

Amelioration of acid soil infertility by phosphogypsum

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Abstract

Amelioration of subsoil acidity requires an increase in Ca status along with a decrease in Al status in subsoil. In this study, effects of phosphogypsum (PG) on the amelioration of subsoil acidity have been evaluated, using cultivated and woodland subsoils representing Cecil, Wedowee (both Typic Hapludult) and Bladen (Typic Albaquult) series. Subsoil (0.6–0.8 m) samples were collected and treated with either PG (approximately 2 Mg ha⁻¹ rate), Ca(NO₃)₂ or Mg(NO₃)₂ along with an unamended control treatment. A fertile topsoil amended with NH₄NO₃ was placed on top of all treated subsoils. Top and root growth of alfalfa [*Medicago sativa* (L.) cv. Hunter River] and soybean [*Glycine max* (L.) Merr. cv. Lee] were significantly greater in PG-amended than in unamended pots of the Cecil and Wedowee soils, although most growth was observed with the Ca(NO₃)₂-amended treatment. In the Bladen soil, however, none of the amendments evoked a significant growth response in either alfalfa or soybean. The concentration of Ca in the displaced soil solution (in soils with no plants) as well as tissue levels of Ca suggest that the growth response was partly due to an improved Ca availability in both PG or Ca(NO₃)₂-treated soils. Exchangeable Al decreased in PG-amended soils. The self-liming effect of PG, which is a release of OH⁻ due to ligand exchange between SO₄²⁻ and OH⁻, as well as a decrease in exchangeable Al in PG-amended soil is greater in predominantly kaolinitic Cecil and Wedowee soils than in smectitic Bladen soil. As a result, significant growth response to PG amendment was observed in the Cecil and Wedowee soils, but not in the Bladen soil.

Introduction

The major deleterious effects of soil acidity on crop growth are Al toxicity and Ca deficiency. Liming to raise soil pH has been a widely accepted practice to alleviate soil acidity, but, the movement of surface-applied lime down the soil profile is extremely slow. Therefore, a conventional liming practice has very little effect in alleviation of acid subsoil infertility. Although deep liming is an effective way to alleviate subsoil acidity, it requires extremely expensive tillage operations. As an alternative approach, amelioration of subsoil acidity by surface appli-

cation of gypsum was demonstrated for the first time by Sumner (1970). Subsequent studies conducted in Brazil, South Africa and Southeastern United States on the use of gypsum or industrial by-products including phosphogypsum (PG) or hydrofluorogypsum as ameliorants of subsoil acidity have been summarized by Shainberg *et al.* (1989). In those studies, the application of gypsum or PG to topsoil resulted in an increased Ca status of the subsoil along with alleviation of Al toxicity.

The alleviation of Al toxicity by gypsum is due to one or more of the following mechanisms: 1) A “self-liming” effect (Reeve and Sumner,

1972), whereby OH^- release as a result of ligand exchange between SO_4^{2-} and OH^- results in polymerization or precipitation of Al; 2) Precipitation of aluminum sulfate minerals (Adams and Rawajfih, 1977) due to an increase in SO_4^{2-} concentration in subsoils; and 3) Formation of the AlSO_4^+ ion-pair, which is less toxic to root growth than the other monomeric species (Pavan and Bingham, 1982). In addition, since PG contains F^- , application of PG results in an increased F^- concentration in soil solution resulting in Al-F ion pairs (Alva *et al.*, 1988) which are less toxic than the uncomplexed Al (Alva and Sumner, 1989; Cameron *et al.*, 1986; Noble *et al.*, 1988; Tanaka *et al.*, 1987).

Although gypsum applications to acid soils have generally resulted in positive crop growth responses, some studies have shown either no response or even negative responses (Buyeye, 1986), thus indicating the importance of soil properties in determining the effectiveness of gypsum as an ameliorant of acid soil infertility factors.

Surface charge properties of soils are of central importance in soil management, because response to an amendment is primarily determined by the reactions at soil surfaces. Soil mineralogy and cultivation history influence the surface

charge properties, which in turn may influence the response to gypsum application. However, studies on the comparison of the effectiveness of gypsum as an ameliorant of subsoil acidity in soils with varying surface charge characteristics and past cultivation practices have not been conducted.

