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Effects of Exchangeable Ca:Mg Ratio on Soil Clay Flocculation, Infiltration and Erosion

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ABSTRACT

Soil erosion due to surface sealing is detrimental to soil resources and agricultural production. We would like to verify if Mg could cause surface sealing in Midwestern USA soils. It is generally accepted for sodic soils that Mg can have a negative effect on soil physical properties when its concentration is relatively high compared to Ca. However, for soils that do not have sodic properties there is also a possibility for deterioration of soil structure due to high Mg with consequent surface sealing, decreased infiltration, increased runoff and erosion during rainfall events. High Mg concentration in the soil solution can be natural or induced by input of dolomitic limestone. In this paper, we studied the influence of modified Ca:Mg ratios on surface sealing of four soils varying in organic matter content, clay content and mineralogy from the Midwestern USA. In a laboratory experiment flocculation behaviors of soil clays were studied at different Ca:Mg ratios and solution electrolyte. We also modified Ca:Mg ratios of bulk soils and measured infiltration, runoff and soil detachment under simulated rainfall. We showed that Mg has a specific effect on soil clay flocculation and surface sealing due to hydration behavior differing from Ca. There was a highly significant linear relationship between Ca percentage on the clay surface and in solution and optical transmittance of clay suspension as an indicator of clay flocculation. In rainfall experiments, Ca-treated well-structured soils (two out of four soils used) had final infiltration rates double that of Mg-treated soils, total infiltration was increased 20 to 100%. The Ca treatment decreased soil losses to half of those from Mg treatment. Thin sections of the surface seals showed evidence of greater aggregate destruction and clay translocation under the Mg treatment. This research presents evidence that it is beneficial to manage soils to high Ca:Mg ratio if they are prone to sealing.

INTRODUCTION

Liming is a customary field procedure on naturally acidic soils of the Midwest US, the main corn and soybean-producing region of the United States. There are a number of different materials that can be used for liming, but the most common ones are limestone containing calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$). Dolomite is widespread, less expensive, and has a greater acid neutralization capacity than calcitic limestones. Therefore, farmers often prefer it. However, application of dolomite can be detrimental to soil physical properties, because it introduces Mg into the soil system - both in solution and on exchange sites. Mg is believed to cause dispersion of soil colloids and enhance surface sealing during rainfall (Curtin et al., 1994; Keren, 1991). Considering the high rainfall intensity and often clayey soils found in the Midwest, increased surface sealing can cause a wide range of problems, such as delayed emergence due to lack of oxygen, runoff, erosion and sedimentation. Negative effects of Mg (whether indigenous or applied with dolomite) on soil structure are well established for sodic soils, and several soil classification systems recognize sodicity due to Mg (Panov, 1989; Soil Survey Staff, 1996). However, it is not very well recognized for the Midwest, with no salinity problems and few sodic soils. Still, the possibility of soil physical deterioration with Mg on exchange sites is high. A possible reason for a specific Mg effect is that the hydration energy of Mg is greater than Ca, therefore, the hydration radius is also greater (Bohn et al., 1985, p. 29). This causes a larger separation distance between clay layers and less attraction between them to cause flocculation. Norton and Dontsova (1998) reported that midwestern soils with a high percentage of Mg on exchange sites had deteriorated soil structural properties and lower infiltration rates during simulated rainfall compared to similar soils high in Ca. The aim of the reported study is to separate effect of Mg on soils' interaction with rainwater by treating same soil to different Ca:Mg ratios.

The objective of this study was to determine effect of exchangeable Ca and Mg on flocculation of soil clays, soil infiltration, runoff and erosion under simulated rainfall using four soils representative of the United States corn belt.

Our hypothesis is that Mg on exchange sites will increase dispersion of soil clays and consequently decrease infiltration and increase erosion.

