Effect of exchangeable Mg on saturated hydraulic conductivity, disaggregation and clay dispersion of disturbed soils

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Abstract

Different opinions exist regarding the specific effect of Mg on soil physical and chemical properties. We hypothesized that Mg^{2+}, compared with Ca^{2+}, reduces saturated hydraulic conductivity (K_s) via promoting clay swelling, disaggregation, and clay dispersion. Two soils (mixed, mesic Typic Hapludalfs) in packed soil columns were leached with either Ca- or Mg-containing solutions at the successive concentrations of 250, 10, 2, 0.5, and 0 mM. Critical flocculation concentration (CFC) in either Ca or Mg systems was determined with flocculation series tests. Aggregate stability and mean weight diameter (MWD) were assessed by wet-sieving. The CFCs were higher in Mg than in Ca for both soils, indicating that Mg is more dispersive than Ca. The MWDs measured using 1–2 mm aggregates of both soils were significantly larger for Ca-soils than for Mg-soils ($P = 0.05$). The K_{sr} (normalized with initial K_s) started to decline at higher concentrations for Mg than for Ca, and the reduction was much greater in Mg than in Ca above 0.5 mM. The K_{sr} and percent transmittance (inversely related to turbidity) of leachate at a given eluted pore volume following 'steady state' were higher in Ca than in Mg for both soils ($P = 0.1$), indicating lower permeability and more clay dispersion with the Mg treatment. Swelling and disaggregation, which reduced large pores, appeared to be the dominant process causing the rapid initial decline of K_{sr}. Clay dispersion and subsequent pore plugging became progressively important when electrolyte concentration was reduced to below CFCs. Published by Elsevier Science B.V.

Keywords: Hydraulic conductivity; Aggregate stability; Clay dispersion; Exchangeable Mg

1. Introduction

Calcium and Mg have, for practical purposes, generally been grouped together as similar ions in maintaining soil structure when quantifying sodicity of soils and irrigation waters (US Salinity Lab. Staff, 1954). However, it has long been suspected that Mg, compared with Ca, has deleterious effects on soil structure under certain circumstances. For example,

Quirk and Schofield (1955) observed that the saturated hydraulic conductivity (K_s) of Mg-saturated, illitic soil was much lower than that of Ca-saturated soil. McNeal et al. (1968) noticed that K_s was consistently lower in Na–Mg systems than in their Na–Ca counterparts.

A distinction has been made between a direct effect of Mg on decreasing soil structural stability, and an indirect effect of Mg on accumulation of Na on soil exchange sites (Curtin et al., 1994; Yousaf et al., 1987). The nature and extent of these effects may vary with clay type and electrolyte concentration. The direct effect, also termed a specific effect of

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Table 1
Selected chemical properties of Mg and Ca ions (from John Burgess (1988))

Ion	Ionic radius (nm)	Ionic potential (l/nm)	Hydration number	Hydration enthalpy (kJ/mol)	Std molal entropy (J/K mol)
Mg	0.065	30.77	12–14	− 1922	− 138
Ca	0.099	20.20	8–12	− 1592	− 53

Mg, appears to be significant for vermiculitic and illitic soils, but not for montmorillonitic soils (Emerson and Chi, 1977; Rahman and Rowell, 1979). This could be because clays vary in their affinities for Mg and differ in their dispersibilities in Mg systems. Montmorillonite showed a preference for Ca over Mg (Hunsaker and Pratt, 1971), while illite and vermiculite showed a preference for Mg over Ca (Peterson et al., 1965; Rahman and Rowell, 1979). Emerson and Chi (1977) reported that an illitic soil was more easily dispersed in Na–Mg systems than in Na–Ca systems. However, Rowell and Shainberg (1979) reported that Mg had a specific effect on hydraulic conductivity of a sodic soil containing montmorillonite and kaolinite when leached with deionized (DI) water. The indirect effect is caused by differences in relative affinity of the clay for Na when Mg, as compared to Ca, is the complementary cation (Curtin et al., 1994). A preference by soils for Ca over Mg could result in a higher exchangeable sodium concentration in Na–Mg systems than in Na–Ca systems.

Electrolyte concentration is another factor affecting the responses of soil to Mg. Rowell and Shainberg (1979) reported that Mg had no specific effect on K_s of a soil dominated by montmorillonite and kaolinite clay minerals when leached by solutions with electrolyte concentration >10 mmol$_c$/l, but Mg showed a specific effect when leached with distilled water. Shainberg et al. (1988) reached a similar conclusion using smectite-sand mixtures. Alperovitch et al. (1981) found that the specific effect of Mg was dependent on ability of soils to release electrolyte. They reported that Mg had no specific effect on hydraulic conductivity or clay dispersion in calcareous soils, whereas for well-weathered, non-calcareous soils, a specific effect existed.

