

## Evaluate Changes in Soil Chemical Properties Following FGD-Gypsum Application

Yong Bok Lee<sup>1)\*</sup>, Jerry M. Bigham<sup>2)</sup>, and Pil Joo Kim<sup>3,4)</sup>

<sup>1)</sup>National Institute of Agricultural Science & Technology, RDA, Suwon 441-707, South Korea

<sup>2)</sup>School of Environment and Natural Resources, The Ohio State University, Columbus, OH 43210, USA

<sup>3)</sup>Division of Applied Life Science (BK21), Gyeongsang National University, Jinju 660-701, South Korea

<sup>4)</sup>Institute of Agriculture and Life Science, Gyeongsang National University, Jinju 660-701, South Korea

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**ABSTRACT:** Natural gypsum has been used as a soil amendment in the United States. However, flue gas desulfurization (FGD)-gypsum has not traditionally been used for agricultural purpose although it has potential benefit as a soil amendment. To expand use of FGD-gypsum for agricultural purpose, the effect of FGD-gypsum on soil chemical properties was investigated in the field scales. Application rates for this study were 0 (control), 1.1, and 2.2 Mg ha<sup>-1</sup> of FGD-gypsum. After two year application, the soil samples were taken to 110 cm depth and sub-sampled at 10 cm intervals. The heavy metal contents in FGD-gypsum were lower than ceiling levels allowed by regulations for land-applied biosolids. Soil pH was not largely affected by FGD-gypsum application. Although degree of calcium (Ca) saturation in surface horizons increases only slightly with respect to the control, there is a clear decrease in exchangeable aluminum (Al). FGD-gypsum clearly increases the soil electrical conductivity (EC) with increasing application rate. Water-soluble Ca and sulfate is increased with FGD-gypsum application and these ions moved to a depth of at least 80 cm after only 2 years. We conclude that surface application of FGD-gypsum can mitigate toxicity of Al and deficiency of Ca in subsoil of acid soil.

**Key Words:** Flue gas desulfurization (FGD)-gypsum, Al toxicity, soil amendment

### INTRODUCTION

Coal is the nation's most important fuel for electricity production and will remain so for many years provided economical and socially acceptable methods are identified to counter the emission of atmospheric pollutants from coal combustion. To comply with the Clean Air Act Amendments of 1990, various technologies have been introduced for SO<sub>2</sub> removal from the emissions of coal-fired power plants. These technologies give rise to large quantities of flue gas desulfurization (FGD) materials that include SO<sub>2</sub> reaction products such as gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O).

Gypsum is one of the earliest forms of fertilizer used in the United States, having been applied to agricultural soils for over 250 yr<sup>1)</sup>. It is a quality source of both calcium (Ca) and sulfur (S) for plant nutrition and is much more soluble than calcite or dolomite. Whereas the beneficial effects of calcite or dolomite are mostly limited to the zone of incorporation, surface applications of gypsum may affect soil physical and chemical properties at depth. Gypsum application to Ca-deficient soils in humid regions have shown beneficial effects because of Ca movement into the subsoil, thereby improving root growth and lowering water stress<sup>2-4)</sup>. Ritchey et al.<sup>5)</sup> reported that application of FGD-gypsum to the plow layer reduced subsurface Al toxicity and improved deep rooting so that water and nutrient uptake by corn, wheat, and leuceana was dramatically

\*Corresponding author:  
Tel: +82-31-290-0315 Fax: +82-55-757-0178  
E-mail: soiltest@daum.net

improved.

Farmers have not traditionally used gypsum in Ohio (USA) due to the cost of mined gypsum and the perception that benefits are limited. High-purity gypsum recovered from the slipstream process at the Zimmer Station of Cinergy in Ohio, USA produced over 1.2 Mg of gypsum per hour when the system was established in 1994<sup>6</sup>. Because of its quality, this gypsum can be used for a variety of commercial applications, including production agriculture. The availability of high quality FGD-gypsum and demonstrated improvements in soil chemical properties that translate to higher yields could dramatically boost agricultural demand. Therefore, the objectives of this study were to determine the effects of FGD-gypsum on the chemical properties of soils to demonstrate the agricultural benefit by application of FGD-gypsum.

