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Plant Nutrition and the Hydrogen Ion: VI. Calcium Carbonate, a Disturbing Fertility Factor in Soils

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Plant Nutrition and the Hydrogen Ion: VI. Calcium Carbonate, a Disturbing Fertility Factor in Soils[1]

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The extent to which the exchangeable cations on the colloidal exchange complex within the humid soils of the eastern United States have been replaced by hydrogen ions has been used as a criterion of the high degree of soil development there. It has likewise represented the magnitude of the fertility problems associated with the acid soils. Conversely, then, the accumulation of calcium carbonate in the soils of the arid west to the extent that the adsorbed cations consist mainly of calcium should similarly serve as a criterion of their low degree of soil development. It should likewise represent the complexity of the fertility problems associated with crop production on these soils.

With the concentration of agriculture on the humid soils and the numerous fertility problems associated with them, especially the need to apply calcium carbonate, it may seem somewhat of an exaggeration to venture the statement that soils with excessive calcium carbonate present more complex fertility problems than those with excessive acidity. However, the arid soils of the West are demonstrating this truth. The fertility problems of these arid soils include not only those associated with irrigation practices, but also that of coping with the tremendous influence which free calcium carbonate exerts upon the availability of phosphorus, iron, manganese, and boron, and upon the colloidal exchange complex to bring about ultimately an ionic monopoly of it by calcium.

Soil development in the light of the transformation of parent materials into soil by their weathering into new minerals and into solution indicates that soils exist in all degrees of development. They range from these calcareous soils insufficiently developed for crop production and still in the earlier stages to those acid soils excessively developed for this purpose and in the later stages of these transformations. Therefore, the soils within the regions of low rainfall and high evaporation rates, respectively 8 and 95 inches annually in southern New Mexico, exist in the earlier stages of the soil development processes. As a result, there has been little chance for a breakdown of the calcium carbonate regime. The colloidal clay complex has become saturated by calcium to as much as 80 to 90% as is the case of the Gila clay series located in the Rio Grande River Valley of southern New Mexico and used in the studies reported herewith.

It is our belief that this free calcium carbonate in the soil, such as is found in the Gila Adobe clay, for example, should represent a nutrient deficiency for plants grown on this soil since the colloidal exchange complex is continually under the influence of a soil solution so dominated by calcium as to give rise to a colloidal complex approaching saturation by calcium alone. This is analogous, therefore, to the case of hydrogen-saturated soils which give an insufficient saturation of the colloidal complex by other nutrients essential for crop production.

IONIC MONOPOLY OF EXCHANGE COMPLEX

Some of the more recent fertility investigations carried out by western experiment stations on calcareous soils seem to explain more adequately the relationship existing between nutrient deficiencies and the nature of the ions adsorbed on the exchange complex of the soil. The earlier investigations of these relationships were by Albrecht and Shroeder (1)[3] who showed that poor crop growth on acid soils was due largely to nutrient deficiencies and not to the high concentration of hydrogen ions, as had been formerly thought. In essence, this concept has given a basis for the more recent investigations into the ionic monopoly of the exchange complex by other cations than hydrogen ions in neutral and alkaline soils. The works of Bower and Turk, (3), Hughes (6), Moser (8), Ratner (10), and Thorne (11, 12) can be interpreted as an extrapolation of this theory showing that a fertility deficiency results from an ionic monopoly of the exchange complex by sodium, magnesium, or potassium, for example, and that such a condition is analogous to that of ionic monopoly of the exchange complex by hydrogen so far as the fertility deficiency is concerned.

The results by these investigators clearly indicate that poor crop growth resulting from a single ionic dominance of the exchange complex is due to insufficient amounts of several essential nutrient ions and not primarily a case of alkalinity, high pH, or excessive sodium, magnesium, or potassium, to the point that each of these is toxic to plants. Ionic monopoly of the exchange complex by any single ion — whether nutrient or not — must consequently result in an unfavorable fertility condition for optimum plant growth through deficiencies of other required nutrient ions.

