AGROKÉMIA ÉS TALAJTAN 73 (2024) 1, 42–58
DOI: 10.1556/0088.2024.00170

Investigating the elemental composition of Egyptian glauconite sediments by applying BCR sequential extraction procedure and some single extractants

[1,4]Nada ELDAWWY, [2]Miklós GULYÁS, [1*]Heba NASER, [2]Anita TAKÁCS, [3]Éva LEHOCZKY, [1]Márk HORVÁTH

[1]Department of Environmental Analysis and Environmental Technology, Institute of Environmental Sciences, Hungarian University of Agriculture and Life Sciences, Gödöllő, Hungary
[2]Department of Soil Sciences, Institute of Environmental Sciences, Hungarian University of Agriculture and Life Sciences, Gödöllő, Hungary
[3]Department of Environmental Sustainability, Institute of Environmental Sciences, Hungarian University of Agriculture and Life Sciences, Keszthely, Hungary
[4]Department of Soil and Water Sciences, Faculty of Agriculture, Minia University, Minia, Egypt

(Received: 04 Apr 2024; Accepted: 10 Jun 2024)

Original article

Abstract

This study assesses the elemental composition of Egyptian glauconite sediments, focusing on potentially toxic elements (PTEs) and macronutrients. The primary aim is to evaluate the feasibility of utilizing these sediments as a natural source of potassium for agricultural purposes, besides conventional chemical fertilizers like potassium sulfate. To quantify elemental content, chemical analysis was employed across five distinct grain size fractions after grinding glauconite rock. The assessment included potassium, calcium, sodium, and PTE concentrations, utilizing potassium chloride (KCl) and ammonium acetate lactate (AL Solution) as single extractants, and the BCR extraction protocol, in addition to measuring the pseudo-total content of these elements. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) facilitated a comparative analysis of elemental concentrations. Results indicate PTE concentrations within European Union regulations, with an absence of cadmium. Glauconite samples contain approximately 3–3.3% potassium by weight, alongside significant amounts of essential macronutrients (calcium, magnesium) and micronutrients (copper, nickel, zinc) crucial for agriculture. BCR sequential extraction protocol results closely align with or slightly surpass pseudo-total content results. Notably, the AL Solution demonstrates high efficiency compared to KCl or acetic acid in the first step of the

---

**Corresponding author:* HEBA NASER, Department of Environmental Analysis and Environmental Technology, Institute of Environmental Sciences, Hungarian University of Agriculture and Life Sciences, Páter Károly str. 1., 2100 Gödöllő, Hungary
E-mail: haboosh_1983@yahoo.com

BCR method. BCR sequential protocol provides valuable insights into various elemental forms and potential mobility. Overall, this study reveals that glauconite has the potential to serve as a promising alternative potassium fertilizer without causing adverse environmental impacts.

Keywords: glauconite sediments, fractionation, PTEs contamination, BCR sequential extraction, single extractants, potassium fertilizers.

Introduction

Egypt's increasing demand for potassium as an essential element for plant growth is a critical concern in agriculture. FAO statistics (URL1) reveals a substantial rise in potash fertilizer consumption, from 79.000 tons to 125.000 tons between 2015 and 2020. However, Egypt's heavy reliance on imported potassium fertilizers significantly hinders agricultural development in the country.

Recognising the current agricultural landscape and the potential of potash-rich soluble minerals, such as glauconite sediments, offers a vital opportunity to diversify potassium sources within Egypt and other countries (CASTRO & TOURN, 2003; SHEKHAR et al., 2017; 2020; FRANZOSI et al., 2014; SANTOS et al., 2016; KARIMI et al., 2012; MERCHANT, 2012; RUDMIN et al., 2019). These sediments are distributed globally and are notably prevalent in ancient shallow marine formations (AMORSI et al., 2007; BALDERMANN et al., 2015; 2017; EDER et al., 2007; HEGAB & ABD-ELWAHED, 2016; IVANOVSKAYA, 2009; BANERJEE et al., 2015; 2016; BANSAL et al., 2017; 2019), including extensive regions in Egypt's Western Desert and the New Valley Governorate, characterised by varying sediment thickness (HEGAB & ABD-ELWAHED, 2016; BAIOUMY & BOULIS, 2012).

Glauconite, a dioctahedral micaceous phyllosilicate mineral, boasts high interlayer potassium concentrations, exceeding 6% in specific locations (DRITS et al., 1997; BAILEY, 1980; GUGGENHEIM et al., 2006; ODIN & MATTER, 2003; MEUNIER & EL ALBANI, 2007). Beyond its potassium content, glauconite holds promise as a fertilizer due to its richness in essential macronutrients like phosphorus and calcium, alongside numerous micronutrients such as iron, manganese, copper, cobalt, and nickel (RUDMIN et al., 2017; 2019; 2020; FRANZOSI et al., 2014; OZE et al., 2019). This diversity of macronutrients, crucial for osmotic regulation and plant growth, endows glauconite with significant commercial value (SHIN et al., 2005).

Furthermore, HECKMAN & TEDROW (2004) reported that glauconite is typically found in layers in much sedimentary rock or as rounded aggregates or pellets of unconsolidated grains of scaly particles, sandy, silty, and clayey but often as sand-sized pellets. However, glauconite does not behave like typical sand since it contains many micro-pores with a higher water-holding capacity than true sand and a higher cation exchange capacity. Some types of glauconite are presented as pellets of two textural forms; aggregate composes the bulk of pellets, and both two textural types are different in their mineralogy and chemistry (ODOM, 1976).