There is no general consensus on the existence of a specific effect of Mg. This could be because the effect of Mg on clay behavior (i.e. dispersion and flocculation) may depend not only on soil clay mineralogy but also on electrolyte concentration of the soil. Further-

more, the presence of Na in soil systems often obscures the Mg effect. Yousaf et al. (1987) studied five arid soils and concluded that greater dispersibilities of these soils in Na–Mg systems than in Na–Ca systems were due to greater sodium adsorption ratios (SAR) in Na–Mg systems. The different opinions regarding the existence of a specific effect of Mg is partially caused by difficulties in properly separating out the Na effect. It may be easier to evaluate specific effects of Mg without the presence of Na.

With negligible energy input, disaggregation is predominantly caused by differential swelling, entrapped air, and spontaneous clay dispersion. However, opinions differ regarding the dominant mechanisms that cause marked reductions in K_s. McNeal et al. (1966) and Jayawardane and Beattie (1978) proposed that swelling of soils was the dominant mechanism causing reductions in K_s, whereas Abu-Sharar et al. (1987) concluded that aggregate failure was the major cause of such reductions. Frenkel et al. (1978) and Shainberg et al. (1981) reported that clay dispersion and subsequent plugging of conducting pores by dispersed clay particles were responsible for the dramatic reductions in K_s.

The differing effects of Ca and Mg ions on clay behavior may originate from their basic differences in chemical properties. The ionic radius of Mg is smaller than that of Ca, while the ionic potential and hydration number are greater for Mg than for Ca (Table 1). A larger hydration number means a larger hydration shell. Hydration enthalpy is more negative for Mg than for Ca, indicating a stronger coordination between Mg ions and the surrounding water molecules. Standard partial molal entropy is also smaller for Mg than for Ca. The smaller entropy suggests that water molecules are better ordered around Mg than around Ca, again suggesting a stronger interaction between Mg and water molecules. The fundamental differences between the two ions warrant an in-depth investigation into their effects on clay behavior, aggregation, and structural stability.

To date, most studies regarding the specific effect of Mg on K_s were conducted with soils from arid and semi-arid regions and in the presence of Na. This study was conducted to evaluate the specific effects of Mg on K_s, aggregate stability, and clay dispersion in the absence of Na in the Ca- or Mg-dominated systems using soils from a humid region, and to further elucidate major mechanisms that could be responsible for dramatic reductions of K_s during column leaching.

2. Materials and methods

Two cultivated soils (Fayette silt clay loam (fine-silty, mixed, mesic Typic Hapludalfs), and Miami silt loam (fine-loamy, mixed, mesic Typic Hapludalfs)) were collected from the top 15 cm layer from Iowa and Indiana, respectively. Samples were air-dried and lightly crushed through a 2 mm sieve. Particle size distribution was measured by a pipette method (Franzmeier et al., 1977). Soil pH was measured in a 1:1 soil/water mixture in both DI water and 0.01 M $CaCl_2$. Exchangeable cations were extracted with 1 M NH_4OAc at pH 7 (Franzmeier et al., 1977), and cation exchange capacity (CEC) was estimated by summing Ca, Mg, K, and Na. Calcium and Mg were determined by atomic absorption spectrometry, and Na and K by flame emission spectrometry (Model 2280, Perkin–Elmer Corp., Norwalk, CT). Soil organic carbon (OC) was measured by dry combustion (Model CHN-60, Leco Corp., St. Joseph, MI).

Critical flocculation concentration (CFC) was determined using a flocculation series test by measuring percent transmittance ($T\%$) at the 420 nm wavelength with a spectrophotometer (DU-64, Beckman Instruments Inc., Fullerton, CA) after 24 h settling. Clay suspensions, fractionated from each soil without removal of organic matter, were initially equilibrated in 1 M $MgCl_2$ or $CaCl_2$ solutions. Aliquots of suspensions were then repeatedly washed with $MgSO_4$ or $CaSO_4$ solutions at five concentrations between 0 and 5 mM. The concentration range was subsequently narrowed, if necessary, to accurately estimate CFC. The calcium or magnesium sulfate concentration that corresponded to the inflection point in the $T\%$ versus concentration plot was defined as CFC. Mineralogy was characterized by X-ray diffraction analyses of oriented slurry mounts. Mg-saturated (glycerol treated) and K-saturated suspension samples were plated onto microscope slides, air-dried, and analyzed at 25 °C. The K-saturated slides were also heat-treated to 100, 300, and 550 °C before analysis.

A wet-sieving machine (Yoder, 1936) with a displacement of 38 mm and a frequency of 36 cycles/min was used to measure aggregate size distributions. Four replicates were used for all wet-sieving experiments. For the untreated, sieved soils (<2 mm, which were used to pack soil column), 40 g of air-dried soils were pre-wetted slowly with DI water under 0.5 J/kg suction on a 1/3 bar suction plate for >7 h. Following wetting, soils were sieved in DI water for 5 min using a series of 127 mm diameter sieves (opening: 2, 1, 0.5, and 0.21 mm). After sieving, the suspension was filtered through a 0.05 mm sieve to obtain an additional size class. The same procedure was used for the 4–6 mm untreated soil aggregates, except that aggregates were pre-wetted and sieved in both DI water and 10 mM $CaSO_4 \cdot 2H_2O$ (analytical-grade gypsum) solution for 10 min and an additional sieve with 4.75 mm opening was used. The mean weight diameter (MWD) was computed as a weighted mean diameter as given by Kemper and Rosenau (1986).