## MATERIALS AND METHODS

### Flue gas desulfurization gypsum

The wet FGD-gypsum was obtained from the Zimmer Station Power Plant operated by CENERGY Corporation near Cincinnati, OH. Total S was measured using a LECO Model 521 induction furnace and Model 518 semi-automatic titrator with K iodate titration of SO<sub>2</sub> evolved by combustion of a 10 mg sample at 900°C. Total Ca and Mg were determined by atomic absorption spectrometry using a Varian SpectrAA5 instrument following complete dissolution of the samples in an acid digest prepared according to Kost et al.<sup>7</sup>. Trace element concentrations were obtained from samples digested according to Method 3050B<sup>8</sup> with subsequent analysis of the digests using a Varian VISTA-AX inductively coupled plasma-atomic emission spectrometer (ICP-AES).

### Field experiment and Soil analysis

The field experiment was conducted in Crawford County, Ohio which had not received gypsum application in previous years. FGD-gypsum was applied at rates of 0, 1.1, and 2.2 Mg ha<sup>-1</sup> on April, 2003 and 2004. These treatments were surface-applied by broadcast to plots 10 by 10 m arranged in a randomized block design with three replicates. In October, 2004, four undisturbed cores were

collected from three replicates of each treatment. The cores were taken to 110 cm depth and sub-sample at 10-cm intervals. The sub-samples were then mixed to obtain a single sample for each depth increment in each plot (11 depth intervals × 9 plots = 99 samples). Soil pH was determined from 1:1 (soil:water) mixtures and 1:2 (soil:0.02 M CaCl<sub>2</sub>) mixtures using a pH meter. Particle size distribution of the <2-mm soil material was determined by using modification of the pipette method of Kilmer and Alexander<sup>9</sup>. Electrical conductivity (EC) and water-soluble Ca, Mg and SO<sub>4</sub>-S were measured as follows. Water was added to 50 g of soil in a 250 ml beaker with stirring until the mixture glistened and flowed slightly when the container was tipped. The mixture was allowed to equilibrate overnight and was then transferred to a 250 ml centrifuge bottle and centrifuged at 3000 rpm for 20 min to separate the soil solids and pore water. The supernatant liquid was decanted and filtered through a 0.45 micron membrane filter. After filtration, the water-soluble Ca and Mg were analyzed by atomic absorption spectroscopy, and water-soluble SO<sub>4</sub>-S was obtained by using ion chromatography.

The procedure for total C was adapted from that of Nelson and Sommers<sup>10</sup>. Exchangeable bases were determined using the procedure of Holmgren<sup>11</sup> and total extractable acidity was determined by the method of Peech<sup>12</sup>. Available phosphorus was analyzed using the method of Kuo<sup>14</sup>. Cation exchangeable capacity (CEC) was calculated by sum of extractable acidity and exchangeable K, Ca, Mg, and Na. The method for determination of extractable Al was taken from Lin and Coleman<sup>13</sup>.

## RESULTS AND DISCUSSION

The total content of Ca and S in FGD-gypsum was higher than that of natural mined gypsum that has been used for many years as an agricultural amendment in USA<sup>15</sup> (Table 1). The heavy metal contents in FGD-gypsum were much lower than ceiling levels permitted by government regulations for land-applied biosolids using U.S. EPA 503 standards<sup>16</sup>. The calculated metal loading with FGD-gypsum application rates of 5 Mg ha<sup>-1</sup>

**Table 1. Total concentration of major and minor elements in FGD-gypsum.**

Ca	Mg	S	Al	As	B	Cd	Co
----- g kg <sup>-1</sup> -----			----- mg kg <sup>-1</sup> -----				
287	0.31	213	250	<1.24	32	<0.5	<0.5
Cr	Cu	Fe	Mo	Ni	Pb	Se	Zn
----- mg kg <sup>-1</sup> -----							
0.62	<0.5	140	0.25	0.55	<0.5	2.0	1.69

