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Mineralogical Controls on Potassium Availability in Semi-Arid Calcareous Soils of Central Iraq

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Abstract

An investigation into the mineralogical controls on potassium (K) availability in calcareous soils cropped to maize (Zea mays L.) was carried out using two field trials located at 2 sites of central Iraq, Hilla and Al-Tali'a, Babil Governorate. Surface layer (0–30 cm) soil samples were retrieved before the start of the plot measurements, and physical and chemical properties, potassium species, and clay mineral composition by X-ray diffraction (XRD) were quantified. The Center of Gravity (Cg) index was employed to assess the degree of mica–smectite alteration and its impact on potassium availability. However, potassium fixing is strong in the soils, as show that available potassium levels (0.30–0.35 cmolc kg^{-1}) were below the critical limit of 0.36 cmolc kg^{-1} despite relatively high total potassium contents (0.61–0.76 cmolc kg^{-1}). Forty-six–55% of potassium was non-exchangeable, highlighting significant structural fixation in kaolinite-type minerals. XRD revealed predominantly montmorillonite (35–45%), chlorite (26–32%) and illite (up to 30%), with lesser amounts of kaolinite (3–8%). Cg values (0.87–1.26) reflected different stages of mica alteration, but their relationship with the K is weak due to strong fixation processes and competition for retention between Ca^{2+} and Mg^{2+} cations with potassium. Clay content showed a strong positive association ($R = 0.85$, $p < 0.05$) with specific surface area, confirming the predominance of clay mineral composition over bulk total potassium in controlling availability of potassium status.

Keywords:
Calcareous soils, Center of Gravity (Cg), Potassium fixation, 2:1 clay minerals, XRD analysis

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Introduction

Maize *Zea mays L.* is a widespread summer crop and is mainly used for the production of grains and fodder. The crop is rich in carbohydrates, which represent a major source of energy in human and animal diets (USDA, 2022). These carbohydrates provide energy for the synthesis of proteins and oils. Potassium is an essential element for plant growth; however, only a small fraction of total soil potassium is available to plants, particularly in Iraqi soils located in arid and semi-arid regions. In addition, the widespread presence of 2:1 clay minerals, such as smectite and illite, promotes the entrapment of K^+ ions within interlayer sites, reducing their short-term availability to crops (Najafi-Ghiri, Boostani and Hardie, 2023; Shakeri and Abtahi, 2020). Iraqi soils are often characterized by available potassium

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concentrations below the critical level of 0.36 cmolc kg⁻¹ (Al-Zubaidi and Pagel, 1979). This situation may give a misleading impression of soil fertility if total potassium is considered alone. This may lead to an underestimation of potassium requirements, particularly for maize (Zea mays L.), which requires an adequate and continuous potassium supply for proper growth (Bell et al., 2021). Routine laboratory soil analyses do not adequately account for mineral variations that affect potassium behavior. To better understand potassium availability from a mineralogical perspective, Barré et al. (2008) proposed the Center of Gravity (Cg). within the soil matrix. To better understand potassium availability from a mineralogical perspective. The method relies on X-ray diffraction results to show whether mica or smectite minerals are more dominant. Values close to 10 Å are usually linked to mica, whereas values near 14 Å indicate expanded smectite layers, as reflected by the Cg values. Higher Cg-values, particularly above 1.0, indicate the presence of more expansible clay minerals. Potassium could be supplied or released. Low Cg-values are generally attributed to mica minerals that are retained or hold onto potassium. Based on the conditions of semi-arid soils in central Iraq, this study focused on examining potassium status in Zea mays L.-cultivated soils of Babylon Province. The work included determining different potassium forms, identifying the main clay minerals using X-ray diffraction, and examining whether the Center of Gravity index can be useful for evaluating potassium availability. However, limited information is available on the usefulness of the Center of Gravity (Cg) index for assessing potassium availability in calcareous soils of central Iraq.

Therefore, this study aims to:(i) evaluate different forms of potassium in calcareous soils cultivated with maize,(ii) identify the dominant clay minerals using X-ray diffraction (XRD), and (iii) assess the applicability of the Center of Gravity (Cg) index as an indicator of potassium availability under semi-arid conditions in central Iraq.

Materials And Methods

Study Area

The investigation was conducted in two farmland sites in Babylon Province, central Iraq. These two farmland sites were in the regions of Al-Qasim and Al-Tali'a. These regions are well known for their cultivable land and depend largely on the system of surface irrigation. The soil type in these regions is alluvial and is mainly used for *Zea mays L.* cultivation. Sites were chosen according to their cropping history, ease of movement, and similar conditions for irrigation. Geographical coordinates were obtained using a GPS instrument with an accuracy of up to 3 m, while air-dry soil samples sieved through a 2 mm mesh were put in polyethylene bags for chemical analyses. The study was implemented in one growing season, however, the two locations with similar management practices provided sufficient spatial coverage of the studied soils.