The amelioration of acid soil infertility by PG is partly due to an increase in Ca status. The additional beneficial effects of PG through alleviation of Al toxicity could be demonstrated by comparing the effects of PG with that of another source of Ca at equivalent rates of Ca application. In this study, the effects of PG or $\text{Ca}(\text{NO}_3)_2$ on the soil solution composition and on the growth of alfalfa [*Medicago sativa* (L.) cv. Hunter River] and soybean [*Glycine max* (L.) Merr. cv. Lee] were evaluated in cultivated and woodland soils with varying mineralogy.

Materials and methods

Pot experiment

Subsoil (0.6–0.8 m) samples were collected from cultivated and adjacent woodland sites representing three soil series, namely Cecil and

Table 1. Selected properties of the soils^a used in the experiment

Soil series/ vegetation	Soil pH (1:2.5)		Exchangeable cations (c mol _c kg ⁻¹)					Clay mineralogy ^b Major/trace	Fe and Al ^c oxides	Clay ^d content
	Water	1M KCl	Ca	Mg	K	Na	Al			
<i>Wedowee</i>										
Cultivated	4.68	3.87	0.56	0.28	0.08	0.07	4.86	Ka/Cv, Gb, Gt	85.1	320
Woodland	5.00	4.03	0.50	0.20	0.06	0.11	2.25	Ka/Cv, Gb, Gt	89.1	420
<i>Cecil</i>										
Cultivated	5.34	4.40	1.06	0.42	0.41	0.07	0.57	Ka/Cv, Gb, Gt	65.1	470
Woodland	5.28	4.20	0.16	0.24	0.06	0.07	1.23	Ka/Cv, Gb, Gt	104.7	580
<i>Bladen</i>										
Cultivated	4.75	3.66	0.68	1.52	0.19	0.18	7.62	Sm/Ka, Qz	27.3	380
Woodland	4.90	3.57	2.52	2.74	0.17	0.18	10.05	Sm/Ka, Qz	28.3	490
<i>Appling</i>										
Cultivated	6.50	5.56	1.72	0.88	0.80	0.14	0.0	<-----ND ^e ----->		

^aWedowee, Cecil and Bladen soils were sampled at 0.6–0.8 m depth, while Appling soil was sampled at 0–0.2 m.

^bCv = Chloritized vermiculite, Gb = Gibbsite, Gt = Goethite, Ka = Kaolinite, Sm = Smectite, Qz = Quartz.

^cDetermination made using the procedure of Coffin (1963).

^dDetermination made using the procedure of Miller and Miller (1987).

^eAnalyses not done.

Wedowee (both Typic Hapludults) from Watkinsville, Georgia and Bladen (Typic Albauquilt) from Hinesville, Georgia. The woodland sites were undisturbed and unfertilized for more than 30 years and were under natural vegetation. The soils were air dried, ground and sieved to <2 mm. Selected properties and mineralogy of the soils are shown in Table 1. The exchangeable Ca, Mg, K, and Na were determined in 1 M NH₄OAc (Thomas, 1982), and exchangeable Al was determined in 1 M KCl (Barnhisel and Bertsch, 1982).

The treatments included: 1) control; 2) phosphogypsum [1 g kg⁻¹ (or 0.24 g Ca kg⁻¹ soil equivalent to 2 Mg ha⁻¹]; 3) reagent-grade Ca(NO₃)₂·4H₂O [1.416 g kg⁻¹ to supply Ca at a rate similar to treatment 2]; 4) reagent-grade Mg(NO₃)₂·6H₂O [1.54 g kg⁻¹ to supply 0.17 g N kg⁻¹ soil as in treatment 3]. The composition of PG used in this study is presented elsewhere (Alva and Sumner, 1989). The required quantity of amendment was thoroughly mixed with 2 kg soil and transferred to pots made of 0.10 m diameter PVC pipe. The soil when compacted occupied approximately 0.19 m height in 0.3 m-tall pots.

On top of this amended or unamended subsoil, 500 g of a fertile, near neutral Appling topsoil (Table 1) was placed, which occupied 0.08 m depth in the pots. The topsoil was identical in all pots, regardless of subsoils and amendments. For adequate plant growth, the topsoil was mixed with 0.57 g NH₄NO₃ kg⁻¹ soil (200 ppm N). High fertility status of the topsoil, near neutral pH and supply of adequate inorganic N thus provided ideal growing conditions in the topsoil for seedling emergence and initial growth until the roots reached the differentially amended subsoils of varying mineralogy.