That plants may suffer a calcium deficiency in the presence of a sodium-saturated complex despite the presence of free calcium carbonate in the soil is quite readily explained by the extremely low solubility of calcium carbonate in highly alkaline-calcareous soils, the pH of which is above 8.5. Evidence of this fact has been reported by both McGeorge (7) and DiGleria (5). Would it not, therefore, seem apparent that those crops which are quite commonly referred

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[2] Graduate Assistant and Professor of Soils, respectively.

[3] Figures in parenthesis refer to "Literature Cited", p. 347.

to as "pH-sensitive" are actually crops which indicate strong sensitivity to ionic monopoly of the exchange complex by a single ion — the high pH values merely being indicative of this ionic monopoly?

It seems justifiable, therefore, to express the belief that free calcium carbonate exists in the semi-arid and arid calcareous soils as one of the most potent and dynamic influences on the adsorption, retention, and ionic exchange of plant nutrients from the colloidal complex to the plant roots. Furthermore, such free calcium carbonate is probably one of the most persistent and effective obstacles in the process of mineral weathering and release of mineral reserves to the colloidal clay complex.

There has been a limited amount of experimental work on the calcareous soils, especially those under irrigation, dealing with the effect of free calcium carbonate on ionic exchange, cation saturation, and the correlation of these factors with the efficiency of fertilizers and crop responses under different levels of calcium carbonate within the soil. It appears, therefore, that the major fertility problem of calcareous soils consists of a more economical and efficient service from fertilizer applied to a soil whose exchange complex is dominated by and under the influence of a tremendous reservoir of one ion.

PLAN AND PROCEDURE

The studies reported herewith were designed to investigate the effect of free calcium carbonate upon the nutrient uptake by plants from a representative calcareous soil whose colloidal complex was saturated by calcium as much as 81%.

The plan of study included the selection of a representative calcareous soil (Gila Adobe clay),[4] the subsequent analysis of its exchangeable cations, and its preparation for use in a greenhouse experiment. The soil profile of Gila Adobe clay from which the soil for this experiment was taken is shown in Fig. 1. Only the surface 12 inches were used in these studies. The greenhouse experiment was designed to measure the fertility of Gila clay under decreasing levels of calcium carbonate. This decrease in calcium carbonate was brought about through the addition of increasing amounts of acid Putnam subsoil clay. Eight treatments were used, representing successive decreases in calcium carbonate in Gila clay. The electronmicroscope indicates that the fine clay fraction ($<0.02\mu$) of Gila clay, like that of Putnam subsoil clay, is predominately a montmorillonitic type clay mineral (Fig. 2). The amounts of Gila and Putnam clays, the milliequivalents of calcium carbonate, the pH values, and the ionic exchange data for each of these respective treatments are given in Table 1. The method used for total exchange capacity and exchangeable sodium was essentially that of Wilcox (13), for exchangeable calcium essentially that of Chapman and Kelley (4), while potassium was determined by difference. The respective soil mixtures were placed into 2-gallon glazed porcelain pots and zonalite added as a means of alleviating the disturbing physical properties of the Gila and Putnam clay mixtures. These treatments were replicated three times and soybeans of the variety Chief were selected as the indicator crop. The soybeans were germinated in cleaned sand and transplanted 10 seeds to the pot when the radicles were about 2 cm long.

Two crops of soybeans were grown and harvested from these soil mixtures during the course of the experiment. The first crop was grown during the winter months (December through February) under unfavorable growing conditions.

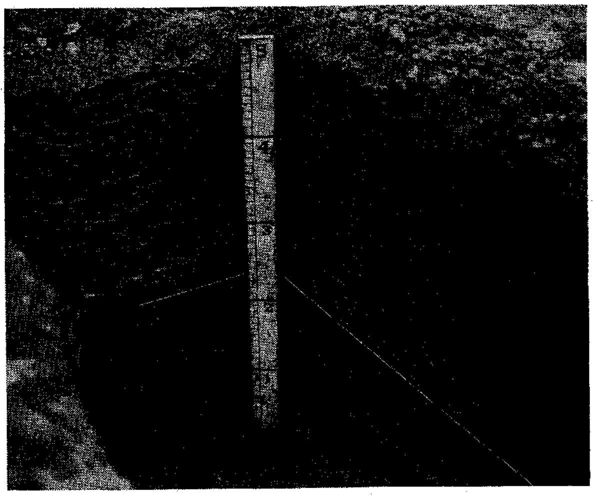

FIG. 1.—Soil profile of Gila (Adobe) clay.

