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KADİR YILMAZ

İSMAİL ÇELİK

SELİM KAPUR

JOHN RYAN

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Clay Minerals, Ca/Mg Ratio and Fe-Al-Oxides in Relation to Structural Stability, Hydraulic Conductivity and Soil Erosion in Southeastern Turkey

Kadir YILMAZ*

Kahramanmaraş Sütçü İmam University, Department of Soil Science, Faculty of Agriculture, Kahramanmaraş - TURKEY

İsmail ÇELİK, Selim KAPUR

Çukurova University, Department of Soil Science, Faculty of Agriculture, 01330, Adana - TURKEY

John RYAN

International Center for Agricultural Research in the Dry Areas, P.O. Box 5466, Aleppo - SYRIA

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Abstract: Studies of clay mineralogy and related chemical composition are rarely connected with implications for soil management in the field. However, this study attempts to manifest the practical utilization of analytical data for determining the susceptibility to soil erosion. The data obtained involve the determination of clay mineral properties, calcium/magnesium ratios, and free aluminum (Al) and iron (Fe) oxides on structure stability, and hydraulic conductivity properties. Nine representative soil pedons developed on serpentine, limestone, and basalt parent materials were selected for the study. The soils were initially grouped into 3 according to their structural stability values. Group 1 soils had the lowest structural stability, highest smectite/kaolinite ratios, and shallow profile depths with the lowest Ca^{2+}/Mg^{2+} ratios. Group 2 soils had moderate structural stability and smectite/kaolinite ratios with moderate profile depths and the highest Ca^{2+}/Mg^{2+} ratios. Group 3 soils had the highest structural stability values, the lowest smectite/kaolinite ratios with deep profiles, moderate Ca^{2+}/Mg^{2+} ratios, and the highest free Al-Fe oxide contents with kaolinite being the dominant clay mineral, whereas smectite was dominant in Groups 1 and 2. Thus, the significance of smectite/kaolinite ratios for structural stability studies in soils, and Ca^{2+} and Mg^{2+} contents, Ca^{2+}/Mg^{2+} ratios, and free Al-Fe oxides are indices reflecting erodibility (such as the shallow Group 1 soils) that should be considered more susceptible to erosion.

Key Words: Clay minerals, structural stability, hydraulic conductivity, erosion, calcium/magnesium ratio.

Kil Mineralleri, Ca/Mg Oranı ve Fe, Al Oksitlerin Strüktür Stabilesi, Hidrolik İletkenlik ve Erozyon İlişkileri

Özet: Toprakların kil mineralojileri ve kimyasal yapıları ile ilgili çalışmalar, toprak yönetimi çalışmalarıyla çok seyrek olarak ilişkilendirilmişlerdir. Bu bağlamda, çalışılan toprakların erozyona duyarlılıklarının saptanması amaçlanarak, toprakların kil mineralleri özellikleri ve kalsiyum/magnezyum oranları ile serbest alüminyum ve demir içeriklerinin strüktür stabilesi ve hidrolik iletkenlikleri ile ilişkileri araştırılmıştır. Bu amaçla farklı ana materyaller üzerinde oluşmuş topraklar çalışmada kullanılmışlardır. Bunlar serpantin, kireçtaşı ve bazalt ana materyalleri üzerinde oluşmuş topraklardır. İncelenen topraklar strüktür stabilesine göre üç grupta yer almaktadırlar. İlk grup topraklar sıg olup, en düşük strüktür stabilesine, en yüksek smektit/kaolinit oranına ve en düşük Ca^{2+}/Mg^{2+} oranına sahiptirler. Buna karşın orta derinlikteki ikinci grup topraklar orta düzeyde strüktür stabilesine ve smektit/kaolinit oranıyla birlikte en yüksek Ca^{2+}/Mg^{2+} oranına sahiptirler. Derin profilli üçüncü grup topraklar ise en yüksek strüktür stabilesine, en düşük smektit/kaolinit oranına, orta düzeyde Ca^{2+}/Mg^{2+} oranına ve en yüksek Al-Fe oksit içeriğine sahiptirler. Birinci ve ikinci grup topraklarda baskın kil minerali smektit olup, üçüncü grup topraklarda baskın kil minerali kaolinitir. Elde edilen bulgularda, toprakların strüktür stabilesinde; smektit/kaolinit oranının, Ca^{2+} , Mg^{2+} içeriğinin, Ca^{2+}/Mg^{2+} oranının ve Al-Fe oksit içeriğinin önemli olduğu saptanmıştır. Bu ölçütler toprakların erozyon ile aşınabilirliği üzerine önemli etki ettiğinden, sıg profilli birinci grup toprakların erozyona daha duyarlı olmaları nedeniyle, yönetim uygulamalarının dikkatle hazırlanmaları gerekliliğini ortaya koymaktadır.

