GYPSUM AS AN AMELIORANT FOR THE SUBSOIL ACIDITY SYNDROME

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FINAL REPORT

GYPSUM AS AN AMELIORANT FOR THE SUBSOIL ACIDITY SYNDROME

Submitted to

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PERSPECTIVE

Dr. Steven G. Richardson, Reclamation Research Director
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Phosphogypsum is a by-product of the wet-acid production of phosphoric acid. More than 600 million tons have accumulated in Florida, and about 30 million tons are being added annually. A high priority research area at the Florida Institute of Phosphate Research has been to investigate potential uses for phosphogypsum in industry and agriculture. This project is one of several funded by the Institute to examine the use of phosphogypsum as an agricultural soil amendment.

In this report, Dr. Malcolm Sumner and his colleagues at the University of Georgia (FIPR Project No. 83-01-024R) have shown that by-product gypsum is effective in increasing yields of several field crops grown on acid soils by ameliorating aluminum toxicity and supply-ing needed calcium. In addition, gypsum application resulted in a decrease in penetration resistance of subsoil hardpan layers. This, coupled with the reduced toxicity of the subsoil, promoted deeper root penetration and greater access to soil moisture, thus reducing drought stress. Phosphogypsum and mined gypsum were equally effective for this purpose. Deep tillage of lime is a practice that has been used to reduce subsoil acidity, but gypsum, because of its greater solubility, can be used effectively through the less-costly method of surface application.

In related work, Miller (1989) has demonstrated how surface-applied gypsum can reduce surface soil crusting, improve infiltration of rainwater, and reduce soil erosion in several highly weathered soils in Georgia. The beneficial effects of gypsum were most striking in a heavier sandy clay loam, but lighter sandy loams also responded.

In another project, Hunter (1989) has described how the application of by-product gypsum alone and in combination with other nutrients and additives affected yield and nutrient content of various crops grown on sandy, low-cation-exchange soils in Florida. Gypsum application resulted in increased yields of several crops, including corn, potatoes, cantaloupes and watermelons. An important point of this research was that the benefits of the calcium and sulfur in gypsum might not be fully realized unless other nutrient deficiencies in the soils are also corrected. The study also found no significant effects of 0.5 to 1.5 tons of phosphogypsum per acre on radioactivity (gross alpha and gross beta emissions) or concentrations of arsenic, copper, iron, manganese, cadmium, vanadium, or zinc in several vegetable and fruit crops.

Also, Mullins and Mitchell (1990) have examined the use of gypsum as a sulfur fertilizer for annual forages. Their research has shown increases in forage quality and yield due to the sulfur in gypsum, which depend not only on the amount but also on the season of application. Soil and plant tissue samples have been analyzed for radium and polonium radionuclide concentrations. The analyses have shown no effects of phosphogypsum, applied at 40 pounds sulfur (260 pounds phosphogypsum) per acre per year for three years, on radionuclide concentrations in either plants or soils.

Some beneficial effects of phosphogypsum on citrus in Florida have been observed by Myhre et al. (1990). Tree health assessments usually improved and the juice brix (sugar) to acid ratio increased slightly in response to gypsum. At one site, fruit yield also increased. When repeated annually for three years, the one-half and one-fourth ton per acre rates of phosphogypsum were generally better than the one ton per acre rate. Phosphogypsum applied annually for three years at rates up to one ton per acre had no effect on Radium-226 content of the fruit. Nemec, et al. (1990) also found that gypsum significantly reduced the incidence of phytophtora foot rot in a new citrus grove. Evidence indicated the effect was on the trees themselves rather than the disease organism.

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SUMMARY

Soil acidity particularly in the subsoil is a major limiting factor in crop productivity in many parts of the world due to aluminum (Al) toxicity and calcium (Ca) deficiency. This syndrome in the topsoil is easily treated with lime but because of the variable charge nature of many acid subsoils, lime does not move down the profile and thus is ineffective. After early observations that gypsum could offset some of the deleterious effects of the subsoil acidity syndrome, a number of experiments in which deep incorporation of lime and phosphogypsum applied to the surface were compared, were laid out in Georgia on a variety of highly weathered soils (Ultisols and Alfisols). Crops studied included alfalfa, corn, soybeans, cotton and peaches. Highly statistically significant and economically profitable yield responses were obtained for all crops. A comparison of phosphogypsum with mined gypsum indicated that as far as crop response and soil reactions were concerned, there were no differences in crop growth but the fluoride content of the phosphogypsum complexed aluminum in the soils. Gypsum (a sparingly soluble salt) applied to the topsoil slowly moves down the profile and in so doing increases labile Ca levels and decreases Al in the subsoil of all soils studied. These effects are intermediate between the control (untreated) and situations where lime had been thoroughly mixed throughout the profile. This amelioration brought about by the gypsum treatments was sufficient to encourage roots to penetrate and proliferate in the subsoil where previous conditions were often so hostile as to prevent root growth. As a result of this improved root penetration, the crops were able to extract subsoil water previously beyond their reach and were consequently able to yield much better,

having partially overcome drought stress. In very sandy soils, gypsum application can have potential deleterious effects in terms of leaching of magnesium (Mg) beyond the root zone. However this can be easily overcome by applying corrective Mg applications to the topsoil once the gypsum has moved down. The longevity of the gypsum effect on medium to heavy textured soils from a single application of 10 t/ha is in excess of 6 years and in some soils may be in excess of 8 years. Not only does gypsum treatment offset subsoil acidity but in addition, there is clear evidence that it has an ameliorative effect on subsoil hardpans making them less of an impediment to root penetration. The ameliorative effects of gypsum on subsoil acidity stem from one or more of the following mechanisms: (a) increased levels of subsoil Ca, (b) complex formation between Al and sulfate (SO_4) and fluoride (F) which detoxifies the Al, (c) ligand exchange of SO_4 for hydroxyls (OH) on sesquioxide surfaces resulting in the so-called "self liming" effect, (d) precipitation of basic aluminum sulfate minerals which renders the labile Al insoluble and (e) salt sorption in which SO_4 is specifically adsorbed which causes the removal of some Al from solution.

INTRODUCTION

Phosphogypsum is an industrial byproduct from the manufacture of phosphoric acid. It is finely crystalline and has calcium (Ca) and sulfur (S) contents usually in excess of 23 and 18%, respectively. In addition, it contains from 0.2 to 1% phosphorus (P) and 0.25 to 1% flouride (F) depending on the efficiency of the manufacturing process. In comparison to gypsum that is mined, phosphogypsum dissolves in water much more rapidly due to its fine cyrstalline nature. Because the production of this byproduct has exceeded demand, large quantities have been stockpiled in stacks in Florida and at other locations where phosphoric acid has been manufactured. There is need to find uses for this material in an attempt to reduce the quantity which must be stored.

Soil acidity has been a major limiting factor to crop production in many parts of the world largely due to the toxic effects of labile aluminum (Al) and manganese (Mn) and to the paucity of available calcium (Ca) on root growth. As far as topsoils are concerned, the cure has been rather simple, involving the addition and incorporation of agricultural limestone. Acid subsoils, on the other hand, have been much more difficult to treat because of the large amounts of expensive energy required to incorporate lime to ever increasing depths. Deep incorporation has been necessary because of the low mobility of lime in variable charge soils. As a consequence, ameliorative strategies to offset the deleterious effects of subsoil acidity were not developed until relatively recently (Shainberg et al., 1989).

No reliable estimates of the soil area on a global basis afflicted with subsoil acidity are available but it is likely to be of the order of 50% of potentially arable

highly weathered soils. In addition, continued ammoniacal nitrogen (N) fertilizer applications on slightly acid soils can result in the development of subsoil acidity even in temperate regions.

Sumner (1970) and Reeve and Sumner (1972) were the first to develop a strategy to overcome the subsoil acidity syndrome in which they showed that by applying gypsum to the soil surface and then instituting a leaching regime, it was possible to reduce labile Al and increase available Ca in the subsoil effectively. Because of differences in the chemistry of Al and Mn compounds in the soil, this strategy has not proved particularly useful in the case of Mn. This initial successful research has been followed up by further work in the United States, Brazil and South Africa which has confirmed and expanded on the original findings and has resulted in substantial yield responses to surface applied gypsum (Freire et al., 1983; Guimaraes et al., 1983; Hammel et al., 1985; Pavan et al., 1982, 1984; Ritchey et al., 1980; Rosolem and Machado, 1984). There has been much further work conducted on this topic which has been conveniently summarized by Shainberg et al. (1989) and therefore will not be discussed in detail here.

PROJECT RESULTS

The major thrust of this project has been an investigation of the potential use of phosphogypsum as an ameliorant for the subsoil acidity syndrome thereby promoting the yield and profitability of crop production. However during the course of the investigation a further beneficial effect of gypsum on subsoil physical properties was discovered. The following discussion will therefore begin with an

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evaluation of gypsum as a yield promoting agent and then will focus on the reasons why crop responses are obtained.

I.   Effect of Gypsum on Crop Production

A.   Materials and Methods

Experiments were laid out at eight sites throughout Georgia in which the effects of gypsum on yields of various crops grown on members of the Cecil (clayey, kaolinitic, thermic Typic Hapludult), Appling (clayey, kaolinitic, thermic Typic Hapludult), Mecklenburg (fine, mixed, thermic Ultic Hapludalf), Altavista (fine-loamy, mixed thermic Typic Hapludult), Dyke (clayey, mixed, mesic Typic Rhodudult) and Ocilla (loamy, siliceous, thermic Aquic Arenic Paleudult) soil series, were assessed.   These soils represented the range of conditions to be found in the Southeastern United States covering the Appalachian Mountains, the Southern Piedmont and the Coastal Plain.   Some of the properties of these soils before experimentation are presented in Table 1.

The crops studied were silage corn, soybeans, alfalfa, cotton, peaches and lespedeza. Basically each experiment consisted of three replications of a series of treatments with various subsoil amendments. The topsoil over all treatments was limed (dolomitic) and fertilized (P and K) according to the best known practices. In a number of experiments, K and Mg treatments were incorporated annually as split plots over the main treatments. In the other experiments, K applications were made in the spring of each year based on replacing the quantities removed in the previous year while Mg (275 kg MgO/ha) was applied once before planting. In all experiments, minor elements (20 kg $ZnSO_4·5H_2O$, 20 kg $CuSO_4·5H_2O$, 20 kg Solubor,

Table 1.   Some properties of the soils studied.

Depth cm	pH KCl	Org C %	Clay %	Ca	Mg	K	Al	ECEC
				Exchange properties		cmol/kg		
Appling								
0-15	5.90	1.33	10.4	6.24	0.33	0.18	.20	6.95
15-30	3.91	0.64	21.6	1.24	0.19	0.10	1.01	2.50
30-45	3.95	0.38	33.8	0.94	0.17	0.08	1.31	2.85
45-60	3.94	0.18	44.6	0.65	0.15	0.05	1.90	2.80
60-75	3.92	0.08	43.0	0.38	0.10	0.08	2.09	2.67
75-90	3.94	0.05	27.6	0.19	0.06	0.04	2.30	2.61
90-105	3.96	0.01	21.8	0.20	0.04	0.06	2.32	2.64
Altavista								
0-15	5.33	1.62	7.4	1.53	0.33	0.15	0.01	2.16
15-30	4.20	0.32	28.0	1.21	0.34	0.15	0.36	2.15
30-45	3.98	0.16	30.2	1.29	0.37	0.09	0.70	2.54
45-60	3.90	0.14	30.8	0.64	0.30	0.06	1.28	2.44
60-75	3.92	0.13	31.2	0.72	0.33	0.07	1.37	2.65
75-90	3.90	0.12	31.4	0.21	0.16	0.05	1.87	2.46
90-105	3.84	0.12	33.4	0.15	0.10	0.05	2.13	2.70
Ocilla								
0-15	4.57	0.90	3.7	1.18	0.25	0.12	0.13	1.81
15-30	4.17	0.23	5.2	0.67	0.15	0.10	0.35	1.40
30-45	4.03	0.05	5.2	0.25	0.07	0.07	0.61	1.12
45-60	4.07	0.02	5.2	0.38	0.07	0.06	0.66	1.29
60-75	4.04	0.03	10.7	0.23	0.07	0.06	0.84	1.34
75-90	4.00	0.06	15.2	0.28	0.08	0.06	1.08	1.64
90-105	3.97	0.05	15.2	0.37	0.10	0.07	1.16	1.84
Dyke								
0-15	5.33	1.19	36.2	3.93	0.75	1.54	0.00	6.26
15-30	5.27	0.50	38.8	3.39	0.80	0.33	0.00	4.58
30-45	5.73	0.40	39.4	2.70	0.90	0.09	0.00	3.75
45-60	4.91	0.31	43.6	1.89	0.86	0.09	0.01	2.89
60-75	4.63	0.25	47.8	0.90	0.66	0.11	0.04	1.74
75-90	4.56	0.23	48.5	0.59	0.88	0.14	0.08	1.71
90-105	4.64	0.17	48.8	0.41	0.99	0.14	0.10	1.65

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Depth	pH	Org C	Clay	Exchange properties				
	KCl			Ca	Mg	K	Al	ECEC
cm		%	%			cmol/kg		
Mecklenburg								
0-15	5.40	1.50	15.0	2.96	1.31	0.26	0.01	4.71
15-30	5.41	0.64	42.6	2.79	1.61	0.14	0.01	4.81
30-45	5.06	0.60	58.4	2.23	1.97	0.09	0.03	4.65
45-60	4.90	0.60	57.9	1.06	2.06	0.16	1.07	4.67
60-75	4.57	0.50	48.9	0.63	2.06	0.15	1.75	4.91
75-90	4.47	0.23	29.1	0.47	1.88	0.17	1.31	5.17
90-105	4.42	0.18	41.6	0.22	1.63	0.18	2.64	5.38
Cecil								
0-15	5.9	0.77	7.6	1.21	0.22	0.08	0.01	1.52
15-30	4.8	0.62	9.8	0.61	0.12	0.08	0.04	0.85
30-45	4.9	0.25	11.9	0.21	0.05	0.04	0.36	0.66
45-60	4.8	0.20	47.8	0.95	0.16	0.15	0.42	1.68
60-75	4.9	0.18	57.2	0.62	0.13	0.06	0.57	1.38
75-90	5.0	0.18	55.5	0.68	0.12	0.04	0.48	1.32
90-105	5.0	0.06	43.6	0.51	0.17	0.02	0.57	1.27

0.5 kg $(NH_4)_2MoO_4$/ha) were applied before planting. In non-gypsum treatments, 100 kg $CaSO_4 \cdot 2H_2O$/ha was applied annually to supply adequate S. In the corn experiment, 125 kg N/ha as NH_4NO_3 was applied before planting. In one experiment, an irrigation treatment was incorporated to offset the deleterious effects of drought. The subsoil treatments were: (a) Control in which no modification was made to the subsoil, (b) Gypsum in which either a constant (10 ton/ha) or variable rates (2.5, 5 and 10 ton/ha) were incorporated into the topsoil, (c) Mixed in which the subsoil was mixed using a backhoe before replacing the topsoil and (d) Mixed and Limed in which sufficient dolomitic lime to neutralize exchangeable Al (Reeve and Sumner, 1970), was mixed into the subsoil while it was being mixed as in (c) with the

topsoil being replaced thereafter. The phosphogypsum used in the experiments contained 24.2% Ca, 18.9% S, 0.037% Mg, 0.08% K, 0.28% P and 0.38% F while the mined gypsum from Nova Scotia contained 21% Ca, 16% S, and no P or F. In the Gypsum treatments, the strategy was to allow the material to dissolve and move down the profile with time. The Mixed treatment reflected conditions after complete disruption of subsurface hardpans whereas the Mixed and Limed treatment represented conditions where there had been complete removal of chemical and. physical barriers to rooting. The Mixed and Limed treatment therefore represents the best profile amelioration against which the other treatments could be compared. In all alfalfa experiments, the cultivar "Apollo" was used except at Tifton where "Florida 77" was used. All alfalfa experiments were seeded at rate of 20 kg/ha. For corn, "PNR 3369A" and for soybeans, "Essex" and "Wright" cultivars were used at 60,000 and 350,000 plants/ha, respectively. In the peach experiment, the variety, "Jefferson" was grown at a spacing of 4 x 2 m.

