on samples being analyzed must be compared to x-ray spectrographic data obtained on similar reference samples analyzed chemically for chromic oxide. Furthermore, the results of a limited study showed that x-ray spectrographic data obtained on reference samples of feces from grazing steers differed markedly from those obtained on samples of excreta from chicks fed a semipurified diet containing chromic oxide.

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PLANT UPTAKE OF MINERALS

Effect of Residual Lime in Soil on Minor Elements in Plants

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Residual lime in the soil resulted in significant changes of the plant composition of peanut foliage, soybean foliage, and orchard grass 7 and 9 years after lime application. Copper, cobalt, manganese, iron, and zinc were significantly lowered in each plant. Molybdenum was significantly increased.

LIME has long been used as a fertilizer and for correcting and controlling soil acidity. The effect of soil acid conditions can be observed by examining plants grown on soils which have incremental dressings of lime. One such study, which illustrates the depressing effects of lime on the levels of cobalt, nickel, and manganese in pasture herbage and its enhancing effect upon molybdenum, was conducted by Mitchell (9). He used the equivalent of 6 and 12 tons of $CaCO_3$ per acre with the pH of the soils at 5.4 for control and 6.1 and 6.4, respectively, for the levels of $CaCO_3$. He found marked depression in cobalt, nickel, and manganese content with decided increases in molybdenum. Taylor (15) and coworkers found that lime significantly decreased the manganese content of plants, significantly increased the molybdenum content, but normally has little influence on the level of copper. Fiskell (7) showed that liming reduced intake of manganese content of blue lupines after 4 years' application and that symptoms of a copper deficiency in ladino clover were intensified by a heavy liming program. Robinson's (14) work under greenhouse studies showed that the molybdenum content of alfalfa, crimson clover, and Austrian winter peas grown on acid soils high in molybdenum may be increased by heavy liming to a point

where these crops are toxic to cattle. Other workers (1, 2, 4, 8, 11, 13, 16, 17) confirm the effects of soil liming on the composition of plants and the uptake of minerals.

The capacity of pastures to supply the mineral needs of grazing stock in adequate amounts, in proper proportions, and without harmful excess depends upon many interrelated factors. Controlled experiments (10) in 1953 and 1954 over wide areas of the state provided opportunity to study residual lime effects for periods up to 7 or 9 years after application. The literature does not report the effects of soil lime treatments on the minor element uptake of plants after years of application.

Procedures

Samples were collected from lime plots in three areas of the state: peanut tissues (leaves) from Norfolk loam fine sandy, deep phase, near the Holland Experiment Station; soybean tissues (leaves) from Sassafras sandy loam, near the Warsaw Experiment Station; and orchard grass from Lodi loam, near Abingdon, Va. The peanut and soybean tissues were collected 7 years and the orchard grass 9 years after lime treatment. The experimental sites were located on private farms. After the lime was applied, the owners continued to crop the areas with normal

practices, except that no additional lime was applied. Fertilization varied, but in most cases the rates used were less than those recommended; and it is believed that neither crops nor fertilization materially influenced pH or base relationships in the soil. No crop yield response was noted except in the case of soybeans, where approximately a 25% increase was obtained from the use of lime compared to no lime. No grazing was done on the peanut or soybean soils, but the orchard grass was in continuous pasture for dairy cattle.

Mineralogically, the three soils were composed primarily of vermiculite (70 to 75%) and contained smaller quantities of illite and kalonite (10 to 25%). Total exchangeable cations present in the unlimed soils were 5.6, 5.9, and 9.6 meq. per 100 grams of soil for the peanut, soybean, and orchard grass soils, respectively. Soil pH was determined on a Model G, Beckman pH meter, using a 1 to 1 soil-water ratio and a half-hour equilibration period. Other soil properties are discussed fully by Moschler (10).

Cobalt, copper, iron, manganese, and zinc were determined according to official methods of the AOAC (3). Molybdenum was determined by the thiocyanate stannous chloride method of Evans (6). The analyses are reported on a dry weight basis, and wet digestion (nitric and perchloric acids) was used instead of dry ashing.

