Glasnik hemičara i tehnologa Bosne i Hercegovine

Bulletin of the Chemists and Technologists of Bosnia and Herzegovina

2025

64

Original Scientific Article

Print ISSN: 0367-4444

Online ISSN: 2232-7266

DOI: 10.35666/2232-7266.2025.64.03

UDK:552.23[543:546]

23-31

New insight into the geochemical behavior of alkali and alkaline earth metals in a frequently subsampled clay pit sample with and without Al-normalization

Jurković, J.*, Sijahović, E., Bašić, F.

Faculty of Agriculture and Food Science, Zmaja od Bosne 8, University of Sarajevo, Sarajevo, Bosnia and Herzegovina

Article info
Received: 16/01/2025
Accepted: 19/05/2025

Keywords:
Clay
Alkali
Alkaline earth
Metals
Behavior
PCA

***Corresponding author:**
Josip Jurković
E-mail: j.jurkovic@ppf.unsa.ba
Phone: +387 63 876 658

Abstract: Clays are fine-particle-size materials (less than 2 μm) comprised mainly of clay minerals, which are hydrated aluminum silicates with associated alkali and alkaline earth elements. The small particle size and complex porous structure result in a high specific surface area, which allows strong physical and chemical interactions with dissolved species. Metals can also be incorporated within the clay structure, which can be made of octahedral and/or tetrahedral sheets. Depending on the composition of the tetrahedral and octahedral sheets, the layer will have no charge or will have a net negative charge. If the layers are charged, this charge is balanced by interlayer cations. The recent research of metals in clays mainly focused on heavy metals, while investigations of light metals are rather rare. For the investigation of the behavior of alkali and alkaline earth metals in clay samples, 110 subsamples of cored samples were taken. The total contents of potassium (K), magnesium (Mg), calcium (Ca), sodium (Na), strontium (Sr), and barium (Ba) were determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES). Descriptive statistics were conducted using maximum, minimum, average, and median values. Correlation and PCA analysis with and without Al-normalization were calculated to determine the different behavior of metals, The contents of metals lie in the following sequence: K>Mg>Ca>Na>Ba>Sr. The highest correlation between metals was found between Mg and K (r=0.87) and Ba and Sr (r=0.65). PCA analysis revealed two subgroups: 1) K, Mg, Na. 2) Ba, Sr. After the Al normalization was applied, Ba and Sr showed the highest correlation (r=0.81). Ca did not significantly contribute to any of the PCA subgroups, suggesting a possible different source and behavior.

INTRODUCTION

Fine-grained clays are naturally occurring materials, found in silt, rocks, and soil. According to Pinnavaia (1983), they are mostly composed of hydrous aluminosilicates, which make up the majority of the colloidal fraction (particle size below 2 m) of rocks, sediments, and soil. The small particle size, complex and porous structure, and high specific surface area of clays and clay minerals enable robust physical and chemical interactions with dissolved species (Uddin, 2017). Clays are abundant, and the clay-based minerals are derived from versatile raw materials (Aboudi Mana et al., 2017). The layered structure of the clay minerals oversees several chemical and physical characteristics. Understanding the intricate clay mineral structure and the mechanisms that keep ions and molecules attached to their surface is challenging (Cygan et al., 2009). The mineralogy and reactive character of clays are the main factors that influence their behavior and ion adsorption kinetics. The adsorption properties are mostly controlled by the surface area of the clay minerals and the porosity of the interlayer (Deng et al., 2017). Clays are particularly good at removing cations, or heavy metals, from solutions due to their high cation exchange capacity (Edi et al., 2015). The surface activity of clays is controlled by various factors, including their chemical composition, the type of exchangeable cations present, the charge of the layer, and the character of the surface atoms (Schoonheydt and Johnston, 2012). The surface of the clay allows for the selective adsorption of various cations. One of the two cations will be more strongly attracted if both are present. The different adsorption strengths are difficult to explain. It depends on the charge, its origin and structure. The size of the ion will determine how two cations with the same charge will adsorb to each other. Water molecules are dipoles. Therefore, positively charged cations attract

partially negatively charged water molecules. The hydrated cation is small because the smaller cation has a higher positive charge density. Deeper sediments, however, are more stable due to the decreased degree of change (Bauer and Velde, 2014). When it comes to determining the metal content of clays, there are several studies on the content of heavy metals (Sen Gupta & Bhattacharyya, 2012; Chen et al., 2016; Nkansah et al., 2016; Uddin, 2017), while studies on alkali and alkaline earth metals are very rare. Therefore, in this study, an analysis of alkali and alkaline earth metals was performed. Although alkali and alkaline earth metals are quite similar in chemical characteristics, their behavior in clay minerals is different. Some of them (K, Rb) are easily replaced by another element, and some are mainly adsorbed on clay particle or incorporated into the interlayer space (Annabi-Bergaya et al., 2006; Arevalo, 2018). With this research, we intend to address this rarely investigated topic. It is challenging to identify which part of nature comes from which source, since metals come from both anthropogenic and natural sources. Natural sedimentary metal content can vary by several orders of magnitude based on the origin, character, and grain size of the metal-rich bedrock. A geochemical strategy is often used to address these issues, This method uses conservative elements (Al, Fe, Li, Rb, Sc) that represent one or more important metal carriers in nature (such as clay minerals, iron and manganese oxides, and organic matter) for geochemical normalization (dividing the metal content) (Covelli and Fontolan, 1997). Schropp and Windom (1988) stated that Al is one of the best markers for terrestrial materials for several reasons, including its abundance in nature, high immobility, resistance to anthropogenic influences, and resistance to diagenesis and strong redox effects in sediments that could change the metal content in sediments. Al-normalization is necessary for interpreting the source of metals (Ho et al., 2012). To enable the Al normalization, the content of all alkali and alkaline earth metals was divided by the content of aluminum. Following the formation of the ratios, the correlations between them were used. The clay content of the clay pit sediment might be less variable due to the normalisation to Al. When there are more samples, it makes more sense to statistically evaluate the correlation results. This makes the correlations more reliable. If a comparative study is based on a data set that is truly too small, which is not uncommon in the literature, its conclusions are subject to a low level of reliability (Yang et al., 2019). The aims of the study were:

a) To estimate the content of alkali and alkaline earth metals (K, Na, Mg, Ca, Ba and Sr) in 110 subsamples of the core clay pit sample.
b) To gain insight into the similarities and differences of metals in geochemical behavior and origin, through correlations and PCA analysis, with and without Al-normalization.
c) The pH in water, pH in $CaCl_2$ and electrical conductivity were measured in order to gain insight into the acidity/alkalinity of the samples and the content of water-soluble ions.