Soil samples (20 cores/plot) down to 1 m depth were taken from all experiments at various stages for analysis of pH and exchangeable cations and sulfate by standard methods (Page, 1982). A neutron moisture meter was used to assay water content of the profiles at depth increments of 0.15 m. Bulk density was determined by the core method (75 mm diameter). Soil solution was expressed using the method of Gillman and Sumner (1987). Root distribution down the profile was obtained by taking cores down the profile and extracting the roots using a Gillison

root washer as described by Sumner and Carter (1988). Cone index values which measure resistance to penetration were obtained using a tractor-mounted computer driven penetrometer as described by Radcliffe et al. (1986).

Salt sorption studies were conducted by equilibrating 10g soil with 25ml of one of the following solutions: 0.005M $CaSO_4 \cdot 2H_2O$, 0.005M $MgSO_4 \cdot 7H_2O$, 0.005M $CaCl_2$ and distilled water. After centrifugation, pH and electrical conductivity (EC) were measured in the supernatant solutions (Alva et al., 1991).

B.   **Yield results**

Because there are basically two sources of gypsum available for use in agriculture, namely, mined and phosphogypsum, it was necessary to conduct an experiment to evaluate whether the response of the crop differed depending on type of gypsum used. In this experiment the results of which are presented in Table 2 phosphogypsum was compared with mined gypsum supplied by the US Gypsum Company at two rates (5 and 10 t/ha).

Table 2.   Effect of mined and phosphogypsum on the yield of alfalfa.

Treatment	Rate t/ha	Yield			
		1987	1988	1989	Total
			kg/ha		
Control	0	2375	5769	7704	15848
US Gypsum	5	3237	6424	8472	18133
US Gypsum	10	3828	7323	9726	20877
Phosphogypsum	5	3783	7068	8816	19667
Phosphogypsum	10	4041	7647	9453	21141
$LSD_{.05}$		618	775	869	

There were no significant differences between sources of gypsum although there was a slight tendency for phosphogypsum to be better at the 5 ton/ha level over all P levels. In the same experiment, there was a slight response to applied P but the interactions between P and gypsum sources were not significant.

In two of the experiments, factors (constant grazing by deer and drought) beyond the control of the investigators led to the abandonment of these sites in the second year of experimentation. Thus the data presented are only from those experiments which were successful in accomplishing the original goals of the project. Because many of the yield results for the successful experiments have already been published in the literature (Hammel et al., 1985; Shainberg et al., 1989; Sumner et al., 1985; Sumner et al., 1986; Sumner et al., 1987), only the cumulative yield responses above the yield of the Control treatment over time will be presented here in Figure 1 for alfalfa and Figure 2 for the other crops. In general, yield responses to Gypsum have only been obtained in the second and subsequent years after application because time is required for the gypsum to dissolve and move down the profile to effect amelioration.

In the case of the Appling coarse sandy loam soil (Figure 1), significant yield responses over the Control after the second year of cropping were obtained for the Gypsum and Deep Lime incorporation treatments with the latter being significantly better than the former throughout the life of the experiment. The Mixed treatment was significantly worse than the Control throughout the experiment. These results indicate that the yield responses obtained were due primarily to the amelioration of the chemical barrier to rooting with possibly some effect due to the elimination of the
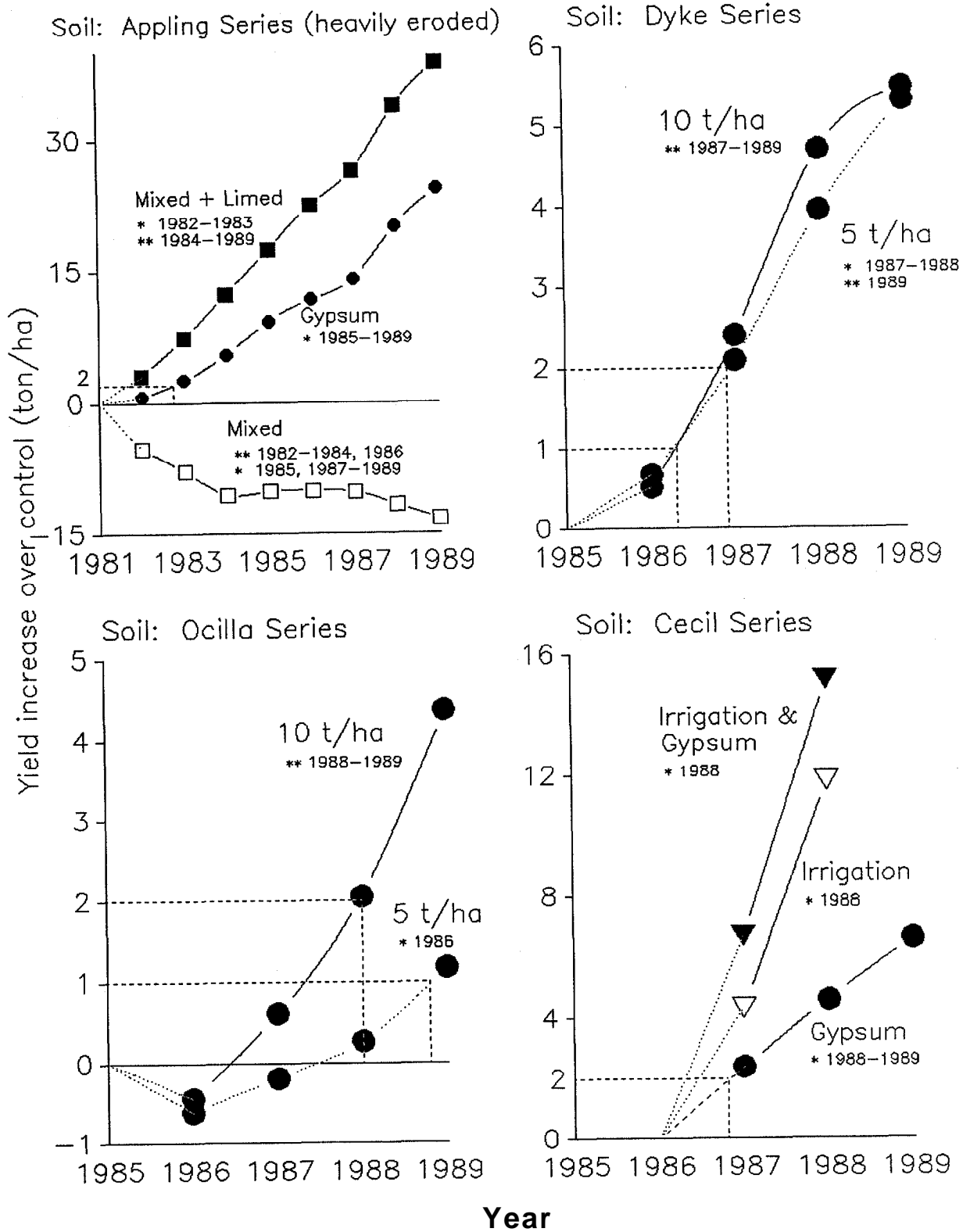
Figure 1. Cumulative yield response (difference from control) of alfalfa grown on four soils to subsoil modification treatments.
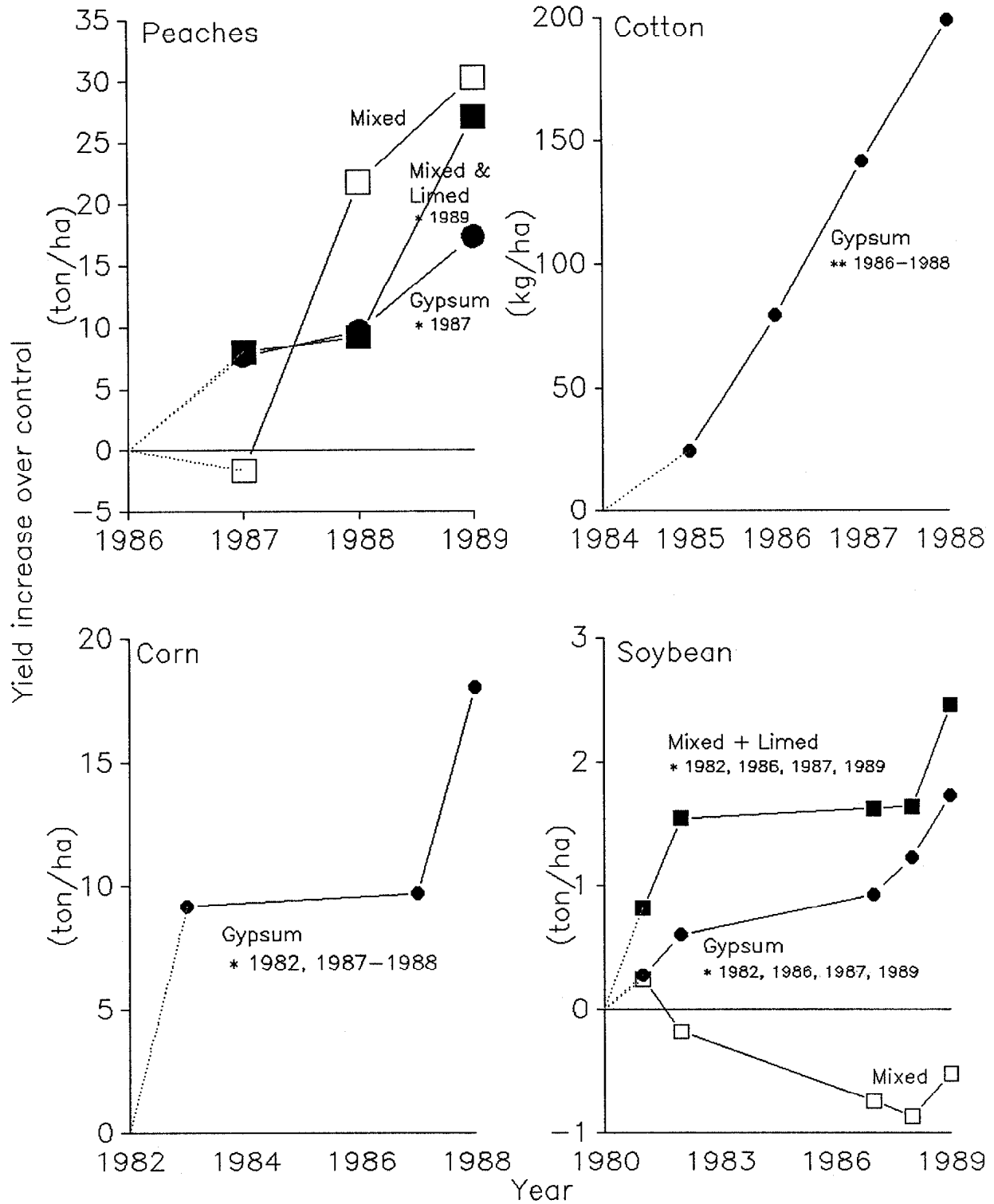
Figure 2. Cumulative yield response (difference from control) of peaches, cotton, corn and soybeans grown on Cecil soil to subsoil modification treatments.

subsoil hardpan. In experiments at other locations, a similar relationship between the Gypsum and Mixed and Limed treatments was observed. These data clearly indicate that a single application of gypsum can induce an effect which lasts more than seven years as evidenced by the fact that the Gypsum response curve is continuing to rise with time.

In the case of the Dyke clay loam soil (Figure 1), a significant response to Gypsum was obtained in the second and subsequent years but there were no significant differences between the rates of gypsum applied. On the Ocilla loamy coarse sand soil, significant positive yield responses to Gypsum were not recorded in the first two years because on this very sandy soil, magnesium (Mg) was preferentially leached from the topsoil by the Gypsum treatments which in fact resulted in a slight yield reduction in the first year. This negated any beneficial effects of the Gypsum on the subsoil which only became apparent after the induced Mg deficiency had been corrected by the application of a broadcast treatment of 50 kg Mg/ha over the entire experiment. From the shape of the curves for the two rates of gypsum applied, it appears that the higher rate will continue to outyield the lower. On the Cecil coarse sandy loam, there was a significant yield response to Gypsum over the Control but when irrigated so that drought stress was essentially eliminated, the response to Gypsum largely disappeared which strongly supports the view that the Gypsum response is to increased water utilization by the crop. Thus the irrigation treatment supplied the crop with adequate moisture so that there was no longer need to extract additional water from the subsoil.

With cotton growing on a Cecil coarse sandy loam (Figure 2), a significant yield response to Gypsum was first observed in the second year and continued thereafter. **A** similar pattern of response to Gypsum was observed for soybeans on an Appling coarse sandy loam. However on this soil, the Mixed treatment performed worse than the Control while the Mixed and Limed treatment proved overall to be slightly superior to the Gypsum treatment which would again suggest that soybeans are more sensitive to the chemical than the physical barrier to rooting. In three of the five years on this experiment, silage corn was double-cropped with the soybeans but significant yield responses to gypsum were only obtained in three of the years. In the case of peaches growing on an Appling coarse sandy loam, only a slight response to gypsum was observed whereas the treatments involving soil disturbance (Mixed, and Mixed and Limed) resulted in much larger yield increases. These results would indicate that peaches unlike the other crops investigated are more sensitive to the physical than chemical barriers in these soils. With lespedeza growing on a Cecil coarse sandy loam, no yield response to Gypsum application was observed (data not presented). This result is not surprising in view of the known tolerance which this crop has for Al toxicity and subsoil hardpans.

C. **Economic Analysis**

Despite the fact that the yields on the gypsum treatments obtained above are significantly better than those of the Control, it is necessary to economically evaluate the results in terms of the potential profitability of the practice of applying gypsum. The data in Table 3 clearly illustrate the profitability of a 10 ton/ha gypsum application to valuable crops such as alfalfa, peaches and cotton. However for a

Table 3. Net profit from the application of gypsum to highly weathered soils.