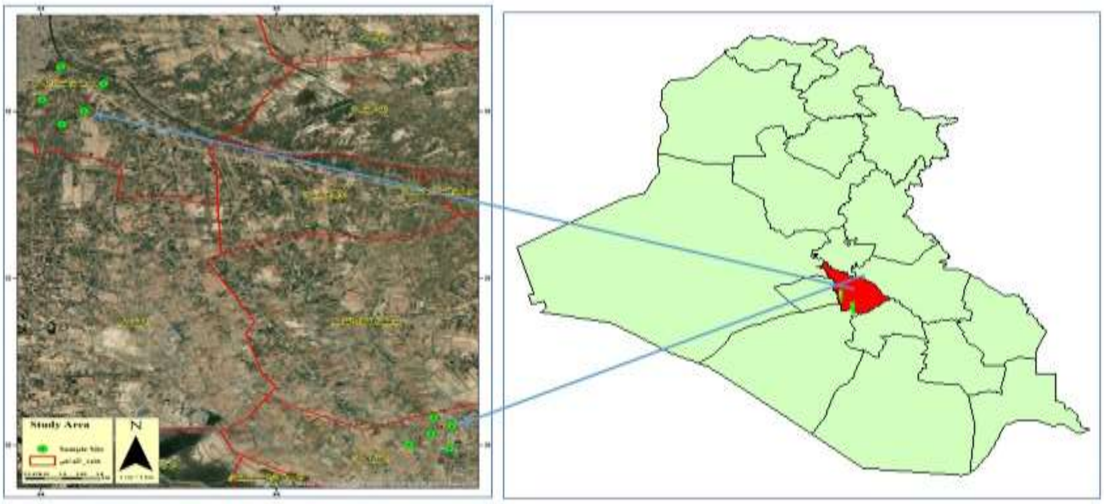

Figure 1. Location of the study area in Babylon Province, central Iraq, showing the distribution of soil sampling sites in Al-Qasim and Al-Tali'a regions.

Sampling Design

At each study site, ten sampling points were positioned in a 5 by 5 m grid. Soil samples at a depth of 0–30 cm were collected during the vegetative stage of corn (40–50 days after sowing) using a stainless-steel auger. The samples were dried and sieved to get large particles out.

Chemical and Mineralogical Analysis

Basic chemical and physical soil properties of the surface layer (0–30 cm) were determined using standard methods described by Jackson et al. (1958). These included soil pH, electrical conductivity (EC), organic matter content, and exchangeable base cations (Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}).

Potassium Fractionation

Available potassium was determined using the method described by Richards (1954). Exchangeable potassium was calculated by subtracting soluble potassium from the available fraction according to Page et al. (1982). Total potassium was measured using acid digestion as described by Sturgeon et al. (1982). Non-exchangeable potassium was estimated as the difference between total and available potassium following Rahi and Al-Ani (1991).

The different potassium fractions were calculated using the following relationships:

- Exchangeable K = Available K − Soluble K
- Non-exchangeable K = Total K − Available K

These calculations were used to distinguish between readily available and structurally fixed potassium forms in the soil.

Clay Separation and XRD Analysis

Clay-sized fractions were separated after removing carbonates, organic matter, and free iron oxides. Oriented clay samples were prepared and treated with magnesium or potassium saturation, followed by ethylene glycol solvation. Selected samples were heated at 350°C and 550°C. X-ray diffraction analysis was performed using a Philips PW1840 diffractometer to determine basal spacing's at the laboratories of the Ministry of Science and Technology, Baghdad.

Calculation of Center of Gravity (Cg)

The Center of Gravity (Cg) index was calculated based on the relative intensities and positions of X-ray diffraction peaks corresponding to basal spacings of mica (~10 Å) and smectite (~14 Å), following Barré et al. (2008). The index was computed using the equation:

- $Cg = \Sigma(a_i \times p_i) / \Sigma a_i$
- where a_i represents the relative peak area and p_i represents the corresponding basal spacing (Å).

Higher Cg values indicate a greater contribution of expandable clay minerals, while lower values reflect mica dominance.

Results And Discussion

Physical and Chemical Characteristics of the Studied Soils

As shown in Table 1, the Hilla soils differ in their physical and chemical attributes. pH values, which were between 7.2 and 7.8, demonstrated neutral to alkaline conditions This suggests As per Richards (1954), values for electrical conductivityware varied from 1.5 to 2.2 dS m^{-1} that were non-saline conditions The organic matter content was low, varying between 1.1 and 1.8%. Cation exchange capacity ranged from 20.7 to 22.3 cmolc kg^{-1}, which is the expected values for a soil rich in clay minerals of the type 2:1, such as illite and montmorillonite. The quantity of dissolved potassium ranged from 0.21 to 0.30 cmolc kg^{-1}. These values indicate the available potassium, which is ready for uptake from the soil solution, and were less than the critical value of 0.36 cmolc kg^{-1} reported in Iraqi soils. Soil texture varied from clayey to silty clay loam. Higher clay content in T1, T3 and T9 resulted in higher water retention capacity and consequently, higher potassium retention (Brady et al., 2016).

