Renovation of Acidic Appalachian Soil with FGD Gypsum and FBC Residue: Soil Leachate Evaluation

K. Dale Ritchey[1], M. Zaifnejad[2,3], Ralph B. Clark[1], V.C Baligar[1], and D. C. Martens[2]

[1]Appalachian Farming Systems Research Center, U.S. Department of Agriculture, Agricultural Research Service, 1224 Airport Road, Beaver, WV 25813-9423; [2]Dept. of Crop and Soil Environmental Sciences, Virginia Tech, Blacksburg, VA 24061; [3]Present address: P.O. Box 2165, Camarillo, CA 93011-2165.

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ABSTRACT

Appalachian pasture and woodland soils are often acidic and low in Ca and Mg. Limestone supplies Ca and insolubilizes toxic Al and Mn, but incorporation below the surface 15-cm soil layer is impractical. Addition of coal combustion scrubber products rich in $CaSO_4$ allows Ca leaching into subsurface horizons to reduce limitations to root growth. The top 15 cm of columns of a Typic Hapludult (Lily) loam soil were treated with dolomitic limestone (Ca_{2-x} Mg_x $(CO_3)_2$) (Aglime), flue gas desulfurization (FGD) gypsum, Aglime + FGD gypsum, FGD gypsum + 6% $Mg(OH)_2$, and a fluidized bed combustion residue (FBC). The 105 cm tall columns were leached with 138 cm water, the equivalent of approximately one year of rainfall. From 11% to 16% of the Ca in the gypsum treatments leached out of the columns. In the Aglime + FGD gypsum treatment 38% of the total Mg, an important plant nutrient, was lost as leachate. Percentage retention of Mg from the FGD gypsum + 6% $Mg(OH)_2$ treatment was even lower. Soil Al decreased, partly due to Al leaching from the column. Leachate Al concentrations reached 11 mg/L.

INTRODUCTION

Many Appalachian soils are infertile and acidic, and plant growth is limited by Al and Mn toxicity. Incorporation of ground limestone (Aglime) in surface horizons increases soil pH and neutralizes Al toxicity, but this management practice does not reduce Al toxicity in deeper horizons.[4] Due to its relatively high solubility, gypsum is able to leach below the zone of incorporation and improve soil Ca status. In addition, sulfate anions form non-toxic complexes with Al, and in some acid soils displace hydroxyl groups to raise soil pH.[5]

Gypsum is an major component of various types of coal combustion products (CCP) resulting from industrial scrubbing processes designed to reduce flue gas discharge of S into the atmosphere. Some of these products are of relatively high purity and available in considerable quantities, making their use as agricultural soil amendments attractive within economically feasible transportation distances.

One side effect of gypsum application is enhancement of leaching and subsequent loss of Mg, a plant nutrient often deficient in acidic soils. Concomitant application of dolomitic limestone is recommended to maintain adequate Mg supplies when gypsum is used. Another approach recently proposed[2] is the enrichment of gypsum with $Mg(OH)_2$.

In this laboratory column study we investigated chemical composition of leachates resulting from application of several gypsum-containing soil amendments to evaluate potential effects on the environment and amendment effectiveness in controlling leaching losses of native and applied Mg.

MATERIALS AND METHODS

Polyvinyl chloride (PVC) cylinders, 120 cm long, were lined with two layers of 4 mil plastic film (resulting in an effective diameter of about 10 cm), and filled to 90 cm with air-dried Lily soil (fine-loamy, siliceous, mesic, Typic Hapludult) packed to 1.1 g/cm^3 bulk density. The bottom of each column was covered with landscaping cloth through which the percolating soil solution could drain and be collected. Some properties of the original acidic Lily soil were: 63% sand, 31% silt, 7% clay, 5.0% organic matter; pH 4.7 (1 soil/1 water) and 4.0 (1 soil/1 0.01 *M* $CaCl_2$); 0.06 dS/m electrical conductivity (1 soil/1 water); 3.02 $cmol_c/kg$ exchangeable acidity and 2.55 $cmol_c/kg$ exchangeable Al (1 *M* KCl-extractable). Extractable nutrients (1 *M* ammonium acetate) (in mg/kg) were 56 Ca, 57 K, 9.8 Mg, 9.0 Na, and 67 S. Aluminum saturation was 65%.