Soil	Crop	Gypsum Applied ton/ha	Cumulative yield increases due to gypsum ton/ha	Cost of gypsum	Value[*] of yield increase	Net profit due to gypsum application
					$/ha	
Appling (7 yrs)	Alfalfa	10	25	300	3750	3450
Dyke (4 yrs)	Alfalfa	5	5.5	150	825	675
		10	5.8	300	870	570
Ocilla (3 yrs)	Alfalfa	5	1.5	150	225	75
		10	4.0	300	600	300
Cecil (3 yrs)	Alfalfa	10	5.0	300	750	450
Cecil (4 yrs)	Cotton	10	0.9	300	1235	935
Appling (3 yrs)	Peaches	10	7.5	300	3947	3647
Appling (5 yrs)	Soybeans	10	1.73	300	358	58

[*] Alfalfa = $150/ton
Cotton = $1372/ton
Peaches = $526/ton
Soybeans = $207/ton

relatively low value crop such as soybeans, such a treatment can hardly be recommended because of the relatively low return despite the fact that the yield responses were statistically highly significant. In Figures 1 and 2, a horizontal dotted line which represents the yield increase which must be realized in order to offset the cost of the gypsum application has been inserted. This line has been computed based on the cost of gypsum at each site and the average market value of each crop. In nearly all cases, the cost of the gypsum application can be recouped within a few years which makes the treatment highly profitable in view of the length of time the Gypsum treatment effect is likely to last.
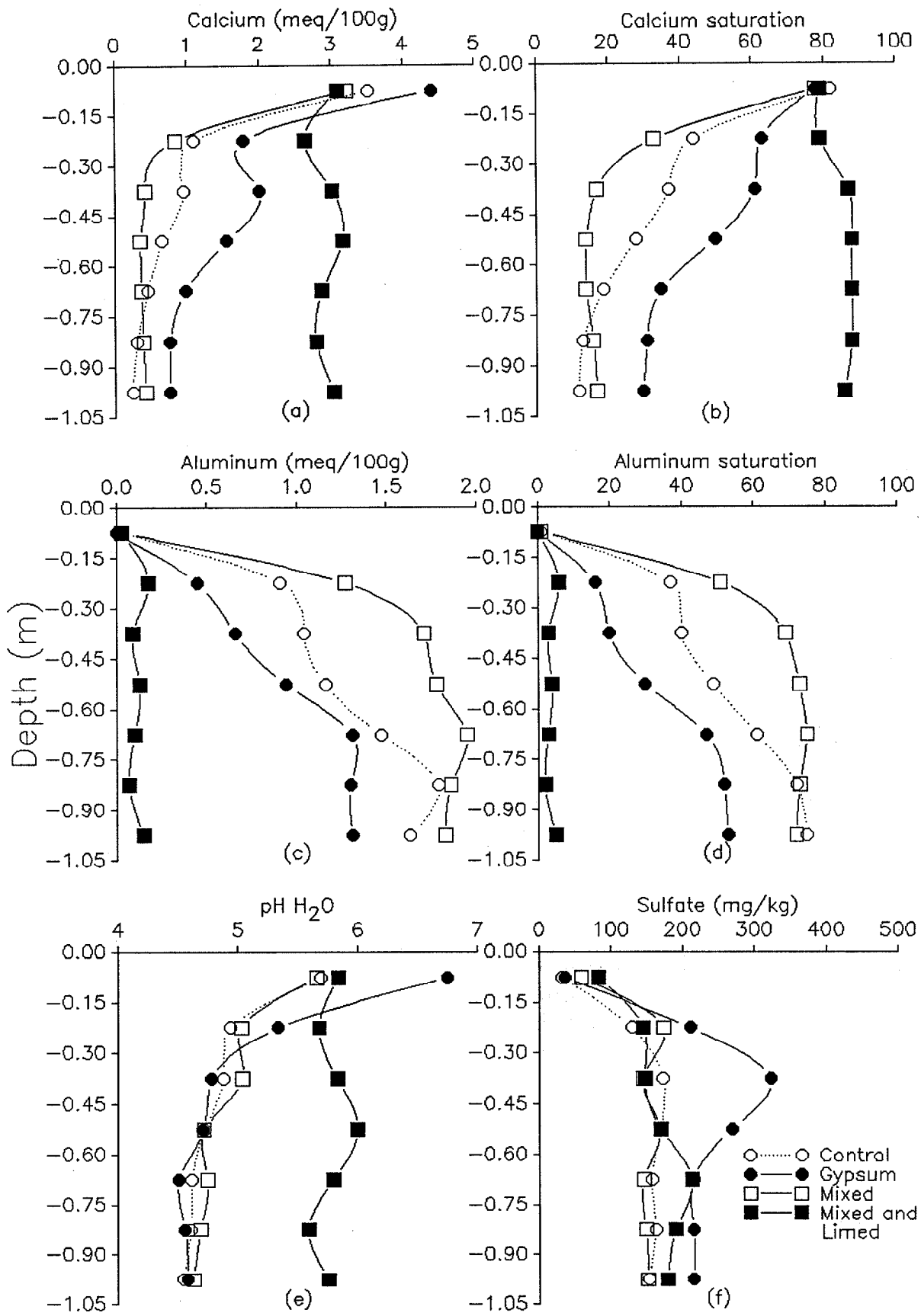
Figure 3.   Effect of subsoil modification treatments on chemical properties of the Appling soil at the end of the experiment in 1989.
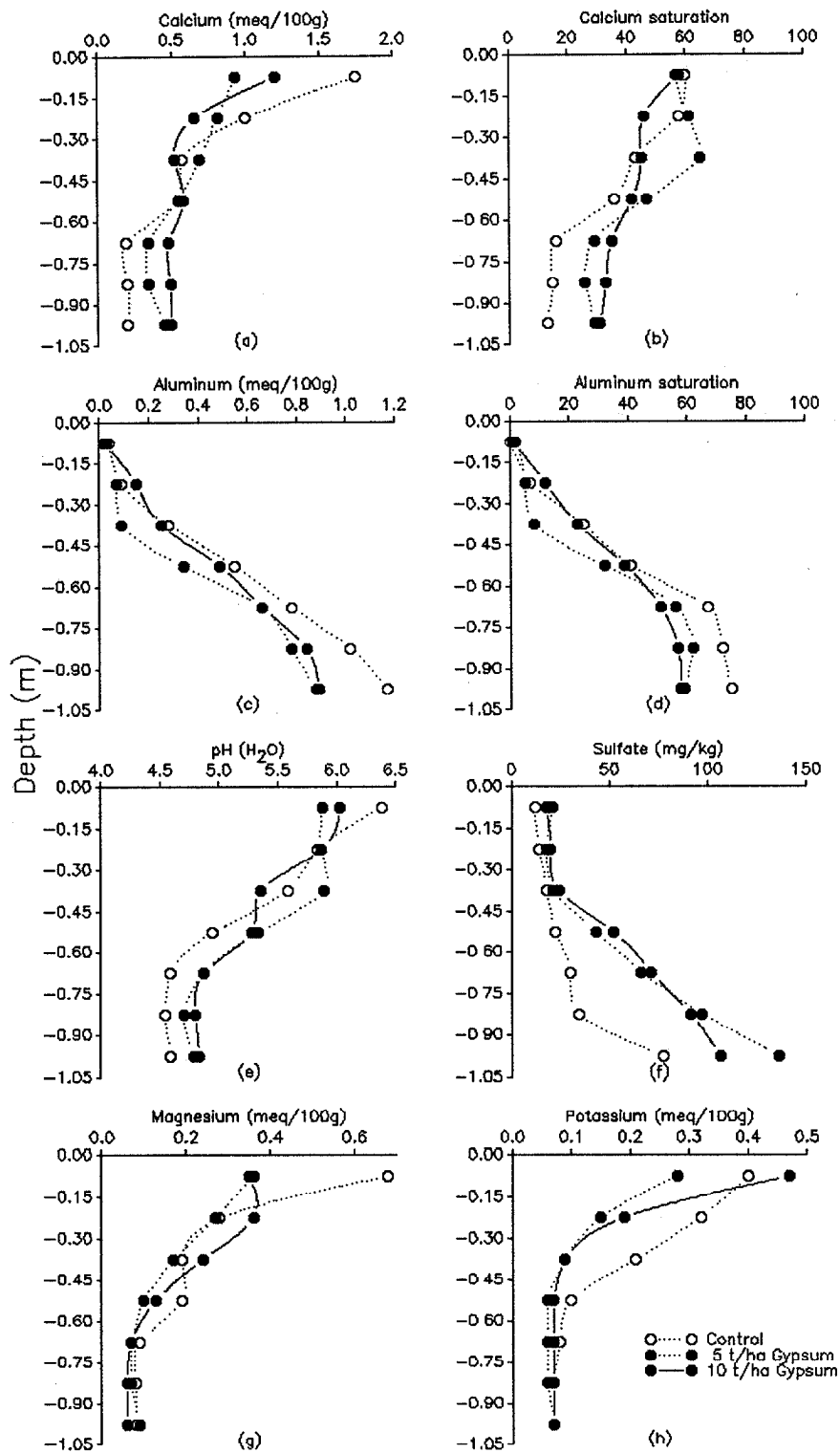
Figure 4.   Effect of subsoil modification treatments on chemical properties of the Ocilla soil at the end of the experiment in 1989.

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II.   Effect of Gypsum on Soil Chemical Properties

A.   Exchangeable Ions

The overall effect of the various subsoil treatments on soil chemical properties have been illustrated in Figures 3 to 7 by plotting curves for the Control against curves for each treatment sampled in 1989 at the end of the experiment for three different soils. For Ca in the Appling coarse sandy loam soil (Figure 3 a and b), the Mixed and Lime treatment resulted in the greatest amounts being retained in the. profile whereas in the Gypsum treatment, amounts intermediate between the Mixed and Limed and the Control were present. Calcium saturation reflected the same picture. There were essentially no differences between the Control and Mixed treatments. These differences in Ca retention between the Mixed and Limed and Gypsum treatments are due to the increase in exchange capacity (Grove et al., 1982) of this variable charge soil brought about by the lime and not the gypsum. Lime has been shown to increase the cation exchange capacity of such soils by an amount equivalent to the Ca added which results in almost complete adsorption and retention of the added Ca whereas in the case of gypsum which does not increase pH appreciably, only a slight increase in variable charge occurs. This effect will be discussed in Section VII. Both Mixed and Limed and Gypsum treatments reduced the level and saturation of the soil with Al (Figure 3c and d), but as expected, liming is more efficient than gypsum. However because the Mixed and Limed treatment is somewhat impractical and expensive, the amelioration by Gypsum is more attractive for economic reasons albeit a little less effective than lime chemically. Soil pH down the profile was changed only by the Mixed and Limed treatment (Figure 3e). None

of the treatments brought about any appreciable changes in K and Mg down the profile and therefore the data have not been presented. The distribution of sulfate down the profile is presented in Figure 3f from which it is clear that only the Gypsum treatment has increased the levels down the profile. From these data, it is possible to calculate the quantity of gypsum remaining in the profile to a depth of 1 m at the end of the experimental period using the Ca and sulfate values in Figure 3a and f. To do this one has to correct for the amount of Ca added in the lime and phosphate. applications made to the topsoil and for the amount of sulfate which has been immobilized in the formation of the insoluble solid phases formed during the precipitation of Al (Sumner et al., 1987). When such calculations are carried out, the results indicate that between 4.8 and 6.0 t/ha of gypsum still remain based on the sulfate and Ca values, respectively. These two independent calculations are in remarkably good agreement and one can therefore state that at least half the gypsum originally applied, is still present in this soil profile.

In the case of the much sandier Ocilla soil on the other hand, an entirely different picture emerges. Most of the residual effect of the 5 and 10 t/ha Gypsum treatments on exchangeable Ca and Ca saturation is to be found below a depth of 0.45 m (Figure 4a and b) which agrees with the reduced levels of Al and Al saturation (Figure 4c and d). Both Gypsum treatments have resulted in a consistent increase in soil pH down the soil profile below 0.45 m (Figure 4e). Both K and Mg have been reduced down the profile to a minimal extent by the Gypsum treatments (Figure 4g and h). In the first year of experimentation, the Gypsum treatments resulted in the almost complete removal of Mg from the upper part of the profile

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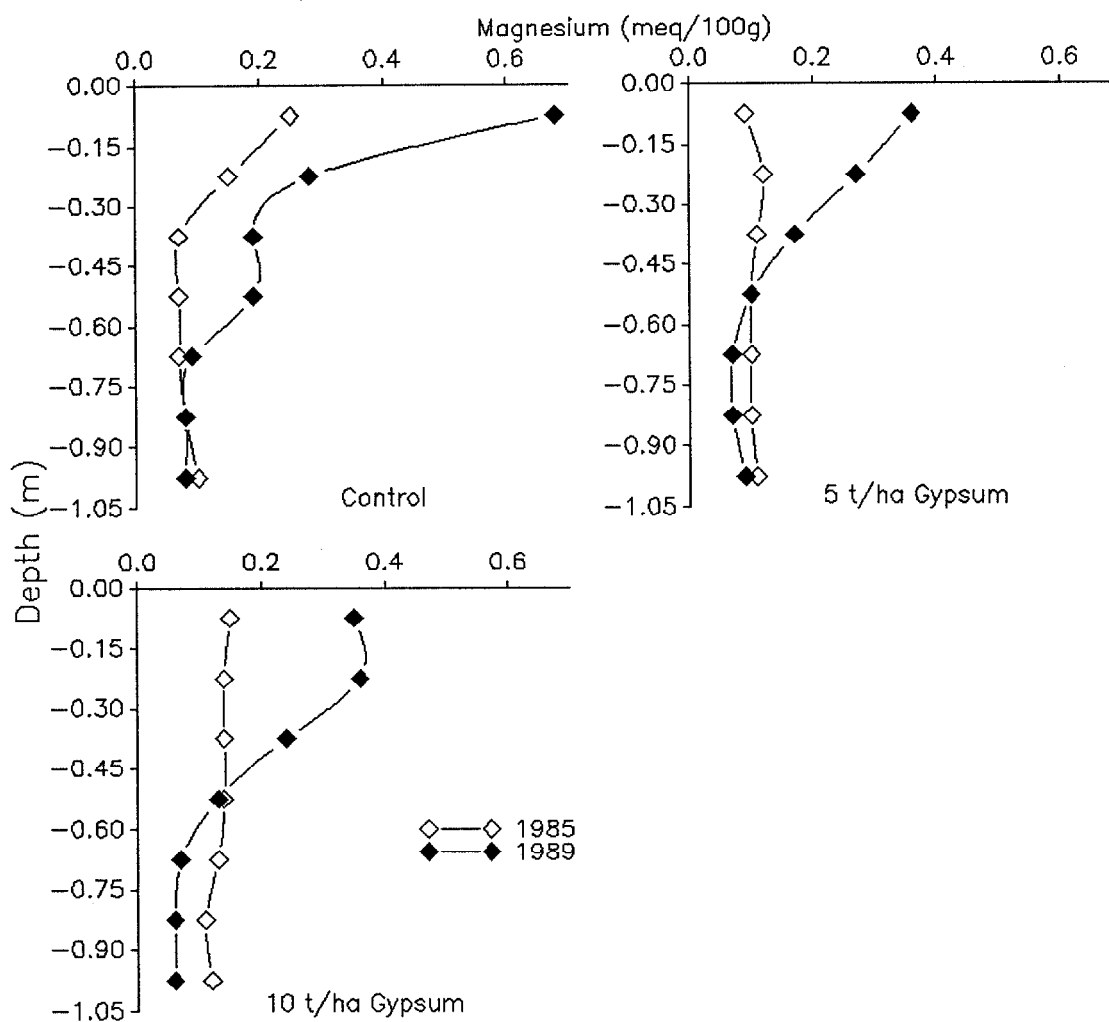
Figure 5.   Comparison of the effects of two levels of gypsum on exchangeable Mg in the Ocilla soil in 1985 and 1989.

