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SOIL ACIDITY AND RESPONSE TO LIMING

E. J. Kamprath

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SOIL ACIDITY AND RESPONSE TO LIMING

E. J Kamprath

Soils in the humid region are or. arily quite acid throughout the profile. Without the application of lime, the growth of many plants on acid soils is reduced and the efficient use of fertilizer is decreased. The purpose of this article is to discuss current ideas on soil acidity and plant growth response to liming. No attempt has been made to include all of the articles dealing with this subject but rather to use certain ones to illustrate the concepts discussed.

NATURE OF SOIL ACIDITY

Exchangeable Acidity

Exchangeable Aluminum. When an acid soil is extracted with a neutral unbuffered salt sulution, a measure can be obtained of the exchangeable acidity which affects plant growth. As early as 1902, Veitch (38) showed that this exchangeable acidity was due to aluminum. Later Paver and Marshall (28) found that aluminum was the predominant exchangeable cation extracted from acid clays with a neutral salt solution. The titration curve of a hydrogen saturated montmorillonite is similar to that of a strong mineral acid and aluminum saturated montmorillonite has a titration curve representative of weak acids (5). Coleman, et al. (8) found that the acid subsoils of the Ultisol (Red and Yellow Podzolic) soils have a large portion of their "effective" CEC (cation exchange capacity) countered with exchangeable aluminum. A large number of other workers also have shown that aluminum is the principal component of exchangeable soil acidity as determined by extraction with a neutral salt.

Exchangeable Hydrogen. Very little exchangeable hydrogen as such exists in mineral soils. On moist storage, H saturated montmorillonites and kaolinites change spontaneously to form either Al, Mg saturated clays, or Al saturated clays (4). Only in acid soils with a high organic matter content is some exchangeable H found.

Nonexchangeable Acidity

Certain soils still have a large amount of titratable acidity after the exchangeable aluminum has been removed with a neutral salt solution. A portion of this titratable acidity in soils is associated with the organic matter. The negative exchange sites of organic matter are weakly acidic (2). At soil pH values of 7 or less the carboxyl groups would be primarily involved. At a pH of 7 the CEC or organic matter in Costal Plain soils varied from 62 to 279 me per 100 grams of organic matter with an average value of 127 me (17). The CEC of soil organic matter in Wisconsin soils was 75 me per 100 grams at pH 3.5, 163 me at pH 7, and 213 me at pH 8 (14).

Many soils of the Ultisol (Red and Yellow Podzolic) and Oxisol (Latosol) groups have a large amount of nonexchangeable acidity which can be replaced by buffered solutions of pH 8.1 but cannot be removed by a neutral salt. For example, a Cecil subsoil which had 5.5 me per 100 grams of acidity replaceable with $BaCl_2$-TEA at pH 8.1 had only 0.5 me of exchangeable acidity replaced with 1N KCl (8). Recently Coleman, et al. (7) have postulated that a large portion of this titratable nonexchangeable acidity may be due to the ionization of H from ferric and aluminum hydrous oxides which exist either on clay surfaces or in the interlayer space. They found that montmorillonite-sesquoxide mixtures had appreciable amounts of titratable nonexchangeable acidity. Others

attribute the titratable nonexchangeable acidity of subsoils to completion of hydrolysis of interlayer hydroxy aluminum (34,35).

Another mechanism which can contribute to the buffer capacity of a soil is anion adsorption by soils. Mehlich (22) has shown that a soil with a large amount of adsorbed sulfate had a higher buffer capacity than when the sulfate was removed. The addition of lime causes a rise in pH and an increase in hydroxyl ions. The hydroxyl ions replace the sulfate ions which react with calcium to form calcium sulfate. The lime used in this manner does not neutralize any exchangeable Al or H.

Measurement of Soil Acidity

Extraction of soil acidity often has been made with solutions buffered at a given pH. These solutions not only extract exchangeable Al and H but also nonexchangeable H. In recent years there has been considerable interest in the measurement of exchangeable Al, since it has been found to be the predominant cation in very acid soils.

Lin and Coleman (19) reported that a neutral salt solution such as N KCl replaced Al^{+3} from soils but did not replace the hydroxy aluminum. The exchangeable aluminum can be estimated by titrating the solution with NaOH. The aluminum is aproximately equal to the amount of base used between the methyl orange and phenolphthalein endpoints.