At the top of each soil column was placed an additional 15 cm layer of Lily soil at bulk density 1.1 g/cm^3 mixed with the different CCPs and dolomitic limestone. The treatments were (in g product per column): no CCP or limestone (Check), agricultural dolomitic limestone (Aglime) at 4.69; high-$CaSO_4$ flue gas desulfurization (FGD) gypsum low in Mg at 18.74; combination of limestone plus FGD (Aglime+FGD) at 4.69 + 18.74, respectively; high-$CaSO_4$ FGD containing 6% $Mg(OH)_2$ (FGD+Mg) at 18.74; and fluidized bed combustion residue (FBC) at 7.61. On an area basis, these rates are equivalent to 5977 kg/ha (or 5296 lb/acre) aglime, 9694 kg/ha FBC and 23,873 kg/ha FGD.

The FGD gypsum contained 23.8% Ca, 0.02% Mg, and 17.7% S. The FDG+Mg byproduct contained 20.9% Ca, 2.3% Mg, and 16.3% S. The FBC material contained 41.4% Ca, 0.4% Mg and 16.0% S. The Aglime contained 22.8% Ca, 11.6% Mg, and 0.2% S. The neutralizing capacity of the materials (in g $CaCO_3$ equivalent per 100g) was 5.0 for FDG gypsum, 13.1 for FGD+Mg, and 55.2 for FBC.[1]

Fertilizer P and K (1690 kg/ha P and 2140 kg/ha K as KH_2PO_4) were added to the soil before leaching, and nitrogen (255 kg/ha as NH_4NO_3) and K (50 kg/ha as KCl) were dissolved in leaching water and added to the columns 28 days after leaching started. The fertilizer levels approximate those that would be found under a field band application for maize.

Deionized distilled water equivalent to 138 cm rainfall, which is approximately equal to the annual average in West Virginia, was added to the columns over 39 days to leach the soil. Water was added in 10-cm increments three times per week. Leachates were collected 2 days after each irrigation. Elemental composition of leachate was determined by ICP spectroscopy. The experimental design was a randomized complete block with four simultaneous replications.

RESULTS AND DISCUSSION

pH

The pH of the leachate from the check soil rose from its initial value of 4.6 for the first 11 cm of leachate collected to nearly 5.5 for the 21-31 cm leachate fractions, then varied between 5.6 and 4.9 (Fig. 1). The initial behavior of the leachate from the Aglime treatment was similar, but slightly lower for the 31-95.7 cm leachate fractions. The leachate from the FBC treatment initially behaved similarly to the Check and Aglime treatment leachates, but then pH began to decrease and reached 4.3 in the 76-95.7 cm fractions similar to the FGD treatments. In the three FGD-containing treatments, pH was relatively stable with a small increase in pH initially, and a final pH near 4.3.

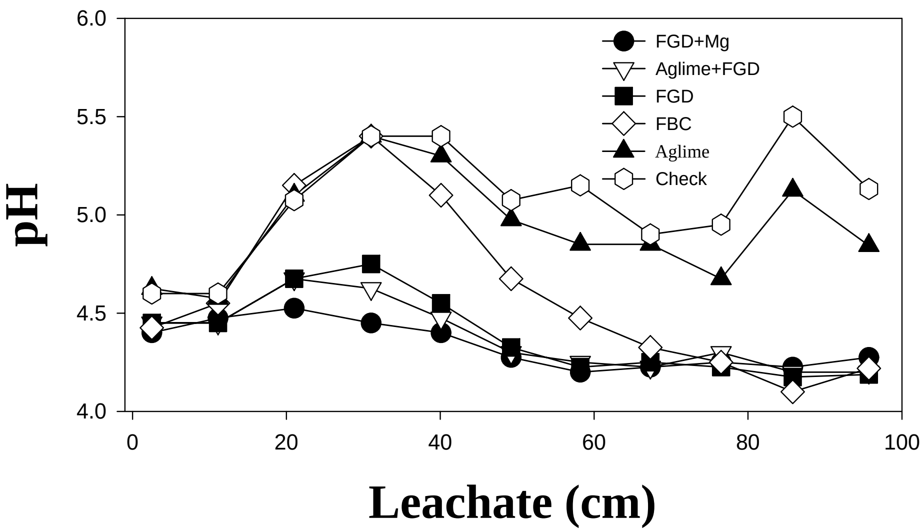

Figure 1. Values of pH for leachates from soil columns that received six surface layer treatments, as a function of cumulative amount of leachate.