Profile Description

Location: New Mexico Agricultural Experiment Station, State College, N. M., exposed August, 1946 (field 25).

0–12 inches — Gila clay, desert grey to reddish brown. Hard and fragmented when dry. Very plastic when moist. 1.98% organic matter, 6.08% free calcium carbonate. 64.72% $<2\mu$ clay.

12–32 inches — Gila clay, reddish brown, similar to the 0–12 inch horizon, changing abruptly at 32 inches to loamy fine river sand. 1.05% organic matter, 6.88% free calcium carbonate. 65.35% $<2\mu$ clay.

32–56 inches — Clay loam, laminated with fine river sand, reddish yellow.

56–60 inches — Fine river sand, reddish yellow.

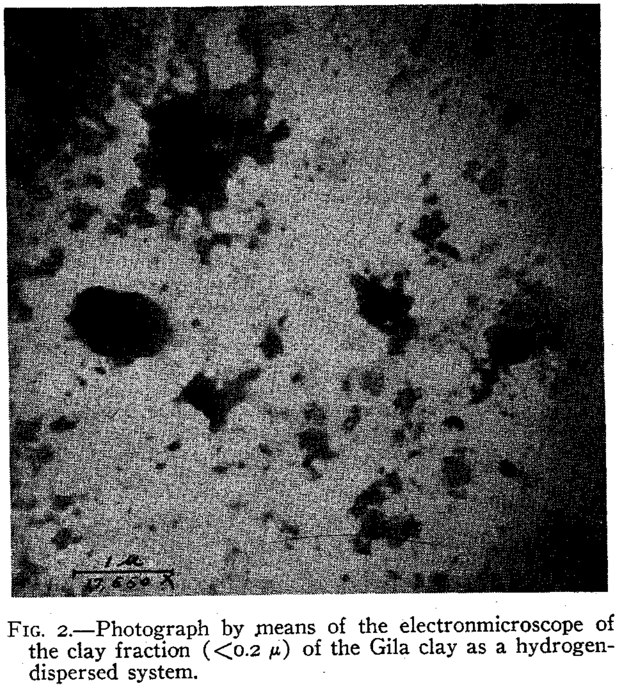

FIG. 2.—Photograph by means of the electronmicroscope of the clay fraction ($<0.2\ \mu$) of the Gila clay as a hydrogen-dispersed system.

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[4] Gila Adobe clay comprises about 13% of the total irrigated land in New Mexico and about 26% (31,000 acres) of the irrigated acreage in the lower Rio Grande River Valley in that state, according to private correspondence from H. T. Maker, State Soil Scientist of New Mexico, June 24, 1947.

TABLE 1.—*Ionic exchange data for the respective treatments.*

	Treatments							
	1	2	3	4	5	6	7	8
Grams Gila clay	1,200	1,000	800	600	400	200	50	——
Grams Putnam clay	——	200	400	600	800	1,000	1,150	1,200
Per cent Gila clay	100	83.33	66.67	50.00	33.33	16.67	4.17	——
Total m.e. Ca*	178.46	151.10	123.75	96.90	69.45	42.20	18.89	14.89
Total m.e. Ca remaining as $CaCO_3$	121.51	93.10	70.25	50.59	28.07	6.77	——	——
Total exchange capacity†	70.35	64.58	57.62	49.80	42.98	36.12	31.18	29.05
Exchangeable Ca†	56.95	58.00	53.50	46.21	41.38	35.43	23.30	14.89
Per cent Ca saturation	80.95	89.81	92.85	92.78	96.27	98.09	74.73	51.26
Exchangeable Mg	8.50	7.10	5.67	4.18	2.92	1.42	0.353	——
K	1.90	1.56	1.26	0.94	0.61	0.31	0.079	——
Na	3.00	2.50	2.00	1.50	1.00	0.50	0.075	——
Initial pH‡	8.39	8.30	8.20	8.09	8.00	7.89	6.71	5.46
Final pH‡	8.12	8.05	7.85	7.70	7.50	7.40	6.50	5.35

*Represents exchangeable Ca + Ca as $CaCO_3$.
†M.e. per 100 grams soil.
‡Values based on the average of three replications.