A plexiglas cylinder (76.2 mm in diameter) with a drainage hole in the center of the base overlain by a metal screen was packed with a 15 mm layer of acid-washed sand (<0.2 mm). The air-dried, untreated soil (<2 mm) was then packed over the sand layer in 10 increments, 15 mm each. For each increment, a pre-determined amount of soil was funneled into the cylinder, mixed, and gently pressed with a rubber stopper to a pre-determined volume. The soil surface was then gently scratched to improve uniformity with the next layer. The bulk densities were 1.24 and 1.28 mg/m^3 for the Miami and Fayette soils, respectively. The differences between individual soil columns were within ±0.003 mg/m^3 for each soil.

Soil columns were flushed with a stream of CO_2 through the bottom holes for more than 30 min, and then wetted from the bottom by capillarity with 250 mM $CaCl_2$ or $MgCl_2$ equilibrating solution for >8 h. The solution level was raised ~40 mm every 2 h until it reached the soil surface. After wetting, soils were allowed to equilibrate overnight before initiation of leaching. To remove dissolved air, all

leaching solutions and DI water were boiled, and the experiment was conducted at ~25 °C. Microbial activities were not controlled, assuming that microbial effects would be similar between the two treatments.

Two treatments (Ca versus Mg salt) were used, with two replicates each. Mariotte bottles were used to maintain a constant water head of 30 mm above the soil surface. Initially, soil columns were leached with 4–5 pore volumes of the equilibrating solutions following overnight equilibration and then with the corresponding sulfate salt solutions (prepared using analytical-grade $CaSO_4 \cdot 2H_2O$ or $MgSO_4$) at the successive concentrations of 10, 2, and 0.5 mM. For each concentration, approximately 4–6 pore volumes of solution were allowed to percolate through the columns. Finally, DI water was introduced and the leaching continued as long as desired. Due to the low solubility of gypsum, chloride salts were used to obtain a higher degree of cation saturation on the soil exchange sites. The use of sulfate salts at lower concentrations was to directly assess the potential effects of gypsum (an abundant industrial by-product), compared with the $MgSO_4$ salt, on soil structural stability including a possible anion effect.

Effluents were collected periodically and the volumes were determined gravimetrically. Electrical conductivity (EC) and pH of effluents were determined for all samples. Total carbon and inorganic carbon contents of selected effluent samples were measured with a Total Organic Carbon (TOC) Analyzer (DC-190, Rosemout Analytical Inc., Santa Clara, CA), and the TOC was calculated as the difference. The $T\%$ of selected samples was measured at the 350 nm wavelength. The change in wavelength in this case was unintended. However, a preliminary study showed that $T\%$ was not particularly sensitive to wavelength between 350 and 420 nm. A student t-test was used to test for significance between treatments for selected parameters.

After column leaching, soil cores were gently extruded from columns and air-dried. The 1–2 mm and 1–6 mm aggregates of Ca- and Mg-soils were pre-wetted and sieved in DI water for 10 min using the procedure described earlier. Percent stable aggregates were computed by correcting for the sand fraction in each sieve size, and MWD was calculated

as discussed earlier. Water-dispersible clay was also measured for the leached soils. Five grams of air-dried Ca- or Mg-soils, with four replicates each, were weighed into 50 ml centrifuge tubes. Forty milliliter of DI water was added to each tube and was shaken horizontally for 4 h. Five milliliter suspension samples were withdrawn at the 2.5 cm depth after 2 h settling and were oven dried to gravimetrically determine dispersed clay percentage.

3. Results and discussion

The Fayette soil had 10% more clay than the Miami soil (Table 2). Both soils contained smectite, illite, and kaolinite, with smectite being predominant in the Fayette soil and illite in the Miami soil. Being the most expandable clay, smectite may be particularly vulnerable to the deleterious effect of Mg in these soils. Inferentially, saturated hydraulic conductivity of the Fayette soil would be more sensitive to the Mg effect than that of the Miami soil if these soils are subjected to prolonged, dispersive leaching conditions. The pH was slightly acid for both soils. The CFCs of the Miami soil were greater than those of the Fayette soil in both Ca- and Mg-dominated systems (the greater the CFC, the more the clay dispersion). More importantly, the CFCs were consistently greater in Mg than in Ca for both soils, indicating that Mg was more dispersive than Ca. The larger hydration shell of Mg would result in greater expansion of clay interlayer and the Stern layer, which would inevitably increase clay swelling and dispersion.