Sulfur

There was little native soil sulfur in the leachates from the columns that did not receive CCP materials (Check and Aglime treatments) (Fig. 2). In the FBC treatment, the amount of S leached in the first 95.7 cm was 41% of that leached from the FGD treatment (Table 1), which is consistent with the amount of S added (approximately 37% of that in the FGD treatment). The highest leachate S concentration (21.6 meq/L) was observed in the Aglime+FGD treatment, but it was still lower than what would be present if the solution were saturated with gypsum (28 meq/L).[8] In the two FGD gypsum treatments amended with aglime and $Mg(OH)_2$, 30% and 39% more S leached than from the FGD gypsum treatment (Table 1). The greater amount of S leached may have been associated with decreased S retention in the top section of the column due to higher pH resulting from neutralization of acidity by the aglime and $Mg(OH)_2$, because retention of sulfate by soil is lower at higher pH levels.[3] In addition, greater intensity of leaching of S in the high Mg treatments may be partly due to reaction of dolomitic limestone or $Mg(OH)_2$ with gypsum in an acidic environment to produce $MgSO_4^o$, an uncharged ion pair. The electrically neutral $MgSO_4^o$ can leach through soils more easily because it is not retained by charged soil particle surfaces. In addition, its solubility is higher than that of $CaSO_4$. Researchers in Ohio found that subsurface effects of applied gypsum were greater when large quantities of Mg were also present in the amendment mix, and they attributed this to the action of $MgSO_4$ moving into the subsoil due to its high solubility.[6]

Table 1. Total amounts of elements leached by 138 cm water from acidic Lily soil in 105 cm columns where the surface layer was treated with various amendments. Numbers in parentheses indicate amounts leached expressed as percent of the amount initially present in the soil plus that added as amendment.

	Mineral element (mg/column)							
Treatment	Ca	(%)	Mg	(%)	S	(%)	Al	(%)
Check	29 c†	(6.3)	6 d	(7.7)	145 d	(26.2)	5 c	(2.6)
Aglime	31 c	(2.0)	7 d	(1.1)	160 d	(28.5)	5 c	(2.6)
FGD	524 b	(10.6)	61 c	(71.1)	1119 b	(28.9)	37 b	(19.6)
Aglime + FGD	633 ab	(11.0)	236 b	(37.5)	1457 a	(37.5)	49 a	(25.9)
FGD + Mg	682 a	(15.6)	307 a	(60.5)	1555 a	(43.2)	55 a	(29.1)
FBC	97 c	(2.7)	28 cd	(25.5)	457 c	(25.9)	15 c	(7.9)

†Means in a column followed by the same letter are not significantly different by LSD test ($P \leq 0.05$).

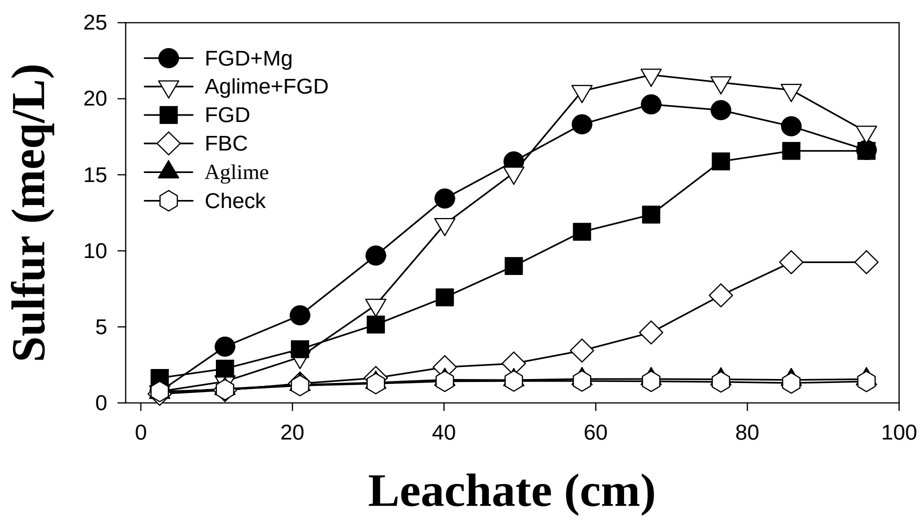

Figure 2. Leachate S concentrations from soil columns that received six surface layer treatments, as a function of cumulative amount of leachate.

Calcium

The levels of Ca in the Check and Aglime treatment leachates were low, and almost identical, beginning at 0.5 meq/L and dropping to 0.2 meq/L, which supports the observation[4] that there is little movement of Ca from moderate limestone applications, due to the lack of an accompanying anion stable at typical soil solution pH levels (Fig. 3).