Table I. Minor Element Content of Plant Tissues and Soil pH

Plant[a]		Lime Added, Tons						Polynomial Fit			
		0	1/2	1	2	4	8	Linear	Quadratic	Cubic	Quartic
Copper, p.p.m.	Peanut[b]	6.47a[c]	6.07a	6.66a	5.41a	4.29b	...	✕✕	...	...	...
	Soybean[b]	14.04a	11.89b	10.84b	10.41b	10.18b	...	✕✕	✕✕	...	...
	Orchard grass[de]	9.72a	...	7.86b	7.37b	7.22b	7.71b	✕	✕✕	...	...
Cobalt, p.p.m.	Peanut	0.03a	0.02b	0.01c	0.01c	0.01c	...	✕✕	✕✕	✕	✕
	Soybean	0.16a	0.04bc	0.05b	0.01c	0.02c	...	✕✕	✕✕	✕✕	✕✕
	Orchard grass	0.05a	...	0.03b	0.02b	0.03b	0.03b	✕	✕	✕✕	...
Iron, p.p.m.	Peanut	78.75abc	78.77ab	83.75a	76.50bc	75.75c	...	✕✕	...	...	✕
	Soybean[f]	115.75	110.50	113.00	115.00	110.75	...	...	...	...	...
	Orchard grass	92.72a	...	80.16b	66.61c	68.28c	67.21c	✕✕	✕✕	✕✕	...
Manganese p.p.m.	Peanut	55.49a	55.40a	27.67b	22.73b	12.94c	...	✕✕	✕✕	...	✕✕
	Soybean	101.06a	79.41b	73.60b	52.90c	45.66c	...	✕✕	✕✕	...	...
	Orchard grass	176.14a	...	157.80b	80.32c	75.61d	64.20d	✕✕	✕✕	✕✕	✕✕
Molybdenum, p.p.m.	Peanut	0.01a	0.01a	0.01a	0.05b	0.09c	...	✕✕	✕✕	✕✕	✕✕
	Soybean	0.01a	0.01a	0.05b	0.15c	0.18d	...	✕✕	✕✕	✕✕	✕✕
	Orchard grass	0.58a	...	0.60a	0.94a	1.52b	2.88c	✕✕	✕	...	...
Zinc, p.p.m.	Peanut	15.82a	12.92b	12.82b	12.80b	11.86b	...	✕✕	...	✕	...
	Soybean	39.84a	37.90a	30.78b	25.77c	26.16c	...	✕✕	✕✕	...	✕
	Orchard grass	25.72a	...	17.68b	17.31b	17.90b	17.36b	✕✕	✕✕	✕✕	...
Soil pH	Peanut	5.96ab	5.89a	6.04ab	6.36bc	6.69c	...	✕✕	...	...	...
	Soybean	5.58a	5.88ca	6.23b	6.74c	7.11d	...	✕✕	✕✕	...	...
	Orchard grass	5.18a	...	5.50b	5.98c	6.32d	6.60d	✕✕	✕✕	...	...

[a] All analyses are averages of 4 replications.
[b] 7 years after lime application.
[c] a, b, c, etc., averages (1% level), any two means not having the same letter are significantly different; any two means having the same letter are not significantly different (5).
[d] 9 years after lime application.
[e] 5% level for copper.
[f] No significant effect.

✕ Significant at 5% level.
✕✕ Significant at 1% level.
... No significance.

Discussion and Results

The effects of various levels of lime application on minor elements in peanut tissues are shown in Table I. Copper levels, although declining progressively, are significantly lowered only at the 4-ton lime level, whereas the 1/2-ton treatment significantly decreased zinc content with no further effect at higher levels. All treatments lowered the cobalt content of the tissues, with the greatest effect at lime levels above 1/2 ton. Although differences were apparent, there was no consistent progressive decrease in iron content with increasing lime application. With manganese, tissue contents were significantly lowered above 1/2 ton, with drastic reduction at higher rates. With increasing lime applications the molybdenum content was significantly increased by the 2-ton and 4-ton levels.

The effects of lime applications on the minor element composition of soybean tissues are shown in Table I. Copper levels were significantly decreased with 1-ton application, but only slightly with higher applications. The most striking decrease in cobalt content occurred with the lime rate of 1 ton, although progressive and significant further decreases occurred with increased liming. Iron contents were unaffected. With manganese, tissue contents were progressively and significantly lowered, with liming rates of 1 and 4 tons exerting the greatest effects. Similar progressive decreases in zinc content were found, with maximum effects at 2-ton and 4-ton lime application. In contrast, molybdenum was significantly increased with increasing lime applications, particularly at the 2-ton and 4-ton levels.

The residual effects of lime application rates on orchard grass are shown in Table I. Copper and cobalt levels were significantly lowered by the 1-ton lime applications, with only minor effects at higher liming rates. Iron content was significantly decreased with the 1-ton and 2-ton liming rates. Manganese was significantly lowered with the 2-ton lime rate, only minor decreases occurring at higher rates. Lime treatments at the 1-ton rate significantly decreased zinc content and higher rates exerted no further effects. Molybdenum content was again significantly increased by 4-ton and 8-ton levels of lime.