The aggregate stability index measured using 4–6 mm aggregates following slow wetting and 10 min wet-sieving, as indicated by MWD, was greater for the Fayette soil than for the Miami soil both in 10 mM gypsum solution (GS) and DI water (Table 2). This might be related to high CFC of the Miami soil and high clay content in the Fayette soil. Generally, soil aggregate stability increases with clay content. More stable aggregates of the Fayette soil would result in larger MWDs. The MWDs of both soils tended to be greater in GS than in DI water, but differences were significant only for the Miami soil at $P = 0.05$. Weight fractions are plotted versus size classes in Fig. 1(a) for both treatments. For both

Table 2
Selected physical and chemical properties of the two soils used in this study

Soil series	Clay (g/kg)	Sand (g/kg)	pH (1:1)		OC (g/kg)	CEC[a] (cmol_c/kg)	CFC[b] (mM)		Mean initial K_s (mm/h)		MWD[c] (mm)			Clay mineralogy[d]
			H_2O	$CaCl_2$			Ca	Mg	Ca	Mg	<2 mm H_2O	4–6 mm		
												H_2O	$CaSO_4$	
Miami	185	104	5.5	5.4	16.0	10.5	1.5–2.5	3.5	17.8	15.6	0.64	4.11	4.42	I(3), K(2), Vr(2), St(1)
Fayette	291	57	5.8	5.7	10.3	14.8	0.5–1	1.6	51.7	33.2	1.00	4.83	4.92	St(4), K(2), I(1)

[a] Cation-exchange capacity, measured in 1 M NH_4OAc at pH 7.
[b] CFC measured in Ca- or Mg- sulfate.
[c] MWD, wet-sieved in DI water for untreated soils (<2 mm) and both in DI water and 10 mM GS for 4–6 mm aggregates.
[d] I = illite, K = kaolinite, Vr = Vermiculite, St = smectite, (1) = very weak, (5) = very strong.
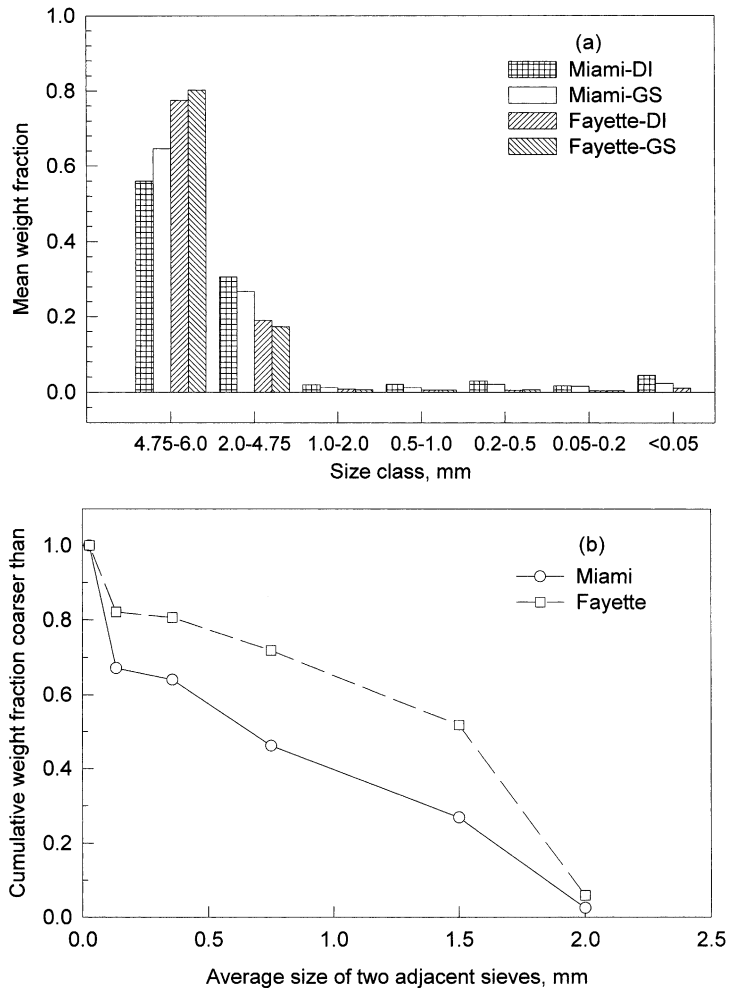
Fig. 1. (a) Size distributions of mean weight fractions of the two untreated soil aggregates (4–6 mm) after sieving in 10 mM GS and DI water, and (b) cumulative weight fractions of the two untreated soils (<2 mm) after sieving in DI water.

soils, fractions in the 4.75–6 mm class size were greater in GS than in DI water, while they were consistently less in the 2–4.75 mm class size, with the rest of the classes being relatively small and indifferent. Clay dispersion was prevented and aggregates were better preserved in 10 mM GS; whereas clay dispersion and slight disaggregation (aggregate failure) occurred in DI water, resulting in a decrease in the 4.75–6 mm class and an increase in the 2–4.75. Size distributions for the untreated soils, which were crushed through a 2 mm sieve and used in column packing, are shown in Fig. 1(b). The Fayette soil was coarser than the Miami soil. The coarser initial

size distributions and more stable soil aggregates with the Fayette soil led to a greater initial saturated hydraulic conductivity for this soil.