MATERIALS AND METHODS

Surface horizons of four previously used soils (Norton and Dontsova, 1998) were used for this study: Blount, fine, illitic, mesic Aeric Epiaqualfs; Catlin, fine-silty, mixed, superactive, mesic Oxyaquic Argiudolls; Fayette, fine-silty, mixed, superactive, mesic Typic Hapludalfs; and Miami, fine-loamy, mixed, active, mesic Oxyaquic Hapludalfs. Classification given is according to U.S. Soil Taxonomy system (Soil Survey Staff, 1996). All are major soils typical

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Table 1. Selected physical and chemical properties of the studied soils.†

Soil	Texture	CEC	pH$_w$	OM	Clay	Sand	Silt	MWD	EC
		cmol$_c$ kg^{-1}		----------	---------- %	----------		mm	dS m^{-1}
Blount	loam (heavy)	21.7	6.0	2.4	25.4	30.6	44.0	1.12	1.7
Catlin	silt loam	23.5	7.1	3.9	18.1	23.4	58.5	1.48	0.6
Fayette	silty clay loam	22.7	5.7	1.4	29.1	5.7	65.2	0.53	1.5
Miami	silt loam	17.4	5.6	2.0	18.5	10.4	71.0	0.45	0.8

† CEC=cation exchange capacity; pH$_w$=pH in DI water at 1:1 ratio; OM=organic matter; MWD=mean weight diameter, wet sieving; EC=electrical conductivity of saturated extract.

of the US Corn Belt. Selected chemical and physical properties of original soils (Table 1) were determined using standard methods as described in Franzmeier et al. (1977). Clay fraction of Fayette soil contained large quantity of smectite, Blount clay was dominated by illite, two other soils had mixed mineralogy. Complete description of soil properties and used procedures and methods can be found in Dontsova (1998).

Flocculation studies were done to study the behavior of soil clays under the influence of different cations. The clay fraction of the soil (< 2 μm) was separated using an automatic fractionator, where no chemical dispersing agent was used and organic matter was not destroyed. Two hundred and fifty milligram aliquots of clay were exchanged to five Ca:Mg ratios (0:100, 25:75, 50:50, 75:25 and 100:0) using 1M solutions of $CaCl_2$:$MgCl_2$ and then washed free of electrolytes. Once the clay samples were ready, $CaSO_4$:$MgSO_4$ solutions of identical electrolyte concentration but with different Ca:Mg ratios were added. Samples were equilibrated overnight and left undisturbed to settle for 24 hours. Then to determine flocculation, transmittance of suspension at 3.5 cm depth was measured using a spectrophotometer with light set at 420 nm wavelength. Analysis of variance for percent optical transmittance was performed using the SAS ANOVA procedure (The SAS Institute, 1990). Following regression using the treatment means, the 95% confidence interval of the predicted means were adjusted for the ANOVA error variance.

A second study was performed to investigate the preference of soils for Ca or Mg in Ca:Mg exchange. For this study, 200 g samples of whole soils were equilibrated with Ca:Mg solutions at target ratios using miscible displacement technique and Ca and Mg contents in the soil were measured by atomic absorption after extraction with neutral ammonium acetate solution. Vanselow selectivity coefficients were determined using TableCurve by Jandel Scientific (Jandel Scientific, 1992) by best fit of the following equation:

$$K_V = (s_{Mg} * c_{Ca}) / (c_{Mg} * s_{Ca}) \qquad [1]$$

where s is molar fraction of cation on soil and c is relative ionic concentration of cation in solution.

A third study used simulated rainfall to estimate infiltration, runoff and erosion of Ca and Mg treated soils. Bulk soils were exchanged to two Ca:Mg ratios – 100:0 and 0:100 – by leaching with Ca:Mg salt solutions. Soil was packed into small interrill plots (0.32 × 0.45 m), wetted to saturation, drained to 5 cm tension and set at 5 % slope. Rainfall was applied at 64 mm h^{-1} for 1 hour using an oscillating V-jet nozzle rainfall simulator (Neibling et al., 1981) and deionized water. Infiltration rate, runoff and soil loss were measured every five minutes. A t-test was used to find significant differences between the treatments at 95% and 90% levels.

Samples of soil crusts for thin sections were taken following the simulations to determine surface porosity. Kubiena pans, 10 cm long, 5 cm wide and 3 cm deep, were pushed into the soil after it was allowed to drain. Then the samples were air-dried for one week and dried in the oven at 105°C for another week. Dry samples were impregnated with Stotchast #3 epoxy resin under vacuum. One thin section (51x75 mm) was prepared for each treatment by Spectrum Petrographics Inc., Winston, OR.

