

Effects of Gypsum Application on Dispersion of an Acid Kunigami Mahji Soil

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Abstract

Gypsum is an useful soil amendment. However, application of gypsum sometimes enhances the dispersion of highly weathered acid soils. The mechanism of the effect of gypsum on the dispersion of a Japanese acid soil is discussed in terms of adsorbed ions and aggregate stability. Leaching of the soil column by NaCl, Na₂SO₄, CaCl₂, and CaSO₄ electrolyte solutions showed that Ca²⁺ could displace Al³⁺ in the soil, and SO₄²⁻ caused more cation retention of the soil. In the slaking experiment, the soil was most dispersive with the CaSO₄, while it was least dispersive with the NaCl. The result goes against the effect that gypsum has on sodic soils. It was concluded that removal of Al³⁺, as a binding agent of the acid soil, by Ca²⁺ and the change in charge characteristic due to SO₄²⁻ adsorption were the mechanisms that enhanced dispersion of the Japanese acid soil following gypsum application.

Key words : gypsum, acid soil, dispersion, chemical amendment, Al, Kunigami mahji

Introduction

Aluminum toxicity is a serious problem in acid soil regions (Noble *et al.* 1988). Calcium salts such as lime, gypsum, and calcium carbonate can remove Al from the exchange sites of acid soil and reduce the problem of Al toxicity. Because of its higher solubility in water, gypsum can decrease the Al status and increase the Ca status of subsoil following the surface application (Pavan *et al.* 1984). Gypsum has been recognized as a dispersion-restricting agent. Many studies have shown the effects of gypsum on the dispersion of saline and sodic soils (Shainberg *et al.* 1989). Gypsum is also effective in preventing dispersion of lower exchangeable percentage (ESP) soils (Miller 1987; Zhang and Miller 1996). However, less is known about the effect of gypsum amendment on the physico-chemical properties of soils of

variable charge. Roth and Pavan (1991) and Nishimura (1996) reported enhancement of the dispersion of acid soils following the application of Ca salt. A possible mechanism for the enhancement of dispersion caused by gypsum amendment might be that the exchangeable Al monomers and/or polymers, which act as binding agents, are displaced from exchange sites by Ca²⁺, induced by the presence of SO₄²⁻ (Roth and Pavan 1991). The detail of this suggested mechanism, however, was not clear. On the other hand, specific adsorption or ligand exchange of SO₄²⁻ on acid soil (Inskeep 1989; Rao and Sridharan 1984; Hue *et al.* 1985), especially on soil of low pH (Wolt 1981) and positive charge, has been reported. Specific adsorption or ligand exchange of SO₄²⁻ can change the charge characteristics of the clay particle (Uehara and Gillman 1981; Rao and Sridharan 1984) and may change the soil dispersion phe-

nomena. This may be suspected as an alternative or an additional mechanism of dispersion enhancement by gypsum application in some acid soils.

Agricultural land reclamation in Okinawa, Japan moved surface soil and forced the acid Kunigami mahji subsoil to be surface soil. This subsoil-derived surface soil has both acidity and erosion problems. Moreover, gypsum application has enhanced the dispersion of the Kunigami mahji soil (Nishimura 1996). The aim of this study was to clarify the effects of Ca^{2+} and SO_4^{2-} on the dispersion of an acid Kunigami mahji soil.

Materials and Methods

Soil

Kunigami mahji soil, an acid red-yellow soil in southern Japan (Typic Hapludult), was used in this study. The soil was collected from a depth of 20 to 40 cm (B horizon) in a non-cultivated field in Nakijin, Okinawa, and sieved through a 3 mm mesh screen. The soil used in the column experiment was kept in a plastic bag to prevent it from drying prior to the experiment, and the rest of the soil was air dried. The texture of the soil was light clay. Clay mineralogy was dominated by Kaolinite, and smaller amounts of gibbsite, vermiculite and goethite were detected by X-ray diffraction. Organic carbon was determined to be 2.5 g kg^{-1} using a total carbon analyzer (LECO Corp., St. Joseph, MI, USA). The electrical conductivity of the soil at a soil : water ratio of 1 : 1 was 0.025 dS m^{-1} , which is equivalent to $0.349 \text{ mmol L}^{-1}$ in ionic strength by Marion-

babcock equation (Sposito 1989). The low electric conductivity of soil suspension suggested that the soil had small amounts of soluble salt. Other selected soil properties are given in Table 1. The exchangeable sodium percentage of the soil was below 0.1 and most of the exchange sites were occupied by Al monomers and/or polymers and protons (Table 2).