Anahtar Sözcükler: Kil mineralleri, strüktür stabilesi, hidrolik iletkenlik, erozyon, kalsiyum /magnezyum oranı.

*Correspondence to: kyilmaz@ksu.edu.tr

Introduction

The chemical and mineralogical compositions of soil materials have a particular influence on the physical properties and soil erodibility of soils in dry climatic conditions (Birkeland, 1984; Reichert and Norton, 1994). An increase in clay does not always result in increased stability. While the clay mineral content is an important factor in aggregation, its influence is modified by the stability of high-clay soils, which depends on the physical-chemical properties of the clay (Warkentin, 1982; Reichert and Norton, 1994). Smectitic clays are more dispersible than kaolinitic clays (Goldberg and Glaubig, 1987) as well as illitic and kaolinitic soils, which contain small amounts of smectite that may be dispersible and as susceptible to sealing as smectitic soils (Stern et al., 1991). Kaolinitic soils have the greatest aggregate stability the montmorillonitic soils the lowest. The greater dispersivity of montmorillonite compared with that of kaolinite decreases the aggregate stability of montmorillonitic soils.

Soil loss through erosion is significantly lowest in the kaolinitic, highest in the montmorillonitic, and intermediate in the non-phyllsilicate soils. Kaolinitic soils, with the lowest soil loss, high aggregate stability, and low soil detachment and runoff transport capacity, are in contrast to montmorillonitic soils, with the lowest aggregate stability and the highest runoff, showing the greatest soil loss. For non-phyllsilicate soils, their intermediate aggregate stability and high runoff rates accounted for the intermediate material losses from these soils (Wakindiki and Ben-Hur, 2002). Six et al. (2000) indicated that free oxides and kaolinite clay minerals are important factors for the stability of soil aggregates. Laboratory studies using synthetic oxide precipitates have shown that Al and Fe oxyhydroxides promote aggregation (Oades, 1984). The structural stability shows the resistance of aggregates to breakdown in water and other external factors. Degradation of the soil structure decreases water permeability, reduces the biomass productivity of the soil, and increases erosivity. Shainberg and Singer (1991) showed that dispersion and deposition of swelling clays in narrow necks of conducting pores reduced the soil's hydraulic conductivity.

Dontsova and Norton (2002) demonstrated that high Mg^{2+} contents had adverse effects on soil structure and that the Mg^{2+} ion had less flocculating effects on soil clays than Ca^{2+} due to its larger hydrated radius; they also

found a significant negative relationship between the fraction of Mg^{2+} on the exchange sites and in the solution and the optical transmittance of the clay suspensions, indicating a lesser degree of flocculation of Mg^{2+} saturated clay. In addition, soil loss was increased significantly by Mg^{2+} , suggesting that erosion rates increased due to increasing soil erodibility and runoff as a result of exchangeable Mg^{2+} having contributed to surface sealing.

The objectives of this study were to determine the effects of (i) clay mineral properties, (ii) Ca^{2+}/Mg^{2+} ratio, and (iii) free oxides on structure stability, hydraulic conductivity, and erosion of a range of soils varying in clay mineral type and contents in southeastern Turkey.

Materials and Methods

The soils selected were high (Group 1, Profiles: 1, 2 and 3), moderate (Group 2, Profiles: 4, 5 and 6) and low (Group 3, Profiles: 7, 8 and 9) in smectite/kaolinite ratio. Nine representative soil pedons with different clay contents, and varying in Ca^{2+} , Mg^{2+} , Al-Fe free oxides and soil depth, were selected on serpentine (shallow) (55 cm) (Group 1), limestone (moderately deep) (80 cm) (Group 2) and basalt (deep) (123 cm) (Group 3) parent materials in southeastern Turkey. These profiles were developed under similar topography, vegetation, and climatic conditions.