Differences in plant growth were apparent but indicated insufficient nutrient uptake for significant differences. After growing 102 days the plants were harvested and the yield and growth data tabulated. The second crop of soybeans was grown for a time of 110 days during the period of April 28 to August 15. Two weeks in the greenhouse were allowed prior to moving the plants to a table outdoors. After 57 days (June 23) it was evident that poor growth was occurring in all treatments due to a deficiency of nitrogen, phosphorus, and possibly iron and manganese. It was evident that without the addition of some fertility the uptake of nutrients by the plants would not occur in sufficient quantities for significant differences and for measurable effects by the calcium carbonate on the nutrient uptake.

Since nutrients were needed for better plant growth and since the experiment was not designed to catalog the several nutrient elements apparently deficient in this soil, the series was divided into three sub-treatments. The first replicate was allowed to grow to maturity with no nutrients added by using only distilled water. The second was continued under the treatment with Rio Grande River irrigation water. The third was grown with added nutrients. The nutrients applied to this last series consisted of an equivalent of 37 pounds of nitrogen, 45 pounds of phosphorus, 24 pounds of potassium, and 14 pounds of magnesium per acre. Those applied to the irrigation series in synthetically prepared irrigation water (2) amounted to the equivalent of 58 pounds of calcium, 10 of magnesium, 10 of potassium, and 50 of sodium per acre. These rates were based on the assumption of an application of 1 acre foot of water during 53 growing days (June 23 to August 15).

The mature plants (roots and tops) were harvested, oven-dried at 60° C, weighed, ground, and digested with perchloric-nitric acids. Analyses of the aliquots of the perchloric-acid digestion included those for calcium, phosphorus, iron, and potassium. Nitrogen was determined by the standard Kjeldahl method (13), calcium was determined by precipitation with oxalic acid and titration with permanganate, phosphorus (9) and iron (13) were determined colorimetrically, while potassium was measured gravimetrically through precipitation of the potassium with cobalti-nitrite solution (13).

RESULTS AND DISCUSSION

The ionic exchange data for each of the treatments in the experiment (Table 1) included the total exchange capacity, exchangeable cations, the percentage calcium saturation, and the total calcium carbonate in each of the soil mixtures. The exchange capacity of the soil in treatment 1 (Gila clay) was 70.35 m.e., including 56.95 m.e. of calcium and giving a calcium saturation of 80.95%. However, the calcium carbonate in that treatment amounted to 121.51 m.e. per 100 grams of soil to give a decided excess of calcium. It will be noted that, with each succeeding dilution, the percentage of calcium saturation of the exchange complex increased as the amount of neutralized calcium carbonate increased, reaching 98.09% saturation in treatment 6. This occurred in part with the transition from a high exchange capacity in the Gila clay of treatment 1 (70.35 m.e.) to a low exchange capacity in only Putnam clay of treatment 1 (29 m.e.).

The application of statistical analysis to the yield and growth data of the first soybean crop gave an increase significant to the 1% level for treatments 3, 4, and 5 over treatment 1. This established the fact definitely that an increased growth and yield of soybeans would occur as the amount of calcium carbonate was decreased.

The nutrient uptake and yield data for the second crop of soybeans are significant for each of the treatments when related to the properties of the soil. The data are given in Tables 2, 3, and 4. According as the calcium carbonate of the Gila clay was partly neutralized by the addition of acid clay, there was a comparable increase not only in the yield of plant material produced but also in the amount of nutrients which these plants were able to get from the soil. This relation is shown for the uptake of nitrogen in Fig. 3. In all three series, i.e., nutrients, irrigation, and check, the trend was similar. The nitrogen uptake increased with a decrease in free calcium carbonate. This was the highest in treatment 4.

