

# Oxidation of FGD-CaSO<sub>3</sub> and Effect on Soil Chemical Properties When Applied to the Soil Surface

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## ABSTRACT

The use of high-sulfur coal for power generation in the United States requires the removal of sulfur dioxide (SO<sub>2</sub>) produced during burning in order to meet clean air regulations. If SO<sub>2</sub> is removed from the flue gas using a wet scrubber without forced air oxidation, much of the S product created will be sulfite (SO<sub>3</sub><sup>2-</sup>). Plants only take up S in the form of sulfate (SO<sub>4</sub><sup>2-</sup>), and SO<sub>3</sub><sup>2-</sup> is toxic to plants and may cause damage to plant roots. For agricultural uses, SO<sub>3</sub><sup>2-</sup> in flue gas desulfurization (FGD) products must oxidize to SO<sub>4</sub><sup>2-</sup> in soils before crops are planted. However, there is little information about the oxidation of SO<sub>3</sub><sup>2-</sup> in FGD product to SO<sub>4</sub><sup>2-</sup> under field conditions. An FGD-CaSO<sub>3</sub> obtained from American Electric Power Company was applied at rates of 0, 1.12 and 3.36 Mg ha<sup>-1</sup> to the surface of an agricultural soil (Wooster silt loam, Oxyaquic Fragiudalf). The SO<sub>4</sub><sup>2-</sup> in the surface soil (0-10 cm) was analyzed on days 3, 7, 17, 45, and 61. The distribution of SO<sub>4</sub><sup>2-</sup> and Ca in the 0-90 cm soil layer was also determined on day 61. Results indicated that SO<sub>3</sub><sup>2-</sup> in the FGD-CaSO<sub>3</sub> rapidly oxidized to SO<sub>4</sub><sup>2-</sup> on the field surface during the first week and much of SO<sub>4</sub><sup>2-</sup> and Ca moved downward into the 0-50 cm soil layer during the experimental period of two months. It is safe for plants if FGD-CaSO<sub>3</sub> is applied to the field surface one month before planting. However, application too long before planting might cause some of the S and Ca for plant uptake to be lost due to leaching or other soil processes.

## INTRODUCTION

The use of high-sulfur coal for power generation in the United States requires the removal of SO<sub>2</sub> produced during burning via some type of scrubbing technology in order to meet clean air regulations. Many FGD technologies including wet limestone, magnesium-enhanced lime, and lime spray drying are currently used in the power industry, and wet limestone processes have predominated in the US (Srivastava and Jozewicz, 2001). Magnesium-enhanced lime FGD and lime spray FGD technologies often produce SO<sub>3</sub><sup>2-</sup>-containing FGD products (Bigham et al., 2005). If SO<sub>2</sub> is removed

from the flue gas using a wet scrubber without forced air oxidation, FGD product created will contain as much as 30-87% of S as  $\text{SO}_3^{2-}$  (Clark et al., 1995). In the Ohio Valley, the wet limestone without forced air process is still used, and a large amount of FGD- $\text{CaSO}_3$  is produced.

Plants take up S mostly in the form of  $\text{SO}_4^{2-}$  (Salisbury and Ross, 1992).  $\text{SO}_3^{2-}$  is toxic to plants and may cause damage to plant roots at low pH (Clark et al., 2001; Ritchey et al., 1995). However,  $\text{CaSO}_3$  can rapidly oxidize to  $\text{CaSO}_4$  in oxygenated environments (Pasiuk-Bronikowska et al., 1992). The reaction rate is strongly affected by dissolved  $\text{SO}_3^{2-}$ , oxygen, pH, temperature, and catalysts such as  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Mn}^{2+}$  (Lancia and Musmarra, 1999; Hao and Dick, 2000; Wu et al., 2004; Lee et al., 2007). Ritchey et al. (1995) reported that  $\text{CaSO}_3$  was completely oxidized to  $\text{CaSO}_4$  in aqueous solutions in 5 weeks, and approximately one-third of  $\text{CaSO}_3$  was oxidized in soil slurry in 8 days. Lee et al. (2007) found that  $\text{CaSO}_3$  was completely oxidized in soil-FGD mixtures in 21 days. Wendell and Ritchey (1996) reported that when FGD- $\text{CaSO}_3$  product was applied to the soil surface, the Al, Ca, and  $\text{SO}_4^{2-}$  movements in the columns of an acid soil were significantly increased.

