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THE ROLE OF MONOVALENT IONS IN THE DETERIORATION OF SOME PHYSICAL PROPERTIES OF CALCAREOUS SOILS IN NORTHERN IRAQ

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ABSTRACT

Twelve soil samples of different textures and carbonate minerals were selected from the great soil group (Calciortheds) in northern Iraq. In order to describe the effect of the concept of mono cations ratios (potassium and sodium) responsible for the stability of soil aggregates CROSS as an alternative to the concept of sodium adsorption ratio, on the water conductivity and the average weighted diameter of soil aggregates, an electrolyte solution consisting of mono cations (potassium and sodium) and divalent cations (calcium and magnesium) with potassium ionic dominance over the rest of the other ionic species was allowed at a concentration of (4.26) mmol.$L^{1/2}$ to undisturbed soil columns with a diameter of 4cm and a length of 6 cm using the miscible displacement technique under the influence of a constant flow solution pressure of 4cm. For ten successive pore volumes for approximately 16 weeks. The flow of electrolyte solution through the columns led to increasing additions of mono cations (K^{+}) that negatively affected the deterioration of different soil groups by sliding their colloids from the original aggregate, causing dispersion of clay colloids dominated by montmorillonite mineral with high ability to swell and disperse clay particles and sliding organic materials, which led to a decrease in the weighted diameter index from 6.18 to 5.43 mm, which led to the deterioration of the soil and a decrease in its water conductivity for all soils from 3.39 to 1.61 cm.h^{-1}. we suggest that the effect of potassium should be taken into account in evaluating soil structure.

INTRODUCTION

Calcareous soils are soils that contain 5% or more calcium carbonate by weight with fine particles and highly specific surfaces which negatively affects the properties of the soil, whether they are physical properties such as the relationship between the soil and water, or chemical properties such as the availability of nutrients (Aljumaily *et al.*, 2022; AL-Hamandi *et al.*,2024). The soil contains many mono and di ions, including (Na^{+1}, K^{+1}, Mg^{+2}, and Ca^{+2}), which are characterized by their negative effects on soil structure due to dispersion and swelling of the clay, as well as water conductivity and permeability. As a single positive ion, potassium causes the clay to disperse and swell, just as sodium does. Many studies have indicated the role of potassium in its effect on soil structure, which is equal to or less than the effect of sodium, and that the bonds between clay and positive ions determine the degree of disintegration of soil and clay particles (Smiles and Smith, 2004; Yotsapon *et al.*, 2018). The role of potassium in the formation and stability of soil aggregates compared to Ca^{+2} and Mg^{+2} ions was in the following order (K<Ca<Mg) or

(Ca<Mg<K). The potassium ion had a more positive effect than sodium in reducing the diffusion of clay, which increased the stability of large soil macro aggregates. They attributed the reason to the fact that the sodium ion has 72% higher hydration energy. The result was found by (Rengasamy, and Marchuk, 2011; Singh *et al*, 2018). With the presence of similarity in the ionic influence of K and Na which. They cause swelling of the clay and increased dispersion, which leads to negative effects on the physical properties of the soil, especially water conductivity (Marchuk and Rengasamiy, 2011; Rengasamy, 2018).

There is a new indicator in the stability of soil aggregates called (CROSS), short for (Cation ratio of soil structural stability), referring to the effects of ions K, Na, Ca, and Mg on the stability of soil aggregates. According to the CROSS concept, any increase in Na or K in the soil will reduce the stability of soil aggregates. The researchers' results showed that K ions have effects similar to Na on percentage stable aggregates and hydraulic conductivity and potassium fertilization may lead to deterioration of soil structure Saturated hydraulic conductivity is a critical parameter that controls how fast water can transmit while the soil is saturated, and it reflects soil conditions such as total porosity, pore size, and tortuosity of pores, as well as characteristics of the soil water, including viscosity and density (Buelow *et al*., 2015). In addition, SHC helps design irrigation, drainage, and wastewater disposal systems, studying runoff characteristics and groundwater recharge. Soil SHC depends on (the content of clay type, EIP, SAR, EC, pH, and organic matter) by affecting soil pore-size distribution. Therefore, soil aggregate stability is an important factor affecting soil SHC. Our research aims to study adding different levels of CROSS on Hydraulic conductivity (HCs) and mean weighted diameter MWD in calcareous soils in north Iraq (Alobaidy and Hassan, 2024).