Table 1. Physicochemical properties of soils from Al-Hilla and Al-Tali’a (0–30 cm)

Sample	pH	EC (dSm^{-1})	OM (%)	CEC (cmolc kg^{-1})	Ca^{2+} (cmolc kg^{-1})	Mg^{2+} (cmolc kg^{-1})	Na^{+} (cmolc kg^{-1})	K^{+} (cmolc kg^{-1})	Texture
T1	7.40	1.80	1.20	21.50	8.20	3.40	2.60	0.25	Silty clay
T2	7.20	2.10	1.80	22.00	7.90	3.10	2.80	0.28	Clay
T3	7.80	1.50	1.10	20.70	8.50	3.60	2.20	0.21	Clay loam
T4	7.30	2.20	1.30	21.90	8.10	3.30	2.60	0.26	Silty clay loam
T5	7.50	1.90	1.40	22.30	8.30	3.20	2.70	0.30	Clay loam
T6	7.35	2.07	1.39	21.70	7.99	3.13	2.72	0.26	Clay
T7	7.48	1.51	1.49	22.05	8.01	3.19	2.38	0.26	Clay loam
T8	7.37	1.67	1.34	21.01	8.12	3.33	2.67	0.23	Silty clay loam
T9	7.41	1.86	1.12	21.71	7.94	3.57	2.78	0.28	Silty clay
T10	7.32	1.56	1.37	21.46	8.20	3.12	2.75	0.23	Clay

3.2 Potassium Forms and Availability

Figure 6 shows that, despite relatively high total potassium contents, the amount of available potassium in the studied soils was low and remained close to the critical level reported for Iraqi soils by Al-Zubaidi and Pagel (1979). Most potassium occurred in non-exchangeable forms, indicating strong fixation within clay mineral interlayers, a behavior commonly observed in calcareous soils rich in 2:1 clay minerals such as smectite and illite (Bell and Guppy, 2022; Zhang et al., 2023; Ye et al., 2024). As a result, soluble and available potassium represented only small fractions of total K, which explains the limited potassium supply to crops despite high total reserves, as also reported for similar soils with high total potassium content in semi-arid environments (Bell and Guppy, 2022; Chen et al., 2021).

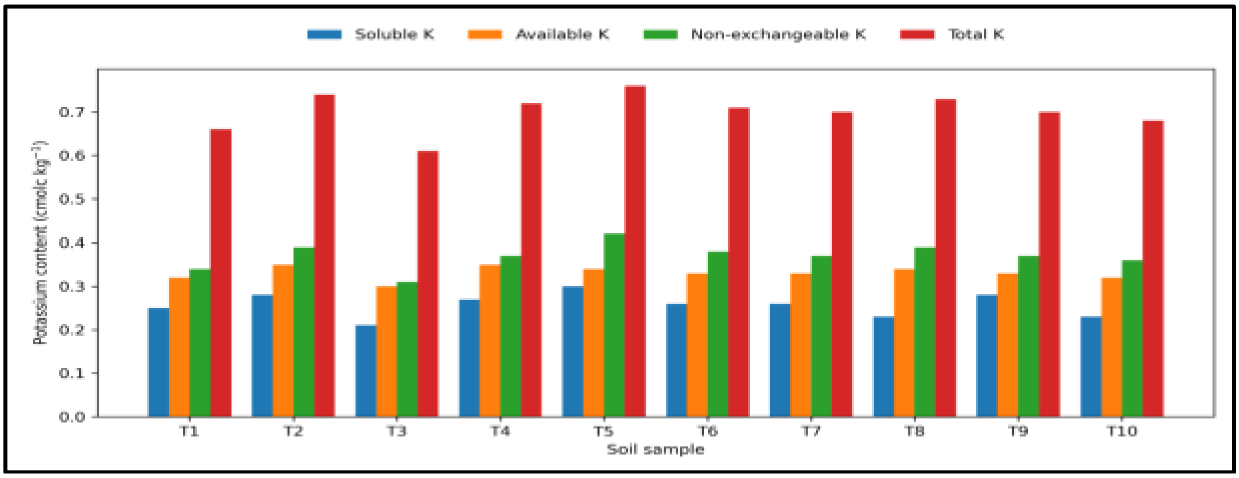

Figure 2. Distribution of potassium forms (soluble, exchangeable, non-exchangeable, and total) in the studied soils at 0–30 cm depth.