In agricultural use, FGD products are often applied to the surface of the fields. However, there is no report on the oxidation of FGD- $\text{CaSO}_3$  and movement in cultivated soils under field conditions. The objectives of this study were to determine the oxidation rate of FGD- $\text{CaSO}_3$  in the surface of an agricultural field and to evaluate the impact of FGD- $\text{CaSO}_3$  on the movement of plant nutrients and toxic elements in the soil.

## MATERIALS AND METHODS

Field studies were conducted on an agricultural soil (Wooster silt loam, Oxyaquic Fragiudalf) located near Wooster, OH. Selected characteristics of the soils are presented in Table 1. The Wooster field had been in continuous corn for three years from 2003 to 2006 under a conventional tillage management system. FGD- $\text{CaSO}_3$  was obtained from American Electric Power Company, Conesville, OH, and FGD-gypsum was obtained from Cinergy Corporation, Cincinnati, OH (Table 2). FGD- $\text{CaSO}_3$  was applied at rates of 0, 1.12, and 3.36  $\text{Mg ha}^{-1}$  to the surface of the agricultural soil, and FGD-gypsum was applied at only a single rate of 1.12  $\text{Mg ha}^{-1}$  as a positive comparison. Rates used were normal field recommended rates required to improve soil physical properties such as water and air infiltration. These treatments were applied to 1 x 1 m plots arranged in a randomized block with four replicates.

Table 1. Organic matter, pH, and concentrations of plant nutrients extracted from experimental field soil (0-20 cm) by Mehlich-III.

pH	Organic matter	P	K	Ca	Mg	S	B	Cu	Fe	Mn	Mo	Zn
	%	-----mg kg <sup>-1</sup> -----										
7.1	3.14	50	111	1440	311	51	0.43	1.45	195	94	0.03	6.74

Table 2. Characteristics of the FGD-CaSO<sub>3</sub> and FGD-gypsum used.

Parameter	FGD-CaSO <sub>3</sub>	FGD-gypsum
Sulfur component (%)		
SO <sub>3</sub> -S	22.7	0
SO <sub>4</sub> -S	2.0	18.7
Major elements (g kg <sup>-1</sup> )		
Al	0.577	0.228
Ca	304	213
Fe	0.654	0.222
Mg	3.66	0.112
S	247	187
Trace elements (mg kg <sup>-1</sup> )		
As	<1.3	<11
B	165	5.8
Ba	20.7	5.5
Cd	<0.05	<1.0
Cr	<0.19	<1.0
Cu	1.69	<3.0
Mn	20.5	1.3
Mo	<0.225	<3.0
Ni	3.66	<3.0
Pb	<0.77	<5.0
Se	<2.3	<25.0
Zn	7.1	4.8

The field experiments were carried out from May 19 to July 19, 2006. Weekly precipitation and average temperature at the experimental site and soil moisture on the sampling days are presented in Table 3. On days 3, 7, 17, 45, and 61 after treatments, five soil cores from depth of 0 to 10 cm were collected from each plot and combined to form one sample. Immediately after returning to the lab, a subsample of 20 g soil was put in a test tube, and 30 mL double deionized water was added. After reciprocating shaking one hour, the soil suspension was centrifuged, and the supernatant was filtered through a 0.45 µm membrane filter. The pH and electrical conductivity (EC) of the extracts were measured using a pH meter and a combination glass electrode. The elements Ca, Mg, K, Al, Fe, Mn, and Zn in the extracts were analyzed by inductively coupled plasma (ICP) emission spectrometry, and SO<sub>4</sub>-S was determined by ion chromatography (IC). A subsample of 30 g soil was dried in a forced air oven at 65°C for four days for moisture determination. On day 61 after treatment, soil samples were collected to a depth of 90 cm in increments of 10 cm using a hydraulic coring device, and soil solution was extracted and analyzed as described above.

Table 3. Weekly precipitation and average temperature for the duration of the experiment in 2007 and soil moisture on sampling dates at Wooster.

Date	Precipitation cm	Average temperature °C	Date	Soil moisture % by mass
5/19-25	3.7	12.2	5/19	22.5
5/26-6/1	2.28	22.2	5/22	20.5
6/2-6/8	2.00	17.9	5/26	21.5
6/9-6/15	0	15.6	6/5	19.8
6/16-6/22	6.17	21.8		
6/23-6/29	1.60	20.2		
6/30-7/6	2.38	21.0	7/3	20.1
7/7-7/13	5.56	21.2		
7/14-7/19	1.98	22.2	7/19	18.3
Total	25.7			

## RESULTS AND DISCUSSION

All treatments of FGD-CaSO<sub>3</sub> and FGD-gypsum gradually decreased the surface (0-10 cm) soil pH on the first 17 days, and then pH gradually recovered over time (Fig. 1). The EC in the soil extracts was significantly increased by FGD-CaSO<sub>3</sub> or FGD-gypsum treatment. The EC trended to decrease over time and was similar for the treatments of 1.12 Mg ha<sup>-1</sup> FGD-CaSO<sub>3</sub> or FGD-gypsum.