MATERIALS AND METHODS

Sampling and Samples

In Central Bosnia and Herzegovina (43° 51′ 54′′ N, 18° 13′ 36′′ E), a clay pit sediment core sample was obtained from the "Rapailo" clay deposit. The site is situated in the Sarajevo Canton, not far from the state capital Sarajevo (Figure 1). Clay in this region is mined for brick making. The area of the clay pit is 300 m wide and 1300 m long. The region with the clay deposits has a temperate continental climate. The average annual temperature in this climate zone is 12°C, with an average high of 1°C in January and an average low of 22°C in July. Precipitation averages up to 1000 mm per year.

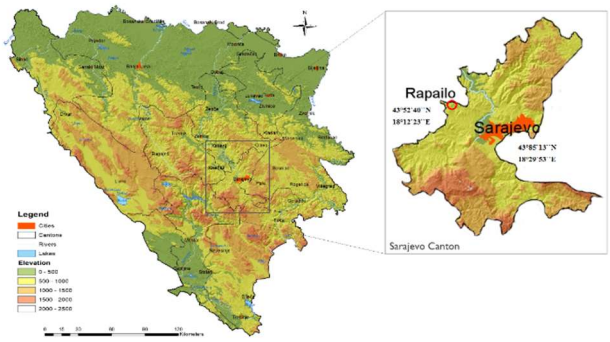

Figure 1. Bosnia and Herzegovina with sampling position (Jurković et al., 2021)

The mineral composition in order of increasing abundance is shown in Table 1.

Table 1. Mineral composition of the Rapailo clay samples (Kapetanović, 2004)

Mineral	Chemical formula
quartz	SiO_2
illite, 2M2	$K_{0.7}Al_{2.1}(SiAl)_4O_{10}(OH)_2$
illite, 2M	$(K, H_3O)Al_2Si_3AlO_{10}(OH)_2$
kaolinite	$Al_2Si_2O_5(OH)_4$
muscovite, 3T	$KAl_2(Si_3Al)O_{10}(OH)_2$
muscovite, 2M1	$KAl_2(Si_3Al)O_{10}(OH, F)_2$
muscovite, 2M2	$(K, Ca)Al_2(SiAl)_4O_{10}(OH)_2$
chlorite, chrome	$(Mg, Cr)_6(SiAl)_4O_{10}(OH)_8$
chlorite	$(Mg, Fe)_6(SiAl)_4O_{10}(OH)_8$

The clay deposits of the Sarajevo basin are part of the sedimentary genetic types that are created by the decomposition and leaching of all types of aluminosilicate rocks. The source material was always somewhat distant from the process of mechanical redeposition. Due to the sorting, which is most often expressed in the form of layers, water was used as a transport medium. Rapid variations in the type of material and grain size can also be seen in lenticular structures. In Bosnia and Herzegovina, clay deposits were primarily formed during the Quaternary and Neogene under external conditions. Further evidence that allochthonous clays exist in fully humid conditions comes from their close association with the production of coal deposits. The geological map of the research area is shown in Figure 2. (Jovanović et al., 1978).

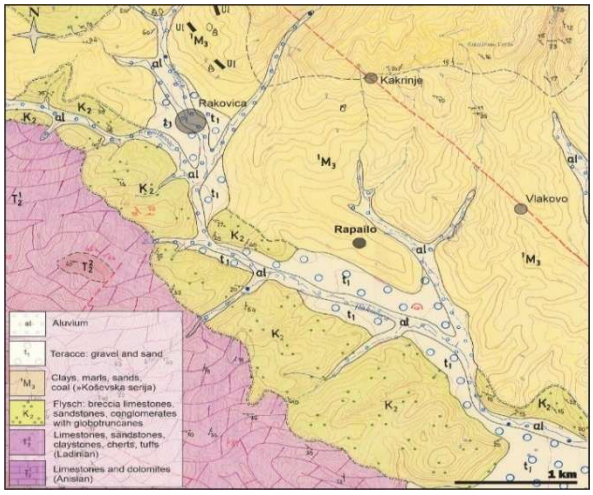

Figure 2. Geological map of research area(Jovanović et al., 1978)

A 33 m-long clay mine core sample was extracted (Figure 3). The core sample was divided into subsamples on site. A separate subsample was extracted from the core sample very frequently (every 30 centimeters). By dividing the sample into subsamples, 110 subsamples were obtained. Five hours after extraction, the samples were packed in sterile polypropylene bags and sent to the laboratory. The samples were transported at 4°C in a refrigerator. The subsamples, or cores, exhibited a unique spectrum of colors at the bottom of the sediment, which included off-white, pale grey, dark black, orange, and dark grey (Figure 3).

Figure 3. Motor-operated sediment corer and samples

Sample preparation

The clay pit core samples were homogenized, allowed to air dry, and then sieved through a 2-mm sieve. Teflon tubes were filled with approximately 0.2 g (accuracy of 0.001 g) of the sample. Concentrated hydrofluoric acid and concentrated nitric acid were then added. The samples were then prepared in forty tubes using microwave digestion. Three microwave digestion sessions were required to process all 110 samples. Under conditions of pressure of 55 bars and a constant temperature increase from 25 to 230°C, the digestion process lasted three hours.