Soil pH was determined in 1:2.5 soil/water suspensions (McLean, 1982). Exchangeable cations and cation exchange capacity (CEC) were determined by the sodium-ammonium acetate method and analyzed by atomic absorption spectrophotometry (Soil Survey Staff, 1993). Particle size distribution was determined by the hydrometer method (Bouyoucus, 1951). Aggregate analysis was performed on disturbed soil samples sieved through 4-mm mesh screens under air-dry conditions. Undisturbed soil samples of about 100 cm³ were used for the measurements of bulk density, hydraulic conductivity, and porosity. The dry bulk density, porosity and structural stability of aggregates were determined by the methods described by Blake and Hartge (1986), Danielson and Sutherland (1986) and Leo (1963), respectively. Saturated hydraulic conductivity was determined using undisturbed soil samples of 100 cm³ volume (Klute and Dirksen, 1986). The total porosity was determined in undisturbed water saturated samples of

100 cm³. Micropores were measured by determining the volumetric water contents, using a pressure membrane apparatus at field capacity. Macropores were calculated as the difference between the total porosity and micropores.

The total carbonate contents were measured using a Scheibler calcimeter (Allison and Moodie, 1965). Organic matter was determined by the Walkley-Black wet oxidation method (Allison, 1965). For the determination of oxides (Al₂O₃, Fe₂O₃) soil samples (<2 mm) were treated with citrate-bicarbonate-dithionite (CBD) (Jackson, 1969). Aluminum and iron oxides were determined using the methods described in Jackson (1969) and Hsu (1963), respectively.

Clay minerals were determined in surface and subsurface horizons of all the profiles. The soil samples for mineralogical analysis were pre-treated with 1 N NaOAc, adjusted to pH 5, to remove carbonates, and with 30% H₂O₂ to remove organic matter, and with sodium dithionite-citrate-bicarbonate to remove Si-Al-Fe oxides (Jackson, 1969). The soils were then adjusted to pH 9.5 with 1 M Na₂CO₃ for dispersion. The sand fraction was separated by wet sieving, and clay and silt fractions were separated by sedimentation and decantation (Jackson,

1969). Diffractograms were obtained from Mg- and K-saturated clay slides by scanning from 3 to 13 2 θ , with nickel-filtered Cu K α radiation using a Philips X-ray diffractometer (Jackson, 1969). The diffraction intensity of the clay minerals was determined by calculating the peak areas. Vermiculite minerals were determined by the differences between Mg- and K-saturated clay slides at the 10 Å peak. The multiplication factors determined by Yılmaz (1990), and Yılmaz and Sayın (1998) for the Harran and Çukurova Plain soils, respectively, were used for quantitative clay analysis. According to both studies, the multiplication factors were 3.37 for smectite-palygorskite, 2.25 for smectite-illite and 3.29 for smectite-kaolinite. Duncan's multiple range statistical tests were used for comparing the means (Hays, 1988).

Results and Discussion

The physical, chemical and mineralogical distributions of the soils are presented in Tables 1, 2 and 3, respectively. For the 9 soils studied, the structural stability values were divided into 3 groups. Group 1 soils had the lowest structural stability, whereas Group 2 and Group 3 soils had intermediate and the highest values

Table 1. The physical properties of the soils.

Levels	Particle Size Distribution (%)			Bulk Density (Mg m ⁻³)	Hydraulic Conductivity (cm h ⁻¹)	Porosity (%)			Structural Stability
	Sand	Silt	Clay			Total	Micro	Macro	
GROUP 1 (Smectite/Kaolinite: 7.81)									
Max.	44	40	37	1.41	3.3	69	40	34	36
Min.	27	29	25	1.00	0.7	54	35	18	21
Mean	33a	34	33b	1.15	1.8a	62a	37	24a	27b
GROUP 2 (Smectite/Kaolinite: 1.26)									
Max.	17	36	65	1.26	2.3	66	40	28	66
Min.	6	27	47	1.02	0.2	55	33	17	42
Mean	10b	31	59a	1.13	1.0b	62a	38	24a	56a
GROUP 3 (Smectite/Kaolinite: 0.49)									
Max.	12	39	64	1.55	3.4	67	50	28	69
Min.	7	28	49	1.04	0.1	44	30	8	53
Mean	9b	32	59a	1.27	1.2b	55b	40	16b	62a
	***	NS	***	NS	***	*	NS	*	***

Mean separation within columns by Duncan's multiple range tests, $P \leq 0.05$

NS, ***, **, *Non-significant or significant at $P \leq .001$, 0.01 and 0.05, respectively

Table 2. The chemical properties of the soils.