A measure of the total soil acidity can be obtained by extracting a soil with $BaCl_2$-triethanolamine solution, pH 8.2, as outlined by Mehlich (21). By subtracting the exchangeable acidity obtained with a neutral unbuffered salt from the $BaCl_2$-TEA pH 8.2 acidity, a measure can be obtained of the nonexchangeable acidity.

Estimations of total soil acidity also can be obtained from potentiometric titration of soils with a base when done in a salt solution.

CAUSES OF POOR PLANT GROWTH ON ACID SOILS

The poor growth of plants on acid soils has been attributed to a number of factors. The principal direct factors causing poor growth are aluminum toxicity, magnesium deficiency, calcium deficiency and molybdenum deficiency.

Aluminum Toxicity

The studies of Vlamis (37) showed Al toxicity was one of the major factors contributing to poor growth of plants on acid soils. Previously, Ligon and Pierre (18) had demonstrated the toxic effect of soluble Al on plant growth. The growth of corn was decreased when the concentration of Al in the soil solution was greater than 1 ppm. The growth of sorghum roots was severely reduced in acid soils until 80 percent of the exchangeable Al was neutralized (30). Cotton roots died when the concentration of Al in the soil solution was 1 ppm and at 0.5 ppm the growth of roots was decreased and their appearance was abnormal (Table 1) (32).

Table 1. Effect of Al concentration in the rooting medium on roots of cotton. [Taken from Rios and Pearson (32)]

Al concentration in lower rooting medium ppm	Root Yield g	Root Appearance
0	0.23	normal
0.1	0.24	normal
0.5	0.17	thickened, short stubby laterals
1.0	0	dead

Aluminum also affects the uptake and translocation of Ca by plants (16). The uptake of Ca from solution cultures by barley roots was drastically decreased by the presence of soluble Al. The effect of Al on Ca uptake was not solely competition for exchange or carrier sites since the amount by which Al reduced Ca uptake was not changed by adding a large amount of Ca. Transport of Ca to the shoots also was restricted by Al but was not completely stopped.

Foy and Brown (12) observed that cotton plants subjected to soluble Al in solution culture exhibited P deficiency symptoms. Wright (41) suggested that aluminum interferes with the uptake and translocation of P.

Manganese Toxicity

Manganese toxicity also has been regarded as a cause of poor growth in acid soils. The growth of lespedeza, soybeans, and barley was reduced when culture solutions contained 1 to 4 ppm of Mn (25). Foy (11) found in a number of acid soils that Mn toxicity was the primary limiting factor in the growth of alfalfa. Liming reduced the high exchangeable Mn levels (>48 ppm) of these acid soils and eliminated the toxicity symptoms. When the soils had a high level of available P the growth of alfalfa was much better. This suggests that P may detoxify Mn within the plant.

Magnesium Deficiency

In North Carolina, Mg deficiencies generally have been observed on acid, sandy soils with pH's of 5 or less and containing a high saturation of exchangeable Al. Corn plants showed Mg deficiency symptoms when Coastal Plain soils contained less than 0.047 me exchangeable Mg and 50 percent or more of the effective CEC was saturated with exchangeable Al (31). Neutralization of the exchangeable Al with calcitic lime eliminated the Mg deficiency symptoms.

Milan and Mehlich (24) found that Mg deficiencies disappeared when the Ca saturation of the soil was increased. Ferrari and Sluijsmans (10) reported that oats adsorbed less Mg when the pH was below 4.8 which might indicate Al antagonism to Mg uptake.

Calcium Deficiency

It is difficult to separate the effects on plant growth of low soil calcium levels in acid soils from the toxic effects of Al and/or Mn. The addition of soluble Ca salts to acid soils usually does not increase plant growth and often results in decreased growth (20, 33). The soluble Ca salts will replace the Al and Mn from the exchange sites and thereby increase the amounts of Al and Mn soil solution to toxic levels. Fried and Peech (13) found the addition of 1000 lbs. of $CaSO_4$ per acre increased considerably the Al and Mn in the soil solution.

A certain amount of available Ca is necessary for adequate plant growth. Root growth of cotton was inhibited when the calcium saturation of the soil was less than 20 percent (15). For the growth of lettuce and barley 20 percent of the exchange complex had to be saturated with Ca (36).