Methods of Analysis

Basic quality parameters

To assess the acidity/alkalinity and soluble ions amount, pH in H_2O (pH_W), and $CaCl_2$ (pH_{Ca}) and electrical conductivity (EC) were measured., The pH of the core samples was determined using a Mettler Toledo MP 220 device.

The instrument was calibrated with buffers with a pH value of 4.21 and 7.00. The clay extraction solution ratio was 1:5 (10 g clay and 50 mL extraction solution), according to ref 31. The measurement was performed with two different extraction solutions: ultrapure water and calcium chloride (0.01 mol/L).

Electrical Conductivity (EC), was measured in the claypit sample/ultrapure water (1:5) ratio, with a Mettler Toledo MC 126 instrument. Using the procedure described in the EPA 9050 approach, the instrument was calibrated with the standards of known EC.

Metals

The total of elements content was determined using optical emission spectrophotometry with inductively coupled plasma. Agilent 7000 ICP-OES apparatus was used to perform measurements. In this way, the total contents of K, Na, Mg, Ca, Ba and Sr were analyzed. The standards of known contents of the investigated elements were utilized for measurement. To prevent excitation interference, 1% CsCl was added to all samples used for iron measurement. The analytical results were in good agreement with the reference materials used (sandy loam and BAM 112 a),

Statistical evaluation

The results of the study were statistically evaluated using SPSS 20.0 SPSS Inc., Chicago, IL and United States Statistical Programs.

Descriptive Analysis: Descriptive statistics were presented as maximum, minimum, mean, average, and median value, along with standard deviation (SD) and coefficient of variance (CV). Standard deviations and coefficients of variance were used to show the distribution of heavy metals (Yongming et al., 2006).

Correlation: The degree of similarity between two sets of results can be measured by correlation. The following is a description of the correlation coefficients, which indicate how strongly two variables are related: (0.0–0.19), weak connection (0.2–0.39), moderate connection (0.40%–0.59), strong connection (0.60%–0.79), and extremely strong connection (0.80%–1.0). When the correlation coefficient (r) is positive, the connection is uphill; when it is negative, the correlation is downhill.

The correlation between the results for heavy metals was also normalized, as it has been shown to be one of the best indicators of terrigenous material, in order to take into account for the different proportions of clay mineral fractions. (Brown et al., 2000).

Principal component analysis (PCA): PCA is very often used in statistical evaluation in environmental studies (Díaz et al., 2002). In order to reduce the data sets and obtain a smaller number of recorded variables or PCs, PCA is commonly applied. An eigenvalue >1 was the cutoff point for retains of PCs, indicating that these PCs accounted for more variance than was accounted by one of the original data sets. These variables are used to analyze the relationship between variables (Loska and Wiechuła, 2003). If there is a high variability in the correlations and standard deviations of the variables, the PCA results will also vary. (Farnham et al., 2003). PCA is applied to the correlation matrix if there are significant differences in order of magnitude and each parameter makes an equal contribution. The VARIMAX normalized rotation method,

where the maximized variation of the factor loadings is carried out, can be used to better understand multivariate analysis. The factor loadings between 0.71 and 0.32 are considered very good, while those below 0.32 are regarded extremely poor. (Yongming et al., 2006).

RESULTS AND DISCUSSION

Basic quality parameters (pH_w, pH_{ca}, EC) and descriptive statistics parameters (average, max, min, median, SD, CV) for the determined alkali and alkaline earth metals are presented in Tables 2 and 3. Vertical distributions of the measured elements are shown in Figures 4 to 9.

Table 2. Basic quality parameters

	pH_w	pH_{Ca}	ΔpH	EC (mS/cm)
Average	6.61±0.16	6.09±0.15	0.5	3.1±0.1
Maximum	8.50	7.69	0.9	16.0
Minimum	3.72	3.63	0.0	0.5
Median	6.42	5.09	0.6	1.9
SD	1.14	0.97	0.2	3.2
CV, %	17.2	16.0	43.0	102.9

	Average (mg/kg)	Max. (mg/kg)	Min. (mg/kg)	Median (mg/kg)	SD (%)	CV (%)
K	19655.2±786.2	33253.2	3181.6	19834.3	7325.8	37.3
Mg	8069.4±484.64	15702.9	1561.4	8233.8	3070.1	38.0
Ca	3629.5±108.9	15360.0	739.1	2816.6	2544.2	70.1
Na	756.0±37.8	2892.8	181.8	710.8	349.6	46.2
Sr	76.7±2.3	400.4	23.8	49.1	76.2	104.1
Ba	44.6±1.3	267.4	7.6	76.7	37.7	84.6

Table 3. Alkali and alkaline earth metals determination

Vertical distributions of measured elements:

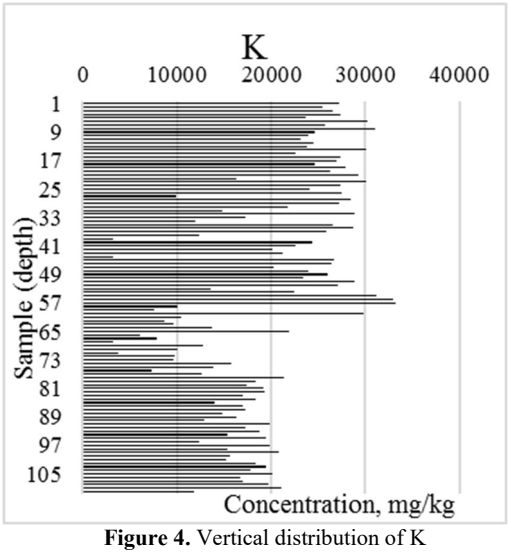

Figure 4. Vertical distribution of K

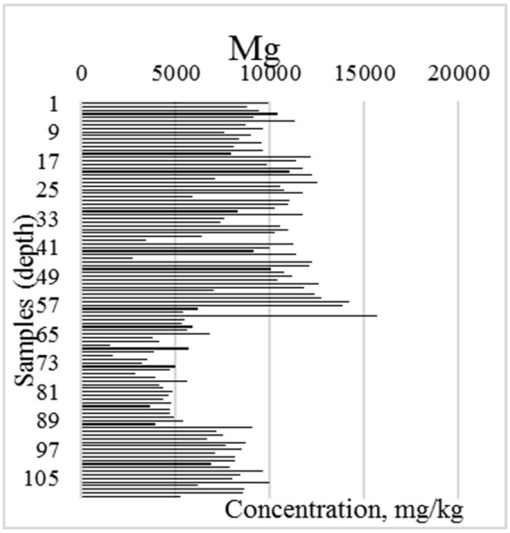

Figure 5. Vertical distribution of Mg

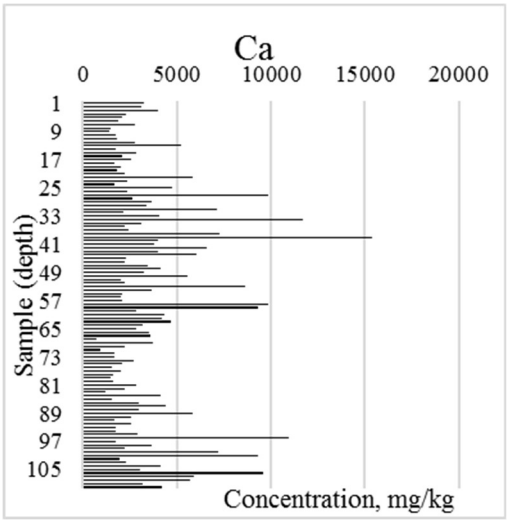

Figure 6. Vertical distribution of Ca

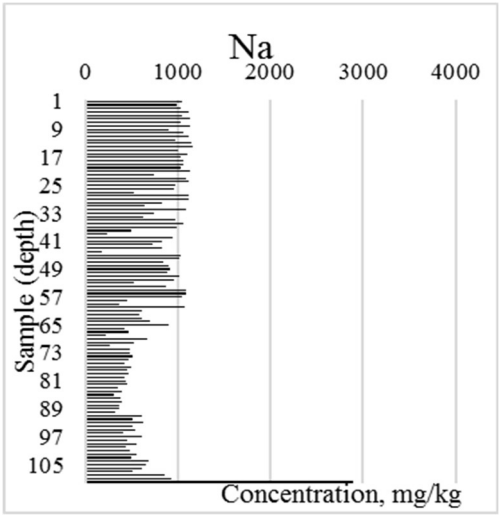

Figure 7. Vertical distribution of Na

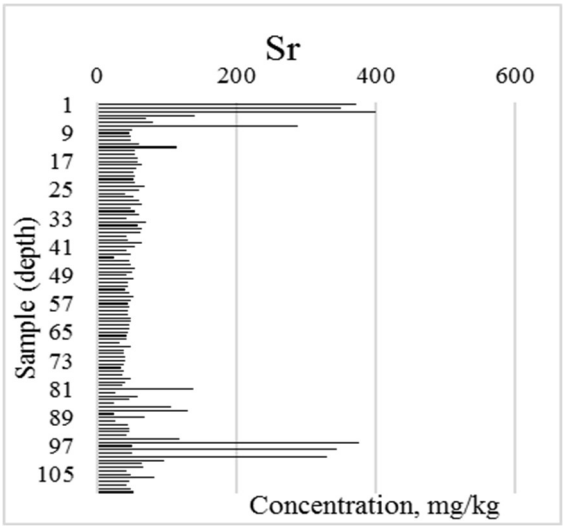

Figure 8. Vertical distribution of Sr

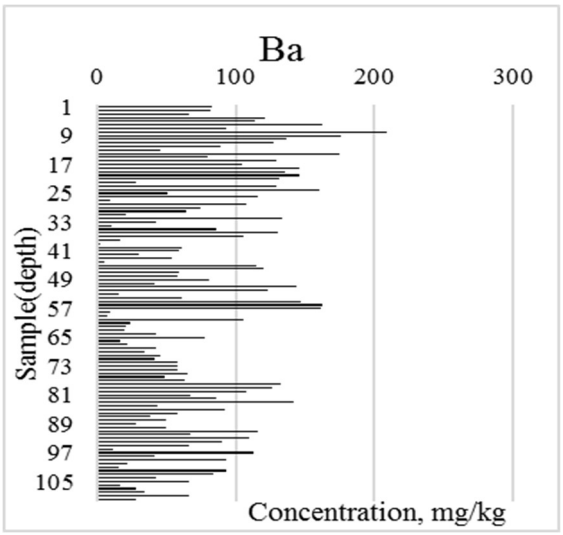

Figure 9. Vertical distribution of Ba

The pH (in H_2O and $CaCl_2$) varied greatly among samples. pH increased with sample depth. The highest pH value was found in sample 96 (8.50 and 7.69), and lowest in the sample 39 (3.72 and 3.63). Alkaline pH promotes metals precipitation and adsorption on the clay surface (Lukman et al., 2013). Characteristics of metals adsorption differ for different clay minerals (Farrah & Pickering, 1978). Natural clay is a mixture of different minerals which makes it difficult to say the exact reason for adsorption of metals. EC was higher in the upper parts of the cored sample. The highest value was found in sample number 42 (16.0 mS/cm). The minimum value was found in the sample 106 (0.5 mS/cm). Higher EC means a higher amount of easily desorbed ions (metals) from the clay particle (Choo et al., 2022).