Levels	pH (1:2.5)	Organic Matter	CaCO ₃	Free Al ₂ O ₃	Free Fe ₂ O ₃	CEC (cmol kg ⁻¹)	Exchangeable Cations (cmol kg ⁻¹)				Ca ²⁺ /Mg ²⁺
							Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	
(%)											
GROUP 1 (Smectite/Kaolinite: 7.81)											
Max.	7.1	4.3	3.5	2.71	0.80	35.3	0.14	1.70	11.08	28.37	1.03
Min.	6.8	1.2	0.3	1.11	0.57	19.3	0.04	0.36	4.05	10.73	0.23
Mean	6.9ab	2.4	1.1b	1.88	0.63	23.7b	0.07	0.76	7.26c	15.64a	0.53b
GROUP 2 (Smectite/Kaolinite: 1.26)											
Max.	7.7	3.4	48.1	2.46	0.96	64.2	0.08	1.78	58.28	8.64	15.34
Min.	7.5	1.4	6.5	0.43	0.46	45.1	0.03	0.52	41.38	2.70	4.88
Mean	7.6a	2.4	17.6a	1.59	0.61	56.5a	0.05	1.15	49.63a	5.69b	10.41a
GROUP 3 (Smectite/Kaolinite: 0.49)											
Max.	7.5	3.2	3.7	5.01	1.22	66.7	0.08	1.20	54.10	11.61	4.93
Min.	5.2	0.8	0.2	0.73	0.30	10.3	0.05	0.17	6.23	2.83	0.82
Mean	6.5b	1.9	1.2b	2.49	0.70	33.1b	0.07	0.88	25.09b	7.03b	3.08b
	**	NS	***	NS	NS	**	NS	NS	***	**	***

Mean separation within columns by Duncan's multiple range tests, P ≤ 0.05
 NS, ***, **, *Non-significant or significant at P ≤ 0.001, 0.01 and 0.05, respectively

Table 3. The mineralogical distributions of the soils.

Levels	Profile Depth (cm)	Clay Fraction				
		Smectite	Paligorskite	Illite	Kaolinite	Vermiculite
(%)						
GROUP 1 (Smectite/Kaolinite: 7.81)						
Max	65	18.58	4.85	3.50	2.58	1.39
Min	43	10.56	3.13	1.40	1.53	0.73
Mean	55	16.01a	3.72c	2.45c	2.05c	1.15b
GROUP 2 (Smectite/Kaolinite: 1.26)						
Max	105	17.90	12.74	8.98	12.19	7.56
Min	65	11.14	11.27	5.37	9.78	2.07
Mean	80	13.98a	11.99b	7.12b	11.09b	4.62a
GROUP 3 (Smectite/Kaolinite: 0.49)						
Max	150	8.48	15.97	15.95	16.88	4.62
Min	100	5.38	12.40	9.89	10.63	2.04
Mean	123	7.05b	14.11a	13.51a	14.37a	3.35a
		***	***	***	***	**

Mean separation within columns by Duncan's multiple range tests, P ≤ 0.05
 NS, ***, **, *Non-significant or significant at P ≤ 0.001, 0.01 and 0.05, respectively

(Table 1). The soils with the highest structural stability contained the highest kaolinite content and the lowest smectite/kaolinite ratio (Table 3). Group 1 soils were determined to have the lowest structural stability due to the highest smectite/kaolinite ratios and the lowest $\text{Ca}^{2+}/\text{Mg}^{2+}$ rates. In addition, the coarser textures of Group 1 soils most probably contributed to the development of low structural stabilities. The lowest structural stability values of Group 1 soils were indicated by the coarse textures and low $\text{Ca}^{2+}/\text{Mg}^{2+}$ rates (Table 2) and also shown by the highly negative correlation between structural stability and sand, and the positive clay content (Figures 1a,b). Similarly, Kemper and Koch

(1966) found that aggregate stability increased with increasing clay contents.