Calcium deficiency symptoms in crops growing in acid soils rarely have been reported. Plants grown in a solution displaced from a limed soil were not adversely affected when sufficient H ion was added to lower the pH to 4.2 (37). This suggests that if adequate Ca is present a low pH as such will not be detrimental. Thus it appears that Ca deficiency as such does not limit plant growth on acid soils but rather the toxic effects of Al and/or Mn.

Molybdenum Deficiency

The solubility and availability of Mo is low in acid soils and increases considerably on liming (9). Since Mo is essential to the symbiotic fixation of nitrogen, legumes are the first crops to show molybdenum deficiency.

LIMING ACID SOILS

Soils are limed for the purpose of (a) neutralizing exchangeable aluminum, exchangeable hydrogen where it is present, and/or exchangeable manganese, and (b) supplying calcium and magnesium.

Neutralization of Soil Acidity

When exchangeable Al is replaced from a soil it hydrolyzes in solution to form hydroxy aluminum and H^+ as indicated by the following reaction:

$$Al^{+3} + HOH \longrightarrow Al\ (OH)^{+2} + H^+$$

As the pH of the solution is increased the hydrolysis continues with the formation of $Al\ (OH)_3$.

The addition of $CaCO_3$ to water results in the following reaction:

$$CaCO_3 + HOH \longrightarrow Ca^{+2} + HCO_3^- + OH^-$$

When lime is added to an acid soil the H^+ resulting from hydrolysis of aluminum reacts with the OH^- to form water. The neutralization of an acid soil with lime can be written as follows:

$$2Al\ Soil + 3CaCO_3 + 6HOH \longrightarrow 3Ca\ Soil + 2Al\ (OH)_3 + 3H_2CO_3$$

Growth as Related to Percent Al Saturation

Mineral Soils. Coleman, et al. (8) suggested a realistic value of the effective cation exchange capacity of a soil is obtained using the sum of the exchangeable cations Al, Ca and Mg replaced by an unbuffered neutral salt such as KCl. A cation exchange capacity determined by this method would measure the sites participating in exchange reactions. The percent Al saturation would be given by the equation, $\% \text{ Al saturation} = \frac{Al}{Al + Ca + Mg + K} \times 100$, with the amounts of the cations expressed as me per 100 grams.

Nye, et al. (27) stated that soils with small amounts of electrolyte would have low concentrations of Al in the soil solution when the Al saturation is less than 60 percent. This was verified by Cate and Sukhai (3) who found less than 1 ppm of Al in the soil solution when the Al saturation was less than 60 percent. The growth of corn on Coastal Plain soils was drastically reduced when the Al saturation of the effective CEC was greater than 55 percent (Table 2) (31).

Table 2. Effect of liming on growth of corn as related to Al saturation and pH. [Data of Rice (31).]

Soil	Al saturation %	pH	Relative plant growth on unlimed as compared to limed soil
Goldsboro	44	4.5	98
Goldsboro	48	4.5	98
Lynchburg	56	4.2	80
Klej	68	4.4	18
Rains	85	4.2	18

At lower Al saturation no response was obtained to liming even though the pH was less than 5. A field experiment with soybeans on a Norfolk soil showed that yields were reduced when the Al saturation was 40 percent or greater (Table 3). Liming beyond pH 5.4 did not increase yields the first year.

Table 3. Yield of soybeans on a Norfolk soil as related to Al saturation and pH.

Lime added lbs/acre	pH	Al me/100g	Ca + Mg me/100g	% Al saturation	Yield bu/a
0	4.9	1.04	1.32	44	11
1000	5.4	0.63	1.93	20	35
2000	5.9	0.16	2.55	6	35

Liming acid sandy Coastal Plain soils which had initial pH's of less than 5 to pH's of 5.3 to 5.5 markedly increased the growth of cotton (20). Data for a Norfolk soil are shown in Table 4.

Table 4. Effect of lime and $CaSO_4$ on the growth of cotton on a Norfolk soil. [Data from McCart and Kamprath (20).]

Treatment		Initial pH after liming	Exch. Al me/100 g	Dry Matter g/pot	Ca uptake me/pot
Lime Ca added me/100g	$CaSO_4$				
0	3	4.6	0.83	3.7	2.3
1	0	5.3	0.32	8.6	5.4
1	1	5.3	0.32	9.1	6.2
1	2	5.3	0.32	8.8	6.6
3	0	6.2	0.13	10.2	9.2
3	1	6.2	0.13	10.7	10.1
	L.S.D.	(05)		1.01	.92

Although the cotton growth was increased by liming to a pH of 6.2, the largest increase was obtained with the first increment of lime which raised the pH from 4.6 to 5.3 and neutralized almost two-thirds of the exchangeable Al initially present.