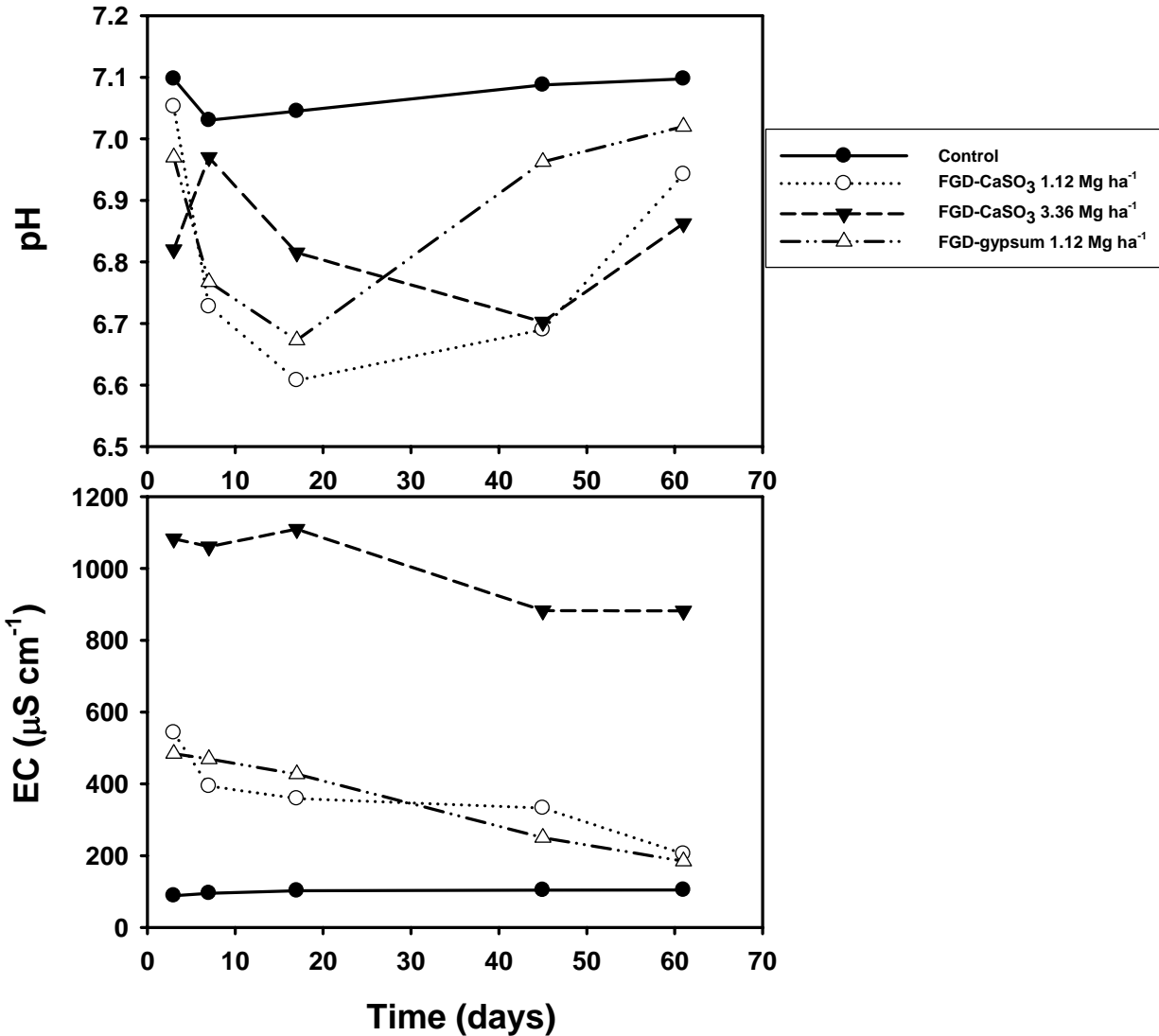


Fig. 1. Changes in pH and electrical conductivity (EC) in water extracts of soils (0-10 cm) over time after surface application of FGD-CaSO<sub>3</sub> or FGD-gypsum.