MATERIALS AND METHODS

Twelve soil samples were collected from Ninavha, Dohuk, and Erbil provinces of northern Iraq, according to different clay, SOM, and CaCO3 contents of the soil rhizosphere layer (0 – 0.30) m. The research region experiences semi-arid weather with an average of 210 to 835 mm of yearly rainfall. Soils are classified as (Calciorthid), according to (Soil Survey Laboratory Staff, 2017). The soil samples the determining chemical and physical characteristics determined by the proposed methods (Sparks, 2017). (EC) and soil pH using 1:1 soil-to-water suspension. SOM was estimated by dichromate oxidation; Total Carbonate minerals were estimated by calcimeter (El Mahi *et al*., 1987). Particle size distribution was determined by the hydrometer method according to (Gee, 2002). Effected cation exchange capacity (CEC) determined by dissolving soil with 1N NH4Cl. Potassium and sodium were determined by a flame photometer (Al-Hamandi *et al*.,2019; Aljumaily *et al*., 2022).

CROSS solution (4.26) content 20 mmolc.L^{-1} with a constant SAR value (1.2) was prepared by using electrolyte solutions with a concentration of (0.1M) of chlorides (Na^+, K^+, Ca^{+2} and Mg^{+2}) according to (Marchuk, 2013). CROSS solutions were calculated by using the following equation:

$$CROSS = [Na + 0.56K] / ([Ca + 0.6Mg]/2)^{1/2} \ (mmolc\ l^{-1})$$

Effect of CROSS Solution on Hydraulic Conductivity Saturation

CROSS solution concentration (4.26) with SAR (1.2) mmolc.$L^{1/2}$ was added in disturbed soil columns with 4cm in diameter and 6cm in length by using continuous a miscible displacement technique through continuous Leaching with a constant head of 4cm. Continuous leaching was made to fill the pore volumes and repeated ten times for about 16 weeks. After that soil columns were dried and then the physical measurements. Hydraulic Conductivity was estimated Using the constant head solution compressor method according to (Klute and Dirkson, 1986). The average weighted diameter is estimated using the dry sieving method using a set of sieves (6.00, 4.75, 2.36, 1.18, 0.5 mm) to express the stability of soil aggregates using the dry sieving method, as stated in (Kemper and Rosenau, 1986) according to the equation and as follows:

$$M.W.D. = \sum_{i=1}^{i=n} X_i^{-} W_i$$

Whereas:
M.W.D.= average weighted diameter (mm).
X= average diameter of each two successive sieves (mm).
W=Weight of soil remaining on top of each sieve relative to the weight of the total sample.

RESULTS AND DISCUSSION

The results show that the studied soils were classified as Mollisols in all samples of the Dohuk and Erbil governors, and Nineveh soils were classified as Inceptisols (Soil Survey Staff, 2017). Table (1) shows that the study soil environment was characterized as calcareous with a high content of carbonate minerals (315 - 375) $g.kg^{-1}$ and high pH (6.80 - 8.10).

Table (1): Some physical and chemical properties of the study soils

Soil no.	Soil sites	EC dS m^{-1}	pH	CEC	$CaCO_3$	O.M	Sand	Silt	Clay	Texture
				$Cmole_c.kg^{-1}$	$g.kg^{-1}$					
1	Buddy	0.77	7.66	24.06	365	17.4	528	18	449	C
2	Bakira	0.76	7.07	33.55	345	14.8	403	23	367	SC
3	Suaruhtuka	0.69	7.12	35.23	370	21.6	303	25	442	C
4	Kiflsen	0.81	7.59	24.50	375	27.1	421	28	297	L
5	Mosul Dam	0.85	7.52	37.88	315	15.6	371	18	447	C
6	Fayda	0.15	6.80	43.90	335	29.3	246	30	723	C
7	Sheikhs	2.13	8.10	48.77	335	29.7	158	27	569	C
8	Talkif	1.42	8.10	34.87	355	28.7	258	32	420	CL
9	Sulak	0.40	7.18	44.16	345	21.7	181	35	467	C
10	Hiran	0.40	7.44	30.75	375	10.3	431	20	367	CL
11	Sinja Castle	0.48	7.14	26.28	325	26.6	581	10	317	SCL
12	Ziarat	0.32	6.82	42.78	350	19.0	256	22	517	C