Internationally, glauconite has been employed as a chemical fertilizer and soil conditioner for agricultural and land reclamation in regions like Russia (LEVCHENKO et al., 2008). In Egypt, extensive research has explored glauconite sediments across various disciplines, including petrology, mineralogy, chemistry, agriculture, and geochemistry (EL-SHARKAWI, 1977; MESAED, 1999; BAIOUMY et al., 2012; HASSAN & BAIOUMY, 2006; EID, 2013; EL-HABAAK et al., 2016; MORSY et al., 2016). Nonetheless, while recent years have witnessed some investigations into the agricultural use of glauconite sediments, there has been limited exploration of their potential toxic element content and associated pollution effects upon agricultural application.

Assessing mobile toxic element fractions in soils is pivotal in understanding the potential risks these elements pose to the biosphere, groundwater quality, and their availability to plants. Environmental contamination sites are rising globally, underscoring the need to evaluate environmental impact (RAO et al., 2008).

Single and sequential extraction methods are highly valuable tools in the field of environmental science, particularly in studies focusing on the fate of environmental pollutants. These extractants offer insights into the availability of elements in various matrices. Although less specific, single extraction methods provide a rapid means of determining element availability. However, they have limitations, such as the potential to target multiple sites or incomplete release from target sites (RAO et al., 2008; JAKUBUS, 2020). RAO et al. (2008) have categorized ideal single extractants based on their capacity to release elements from specific soil phases, aiding in studying soil chemistry and understanding metal binding, transformation, or release mechanisms in soils.

In assessing heavy metal contamination risk in environmental samples, two critical factors come into play: the chemical species form of the element, which determines its biological impact, and the solubility (availability) of the elemental species. These factors are inherently interconnected within a given medium, such as water, sediment, soil, or other environmental samples (TEMPLETON, 2000).

Measuring “pseudo-total” element concentrations in environmental samples, achieved through strong acid or aqua regia digestion, provides a valuable means of evaluating elemental contamination within an environmental context. Pseudo-total content reflects the maximum potential hazard associated with metal contaminants that are not bound in silicates, aiding in understanding the long-term implications of introducing environmental samples, such as glauconite, into soils (RAO et al., 2008; URE & DAVIDSON, 2002) .The legal requirements typically focus on the total content of PTEs, these quantities do not adequately represent the actual environmental impact of metals. Consideration of metal solubility and availability for plants is essential. Thus, the chemical fractions of metals play a pivotal role in influencing the mobility of PTEs in the soil environment (JAKUBUS, 2020).

Various techniques have been employed to determine metal fractionation and assess their availability in solid materials. The Community Bureau of Reference (BCR) procedure is a valuable method, offering simplicity and comprehensive metal mobility information. The BCR approach categorises fractions into four groups: exchangeable, bound to iron and manganese oxyhydroxides, bound to organic matter and sulfides, and residual (JAKUBUS, 2020; HORVATH et al., 2010; 2013; HELTAI et al., 2015; 2018; 2019).

Sequential extraction, an essential tool, provides insights into the conditions of elements in soils, shedding light on their potential mobility, bioavailability, and chemical nature. It offers a more precise estimate of the true environmental impact (UMOREN et al., 2007; YANG et al., 2009; SALEEM et al., 2018). Previous studies have not utilised the BCR sequential extraction protocol on glauconite sediments.

This research fills a gap by applying the BCR sequential extraction protocol to glauconite deposits to quantify various elements and assess their potential availability when added to the soil while evaluating the content of potentially toxic elements to ensure environmental safety. Additionally, this study compares the BCR method with single extractant techniques, offering a faster, simpler, and more cost-effective approach to determining element availability. Based on the results, the environmental suitability of glauconite for use as a soil fertilizer can be determined. This multifaceted approach aims to comprehensively understand glauconite's potential as a sustainable potassium source for agriculture in Egypt.

Materials and methods

Samples

Representative samples of Glauconite were collected from El-Baharia Oasis in the Western Desert of Egypt close to El-Gedida mining area with coordinates 28°28′26″.11 N and 29°11′4.18″E at 187 m above sea level. Egypt has abundant mineral resources, including significant ironstone reserves in the El-Gedida mine (SALAMA et al., 2012). The mining area includes iron ores and high amounts of glauconite sediments (HASSAN & BAIOUMY, 2007). The sediments are mined as overburden and are removed to reach the commercial iron ore deposit. Glauconite sediments are widespread throughout many locations in the Western Desert.

The first step in preparing the samples for the analysis involved grinding the glauconite rock with a jaw crusher to less than 2 mm. Secondly, the fractionation of the sample is done by dry sieving, resulting in different five-size fractions (<2–1, <1–0.5, <0.5–0.2, <0.2–0.1, and <0.1 mm) which were used then in the chemical analysis. The main objective of sieving is to study the impact of sieving on the beneficiation of glauconite in these five mentioned samples after estimating their content of essential elements and the PTEs.

Chemical analysis

pH measurement

The pH of glauconite was measured using a digital pH meter (WTW MULTI 3420i) at 1:5 for the glauconite/water mixture and glauconite/KCl mixture, according to KALRA (1995). For each glauconite sample, a 2.00 g portion was weighed and dried at 60 °C for 1 h. The dried sample was put into a 50 ml beaker, and 10 ml of the liquid was added. The mixture was stirred for one hour and allowed to stand for 30 min. After the calibration of the pH meter using two buffer solutions of pH 7.01 and 4.01, the pH was measured at 25 °C.

(BCR) Sequential Extraction Procedure

Table 1 describes the steps of the improved BCR sequential extraction procedure. According to the protocol, the sample-to-extractant ratio was 1:40, as each sample's initial weight was 1.000 g. In the present investigation, the extraction and digestion procedures were repeated three times (n = 3) for each sample. A procedure blank was also prepared according to the BCR protocol.