RESULTS AND DISCUSSION

The percentage of Ca on the exchange sites and in solution had a significant influence on the flocculation of the clay fraction in all studied soils. The effect was clear and could be detected visually (Fig. 1). Results agreed with the findings of Curtin et al. (1994) for montmorillonitic soils and Emerson and Chi (1977) for specimen and soil illites. These authors explained the difference in behavior between Ca and Mg as due to a slightly greater hydrated radius of the Mg^{++} ion (0.47 vs. 0.42 nm) and consequently lower electrostatic force with which a hydrated Mg^{++} ion is held at the clay surface.

In our study, a highly significant positive linear relationship between the percentage of Ca in solution and that on exchange sites and light transmittance of clay suspensions as a measure of flocculation was found for all soils (Fig. 2). For the Blount soil a quadratic relationship was also significant indicating that the effect of Mg on dispersion was more pronounced the greater the fraction of the exchange sites was occupied by Mg ions. This behavior can possibly be due to the fact that its clay fraction was dominated by illite. Emerson and Chi (1977), who used illitic soils as well, established a similar trend. There was no threshold value of Ca:Mg ratio at which Mg had no specific effect on dispersion. It should be, however, remembered that Mg is an important macronutrient and plants require some amount of Mg for normal growth. According to Tisdale et al. (1993, p.298), generally, there is a possibility of Mg deficiency when Mg accounts for less than 10% of cation exchange capacity of the soil, but this number greatly depends on soil and crop type.

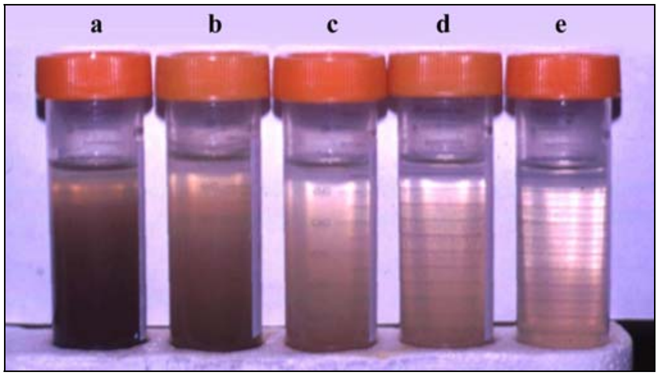


Figure 1. Photograph of the Catlin flocculation series after 24 hours of sedimentation. Treatments are a) 0:100, b) 25:75, c) 50:50, d) 75:25, and e) 100:0 ratios of Ca:Mg in 2.1 mmol L^{-1} solution of calcium:magnesium sulfate.

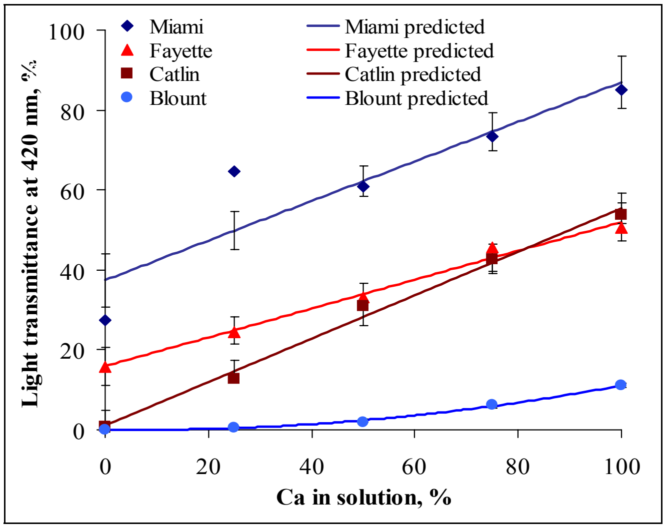


Figure 2. Relationship between clay flocculation as described by the percentage of light transmittance at 420 nm and percentage of Ca in solution for studied soils. Error bars equal one half of the least significant difference at probability level 0.05. Predicted means are significantly different where error bars do not overlap within one soil.