resulting in crop failure.   As a result, MgO applications were made in the second season to restore the fertility. The relatively high level of Mg in the top 15 cm of the Control treatment reflects this application which was only partially leached from the Gypsum treatments because much of the gypsum had probably already dissolved and been removed from the topsoil.   The effect of the Gypsum treatments on the movement of Mg after the MgO application is illustrated in Figure 5 in which Mg
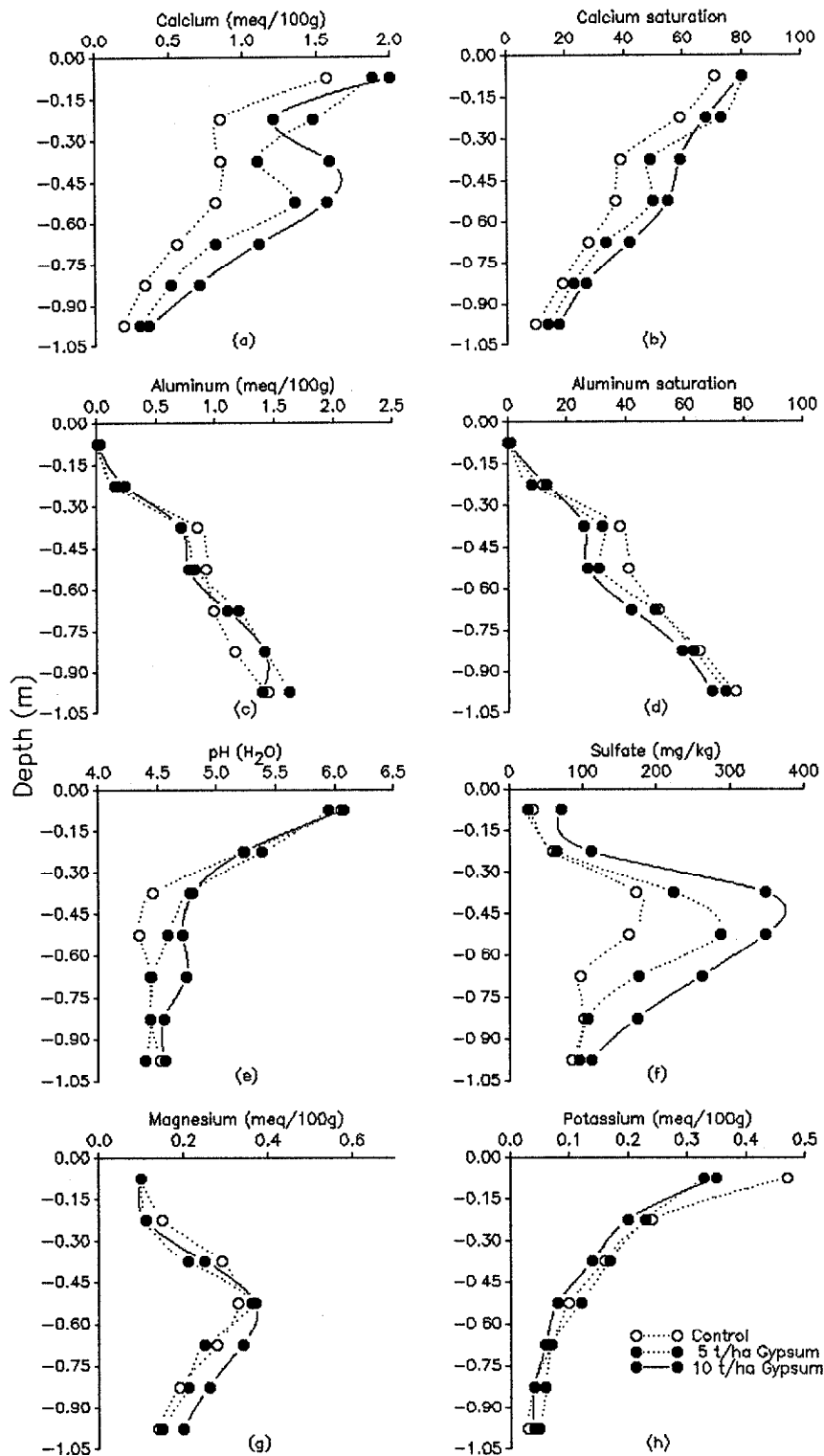
Figure 6. Effect of subsoil modification treatments on chemical properties of the Altavista soil at the end of the experiment in 1989.
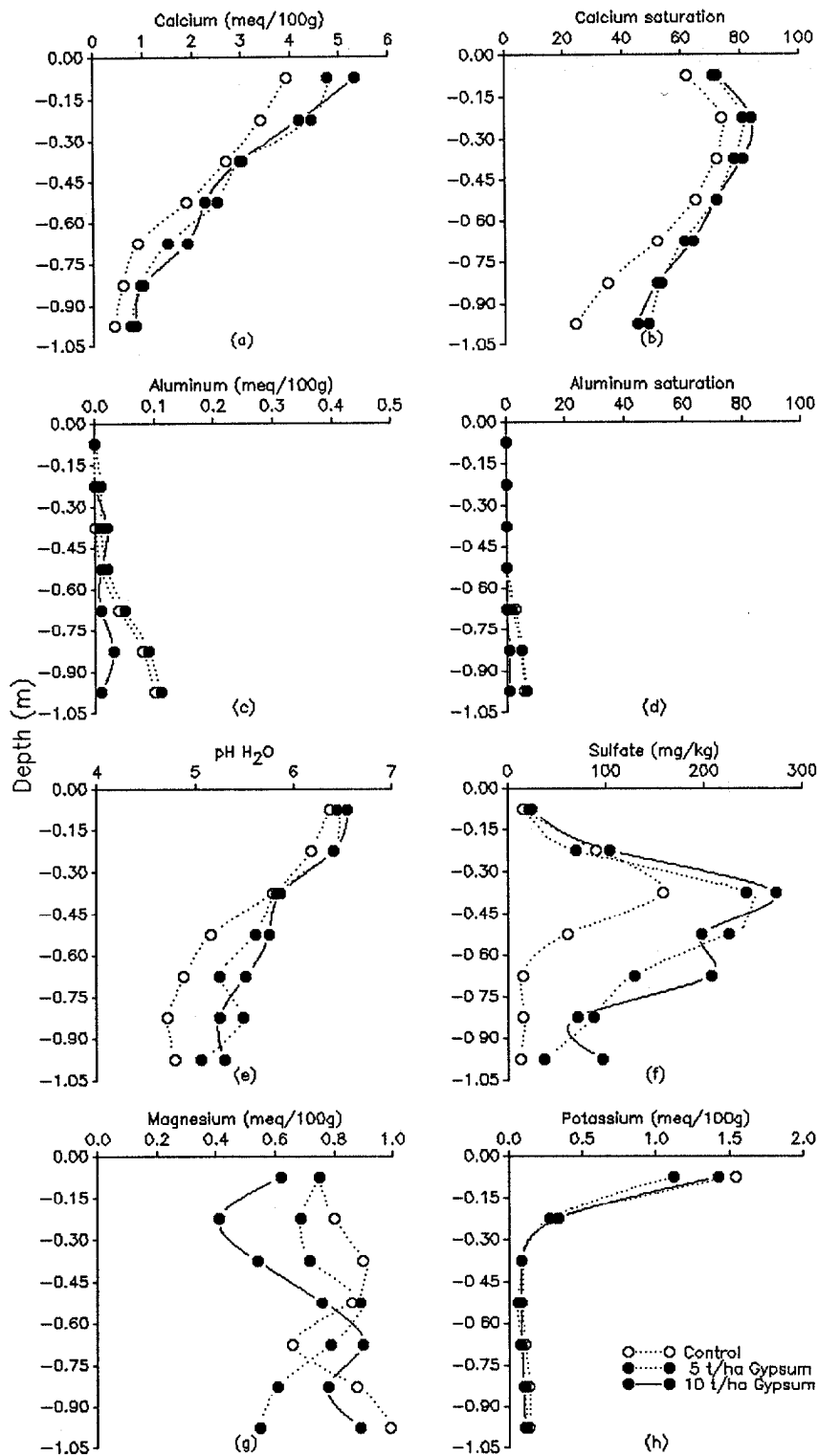
Figure 7.   Effect of subsoil modification treatments on chemical properties of the
Dyke soil at the end of the experiment in 1989.

values in 1985 and 1989 are compared. The Mg levels in the Control topsoil in 1989 are much higher than those for the Gypsum treatments. The effect of the Gypsum treatments on increasing extractable sulfate down the profile is still apparent (Figure 4f). When one makes the calculation as above to estimate the amount of gypsum remaining in the profile, one finds values of 0 and 1.8 t/ha based on the Ca and sulfate levels, respectively. This suggests that in this loamy sand soil, most of the gypsum applied will be leached out of the profile in a period of 5 years. In view. of the relatively modest yield responses obtained on this soil and the problems of maintaining adequate Mg in the topsoil in the initial stages after gypsum application, it is doubtful whether gypsum treatments to ameliorate subsoil acidity of such sandy soils can be recommended.

The distribution of chemical properties down the profile on the Altavista loamy coarse sand is intermediate between that of the Appling and Ocilla soils (Figure 6). By the same calculation as used above, the amount of gypsum remaining in the profile is between 3 and 5 t/ha.

In the case of the Dyke clay loam, the effect of the Gypsum treatments on exchangeable Ca and Ca saturation is clearly visible down the entire profile (Figure 7). The Gypsum treatments have increased the pH in the lower part of the profile' corresponding to a decrease in exchangeable Al. In the case of Mg, there is evidence of some removal from the topsoil as a result of Gypsum treatment while with K, there are no perceptible differences. Both the Gypsum treatments increased the level of sulfate substantially particularly in the upper part of the profile. Based on the Ca

and sulfate values in Figure 7, the amount of gypsum remaining in this profile is between 4 and 6 t/ha for the 10 t/ha treatment.

The removal of gypsum from the profile follows the general pattern which one might expect. In the sandiest soil profile (Ocilla), most of the gypsum has been leached below 1 m during a 5 year period while during the same period only about 50-60% has been removed from the Altavista soil which is slightly heavier. In the Appling and Dyke soils which are heavier in texture in the subsoil than the other soils, somewhat smaller amounts of gypsum have been leached. These results indicate that the longevity and consequently the efficiency of the gypsum treatment on amelioration of the subsoil acidity syndrome will be greater on the heavier soils.

B.   Soil Solution Ions

The effect of Gypsum treatment on the composition of the soil solution of the various soils incubated at field capacity in closed pots is illustrated in Table 4. On gypsum treatment, the pH in top- and subsoils decreases in all soils except the heaviest soil (Dyke). Presumably in these closed pots with direct addition of gypsum and no leaching, the "salt effect" on pH dominates over the "sulfate effect" in producing alkalinity by the "self liming" effect (Reeve and Sumner, 1972). The two heavier soils (Appling and Dyke) show much smaller increases in Ca, SO_4 and total electrolyte concentration than the sandy soils (Ocilla and Altavista) after gypsum treatment. These data show that substantial salt sorption has taken place, presumably associated with specific adsorption of sulfate on sesquioxide surfaces. In the heavy textured soils, there are very marked decreases in K and Al (despite a decrease in solution pH in the Appling soil) concentrations in the gypsum treated

subsoils indicating that some immobilization of these components has taken place whereas in the sandy soils which are swamped by the gypsum application, K and Al as well as the other cations are increased as would be expected on the basis of exchange reactions with the added Ca. Thus in the clay subsoils, a strong sorption of Ca and SO_4 and a cosorption of K and Al without the release of a corresponding quantity of other ions into the solution, has taken place. Some other effects of gypsum treatment are worth noting, namely, a tendency for soluble Mn, Si, NO_3, Cl and F levels to increase and for soluble PO, to decrease slightly. These trends are more pronounced in the heavier than the sandy soils. However these changes are relatively small and are unlikely to affect root growth to any marked extent.

The presence of ligands, such as SO_4, PO_4 and F which are introduced into the system in large quantities by phosphogypsum, have a profound effect on the chemistry of Al in solution. The effects of reagent grade, phosphogypsum (PG) and various ligands on the activities of various Al species in solution (as calculated according to the GEOCHEM program, Sposito and Mattigod, 1980) are illustrated in Table 5. All solutions in this experiment contained 500 μM $CaSO_4 \cdot 2H_2O$ as a background electrolyte which explains why some of the Al in the pure Al solution (#3) was complexed as $AlSO_4^+$ and $Al(OH)_x$. This effect was more pronounced, in treatment #5 where the gypsum level was much higher. In the pure PG treatment (#2), the Al which is an impurity, occurs entirely in AlF_x forms as it does in treatment #4 where Al had been added. The addition of F to the mixture containing Al and pure gypsum (treatments #6 and 8) results in a shift from $Al(OH)_x$ and $AlSO_4^+$ species to the much more stable AlFx forms. The addition of PO_4 to

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Table 4. Composition of the soil solution after incubating soils in pots for 3 months at field capacity with or without 100 mg kg^{-1} of CaSO$_4$·2H$_2$O.

Soil	Horizon	Treatment	pH	Cations (mmol l^{-1})							Anions (mmol l^{-1})						Electrolyte concentration
				Ca	Mg	K	Na	NH$_4$	Al	Mn	SO$_4$	NO$_3$	Cl	PO$_4$	F	Si	[mmol(c) l^{-1}]
Appling	Topsoil	Control	4.33	1.68	0.55	0.33	0.84	0.17	0.008	0.015	0.13	4.53	0.42	0.005	0.020	0.259	5.6
	(loam)	Gypsum	4.35	8.47	1.06	0.36	1.11	0.14	0.071	0.251	6.95	6.30	0.40	0.006	0.055	0.340	20.9
	Subsoil	Control	5.31	0.02	0.01	0.10	0.91	0.17	0.005	-	0.12	0.22	0.27	0.004	0.037	0.218	1.0
	(clay)	Gypsum	4.87	0.83	0.22	0.04	1.58	0.17	0.003	0.002	1.12	0.71	0.42	0.002	0.041	0.392	3.9
Dyke	Topsoil	Control	5.94	2.75	1.58	0.71	1.44	0.17	0.014	-	0.17	10.00	0.63	0.012	0.018	0.234	
	(clay)	Gypsum	6.10	6.76	2.40	0.46	1.74	0.17	0.009	-	7.59	8.31	0.52	0.003	0.026	0.245	
	Subsoil	Control	5.32	1.70	0.85	0.29	1.12	0.17	0.010	-	0.13	3.16	0.40	0.008	0.013	0.199	
	(clay)	Gypsum	5.41	6.03	2.00	0.03	1.41	0.17	0.005	-	6.02	6.76	0.42	0.002	0.012	0.275	
Ocilla	Topsoil	Control	6.00	3.00	0.99	1.33	0.68	0.17	0.011	0.001	0.77	5.04	0.46	0.020	0.011	0.141	9.0
	(sand)	Gypsum	5.74	14.41	3.27	2.15	1.09	0.16	0.015	0.001	12.85	8.00	0.54	0.014	0.078	0.140	38.8
	Subsoil	Control	4.72	0.15	0.04	0.46	0.70	0.19	0.014	0.002	0.29	0.63	0.57	0.007	0.003	0.287	1.7
	(sand)	Gypsum	4.13	14.43	0.60	0.93	1.21	1.12	0.700	0.061	13.29	0.40	0.40	0.001	0.085	0.333	35.2
Altavista	Topsoil	Control	6.26	6.45	2.95	9.33	1.09	0.17	0.022	-	0.14	28.84	0.43	0.043	0.010	0.117	
		Gypsum	5.35	14.45	4.36	9.77	0.93	0.15	0.023	-	12.30	18.19	1.62	0.003	0.012	0.112	
	Subsoil	Control	5.98	1.58	0.48	2.04	0.68	0.17	0.009	-	0.37	4.36	1.12	0.009	0.011	0.195	
		Gypsum	5.80	9.12	1.51	2.88	0.71	0.18	0.005	-	8.91	5.37	0.52	0.004	0.015	0.199	

Table 5. Aluminum speciation using the GEOCHEM program (Sposito and Mattigod, 1980) in dilute nutrient solutions containing Al with various amendments.