As would be expected, the increments of lime applied in these investigations resulted in progressive shift of the pH of the soil from acid range to a level approaching or exceeding neutrality. However, because of plant, soil, or climatic influences, it is not possible to predict significant liming effects from the pH values alone. In some instances significant composition effects were noted with little or no change in soil pH.

A polynomial was fitted to the levels of lime, and the results of this fit for each of the minerals and crops are indicated in Table I.

These observations, in general, confirm the published literature concerning the relationship between soil acidity and plant uptake of minor elements. However, most previous studies have examined these relationships only during brief periods following lime applications. These results emphasize the sustaining effects of lime treatments in the soil on plant composition 7 and 9 years after application. Obviously, they have important implications in terms of sustaining optimum health in grazing animals with respect to minor elements (12).

Summary

With one exception, the negative effect on iron content of soybean tissues, lime treatments of the soil significantly decreased the copper, cobalt, manganese, iron, and zinc in peanut tissues, soybean tissues, and orchard grass, but significantly increased the molybdenum content found 7 and 9 years after lime application.

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FERTILIZER SOLUBILITY

Effect of Polyphosphate Content on Properties and Use of Liquid Fertilizers

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The solubility and other properties of liquid fertilizers made from electric-furnace phosphoric acids containing 55, 76, and 79% P_2O_5 (24, 33, and 34% P) are compared; the proportion of P_2O_5 in the polyphosphate form in fertilizer solutions made from these acids was about 0, 45, and 70%, respectively. The solubility at 32° F. of the ammoniated acids increased as the polyphosphate content was increased. When 70% of the P_2O_5 was in the polyphosphate form, variations in the N:P_2O_5 weight ratio in the range of 0.28 to 0.32 (N:P ratio 0.64 to 0.73) had very little effect on plant nutrient solubility, which was about 48% N + P_2O_5 (27% N + P). Solubility data are given for liquid fertilizers made from the ammoniated acids, urea–ammonium nitrate solution, and potassium chloride. The effectiveness of the polyphosphates in dissolving micronutrients and in sequestering the impurities in liquid fertilizers made from wet-process acid is discussed. Factors affecting the rate of hydrolysis of the polyphosphates to orthophosphate were pH and temperature.

UP TO 5 years ago, furnace-grade orthophosphoric acid was the source of essentially all the phosphate in liquid fertilizers. TVA (6) and others (2, 8) have published solubility data on that system. About 5 years ago, TVA introduced superphosphoric acid (9) which contains phosphate in the form of polyphosphates as well as orthophosphate. As the P_2O_5 content of the acid increases, the proportion of P_2O_5 in polyphosphate form increases and the proportions present as different species of polyphosphate change. Ammoniation of the acid is possible with little change in polyphosphate content. Acid of 76% P_2O_5 (33% P) concentration (shipping grade) contains about 50% of its P_2O_5 in polyphosphate form. Ammoniation yields a liquid fertilizer containing about 45% of its P_2O_5 in polyphosphate form; results of solubility studies on this system have been presented (7). When this work was done, TVA was producing a

solution having an N:P_2O_5:K_2O grade of 10–34–0 (N:P:K grade, 10–15–0) from acid containing 76% P_2O_5 (33% P).

Acid containing 78 to 80% P_2O_5 (34 to 35% P) has since been produced, and the ammoniated product has been increased in grade to 11–37–0 (11–16–0). The increase in grade was made after studies had shown that the use of 78 to 80% P_2O_5 (34 to 35% P) acid (some 70% of its P_2O_5 as polyphosphates) resulted in a product of higher solubility than that made from acid containing 76% P_2O_5 (33% P). Results of these studies are presented here. Effects of polyphosphate content of ammoniated superphosphoric acid on solubility are discussed, and a solubility diagram is presented for N:P:K liquid fertilizers made by adding supplemental nitrogen and potassium to 11–37–0 (11–16–0). Also given are results of studies on use of polyphosphates to solubilize micronutrients and

to sequester impurities in liquid fertilizers made from wet-process phosphoric acid.

Procedure

Superphosphoric acids were obtained from the TVA plant or were prepared by dissolving phosphorus pentoxide in reagent-grade orthophosphoric acid. Source of the acid made little difference in solubility measurements, except that the small amount of impurities in the plant acid promoted supercooling and thus lengthened the time required for measurements.

The phosphoric acids were ammoniated to different degrees either in the plant or in the laboratory to produce solutions that are conveniently called "base solutions," since other fertilizer materials usually are added to produce the final liquid fertilizer. To minimize hydrolysis, the pH was kept above 5.5 and the temperature below 180° F.