Table 1
BCR Sequential Extraction Protocol

BCR Steps	**Fraction/phase extracted**	**Extractants**
1	Exchangeable, water, and acid-soluble	0.11 mol dm^{-3} HOAc
2	Reducible e.g., bound to iron and manganese oxyhydroxides	0.5 mol dm^{-3} $NH_2 - OH.HCl$ (adjusted to pH=1.5 by adding 25 cm^3, 2 mol*dm^{-3}HNO_3)
3	Oxidizable e.g., bound to organic matter and sulfides	8.8 mol dm^{-3} H_2O_2 then 1 mol dm^{-3} NH_4OAc (pH=2)
4	Residual. Non-silicate bound metals	Aqua regia/(HNO_3/H_2O_2)

The results were statistically analysed using a one-way analysis of variance (ANOVA). The data in *Table 2* are presented as means±standard deviation, and the differences between the samples are indicated by the least significant difference (LSD) with $P < 0.05$.

Table 2
Element concentration in the BCR steps compared with Pseudo total element content (mg kg^{-1}) related to dry weight, mean± standard deviation). (n.d.: not detected). LSD 5%: Least significant difference according to Fisher test (at $P < 0.05$)

Element	**Sample**	**BCR 1**	**BCR 2**	**BCR 3**	**BCR 4**	**(1+2+3+4)**	**Pseudo total**
Ca	**1**	269±3	1214±15	57.5±6.4	46.8±0.3	1587	1410
	2	265±10	1191±20	47.4±3.1	41.0±2.1	1544	1238
	3	276±11	1275±19	50.3±0.6	44.5±2.7	1645	1316
	4	250±14	1331±17	53.2±1.2	49.5±0.7	1683	1354
	5	254±1	1427±6	64.3±6.0	48.0±0.3	1793	1733
	LSD %5	*21*	*36*	*9.6*	*3.6*		
	Extractable (%)*	18.66	91.31	3.87	3.26	117.09	100
Cd	**1**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	LSD %5						

Table 2 cont.

Element	Sample	BCR 1	BCR 2	BCR 3	BCR 4	(1+2+3+4)	Pseudo total
Cr	**1**	0.091±0.022	0.110±0.200	0.70±0.00	45.3±1.0	46.2	51.27
	2	0.073±0.032	0.140±0.090	0.65±0.05	47.6±0.1	48.54	50.15
	3	0.092±0.031	0.052±0.013	0.78±0.02	49.9±0.7	50.82	48.09
	4	0.120±0.100	0.081±0.012	0.98±0.07	52.1±1.0	53.28	52.11
	5	0.092±0.031	0.130±0.010	1.06±0.02	52.4±0.4	53.68	54.12
	LSD %5	*0.07*	*0.1*	*0.1*	*1.7*		
	Extractable (%)	0.18	0.20	1.63	96.79	98.81	100
Cu	**1**	n.d.	0.40±0.40	n.d.	7.6±0.1	8	8.1
	2	n.d.	0.51±0.04	n.d.	7.7±0.1	8.2	8
	3	n.d.	0.66±0.12	n.d.	8.0±0.4	8.7	8.4
	4	n.d.	1.05±0.20	n.d.	8.2±0.3	9.3	9.2
	5	n.d.	1.20±0.07	n.d.	8.5±0.1	9.7	15.9
	LSD %5		*0.48*		*0.5*		
	Extractable (%)	0.00	8.31	0.00	86.67	94.98	100
K	**1**	811±12	536±86	255±8	29561±257	31163	30690
	2	789±12	575±2	262±8	30553±301	32179	32323
	3	782±12	573±4	269±3	31819±482	33443	32408
	4	789±12	567±4	263±3	31079±831	32698	33255
	5	801±8	550±8	263±5	29950±612	31564	33363
	LSD %5	*26*	*88*	*13*	*1223*		
	Extractable (%)	2.45	1.73	0.81	94.40	99.39	100
Mg	**1**	272±4	983±27	164±3	9552±157	10971	10894
	2	264±5	1002±4	157±2	10068±153	11491	11500
	3	256±3	1002±10	155±3	10345±71	11758	11115
	4	223±12	1003±17	144±3	10094±179	11464	11494
	5	282±4	951±22	158±3	9735±265	11126	11718
	LSD %5	*15*	*42*	*6*	*400*		
	Extractable (%)	2.29	8.71	1.37	87.79	100.16	100
Na	**1**	9239±140	128± 15	35.4±2.0	175±5	9577	7124
	2	9032±62	139± 0	39.0±2.0	189±6	9398	6821
	3	8514±29	131± 1	42.6±4.0	196±4	8882	6442
	4	8236±83	141± 4	38.9±1.0	200±1	8615	6267
	5	9109±25	119± 6	43.6±2.5	248±3	9520	7468
	LSD %5	*181*	*17*	*5.7*	*9*		
	Extractable (%)	129.32	1.92	0.58	2.84	134.67	100
Ni	**1**	n.d.	0.2	n.d.	13.9±0.3	14.1	16.2
	2	n.d.	n.d.	n.d.	14.6±0.2	14.6	15.9
	3	n.d.	n.d.	n.d.	16.2±0.3	16.2	16.2
	4	n.d.	n.d.	n.d.	16.5±0.2	16.5	17.5
	5	0.1	0.4	n.d.	15.9±0.3	16.4	18.5
	LSD %5				*0.6*		
	Extractable (%)	0.00	0.00	0.00	89.80	89.80	100

Table 2 cont.