The total potassium content remained relatively high in all samples, ranging from 0.61 to 0.76 cmolc kg^{-1}, confirming the presence of substantial potassium reserves in the soil. However, the low mobility of potassium is mainly attributed to fixation processes associated with 2:1 clay minerals, particularly smectite and illite, which retain K^+ ions within interlayer positions and reduce their short-term availability (Zhang et al., 2023; Ye et al., 2024). Recent studies have demonstrated that clay mineral composition and structural characteristics strongly control potassium retention and release patterns in agricultural soils (Cuadros & Altaner, 2020; Chen et al., 2021). Accordingly, total potassium content alone does not provide a reliable indication of soil potassium availability. The integration of mineralogical indicators, such as indices derived from X-ray diffraction (e.g., Center of Gravity), provides a more accurate assessment of plant-available potassium in soils with high fixation capacity (Bell and Guppy, 2022).

X-ray Diffraction (XRD) -Tali'a Site

The XRD analysis of the clay fraction samples collected from the Tali'a site (Figures 3a) revealed the presence of characteristic peaks associated with mica minerals and 2:1 expanding clay minerals, particularly smectite and real chlorite. These features reflect both the mineral weathering extent and inheritance, which impacts K^+ availability in the studied soils. All samples exhibited a prominent diffraction peak at 13.92–14.72 Å when Mg-saturated and air-dried (Figure 3), residuals indicative of the presence of 2:1 expanding clays within each sample. This peak extended to 15.78–17.04 Å after treatment with ethylene glycol (EG) (Figure 3b), confirming the identity of smectite due to its capacity to intercalate organic molecules [30,31]. The original peak in the range of 13.926–14.718 Å remained stable, indicating that some real chlorites are also thermally resistant and can still be found in the clay fraction after heat treatment. Further K-saturation and heating to 350 °C and 550 °C (Figure 3b) facilitated a collapse of the 17.04 Å peak, with no change on either heating treatment of the long-range ordered phase at 13.92–14.72 Å was observed. This trend reinforces the identification of authentic chlorite and smectite, with the latter exhibiting thermal instability characteristic of 2:1-expanding clays. The presence of mica, especially biotite, was identified by a single, broad peak at 9.87–10.27 Å common to all treatments (Figures 3a-e) and an additional weaker second-order reflection at 5.00 Å. The scenario providing stability of these peaks through all situations is comparable with the behavior of biotite actually found in Iraqi soil, which is more weatherable than muscovite and controlled the alluvial sediments of Euphrates and Tigris rivers (Al-Qaisi, 2017).Additional peaks at 12.11–12.99 Å were identified under the Mg-saturated air-dried condition (Figure 3), indicating the presence of randomly interstratified mica–smectite minerals. Upon EG treatment, this peak shifted to approximately 13.26 Å (Figure 3b), suggesting limited swelling response by the smectite layers embedded within the interstratified structure.The non-exchangeable form of potassium, although quantitative, is largely inaccessible to plants in the short term until it is gradually released through weathering or microbial processes (Zhang et al., 2023). The total potassium level was continuously high in all samples, from 0.61 to 0.76 cmolc kg^{-1}, confirming the presence of large K shares in the soil. However, the low mobility of K is attributed to K fixation in these systems. Fixation by 2:1 clay minerals, mainly smectite and illite, are known to retain K^+ ions in interlayer positions, which reduces their availability (Chen et al., 2021).These findings are in line with previous studies in Iraqi soils, such as Al-Law (2017), who reported that mineral-bound K is more than 96% of total K in many agricultural sectors. Similar conclusions were presented (Al-Shammari ,2020), all emphasizing the role of clay minerals and original materials in determining the potassium release patterns. In light of these results, it is clear that the total potassium content alone is not a reliable indicator of nutrient status. The data supports the integration of mineral indicators for example, the Center of Gravity (Cg) that assess the degree of weathering and changes from mica, which affect the bioavailability of K. Such integrated indices provide a more accurate representation of plant-accessible K, especially in soils with high fixation capacity. This mātauranga directly affect potassium fixation and release dynamics. As shown by the presence of interstratified phases and real chlorite, in addition to expandable smectite (one example here is that K^+ was identified as excess in calcareous clay soils) [2], the availability of K^+ in these soils is complex. These mineralogical traits need to be integrated into fertilization management decisions in the fields devoted to Zea mays L.