However, an increase in clay does not always yield an increase in stability, since the clay mineral content of a soil is an important factor in aggregation, and the stability of high-clay soils depends on the physical-chemical properties of the clays (Warkentin, 1982). A significant positive correlation was found between kaolinite contents and structural stability, whereas significant negative correlations were found between smectite contents and structural stability, and between smectite/kaolinite ratios and structural stability (Figures 1c,d,e). These indicated that clay types and contents of the investigated soils had

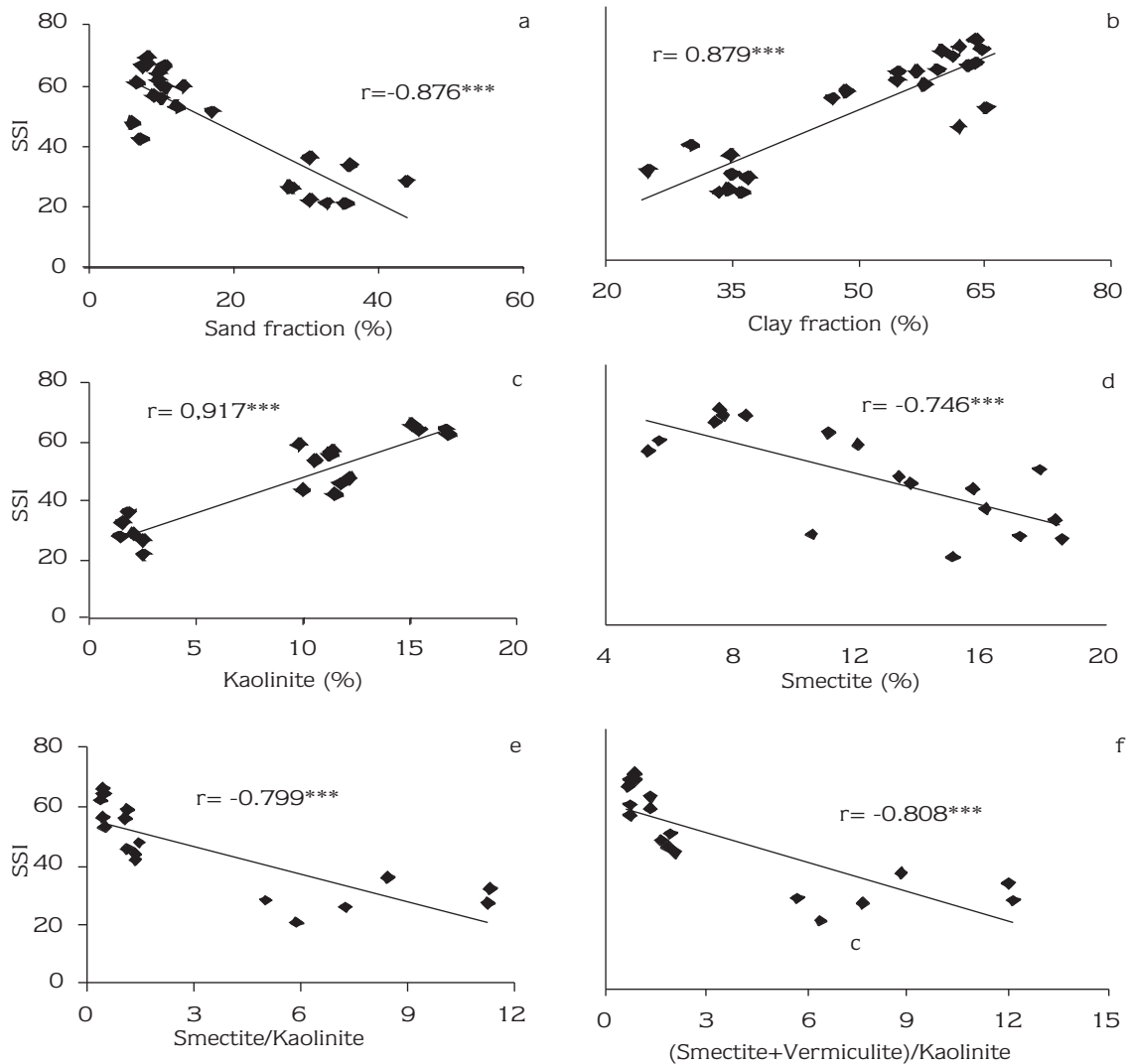


Figure 1. The relationship between clay types and structural stability index (SSI).