The Ca:Mg exchange studies indicated a preference for Ca in all studied soils. Vanselow selectivity coefficients of Mg over Ca differed between the soils, but were close to 0.5 on average. Soils by their preference for Ca can be ranked in the order Catlin ≥ Miami > Blount >> Fayette. Differences in preferential exchange between the soils can possibly be explained by different organic matter contents, since soils were arranged in organic matter in the same order Catlin >> Miami ≥ Blount > Fayette. The strong correlation between organic matter content and soils preference for Ca was also observed by Curtin et al. (1998). Mineralogical composition of the clays did not offer an explanation for their exchange behavior. A greater affinity of soils for Ca than Mg should not influence the results of the experiment, because soils were leached to contain no appreciable amount of Na or other ions. All differences between treatments should only be due to difference in the Ca:Mg ratio. On the other hand, availability of potassium and ammonium can be effected by a soil's preference for Ca and further study will be needed to explore how distribution of K between solution, exchangeable and non-exchangeable phases is influenced by the Ca:Mg ratio.

In rainfall simulation studies we observed decrease in infiltration rate with time. Catlin soil, unlike other studied soils, exhibited this behavior only after first 10 to 15 minutes during which time the considerable porosity of this soil was filled with water. Rainfall simulation studies showed that Mg had a specific effect on infiltration and erosion of stable soils. Ca-treated Catlin and Blount soils had respectively 1.8 and 2 times greater final infiltration rate than Mg-treated soil (Table 2, Fig. 3). Total infiltration was also significantly increased at 95% level for Blount soil (2.1 times) and at 90% level for Catlin soil (1.2 times). This effect can be attributed mostly to greater structural stability of Ca-saturated aggregates, because if some soluble salts were present in the surface layer of the soil in the beginning of the rainfall event they were washed out quickly by low-electrolyte rainwater. In soils, when ionic strength of the soil solution in the surface layer decreased, several processes of seal formation might have taken place. Low ionic strength directly can lead

Table 2. Final and total infiltration (I_f, I_t), runoff (R_f, R_t) and soil loss (S_f, S_t) for Ca and Mg treated soils.

Soil	Treatment	I_f mm h^{-1}	I_t mm	R_f mm h^{-1}	R_t mm	S_f kg m^{-2} h^{-1}	S_t kg m^{-2}
Blount	Ca	5.7 a	18.8 a	57.6 a†	43.3 b	0.2355 a†	0.1693 b
	Mg	2.8 b	9.2 b	62.7 a†	55.6 a	0.4687 a†	0.3689 a
Catlin	Ca	31.9 a	45.0 a†	29.9 b	12.2 b	0.1170 a	0.0800 a
	Mg	17.7 b	37.9 a†	48.6 a	25.9 a	0.3808 a	0.1377 a
Fayette	Ca	3.8 a	12.3 a	55.6 a	47.5 a	0.3394 a†	0.2715 a†
	Mg	3.0 a	12.4 a	61.8 a	51.4 a	0.5038 a†	0.3749 a†
Miami	Ca	2.3 a	3.9 a	58.4 a	57.0 a	0.4954 a	0.5346 a
	Mg	2.6 a	3.9 a	61.9 a	60.1 a	0.4350 a	0.4672 a

I_f=final infiltration rate, I_t=total infiltration, R_f=final runoff rate, R_t=total runoff, S_f=final soil loss rate, S_t=total soil loss.

Means followed by the same letter in the column within one soil are not significantly different by the t-test at α=0.05. If letter has † after it, means were different at α=0.1.