Of all the metals investigated, K had the highest abundance (0.32%–3.33%). The average content was 1.96%. Very comparable results were found by Cherian et al. (2018). The sample 68 (3181.6 mg/kg) had the lowest content of K in the middle portion of the sediment (depth ranged from 19.30 to 19.60 m). K content was highest in sample 57 (33253.2 mg/kg) (depth ranged from 16.00 to 16.30 m). K content shows a gradual downcore decrease. The lowest CV was found in the case of K, meaning that the K variability in content is lowest throughout the sediment core. Sample 60 (1502.9 mg/kg) had the highest Mg content (depth from 16.90 to 17.20 m). Less Mg was found in deeper sediment layers, according to the vertical distribution of Mg. In sample 69 (1561.4 mg/kg), the Mg measurement yielded the lowest content (depth from 19.30 to 19.60 m). The average Mg content was comparable to that of a recent study (Diko-Makia and Ligege, 2020). The maximum Ca content was found in the upper parts of the clay sediment in sample 39 (15360.0 mg/kg) (depth from 11.40 to 11.70 m). The minimum content was found in the sample 68 (739.1 mg/kg) (depth from 19.30 to 19.60 m). The average amount of Ca was similar to the study of Cherian et al. (2018). The Ca content varied greatly throughout the sediment. Up to about 20 meters below the surface, the Na content was quite uniform. The average Na content was 756.04 mg/kg. The middle portions of the clay sediment, sample 44 (181.8 mg/kg), had the lowest Na content (depth from 12.10 to 12.40 m). The last sample (110) (2892.8 mg/kg) had the highest content (depth range: 32.10 to 32.40 m). The average Na content in the soils is slightly lower than that found in the study by Williams et al. (2008). Sample 3 (400.4 mg/kg) had the highest Sr content (depth from 0.6 to 0.9 m). Less Sr was found in the middle sediment layers, according to the vertical distribution of Sr. In sample 85 (23.8 mg/kg), the Sr measurement yielded the lowest content (depth from 24.40 to 24.70 m). The average Sr content was lower than in a recent study (Mohamed et al., 2022). The highest CV was found for Sr, meaning that the variability of Sr content was the highest throughout the sediment core. Ba had the lowest average content of all the metals under investigation (7.63 mg/kg-267.39 mg/kg). The average content was 44.60 mg/kg. The amounts of Ba found in the clay samples were lower than average soil content (>19 mg/kg) (Kabata-Pendias, 2010). Sample 69 (7.6 mg/kg) had the lowest amounts of Ba in the middle portion of the sediment (depth ranged from 19.30 to 19.60 m). The Ba content was highest in sample 14 (267.4 mg/kg) (depth ranged from 3.90 to 4.20 m). Ba showed the lowest standard deviation of all measured metals. The minimal contents of K, Mg, and Ca were found in sample 68, (depth ranged from 19.30 to 19.60 m).

Correlations

Correlations among measured metals without Al-Normalization are presented in Table 4.

Table 4. Correlations among metals without Al-normalization

	Mg	Na	K	Ca	Ba	Sr
Mg	1.00					
Na	0.63	1.00				
K	0.87	0.64	1.00			
Ca	-0.15	-0.24	-0.41	1.00		
Ba	0.24	0.22	0.21	0.26	1.00	
Sr	0.09	0.05	0.12	0.16	0.65	1.00

High correlation coefficients indicate similar geochemical behavior of the elements. A very strong correlation was observed between K and total Mg (r=0.87). This high correlation is a result of the fact that K and Mg are constituents of aluminosilicate materials, especially

chlorite, which is found in this clay pit. The strong correlation between Sr and Ba (r=0.65) can be explained by their similarity. Both metals are alkaline earth elements, with the same valence state and similar ionic radii (Ba^{2+} - 149 pm, Sr^{2+} - 132 pm with coordination number 6, and Ba^{2+} - 156 pm, Sr^{2+} - 140 pm with coordination number 8) (Luther III, 2016). Since they are members of group II A elements, their behavior is representative of the interaction of alkali-earth elements with clays and soil fractions (Hatipoglu et al., 1990). Strong and positive correlations were also found in the case of K and Na, which are very similar in behavior and characteristics. Na can be found in the interlayers of various clays containing K. (Kumari and Mohan, 2021). A strong correlation (r=0.63) was found between Na and Mg, and the reason for this correlation could be the fact that Na can replace K in the mineral structure or adsorb on clay particles in a similar way. It is significant that Ca showed only negative correlations with other metals, indicating that Ca behaves differently and has different origin.

Correlations among metals with Al-normalization

The Al normalization was used to minimize the effect of the fluctuating clay mineral content. The results of correlation coefficients after Al normalizations are shown in Table 5.

Table 5. Correlations with applied Al-Normalization

	Mg	Na	K	Ca	Ba	Sr
Mg	1.00					
Na	0.48	1.00				
K	0.75	0.44	1.00			
Ca	0.49	0.16	0.04	1.00		
Ba	0.45	0.24	0.32	0.29	1.00	
Sr	0.47	0.21	0.38	0.27	0.81	1.00

After normalization, Sr showed an even higher correlation with Ba than without Al-normalization (r=0.81). The Ba^{2+} ion is bound to different clay minerals. In kaolinite, Ba^{2+} ion sorption occurs mainly at surfaces and edges. In the case of chlorite-illite mixed clay and montmorillonite, appreciable amounts of Ba^{2+} ion are sorbed between the layers. Sorption is reversible in kaolinite, and only partially reversible in chlorite-illite and montmorillonite (Eylem et al., 1990). The correlation between Mg and K is slightly reduced (r=0.75). Ca, which showed only negative correlations before Al normalization, now shows low but positive correlations. It also shows a moderate correlation with Mg (r=0.49). This result may indicate that Ca is found in some other minerals beside clay minerals in this clay pit, for example, calcite or dolomite.