According to the reports of the world food and agriculture organization (FAO, 2017). This indicates that the soils of areas with high temperatures and no guaranteed rainfall are characterized by high accumulation of $CaCO_3$ due to lack of rain, high evaporation, and limited filtration (Taalab *et al*., 2019). Non-saline soils, as their EC values ranged between (0.15 - 2.13) dS m^{-1}. The clay content (367 - 736) $g.kg^{-1}$. And CEC (24.06 - 48.77) $Cmolec.kg^{-1}$. The results show that there is a clear variation in the CEC values between the study soils, which affects the amount of adsorbed ionic species. the amount of SOM was low (10.3 - 29.7) $g.kg^{-1}$.

Effect of added potassium levels on hydraulic conductivity

Results showed in Table (2) a decrease in Ks and MWD, for all soil samples after treating with CROSS solution, the values of Ks decreased, perhaps due to the destruction of the aggregates as a result of slacking during wetting electrolyte solution movement in soil column. It also led to a decrease in MWD and an. Many researchers. The slaking process is controlled by the wetting rate of the soil: the faster the wetting, the stronger the slaking forces and the greater the proportion of aggregates that undergo slaking. documented that slaking occurs when there is the effect of slaking forces such as aggregates not strong enough to withstand the stress produced by different swelling, the rapid release of heat during wetting, the pressure of entrapped air, and the mechanical action of moving water (Sposito *et al*., 2016). Reported that slaking is strongly affected by the wetting rate of soil: the faster wetting occurs, the greater slaking forces; which in turn allows for the preservation of small MWD. The aggregate sizes could affect the slaking, swelling, and dispersion process, and consequently the influence of the soil Ks (Al-Hadedi and Al-Obaidi ،2021).

Table (2): The effect of added potassium CROSS on Ksat and MWD of the study soils

Soil No	M.W.D mm		Hydurolic conductivity cm/h^{-1}	
	Distilled water	Saline Solution	Saline solution	Distilled water
1	4.58	4.27	0.20	0.85
2	5.56	4.87	0.17	5.02
3	5.42	4.76	1.76	3.35
4	6.26	5.41	2.90	4.15
5	6.77	5.80	0.31	1.06
6	6.55	6.41	2.30	5.31
7	7.12	6.64	1.12	2.42
8	6.51	5.65	0.88	1.79
9	6.21	5.05	1.96	3.16
10	6.79	5.62	5.54	8.53
11	6.51	5.04	1.66	2.09
12	5.88	5.68	0.55	2.96
Average	6.18	5.43	1.61	3.39