important effects on structural stability. Although the organic matter content and soil texture of Group 2 and Group 3 soils were similar, their structural stability values were significantly different. Hence, Group 2 soils had a higher cation exchange capacity and pH because of higher smectite contents than Group 3 soils, which most probably form at high pH and cation exchange capacity, whereas kaolinite forms at lower pH conditions and low cation exchange capacity (Sayın, 1999).

A significant negative correlation was also found between smectite + vermiculite/kaolinite ratios and structural stability (Figure 1f). Thus, swelling smectite and vermiculite clays had dispersivity effects on soil structure, whereas kaolinite had a positive effect on structure due to its low swelling capacity; thus, the former was more susceptible to erosion as shown earlier by Reichert and Norton (1994), Singer (1994), Buhmann et al. (1996), Seta and Karathanasis (1996), and Wakindiki and Ben-Hur (2002). Similar results to this paper were shown by Singer (1994), indicating decreasing aggregate stabilities with increasing smectite and inversely with kaolinite content. The high flocculation capacity of kaolinite is due to the electrostatic interaction between the positive charges on the edges of the clay platelets and the negative charges in the body of the crystal (El-Swaify, 1980; Dixon, 1989).

In addition to the stabilizing effects of Fe and Al oxides and kaolinite by themselves, interactions between the 2 components have been reported (El-Swaify, 1980; Seta and Karathanasis, 1996). Group 3 soils have the highest free Al_2O_3 and Fe_2O_3 contents, positively affecting structure stability, as indicated by Reichert and Norton (1994), who determined the highest increase in aggregate stability in soils rich in kaolinite and Fe-Al

oxyhydroxides. Further adsorption of Fe and Al oxides on the few negatively charged sites of kaolinite reduces its cation exchange capacity and increases its positive charge (Dixon, 1989). Therefore, this interaction between Fe and Al oxides and kaolinite is synergistic and increases the aggregation potential of kaolinite.

Since Group 3 soils were highly weathered, kaolinite was the dominant clay mineral (Table 3), and Fe-Al free oxides of this soil were higher than those of Group 1 or 2 soils. The high Fe-Al free oxides and dominant kaolinite clay mineral of Group 3 soils caused increasing structural stability. In addition, the reason for the high structure stability of Group 2 soils may be the high CaCO_3 contents correlating with the structural stability (Table 2; Figure 2a) increasing with soil depth. Group 3 soils, with the highest mean soil depth (123 cm), were determined to have the highest structural stability, whereas Group 2 soils, with moderate depth (80 cm), were determined to have moderately high structural stabilities, with the lowest values obtained in Group 1 soils with probable high soil losses (55 cm) (Table 2). Thus, Group 1 soils are more vulnerable to erosion than the soils of Groups 2 and 3, with their corresponding lowest structural stability and thinner/shallower A and B horizons along with the highest smectite/kaolinite contents compared with Groups 2 and 3.

Significant statistical variances were determined between the $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratios and the soil groups (Table 2). The negative correlation between the structure stability and Mg^{2+} contents (Figure 2b), and the positive correlation of the $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratios (Figure 2c) were similar to Dontsova and Norton's (2002) low $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratios and high Mg^{2+} contents causing dispersion in soils that had different mineralogical compositions. For all soil