The addition of lime beyond that needed to neutralize 85 percent of the exchangeable Al of a Red and Yellow Podzolic soil did not increase the yield of alfalfa (Table 5) (26). At a pH of 5.7 practically all of the exchangeable Al had been neutralized.

Table 5. Effect of exchangeable Al on growth of alfalfa. [Data from Moschler, et al. (26).]

Lime Treatment tons/acre	pH	Exch. Al me/100 g	Exch. Ca + Mg me/100g	Alfalfa Yield (3 years) tons/acre
0	4.9	0.74	1.24	0.26
0.5	5.3	0.40	2.26	3.94
1	5.7	0.14	3.15	6.94
2	5.7	0.12	3.24	7.67
4	6.2	0.10	3.62	7.81
8	6.5	0.03	4.74	7.80
16	6.8	0.02	5.98	8.00

Where high rates of fertilizer are applied it is desirable to have a low level of exchangeable Al, since the cations in the fertilizer salts will replace some Al from exchange sites and increase the Al in the soil solution. In one study the addition of 1000 lbs. of $CaSO_4$ per acre to an acid soil increased the Al in solution by 50 percent (13).

Another reason for neutralizing practically all of the exchangeable Al before fertilization is the effect of Al on the amount of P required for maximum growth. Foy (11) showed that in nutrient solutions containing soluble Al much higher concentrations of P were required to give normal plant growth. When soils with a high saturation of exchangeable Al were limed to neutralize the Al only one-half as much P needed to be added to the soils to give maximum growth (Table 6).

Table 6. Effect of neutralization of exchangeable Al on the amount of fertilizer P required to give maximum growth of millet. [Data of Woodruff and Kamprath (40).]

Soil	pH	Exchangeable Al me/100 g	P added ppm	Dry Matter g/pot
Norfolk	4.6	0.60	38	1.6
	7.0	0.05	18	2.0
Hyde	4.4	10.1	226	1.9
	5.2	3.6	111	3.0
Cecil	4.8	1.1	116	2.3
	6.6	0.2	52	2.4

The evidence currently available suggests that liming recommendations should be based on the amount of exchangeable Al which is replaced by a neutral unbuffered salt such as KCl. In most mineral soils adding sufficient lime to raise the soil pH in the range of 5.6 to 6.0 results in most of the exchangeable Al being precipitated. In most soils where Mn toxicity is a problem, increasing the soil pH to 5.6 to 6.0 will also decrease solubility of Mn compounds sufficient to prevent toxicity. Thus with most crops very little response to lime would be expected on mineral soils when the soil pH (measured in water) is in the range of 5.6 to 6.0.

High Organic Matter Soils. The pH range in which optimum plant growth is obtained on mineral soils does not apply to high organic matter soil. Soybean yields on a Hyde soil (18% organic matter) were not increased by raising the pH above 4.9 (Table 7) (39).

Table 7. Yield of soybeans at different pH levels on a Hyde soil, 18% O.M. [Data of Welch and Nelson (39).]

pH	Yield bu/acre
4.2	16
4.9	28
5.6	29

Greenhouse studies showed that soybean growth on a peat soil was considerably increased as the exchangeable Al content was reduced (Table 8). However, the changes in pH of the peat soil were not very great and well below that deemed desirable for mineral soils.

Table 8. Growth of soybeans on a peat soil as related to pH and exchangeable Al content.

Lime Treatment lbs./acre	pH	Exchangeable Al me/100 g	Dry Matter g/pot
None	4.1	3.1	2.4
1500	4.2	2.9	2.7
3000	4.4	2.3	3.6
6000	4.5	1.3	4.0

The effective cation exchange capacity of soil organic matter is due mainly to ionization of carboxyl groups and is pH dependent. Trivalent cations such as Fe and Al are bound much more tightly by carboxyl groups than the divalent cations, Ca and Mg. Pierre, et al. (29) stated that high organic matter soils had less Al in the soil solution at given pH than soils with a low organic matter content. Organic matter has a high buffer capacity and relatively large amounts of lime are needed to raise the pH very much.