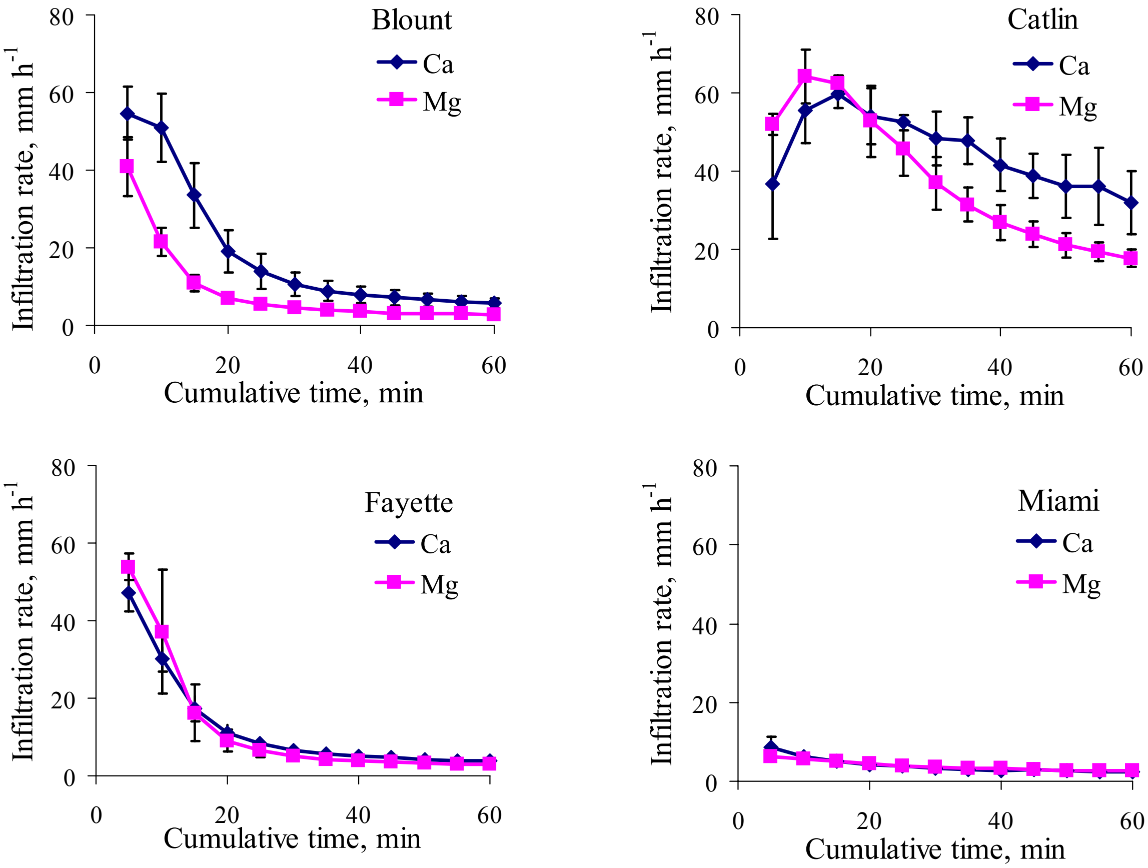


Figure 3. Infiltration rate (average of four replications) as a function of cumulative time for Ca- and Mg-saturated soils. Error bars equal one standard deviation.

to clay dispersion, but it may also enhance slaking and susceptibility of soil aggregates to raindrop impact through a decrease in stability of soil aggregates. Separated particles and smaller aggregates resulting from these processes will block pores and decrease infiltration. Swelling could also have been increased by the low concentration of electrolyte in the water. Expansion in volume associated with swelling will lead to decrease in pore diameter and infiltration rate. We expect that Ca can be more effective in preventing all of the listed processes than Mg, because of its smaller hydration number and, as showed in the preceding flocculation study, greater flocculating power. In agreement with the flocculation study, results of rainfall simulations for Blount and Catlin soils showed that surface sealing is less in Ca-saturated than in Mg-saturated soil. There was no significant difference in infiltration for Miami and Fayette soils in Ca and Mg-saturated plots. Lower aggregation of both soils or insufficiently long time of contact between soils and cation can explain this finding. However, greater flocculation in $CaSO_4$ than in $MgSO_4$ suggests that long-term effect of presence of Ca on exchange sites may lead to formation of stronger aggregates.