**Table 2. Selected characteristics of soil used in this experiment.**

Soil depth (cm)	PSD (%)			pH		OC (g kg <sup>-1</sup> )	Ex. Cation (cmol <sup>+</sup> kg <sup>-1</sup> )		
	Sand	Silt	Clay	H <sub>2</sub> O	CaCl <sub>2</sub>		Ca	Mg	K
0-10	25.0	58.4	16.6	6.0	5.5	15.2	10.2	1.5	0.38
10-20	24.3	48.9	26.8	5.3	4.5	12.5	8.5	1.4	0.26
20-30	25.6	46.9	27.5	5.0	4.5	8.0	9.3	1.8	0.23
30-40	18.1	49.5	32.4	5.3	4.9	5.8	11.9	2.5	0.31
40-50	20.5	50.7	28.8	5.9	5.6	5.4	12.8	3.3	0.28
50-60	23.2	54.0	22.8	6.4	6.1	5.0	13.9	3.8	0.24
60-70	22.0	57.8	20.2	6.7	6.5	5.2	16.8	4.0	0.22
70-80	24.4	54.1	21.5	7.1	6.6	5.6	15.9	3.5	0.21
80-90	23.7	53.8	22.5	7.3	6.9	6.6	18.0	3.7	0.20
90-100	23.9	52.9	23.2	7.5	7.1	11.1	25.5	4.0	0.19
100-110	22.8	52.9	24.3	7.5	7.1	10.1	24.8	4.0	0.18

PSD = Particle size distribution; OC = Organic carbon

yr<sup>-1</sup> were 100 to 10,000 times lower than annual loading rates permitted by these same regulations. Thus, FGD-gypsum could be applied without restriction for trace metal loading when it was applied with recommended rates.

The farm used in this study had been a corn-soybean rotation field. The surface soil selected for this study was silt loam with relatively low organic carbon content (15.2 g kg<sup>-1</sup>) (Table 2). The depth distribution of soil characteristic was determined in order to assess changes in soil chemical properties with depth as a result of FGD-gypsum application.

Several studies have proposed that gypsum applications may affect pH by two opposing reactions. One is a so-called self-liming effect involving the displacement of surface OH groups by sorption of SO<sub>4</sub>, which should increase the soil pH. The other is a salt effect with the potential to decrease soil reaction<sup>17,18, 23</sup>. Thus, an increase or decrease of soil pH after gypsum application should be governed by whichever reaction is dominant.

In this study, no consistent impact on soil was observed after FGD-gypsum application (Fig. 1),

thereby indicating that OH released as a result of self-liming was balanced by protons displaced through a salt effect. But pH (H<sub>2</sub>O) of the surface horizons (0-10 cm) was slightly decreased due to a salt effect.

Although % saturation of the cation exchange capacity (CEC) with Ca in the upper soil horizons increased only slightly with respect to the control, there is a clear decreased in exchangeable Al (Fig. 2). The decrease in exchangeable Al without neutralizing soil acidity can be explained by the formation of insoluble basic Al hydroxysulphate compounds as suggested by Adams and Rawajfih<sup>19</sup> and Hue et al.<sup>20</sup>. The previous study clearly demonstrates that gypsum can be applied to acid soils to mitigate the detrimental effects of Al toxicity and Ca deficiency<sup>2,21,22</sup>.

FGD-gypsum clearly increases the soil EC in proportion to the amount of material applied in this study (Fig. 3). The higher EC value are also reflected in elevated concentrations of water-soluble Ca and sulfate and indicate that leachates from surface applied FGD-gypsum have influenced soil chemistry to a depth of at least 80 cm after