The concentrations of water-soluble SO<sub>4</sub>-S, Ca, Mg, and K in the soil from surface to 10 cm were significantly increased by FGD-CaSO<sub>3</sub> or FGD-gypsum treatment and gradually decreased over time (Fig. 2). The concentrations of SO<sub>4</sub>-S, Ca, Mg, and K by treated with 1.12 Mg ha<sup>-1</sup> FGD-CaSO<sub>3</sub> were similar to those treated with FGD-gypsum at all days measured. These results suggested that the SO<sub>3</sub><sup>2-</sup> in the FGD-CaSO<sub>3</sub> was rapidly oxidized in 3 days after surface application. Wendell and Ritchey (1996) also found that S in leachate was mostly in the form of SO<sub>4</sub>-S when FGD-CaSO<sub>3</sub> was surface application on soils and leached with deionized water. Lee et al. (2007) reported that oxidation of SO<sub>3</sub><sup>2-</sup> in soil- FGD mixtures needed 21 days, but oxygen was probably limiting the rate of oxidation in the soil-FGD mixture. Even though FGD-CaSO<sub>3</sub>

and FGD-gypsum contained little or no Mg and K, water-soluble Mg and K were significantly increased by FGD-CaSO<sub>3</sub> or FGD-gypsum treatment. This is because Ca ions have greater affinity for exchange sites on soil particles than Mg and K ions, and application of FGD-CaSO<sub>3</sub> and FGD-gypsum displaced and mobilized Mg and K.

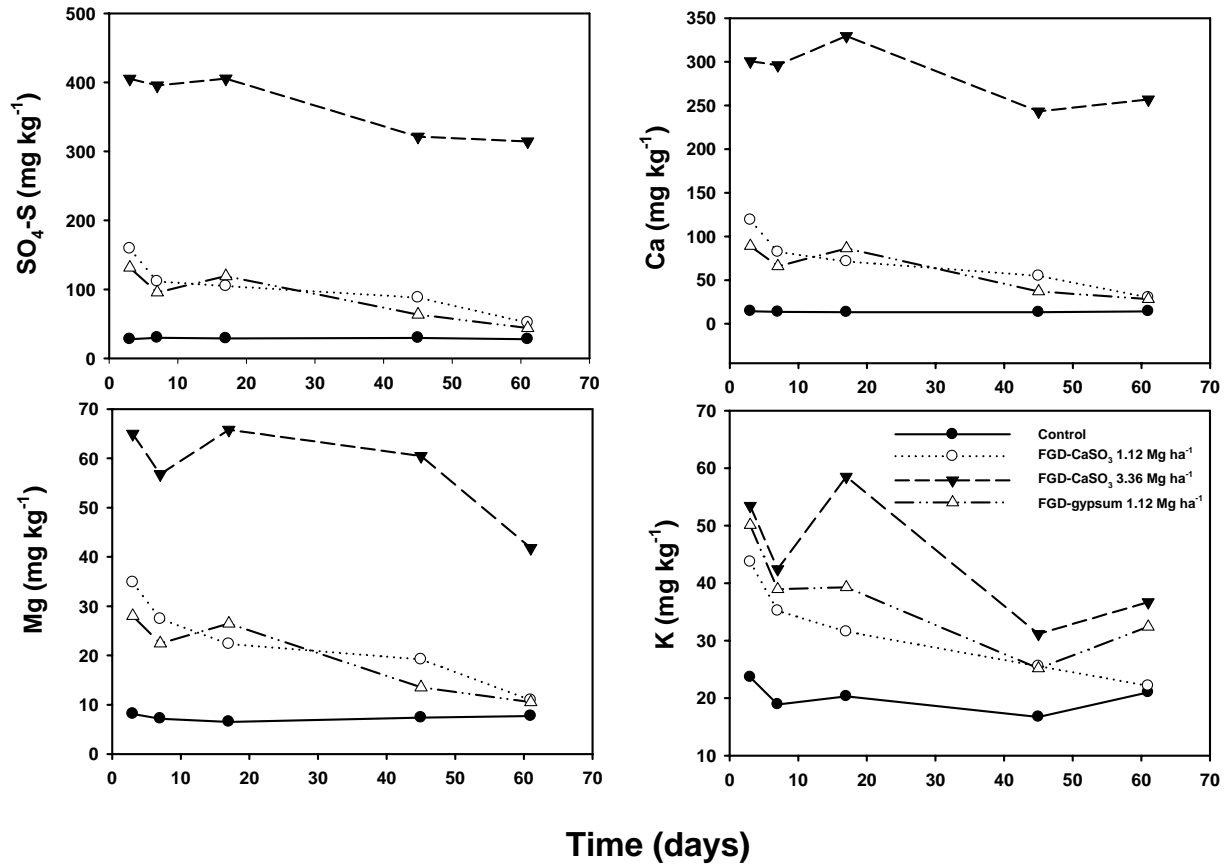


Fig. 2. Changes in water-soluble SO<sub>4</sub>-S, Ca, Mg, and K in the surface 10 cm soil layer over time after surface application of FGD-CaSO<sub>3</sub> or FGD-gypsum.