Liming of high organic matter soils should be aimed at reducing the exchangeable Al to a level which is not detrimental to plant growth and providing adequate amounts of Ca. Arnon and Johnson (1) found that lettuce made as good growth at pH 5 as at 6 in a nutrient solution provided adequate calcium was present. As a general rule when sufficient lime is added to bring the pH of high organic matter soils to 4.8 to 5.1 the exchangeable Al is sufficiently reduced and enough Ca is added for good plant growth. However on peat and muck soils good plant growth may be obtained at lower pH's.

Lime Recommendations

Lime recommendations should be based on the amount of exchangeable acidity extracted with an unbuffered neutral salt solution. In mineral soils the exchangeable acidity will be mostly aluminum while in high organic soils there may be some exchangeable H in addition to the exchangeable Al. The exchangeable acidity can be extracted using 10 grams of soil and 50 milliliters of 1 N KCl. The soil plus the KCl solution should be shaken for 30 minutes, filtered and then washed with 50 ml of 1 N KCl added in 10 ml increments. For routine determinations the washing with the additional KCl can be eliminated. The filtrate should be titrated with 0.01 N or 0.05 N NaOH using phenolphthalein as the indicator. The exchangeable acidity expressed as me per 100 grams of soil is calculated as follows:

$$\text{Exchangeable acidity (me/100 g)} = \text{normality of base} \times \text{mls of base} \times \frac{100}{\text{weight of soil}}$$

The rate of lime needed depends not only on the amount of exchangeable Al present but also on the purity and fineness of the lime. Meyer and Volk (23) found that lime finer than 100 mesh reacted quite fast but that 30 to 60 mesh lime took 6 to 18 months to neutralize the acidity neutralized in one month by 80 mesh lime.

Incubation studies were conducted by the author with three mineral soils and a peat soil to determine the percent neutralization of exchangeable Al with lime rates based on the amount of exchangeable Al extracted by the procedure previously discussed. One hundred mesh lime was thoroughly mixed with the soils and they were incubated four weeks at field moisture capacity. After incubation the exchangeable Al and pH were determined.

The percent neutralization of exchangeable Al with lime rates based on the exchangeable Al originally present is shown in Figure 1. Lime rates on an equivalent weight basis ranging from 60 to 150 percent of the exchangeable Al originally present gave a linear relationship between lime added and the percent of Al neutralized in the mineral soils. When the lime rate was 150 percent of the exchangeable Al, about 80 percent of the exchangeable Al was neutralized. Rates above this were much less efficient in neutralizing the remaining exchangeable Al. For mineral soils lime rates based on the exchangeable Al multiplied by a lime factor of between 1.5 and 2 should neutralize enough Al to eliminate it as a cause of poor growth in acid soils.

A larger lime factor is probably needed for peat soils than for mineral soils. A lime application equivalent to 187 percent of the exchangeable acidity neutralized only 60 percent of the exchangeable Al and H. A consid-