The total soil loss was significantly decreased by Ca-treatment at the 95% level in the Blount soil, and at the 90% level in Fayette (Table 2, Fig. 4). Mg-treated Catlin soil had a greater soil loss, but the difference was not statistically significant. The erosion for Miami soil treatments was essentially the same. Differences in final soil loss were not significant at the 95% level in all soils, but at the 90% level Ca-treated Blount and Fayette soils had a significant decrease in final soil loss compared to the Mg-treated soils. It is worth mentioning that for Fayette soil final runoff was 1.1 times greater, but final soil loss 1.5 times greater for Mg than for Ca-treated soil. This supports the hypothesis of Keren (1991), who suggested that Mg increases repulsion between clay tactoids and enhances erosion through redistribution of forces that act on soil particles.

Results were highly dependent on the degree of aggregation of the original soil. Better structured Blount and Catlin soils (mean weight diameter (MWD) of 1.12 and 1.48 mm respectively) showed bigger differences in infiltration between treatments, than soils with poorer structure - Miami and Fayette (MWD of 0.45 and 0.53 mm respectively). It is likely that less stable aggregates of these soils could not withstand the impact of raindrops, regardless of the treatment.

Intensity and kinetic energy of the rainfall were shown by Keren (1990) to affect soils' response to the Ca:Mg ratio: at higher intensities, differences between the treatments were decreased. One reason for not finding significant differences between some Ca- and Mg-treated soils in our study, which is contrary to results of Keren (1991), may be the greater

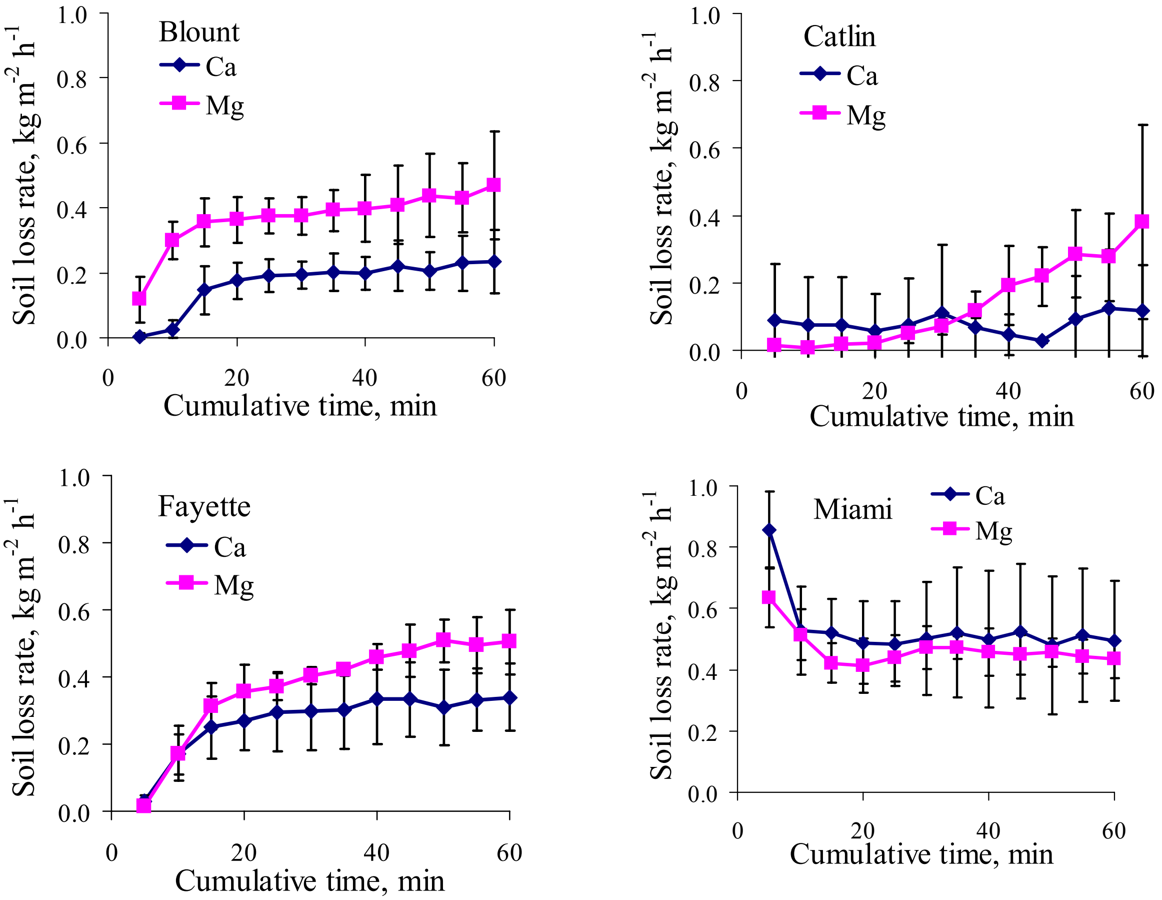
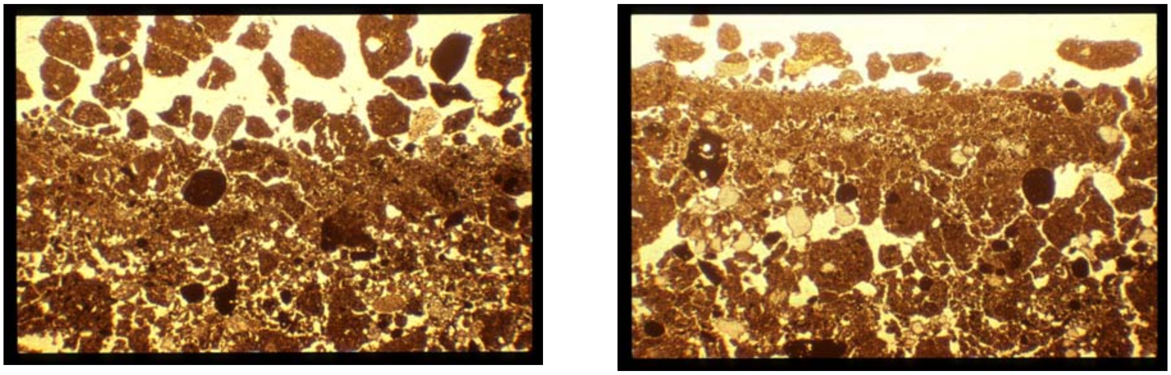