Element	Sample	BCR 1	BCR 2	BCR 3	BCR 4	(1+2+3+4)	Pseudo total
Pb	**1**	n.d.	1.21±0.41	n.d.	6.50±0.42	7.7	6.8
	2	n.d.	0.52±0.21	n.d.	7.40±0.23	7.9	6.7
	3	n.d.	0.63±0.12	n.d.	7.50±0.51	8.1	7
	4	n.d.	0.73±0.22	n.d.	7.37±0.28	8.1	6.8
	5	n.d.	1.40±0.10	n.d.	7.61±0.17	9	8.7
	LSD %5		*0.5*		*0.79*		
	Extractable (%)	0.00	12.00	0.00	101.08	113.08	100
Zn	**1**	3.0±0.01	7.2±1.9	n.d.	101.6±2.3	111.7	112.3
	2	3.1±0.18	7.8±0.5	n.d.	105.6±0.3	116.4	115.7
	3	1.9±0.38	8.0±0.2	0.1	111.0±1.6	121	112.8
	4	1.2±0.40	8.3±1.1	n.d.	111.0±1.9	120.5	118.4
	5	2.4±0.96	10.1±0.7	0.8	107.8±1.3	121.2	127.1
	LSD %5	*1.14*	*2.5*		*3.7*		
	Extractable (%)	1.97	7.07	0.00	91.62	100.67	100

*The mean percentage of extractable element content in each BCR step compared with pseudo total content

The samples were analysed for “pseudo-total” content of all measured elements by digestion using nitric acid/H_2O_2 on the different sample sizes in the CEM MARS5 microwave digestor. The microwave digestion method was conducted according to the Hungarian Standard MSZ 21470–50:2006 (2006). The microwave digestion vessels containing samples were assembled and placed in a CEM Mars 5 Xtraction 230/60 Microwave Accelerated Reaction System 907501. The microwave digestion system was set at the following parameters: Ramp time – 20 minutes (450 Psi or 180 °C), Hold time – 18 minutes, Still time – 5 minutes (0 Watt), Hold time – 10 minutes (800 Watt, 450 Psi and/or 180 °C) and Cooling time – 20 minutes. After digestion, each sample was filtered using a 90 mm Filter Discs (Quant.) Grade 389 into a 25 ml volumetric flask and made up to 25 ml with distilled water. Each sample was physically homogenised by shaking it and transferred into a centrifuge tube for the trace element analysis.

Extracting by single extractants

Two different single extractants were used in this study. The first one was 1M KCl, and each sample weight was 20.00 g extracted in 50 ml potassium chloride. The second extractant was AL solution (diluted 1:10 with distilled water) using the AL method by EGNER et al. (1960), the glauconite sample ratio to extractant was 1:20. All samples were placed on the shaking system for 2 hours before starting the filtration.

All these elements (Cd, Zn, Pb, Ni, Cr, Cu, K, Mg, Ca and Na) were determined in the Extractants using ICP-OES (HORIBA Jobin Yvon ACTIVA-M Inductively Coupled Plasma Optical Emission Spectrometry) in the Hungarian University of Agriculture and Life Sciences, Institute of Environmental Science.

Results

The Elemental content of the five sample sizes applying BCR sequential extraction procedure and pseudo total

Table 2 provides a comprehensive presentation of the elemental content analysis results for glauconite samples, encompassing elements such as (Ca, Cd, Cr, Cu, K, Mg, Na, Ni, Pb and Zn); these concentrations are reported in milligrams per kilogram (mg·kg^{-1}) at each stage of the BCR procedure, alongside the pseudo-total content, across five different sample sizes of glauconite.

The samples contain about 3–3.3 wt% of potassium; the available potassium content found in the non-residual fractions (BCR 1+2+3) ranged between 1600–1625 mg kg^{-1} as indicated in *Table 2*. Additionally, the results showed that the samples were free of cadmium. The elemental content followed the following descending order K>Mg>Na>Ca>Zn>Cr>Ni>Cu>Pb, and the total content of the elements (Cr, Cu, Ni and Pb) was below the standard limits on fertilizers in the EU REGULATION (2019/1009) of the European Parliament and of the Council as shown in *Table 3*.

Table 3
Comparison between the concentrations (mg kg^{-1}) of the PTEs in glauconite sediments and the limits in fertilizers in the guidelines in the EU REGULATION (2019/1009)

Potentially toxic Elements	Cr	Cu	Pb	Ni	Cd
Glauconite	51.1	9.9	7.2	16.8	0.0
EU limits on fertilizers	200	600	120	100	1.5

Table 2 presents the mean in each step of BCR compared with the mean of Pseudo total content of the five samples calculated in percentage. The results indicate that for the elements whose concentrations were much over the detection limit, the sum of the element concentrations in the BCR fractions (1+2+3+4) equals or is slightly higher than the pseudo total concentration, such as Ca, Na and Pb. *Table 2* illustrates that the highest amount of detected calcium content was found in the reducible fraction (BCR 2), while sodium is located mainly in the easily mobilizable fraction (BCR 1), whereas Cr, Cu, K, Mg, Ni, Pb and Zn are typically found in the residual Fraction (BCR 4).

Single Extractants

The results of the BCR sequential analysis provide valuable information about the potential mobility of metals in the environment if glauconite sediments are used for agricultural purposes; however, we should look for another method to practice fast, low-cost assaying of metal levels that theoretically may contaminate the environment. Therefore, we compared the use of AL solution and KCl as single extractants to the results obtained from step 1 of the BCR process for all elements determined using the BCR technique, as shown in *Table 4*. In the case of Ca, Cu, K, and Mg, the extracted quantities by AL solution or KCl were more than the quantities gained from step 1 in BCR. As shown in *Table 4*, In the case of calcium, the results obtained with the KCl or AL solution were three times higher than those determined in BCR step 1; about 80–90% of the results gained in the reducible fraction. In Mg, the increase in findings extracted by single extractants was approximately double the results obtained in the exchangeable fraction.