Alfalfa cv. Hunter River (approximately 20–25 seeds per pot) or soybean cv. Lee (4 seeds per pot) were planted. Five days after emergence, the stands were thinned to 2 and 15 seedlings per pot, for soybean and alfalfa, respectively. The pots were watered daily by weight to -0.005 MPa soil water potential for about a week and then to -0.01 MPa soil water potential for the rest of the growing period. Fifty-five days after planting the tops were clipped, roots washed free of soil, and dry weights (at 80°C for

48 h) were determined. The experiment was conducted with three replications. The pots were rotated in the greenhouse once a week to eliminate possible differences in lighting conditions.

Dry matter of tops was ground. One-gram samples were ashed in a muffle furnace at 500°C for 8 h. The ash was dissolved in 10 mL of 3 M HCl and filtered through Whatman No. 42 filter paper into a 100-mL volumetric flask. The crucible was rinsed with 10 mL of 3 M HCl and the contents transferred to the volumetric flask. The filter paper was washed with approximately 50 mL distilled water before diluting the extract to 100 mL. The concentrations of Ca, Mg, K and Al were measured by inductively coupled plasma emission spectroscopy (ICPES).

Soil solution studies

Subsamples of the subsoils used in the above experiment were treated as explained above without the placement of topsoil and incubated in the greenhouse at -0.01 MPa soil water potential. Soil moisture was adjusted once a day by weighing. On 14, 30 and 50 days after incubation, approximately 200 g of moist soil was taken from each pot and the soil solution was displaced by centrifugation (Gillman, 1976) at 2500 rpm for 30 min. The pH of the soil solution was measured 3–4 min following displacement of soil solution before filtration through a 0.45 μm micronsep membrane filter and the concentrations of Ca, Mg, K, Na, Al, Si, Mn and P were determined by ICPES. The concentrations of F, P, Cl, NO₃ and SO₄ were determined by ion chromatography. Concentrations of P were <10⁻⁸ M in all soil solutions. The concentrations of various cations and anions and solution pH were employed to calculate ionic strength by using the MINTEQ computer program (Brown and Allison, 1987).

Results

All subsoils employed in this study are extremely acidic (pH-KCl values <4.4) (Table 1). Exchangeable Al was highest in the Bladen soil followed by the Wedowee and Cecil soils. The Cecil and Wedowee soils are predominantly kao-

linitic with higher free Fe and Al oxide content than the Bladen soil which is smectitic (Table 1). Therefore, permanent charge sites dominate in the Bladen soil, while the Cecil and Wedowee soils contain substantial variable charge sites.

The top and root weights of alfalfa and soybean were significantly influenced by type of subsoil, past cultivation practice, and type of amendments (analysis of variance data are not presented). Furthermore, soil \times cultivation and soil \times amendment interactions were also significant. Therefore, top and root weight data are presented for each cultivated and woodland soil for each amendment treatment (Table 2). Top and root weights of alfalfa were significantly greater on Cecil and Wedowee than on Bladen subsoil (summary data not presented). Top weight of soybean was significantly greater on Bladen and Wedowee than on Cecil subsoil, while root weight was significantly greater for Wedowee than for Bladen and Cecil subsoils.

Mean dry weights of tops and roots of alfalfa and soybean were significantly higher on cultivated than on woodland subsoils.

For the Cecil and Wedowee subsoils (both cultivated and woodland), the top and root weights of alfalfa and soybean were significantly greater in PG amended than in control treatments (Table 2), although the $\text{Ca}(\text{NO}_3)_2$ treatment resulted in by far the highest top and root growth, with few exceptions. Top and root weights in the $\text{Mg}(\text{NO}_3)_2$ treatment were generally similar to those in the PG treatment. In the Bladen soil, however, none of the subsoil amendments significantly raised top or root weights of alfalfa or soybean.