MWD was higher initially than decreased. The -22.89 % decreases were higher in soil no 11, it may be indicated that soil was more affected by the destruction of aggregates. As shown in Figure (1) Found that the binding agent between particles in the aggregates varies according to aggregate sizes. They indicated that Macro-aggregates are being held together by weaker forces than micro-aggregates, which are being held together strongly and can form macro-aggregates. The highest MWD for soil no 11 compared to soil no 6 indicated that more macro-aggregates existed in soil 11which might bind weakly and be exposed to destruction. Our results agree with (Al-Hadedi and Al-Obidi, 2021). Hypothesized that the effect of aggregates on Ks reduction was more pronounced in soil with aggregates sizes of 2-4mm than those with sizes < 2mm. They suggested that there is an interaction between aggregates slaking and aggregate sizes in their combined effect on soil Ks mentioned that during leaching soil with diluted electrolyte solutions, the main reason for the differences in the structure and the Ks of soil was due to variation in aggregates size distribution. reported that there are fundamental problems in characterizing the pore spaces in the soil, which become much more complicated as mentioned by (Dikinya *et al*., 2007) when the soil structure is changed during its wetting and leaching. Figure (1) also shows the decrease in each parameter compared to initial values. The highest decrease in KS of 2 soil was (-96.81) while it was (-19.12%) in soil no 11, Soil treated with ten continuous irrigation cycles, the length of one cycle being equivalent to the duration of flow of one pore volume, as treating the soil with an electrolyte solution containing increasing ions of potassium led to a deterioration in the values. Hydraulic conductivity in varying proportions depends on the difference in soil texture. The coarse-textured soil was higher than the fine-textured soil in the comparison sample (using distilled water). This is due to the high percentage of large-sized pores (micropores) responsible for effective transport according to Bozel's law in primary soils, and when these values were examined, it was found that they are within the limits of the saturated water conductivity values for different soil textures measured according to this is consistent with what (Al-Hadidi and Al-Obaidi, 2021) reached. The results indicate that the decrease in soil Ks values is due to the combined role of potassium and sodium ions. It is concluded that increasing the percentage of single ions (K^+, Na^+) as a function of CROSS in the water leads to an increase in the percentage of EKP in the soil and an increase in the thickness of the impediment layer and the dispersal of fines. Clay and redistribute it. Which resulted in a decrease in the pore diameters. This is in addition to the effect of swelling in the clay mixture soil, which leads to the narrowing of the soil pores and a decrease in the values of saturated water conductivity, thus increasing the movement of water. Ks values reflect the rate of structure collapse and the closing of pores, which may lead to It occurring during the movement of water in the soil (Marchuk and Marchuk, 2018). Which may affect the movement of water. The Ks values depend on the composition of exchangeable ions and the concentration of the soil solution (Laurenson *et al*., 2011).

This is consistent with (Marzchuk and Rengasamy, 2011) and what he pointed out confirms the findings of (Marchuk, 2013) in his study on two different soils. In the texture and mineral composition, the first, Illite - Kaoline, and the second, Smectite, were exposed to three cycles of wetting and drying using solutions containing increasing concentrations of potassium in terms of CROSS at a fixed SAR value, which showed a significant decrease in the value of Ks values in both cultures at high CROSS values. Potassium is one of the monovalent cations that can cause swelling of clay and disperse it, just as sodium does. International research has indicated that the role of potassium in influencing soil structure is almost equal to or less than the role of sodium (Smith *et al*., 2015).