Upon initial wetting with 250 mM $CaCl_2$ or $MgCl_2$ solution, the soil surface rose approximately 4–5 mm for the Fayette soil and no discernable change was observed for the Miami soil. The observation agreed well with the relative abundance of smectite in two soils. This result indicates that significant swelling can take place even when electrolyte concentration is far above CFC values. In general, the macroscopic swelling is caused by hydration of clay surfaces and exchangeable cations, and osmotic pressure due to
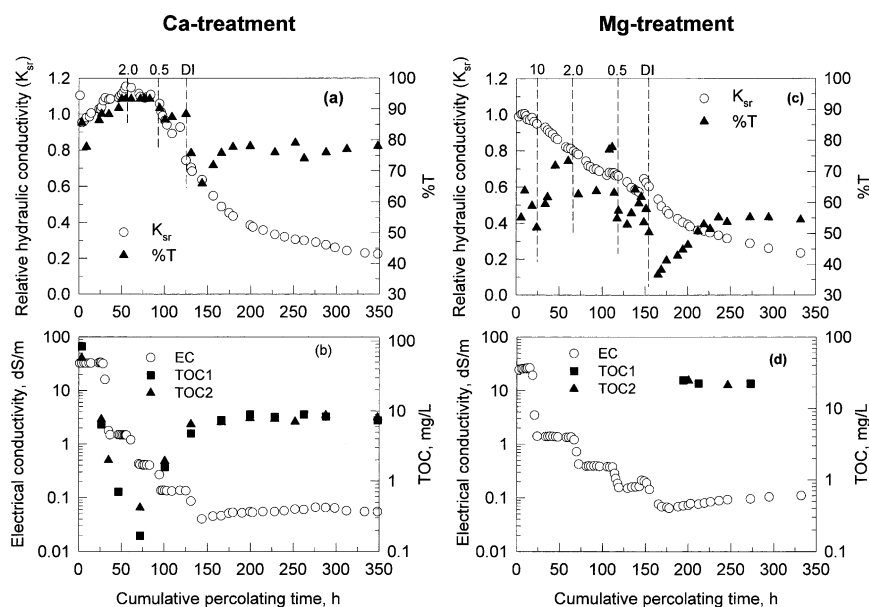
Fig. 2. Plots of K_{sr}, $T\%$, EC, and TOC versus percolating time for both Ca and Mg treatments of the Miami soil. Individual replicates of TOC, instead of replicate means, are plotted due to asynchronous measurements. Arrows indicate the onset of selected concentrations in mM.

concentration gradient between the diffuse double layer and bulk solution. Surface hydration predominates when the distances between clay platelets are less than 2 nm (Viani et al., 1983; Rengasamy and Olsson, 1991). Viani et al. measured swelling pressures and interlayer distances of montmorillonite-water suspensions, and concluded that surface hydration of montmorillonite layers was a major force causing interlayer swelling. The osmotic swelling prevails when clay platelets are further apart and their double layers are overlapped. The excessive osmotic swelling due to low electrolyte concentration in bulk solution could ultimately lead to clay dispersion. Cation hydration can take place near clay surfaces or in free solution; however, the extents to which cations are hydrated vary. Overall, swelling upon wetting increased the proportion of smaller pores, and therefore lowered the baseline or initial K_s. The averaged initial K_s values were generally greater in the Ca treatment than in the Mg treatment for both soils (Table 2). This apparent trend might be attributed to the differences in hydration (swelling) potentials between Mg and Ca ions.

To reduce variation between individual columns, the relative saturated hydraulic conductivity (K_{sr},

normalized by initial K_s) was presented. Overall, K_{sr} increased somewhat following the initiation of leaching in both treatments; however, a much greater increase occurred with the Ca treatment (see Figs. 2 and 3). Moutier et al. (1998) reported a similar initial increase in their studies, and have attributed this increase to the development of cohesive bonds between clay particles during leaching (termed as reaggregation by the authors). They found that the initial increase depended upon initial soil condition or treatment, SAR of leaching solution, as well as hydraulic gradients. The initial K_s increase was suppressed as higher SAR leaching solution was used due to the dispersive nature of Na. Based on the reaggregation theory, new soil structures resulted from cohesive bond formation might have been developed in both soils when leached with 250 and 10 mM solutions. The greater increases with the Ca treatment indicate that Ca favors cohesive bond formation due to its smaller hydration shell.

The K_{sr}, $T\%$, EC, and TOC values for the Miami soil are plotted versus time for both treatments in Fig. 2. Time, instead of eluted pore volumes, was used to better show the rate of change in K_{sr}. For the Ca treatment, K_{sr} increased gradually during the

leaching of 250 and 10 mM solutions, and remained largely unchanged at the 2 mM concentration level, suggesting that little change in soil structure occurred at the 2 mM level. This was in good agreement with the measured CFC (1.5–2.5 mM). A rapid decline in K_{sr} initiated after the introduction of the 0.5 mM solution and continued after DI water was applied, followed by a slower decline in the tailing region.