The concentration of Ca in alfalfa tops was significantly higher in the $\text{Ca}(\text{NO}_3)_2$ than in the PG treatment in the case of cultivated Wedowee and Cecil soils (Table 3), while in the other soils, no significant difference was observed. The concentration of Ca in soybean tops was not signifi-

Table 2. Effects of subsoil amendments of either phosphogypsum (PG), $\text{Ca}(\text{NO}_3)_2$ or $\text{Mg}(\text{NO}_3)_2$ on root and top growth of alfalfa cv. Hunter River, and soybean cv. Lee

Treatments	Wedowee		Cecil		Bladen	
	Cultivated	Woodland	Cultivated	Woodland	Cultivated	Woodland
Alfalfa						
<i>Root dry weight (g per pot)</i>						
Control	1.07 c ^a	1.00 c	1.80 c	1.01 c	0.94 a	0.85 a
PG	1.58 b	1.50 b	2.42 a	1.28 b	0.88 a	0.83 a
$\text{Ca}(\text{NO}_3)_2$	2.10 a	1.95 a	2.11 b	1.47 a	0.96 a	0.94 a
$\text{Mg}(\text{NO}_3)_2$	1.61 b	1.56 b	1.98 b	1.17 b	1.05 a	0.74 a
<i>Top dry weight (g per pot)</i>						
Control	0.87 c	1.05 c	1.30 c	0.72 c	0.79 a	0.79 a
PG	1.06 b	1.18 b	1.88 a	0.98 b	0.76 a	0.67 a
$\text{Ca}(\text{NO}_3)_2$	1.40 a	1.34 a	1.55 b	1.23 a	0.95 a	0.84 a
$\text{Mg}(\text{NO}_3)_2$	1.10 b	1.24 b	1.63 b	1.01 b	0.91 a	0.67 a
Soybean						
<i>Root dry weight (g per pot)</i>						
Control	1.05 c	0.87 c	1.08 c	0.66 c	1.09 a	0.91 a
PG	1.21 b	1.02 b	1.23 b	0.89 b	1.27 a	0.89 a
$\text{Ca}(\text{NO}_3)_2$	1.61 a	1.31 a	1.43 a	1.34 a	1.33 a	1.00 a
$\text{Mg}(\text{NO}_3)_2$	1.16 b	1.03 b	1.11 c	0.99 b	1.07 a	1.01 a
<i>Top dry weight (g per pot)</i>						
Control	1.99 c	2.08 b	2.51 c	1.10 d	2.57 a	0.90 a
PG	2.65 b	2.65 a	2.87 b	1.50 c	2.65 a	0.91 a
$\text{Ca}(\text{NO}_3)_2$	2.99 a	2.82 a	3.20 a	2.58 a	2.72 a	1.00 a
$\text{Mg}(\text{NO}_3)_2$	2.68 b	2.77 a	2.94 b	2.04 b	2.75 a	1.01 a

^aTreatment means followed by the same letter within crop species and plant part within each soil are not significantly different at $P = 0.05$.

Table 3. Concentration of Ca (g kg⁻¹ dry matter) in alfalfa and soybean tops as influenced by phosphogypsum (PG), Ca(NO₃)₂ or Mg(NO₃)₂ amendment in various soils

Treatments	Wedowee		Cecil		Bladen	
	Cultivated	Woodland	Cultivated	Woodland	Cultivated	Woodland
Alfalfa						
Control	0.172 b ^a	0.162 b	0.145 b	0.106 b	0.125 b	0.117 b
PG	0.190 b	0.190 a	0.150 b	0.151 a	0.143 a	0.139 a
Ca(NO ₃) ₂	0.213 a	0.199 a	0.172 a	0.172 a	0.145 a	0.137 a
Mg(NO ₃) ₂	0.182 b	0.155 b	0.132 b	0.150 a	0.130 b	0.124 b
Soybean						
Control	0.128 b	0.110 c	0.126 b	0.092 c	0.089 b	0.105 b
PG	0.158 a	0.137 b	0.169 a	0.133 a	0.144 a	0.115 a
Ca(NO ₃) ₂	0.180 a	0.171 a	0.193 a	0.136 a	0.166 a	0.118 a
Mg(NO ₃) ₂	0.131 b	0.116 c	0.124 b	0.120 b	0.089 b	0.107 b

^aTreatment means followed by the same letter within crop species and plant part within each soil are not significantly different at $P = 0.05$.

cantly different between the PG and Ca(NO₃)₂ treatments, except for the woodland Wedowee soil. The concentration of Ca in tops was generally lower for Mg(NO₃)₂-amended or control treatments than for PG or Ca(NO₃)₂ treatments in all soils. The concentration of Mg in alfalfa or soybean tops was greater for Mg(NO₃)₂-amended than for other treatments in all soils (data not shown).