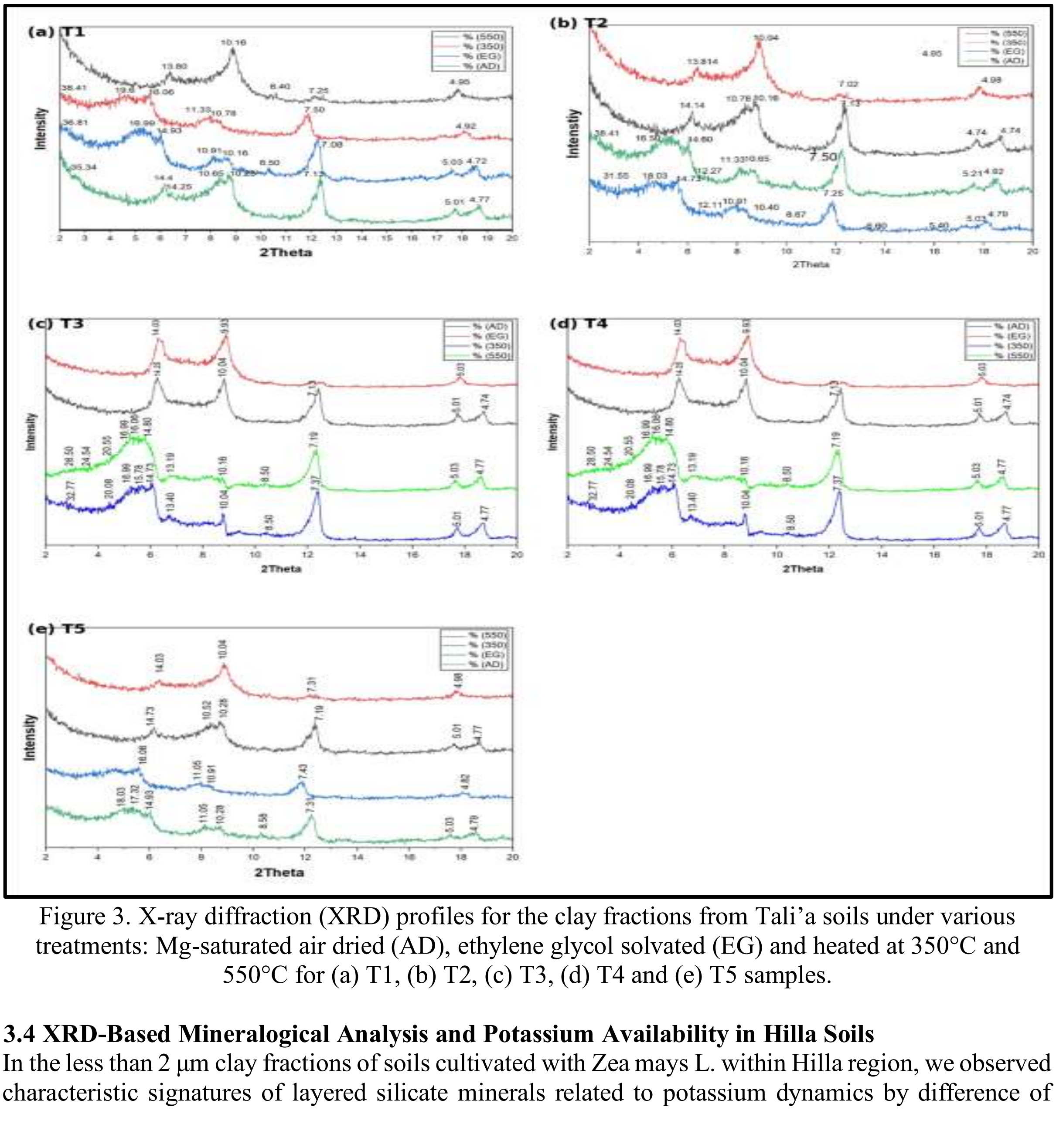

Figure 3. X-ray diffraction (XRD) profiles for the clay fractions from Tali'a soils under various treatments: Mg-saturated air dried (AD), ethylene glycol solvated (EG) and heated at 350°C and 550°C for (a) T1, (b) T2, (c) T3, (d) T4 and (e) T5 samples.