The Mg treatment, in contrast to Ca, exhibited a decrease in K_{sr} even at the 10 mM concentration (Fig. 2(c)), which was well above the CFC (3.5 mM). This suggests that continuing swelling and its resulting disaggregation were responsible for K_{sr} reduction at this stage. Another plausible mechanism for the disaggregation could be the overburden load and the dragging force of flowing water that might have caused shearing at the weakened contact points and along weakened planes of aggregates induced by swelling. The K_{sr} at the introduction of 0.5 mM solution was less than 0.7 for the Mg treatment, while it was about 1.1 for the Ca treatment, indicating that greater swelling, disaggregation, and clay dispersion occurred in the Mg treatment. The rapid decrease in K_{sr} continued linearly with time until the 200 h mark, followed by a slower rate of decrease. It should be pointed out that the differences in K_{sr} between the Ca and Mg treatments as displayed in Fig. 2 became increasingly smaller following DI water addition. This is partially because more DI water has eluted through soil columns in the Ca treatment than in the Mg treatment at any given time. If K_{sr}s were plotted with eluted pore volumes, the differences would be more apparent.

The rapid decline in K_{sr} was accompanied by a decrease in $T\%$ (Fig. 2(a) and (c)). The minimum $T\%$ occurred shortly after the introduction of DI water, indicating accelerated clay dispersion. The minimum values of $T\%$ were about 65% in Ca and 35% in Mg, reflecting more severe clay dispersion with Mg. The greater turbidity with Mg shows that Mg is more dispersive than Ca. Following the minima, $T\%$ started to increase even though the conditions still favored clay dispersion (i.e. EC < CFC, note 1 dS/m ≈ 10 mmol$_c$/l of total electrolyte concentration). The increase was probably not caused by increasing interception of mobile clay particles, because the maximum clay concentration in leachate was less than 0.023 g/l for Ca at $T\% \approx 65$ and 0.098 g/l for Mg at

$T\% \approx 35$. It could be better explained by a slowed release of dispersed clay particles following a rapid release during the rapid disaggregation resulted from the excessive swelling. The rapid disaggregation upon leaching with DI water might also have been caused by osmotic explosion as proposed by Emerson and Bakker (1973). The salt gradient between aggregate micropores and conducting macropores could cause osmotic water movement into aggregates, which could disrupt weakened soil aggregates.

The gradual decrease in K_{sr} in the tailing region (Fig. 2) was probably caused by slowed disaggregation (due to limited remaining aggregates), continued clay dispersion as well as by slight pore plugging resulted from progressively reduced flow velocities and pore sizes. These results are in agreement with the conclusion drawn by Abu-Sharar et al. (1987), who measured K_{sr} for three California soils under different levels of sodicity and reported that reduction in large conducting pores resulting from aggregate failure was the major cause for K_{sr} reduction.

The initial increase in $T\%$ in Fig. 2(a) and (c) was due to flushing of soluble organic matter dissolved during wetting (initial leachate was amber but clear), as evidenced by the initially high TOC in Fig. 2(b) (TOC of the Mg treatment was measured after the introduction of DI water). A supplementary study showed that $T\%$ measured at the 350 nm wavelength decreased linearly with TOC in 10 mM gypsum extracts of both soils, with a regression of $T\% = 89.3 - 0.229 \times$ TOC and an r^2 of 0.92. Following the initial decrease, TOC started to increase rapidly at the time when K_{sr} started to decrease, and then leveled off as K_{sr} approached the steady state (Fig. 2(a) and (b)). This close correlation between TOC and K_{sr} revealed not only a flow rate effect on TOC concentration but also a sizable disaggregation. With breakdown of soil aggregates, larger surface area was exposed and more soluble OC released into flowing water.

The minimum EC in leachate coincided with the minimum $T\%$, reflecting the maximum clay dispersion. Following the minima, EC increased slightly as K_{sr} gradually approached the steady state (Fig. 2(b) and (c)). As water flux reduced and travel time increased, more salts were released by matrix leaching and weathering. It should be noticed that EC was actually higher in the Mg treatment than in the Ca
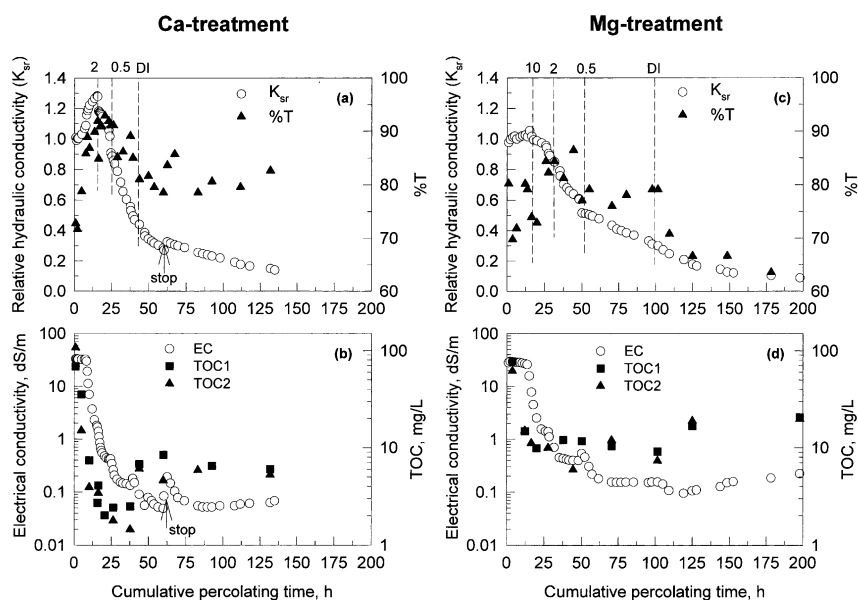
Fig. 3. Plots of K_{sr}, $T\%$, EC, and TOC vs. percolating time for both Ca and Mg treatments of the Fayette soil. Individual replicates of TOC are plotted due to asynchronous measurements. Arrows indicate the onset of selected concentrations in mM.

treatment in the tailing region due to lower water flux in the Mg treatment.