PCA Analysis

Varimax rotation was used for principal component analysis (PCA). The metal content (K, Mg, Ca, Na, Sr, and Ba) was employed as possible variables, both with and without previously completed normalization.

3.3.1. PCA analysis without Al-Normalization

The six main components detected by monitoring the total amount of the metals under examination without normalization comprised 100.00% of the experiment's overall variance, according to an analysis of the key components using oblimin rotation (Table 6). The experiment's total variability was comprised of 73.429% of the first two major components. Table 6. shows the principal components' eigenvalues, the percentage of variance, and the cumulative variance.

Table 6. Total variance without Al-Normalization

	Initial Eigenvalues		
	Total	% of Variance	Cumulative %
1	2.669	44.482	44.482
2	1.737	28.947	73.429
3	0.768	12.806	86.236
4	0.443	7.376	93.612
5	0.304	5.061	98.672
6	0.080	1.328	100.000

The most significant variables for PC1 were the contents of K, Mg, and Na with contents of eigenvectors (loadings) greater than 0.8 and a significant positive result; for PC2, the most significant variables are the content of Ba and Sr with similarly high contents of eigenvectors greater than 0.8, according to the indicators of the relationship between the main components and the analyzed variables (Table 7).

Table 7. Component matrix without Al-Normalization

	Component	
	1	2
Mg	0.895	-0.076
Na	0.809	-0.115
K	0.933	-0.178
Ca	-0.339	0.615
Ba	0.400	0.813
Sr	0.261	0.805

A two-dimensional graph showing the spatial distribution and mutual interaction of the investigated variables (properties) was created utilizing the principal components (PC1 and PC2) as the spatial dimensions (Figure 10). In the graphical presentation, vectors stand in for the examined variables. Graph 10 shows that K, Mg, and Na are grouped in a very small area of the graph, indicating a high similarity in behavior. Sr and Ba are also similar, but Ca behaves differently from the other metals.

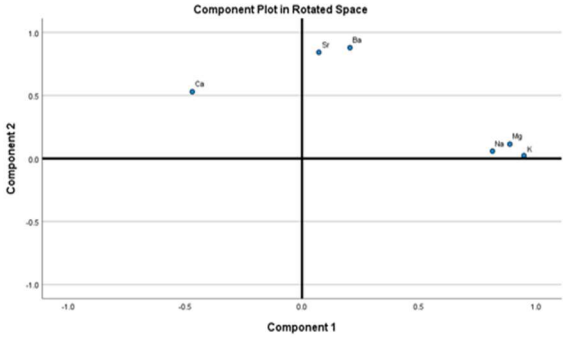

Figure 10. Component plot in rotated space without Al-Normalization

Kleven and Alstad (1996) found that in montmorillonite-$CaCl_2$ systems, a moderate selectivity for Ca^{2+} ions over Na^+ was observed. Also, a higher affinity for Ba^{2+} over Ca^{2+} was found in the clays. Spatially separated metals may indicate that their sources are different from each other.

PCA analysis with Al-normalization

By analysis of the main components using oblimin rotation, the six main components obtained by monitoring the total content of the analyzed metals with normalization contained 100.00% of the total variance of the experiment (Table 8). The first two main components contained 69.331% of the total variability of the experiment.

Table 8. Total variance with Al-Normalization

Initial Eigenvalues		
Total	% of Variance	Cumulative %
3.026	50.441	50.441
1.133	18.890	69.331
0.927	15.454	84.785
0.605	10.087	94.873
0.188	3.135	98.008
0.120	1.992	100.000

The indicators of the relationship between the main components and the analyzed variables (Table 9.) show that the most significant variables for PC1 were the content of Mg with contents of eigenvectors (loadings) greater than 0.8 with a significant positive result, while the content of K, Ba, and Sr also has high eigenvectors (greater than 0.7).

Table 9. Component matrix with Al-Normalization

	Component	
	1	2
Mg	0.873	-0.243
Na	0.578	-0.522
K	0.725	-0.501
Ca	0.485	0.326
Ba	0.759	0.484
Sr	0.771	0.458

By using the main components (PC1 and PC2) as spatial dimensions, a two-dimensional graph was constructed showing the spatial distribution and mutual relationship of the analyzed variables (properties). The analyzed variables are represented by vectors on the graphic display. From Figure 11 it can be seen that K and Na, on one side and Ba and Sr are on the other, which is similar to the version without Al-normalization. When we use Al normalization, Ca and Mg show different characteristics. When we use Al-normalization, Mg and Ca are separated from the other elements, which may indicate that they have a different source. The short-term clay-lime interaction involves the adsorption of free Ca ions onto clay minerals (Cherian et al., 2018).

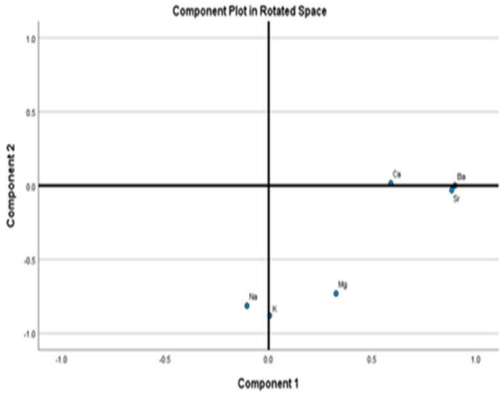

Figure 11. Component plot in rotated space with Al-Normalization

CONCLUSIONS

The present study focused on evaluating the behavior of alkali and alkali earth metals (K, Na, Mg, Ca, Sr, and Ba), with and without the application of Al normalization. The results were evaluated using correlations and PCA analysis. From the results obtained it can be concluded that:

- The investigated metal contents lie in the following sequence: K>Mg>Ca>Na>Ba>Sr.
- The metal pairs: Sr and Ba; K and Na, K and Mg show similar geochemical behavior and origin.
- Ca showed almost no similarity to other metals when Al-normalization is applied, indicating that Ca has a different behavior and origin, perhaps from carbonates.