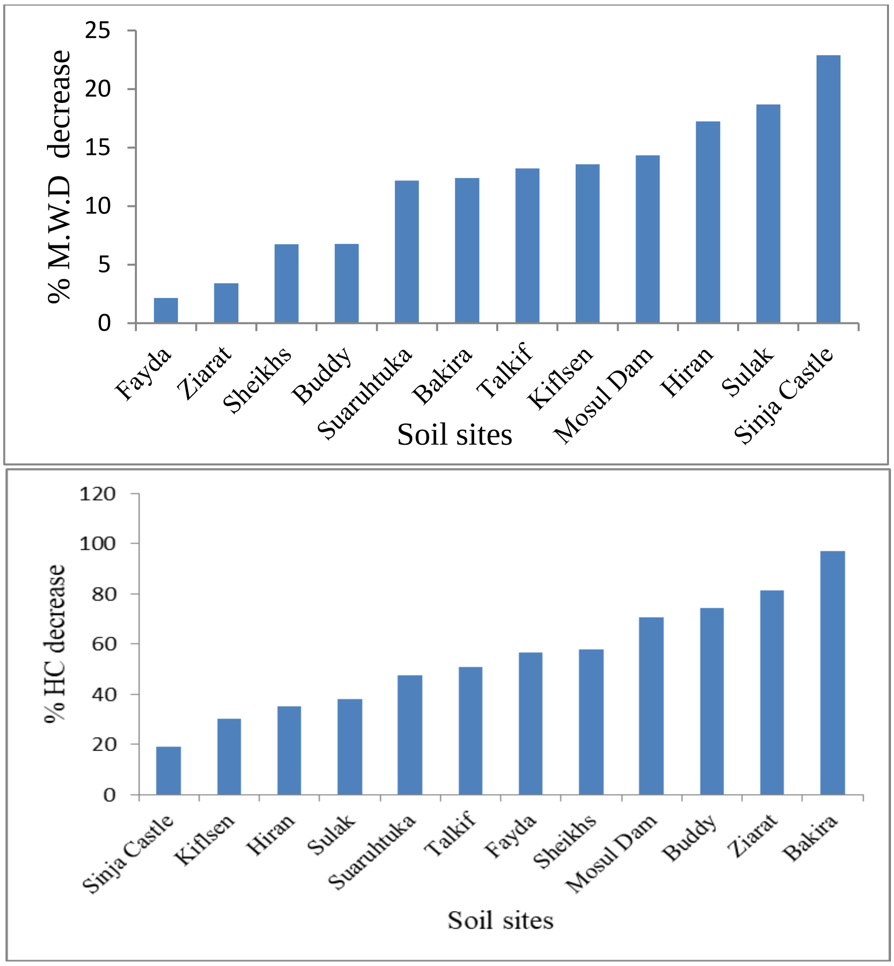

Figure (1): Soil site arrengment according to % decrease in MWD and HC

The researchers (Liu *et al*., 2016) hypothesized that the strength of the ionic bonds between clay and positive ions determines the degree of dissociation of clay particles and that the interfering effect of polar water molecules on these bonds arises from the forces of attraction and repulsion of positive ions, as it is considered the main determinant of the effect of high CROSS in used water on the transport of the movement of water in the soil due to the high effectiveness of clay in showing the effect of increasing the thickness of the double layer of carbon and forming the obstruction layer Drag layer and soil dispersion, in addition to the appearance of some swelling in the mixed clay soil due to its high clay content, may be one of these reasons. Carbonate minerals can act as a substance that increases the cohesion of the particles, reducing the disruption of the aggregates (less than 2mm) when moving water with a high CROSS content and reducing from the rate of dispersion and swelling in it. The optical density increased due to the increase in the density of the suspension (the amount of dispersed particles) (Sposito *et al*.,2016), and this is due to the destruction of the structure (Li *et al*., 2015). Which leads to a modification in the geometric structure of the spaces with a change in the state of the clay minerals and the release of ions present on the tactoic clay mineral sheets, thus increasing the colloidal clay suspension and increasing its turbidity. (Luo *et al*., 2018b) illustrated that hydration and osmotic forces among soil particles on water infiltration. (Liu, 2017) referred to Position of shear plane at the clay–water interface by making a strong polarization effects of counter ions also (Luo *et al*., 2018a). showed on the relationship between ion adsorption energy and particle aggregation activation energy. Soil macropores play a crucial role in water and solute transport, accounting for 85% of the total infiltration volume. For saline water with the same EC, a decrease in KC concentration may enhance soil clay dispersion, resulting in the loosening of clay particles from the aggregates. The dispersed clay particles moving with the water could clog the soil macropores, promoting the conversion of macropores to micropores (Cameira *et al*., 2003) thus reducing the macropore volume (Akrawi and Alkhaled, 2024).

Aggregate stability

The results shown in Table (3) indicate that all remaining masses on the five sieves of the original soils were superior to their counterparts in the soils treated with the electrolytic solution containing mono ions. This may be due to the low content of the original soils of dissolved and exchanged mono ions responsible for this deterioration. However, after treating the soils with the electrolytic solution, the solid and liquid phases of the soil were enriched with monoions (potassium and sodium), which contributed negatively to the deterioration of the aggregates and their distribution on the sieves. The highest remaining aggregate mass was above the 7.5mm sieve, then it decreased until it reached the lowest values above the last sieve. The continued decrease in the masses of large aggregates and their transformation into smaller mass sizes clearly indicates the role of mono cation ions.

Table (3): Effect of adding potassium-bearing electrolyte solution on the masses of soil aggregates remaining on the sieves

Soil No	Soil aggregates remaining on the sieves									
	Average sieve diameter mm									
	7.55		5.38		3.56		1.77		0.84	
	before	after	before	after	before	after	before	after	before	after
1	30	26	22	18	19	23	16	23	13	11
2	41	32	35	24	8	21	11	17	6	6
3	34	37	19	30	22	22	13	7	12	4
4	46	70	17	6	20	9	9	7	8	8
5	47	70	28	18	16	9	5	2	5	1
6	57	67	30	17	9	10	2	4	2	2
7	66	80	25	15	3	4	3	1	3	1
8	54	67	13	16	12	11	12	3	8	2
9	41	58	16	20	20	15	11	5	12	2
10	50	71	18	18	14	7	9	3	9	2
11	31	73	27	8	26	7	12	7	4	5
12	46	50	28	22	12	19	9	6	6	3
average	45.25	58.42	23.17	17.67	15.08	13.08	9.33	7.08	7.33	3.92