Effects of amendments on soil solution properties

Values of soil solution pH displaced from unamended soils were lower by 0.1 to 0.3 pH units after 50 than after 14 days of incubation (Table 4). Soil solution pH was lower in the PG-amended than in the control treatment in all soils, but, the magnitude of the decrease was greatest in the Bladen soil. The soil solution pH was lower by 0.2 to 1.0 pH unit in Ca(NO₃)₂- and Mg(NO₃)₂-amended than in untreated or PG-amended soil.

Soil solution ionic strengths displaced from unamended soils were <2.11 mM after 14 days of incubation (Table 4) with little change on further incubation, except in the cultivated Cecil soil, where ionic strength increased from 2.11 to 12.03 mM between 14 and 50 days of incubation. Soil solution ionic strengths were much greater in soils incubated with Ca(NO₃)₂- or Mg(NO₃)₂- than PG-amended soils.

In unamended cultivated soils, soil solution Ca concentration after 14 d of incubation was greater in the Cecil and Wedowee soils than in Bladen

soil with the reverse being true for the woodland sites (Table 4). The magnitude of increase in concentration of Ca in soil solution due to incubation of the soils with PG or Ca(NO₃)₂ was much greater in the Cecil than in Wedowee or Bladen soils. However, the increase in concentration of Ca in the soil solution in PG or Ca(NO₃)₂ amended than in the unamended treatment was greater in the Wedowee than in Bladen or Cecil soils. Concentration of Ca in the soil solution was greater in Mg(NO₃)₂ amended than in unamended soils especially after 50 d of incubation.

The concentration of exchangeable Al measured 50 d after incubation was lower in PG amended than in unamended treatment in all the soils (Table 5). However, the exchangeable Al status in the Ca(NO₃)₂ or Mg(NO₃)₂ amended treatments were very similar to that in unamended treatment.

Discussion

Since topsoil was similar in all the pots, plant growth reflects the differences in subsoil amendments and soil types. Because the topsoil has been adequately fertilized with N, alfalfa and soybean growth was unlikely to be dependent on symbiotic N fixation.

The lower root growth of alfalfa and soybean in the Bladen soil as compared to Cecil and Wedowee soils (Table 2) was probably due to

Table 4. Effects of various amendments on pH, ionic strength and concentration of Ca in displaced soil solution

Soil/treatments	Soil solution pH		Ionic strength (mM)		Conc. of Ca in soil solution (cmol _c L ⁻¹)	
	14 d	50 d	14 d	50 d	14 d	50 d
<i>Bladen-cultivated</i>						
Control	5.18	4.94	1.07	2.27	0.016	0.026
PG	4.31	4.29	1.99	9.58	0.090	0.210
Ca(NO ₃) ₂	5.03	4.00	3.03	20.23	0.122	0.609
Mg(NO ₃) ₂	4.90	4.00	3.15	18.95	0.017	0.240
<i>Bladen-woodland</i>						
Control	5.26	5.14	1.18	1.76	0.024	0.032
PG	4.38	4.41	1.55	7.72	0.092	0.200
Ca(NO ₃) ₂	5.03	4.17	2.97	8.71	0.123	0.474
Mg(NO ₃) ₂	5.02	4.22	2.91	6.29	0.018	0.145
<i>Cecil-cultivated</i>						
Control	5.95	5.65	2.11	12.03	0.037	0.469
PG	5.56	5.40	2.90	30.81	0.137	1.577
Ca(NO ₃) ₂	5.26	4.44	3.85	40.60	0.246	2.246
Mg(NO ₃) ₂	5.21	4.50	3.57	37.39	0.184	0.938
<i>Cecil-woodland</i>						
Control	5.99	5.68	1.21	1.81	0.006	0.004
PG	5.71	5.52	1.98	4.79	0.021	0.028
Ca(NO ₃) ₂	4.94	4.77	2.85	7.56	0.118	0.359
Mg(NO ₃) ₂	4.84	4.62	2.97	7.87	0.033	0.048
<i>Wedowee-cultivated</i>						
Control	5.27	5.06	0.96	1.44	0.031	0.049
PG	4.92	4.75	3.91	6.20	0.148	0.293
Ca(NO ₃) ₂	4.37	4.19	5.09	18.78	0.232	0.950
Mg(NO ₃) ₂	4.48	4.25	4.37	19.11	0.090	0.409
<i>Wedowee-woodland</i>						
Control	5.59	5.25	0.67	0.98	0.012	0.018
PG	5.10	4.83	2.85	5.13	0.106	0.223
Ca(NO ₃) ₂	4.42	4.10	4.88	14.61	0.260	1.146
Mg(NO ₃) ₂	4.40	4.13	3.72	15.84	0.108	0.349

PG = Phosphogypsum.