Similar plots are shown in Fig. 3 for the Fayette soil. The general trends of the selected parameters with respect to time were similar to those of the Miami soil in both treatments, except that no apparent concavity was observed for $T\%$ in either treatment. The minimum values of $T\%$ following DI water were about 78% in Ca and 65% in Mg (equivalent to 0.013 g clay/l for Ca and 0.023 g clay/l for Mg). For the Ca treatment, K_{sr} increased gradually during leaching of 250 and 10 mM solutions, and then decreased rapidly following the introduction of 2 mM solution. Comparatively, K_{sr} started to decline at the 10 mM concentration level in the Mg treatment, followed by a rapid decline throughout the 2 mM level. K_{sr}s declined rapidly at the 2 mM concentration in both treatments, though the 2 mM concentration was well above the CFCs (cf. Table 2). This suggests that swelling and perhaps disaggregation (facilitated by dragging forces of flowing water and shear of the overburden load) rather than clay dispersion was responsible for the decrease at this stage, and was strongly supported by the fact that the maximum values of $T\%$ were measured at this concentration. The disaggregation could be affected by pH increase due to cation hydrolysis and reduction reactions under

anaerobic conditions (elaboration will follow). However, a greater decline for the Mg treatment, compared with Ca, at the 2 mM concentration indicated a deleterious effect of Mg on soil structural stability. At the onset of 0.5 mM solutions, K_{sr} was about 0.9 for the Ca treatment, while 0.5 for the Mg treatment.

To check the effect of aging and released salts on K_{sr}, the drainage tube was clamped for two days during the DI leaching as indicated in Fig. 3(a) and (b). Following the stop, electrolyte concentration increased to about 2 mmol$_c$/l, which was around the CFC (0.5–1.0 mM). The EC increase also caused a slight increase in K_{sr}, partially due to flocculation of dispersed clay particles or the development of cohesive bonds between clay particles. This implies that local movement of dispersed clay and subsequent plugging of conductive pores might have occurred in the tailing region. This could be because clay particles were more likely to be intercepted by smaller pores at lower flow velocity resulted from the prior disaggregation. Hence, pore plugging by dispersed clay particles could play a role in decreasing K_{sr} in the tailing region, or at least supplemented the continued swelling and disaggregation process.

The K_{sr}s in the tailing region at any given eluted pore volumes were significantly lower in the Mg
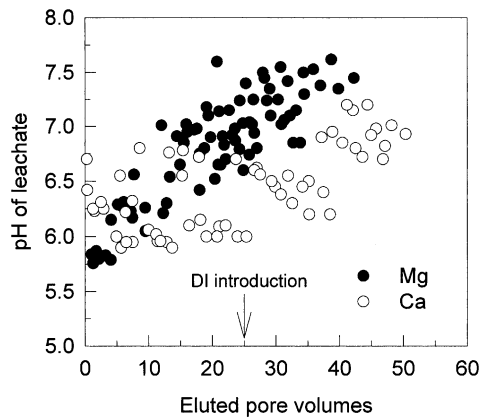
Fig. 4. Plot of leachate pH versus eluted pore volumes for both Ca and Mg treatments of the Miami soil. Individual replicates are shown.

treatment than in the Ca treatment for both soils at $P = 0.1$ (cannot be visualized in Figs. 2 and 3). The differences were in the range of one fold for Miami and six folds for Fayette. The greater sensitivity of the Fayette soil to the Mg effect was due to its high smectite content, which is highly expansible. Such Mg effects were not caused by differences in EC because EC was slightly higher in Mg as mentioned earlier due to slower flow rates. The $T\%$ at any given pore volumes in the tailing region was lower in Mg than in Ca for both soils ($P = 0.05$), indicating more severe clay dispersion with Mg.

Changes of leachate pH with eluted pore volumes for the Miami soil are depicted in Fig. 4. Similar trends were exhibited by the Fayette soil. In general, pH increased with eluted pore volumes or time due to reduction reactions and cation hydrolysis. The increase was greater in the Mg treatment than in the Ca treatment after the DI introduction. This could be caused by a greater hydrolysis of Mg^{2+}, compared with Ca^{2+}. A pH increase during leaching was also reported by Chiang et al. (1987) and Frenkel et al. (1978) for kaolinitic soils. An increase in pH tends to enhance clay dispersion and therefore to reduce K_{sr} since an increase in pH increases negative charges on the clay edge surfaces. The increased negative charges elevate repulsive forces between negatively charged clay particles. This effect would be more severe for 1:1 clay minerals than for 2:1 clays, because there are fewer variable-charge sites on the

2:1 clay edge surfaces. Undoubtedly, the pH increase enhanced clay dispersion and hence K_{sr}. Since pH was not controlled, its effect could not be isolated. However, the remarkable differences between the two treatments were unlikely caused largely by differences in pH. Firstly, pH values were similar before the introduction of DI water (Fig. 4), before which significant differences in K_{sr} already existed between the two treatments. Secondly, soils used in this study contained predominant amounts of 2:1 clay minerals. Thirdly, the pH differences were generally within one pH unit.