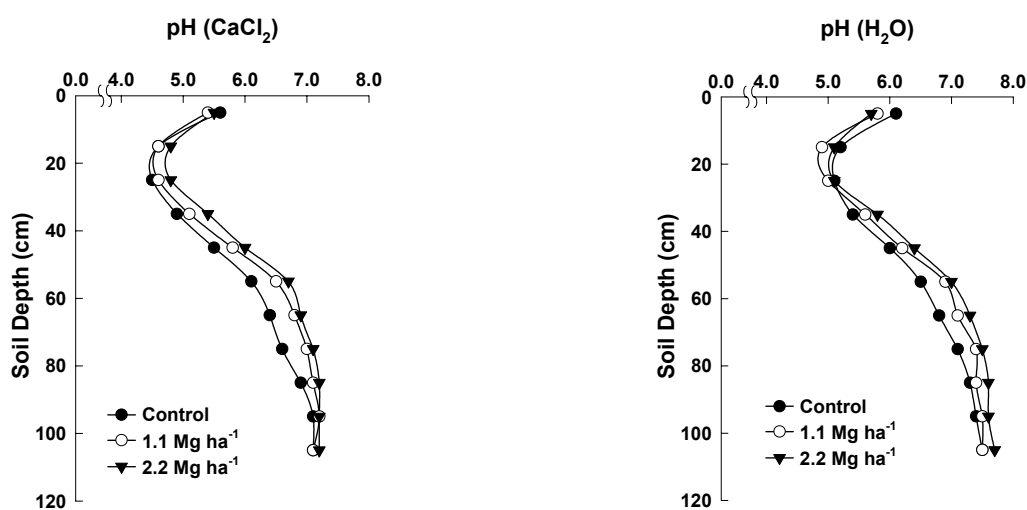


Fig. 1. Effects of surface-applied FGD-gypsum on pH at different soil depths.

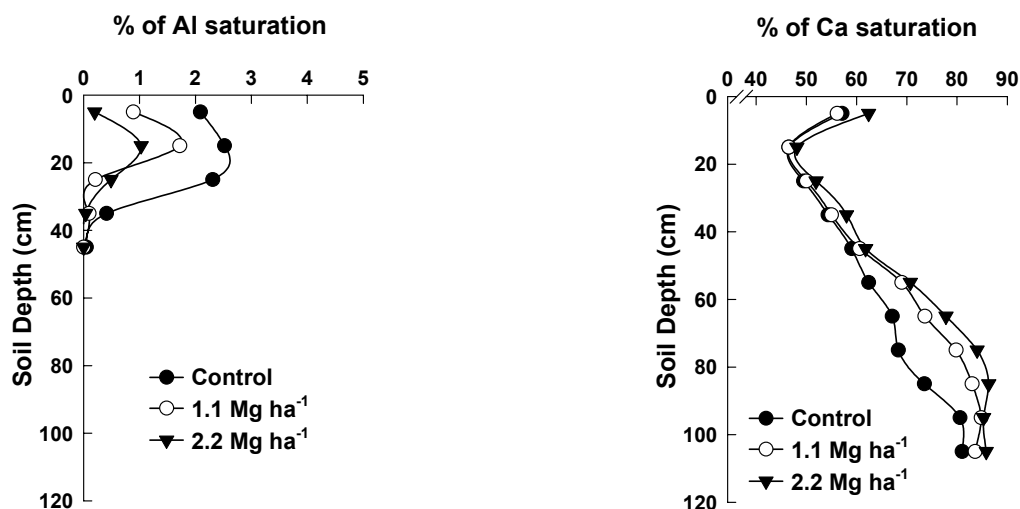


Fig. 2. Effects of surface-applied FGD-gypsum on degree of base saturation at different soil depths.