Application of FGD-CaSO<sub>3</sub> or FGD-gypsum significantly decreased the concentrations of water-soluble Al, Fe, Mn and Zn in the soil from surface to 10 cm (Fig. 3). These decreases were attributed to leaching losses of these elements by Ca replacement.

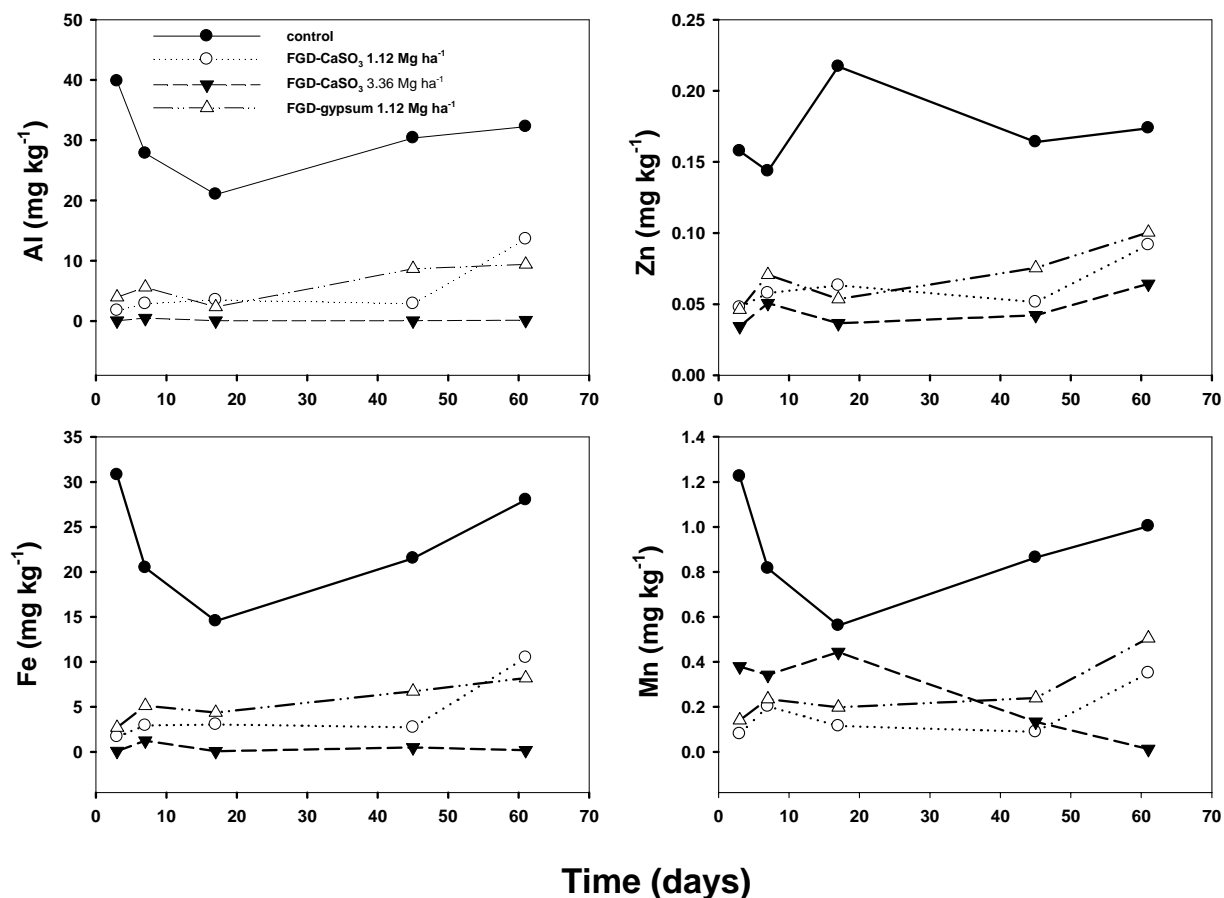


Fig. 3. Changes in water-soluble Al, Fe, Mn and Zn in the surface 10 cm soil layer over time after surface application of FGD- $\text{CaSO}_3$  or FGD-gypsum.