3.4 XRD-Based Mineralogical Analysis and Potassium Availability in Hilla Soils

In the less than 2 µm clay fractions of soils cultivated with Zea mays L. within Hilla region, we observed characteristic signatures of layered silicate minerals related to potassium dynamics by difference of diffraction patterns (Figures 4 a-e). An indication at 20.01–20.53 Å from the EG-treated samples is consistent with the d_{001} basal spacing of a pseudo-stable interstratified mica–illite phase, which supports evidence for transitional illite structure (further discussion provided below). Two competing hypotheses are proposed to explain the origin of this phase. Hower et al. proposed the first explanation, which argued that they were not naturally occurring. (1976); Pearson and Small (1988)] to an ordered smectite–mica interstratification in which layers of smectite (9.5 Å) alternate with untethered mica (10.5 Å) units. Under this mechanism, smectite is altered to illite with the process of Al^{3+}- and K^{+}-rich stage (enriched in Al^{3+} and K^{+} after maturing) to the illitic stage. This process, however, needs acidic to neutral pH conditions favoring Al^{3+} mobility, which are mostly lacking in the calcareous soils studied (pH 7.3–7.8). On the other hand, based on (Srodon, 1999; Nakao et al.,2009) interpretation of the 20 Å reflection result from regular illite–mica interstratification due to edge-weathering of mica into illite and frayed edge sites under mild pyogenic alteration. This hypothesis is more agreeable with the alkaline, calcium-rich condition of Hilla soils and non-paddy limited weathering intensity. The 20 Å reflection was only observed in soils from paddy environments, indicating greater degrees of mica transformation when flooded. This coincides with increased potassium availability (Cg values: 0.98–1.26), likely from the partial alteration of mica to illite and smectite. Other reflections at 14.25–14.73 Å (air-dried, Mg-treated samples) expanded to 16.60–17.76 Å after ethylene glycol (EG) treatment followed by collapse to 10.10–10.50 Å after K-saturation and heating at temperatures between 350°C-550°C confirmed those of expandable smectites. The presence of 10.10 Å peaks at different treatments also indicates that mica (biotite/muscovite) were present in various conditions. Bowen (1990) and Dixon et al. (1977) peaks at 5.00 Å suggest biotite presence. In addition, diffuse and variable reflections in the 11.0–13.5 Å d-region of some samples indicate randomly interstratified phases (mica–smectite), suggesting progressive mineral alteration. Peaks at ~7.10 Å in each of the Mg–air dried treatments confirm that kaolinite was present. This indicates that total K availability in Hilla soils is controlled by the glassy and interstratified proportion of micas. These alterations are further accentuated under hydromorphic (paddy) conditions, thus validating the use of Center of Gravity (Cg) index as a diagnostic dichotomous tool for gauging pyogenic release potentiality of structural potassium.

The noted low-availability of potassium despite the high total potassium content here agrees with previous field studies on calcareous soils largely controlled by 2:1 clay minerals (Chen et al., 2021; Zhang et al., 2023), that did show powerful K+ fixation within interlayer sites. Likewise, Bell and Guppy (2022) stated that the total potassium content of soil is not a good index of plant-available potassium in soils with a high ability to fix K.

On the other hand, unlike Barré et al., from this study, we found a weak correlation between Cg index and extractable K. (2008) proposed that the mineral transformation indices were good predictor of potassium availability. The non-relation is possibly due to high levels of total calcium carbonate and soil alkalinity in the soils under study which favour potassium fixation and limit its release from structural particles into soil solution.

These results show that potassium dynamics in semi-arid calcareous soils are more-strictly controlled by fixation processes as opposed to mineral transformation alone.