Treatment[a]		Predicted activities of Al species in solution, μM[b]									
		Al^{3+}	$Al(OH)^{2+}$	$Al(OH)_2^+$	$Al(OH)_3^0$	$AlSO_4^+$	AlF^{2+}	AlF_2^+	AlF_3^0	AlF_4^-	Σactivity
2	No Al + PG (2 gL^{-1})	t	t	t	t	t	0.02	2.63	12.0	0.85	15.5
3	40 μM Al	10.80	3.40	5.43	0.43	9.93	0.0	0.0	0.0	0.0	29.9
4	40 μM Al+PG (2 gL^{-1})	t	t	t	t	t	0.12	12.1	39.2	2.07	53.49
5	40 μM Al+CaSO$_4$·2H$_2$O (2.07) gL^{-1})	3.01	0.94	1.52	0.09	21.7	0.0	0.0	0.0	0.0	27.26
6	as in trt. 5 + 400 μM F	t	t	t	t	t	0.101	9.43	27.6	1.27	38.40
7	as in trt. 6 + 30 μM P	t	t	t	t	t	0.103	9.42	27.6	1.27	38.39
8	as in trt. 3 + 400 μM F + 30 μM P	t	t	t	t	t	0.087	8.86	28.8	1.49	39.24

[a] Treatment 1 is control with no Al added. The calcium concentration in treatments 1,3, and 8 was 500 PM (as CaSO$_4$·2H$_2$O).

[b] Predicted activities of Al-PO$_4$ and Al-EDTA complexes were <10^{-10} M in all solutions. t = predicted activities < 10^8 M.
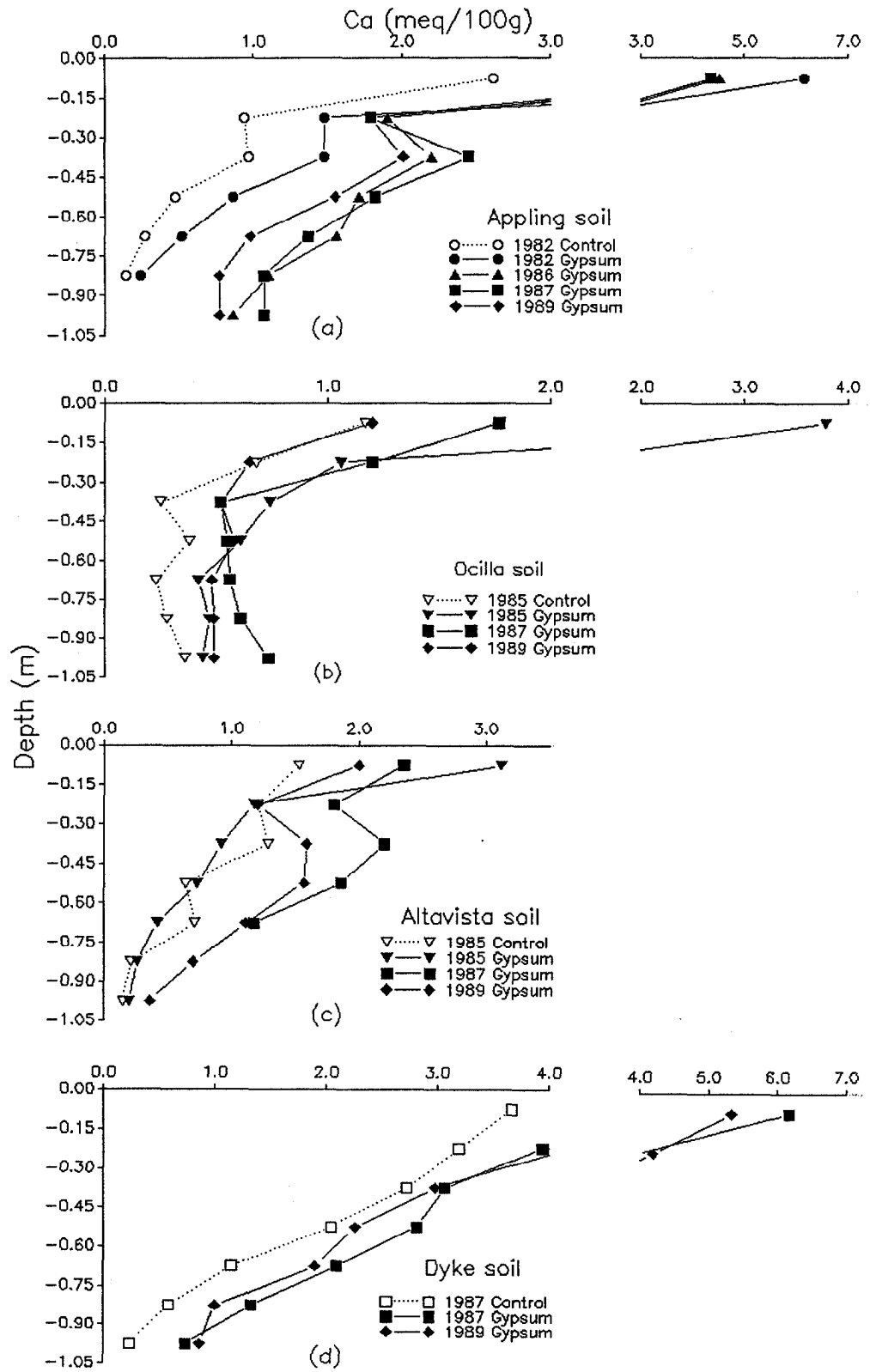
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Figure 8.   Effect of time on redistribution of surface applied gypsum down the profile of four highly weathered soils.

treatments containing F does not alter the distribution of species to any appreciable extent. The data in Table 5 clearly show that in the presence of SO_4, the activity of Al^{3+} is substantially reduced while in the presence of F, it is totally eliminated in favor of the less toxic species $AlSO_4^+$ and AlF_x.

III.   Kinetics of Gypsum Movement

Because gypsum is a sparingly soluble salt which moves gradually down the profile with time, it is important to obtain an estimate of the rate at which it moves in different soils so that predictions of the time its effects are likely to last can be made. The current set of experiments present the ideal conditions to make these estimates.

The changes in exchangeable Ca with time over the life of these experiments are presented in Figure 8 for four locations on quite widely differing soils. In the experiment on the Appling soil, the levels of Ca lower down the profile increased at the expense of topsoil levels until 1987. In the 1989 sampling, there is distinct evidence that the levels are now beginning to decline. Thus one can estimate that the beneficial effects of gypsum on this soil are likely to last for at least 8 and possibly 10 years after a 10 ton/ha application of gypsum on the surface. This pattern of behavior corroborates the estimate of the amount of gypsum remaining in the profile made above (Section II A). The other three soils all exhibit a pattern of behavior similar to that of the Appling soil. All these soils are more pervious than the Appling resulting in a somewhat accelerated removal of gypsum from the profile. Nevertheless in all cases the effect of gypsum on the levels of exchangeable Ca is still present to a marked degree after 5 years indicating that the benefits of a surface application are likely to last longer than that in most soils.
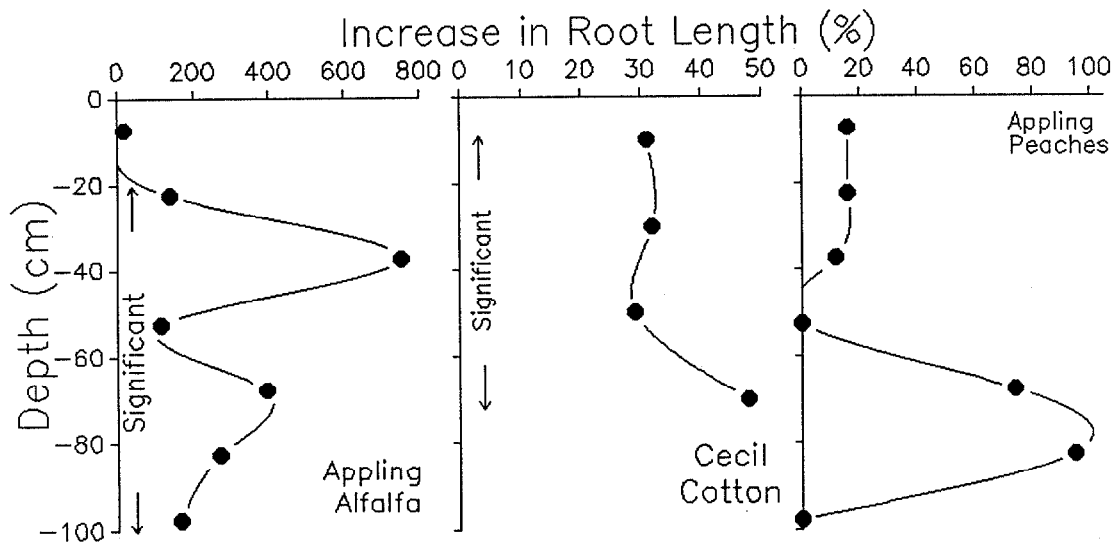
Figure 9.   Increase in root length (RL) with depth of alfalfa, cotton and peaches as a result of the surface application of 10 t/ha gypsum.

Iv.   Effect of Gypsum on Crop Rooting

The effect of gypsum on promoting root proliferation for a number of crops in different soils is presented in Figure 9. In the cases of alfalfa and cotton, Gypsum treatment resulted in significant increases in root length down the entire profile consistent with the yield increases obtained (Figures 1 and 2). This effect is illustrated visually for all the subsoil modification treatments in the alfalfa experiment in Plate 1. The differences between the Control treatment and the Gypsum and Mixed and Limed treatments are most striking. In the Gypsum treatment, the roots appear to have followed preferred routes probably down macropores where amelioration had been more efficient. However for peaches, Gypsum increased root length down the profile but the difference did not reach significance despite the improved chemical conditions in the subsoil (Figure 3). The lack of improved root growth is also consistent with the relatively small increase in yield obtained (Figure 2). It would thus appear that peach roots are probably more sensitive to the physical than

Plate 1.   Effect of profile modification treatments after 8 years on alfalfa rooting habit in an Appling soil (a) control, (b) gypsum, (c) mixed and (d) mixed and limed.

chemical barriers in the soil which is supported by the fact that in the Mixed treatment (no chemical amelioration), increases in root length down the entire profile were much greater than in the Gypsum treatment and reached significance below 60 cm.

V.   Effect of Gypsum on Subsoil Hardpans

The effect of Gypsum treatment on cone index [Cone index is a measure of the resistance to the penetration of a cone shaped probe with high values indicating greater resistance.] (CI) values down the profile at different locations under different crops is illustrated in Figure 10. As the moisture content in the Gypsum treated plots was lower down the entire profile than that in the Control plots in all cases (data not shown), any differences in CI are therefore due to treatment effects and not due to moisture variations. It can clearly be seen that surface application of gypsum resulted in improvement in the ability of the subsoil hardpans to be penetrated although the differences were significant at only three of the locations. However in the case of the cotton experiment, spatial variability was so great that statistical significance was not reached although a significant yield response to Gypsum was obtained (Figure 2). Significant increases in root length below 20 cm in the profile were observed at the two of the three locations where samples for root distribution were taken (Figure 9). The fact that improved penetrability is reproducible with different crop and soil combinations indicates that the Gypsum treatment is probably initiating a chain of events leading to this improvement which may be a direct or indirect effect. To test this, the effects of Gypsum on fallow and alfalfa covered Cecil soil (Figure 10e and f) show that the improvement induced by Gypsum in the fallow treatment is not significant which would tend to indicate that the major part of the effect is probably due to the indirect effects of increased rooting in the subsoil although the direct beneficial effect of Gypsum on