This same relationship is evident (Tables 2, 3, and 4) for the uptake of calcium, phosphorus, iron, and potassium. Despite the fact that all plants con-

TABLE 2.—*The nutrient uptake and yields for the respective treatments of the nutrient series, with all values based on 10 soybean plants, including roots.**

Treatment	M.e. calcium carbonate per 100 grams	Nitrogen		Calcium		Phosphorus		Potassium		Iron		Yield of 10 plants, grams
		%	Total, mgms	%	Total, mgms	%	Total, mgms	%	Total, mgms	%	Total, mgms	
1	121.51	2.259	423.1	0.757	142.0	0.065	12.19	2.39	448.2	0.021	3.94	18.755
2	93.10	2.037	430.2	0.906	191.4	0.069	14.58	—†	—†	0.023	4.86	21.125
3	70.25	2.170	482.4	1.055	235.3	0.070	15.61	2.41	537.4	0.027	6.47	22.300
4	50.59	2.179	539.5	1.062	263.8	0.071	17.64	3.21	797.2	0.029	7.20	24.835
5	28.07	2.012	464.2	0.952	219.9	0.067	15.47	—†	—†	0.032	7.39	23.095
6	6.77	1.80	414.8	0.544	125.4	0.060	9.66	3.05	702.9	0.037	8.53	23.045
7	0.00	1.72	312.8	0.508	92.4	0.053	9.64	—†	—†	0.024	4.36	18.185
8	0.00	1.68	258.0	0.460	70.7	0.049	7.53	—†	—†	0.022	3.38	15.360

*Ten seeds contained 74.0 mgms nitrogen, 1.91 mgms calcium, 8.01 mgms phosphorus, 31.05 mgms potassium, and 8.26 mgms of iron.
†Not determined.

TABLE 3.—*The nutrient uptake and yields for the respective treatments of the irrigation series, with all values based on 10 soybean plants, including roots.**

Treatment	M.e. calcium carbonate per 100 grams	Nitrogen		Calcium		Phosphorus		Potassium		Iron		Yield of 10 plants, grams
		%	Total, mgms	%	Total, mgms	%	Total, mgms	%	Total, mgms	%	Total, mgms	
1	121.51	1.827	275.3	0.622	93.8	0.041	6.18	—†	—†	0.018	2.71	15.080
2	93.10	1.946	320.9	0.631	104.3	0.039	6.44	—†	—†	0.017	4.46	16.525
3	70.25	1.981	414.4	0.600	125.6	0.045	9.42	—†	—†	0.018	3.77	20.930
4	50.59	1.825	391.1	0.706	151.8	0.037	7.96	—†	—†	0.023	4.95	21.500
5	28.07	1.743	374.4	0.712	153.3	0.036	7.75	—†	—†	0.023	4.96	21.525
6	6.77	1.446	251.5	0.560	97.7	0.035	6.11	—†	—†	0.025	4.36	17.450
7	0.00	1.413	233.6	0.540	89.3	0.035	5.79	—†	—†	0.023	3.80	16.530
8	0.00	1.328	193.2	0.464	67.5	0.030	4.37	—†	—†	0.021	3.06	14.550

*Ten seeds contained 74.0 mgms nitrogen, 1.91 mgms calcium, 8.01 mgms phosphorus, 31.05 mgms potassium, and 8.26 mgms of iron.
†Not determined.

TABLE 4.—*The nutrient uptake and yields for the respective treatments of the check series, with all values based on 10 soybean plants, including roots.**