The largest amounts of Ca in leachates were found in the three treatments receiving FGD gypsum (Table 1). For the six treatments, the amount of Ca leached was closely linked with the amount of sulfate leached [Ca (meq/L) = -0.325 + 0.385 S (meq/L), r^2=0.95]. Initially the Ca concentration was highest in the FGD+Mg treatment, but after the 49-58 cm leachate fraction, the Aglime+FGD treatment surpassed it.

Leaching in the FBC treatment was delayed considerably compared with the other byproduct treatments. It was not possible to determine if Ca in FBC leachate had reached a maximum, but in the first 95.7 cm of leachate, only 3% of the Ca added as FBC had leached compared to 12% for the FGD treatment. While some of this difference can be attributed to the smaller amount of Ca added, the lower leachate levels could also be attributed to lower solubility of Ca components of FBC, slower movement of the accompanying anion through the column, and to greater reaction and subsequent retention of FBC components on soil particle surfaces compared to FGD gypsum.

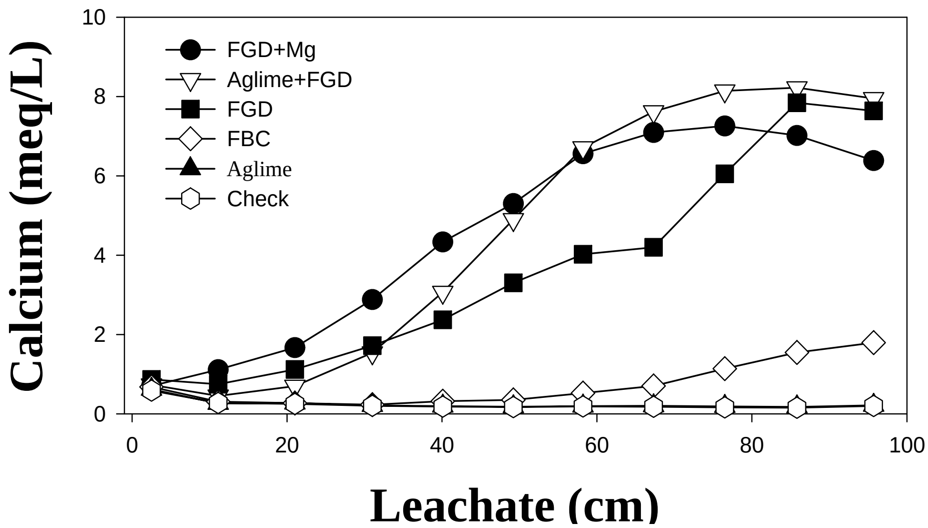

Figure 3. Leachate Ca concentrations from soil columns that received six surface layer treatments, as a function of cumulative amount of leachate.

Aluminum

Little Al was present in the leachate from the Check and the Aglime treatments (data not shown). For the six treatments there was a close association between the concentration of Al and S in the leachate [Al(meq/L) = 0.053 + 0.055 S(meq/L), r^2=0.96], and a slightly less close association between Al and Ca (r^2=0.91). The association of Al with pH was lower (r^2= 0.55), indicating that pH was not as important in promoting leaching as the action of Ca and S. Calcium probably displaced Al from the exchange complex, and sulfate in soil solution facilitated its downward movement. As reported in a separate paper, higher levels of soil Ca and lower levels of Al in the gypsum treatments resulted in improved root growth in subsurface layers.[11] Lower exchangeable Al levels were due to increased soil pH and precipitation/sorption reactions as well as leaching of Al from columns.

Concentrations of Al in some leachate fractions of the gypsum treated columns reached 1.24 meq/L (11 mg/L), which exceeded the Secondary Maximum Contaminant Level for drinking water of 0.05 to 0.2 mg/L.[7] Our column results indicate that water collected from directly below the plow layer where gypsum has been incorporated would probably not meet drinking water standards. However, it is probable that water draining from a treated field would mix with water from other areas and Al concentrations would be considerably reduced, and as leachate filters through subsoil and rock strata, some solutes would be absorbed by mineral constituents.

Magnesium

Maintaining an adequate level of Mg in the surface layer of agricultural soils is necessary for adequate plant growth and to keep plant Mg concentrations above 2 g/kg to avoid problems with hypomagnesia in lactating cows grazing forage with elevated K/Mg ratios.[9] It is difficult to keep Mg levels high in the presence of gypsum because sulfate greatly increases Mg mobility. In the two gypsum treatments with added Mg (Aglime+FGD and FGD+Mg), the patterns of leached S and Mg were similar (Fig. 2, Fig. 4), and the correlation between S and Mg was highly significant [Mg (meq/L) = -0.0377 + 0.241 S (meq/L), r^2=0.95]. The high mobility resulted in a leaching loss of 71% of the Mg in the FGD gypsum treatment. In contrast, the highest percentage of total initial Ca lost in leachate for any treatment was 16% (Table 1).