flocculation and physical condition of the clay in these soils (Miller and Baharuddin, 1986) cannot be ruled out. In one case where water stable aggregates were measured in the hardpan layer (Figure 11), there was a significant increase in large sized aggregates between 30 and 60 cm below the surface which is most likely due to the binding of soil particles by roots and fungal mycelia (Tisdall and Oades, 1982). On the other hand in a laboratory experiment, both CI and moisture content at -0.05 MPa matric potential measured on compacted soil cores (bulk density = 1.5 g/cc) prewetted with distilled water was significantly. higher (1.32 MPa) than in those prewetted with saturated gypsum solution (1.18 MPa). These results indicate that gypsum does have a direct effect on resistance to penetration and the fact that the differences observed in the field did not reach significance (Figure 10c) is probably due to the large extent of spatial variability at the site. Comparison of the moisture release curves at high matric potentials (0-0.2 MPa) (Figure 12) shows that the moisture content in systems wetted with saturated gypsum solution decreased more than those wetted with deionized water indicating that there were more large pores in the Gypsum treated soil further corroborating the direct effect of gypsum on flocculation and aggregation. The results presented here clearly demonstrate that surface applied gypsum contributes to conditions in highly weathered soils which lead to improved penetration of subsoil hardpans by roots resulting in improved utilization of water (cf Section VI) and increased yields. The effects of gypsum appear to be both direct, by influencing the flocculation and aggregation of the subsoil and indirect, by improved rooting leading to greater subsoil aggregation.
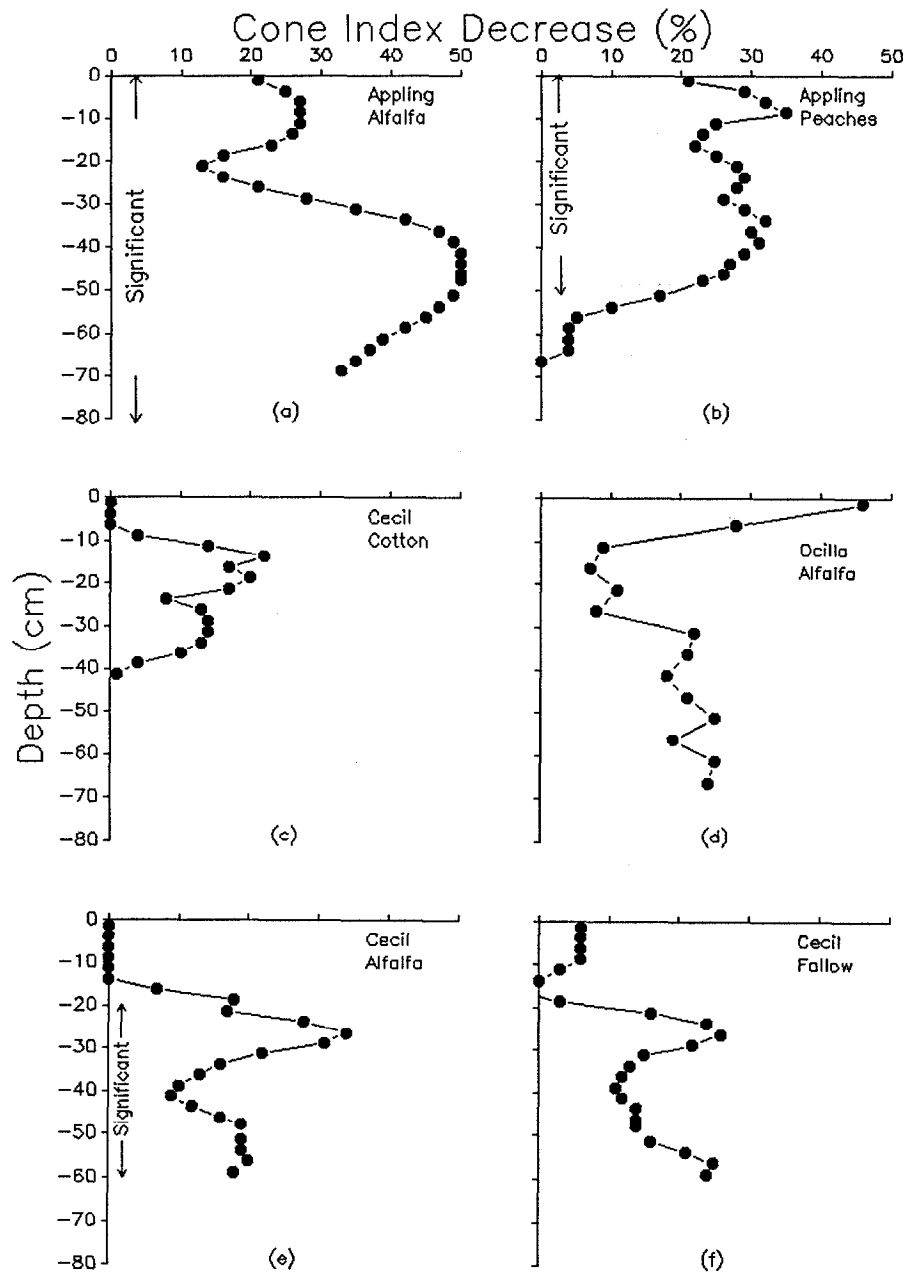
Figure 10.   Decrease in cone index (CI) with depth caused by surface application of 10 t/ha gypsum to different soil/crop combinations at different locations. Measurements were made: a) 48, b) 30, c) 30, d) 33, e) 21 and f) 21 months after treatment. Mean CI values below 20 cm were: a) 3.41, b) 3.44, c) 3.77, d) 3.32 e) 6.41 and f) 3.81 MPa.

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Figure 11. Increase in water-stable aggregates at two depths measured 48 months after surface application of 10 t/ha gypsum to alfalfa on Appling soil.
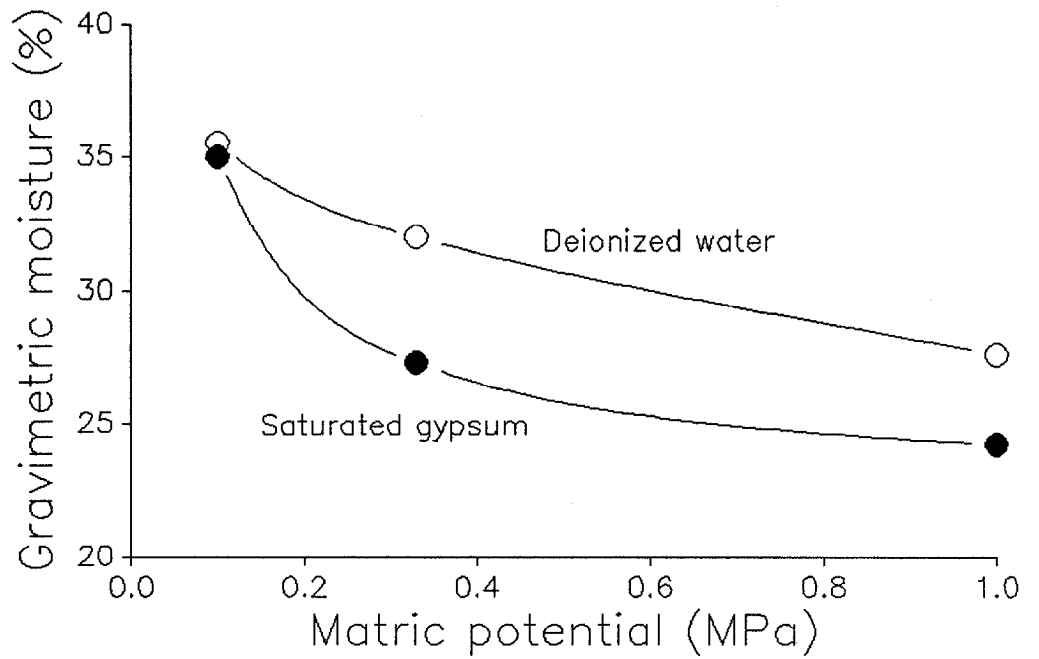
Figure 12. Effect of gypsum in wetting solution on moisture release curve for Cecil soil at high soil water potential.
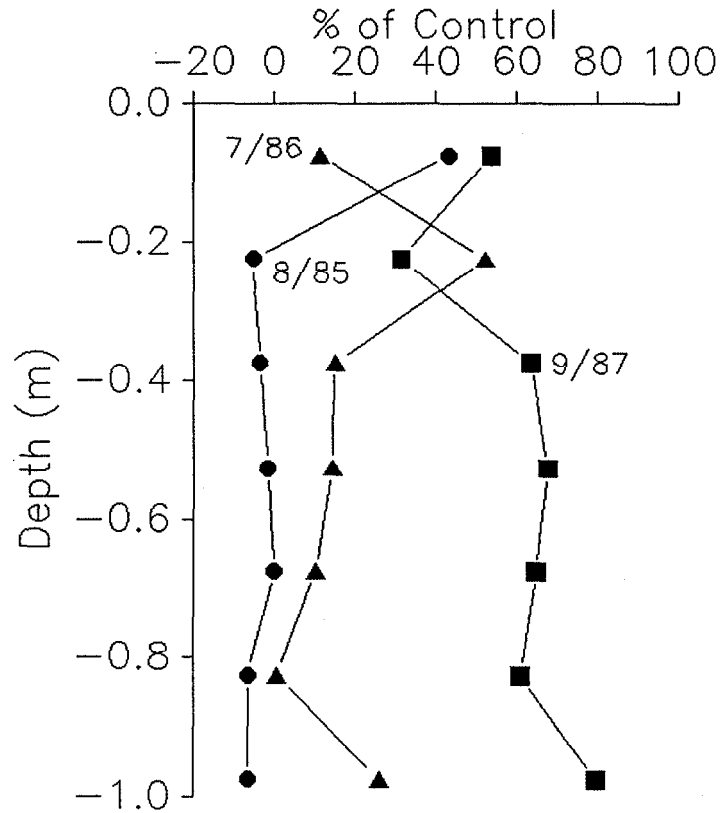
Figure 13.   Increase in water extraction due to gypsum on an Appling soil during three
dry down periods.

VI.   Effect of Gypsum on Water Extraction

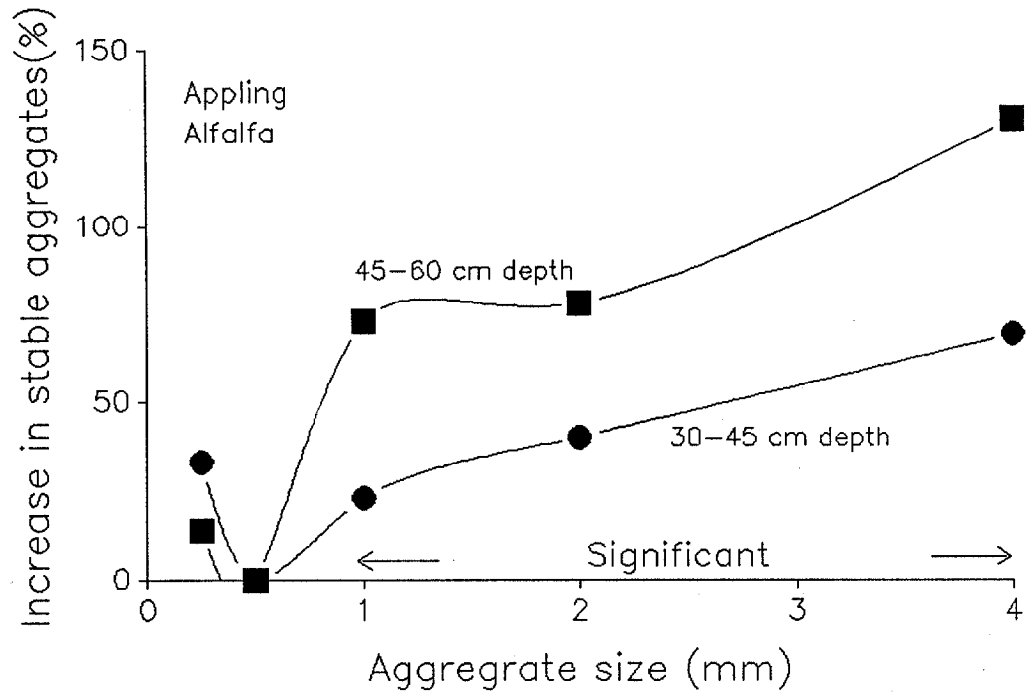Increased water extraction in the Gypsum treatments over the control in three years

are presented in Figure 13. These results were obtained by measuring the profile moisture

content during a drydown period after soaking rains which thoroughly wetted the soil profile.

Soil moisture at 0.15 m increments down the profile was measured using a neutron moisture

meter. In the first year which was only two years after gypsum application, most of the

additional water extracted in the Gypsum treatment was from the topsoil indicating that root

penetration into the subsoil was not yet substantial.   In subsequent years, increasing

quantities of water were extracted from the subsoil corroborating the fact that roots had

entered the subsoil (Figure 9). From these data, it is clear that the Gypsum treatment has

improved the chemical and physical conditions in the subsoil sufficiently to allow root penetration and improved water extraction which has been translated into increased yields.

VII.   Possible Mechanisms for Chemical Amelioration

The objective of this section is to present arguments in support of the mechanisms which offer the most satisfactory explanation of the observed beneficial effects of gypsum application on root growth in acid subsoils.   The most consistent pattern of behavior observed in this and other studies on amelioration by gypsum is one of increased exchangeable Ca and decreased exchangeable Al down the profile (Figures 3, 4, 6 and 7). Usually the levels of these elements in the soil solution follow the same pattern although in the case of Al the effect is somewhat more complex because the activity of Al^{3+} often decreases even when total Al in solution increases as a result of gypsum application. There have also been a number of other chemical effects of applied gypsum on subsoils observed which have not always been consistent such as an increase in pH (Figures 4, 6 and 7), an increase in the activity of silicon in the soil solution (Table 4) and complexation of Al by the fluoride present in phosphogypsum (Table 5).   Because these effects are not always consistent, such mechanisms may not be the primary explanations for improved root growth. Each of the above possibilities will be discussed together with the supporting evidence.

A.   Increased Levels of Subsoil Ca

It has been known for a long time that, in the absence or at very low levels of Ca in a medium, root elongation does not take place (Hanson, 1984). It appears that for roots to elongate satisfactorily, sufficient Ca must be available at the point of elongation.   In many soils, there is typically an inverse relationship between exchangeable Ca and Al (Figures 3, 4, 6 and 7) with leached, Ca-impoverished soils usually being sufficiently acidic to subtend

toxic levels of Al in the soil solution. Consequently subsoils low in exchangeable Ca such as those investigated here (Figures 3, 4, 6 and 7) present a hostile environment for root proliferation and any increase in soluble Ca is likely to promote rooting. The Gypsum treatments have all resulted in substantial increases in subsoil Ca (Figures 3, 4, 6 and 7) which is likely to have contributed partially to the beneficial effects observed. However it is very difficult to distinguish the effects of Ca deficiency from those of Al toxicity on root development. In solution culture studies with soybeans, the toxic effects of Al on root elongation could be negated by increasing the level of Ca in the solution (Table 6). This principle has been formulated in various expressions developed by different workers involving Al saturation of the exchange complex or different measures of the relative proportions of Ca and Al in the soil solution (Lund, 1970; Adams, 1984; Buyeye, 1985; Sumner et al., 1985). A comparison of some of these forms of expression with the Calcium-Aluminum Balance (CAB) $\{2\log(Ca^{2+}) - [3\log(Al^{3+}) + 2\log(AlOH^{2+}) + \log(Al(OH)^{2+})]\}$ developed in this project for the data in Table 6 is presented in Table 7. It can clearly be seen from the coefficients of determination that the CAB expression is superior to all the others. These data bring into clear focus the beneficial effects which soluble Ca has in offsetting the toxic effects of soluble Al. In view of these considerations, it would seem to be futile to try to make a distinction between enhanced Ca status and reduced Al toxicity in explaining improved root growth brought about by Gypsum treatment because both are likely to be important in at least some soils. It would therefore appear to be much more profitable to focus our attention on the mechanisms by which gypsum renders Al less labile (Section VII C-E) because simple cation exchange reactions would suggest that gypsum should exacerbate the problem by forcing more Al into the soil solution.

Table 6.   Effect of varying pH, Ca and Al on the tap root length of soybeans grown in dilute nutrient solutions.

Ca μM	Initial Al conc., μM				
	0	20	40	80	160
	Root length, mm				
pH 4.2					
625	222	182	104	79	84
1250	208	206	162	94	78
2500	222	211	206	145	79
5000	223	223	223	200	126
10000	226	233	218	216	171
pH 4.5					
625	217	168	114	86	89
1250	235	217	139	98	84
2500	227	241	189	121	100
5000	232	234	216	184	97
10000	186	237	242	217	92
pH 4.8					
625	233	192	119	105	85
1250	241	207	152	109	91
2500	233	234	183	157	91
5000	231	239	211	150	111
10000	249	232	209	207	119

LSD (P = 0.05)   pH   NS   pH x Ca   NS
                  Ca   66   pH x Al   NS
                  Al   66   Ca x Al   34
                                  pH x Ca x Al   NS

Table 7.   Regression equation of relative tap root length versus various aluminum parameters.