Column experiment

The soil was packed into a plastic pipe 5 cm in diameter and 10 cm in length, with an end-cap drilled to make an outlet. The soil, with a moisture content of 25% by weight, was packed gradually into the column by hand, with care taken to avoid segregation of the particles. The bulk density was 1.15 Mg m^{-3} , which was referred to the bulk density of the surface soil of a sugarcane field near the sampling site. The actual pore volume of the column was 114 cm^3 .

NaCl , Na_2SO_4 , CaCl_2 , and CaSO_4 electrolyte solutions were used in this study to clarify the effects of Ca^{2+} and SO_4^{2-} on soil dispersion. All the solutions had a concentration of $30 \text{ mmol}_e \text{ L}^{-1}$, and the pH of solutions was between 5.4 and 5.9. The flux density of the

Table 2 Changes in exchangeable cation due to gypsum treatment

Cation	Exchangeable cation [mmol _e kg ⁻¹]
Na ⁺	2.2
K ⁺	2.5
Mg ²⁺	0.79
Ca ²⁺	0.12
Al ³⁺	44

Table 1 Properties of soil material

Texture	LiC (Clay 33.9, Silt 33.7, Sand 32.4%)
Specific surface area	100 [m ² g ⁻¹] (EGME adsorption)
Particle density	2.74 [Mg m ⁻³]
Organic Carbon	2.5 [g kg ⁻¹]
Electrical conductivity	0.025 [dS m ⁻¹] (1 : 5 soil : water ratio)
Cation exchangeable capacity	265 [mmol _e kg ⁻¹] (KCl extraction)
Soil color	2.5 YR 4 or 5/8

solutions was around $5 \times 10^{-3} \text{ cm s}^{-1}$, which was 60% of the saturated hydraulic conductivity of the packed soil sample. The electrolyte solution was supplied onto the top of the column using a peristaltic pump. It took 70 minutes to supply 3 pore volumes of solution onto the column. The top of the column was covered with a few layers of gauze to prevent soil dispersion by drops. Drainage from the bottom of the column was sampled periodically and the concentrations of cations and anions and the pH were measured. Atomic absorption spectrometry and ion chromatography (both Shimadzu Co., Japan) were used to determine cation and anion concentrations, respectively. Each experiment was replicated twice, but the pH was only measured once.

Dispersion experiment

The dispersion experiment was carried out according to the procedure modified from Sato *et al.* (1969). A spread of 30 g of air-dried soil was passed through a 3 mm mesh screen onto a 2 mm mesh sieve, 15 cm in diameter. The sieve and the soil were immersed in the electrolyte solution gently and completely, and left to stand for one hour. The sieve and the soil were then gently removed from the solution and the soil left on the sieve was weighed. The amount of soil dispersed was the difference between the weight of the soil on the sieve before and after the immersion. The concentrations of the electrolyte solutions used in the dispersion experiment were the same as those used in the column experiment. Replicates of the experiment were twice or more.

Results and Discussions

Breakthrough curve of ions

Packing of the soil may be the biggest factor affecting water flow through an artificially packed soil column. In this study, the drainage rate of each column was quite consistent, $(4.89 \pm 0.04) \times 10^{-3} \text{ cm s}^{-1}$, which indicated that packing of the soil was successful. Breakthrough curves (BTC) of each treatment were consistent, too, thus the BTC of one treatment

could be compared with the other ones.

The Na^+ and Cl^- breakthrough curves (BTCs) coincided well (Fig. 1), and BTCs of Cl^- in the CaCl_2 and NaCl treatment coincided well even though Ca^{2+} in the CaCl_2 treatment might remove Al^{3+} from the soil (Fig. 2). It is possible to interpret Cl^- as the reference tracer in this study. Recently, Bellin *et al.* (1996) showed that the application of Cl^- as a non-reactive tracer is questionable for acid soil of variable charge. The present study used an acid Japanese soil of variable charge. However, Cl^- could be a reference tracer in the present study since the variations in pH for each treatment were small (Fig. 3). As to the BTC, there was almost no cation except Na^+ in the

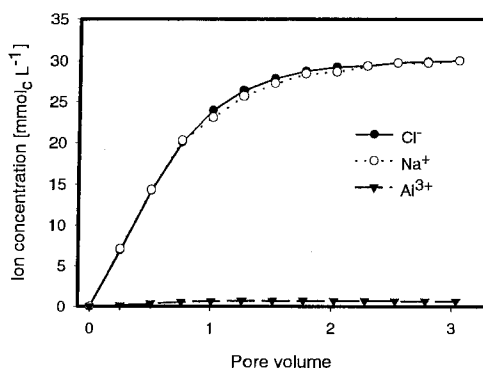


Fig. 1 Changes in ion concentrations in effluent from the Kunigami mahji soil column, NaCl treatment.