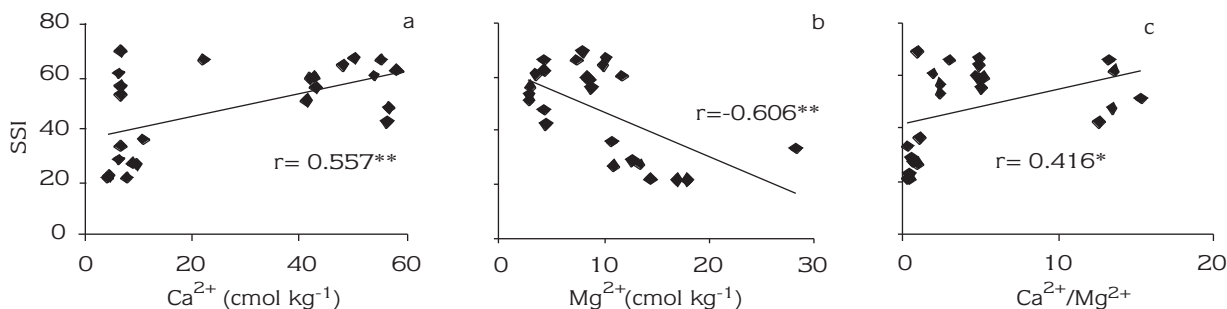


Figure 2. The relationship between exchangeable cations and structural stability index (SSI).

clays, a negative linear relationship was determined between the Mg^{2+} percentage in solution and the optical transmittance of clay suspension as an indicator of clay flocculation, documenting increased surface sealing and erosion (Dontsova and Norton, 2002). Keren (1991) also established that Mg^{2+} in soil could affect erosion rates, explained by the hydration number of the Mg^{2+} ion being about 50% greater than that of the Ca^{2+} ion.

Group 1 soil had the lowest Ca^{2+}/Mg^{2+} ratios and highest Mg^{2+} contents along with dominant smectite at the surface horizons compared with the Group 2 and 3 soils. Thus, the low Ca^{2+}/Mg^{2+} ratios, high Mg^{2+} contents, and dominant smectite caused dispersion in Group 1 soils. Saturated hydraulic conductivities of the surface soils of Group 1 (0.73 cm h^{-1}) were 3 to 4 times lower than those of the subsurface horizons (2.36 cm h^{-1}) (Figure 3). This is most probably due to the dominant smectite and Mg^{2+} contents, as well as the low Ca^{2+}/Mg^{2+} ratios in Group 1 soils.

Saturated hydraulic conductivity values were higher in Group 1 soils that have coarse texture and macroporosity than the Group 2 and 3 soils that have a fine texture (Table 1). Texture variation between Group 1 and Groups 2 and 3 was found at the 0.1% significance level. Hydraulic conductivities of Group 2 and Group 3 soils were present in the same statistical group and similar

texture, whereas the hydraulic conductivity of Group 3 soils was higher than that of Group 2 soils (Table 1). The structural stability variation with the organic matter contents was non-significant in all soils, indicating the significance of soil texture and clay types on the hydraulic conductivity of soils. Group 1 soils had higher hydraulic conductivity values than Group 2 and Group 3 soils due to the coarser textures and higher macroporosity of the latter.

The differences in the hydraulic conductivities of Group 2 and Group 3 soils with similar texture were explained by the differences in clay mineralogy, free Al-Fe oxide levels and structural stability. Namely, Group 2 soils had higher smectite and smectite/kaolinite ratios, and lower free Al-Fe oxides and structural stability than Group 3 soils. The higher smectite contents were negatively associated with the hydraulic conductivity of Group 2 soils. Group 3 soils had higher kaolinite contents and lower smectite/kaolinite ratios with higher Al-Fe oxide contents than Group 2 soils, and accordingly higher hydraulic conductivity and structural stability values than Group 2 soils. Similar results between the clay mineralogy and hydraulic conductivity were found by Romkens et al. (1995), and Mermut et al. (1997), concluding that the presence of more smectite clay in the soil resulted in a rapidly decreasing infiltration rate despite the high organic matter contents.

Thus, this study, together with previous ones, revealed that the high hydraulic conductivity of Group 1 soils is associated with coarser textures, whereas, as in Group 1, the higher hydraulic conductivity values of soil groups with similar textures is explained by the differences in the clay types. However, the values of hydraulic conductivity and structural stability of Group 1 and Group 2 soils varied despite their dominant clay types. This was most probably due to differences in the texture of the soils of Groups 1 and 2.