As to the effect of mineralogy, this study shows that the two humid-region soils containing variable amounts of smectite, kaolinite, illite, and vermiculite were susceptible to the deleterious effects of Mg. The results were in agreement with earlier findings with soils from arid and semi-arid regions, which contained various types of clay minerals (Rowell and Shainberg, 1979; Rahman and Rowell, 1979; Emerson and Chi, 1977). A general explanation is that Mg, compared with Ca, has greater hydration energy and a larger hydration shell, which results in greater clay swelling. The greater swelling inevitably leads to weaker aggregate bonds and hence lower aggregate stability.

With negligible energy input, disaggregation is predominantly caused by differential clay swelling and spontaneous dispersion. For expansible clay, greater clay swelling with Mg would result in more disaggregation. This explains why the Fayette soil was more sensitive to Mg than was the Miami soil. Excessive clay swelling is a major mechanism causing disaggregation. Breakdown of soil aggregates promotes clay dispersion by exposing more dispersive surfaces to flowing water. Clay dispersion, on the

Table 3
Exchangeable cation compositions of the two soils after leaching with Mg- or Ca- salt solutions

Soil series	Treatment	Exchangeable cation percentage (%)			
		Ca	Mg	Na	K
Miami	Ca	94.8	1.8	0.23	3.2
	Mg	7.3	89.9	0.25	2.6
Fayette	Ca	96.5	1.8	0.13	1.6
	Mg	5.2	93.0	0.21	1.7

other hand, could enhance disaggregation resulting from the loss of the 'cementing' agent.

After leaching, soils were analyzed for exchangeable cation composition (Table 3). The concentrations of exchangeable sodium and potassium were very low and not significantly different between the two treatments for both soils. This demonstrates that the Mg effect discussed earlier was not caused by sodium and was indeed a specific effect of Mg. In addition, both soils show a varying degree of preference for Ca over Mg (the degree of Ca saturation in the Ca treatment was greater than that of Mg saturation in the Mg treatment, Table 3). If such preferences did not exist, the specific effect of Mg would be even greater.

The foregoing findings were further substantiated by aggregate stability analyses measured using the column-leached soils. The water-dispersible clay percentages were 5.1 and 5.3 for the Ca- and Mg-Miami, and 4.8 and 5.7 for the Ca- and Mg-Fayette. The differences between the two treatments were significant for both soils ($P = 0.05$), indicating that the Mg-soils were more dispersive than the Ca-soils. The percent stable aggregates (stability index) measured using 1–6 mm aggregates were 81.8 and 79.5 for Ca- and Mg-Miami, and 94.1 and 88.9 for the Ca- and Mg-Fayette; and the MWDs were 2.0, 1.6, 2.4, and 1.8 mm, respectively. The differences were significant only for the Fayette soil at $P = 0.05$. The insignificant test results for the Miami soil could have resulted from differences in initial aggregate-size distributions. To test this hypothesis, 1–2 mm aggregates were tested, and results revealed that differences were significant at $P = 0.05$ for both soils. The larger MWDs indicate that aggregates were more stable in Ca-soils than in Mg-soils. The overall testing results from the aggregate stability analyses show that Fayette soil, compared with the Miami soil, was more susceptible to the deleterious effect of Mg due to its greater smectite content. This result substantiates the K_{sr} findings reported earlier.

4. Conclusions

There was a specific effect of Mg, compared with Ca, on aggregate stability, clay dispersion, and K_{sr} for the two humid region soils containing smectite, kaolinite, vermiculite, and illite. The K_{sr} started to decline

at higher electrolyte concentrations in Mg than in Ca, and the reduction of K_{sr} was greater in Mg than in Ca prior to the introduction of 0.5 mM solution. The K_{sr} and $T\%$ in the tailing region at any given pore volume were lower in Mg than in Ca for both soils. The deleterious effect of Mg on soil aggregate stability and hydraulic conductivity was caused by its greater hydration energy and larger hydration shell, which resulted in more clay swelling.

Reduction of large pores resulting from clay swelling and disaggregation appeared to be the major cause of the rapid decline in K_{sr} for the two soils studied. Clay dispersion and subsequent dislodgement (along with some pore plugging) supplemented the swelling and disaggregation processes, and became progressively important in reducing K_{sr} in the tailing region. Clay swelling due to clay surface and cation hydration as well as osmotic pressure is the major force weakening soil aggregates. The dragging force of flowing water and the overburden load in the column may have facilitated disaggregation by causing shearing at the points of contact of aggregates and along planes of weakness induced by swelling. Disaggregation promotes clay dispersion by exposing larger dispersive surfaces to flowing water. Clay dispersion, on the other hand, could enhance disaggregation due to loss of clay particles that bind soil particles.

Acknowledgements

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