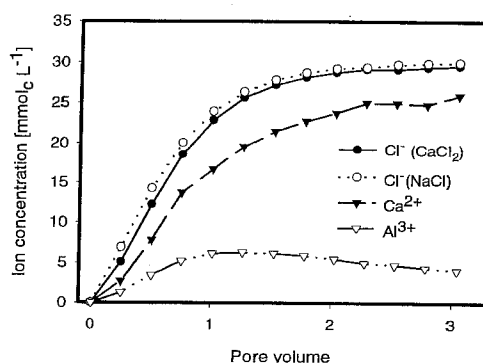


Fig. 2 Changes in ion concentrations in effluent from the Kunigami mahji soil column, CaCl_2 treatment.

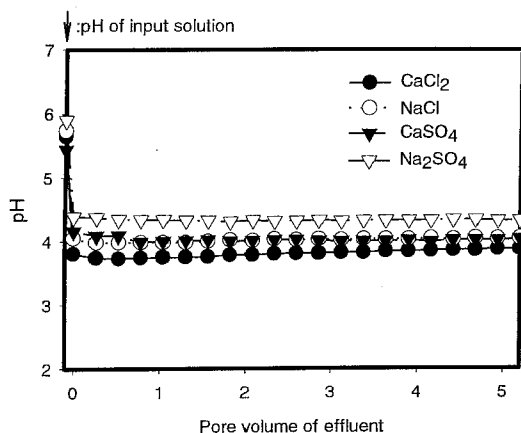


Fig. 3 pH of the effluent from the Kunigami mahji soil column.

effluent of the NaCl treatment. This indicated that Na^+ could not remove Al^{3+} from the soil in this study.

In the CaCl_2 treatment, Ca^{2+} has replaced Al^{3+} in the cation exchange sites of the soil (Fig. 2). The amount of Ca^{2+} retained by the soil was estimated from integration of the area between the Cl^- and the Ca^{2+} BTCs. In the CaCl_2 treatment, the pH of the effluent (Fig. 3) suggested that most of the Al was an Al^{3+} -monomer (Sparks 1995), and that the integration of the Al^{3+} BTC could represent the amount of Al removed from the soil. Additionally, removal of H^+ adsorbed on soil clay by Ca^{2+} and Na^+ might be a reason of lower pH of effluents compare to the input solutions.

The amount of Na^+ and SO_4^{2-} retentions were closely related in this study. The BTC of Cl^- in the NaCl treatment is plotted in the BTCs of the Na_2SO_4 treatment as the reference BTC (Fig. 4). The retention of ions was determined by the same method that was used for the CaCl_2 treatment, that is, the areas between the BTC of the ions and the BTC of the reference tracer (Cl^-) represented the amount of ions retained by or removed from the soil. The amount of Na^+ retained by the soil was greater in the Na_2SO_4 treatment than in the NaCl treatment, and the amounts of Na^+ and SO_4^{2-} retained by the soil were quite similar at

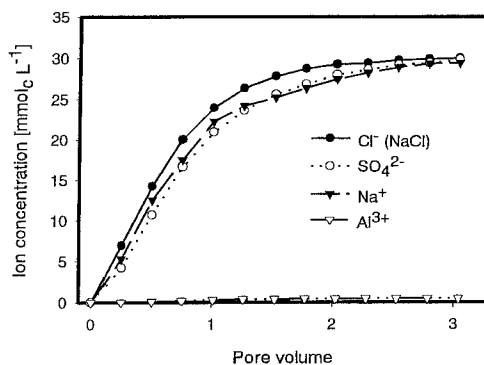


Fig. 4 Changes in ion concentrations in effluent from the Kunigami mahji soil column, Na_2SO_4 treatment.

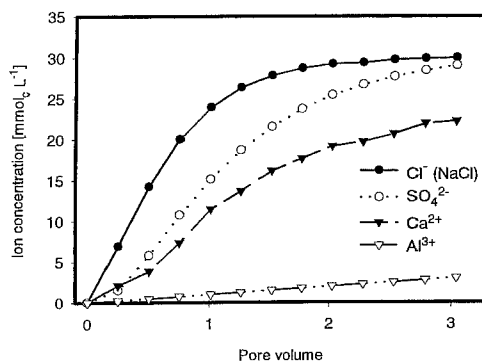


Fig. 5 Changes in ion concentrations in effluent from the Kunigami mahji soil column, CaSO_4 treatment.

the end of both treatments.