On day 61, FGD-gypsum slightly increased the pH in the 10 to 30 cm soil layers, while FGD- $\text{CaSO}_3$  at the rate of 3.36  $\text{Mg ha}^{-1}$  decreased the pH in the 10-20 cm soil layer (Fig. 4). All treatments of FGD- $\text{CaSO}_3$  and FGD-gypsum significantly increased the EC in the soil layers from 0-50 cm, and FGD- $\text{CaSO}_3$  at the rate of 3.36  $\text{Mg ha}^{-1}$  increased the EC much more in these soil layers than other treatments.

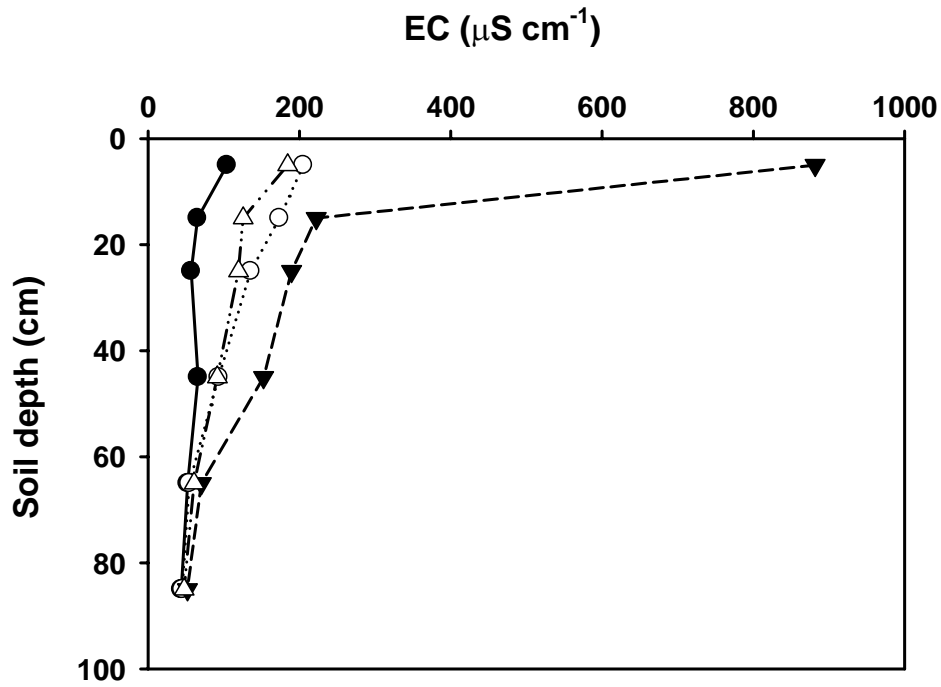
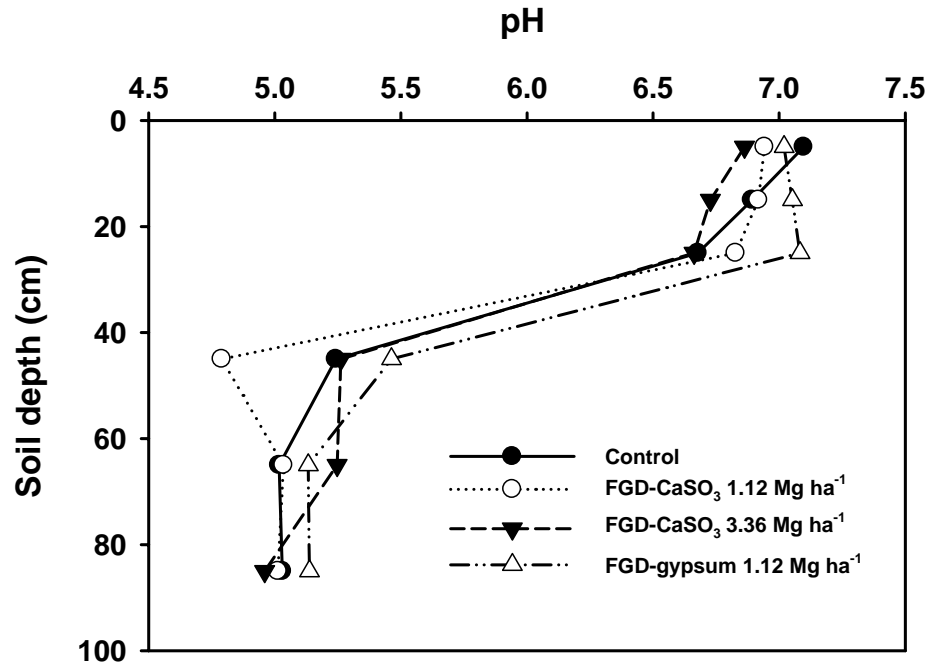


Fig. 4. Changes in pH and electrical conductivity (EC) in water extracts of soil collected at different depths 61 days after surface application of FGD-CaSO<sub>3</sub> or FGD-gypsum.