Table 4

Element concentration in the BCR step 1 compared with element content by using single extractants (mg kg^{-1} related to dry weight)

Element	**Sample**	**BCR 1**	**KCl**	**AL**
Ca	1	269	962	1019
	2	265	963	1297
	3	276	947	1300
	4	250	976	1270
	5	254	1022	1305
Cr	1	0.1	n.d.	n.d.
	2	0.1	n.d.	n.d.
	3	0.1	n.d.	n.d.
	4	0.1	n.d.	n.d.
	5	0.1	n.d.	n.d.
Cu	1	n.d.	0.7	0.3
	2	n.d.	0.1	0.0
	3	n.d.	0.0	0.9
	4	n.d.	0.9	2.1
	5	n.d.	0.6	1.9
K	1	811	-	1197
	2	789	-	1029
	3	782	-	954
	4	789	-	936
	5	801	-	890
Mg	1	272	592	657
	2	264	568	679
	3	256	557	666
	4	223	531	661
	5	282	523	581
Na	1	9239	3515	7271
	2	9032	3509	7229
	3	8514	3491	6718
	4	8236	3550	6486
	5	9109	3539	6879
Zn	1	3.0	1.2	7.4
	2	3.1	1.3	11.0
	3	1.9	2.0	9.1
	4	1.2	1.4	9.9
	5	2.4	0.7	12.6

- not measured

In contrast, in the case of Na, the extracted quantity of sodium was higher in step 1 in BCR compared to the single extractants. It could be because of the high solubility of sodium in water, which allowed most of the sodium amount to dissolve directly. Using AL solution, which consists of (lactic acid, acetic acid, and ammonium hydroxide) was more effective than using KCl or water with acetic acid in the case of BCR step1 for determining the mobility of Zn. The extracted amount of element using AL solution was approximately equals the extracted amount in the exchangeable fraction and the reducible fraction together as shown in *Table 2 and 4*.

In Pb and Ni elements cases, the single extractants did not affect their release, with concentrations remaining below the detection limit, consistent with the results observed in the first step of the BCR protocol.

Discussion

In the current study, the size fractionation of the glauconite sediments had a negligible impact on the element concentration content. The differences between the concentrations in most of the data appear to be small and not highly significant, but in sample 5 (the smallest fraction size), the concentrations were slightly higher than in the other samples; this might be because the specific surface area of the glauconite pellets has increased. Following FRANZOSI et al. (2014) findings in a prior study on glauconite in Patagonia, Southeast Argentina, the fractionation was unnecessary in their investigation since employing two different fraction sizes from glauconite sediments as a potassium fertilizer gave similar results. In contrast, a study by EL-HABAAK et al. (2016) on two glauconite samples from the El-Bahariya Oasis area in Egypt demonstrated that potassium concentrations varied depending on particle size. Using five different size fractions, the potassium concentrations in the samples ranged from 4% to 7% K_2O.

Among the various factors influencing the mobility of potentially toxic elements (PTEs) within the soil matrix, pH emerges as a prominent determinant, as expounded upon by SHIVA KUMAR & SRIKANTASWAMY (2014). In the present study, the pH value measured with distilled water was 6, calculated as a mean of 5 replicates (standard deviation of 0.09), and the pH value measured with KCl was 5 (standard deviation of 0.09). These pH results collectively underscore the suitability of using glauconite sediments in the soil to support the growth of a wide range of plants, as they align within the generally accepted pH range of 5.5 to 7 (KIDD & PROCTOR, 2001).

The comparison of the sum of the cumulative BCR concentrations with the concentrations derived from the pseudo total provided acceptable findings. The BCR results exceeded the Pseudo-total in the measurements of some elements such as Ca, Na, and Pb, this might be due to the accumulated inaccuracy from each extraction measurement (VAN HERREWEGHE et al., 2003). In addition, the fact that pseudo total content reflects the maximum potential hazard associated with metal contaminants that are not bound in silicates.

In the single extractant results, the AL solution extracted a higher amount than KCl or the reagents in the BCR step 1 for Ca, Cu, K, Mg, and Zn elements, which could be because the formation of metal complexes with acetate ions is somewhat more stable than the formation of metal chloro-complexes. This increases the rate of exchange and decreases the rate of re-adsorption or precipitation of the metals that have been removed (PICKERING, 1986).

Glauconite as a potential fertilizer

The samples contain about 3–3.3 wt% of potassium, which equals 3.7–4 K_2O wt% calculated according to RICHERT et al. (2010), which is in the acceptable range as potassium fertilizer according to previous studies reported by FRANZOSI et al. (2014); HECKMAN & TEDROW (2004) and KARIMI et al. (2012). Additionally, the samples contain secondary macronutrients, including approximately 1.1 wt% magnesium, 0.15–0.17 wt% calcium, and 0.8–0.9 wt% sodium.

Based on the results obtained in *Table 4*, the compared elemental concentrations of PTEs and the permissible limits in EU REGULATION (2019/1009) ensure that using glauconite sediments as an alternative soil fertilizer does not have hazardous impacts on the environment. These results are consistent with EL-HABAAK et al. (2016), who studied the Egyptian glauconite sediments and reported that the chemical composition of El-Gedida glauconites is identical to the commercial New Jersey (USA) glauconite. which indicates that El-Gedida glauconite sediments contain sufficient potassium for land reclamation and agricultural uses and are considered an eco-friendly fertilizer, releasing their potassium content slowly (RUDMIN et al., 2020).

Conclusion

This study analysed the Egyptian glauconite sediments for their suitability as a soil fertilizer.

The investigation revealed that fractionation of glauconite sediments through sieving is unnecessary, as grinding alone satisfies their suitability. Pellets falling within the size fraction (<2.0–0.1mm) can be employed without sieving, as sieving has a negligible impact on elemental release enhancement.

Glauconite samples contained around 3–3.3% potassium and had potassium content within the acceptable range for fertilizers. Cadmium was not detected. The order of elemental content was K>Mg>Na>Ca>Zn>Cr>Ni>Cu>Pb. Importantly, the Cr, Cu, Ni, and Pb levels were below the limits in EU fertilizer regulations.