The BTC of Cl^- in the NaCl treatment is also plotted in the BTCs of the CaSO_4 treatment as the reference BTC, and the amounts of Ca^{2+} and SO_4^{2-} retained by the soil and Al^{3+} removed from the soil were determined by the same method used for the CaCl_2 and Na_2SO_4 treatments. The retention of SO_4^{2-} was almost completed with 3 pore volumes of effluent for electrolyte solutions containing SO_4^{2-} , independent of co-cation types (Figs. 4 (Na_2SO_4) and 5 (CaSO_4)), while Al^{3+} displacement steadily continued in the CaCl_2 treatment after 3 pore volumes of effluent (Figs. 2 (NaCl) and 5).

The sum of retained or removed ions for the

Table 3 Retention of ions by Kunigami mahji soil during 3 pore volumes of effluent (Concentration of percolated electrolyte solutions was 0.03 cmol_c kg⁻¹)

Electrolyte solution	Al ³⁺ displaced [mmol _c kg ⁻¹] (A)	Ca ²⁺ retained by the soil [mmol _c kg ⁻¹] (B)	Na ⁺ retained by the soil [mmol _c kg ⁻¹] (B)	SO ₄ ²⁻ retained by the soil [mmol _c kg ⁻¹]	(B) - (A) [mmol _c kg ⁻¹]
NaCl	0.96	—	0.3	—	- 0.66
Na ₂ SO ₄	0.54	—	3.9	4.3	3.36
CaCl ₂	7.4	7.3	—	—	- 0.1
CaSO ₄	3.6	13.8	—	6.5 (5.9*)	10.2

* SO₄²⁻ retention after AlSO₄⁺ correction

3 pore volumes of effluent are summarized in Table 3. Measured concentration data were converted into a base value of soil mass. The SO₄²⁻ retention was determined by the difference between the SO₄²⁻ concentrations of the input and the effluent solutions as measured by ion chromatography. Integrals of the differences in measured concentration of SO₄²⁻ were 4.3 and 6.5 mmol_c kg⁻¹ for the Na₂SO₄ and CaSO₄ treatments, respectively. Some SO₄²⁻ could exist as the AlSO₄⁺ form in the effluent of the CaSO₄ treatment that had higher Al³⁺ and SO₄²⁻ concentrations (Van Breemen 1973). The AlSO₄⁺ form of SO₄²⁻ complex cannot be detected as SO₄²⁻ by ion chromatography, which could cause overestimation of SO₄²⁻ retention in the CaSO₄ treatment. It is possible to estimate the concentration of AlSO₄⁺ by using the following equation :

$$[AlSO_4^+] = \frac{10^{3.20} [SO_4^{2-}]}{10^{3.20} [SO_4^{2-}] + 1} \times [\text{measured concentration of Al}]$$

(From Lindsay 1989).

The available concentration of AlSO₄⁺ with the existence of gibbsite and 5 mmol_c L⁻¹ of SO₄²⁻ at pH 4, which were similar conditions to those of the effluent of the CaSO₄ treatment in this study, was 3 mmol_c L⁻¹. The value was close to the difference between the measured SO₄²⁻ concentration and the reference Cl⁻ BTC at the 3 pore volumes of effluent (Fig. 5). After the AlSO₄⁺ correction, the amount of SO₄²⁻ retained by the soil was 5.9 mmol_c kg⁻¹ in the

CaSO₄ treatment. According to Rao and Sridharan (1984) and Inskeep (1989), the maximum sulfate retention of kaolinitic soil clay was found to be around 20 mmol_c kg⁻¹ using the batch technique. The smaller SO₄²⁻ retention of the present study was not anomalous since the present study was using actual soil (clay fraction was 34%), and did not employ the batch technique which usually shows more exchange than the flow-through or the miscible-displacement method (Sparks and Rechcigl 1982). Hue *et al.* (1985) reported 4 mmol_c kg⁻¹ for an actual soil, Benndale sandy loam, after CaSO₄ incubation. Adsorption of the CaSO₄ ion pair (Bolan *et al.* 1993) could be a reason for the soil showing more SO₄²⁻ retention with the CaSO₄ treatment than with the Na₂SO₄ treatment.