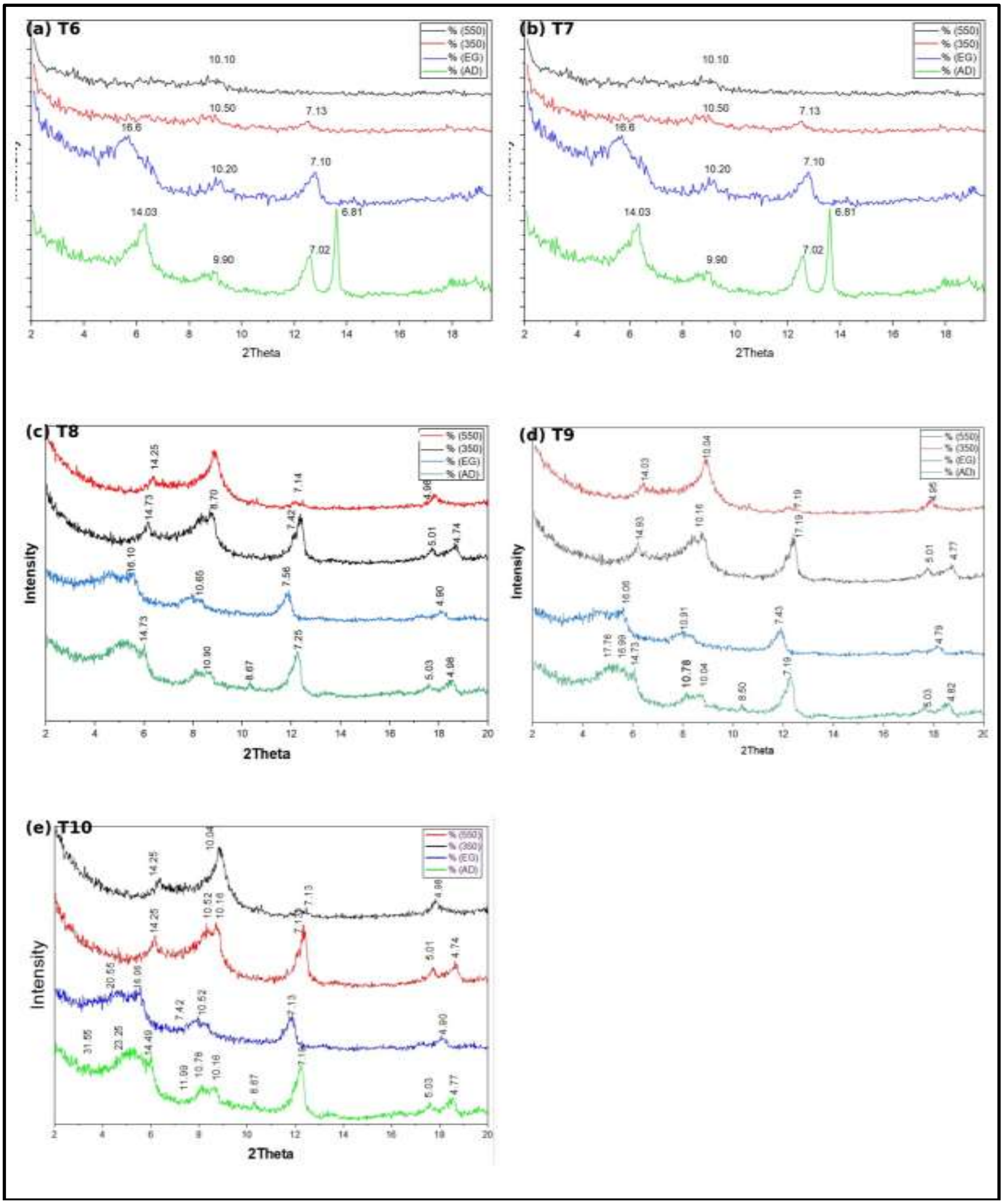

Figure 4. X-ray diffraction (XRD) patterns of clay fractions from Hilla soils under different treatments: (a) T6, (b) T7, (c) T8, (d) T9, and (e) T10. Samples were Mg-saturated (air-dried), ethylene glycol solvated, and heated at 350 °C and 550 °C.

Cg–Available Potassium Relationship

Ten samples were taken of Zea mays L. cultivated soil, from the Hilla and Tali'a regions, where the relationship between Cg index and available K+ was studied. Cgc values varied from 0.89 to 1.26, including different levels of mineralogical transformation (i.e., alteration of mica to smectite or illite types), possibly due to the lack of clear anaerobic conditions in this sedimentary environment since nanometer-sized precipitate grains may be artefacts resulting from textural change at low temperature [14]. Nevertheless, K content ranged only slightly from 0.33 to 0.35 cmolc kg^{-1} for all samples tested. The low variation indicates that higher Cg does not always mean more short-term K available. Results indicate a weak correlation ($r \approx 0.20$; Figure 5) between Cg and available potassium implying that only mineralogical transformation intensity does not properly predict plant-available K under calcareous soil conditions.

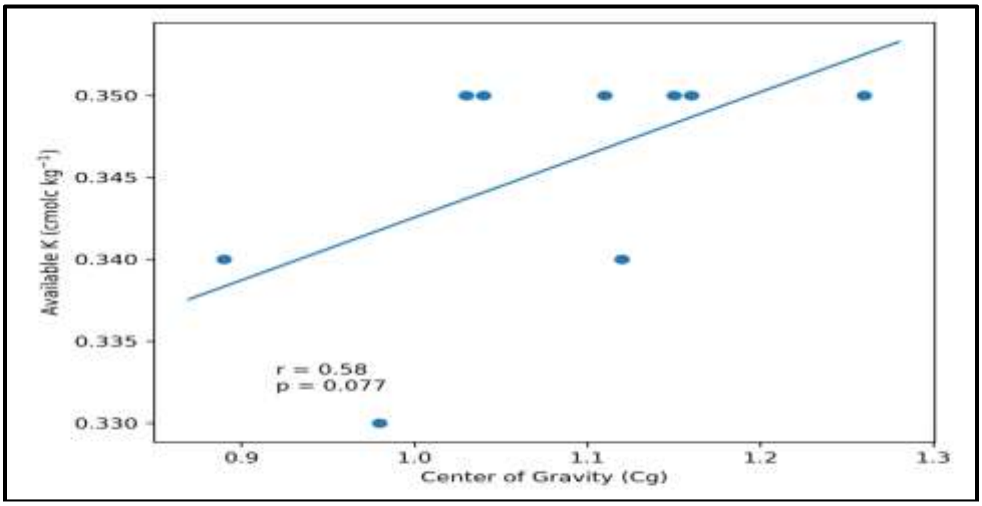

Figure 5. Relationship between Center of Gravity (Cg) index and available potassium in calcareous soils cultivated with maize (Zea mays L.).