REFERENCES

Aboudi Mana, S. C., Hanafiah, M. M., & Chowdhury, A. J. K. (2017). Environmental characteristics of clay and clay-based minerals. *Geology, Ecology, and Landscapes*, *1*(3), 155–161. https://doi.org/10.1080/24749508.2017.1361128

Annabi-Bergaya, F., Theng, B. K. G., & Lagaly, G. (2006). *Handbook of Clay Science*.

Arevalo, R. (2018). *Alkali and Alkaline Earth Metals BT - Encyclopedia of Geochemistry: A Comprehensive Reference Source on the Chemistry of the Earth* (W. M. White (ed.); pp. 23–26). Springer International Publishing. https://doi.org/10.1007/978-3-319-39312-4_211

Bauer, A., & Velde, B. D. (2014). *Geochemistry at the Earth Surface*. Springer International Publishing.

Brown, E. T., Le Callonnec, L., & German, C. R. (2000). Geochemical cycling of redox-sensitive metals in sediments from Lake Malawi: A diagnostic paleotracer for episodic changes in mixing depth. *Geochimica et Cosmochimica Acta*, *64*(20), 3515–3523. https://doi.org/10.1016/S0016-7037(00)00460-9

Chen, Y. M., Gao, J. bo, Yuan, Y. Q., Ma, J., & Yu, S. (2016). Relationship between heavy metal contents and clay mineral properties in surface sediments: Implications for metal pollution assessment. *Continental Shelf Research*, *124*, 125–133. https://doi.org/10.1016/j.csr.2016.06.002

Cherian, C., Kollannur, N. J., Bandipally, S., & Arnepalli, D. N. (2018). Calcium adsorption on clays: Effects of mineralogy, pore fluid chemistry and temperature. *Applied Clay Science*, *160*, 282–289. https://doi.org/https://doi.org/10.1016/j.clay.2018.02.034

Choo, H., Park, J., Do, T. T., & Lee, C. (2022). Estimating the electrical conductivity of clayey soils with varying mineralogy using the index properties of soils. *Applied Clay Science*, *217*, 106388. https://doi.org/https://doi.org/10.1016/j.clay.2021.106388

Covelli, S., & Fontolan, G. (1997). Application of a normalization procedure in determining regional geochemical baselines. *Environmental Geology*, *30*(1–2), 34–45. https://doi.org/10.1007/S002540050130

Cygan, R. T., Greathouse, J. A., Heinz, H., & Kalinichev, A. G. (2009). Molecular models and simulations of layered materials. *Journal of Materials Chemistry*, *19*(17), 2470–2481. https://doi.org/10.1039/B819076C

Deng, L., Yuan, P., Liu, D., Annabi-Bergaya, F., Zhou, J., Chen, F., & Liu, Z. (2017). Effects of microstructure of clay minerals, montmorillonite, kaolinite and halloysite, on their benzene adsorption behaviors. *Applied Clay Science*, *143*, 184–191. https://doi.org/https://doi.org/10.1016/j.clay.2017.03.035

Díaz, R. V., Aldape, F., & Flores M., J. (2002). Identification of airborne particulate sources, of samples collected in Ticomán, Mexico, using PIXE and multivariate analysis. *Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms*, *189*(1–4), 249–253. https://doi.org/10.1016/S0168-583X(01)01073-4

Diko-Makia, L., & Ligege, R. (2020). Composition and Technological Properties of Clays for Structural Ceramics in Limpopo (South Africa). In *Minerals* (Vol. 10, Issue 8). https://doi.org/10.3390/min10080700

Edi, S. F., Ismadji, S., & Ayucitra, A. (2015). *SPRINGER BRIEFS IN MOLECULAR SCIENCE Clay Materials for Environmental Remediation*.

Eylem, C., Erten, H. N., & Göktürk, H. (1990). Sorption-desorption behaviour of barium on clays. *Journal of Environmental Radioactivity*, *11*(2), 183–200. https://doi.org/https://doi.org/10.1016/0265-931X(90)90061-Y

Farnham, I. M., Johannesson, K. H., Singh, A. K., Hodge, V. F., & Stetzenbach, K. J. (2003). Factor analytical approaches for evaluating groundwater trace element chemistry data. *Analytica Chimica Acta*, *490*(1–2), 123–138. https://doi.org/10.1016/S0003-2670(03)00350-7

Farrah, H., & Pickering, W. F. (1978). Extraction of heavy metal ions sorbed on clays. *Water, Air, and Soil Pollution*, *9*(4), 491–498. https://doi.org/10.1007/BF00213544

Hatipoglu, S., Eylem, C., Gokturk, H., & Erten, H. N. (1990). Sorption of strontium and barium on clays and soil fractions. *Sciences Geologiques - Memoire*, *86*, 79–86.

Ho, H. H., Swennen, R., Cappuyns, V., Vassilieva, E., & Van Tran, T. (2012). Necessity of normalization to aluminum to assess the contamination by heavy metals and arsenic in sediments near Haiphong Harbor, Vietnam. *Journal of Asian Earth Sciences*, *Complete*(56), 229–239. https://doi.org/10.1016/J.JSEAES.2012.05.015

Jovanović, R., Mojićević, M., Tokić, S., & Rokić, L. (1978). *Basic geological map of SFRY (1:100.000), Interpreter of the Sarajevo sheet K34-1*.