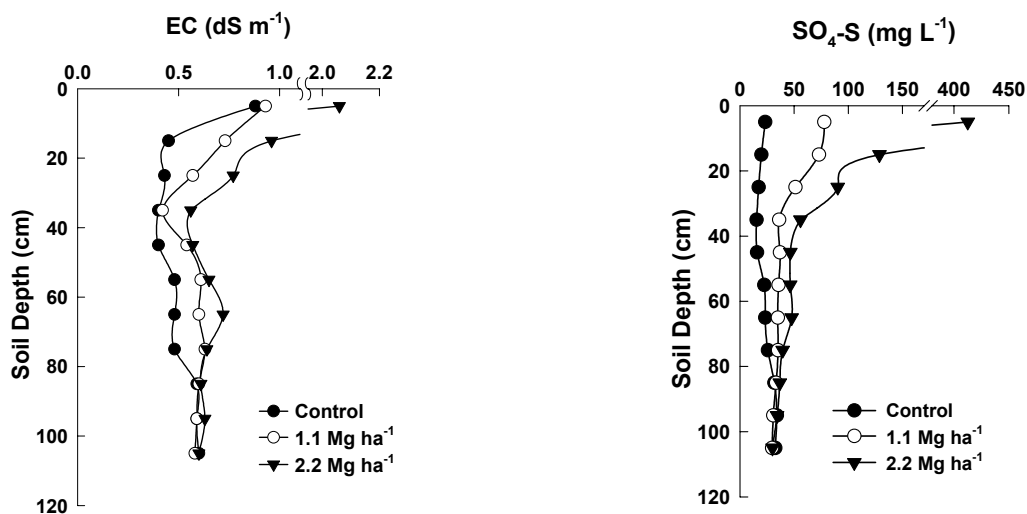


Fig. 3. Effects of surface-applied FGD-gypsum on EC and water soluble SO<sub>4</sub>-S at different soil depths.

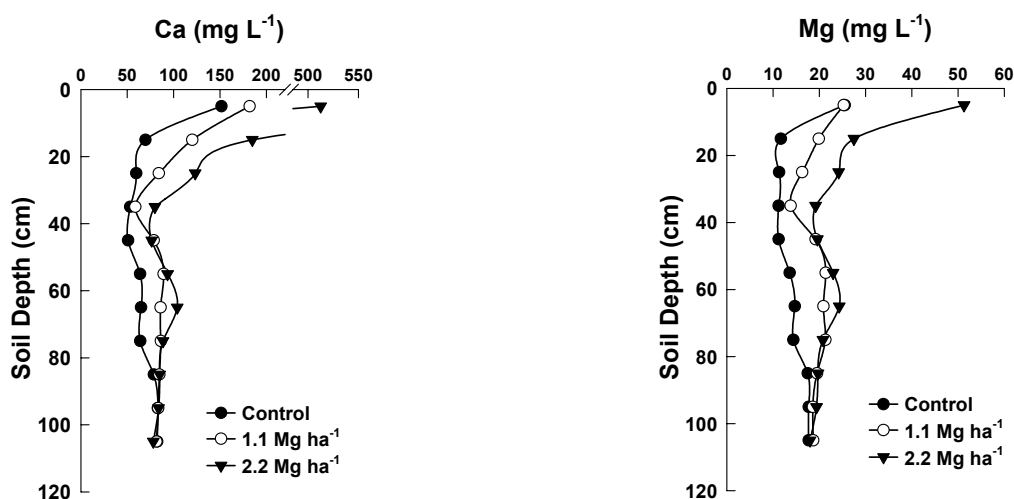


Fig. 4. Effects of surface-applied FGD-gypsum on water soluble Ca and Mg at different soil depths.

only 2 year. FGD-gypsum treatments have also increased the water-soluble Mg concentrations (Fig. 4). The observed increase in water-soluble Mg concentrations can be attributed to the replacement of Mg by Ca because content of Mg in FGD-gypsum was not significant. Many researchers reported exchangeable Mg was decreased by gypsum application in arable soil<sup>4,18,23</sup>. Sumner<sup>24</sup>, in fact, suggested that Mg should be added to some soils after gypsum applications in order to maintain an adequate Mg level.

The detrimental effects on plant growth of factors associated with soil acidity, particularly of high levels of exchangeable Al and Ca deficient in subsoil, are well known. In order to reduce these detrimental effects, possible strategies which have been proposed include the use of Al tolerant crops, physical modification of the profile involving deep liming. However, incorporation of lime into the subsoil is not feasible in general because of costs of deep plowing, plant spacing, and population. Our results indicate that application of FGD-gypsum can mitigate Al toxicity and Ca deficiency without mechanically incorporation the amendments into the subsoil.

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