Potassium works to reduce large aggregates and increase small aggregates, and thus has a role similar to sodium ions by demolishing the soil structural aggregates through three mechanisms: the first is the sliding of the aggregates, then the swelling of the clay, then its dispersion, which creates confined air pressure accompanied by hydration heat that contributes to accelerating the demolition of the structural aggregates and the large aggregates not having high resistance to overcome the forces of mono cation ions in the face of the fragmentation and sliding of the structural aggregates (Khalid, 2012).This depends on the soil content of cementing materials, clay silicates, organic soil material, carbonate minerals, and hexagonal oxides, which contribute a positive role in building stable soil aggregates that are resistant to dispersion (Ben-Har *et al*., 2009).

CONCLUSIONS

The study soils, which are located in the rain-fed region of northern Iraq, were characterized by relatively high values of the potassium to sodium ratio in their liquid and solid phases, which makes them susceptible to dynamic dispersion of clay colloids and thus reduces their physical properties affecting plant growth (soil aggregate stability and water conductivity). The experiment of adding electrolyte solutions with increasing potassium content, expressed by the term CROSS, revealed a significant deterioration in the physical properties of the soil (weighted diameter ratio and water conductivity).

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CONFLICT OF INTEREST

The researchers declare that they do not have any competing tests and there is no conflict of interest.

دور الأيونات الأحادية التكافؤ في تدهور بعض الخصائص الفيزيائية للتربة الكلسية في شمال العراق

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الخلاصة

اختيرت اثني عشر عينة تربة ذات نسجة ومعادن الكربونات مختلفة ضمن مجموعة الترب العظمى Calciortheds من شمال العراق. بهدف وصف تأثير مفهوم نسب الايونات الاحادية (البوتاسيوم والصوديوم) المسؤولة عن ثباتية تجمعات للترب CROSS كبديل عن مفهوم نسبة الصوديوم الممتز على الايصالية المائية ومعدل القطر الموزون لمجاميع التربة، إذ تم السماح لمحلول إلكتروليتي مكون من كاتيونات أحادية (البوتاسيوم والصوديوم) وكاتيونات ثنائية التكافؤ (الكالسيوم والمغنيسيوم) ذات سيادة أيونية للبوتاسيوم على بقية الأنواع الأيونية الأخرى بتركيز (4.26) مليمول.لتر $^{-1/2}$ الى أعمدة تربة غير مستثارة بقطر 4سم وطول 6سم باستخدام تقنية الإزاحة الامتزاجية الهادئة تحت تأثير ضاغط لمحلول الجريان ثابت 4 سم لعشرة أحجام مسام متتالية لمدة 16 أسبوعًا تقريبًا. أدى تدفق المحلول الالكتروليتي عبر الأعمدة إلى إضافات متزايدة من الكاتيونات أحادية (K^+) التي أثرت سلبًا على تدهور مجاميع الترب المختلفة من خلال انزلاق غروياتها من التجمعات الأصلية

مما تسبب في تشتت الغرويات الطينية ذات سيادة لمعدن المونتموريلونيت ذو القدرة العالية على الانتفاخ وتشتيت جزيئات الطين والمواد العضوية المنزلقة، ادت الى انخفض مؤشر القطر الموزون من 6.18 الى 5.43ملم وان الغرويات المشتتة ملئت مسام التربة مما ادى الى تدهور الترب وانخفاض ايصاليتها المائية لجميع الترب من 3.39 إلى 1.61 سم.ساعة$^{-1}$. ووفقا للنتائج نقترح أن يؤخذ بعين الاعتبار تأثير البوتاسيوم في تقييم بناء التربة.

الكلمات المفتاحية: البوتاسيوم، التشتت، الايصالية المائية، تدهور التربة، معدل القطر الموزون.

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