Utilizing the BCR protocol yielded valuable insights into the mobility of potentially toxic elements (PTEs) and other essential elements like K, Ca, Na, Cu, and Mg. The cumulative BCR steps closely approximated or slightly exceeded pseudo-total content measurements for most elements.

AL solution and KCl were tested as single extractants and compared to BCR step 1 results. AL solution was more effective than KCl for certain elements, notably Zn.

Glauconite sediments were found to be suitable as solid inorganic fertilizers containing potassium and other essential elements.

Future research should investigate additional elements, including iron and phosphorus, and examine the effect of glauconite acidification on elemental release and potassium beneficiation. Additionally, studies should explore the potential of washing glauconite to reduce sodium content before its use in agriculture.

Acknowledgements

The research was supported by the project ‘The feasibility of the circular economy during national defense activities’ of 2021 Thematic Excellence Programme of the National Research, Development and Innovation Office under grant no.: TKP2021-NVA-22, led by the Centre for Circular Economy Analysis. The authors thank The Cultural Affairs and Missions in Egypt, and TEMPUS Public Foundation for their support.

References

AMOROSI, A., SAMMARTINO, I., TATEO, F., 2007. Evolution patterns of glaucony maturity: A mineralogical and geochemical approach. Deep Sea Research Part II: Topical Studies in Oceanography. **54**. (11–13) 1364–1374.

BAILEY, S. W., 1980. Summary of recommendations of AIPEA nomenclature committee on clay minerals. American Mineralogist. **65**. (1–2) 1–7.

BAIOUMY, H. M., BOULIS, S. N., 2012. Glauconites from the Bahariya Oasis: an evidence for Cenomanian marine transgression in Egypt. Journal of African Earth Sciences. **70**. 1–7.

BAIOUMY, H. M., BOULIS, S. N., HASSAN, M. S., 2012. Occurrences and petrographical variations among the glauconite sediments from Egypt. In: Proceedings of the 10th international congress for applied mineralogy (ICAM). Springer, Berlin. pp. 39–47.

BALDERMANN, A., WARR, L. N., LETOFSKY-PAPST I., MAVROMATIS, V., 2015. Substantial iron sequestration during green-clay authigenesis in modern deep-sea sediments. Nature Geoscience. **8**. (11) 885–889.

BALDERMANN, A., DIETZEL, M., MAVROMATIS, V., MITTERMAYR, F., WARR, L. N., WEMMER, K., 2017. The role of Fe on the formation and diagenesis of interstratified glauconite-smectite and illite-smectite: A case study of Upper Cretaceous shallow-water carbonates. Chemical Geology. **453**. 21–34.

BANERJEE, S., MONDAL, S., CHARKABORTY, P. P., MEENA, S. S., 2015. Distinctive compositional characteristics and evolutionary trend of Precambrian glaucony: Example from Bhalukona Formation, Chhattisgarh basin, India. Precambrian Research. **271**. 33–48.

BANERJEE, S., BANSAL, U., PANDE, K., MEENA, S. S., 2016. Compositional variability of glauconites within the Upper Cretaceous Karai Shale Formation, Cauvery Basin, India: implications for evaluation of stratigraphic condensation. Sedimentary Geology. **331**. 12–29.

BANSAL, U., PANDE, K., BANERJEE, S., NAGENDRA, R., JAGADEESAN, K. C., 2019. The timing of oceanic anoxic events in the Cretaceous succession of Cauvery Basin: Constraints from 40Ar/39Ar ages of glauconite in the Karai Shale Formation. Geological Journal. **54**. (1) 308–315.

BANSAL, U., BANERJEE, S., PANDE, K., ARORA, A., MEENA, S. S., 2017. The distinctive compositional evolution of glauconite in the Cretaceous Ukra Hill Member (Kutch basin, India) and its implications. Marine and Petroleum Geology. **82**. 97–117.

CASTRO, L., TOURN, S., 2003. Direct application of phosphate rocks and glauconite as alternative sources of fertilizer in Argentina. Exploration and Mining Geology. **12.** (1–4) 71–78.

DRITS, V. A., DAINYAK, L. G., MULLER, F., BESSON, G., AND MANCEAU, A., 1997. Isomorphous cation distribution in celadonites, glauconites and Fe-illites determined by infrared, Mössbauer and EXAFS spectroscopies. Clay minerals. **32**. (2) 153–179.

EDER, V. G., MARTÍN-ALGARRA, A., SÁNCHEZ-NAVAS, A., ZANIN, Y. N., ZAIRAILOVA, A. G., LEBEDEV, Y. N., 2007. Depositional controls on glaucony texture and composition, Upper Jurassic, West Siberian Basin. Sedimentology. **54**. (6) 1365–1387.

EGNER, H., RIEHM, H., DOMINGO, W. R., 1960. Investigations on the chemical soil analysis as a basis for assessing the soil nutrient status. II: Chemical extraction methods for phosphorus and potassium determination. Kungliga Lantbrukshügskolans Annaler. **26**. 199–215.

EID, M. A, 2013. Some Adsorption Characterization of the Egyptian Glauconite Ore. Egyptian Journal of Soil Science. **53**. (1) 75–88.

EL-HABAAK, G., ASKALANY, M., FARAGHALY, M., ABDEL-HAKEEM, M., 2016. The economic potential of el-gedida glauconite sediments, el-bahariya oasis, western desert, Egyptian Journal of African Earth Sciences. **120**. 186–197.

EL-SHARKAWI, M. A, 1977. Glauconite, a possible source of iron for El Gidida iron sediments, Bahariya Oases, Egypt. Egyptian Journal of Geology. **1**. 109–116.

FRANZOSI, C., CASTRO, L. N., CELEDA, A. M., 2014. Technical evaluation of glauconies as alternative potassium fertilizer from the Salamanca Formation, Patagonia, Southwest Argentina. Natural Resources Research. **23**. 311–320.