Jurković, J., Murtić, S., Bašić, F., Gavrić, T., Sijahović, E., & Čadro, S. (2021). Relationships between Heavy Metals and Their Connection to Amorphous and Total Iron in a Frequently Subsampled Clay Pit Core Sample. *ACS Earth and Space Chemistry*, *5*(7), 1726–1740. https://doi.org/10.1021/acsearthspacechem.1c00078

Kabata-Pendias, A. (2010). Trace elements in soils and plants: Fourth edition. In *Trace Elements in Soils and Plants, Fourth Edition*. https://doi.org/10.1201/b10158

Kleven, R., & Alstad, J. (1996). Interaction of alkali, alkaline-earth and sulphate ions with clay minerals and sedimentary rocks. *Journal of Petroleum Science and Engineering*, *15*(2–4), 181–200. https://doi.org/10.1016/0920-4105(95)00085-2

Kumari, N., & Mohan, C. (2021). *Basics of Clay Minerals and Their Characteristic Properties* (G. M. Do Nascimento (ed.); p. Ch. 2). IntechOpen. https://doi.org/10.5772/intechopen.97672

Loska, K., & Wiechuła, D. (2003). Application of principal component analysis for the estimation of source of heavy metal contamination in surface sediments from the Rybnik Reservoir. *Chemosphere*, *51*(8), 723–733. https://doi.org/10.1016/S0045-6535(03)00187-5

Lukman, S., Essa, M., Nuhu Mu`azu, A., Bukhari, & Basheer, C. (2013). Adsorption and Desorption of Heavy Metals onto Natural Clay Material: Influence of Initial pH. *Journal of Environmental Science and Technology*, *6*(1–15).

Luther III, G. W. (2016). *Inorganic Chemistry for Geochemistry and Environmental Sciences*. John Wiley & Sons, Ltd.

Mohamed, H. H., Wazan, G., & Besisa, D. H. A. (2022). Natural clay minerals as heterojunctions of multi-metal oxides for superior photocatalytic activity. *Materials Science and Engineering: B*, *286*(October), 116077. https://doi.org/10.1016/j.mseb.2022.116077

Nkansah, M. A., Korankye, M., Darko, G., & Dodd, M. (2016). Heavy metal content and potential health risk of geophagic white clay from the Kumasi Metropolis in Ghana. *Toxicology Reports*, *3*, 644–651. https://doi.org/https://doi.org/10.1016/j.toxrep.2016.08.005

Pinnavaia, T. J. (1983). Intercalated clay catalysts. *Science*, *220*(4595), 365–371. https://doi.org/10.1126/SCIENCE.220.4595.365

Schoonheydt, R. A., & Johnston, C. T. (2012). The surface properties of clay minerals. *Layered Mineral Structures and Their Application in Advanced Technologies*, *January*, 335–370. https://doi.org/10.1180/emu-notes.11.10

Schropp S.J., Windom H.L. (1988). *A Guide to the interpretation of metal concentrations in estuarine sediments*. Florida Department of Environmental Regulation, Florida.

Uddin, M. K. (2017). A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade. *Chemical Engineering Journal*, *308*, 438–462. https://doi.org/10.1016/j.cej.2016.09.029

Williams, L. B., Haydel, S. E., Giese, R. F., & Eberl, D. D. (2008). Chemical and mineralogical characteristics of French green clays used for healing. *Clays and Clay Minerals*, *56*(4), 437–452. https://doi.org/10.1346/CCMN.2008.0560405

Yang, Q., Su, M., Li, Y., & Wang, R. (2019). Revisiting the Relationship between Correlation Coefficient, Confidence Level, and Sample Size. *Journal of Chemical Information and Modeling*, *59*(11), 4602–4612. https://doi.org/10.1021/acs.jcim.9b00214

Yongming, H., Peixuan, D., Junji, C., & Posmentier, E. S. (2006). Multivariate analysis of heavy metal contamination in urban dusts of Xi'an, Central China. *Science of the Total Environment*, *355*(1–3), 176–186. https://doi.org/10.1016/j.scitotenv.2005.02.026

Summary/Sažetak

Gline su materijali sitnih čestica (veličine manje od 2 μm) koji se uglavnom sastoje od minerala gline, koji su hidratizirani aluminijski silikati s pripadajućim alkalnim i zemno alkalnim metalima. Mala veličina čestica i složena porozna struktura rezultiraju visokom specifičnom površinom, što omogućuje snažne fizičke i kemijske interakcije s otopljenim vrstama. Metali se također mogu ugraditi u strukturu gline, koja može biti izrađena od oktaedarskih i/ili tetraedarskih ploča. Ovisno o sastavu tetraedarskih i oktaedarskih ploča, sloj neće imati naboj ili će imati ukupni negativni naboj. Ako su slojevi nabijeni, ovaj naboj se uravnotežuje međuslojnim kationima. Novija istraživanja metala u glinama uglavnom odgovaraju teškim metalima, dok su istraživanja lakih metala prilično rijetka. Za ispitivanje ponašanja alkalnih i zemno alkalnih metala u uzorcima gline uzeto je 110 poduzoraka sondiranog uzorka. Ukupni sadržaj kalija (K), magnezija (Mg), kalcija (Ca), natrija (Na), stroncija (Sr) i barija (Ba) određen je pomoću induktivno spregnute plazme optičke emisijske spektroskopije (ICP-OES). Deskriptivna statistika provedena je pomoću maksimalnih, minimalnih, prosječnih i vrijednosti medijane. Za određivanje različitog ponašanja metala, izračunata je korelacija i PCA analiza sa i bez Al-normalizacije. Sadržaj metala je u sljedećem nizu: K>Mg>Ca>Na>Ba>Sr. Najveća korelacija između metala utvrđena je između Mg i K (r=0,87) te Ba i Sr (r=0,65). Multivarijantnom statističkom analizom izdvojene su dvije grupe: 1) K, Mg, Na. 2) Ba, Sr. Nakon primjene Al normalizacije, Ba i Sr pokazuju najveću korelaciju (r =0,81). Ca nije značajno pridonio ni jednoj grupi PCA, što ukazuje na mogući drugačiji izvor i ponašanje.