Parameter	Equation	Coefficient of determination
Monomeric Al conc.	$Y = 85.18 - 0.43x$	0.208
$\Sigma a_{Al\ monomeric}$	$Y = 99.49 \exp(-0.02x)$	0.647
$\Sigma a_{Al}{}^{3+} + a_{AlOH}{}^{2+}$	$Y = 89.27 \exp(-0.03x)$	0.799
$\Sigma a_{Al}{}^{3+} + a_{Al(OH)2}{}^{+} + a_{Al(OH)2}{}^{+}$	$Y = 86.23 \exp(-0.02x)$	0.729
$\Sigma 3a_{Al}{}^{3+} + 2a_{AlOH}{}^{2+} + a_{Al(OH)2}{}^{+}$	$Y = 89.95 \exp(-0.01x)$	0.801
Ratio activities Al^{3+}/Ca^{2+}	$Y = 58.04 \exp(-30.57x)$	0.509
$(Ca^{2+})/(Al^{3+})^{1/3}$	$Y = 92.89 - (66.54/x)$	0.614
$1/2\log(Ca^{2+}) - 1/3\log(Al^{3+})$	$Y = 102.92x - 1.24$	0.669
$2\log(Ca^{2+}) - 3\log(Al^{3+})$	$Y = 100\{1-\exp[-0.70(x-6)]\}^{7.24}$	0.829
$2\log(Ca^{2+}) - [3\log(Al^{3+}) + 2\log(AlOH^{2+}) + \log(Al(OH)_2{}^{+}]$	$Y = 100\{1-\exp[-0.49(x-20)]\}^{12.22}$	0.900

B.   Ion Pairing

Pavan et al. (1982) have contended that Al toxicity is reduced by gypsum treatment primarily through ion pair formation. According to this hypothesis, the sulfate in the gypsum forms an ion pair $AlSO_4{}^{+}$ despite the fact that the concentration of Al in the solution may even increase. The less toxic nature of $AlSO_4{}^{+}$ is confirmed by the data presented in Figure 14 where the tightness of fit of the relationship between tap root length of soybeans and the sum of the activities of monomeric Al species is improved by taking it into account. Nevertheless this hypothesis has less appeal thermodynamically because the formation of $AlSO_4{}^{+}$ would be at the expense of Al^{3+} and further dissolution of Al would have to occur to reestablish equilibrium which has been shown to be the case by the data of other workers (Buyeye et al., 1985; Pavan et al., 1984). However, in the absence of solid phases as would
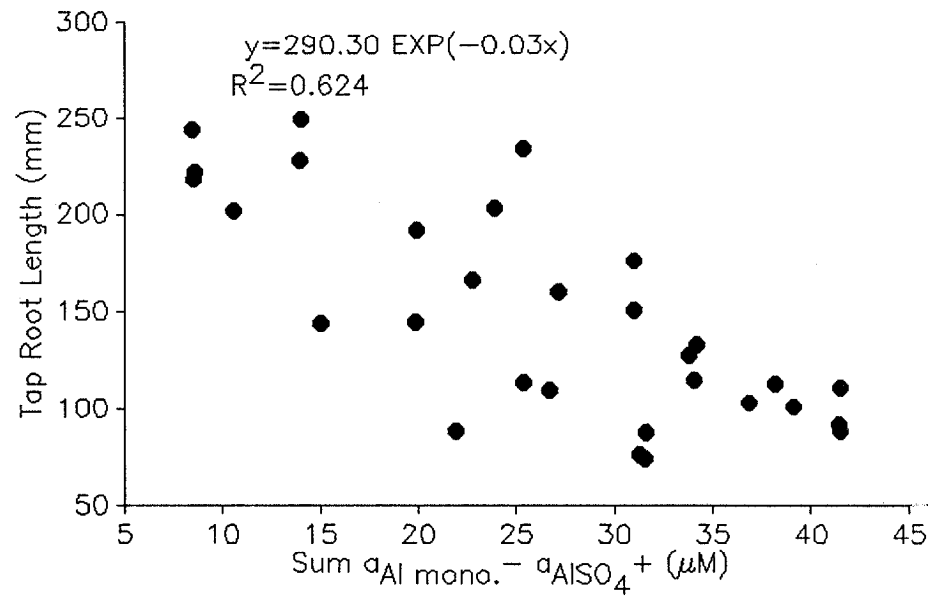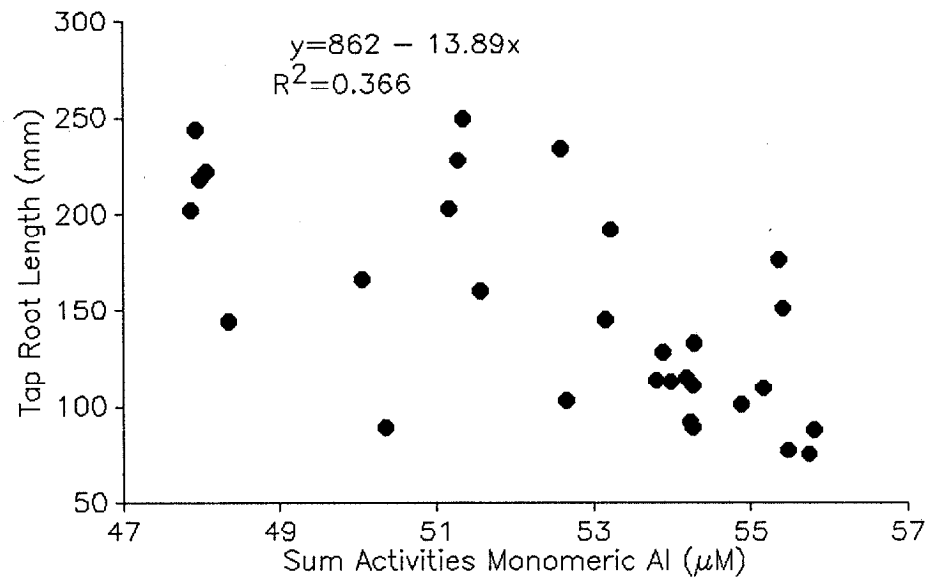
38

Figure 14.   Effect of $AlSO_4^+$ on the relationship between tap root length and sum of the activities of monomeric Al species.

be the case in nutrient solution culture, the mechanism of Al detoxification by gypsum may be quite different. Nevertheless if the kinetics of Al dissolution to replenish that which is converted to $AlSO_4^+$ in solution are slow enough, this mechanism may still be feasible in short-term amelioration. Because phosphogypsum contains fluoride, the potential exists for labile Al to form AlF_x complexes which are known to be less toxic than other monomeric forms (Alva et al., 1988; Cameron et al., 1986; Noble et al., 1988). However because these complexes are very stable, it is unlikely that much uncomplexed F would move into. the subsoil to be available for the detoxification of labile Al.

C.   **"Self-liming" Effect**

The "self-liming" effect was the first mechanism proposed to account for the reduction in exchangeable Al in highly weathered soils after gypsum application by Reeve and Sumner (1972). According to this hypothesis, ligand exchange takes place between the added sulfate and OH groups on sesquioxide surfaces and the alkalinity produced precipitates some Al as illustrated below:

$$3Ca(OH)_2 + 2Al^{3+} \rightarrow 2Al(OH)_3 + 3Ca^{2+}$$
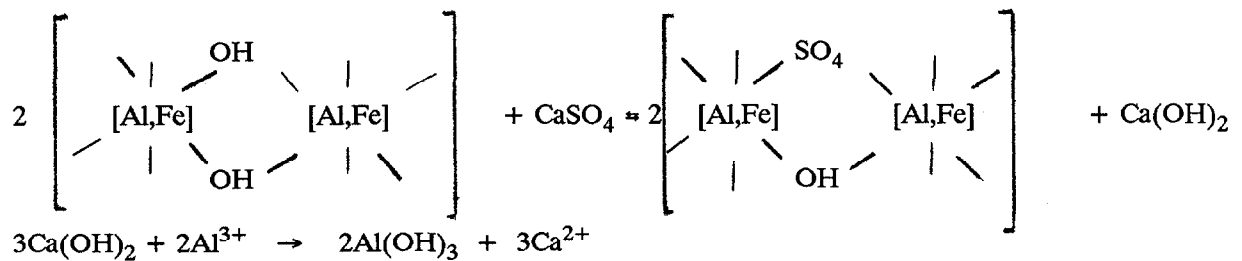
Evidence for this effect can be observed in Figures 4, 6 and 7 (Ocilla, Altavista and Dyke soils) where the pH in the subsoil has increased as a result of gypsum application. However in Figure 3 (Appling soil), gypsum has had little effect on soil pH and it is possible that in this case, the effect has been masked by soil heterogeneity. In order to investigate this possibility, the effect of gypsum and $CaCl_2$ at equal concentrations or ionic strengths on the

p H of Appling subsoil under controlled laboratory conditions was studied (Table 8). Irrespective of conditions, the pH value in $CaSO_4$ is consistently higher than in $CaCl_2$ by about 0.1 to 0.3 pH units suggesting that some replacement of OH by SO_4 does indeed take place when gypsum is added. This effect has also been corroborated by other workers (Couto et al., 1979; Singh, 1982,1984).
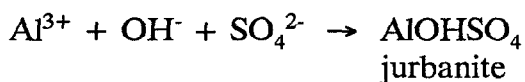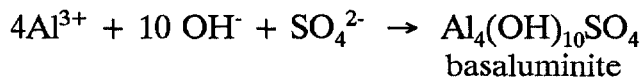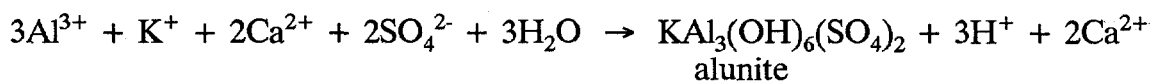
Table 8.   Effect of nature and concentration of electrolyte on pH of Appling soil.

Concentration at given pH mol L^{-1}	pH at given concentration			pH at given ionic strength		
	$CaSO_4$	$CaCl_2$	ΔpH†	$CaSO_4$	$CaCl_2$	ΔpH†
0.0300	--	--	--	4.54	4.20	0.34
0.0140	4.42	4.14	0.28	4.72	4.44	0.28
0.0028	4.72	4.48	0.24	4.95	4.74	0.21
0.0014	4.82	4.62	0.20	5.08	4.91	0.17
0.0007	4.93	4.82	0.11	5.19	5.06	0.13

† $\Delta pH = pH_{CaSO4} - pH_{CaCl2}$

D.   Precipitation of Basic Aluminum Sulfate Minerals

In acid soil environments enriched in sulfate, one or more of the basic Al sulfate minerals have been shown to precipitate (Adams and Rawajfih, 1977; Nordstrom, 1982) as follows:

$$3Al^{3+} + K^+ + 2Ca^{2+} + 2SO_4^{2-} + 3H_2O \rightarrow KAl_3(OH)_6(SO_4)_2 + 3H^+ + 2Ca^{2+}$$
$$\text{alunite}$$
$$4Al^{3+} + 10\ OH^- + SO_4^{2-} \rightarrow Al_4(OH)_{10}SO_4$$
$$\text{basaluminite}$$

$$Al^{3+} + OH^- + SO_4^{2-} \rightarrow AlOHSO_4$$
$$\text{jurbanite}$$

Sposito (1985) has suggested that precipitation of a metastable basaluminite may occur first, particularly if the soil solution was sufficiently enriched in sulfate, followed by a slower

conversion to the more stable jurbanite. From stability diagrams at approximately millimolar levels of sulfate in solution which is quite common in gypsum treated subsoils (Table 4), it appears that alunite is more stable than kaolinite below pH 4.5 with jurbanite becoming most stable below pH 4.0. In terms of reactions with solid aluminous surfaces, the same effect as proposed under "self liming" can be obtained as follows:

$$Al(OH)_3 + CaSO_4 \longrightarrow AlOHSO_4 + Ca(OH)_2$$
gibbsite   jurbanite

$$Al_2Si_2O_5(OH)_4 + 2CaSO_4 + 5H_2O \longrightarrow 2AlOHSO_4 + 2H_4SiO_4 + 2Ca(OH)_2$$
kaolinite   jurbanite
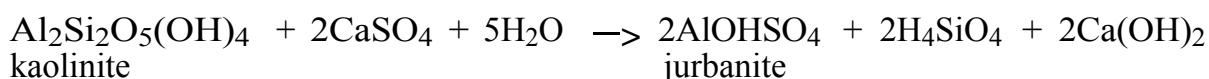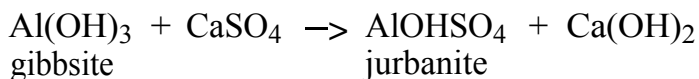
Either reaction explains the decrease in acidity after gypsum treatment although in the second reaction, some of the alkalinity produced could be neutralized by the silicic acid. The second reaction would explain the release of Si in some soils (Table 4). The stability relationships between the different aluminum minerals are presented in Figure 15 together with the shifts in actual values brought about by gypsum application on four of the subsoils studied. Although one cannot use these stability diagrams to prove the existence of a particular mineral, they do serve as a basis for determining the degree of supersaturation or undersaturation with respect to a particular mineral and whether or not the formation of such a new mineral is feasible. In two instances (Appling and Cecil soils) after gypsum application, the soil solutions are undersaturated with respect to all solid phases in Figure 15. In the other cases (Altavista and Dyke soils), the data are consistent with the formation of alunite and/or basaluminite.
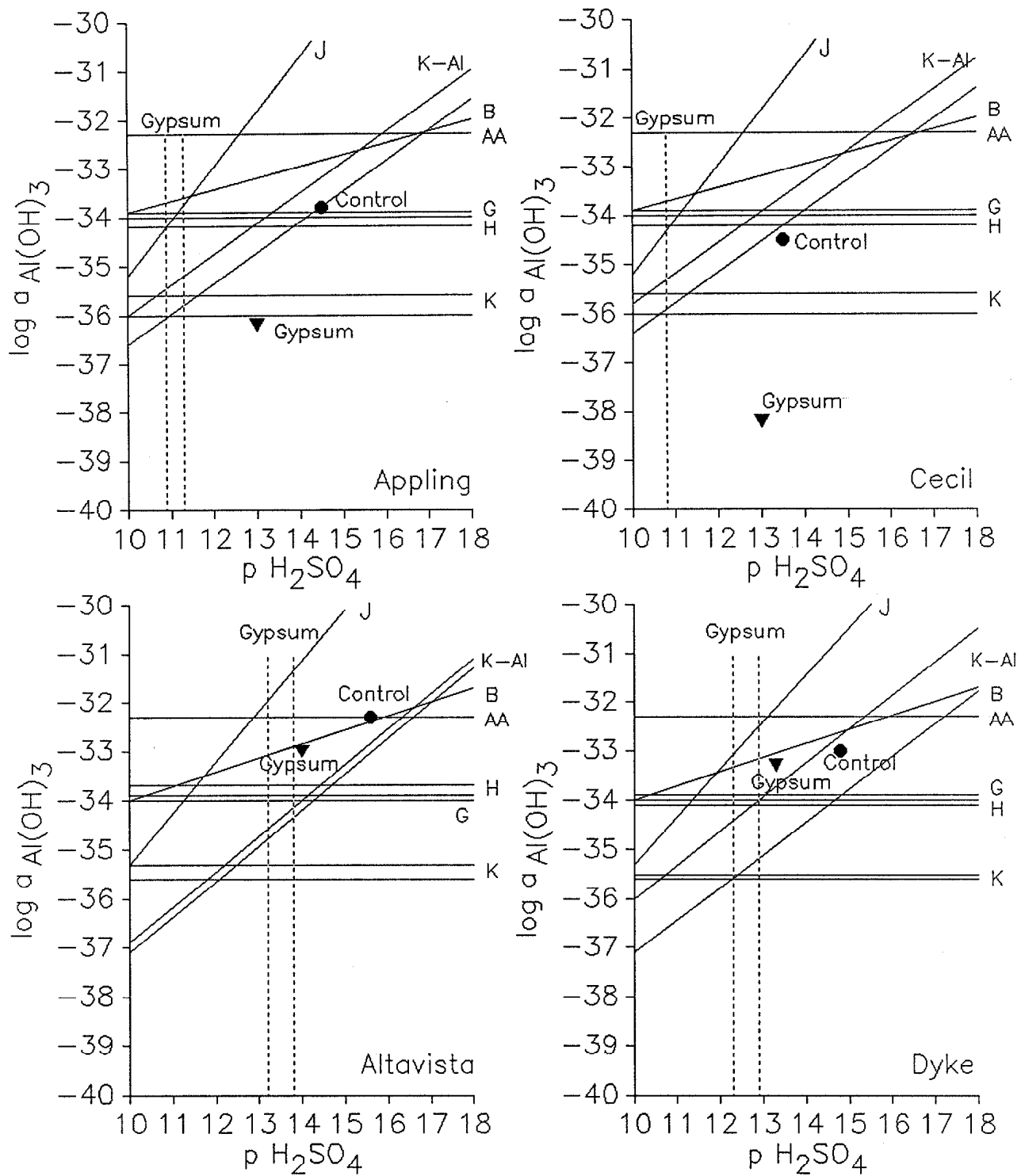
Figure 15. Equilibrium soil solution ion activity products (-log $(Al^{3+})(OH^-)^3$ vs. -log $(H^+)^2(SO_4^{2+})$). Points represent actual solution composition (control and gypsum) and lines or bars represent solubility lines for the minerals indicated (J: jurbanite; K-Al: alunite; B: basaluminite; AA: amorphous $Al(OH)_3$; G: gibbsite; H: halloysite; K: kaolinite).