On day 61, treatment of FGD-CaSO<sub>3</sub> at the rate of 3.36 Mg ha<sup>-1</sup> significantly increased water-soluble SO<sub>4</sub>-S, Ca and Mg in the soil layers of 0-90 cm (Fig 5). Application of FGD-CaSO<sub>3</sub> or FGD-gypsum at the rate of 1.12 Mg ha<sup>-1</sup> increased water soluble SO<sub>4</sub>-S, Ca, and Mg in the soil layers of 0-30 cm. The impact of 1.12 Mg ha<sup>-1</sup> FGD-CaSO<sub>3</sub> was similar to that of FGD-gypsum. Because CaSO<sub>3</sub> is insoluble, the similar downward movement of SO<sub>4</sub>-S and Ca in the soil treated with FGD-CaSO<sub>3</sub> or FGD-gypsum also suggested that the CaSO<sub>3</sub> had been oxidized to CaSO<sub>4</sub> in the soil surface.

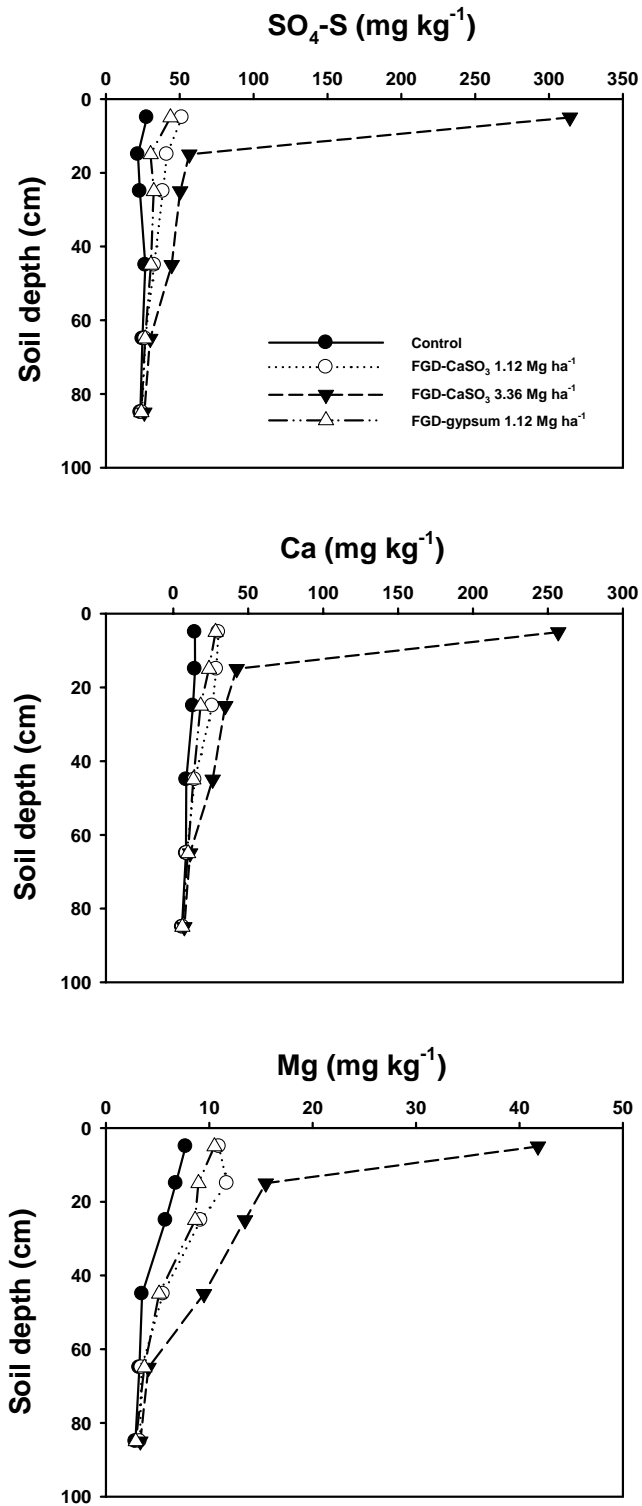


Fig. 5. Changes in water-soluble SO<sub>4</sub>-S, Ca, and Mg in the soil at different depths 61 days after surface application of FGD-CaSO<sub>3</sub> or FGD-gypsum.