Sulfate retention may change the surface charge and cation-adsorption characteristics of clay particles (Uehara and Gillman 1981). In the present study, the difference between the amount of Al³⁺ removed from the soil and the amount of cation, Ca²⁺ or Na⁺, retained by the soil increased as SO₄²⁻ was retained. Na⁺ retention increased by 3.6 mmol_c kg⁻¹ from the Cl⁻ treatment to the SO₄²⁻ treatment, while SO₄²⁻ was retained in an amount of 4.3 mmol_c kg⁻¹ with the Na₂SO₄ treatment. For the Ca salt treatments, the difference between the retained Ca²⁺ of the SO₄²⁻ and the Cl⁻ treatments was 6.5 mmol_c kg⁻¹, and the retained SO₄²⁻ in the CaSO₄ treatment was 5.9 mmol_c kg⁻¹. The [enhanced cation retention]/[SO₄²⁻

retention] ratio was 0.84 and 1.10 for monovalent Na^+ and divalent Ca^{2+} , respectively. This result seemed to agree with the result of Hue *et al.* (1985) for kaolinitic soil, in which the increase in cation exchange capacity (CEC) was equivalent to the moles of SO_4^{2-} adsorption in the highest gypsum application. Alva *et al.* (1990) reported Cecil and Wedowee soils in their study behaving like the soils in the present study. They explained that the result was due to the effect of the ionic strength of the electrolyte solution on soil of variable charge. It was concluded that SO_4^{2-} retention enhanced cation retention by the soil. Only specific adsorption (Alva *et al.* 1990) or ligand exchange (Rao and Sridharan 1984) may cause such an enhancement in cation retention, especially for soils of low pH (Hue *et al.* 1985). Effluents of the SO_4^{2-} treatments had a higher pH than the effluents in the Cl^- treatments for the same cation (Fig. 3). The higher pH of the effluents of the SO_4^{2-} treatments qualitatively reinforced the ligand exchange of SO_4^{2-} with hydroxides on clay surfaces.

Effect of electrolytes on soil dispersion

In the dispersion experiment, the ionic strength of the electrolyte solutions was the same as in the column experiment, but the soil/solution ratio was higher for the column experiment. The CaSO_4 solution caused the Kunigami mahji soil to be most dispersive, although gypsum generally is recognized as a dispersion

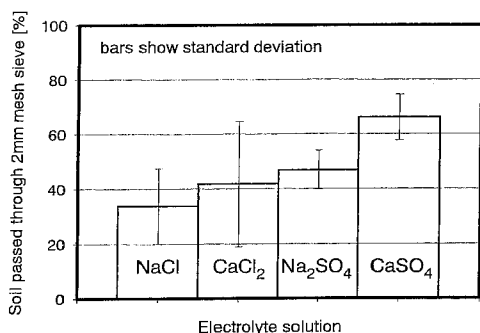


Fig. 6 Effects of compositions of electrolyte solution on dispersion of the Kunigami soil.

-restricting agent (Fig. 6). A reason for this unexpected result was the contribution of Al^{3+} to the clod stability of acid soils. As shown in the column experiment, Na^+ could not remove exchangeable Al^{3+} , but Ca^{2+} could. The Ca soil is more dispersive relative to Al soil in terms of the diffuse double-layer theory; thus the soil showed less dispersion in Na^+ electrolyte solutions where adsorbed Al^{3+} was not affected by Na^+ . Adsorption of SO_4^{2-} was suspected of making another contribution to soil dispersion. The acid Kunigami mahji soil showed more dispersion in the SO_4^{2-} electrolyte solutions than in the Cl^- solutions. Specific adsorption, or ligand exchange, of SO_4^{2-} may decrease the positive charge of the soil, or increase the negative charge of the soil (Rao and Sridharan 1984; Uehara and Gillman 1989; Hue *et al.* 1985). Furthermore, when soil particles have a sufficient positively charged edge, they can form a card house edge-to-face structure and are easy to flocculate. On the contrary, if most of the positive charge turns into negative charge, only a face-to-face structure would be dominant and the soil would tend to be more dispersive. This mechanism might be the second reason behind the enhanced dispersion of acid soil following gypsum application. The point of zero salt effect (PZSE) of this Kunigami mahji soil was 3.8 (Nishimura, unpublished) and the pH of the effluent of the CaCl_2 treatment was 3.7. This suggested that the soil initially had some positive charge, and that the application of CaSO_4 might have canceled those positive charges and increased the pH of the soil solution following the ligand exchange of SO_4^{2-} .

Conclusion

Ca^{2+} and Na^+ retained by Kunigami mahji soil was separated into two fractions, exchanged cations and cations retained subsequent to SO_4^{2-} adsorption. It was concluded that dispersion of the acid Kunigami mahji soil was affected by both Ca^{2+} - Al^{3+} cation exchange and the specific adsorption of SO_4^{2-} .

These processes might be the reasons why Kunigami mahji soil, and other acid soil in previous studies, showed more dispersion following gypsum application. Further study is needed to specify the conditions under which acid soils disperse following gypsum treatment.

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