Controls on Potassium Fixation and Release

While Cg values differed for the soils studied, they did not translate into differences in potassium availability. Potassium was largely retained in the framework of 2:1 clay minerals, restricting its release to the soil solution. Under calcareous soil conditions, the available potassium indicated strong fixation and remained between 75.0-225.00 mg kg-1 (Table 3). Potassium mobility was hindered further through soil pH, calcium carbonate content, and heavy texture. Conclusion Availability of potassium was thus determined more so by fixation processes than total potassium content or degree of mineral transformation ➜ (Jabbar et al., 2025; Al-Silmawy et al., 2025; Roostaei et al., 2026; Al-Juthery et al., 2026)

Clay Mineralogy of the Studied Soils

The studied soils exhibited a marked dominance of montmorillonite clay mineral composition, accounting with values from 35 to 45% (Figure 6). This is in accordance with a general use of 2:1 expanding clay minerals in the alluvial soils of central Iraq propagated under semi-arid and calcareous conditions. In addition, chlorite was present in relatively high amounts (26–32%), suggesting weak chemical weathering and inherited minerals endurance. Illite was also present in moderate proportions (23–30%) and represents partially weathered mica, which is known to tightly fix potassium by its interlayers. In contrast, kaolinite was low (3–8%) and indicative of alkaline soil remains, implying the development of limited weathering within soils. In general, the prevalence of 2:1 clay minerals accounts for the high potassium fixation capacity and the low availability of potassium in those soils.

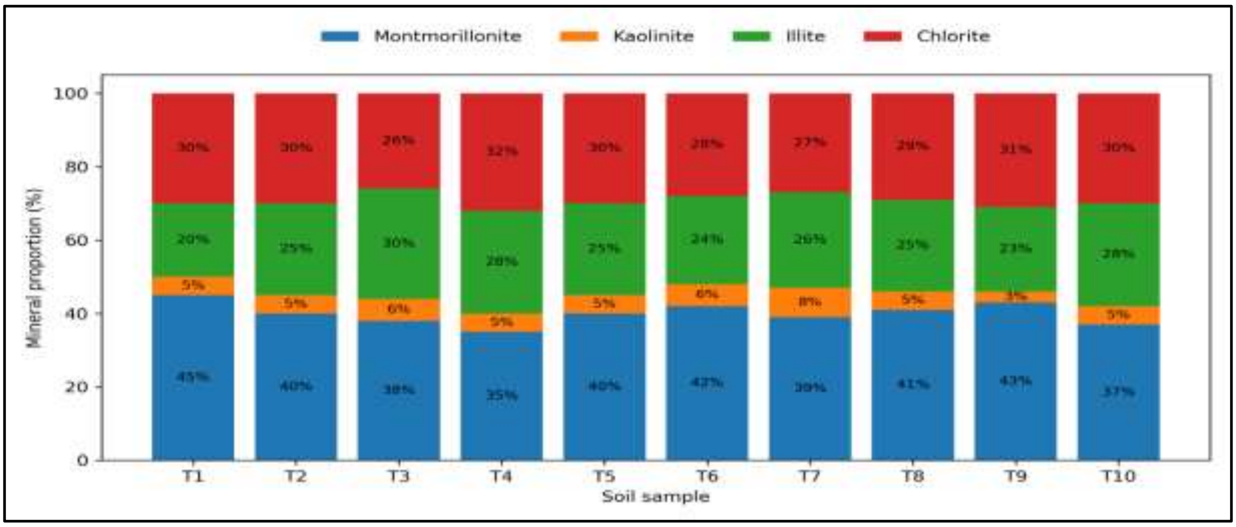

Figure 6. Relative proportions (%) of dominant clay minerals (montmorillonite, chlorite, illite, and kaolinite) in the studied soil samples.

Conclusion

Potassium Availability in Calcareous Soils of Central Iraq as Influenced by Potassium Fixation Mechanisms and Clay Mineral CompositionThis study shows that in calcareous soils of central Iraq potassium availability is not governed solely by total potassium content but rather is highly controlled by clay mineral composition (e.g., illite to smectite ratio) and mechanisms related to potassium fixation. Although total potassium was relatively high, the accessible portion of that potassium remained below the required critical level because it was retained by 2:1 clay minerals such as illite and smectite. X-ray diffraction analysis confirmed these minerals as the dominant phases and identified various interstratified phases, indicating ongoing mineral transformation processes. Nevertheless, the weak correlation between the Cg index and readily available K suggests that simply relying on mineralogical transformation does not adequately distinguish short-term potassium availability in calcareous environments.

This study provides evidence of the need for integrating mineralogical indicators with classical soil analysis to better assess K availability. This can help improve potassium utilization strategies in semi-arid agricultural systems.

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