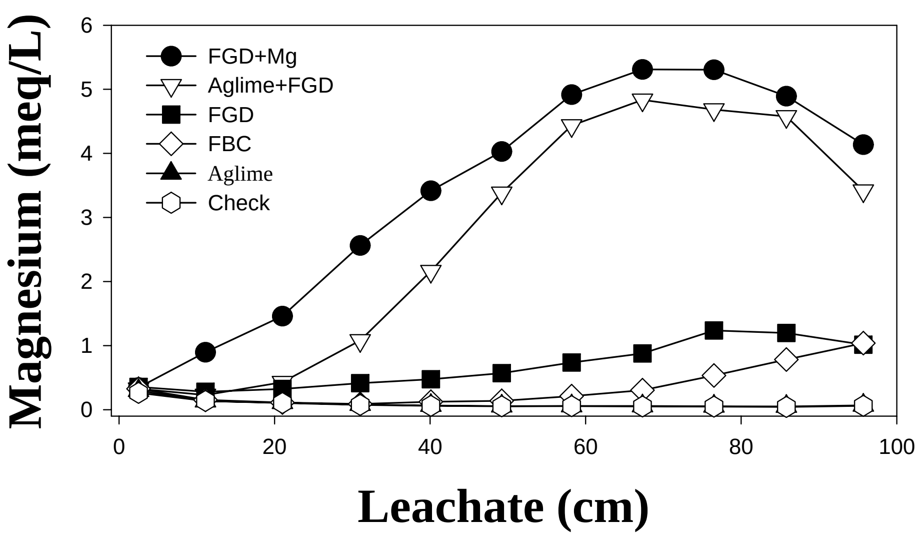

Figure 4. Leachate Mg concentrations from soil columns that received six surface layer treatments, as a function of cumulative amount of leachate.

As discussed elsewhere,[10,11] higher levels of leaching resulted in serious Mg depletion in the top 15 cm of soil. The Mg level decreased from 10 mg/kg in the Check to 4 mg/kg in the FGD treatment, and the Ca/Mg ratio increased from 3 to 184. Wheat plants grown in the FGD-treated columns showed serious Mg deficiency.[10]
One objective of this experiment was to compare the effectiveness of supplementation of gypsum with two Mg sources in maintaining adequate Mg levels in the rooting zone. Supplementation of gypsum with dolomitic limestone was more effective than use of $Mg(OH)_2$-amended FGD gypsum in maintaining adequate levels of Mg in the soil, as final soil Mg levels were 104 mg/kg in the Agime+FGD treatment compared to only 20 mg/kg in the FGD+Mg treatment.[11] Leaf Mg levels of plants grown with Aglime+FGD were 1.74 g/kg compared to 0.54 g/kg in plants grown with FGD+Mg treatment, but both treatments overcame yield depression associated with Mg deficiency.[10]

The total amount of Mg contained in leachate from the Aglime+FGD treatment (236 mg/column) was lower than from the FGD+Mg treatment (307 mg/column) (Table 1), even though the amount of Mg added to the top 15 cm was somewhat higher (550 mg vs. 430 mg in the FGD+Mg treatment). This indicated that dolomitic limestone was an effective Mg source. The decrease in Mg leaching losses where Aglime+FGD was added may have been caused by the higher pH present in the surface soil (pH 5.4 compared to pH 4.6 in the Aglime+FGD treatment); the higher pH would have increased the effective cation exchange capacity of the soil.

SUMMARY AND CONCLUSIONS

Gypsum applications increased downward movement of Al, Ca, S and Mg and improved plant rooting in acidic subsoils, but the increased leaching losses of Mg from surface layers decreased the amount of Mg available to plants. In a low-fertility Appalachian soil, application of FGD gypsum without supplemental Mg increased leachate losses of Mg by a factor of 10 and induced a Ca/Mg imbalance in the surface soil.

Supplementation of gypsum with 6% $Mg(OH)_2$ improved the Ca/Mg balance, but 60% of the applied Mg was still leached. Application of gypsum together with dolomitic limestone eliminated Mg stress, and reduced the amount of Mg found in leachates compared to the Mg-supplemented gypsum treatment.

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