The bulk density of the Group 1 and Group 2 soils was similar, unlike that of Group 3 soils. The lowest organic matter, total porosity and highest free Fe_2O_3 were in Group 3 soils that had the greatest bulk density. The significant correlation found between the bulk density and organic matter, total porosity and free Fe_2O_3 (Figures 4a,b,c) suggests that the bulk density of the soils was reduced by the organic matter content of the soils and increased by free Fe_2O_3 . High bulk densities indicated compaction and decreasing macroporosity in the soils

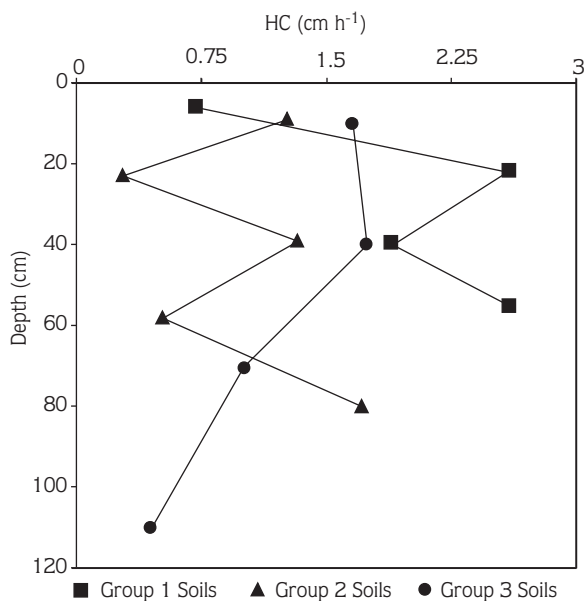


Figure 3. Variation in hydraulic conductivity (HC) with soil depth.

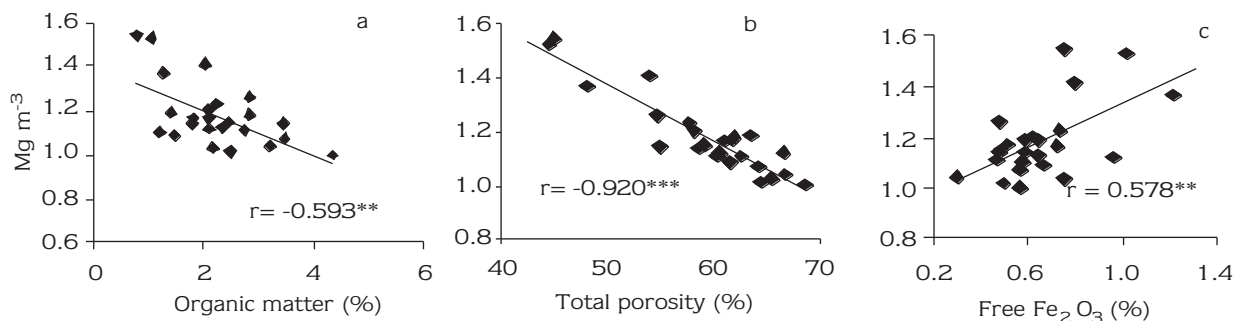


Figure 4. The relationship between bulk density, organic matter, total porosity, and iron oxides.

(Table 1). Zebarth et al. (1999) and Aggelides and Londra (2000) found that increasing organic matter caused a decrease in bulk density and that organic matter contents, free Fe_2O_3 , and mineralogical compositions affected the bulk densities of similar soils.

Conclusion

The structural stability values of the 9 soils studied from southeastern Turkey were negatively affected by an increasing smectite/kaolinite ratio. Statistically significant positive relationships were found between structural stability and kaolinite, and there was a negative relationship with smectite. The structural stability values

of the soils were also positively affected by the increasing ratio of $\text{Ca}^{2+}/\text{Mg}^{2+}$, and Al-Fe oxide contents, i.e. significant positive relationships were determined with increasing Ca^{2+} and Al-Fe oxides and negative relationships with increasing Mg^{2+} . These point to the need for utmost care against erosion in the management of shallow soils such as Group 1.

This study also revealed that high hydraulic conductivity is associated with coarser textures, differences in clay mineralogy, free Al-Fe oxide levels and structural stability. The lowest amounts of palygorskite, illite and kaolinite corresponding to the highest hydraulic conductivity values may point out some relations to be considered for sustainable soil and water management.

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