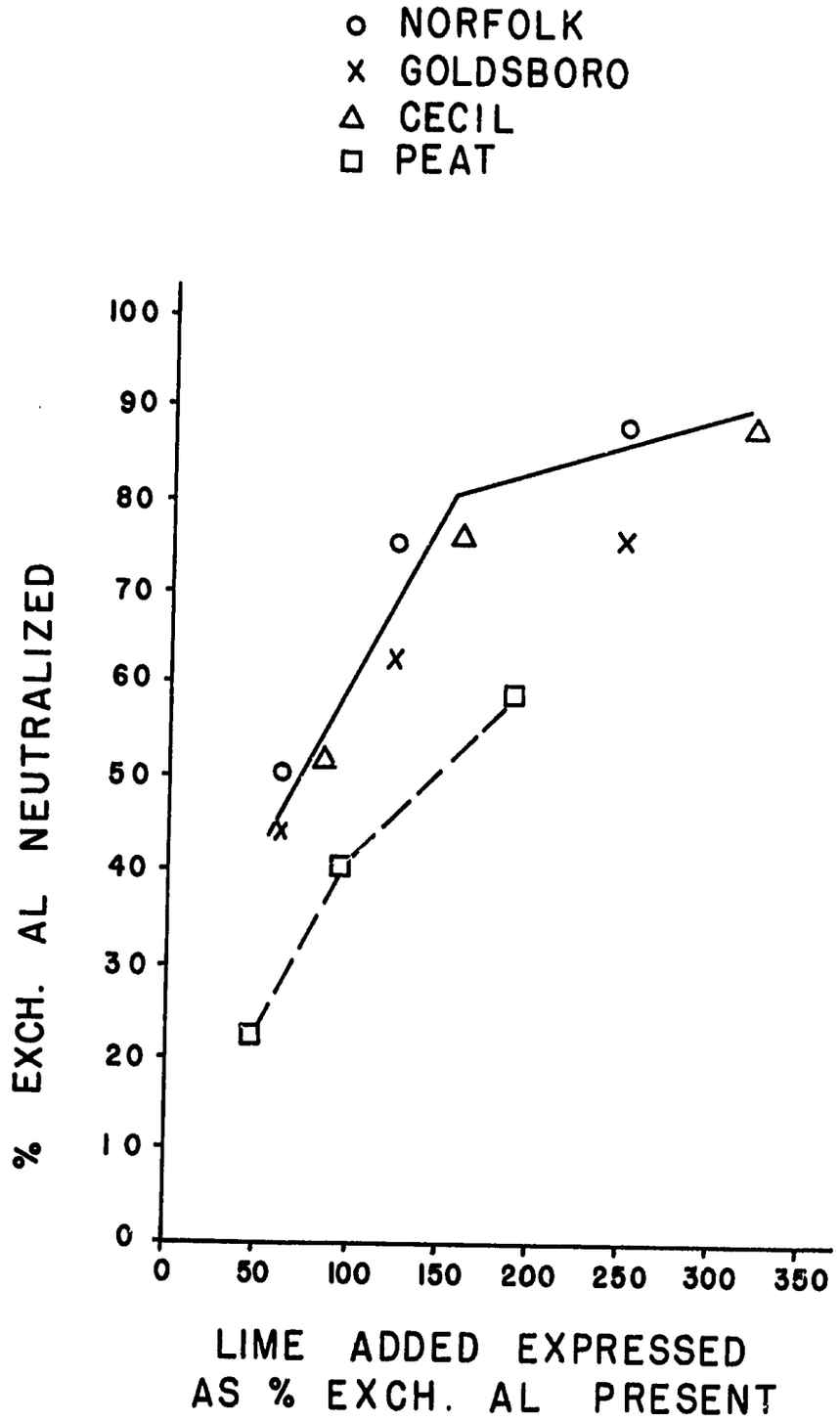

Fig. 1. The percent of exchangeable Al neutralized by various rates of lime based on the exchangeable Al present.

erable portion of the lime probably reacted with the hydrogen of carboxyl groups which is mostly nonexchangeable. A lime factor of 2 to 3 probably should be used with peat and muck soils.

The relationship between the percent of exchangeable Al neutralized and pH is shown in Figure 2. The soil pH was measured in distilled water using a 1:1 soil solution ratio. Around 75 to 80 percent of the exchangeable Al in the mineral soils was neutralized at a pH of 6. Addition of lime to raise the pH above 6 neutralizes mostly hydrogen of carboxyl groups, hydroxy aluminum, and hydrous oxides or iron and aluminum. Liming of soils low in micronutrients to a pH above 6 to 6.2 may induce micronutrient deficiencies. Neutralization of 60 percent of the exchangeable Al and H of the peat soil did not raise the pH very much. The tremendous buffer capacity of the organic matter resulted in very little change in pH.