Figure 4. Soil loss rate (average of four replications) as a function of cumulative time for Ca- and Mg-saturated soils. Error bars equal one standard deviation.



a **b**

Figure 5. Photomicrographs of the Catlin soil treated with a) Ca and b) Mg. Frame width equals 11.5 mm. Pores are seen as yellow and aggregates as brown.

intensity and kinetic energy of the rainfall used in this study, i.e., 64 mm h^{-1} and 24 KJ m^{-3}. Keren (1991) operated at 33 mm h^{-1} and kinetic energy of 12.5 KJ m^{-3}. Levy et al. (1988) in rainfall simulations with 45 mm h^{-1} intensity and kinetic energy of 18 KJ m^{-3} also did not observe differences, even though differences were suggested by hydraulic conductivity studies on the same soils. At higher rainfall intensities chemical processes can become relatively less important compared to mechanical destruction of the aggregates by raindrop impact.

Another possible explanation for difference in results between our study and Keren (1991) might be in the way the soil was prepared. Keren (1991) in his studies washed the soil only once after equilibration with 0.1 mol L^{-1} $CaCl_2$:$MgCl_2$ solution which would yield a much greater electrolyte concentration in the soil solution than in this study.

The thin sections indicated that seal formation is more developed and the seal is more consolidated in Mg-saturated soil (Fig. 5).

CONCLUSIONS

The effects of Mg and Ca on clay flocculation and aggregate stability of soils during rainfall was studied for several major soils from the Midwest United States. It was found that Ca^{2+} ions were more effective than Mg^{2+} in aggregating soil clays. These results were supported by differences in infiltration and erosion between Ca and Mg treatment for two out of four studied soils.

Practically, this research provides further evidence to explain differences in infiltration by varying the Ca:Mg ratio. It can be used to prevent future problems through selection of appropriate liming material (dolomitic vs. calcitic limestones). To remediate an existing problem the application of gypsum ($CaSO_4*2H_2O$) as a source of electrolytes and Ca can be used. It has proved to be effective for studied soils on reducing erosion and improving water entry in an earlier study (Norton and Dontsova, 1998).

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