Sixty-one days after treatments, concentrations of water-soluble Al were significantly decreased in the soil layers of 0-30 cm by all treatments of FGD-CaSO<sub>3</sub> or FGD-gypsum (Fig. 6). Concentrations of water-soluble Zn was decreased in the soil layers of 0-90 cm. The impact of 1.12 Mg ha<sup>-1</sup> FGD-CaSO<sub>3</sub> was similar to that of FGD-gypsum.

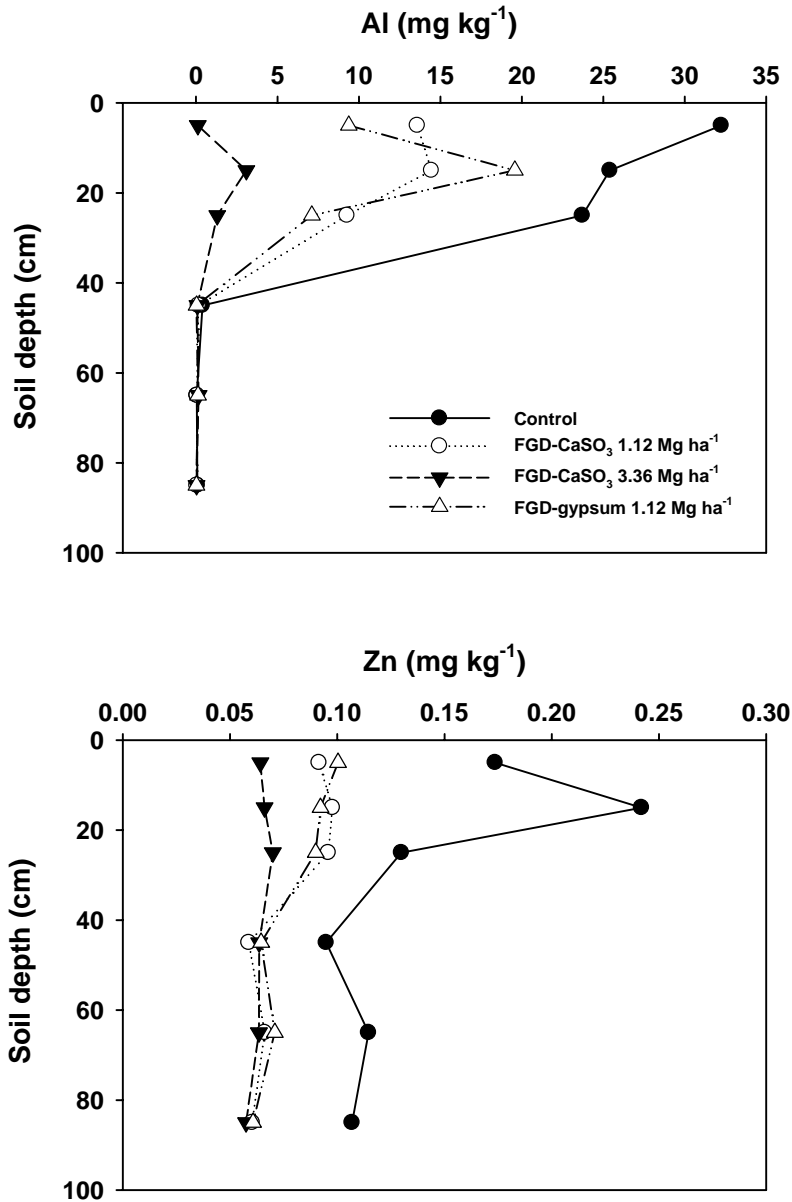


Fig. 6. Changes in water-soluble Al and Zn in the soil at different depths 61 days after surface application of FGD-CaSO<sub>3</sub> or FGD-gypsum.

## CONCLUSIONS

Sulfite in FGD-CaSO<sub>3</sub> was rapidly oxidized to SO<sub>4</sub><sup>2-</sup> within three days when applied to the moist surface of a field in the spring. There were no differences in the concentrations of water-soluble SO<sub>4</sub>-S and Ca in the soil surface (0-10 cm) over time or at different depths 61 days after 1.12 Mg ha<sup>-1</sup> of FGD-CaSO<sub>3</sub> or FGD-gypsum was applied to the soil. Effects of FGD-CaSO<sub>3</sub> on water-soluble Mg, K, Al, Fe, Mn, and Zn in soils were similar to those of FGD-gypsum when applied at the rate of 1.12 Mg ha<sup>-1</sup>. It is safe for plants if FGD-CaSO<sub>3</sub> is applied to the field surface one month before planting.

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