Treatment	M.e. calcium carbonate per 100 grams	Nitrogen		Calcium		Phosphorus		Potassium		Iron		Yield of 10 plants, grams
		%	Total, mgms	%	Total, mgms	%	Total, mgms	%	Total, mgms	%	Total, mgms	
1	121.51	1.791	266.5	0.554	82.5	0.045	6.70	2.16	321.6	0.020	2.80	14.890
2	93.10	1.614	258.9	0.712	114.5	0.042	6.80	—†	—†	0.021	3.38	16.080
3	70.25	1.961	347.3	0.637	125.7	0.045	8.88	2.23	440.1	0.024	4.74	19.735
4	50.59	2.043	423.3	0.706	146.5	0.037	7.68	2.02	419.3	0.029	6.02	20.155
5	28.07	1.906	371.5	0.668	130.5	0.031	6.06	—†	—†	0.031	6.06	19.535
6	6.77	1.727	269.9	0.648	101.6	0.026	4.08	—†	—†	0.037	5.80	15.675
7	0.00	1.691	244.0	0.540	77.9	0.025	3.61	—†	—†	0.023	3.32	14.430
8	0.00	1.662	204.1	0.456	56.1	0.023	2.95	—†	—†	0.013	1.72	12.280

*Ten seeds contained 74.0 mgms nitrogen, 1.91 mgms calcium, 8.01 mgms phosphorus, 31.05 mgms potassium, and 8.26 mgms of iron.
†Not determined.

tained a very little amount of phosphorus and that plants of the irrigation and check series, except treatment 3 (Tables 3 and 4), lost phosphorus back to the soil. This loss was less for the plants under less calcium carbonate. The plants of the nutrient series (Table 2) lost no phosphorus back to the soil and contained more phosphorus according as the calcium carbonate decreased.

The yields of treatments 6 and 7 of the check series were low since they could grow only by means of the small supply of nutrients afforded by small aliquots of Gila clay in these mixtures. The nutrients added in the irrigation and in the nutrient series were insufficient to overcome this same condition.

It is apparent from these data that successive decreases in the amount of calcium carbonate brought about a more balanced nutrient environment for crop growth. This is evident even in the case of the check series where no nutrients whatsoever were added and in the case where plants grew even under the influence of highly mineralized irrigation water. This indicates that over a period of many years this soil has been treated with a calcium-laden irrigation water which brought about not only an accumulation of free calcium carbonate within the soil but also has a high degree of calcium saturation of the exchange complex at the expense of the other essential nutrient ions.

Free calcium carbonate exists within the soil as

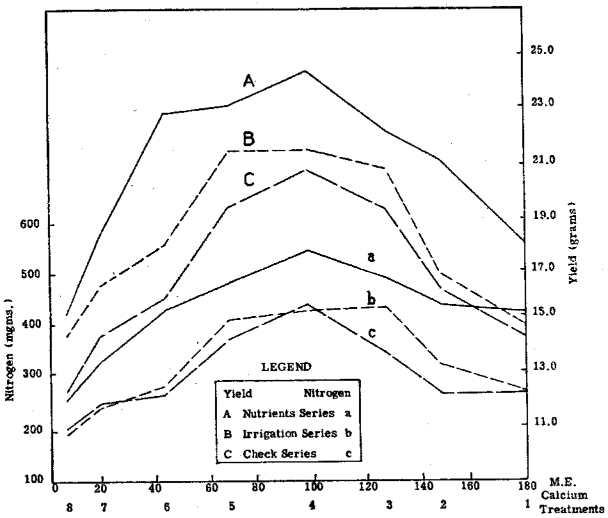

FIG. 3.—Yield and nitrogen uptake by soybeans as related to the total milliequivalents of calcium present.

particles of colloidal dimension in many cases. It exists in spite of the influence of the pressures of carbon dioxide within the soil and in spite of the acid action of root respiration. It represents a continuous reservoir of calcium. Even though its decomposition by carbon dioxide and root respiration may be extremely slow, it means that these acids are expended in releasing primarily calcium, an element already present in abundance on the exchange complex. With such an over-balance of calcium carbonate, these acids are never able to react with the reserve minerals within the silt fraction to decompose them and to furnish a supply of nutrients other than calcium for a nutrient-balance on the exchange complex.

The question then arises as to just what efficiency one gets by the application of fertilizer to a soil the complex of which is saturated as highly as 80 to 90% with calcium. In the case of applied phosphorus there would seem to be an extremely low efficiency, with a continuous accumulation of unavailable phosphates within the soil. The amount of added nutrients held by the exchange complex as a consequence of the addition of fertilizer to such a calcareous soil would seem to be very slight, while that not adsorbed by the complex may well be lost through leaching or through the reaction with calcium carbonate into an unavailable form.