GUGGENHEIM, S., ADAMS, J. M., BAIN, D. C., BERGAYA, F., BRIGATTI, M. F., DRITS, V. A., FORMOSO, M. L. L., GALÁN, E., KOGURE, T., STANJEK, H., 2006. Summary of recommendations of nomenclature committees relevant to clay mineralogy: report of the Association Internationale pour l'Etude des Argiles (AIPEA) Nomenclature Committee for 2006. Clays and Clay minerals. **54**. 761–772.

HASSAN, M. S., BAIOUMY, H. M., 2006. Structural and chemical alteration of glauconite under progressive acid treatment. Clays and clay minerals. **54**. (4) 491–499.

HASSAN, M., BAIOUMY, H., 2007. Characterization and origin of alunite in the El-Gideda iron mine (Egypt). Periodico di Mineralogia. **76**. (1) 11–24.

HECKMAN, J. R., TEDROW, J. C. F., 2004. Greensand as a soil amendment. Better Crops with Plant Food. **88**. (2) 16–17.

HEGAB, O. A., ABD EL-WAHED, A. G., 2016. Origin of the glauconite from the middle Eocene, Qarara formation, Egyptian Journal of African Earth Sciences. **123**. 21–28.

HELTAI, G., FEKETE, I., HALÁSZ, G., KOVÁCS, K., HORVÁTH, M., TAKÁCS, A., BOROS, N., GYŐRI, Z., 2015. Multi-Elemental Inductively Coupled Plasma-Optical Emission Spectroscopic Calibration Problems of the Sequential Extraction Procedure for the Fractionation of the Heavy Metal Content from Aquatic Sediments. Hungarian Journal of Industry and Chemistry. **43**. (1) 7–13.

HELTAI, G., GYŐRI, Z., FEKETE, I., HALÁSZ, G., KOVÁCS, K., TAKÁCS, A., BOROS, N., HORVÁTH, M., 2018. Longterm study of transformation of potentially toxic element pollution in soil/water/sediment system by means of fractionation with sequential extraction procedures. Microchemical journal. **136**. 85–93.

HELTAI, G., GYŐRI, Z., FEKETE, I., HALÁSZ, G., KOVÁCS, K., TAKÁCS, A., KUMHALO, L., HORVÁTH, M., 2019. Application of flexible multi-elemental ICP-OES detection in fractionation of potentially toxic element content of solid environmental samples by a sequential extraction procedure. Microchemical Journal. **149**. 104029.

HORVÁTH, M., HALÁSZ, G., KUCANOVÁ, E., KUCIKNOVÁ, B., FEKETE, I., REMETEIOVÁ, D., HELTAI, G., FLÓRIÁN, K., 2013. Sequential extraction studies on aquatic sediment and biofilm samples for the assessment of heavy metal mobility. Microchemical Journal. **107**. 121–125.

HORVÁTH, M., BOKOVÁ, V., HELTAI, G., FLÓRIÁN, K., FEKETE, I., 2010. Study of application of BCR sequential extraction procedure for fractionation of heavy metal content of soils, sediments, and gravitation dusts. Toxicological & Environmental Chemistry. **92**. (3) 429–441.

IVANOVSKAYA, T. A., 2009. Glauconitites in terrigenous rocks of the Khaipakh Formation (Middle Riphean, Olenek Uplift). Lithology and Mineral Resources. **44**. 348–366.

JAKUBUS, M., 2020. Changes in lead and chromium contents in sewage sludge evaluated using both single extractants and sequential method. Environmental Pollutants and Bioavailability. **32**. (1) 87–99.

KALRA, Y. P., 1995. Determination of pH of soils by different methods: collaborative study. Journal of AOAC international. **78**. (2) 310–324.

KARIMI, E., ABDOLZADEH, A., SADEGHIPOUR, H. R., AMINEI, A., 2012. The potential of glauconitic sandstone as a potassium fertilizer for olive plants. Archives of Agronomy and Soil Science. **58**. (9) 983–993.

KIDD, P. S., PROCTOR, J., 2001. Why plants grow poorly on very acid soils: are ecologists missing the obvious? Journal of Experimental Botany. **52**. (357) 791–799.

LEVCHENKO, E., PATYK-KARA, N., LEVCHENKO, M., 2008. Glauconite deposits of Russia: perspectives of development. In: Abstract for the 33rd International Geological Congress (Oslo, Norway). The Norvegian Academy of Science and Letters, Oslo, Norway. pp. 5059.

MERCHANT, R. J., 2012. Glauconite-the future potash for fertilisers in New Zealand. AusIMM Bull. **1**. 78–81.

MESAED, A. A, 1999. Mineralogy and geochemistry of the Bartonian stratabound diagenetic and latertic glauconitic ironstones of El-Gidada mine, El-Bahariya Oases, Egypt. In: International Conferece on Geology of the Arab World. Cairo University, Cairo, Egypt. pp. 509–540.

MEUNIER, A., EL ALBANI, A., 2007. The glauconite–Fe-illite–Fe-smectite problem: a critical review. Terra nova. **19**. (2) 95–104.

MORSY, M. A., DARWISH, O. H., ELDAWWY, N. G., 2016. Evaluation of glauconite sediments as an amendment for sandy soil: 1-preliminary studies. El-Minia Journal of Agricultural Research and Development. **36**. 343–355.

MSZ 21470–50:2006, 2006. Environmental testing of soils. Determination of total and soluble toxic element, heavy metal and chromium (VI) content. Hungarian Standard Association, Budapest (In Hungarian).

ODIN, G. S., MATTER, A., 2003. De glauconiarum origine. Sedimentology. **28**. (5) 121–151.

