potássio no cultivo do girassol ornamental. *Ciência e Agrotecnologia*, 40(3), 257-264. <https://doi.org/10.1590/1413-70542016403036115>
- Violatti, I. C. A., Gualberto, C. A. C., Silveira, L. H., Santos, G. A., Ferreira, B. C., Machado, P. M. M., & Pereira, H. S. (2019). Glauconitic siltstone as multi-nutrient fertilizer for *Urochloa brizantha* cv. Marandú. *Australian Journal of Crop Science*, 13(8), 1280-1287. <https://doi.org/10.21475/ajcs.19.13.08.p1609>
- Wadt, P. G. S. (2011). *Diagnose foliar e recomendação de adubação para lavouras comerciais* (p. 69). EMBRAPA, Rio Branco.

Copyrights

Copyright for this article is retained by the author(s), with first publication rights granted to the journal.

This is an open-access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).