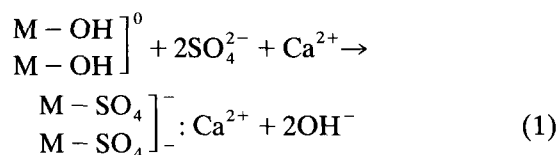
Table 5. Exchangeable Al (cmol_c kg⁻¹) measured in moist soil (-0.01 MPa soil water potential) on the 50th day of incubation (values expressed as corrected for air dry soil)

Treatments	Exchangeable Al					
	Bladen		Cecil		Wedowee	
	Cultivated	Woodland	Cultivated	Woodland	Cultivated	Woodland
Control	7.60	10.06	0.59	1.26	4.84	2.28
PG	6.93	9.45	0.48	0.78	4.29	1.86
Ca(NO ₃) ₂	7.48	9.87	0.57	0.90	4.59	2.07
Mg(NO ₃) ₂	7.62	10.20	0.60	0.99	4.71	2.22

PG = Phosphogypsum.

acidity and the high Al status (Table 1). The low ionic strengths of soil solution of woodland subsoils (Table 4) resulted in substantial sorption of ions in soils amended with either PG, $\text{Ca}(\text{NO}_3)_2$ or $\text{Mg}(\text{NO}_3)_2$. Ionic strengths in woodland soils were much lower than cultivated soils for each treatment.

The growth increases in PG over unamended treatments in the Cecil and Wedowee soils (Table 2), is probably due to improved Ca availability as is evident from the increase in soil solution Ca concentration (Table 4). Although equal rates of Ca were applied in both PG and $\text{Ca}(\text{NO}_3)_2$ treatments, soil solution Ca concentration in the latter was greater than in the former treatment (Table 4). This would suggest that some of the Ca was sorbed in the PG treatment, because of an increase in negative charges developed as a result of the specific sorption of SO_4^{2-} as shown in the following reaction:



Improved Ca availability in $\text{Ca}(\text{NO}_3)_2$ than in PG treatment is probably responsible for the observed increase in root and top growth in the former treatment on the Cecil and Wedowee soils. The increase in soil solution Ca concentration in $\text{Mg}(\text{NO}_3)_2$ -amended soils is due to the Mg induced exchange of Ca into the solution which could be partly responsible for the greater top and root growth in this treatment. Indeed, Ca concentration in the tops (Table 4) parallels the soil solution Ca status and corresponding top growth.

Alleviation of Al toxicity by gypsum or PG application can partly be attributed to the exchange of OH^- ions by SO_4^{2-} termed the "self-liming effect" by Reeve and Sumner (1972). This mechanism will not necessarily result in an increase in soil solution pH, because salt induced changes in pH are due to the competing effects of both cation and anion of the salt for potential acid and base sources. Therefore, although soil solution pH of PG amended soil was lower than that of the control soil, it was greater than that

from either $\text{Ca}(\text{NO}_3)_2$ - or $\text{Mg}(\text{NO}_3)_2$ - amended soil. This indicates that the Cecil and Wedowee soils exhibit the "self-liming" effect.

The decrease in exchangeable Al induced by PG treatment was only 6–9% in the Bladen soil, but 11–18% and 19–38% in the Wedowee and Cecil soils, respectively (Table 5). This suggests a greater ameliorative effect in kaolinitic than smectitic soils due partly to a greater neutralization of Al by the alkalinity produced in the former soils. This, in turn, resulted in increased root and top growth of alfalfa and soybeans in kaolinitic but not in smectitic soils.

In field experiments, substantial decreases in subsoil exchangeable Al especially have taken place 2 to 3 years (Buyeye, 1986) after gypsum application concomitantly with substantial yield increases. The amelioration of subsoil acidity by surface application of PG is due to the enriched leachate moving down into the subsoil. In the field situation this is repetitive, and the resulting increase in crop growth becomes greater with time.

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