ODOM, I. E., 1976. Microstructure, mineralogy and chemistry of Cambrian glauconite pellets and glauconite, central USA. Clays and Clay Minerals. **24**. 232–238.

OZE, C., SMAILL, J. B., REID, C. M., PALIN, M., 2019. Potassium and metal release related to glaucony dissolution in soils. Soil Systems. **3**. (4) 70.

PICKERING, W. F, 1986. Metal ion speciation—soils and sediments (a review). Ore Geology Reviews. **1**. (1) 83–146.

RAO, C. R. M., SAHUQUILLO, A., LOPEZ SANCHEZ, J. F., 2008. A review of the different methods applied in environmental geochemistry for single and sequential extraction of trace elements in soils and related materials. Water, Air, and Soil Pollution. **189**. 291–333.

REGULATION (EU), 2019. Regulation (EU) 2019/1009 of the European Parliament and of the Council of 5 June 2019 Laying down Rules on the Making Available on the Market of EU Fertilising Products and Amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009 and Repealing Regulation (EC) No 2003/2003. 2019. Official Journal of the European Union. **170**. 1–114.

RICHERT, A., GENSCH, R., JÖNSSON, H., STENSTRÖM, T. A., DAGERSKOG, L., 2010. Practical guidance on the use of urine in crop production. EcoSanRes Publications Series. (2010-1). Stockholm Environment Institute, Stockholm, Sweden.

RUDMIN, M., BANERJEE, S., MAKAROV, B., 2020. Evaluation of the effects of the application of glauconitic fertilizer on oat development: A two-year field-based investigation. Agronomy. **10**. (6) 872.

RUDMIN, M., BANERJEE, S., MAKAROV, B., MAZUROV, A., RUBAN, A., OSKINA, Y., TOLKACHEV, O., BUYAKOV, A, SHALDYBIN, M., 2019. An investigation of plant growth by the addition of glauconitic fertilizer. Applied Clay Science, **180**. 105178.

RUDMIN, M., BANERJEE, S., MAZUROV, A., MAKAROV, B., & MARTEMYANOV, D., 2017. Economic potential of glauconitic rocks in Bakchar deposit (SE Western Siberia) for alternate potash fertilizer. Applied Clay Science. **150**. 225–233.

SALAMA, W., EL AREF, M., GAUPP, R., 2012. Mineralogical and geochemical investigations of the middle Eocene ironstones, El bahariya depression, western desert, Egypt. Gondwana Research. **22**. (2) 717–736.

SALEEM, M., IQBAL, J., AKHTER, G., SHAH, M. H., 2018. Fractionation, bioavailability, contamination and environmental risk of heavy metals in the sediments from a freshwater reservoir, Pakistan. Journal of Geochemical Exploration. **184**. 199–208.

SANTOS, W. O., MATTIELLO, E. M., VERGUTZ, L., COSTA, R. F., 2016. Production and evaluation of potassium fertilizers from silicate rock. Journal of Plant Nutrition and Soil Science. **179**. (4) 547–556.

SHEKHAR, S., MISHRA, D., AGRAWAL, A., SAHU, K. K., 2017. Physical and chemical characterization and recovery of potash fertilizer from glauconitic clay for agricultural application. Applied Clay Science. **143**. 50–56.

SHEKHAR, S., SINHA, S., MISHRA, D., AGRAWAL, A., SAHU, K. K., 2020. A sustainable process for recovery of potash fertilizer from glauconite through simultaneous production of pigment grade red oxide. Sustainable materials and technologies. **23**. e00129.

SHIN, R., BERG, R. H., SCHACHTMAN, D. P., 2005. Reactive oxygen species and root hairs in Arabidopsis root response to nitrogen, phosphorus and potassium deficiency. Plant and Cell Physiology. **46**. (8) 1350–1357.

SHIVA KUMAR, D., SRIKANTASWAMY, S., 2014. Factors affecting on mobility of heavy metals in soil environment. International Journal for Scientific Research & Development. **2**. (3) 201–203.

TEMPLETON, D. M., ARIESE, F., CORNELIS, R., DANIELSSON, L. G., MUNTAU, H., VAN LEEUWEN, H. P., LOBINSKI, R., 2000. Guidelines for terms related to chemical speciation and fractionation of elements. Definitions, structural aspects, and methodological approaches (IUPAC Recommendations 2000). Pure and applied chemistry. **72**. (8) 1453–1470.

UMOREN, I. U., UDOH, A. P., UDOUSORO, I. I., 2007. Concentration and chemical speciation for the determination of Cu, Zn, Ni, Pb and Cd from refuse dump soils using the optimized BCR sequential extraction procedure. The Environmentalist. **27**. 241–252.

URE, A. M., DAVIDSON, C. M., 2002. Chemical Speciation in Soils and Related Materials by Selective Chemical Extraction. In: (A.M. URE & C.M. DAVIDSON eds.) Chemical Speciation in the Environment. Blackwell, Hoboken, US. pp. 265–300.

VAN HERREWEGHE, S., SWENNEN, R., VANDECASTEELE, C., CAPPUYNS, V., 2003. Solid phase speciation of arsenic by sequential extraction in standard reference materials and industrially contaminated soil samples. Environmental pollution. **122**. (3) 323–342.

YANG, Z., WANG, Y., SHEN, Z., NIU, J., TANG, Z., 2009. Distribution and speciation of heavy metals in sediments from the mainstream, tributaries, and lakes of the Yangtze River catchment of Wuhan, China. Journal of hazardous materials. **166**. (2–3) 1186–1194.

Internet resource

URL1: Fertilizers consumption in nutrients in Egypt, 1961–2020. FAO, Rome. https://www.fao.org/faostat/en/#country/59

Conflict of interest

Éva Lehoczky is a member of the Editorial Board of the journal. Therefore, a different member of the editorial board handled the submission, and she did not take part in the review process in any capacity.