SUMMARY AND CONCLUSIONS

This investigation was designed to study the effect of free calcium carbonate within a representative arid, calcareous soil upon the nutrient uptake by plants. These effects emphasized the need for a more intensive investigation of the influences by calcium carbonate on the ionic exchange and on the mechanisms of nutrient delivery in calcareous soils. The soil selected for this study was a Gila Adobe clay, a typical alluvial, calcareous soil of the arid Southwest. Soybeans were used as an indicator crop and were grown on eight different soil mixtures. The mixtures ranged from 100% Gila clay, containing 121.5 m.e. of calcium carbonate to 100% Putnam clay (hydrogen clay) with no free calcium carbonate but with 14 m.e. of exchangeable calcium. The latter clay was used to bring about a reduction in the total calcium and in the free calcium carbonate in each of the successive mixtures as soil treatments. Successive increases in dry matter and in nutrient uptake, including nitrogen, phosphorus, potassium, calcium, and iron, were obtained according as the total amount of calcium carbonate was reduced from 121.5 m.e. per 100 grams of soil in treatment 1 (100% Gila clay) to 6.8 m.e. of calcium carbonate in treatment 6 which contained only 16.7% Gila clay in the mixture.

This increased growth and nutrient uptake was obtained despite the fact that with each successive treatment the total amount of nutrients available, as well as the exchange capacity of the mixture, was greatly reduced through the addition of the nutrient-deficient hydrogen clay.

It was found that as the free calcium carbonate was neutralized, the released calcium effected a corresponding increase in calcium saturation of the clay mixture. This degree of calcium saturation increased from 81% in treatment 1 to 98% in treatment 6 where 114.7 m.e. calcium carbonate had been neutralized.

These data indicate further the low availability, as well as absence of, other nutrients in a typical unfertilized calcareous soil. They suggest that even large applications of phosphorus, nitrogen, and certain minor elements to this soil may be very inefficiently taken by plant roots in the presence of the excessive calcium.

This soil suggests itself as one in which apparently the processes of soil development have insufficiently removed, but rather have excessively accumulated one of, the rock-weathering products, i.e., calcium carbonate. It therefore raises the question whether there is not a fertility deficiency in nutrients other than calcium since they are contained in the minerals undergoing slow weathering and giving up few nutrients to be adsorbed and held by the clay complex and thereby available for plant use.

It further suggests that this excessive calcium carbonate neutralizes quickly any hydrogen respiring from the plant root, or any carbonic acid within the soil solution, and serves to aggravate an already calcium-dominated complex.

Thus, in the less developed soils under low rainfall, the colloidal clay complex has seemingly become stocked primarily with calcium. This ionic monopoly may be considered as a fertility deficiency analogous to that as we view it in the acid soils, which have developed under high rainfall and have become deficient in fertility because of excessive hydrogen saturation.

These studies point to the importance of balanced fertility in the soil more than to its degree of acidity or of alkalinity for plant growth. They indicate the similarity of the fertility problems of both acid and calcareous soils. Just as the fertility problem of the acid soils would not be remedied by their neutralization with calcium carbonate, so would the mere removal of excessive calcium carbonate from calcareous soils by acidification without the addition of other nutrients not represent potential crop production.

The concept has been presented here that excessive calcium carbonate within a soil — a concept also applicable to the excessive hydrogen in acid soils — exists as a dynamic factor disturbing the adsorption, retention, and exchange of nutrient and other ions to the plant roots. It represents one of the most serious obstacles to the normal breakdown of reserve minerals and fertility delivery within the soil.

There is a need for a closer study of the relationships among (a) ionic monopoly of the exchange complex by any one ion, whether nutrient or not; (b) the retention of nutrients by the exchange complex; (c) the accumulation of insoluble calcium carbonate minerals; and (d) the economical use made by plants of the heavy application of fertilizers to such calcareous soils as the Gila clay type in the arid West.

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