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E.   Salt Sorption

The cases where the soil solution is undersaturated with respect to all solid phases suggest that surface reactions on sesquioxides rather than mineral dissolution may exert the ultimate control on solution composition. All the subsoils except the sandiest in this study exhibit "salt sorption" to varying degrees as illustrated in Table 9.

Table 9.   Sorption of salt by various soils and corresponding pH values.

| Soil | Depth | pH | | | $CaSO_4 \cdot 2H_2O$ Sorbed |
	cm	water	0.005M $CaSO_4 \cdot 2H_2O$	0.005M $CaCl_2$	$\mu g/g$
Appling	0-15	6.20	5.99	6.04	-1092
	60-75	4.45	4.55	4.23	1932
Altavista	0-15	5.89	5.89	5.73	-1482
	60-75	4.22	4.46	4.11	685
Dyke	0-15	6.47	6.17	6.03	-660
	60-75	4.64	5.74	4.65	1904
Ocilla	0-15	6.57	6.04	6.10	-1287
	60-75	4.45	4.53	4.35	-827

The subsoils with the exception of the lightest in texture (Ocilla) all exhibit substantial "salt sorption" capacity whereas the topsoils have negative values indicating that on addition of a gypsum solution more salts are present than would be accounted for by the gypsum added. The positive values shown by all the topsoils indicate that the soils have behaved in a manner analogous to a mixed bed deionizer having the ability to remove electrolyte from solution. This salt sorption phenomenon can act as a control on the level of Al^{3+} in solution and probably takes the form of a co-immobilization of Ca^{2+}, and some Al^{3+} and SO_4 as illustrated in Figure 16. In this experiment the soil was repeatedly treated with a dilute
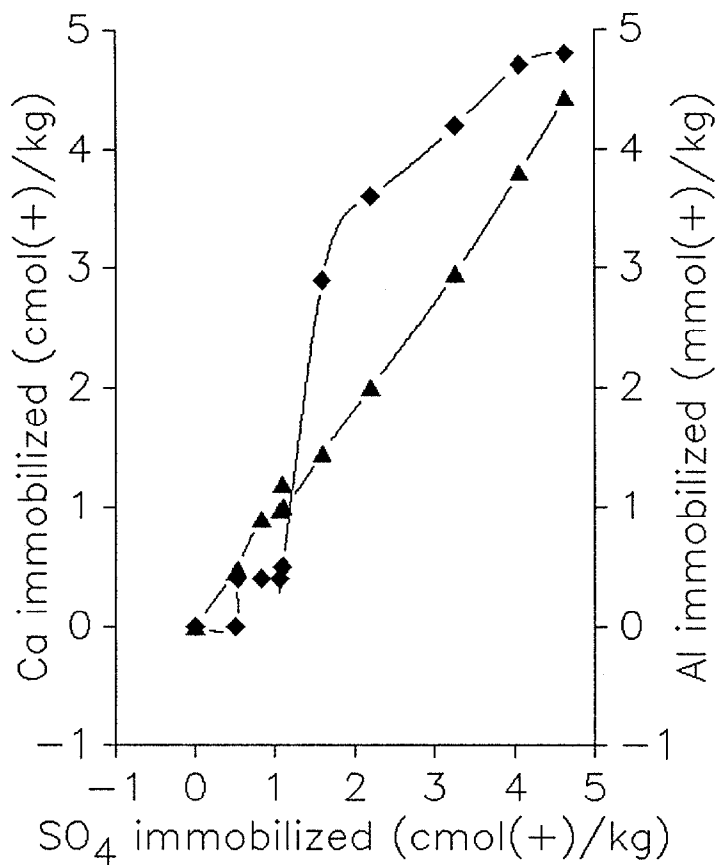
Figure 16.   Cosorption of Ca, Al and SO_4 on an Appling soil.

solution of calcium sulfate and the amounts of Ca and SO_4 adsorbed were measured. There

was virtually no exchange between the added cations and anions and those already present

(excluding H- and OH-) indicating that "salt sorption" was taking place. The Al values in

Figure 16 are the amounts rendered non-extractable with KCl during the equilibrations. The

parallel nature of the curves for Ca and Al supports the likelihood of some type of surface

reaction being involved.   Initially specific adsorption of sulfate would increase the net

negative charge on the surface (Bowden et al., 1980; Zhang et al., 1987) which would in turn,

cause greater Ca^{2+} and Al^{3+} uptake. In addition to much of the original exchangeable Al

being deposited in a form no longer extractable by N KCl, approximately 50% of the Ca
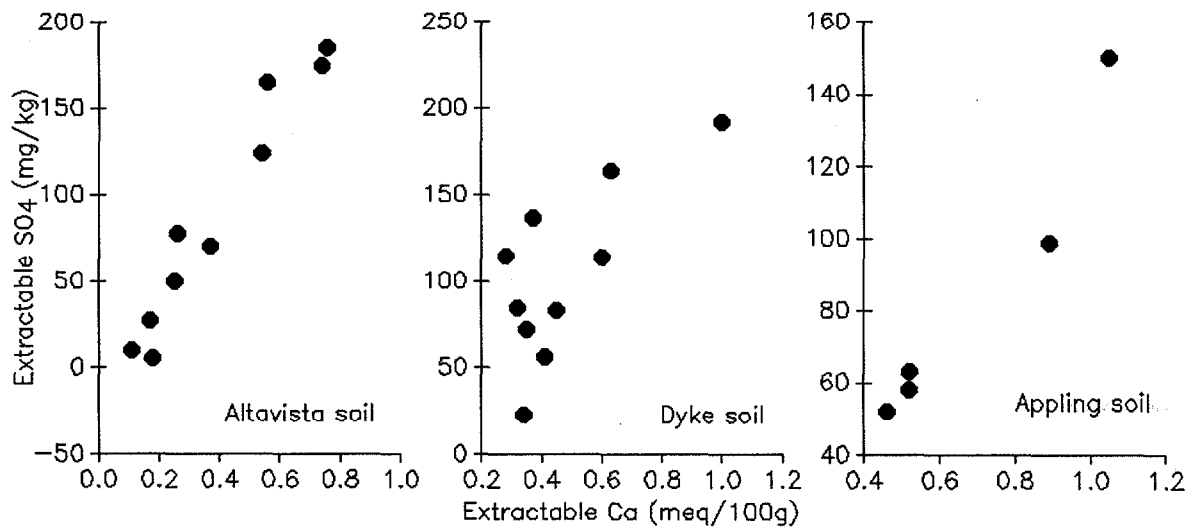
45

Figure 17.   Cosorption of Ca and SO$_4$ in the subsoils from three sites at the end of experimentation.

taken up by the soil during equilibration is no longer exchangeable. The co-sorption of Ca and SO$_4$ is strongly supported by the strong relationship from the field experiments (Figure 17) where extractable Ca has been plotted against extractable SO$_4$ at the end of experimentation.   In cases where soil pH increased as a result of gypsum application, a similar process involving the co-sorption of protons may have occurred. The exact nature of the reactions involved in this co-immobilization is not clear and needs further investigation.

F.   Conclusions

At this stage it is not possible to clearly define which of the above mechanisms are in fact operative under field conditions. Further clarification will probably only be attained when sufficient thermodynamic data for surface reactions involving cation- and ligand-exchange equilibria become available for more quantitative modeling of the system.   It

makes little difference to the outcome whether one invokes the paradigm of adsorption or precipitation to explain the detoxification of Al by gypsum. Changes in soil solution and exchangeable Al observed in this study are consistent with the original "self-liming" hypothesis of Reeve and Sumner (1972) manifested in any one of the following ways: (i) ligand exchange of SO_4^{2-} for OH^- on sesquioxide surfaces, (ii) Al^{3+} and H^+ immobilization on sesquioxide surfaces charged by specific adsorption of SO_4^{2-} and/or (iii) partial conversion of hydroxy Al minerals to solid hydroxy Al sulfates and lime. In all cases, the activity of Al^{3+} in solution and exchangeable Al will decrease often accompanied by an increase in pH.

VIII. Soil Test for Responsiveness to Gypsum

Based on the fact that the soils in this study which responded to gypsum also exhibited substantial salt sorption as well as a higher pH in $CaSO_4$ than in $CaCl_2$ of the same molarity, the following simple test is proposed for further evaluation and use:

Take 3x10 g soil in three separate centrifuge tubes and add 25 ml of either 0.005M $CaSO_4$, 0.005M $CaCl_2$ or distilled water and shake intermittently overnight. After centrifuging, measure the electrical conductivity and pH values of the supematant solutions. Calculate Delta pH as pH in 0.005M $CaSO_4$ - pH in $CaCl_2$ Calculate the amount of salt sorption using the following equation:

Gypsum sorbed µg/g) = 2150 - 3.483(EC_{Gypsum} - EC_{Water})

Responsive soils should lie to the right of the vertical line as illustrated in Figure 18. One can clearly see that the soils taken from sites with known responses fall near or to the right of the line.
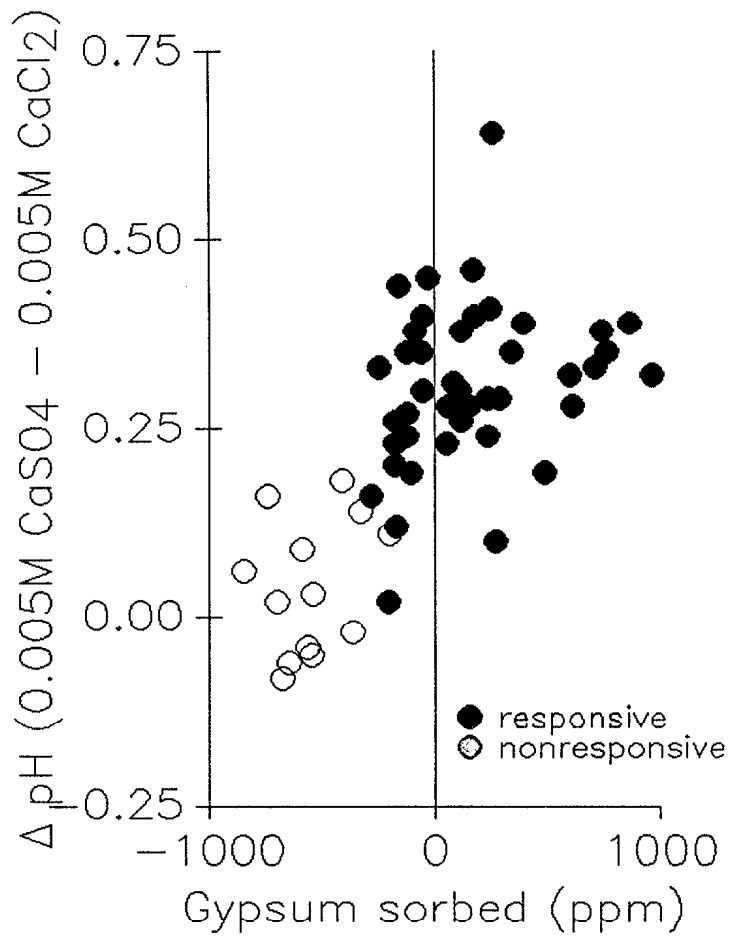
Figure 18.   Relationship between ΔpH and gypsum sorbed for responsive and non-responsive sites.

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions can be drawn from the results of this investigation:

1. Phosphogypsum is a suitable ameliorant for overcoming the subsoil acidity syndrome which limits root penetration into acid Ca deficient and/or Al toxic subsoils.

2. Phosphogypsum and mined gypsum are equally effective for this purpose.

3. Given sufficient time (usually 1-2 years), gypsum dissolves and moves down the soil profile into the subsoil where it immediately supplies Ca for root elongation and induces the partial precipitation of labile subsoil Al allowing roots to explore the subsoil more effectively.

4. Increased root proliferation in the subsoil allows the crop to use water previously beyond reach which ultimately translates into increased yields.

5. These beneficial effects of an initial 10 ton/ha application of gypsum last more than 5 years which makes the economics of this treatment very favorable.

6. Because gypsum causes the preferential leaching of Mg from the topsoil, its use on sandy soils with low Mg levels cannot be recommended as negative responses may be obtained if the Mg falls to deficient levels.

7. With high value crops such as alfalfa, peaches and cotton, net profit due to gypsum application ranged from $100 - $500/ha/yr.

8. Phosphogypsum also had a profound effect in reducing the penetration resistance of subsoil hardpan layers which also allows roots to penetrate subsoils more easily.

PUBLICATIONS

During the course of this project, the following papers were published and contained some of the data generated.

a.   Refereed Books and Chapters:

Sumner, M. E., W. P. Miller, D. E. Radcliffe and J. M. McCray.   1986. Use of phosphogypsum as an amendment for highly weathered soils. Florida Inst. Phos. Res., Bartow, FL.

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b.   Refereed Journal Articles:

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c.   Abstracts and Proceedings

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