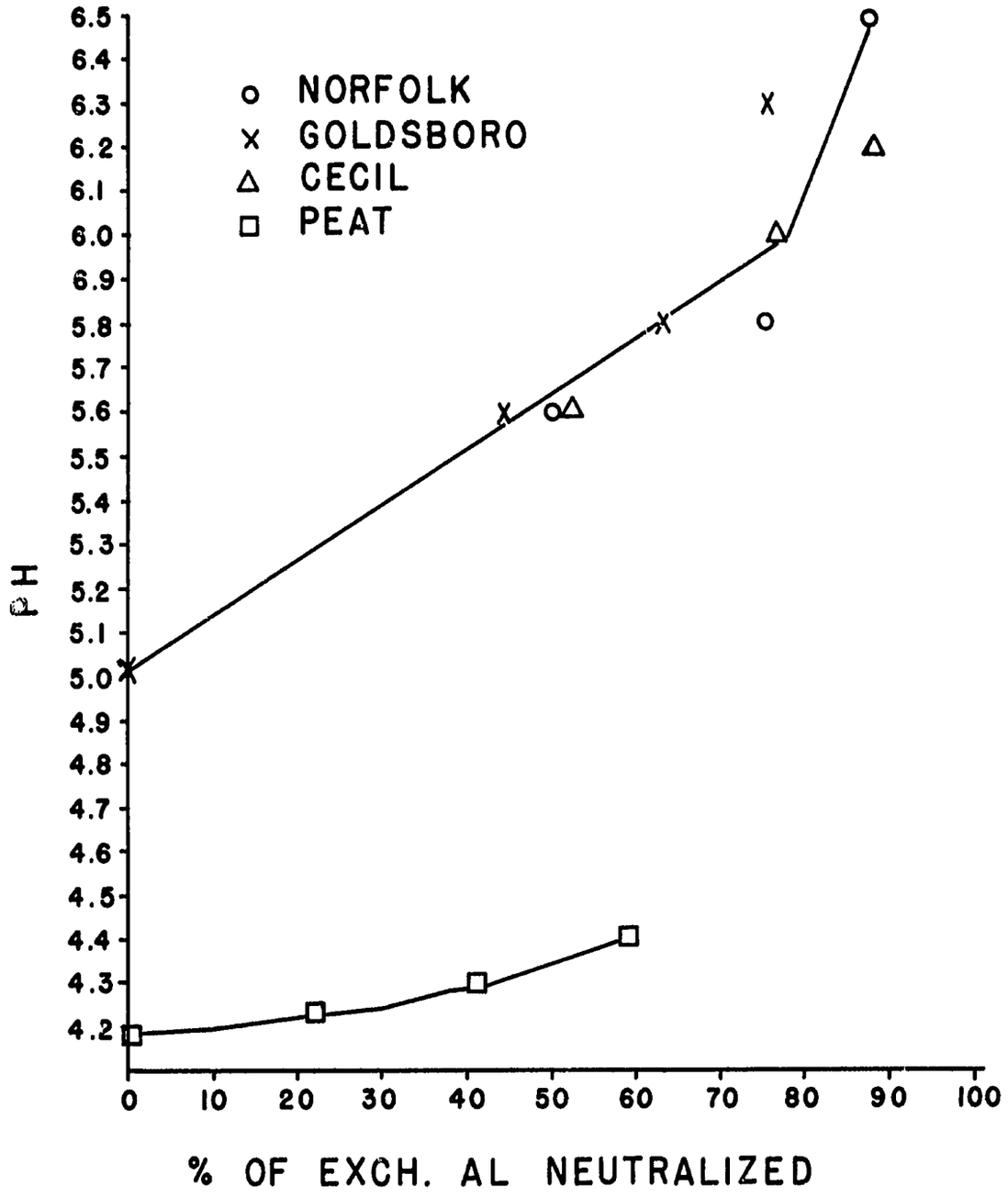

Fig. 2. Relationship between the percent of the exchangeable Al neutralized and the pH of the soil.

SUMMARY

1. Exchangeable Al is the predominant cation of acid mineral soils with a pH of less than 5. Acid soils with a high organic matter content also will have some exchangeable H in addition to the Al.
2. The poor growth of plants on acid soils is due to high levels of exchangeable aluminum and/or manganese. High levels of exchangeable Al will result in:
   (a) Detrimental effects on root growth of plants
   (b) Decreased Ca uptake and translocation
   (c) The need for considerably higher amounts of fertilizer P
3. A measure of the soil acidity effecting plant growth can be obtained by determining the acidity extracted with an unbuffered neutral salt solution such as 1 N KCl. In mineral soils the exchangeable acidity is due to Al and in high organic matter soils Al and some H.
4. Lime additions to acid soils should be based on the exchangeable Al and/or H extracted with an unbuffered neutral salt. Lime rates which neutralize most of the exchangeable acidity will also provide adequate calcium for plant growth.
5. General lime recommendations can be calculated according to the following relationships:

   Millequivalents of exchangeable acidity x 2 = me of lime needed to neutralize exchangeable Al

   1 me of lime per 100 grams of soil = 1000 lbs of $CaCO_3$ per 1 acre six inch slice or 2 million lbs of soil

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