THE RELATION OF BUFFER CAPACITY AND ORGANIC MATTER TO THE SOLUBILITY OF THE NUTRIENT ELEMENTS IN TOA SILT LOAM

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ABSTRACT

The reaction of arable soils varies widely. Since each soil is affected and reacts differently from all others to applications of fertilizers and soil amendments, it is the problem of the soil scientist to make recommendations regarding the value of different soil amendments and fertilizers on the basis of individual soil type. It has been the purpose of this work to study the effect of buffer capacity and organic matter on the solubility of the mineral nutrient elements in Toa silt loam. This is an alluvial soil from the northern coast of Puerto Rico. Sugar cane is the universal crop grown on it. This soil type is very fertile. Since the buffer capacity, resistance to change in reaction, or pH, of Toa silt loam has not been extensively studied it was desired to study it more thoroughly.

The six samples of Toa silt loam received the same treatments throughout the experimental procedure. Each sample was treated with successive increments of a saturated solution of calcium hydroxide or tenth normal sulfuric acid, each addition being equivalent to one, two and three tons of calcium carbonate or sulfuric acid equivalents of calcium carbonate per acre, respectively.

It was found that each sample of Toa silt loam behaved differently in the solubility of its mineral nutrient elements. This behavior was largely dependent on the amount of organic matter present in the sample. Some of the nutrient elements like potassium and manganese were found to be more soluble at higher pH values whenever the sample in question was high in organic carbon content. In samples in which the organic carbon content was not as high the solubility of these two nutrient elements was found to increase only at lower pH values. Liming increased the solubility of calcium but did not decrease the solubility of phosphorus although it always decreased the solubility of potassium, manganese, and iron. Additions of acid always increased the solubility of calcium, magnesium, manganese, iron, and potassium. It was found that in samples high in

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organic carbon content the buffer capacity, resistance to change in reaction, was greatest near neutrality. In the samples with a lower per cent of organic carbon the buffer capacity was found to be greatest at the extreme ranges of acidity and alkalinity. This was represented by pH curves plotted against the amount of acid or base used.

This work bears out the fact that the ability of a soil to resist a change in reaction, buffer capacity, is an individual characteristic for each soil. Without a knowledge of the buffer characteristics of the soil, no definite recommendations can be set forth regarding the effect of a particular fertilizer or soil amendment on the soil. This is of great economic importance to the crop grower since additions of fertilizer materials, both acidic and basic, or soil amendments to the soil is a very common practice in the agricultural field. The effect of additions of acidic or basic materials to the soil will not produce the same results in any two soils. The profits to be derived therefrom will be proportional to the power of the soil in question to yield soluble mineral nutrient elements to be used by the plant grown.

INTRODUCTION

The reaction of arable soils varies between pH 4.0 and 9.0 and depends upon the relative amounts of hydrogen, calcium, and sodium adsorbed by the humus and mineral or clay colloids of the soil. Since the humic or clay acids which form weak combinations with adsorbed cations of hydrogen, sodium, or calcium, are unlike normal acids and have no very definitely fixed capacity for combining with bases, they will exhibit the strong buffer capacities characteristic of weak acids or the calcium or sodium salts of weak acids. The strong buffering effect of the soil acids or salts of the soil acids is due to the fact that only a very small fraction of the acid or salt is dissociated at any one time to give hydrogen, calcium or sodium ions, but increasing amounts dissociate and are neutralized when increasing amounts of base or acid are added. The complexity of these colloidal acids or their salts in the soil makes necessary the use of indirect methods for the study of the acidic or basic properties of a soil. These properties are most conveniently and practically measured by curves which show the pH values plotted against the amounts of standard acid or base which has been added to the soil in question.

Different soils contain widely varying amounts and proportions of the humus and clay colloids and the interaction of the humus and clay in different soils varies. There are also changes in the saturation capacities of the soil colloids with changes in the soil reaction or pH values. Thus the determination of the quantities of bases or acids that must be added to a soil to effect a unit change in reaction is an individual problem for each soil.

Associated with the change in reaction of a soil is the change in the solubilities of the mineral elements in the soil. The changes in the solubilities of the nutrient elements are of especial practical importance. The current practices in the cultivation of crops involve the addition to the soil of both acidic and basic substances as fertilizers or soil amendments. One of the most common basic materials used is lime in some of its forms while the most common acidic materials are ammonium sulfate, sulfur, ammonium chloride, and sulfuric acid.

The study of the effect of the change in reaction of a soil largely resolves itself into a determination of the unit changes in reaction, or pH value, per unit addition of some commonly used basic or acidic substances and the effects of these substances on the solubilities of the nutrient elements. The effects of such additions will be specific for a given soil under a definite set of conditions. Since the buffer capacity, or the resistance to change in reaction, for Toa silt loam has not been extensively studied, it is the purpose of this work to study the effects of additions of calcium hydroxide and sulfuric acid on the changes in reaction of the soil and the solubilities of the mineral nutrient elements in six different samples of Toa silt loam which vary widely in their humus or organic matter content.

REVIEW OF LITERATURE

Comprehensive studies made by Pierre and others (17, 18, 19) show that in most investigations on buffer action of soils the results have been recorded as titration curves representing the amount of acid and base used against the pH obtained. Charlton (17) suggested a method giving fixed numerical values to the buffer capacity of soils by using simple formulae. He states that total buffer capacity toward acid is the amount in milliliters of normal sulfuric acid used to bring 100 grams of soil to pH 4.5. Similarly, he states that the total buffer capacity toward base is the amount in milliliters of normal barium hydroxide used to bring 100 grams of soil to pH 9.5. However, this method is open to question due to the fact that original pH values of soils vary, preventing the indication of the relative power of different soils to buffer given amounts of acid or base. Therefore, Charlton indicated two other expressions which he named ''buffer action per 1.0 pH toward acid and toward base''. He defined the former as the total buffer capacity divided by X-4.5, where X is the original pH of the soil. The buffer capacity toward base is the total buffer capacity divided by 9.5-X. He called this "buffer capacity per 1.0 pH" the "specific buffer capacity".

Pierre and Worley (**18**) found that liming soils in accordance with the amount of exchangeable hydrogen brought the soils to pH 6.5. They also found the average liming factor at pH 6.5 to be 1.43 and at pH 6.0 the average liming factor was 1.52 and so concluded that the exchangeable hydrogen method, unlike the buffer method, gave no indication of the lime needed to bring the soils to pH values other than 6.5.

Runk (**23**) making a lime requirement survey for Delaware soils found that the lime requirements obtained in the laboratory methods could not be applied in the field without harming the crops. It was found that in some instances lower yields were evident and in others yellow color and stunted leaf growth were observed. However, when smaller applications than those indicated by the laboratory tests were applied to these soils very satisfactory results were obtained. Runk concludes that since the differences in buffer capacities of soils are so varied, "it would seem necessary to know the buffer capacity before applying materials which affect soil reaction".

Slipher (**26**) found that while applications of lime were arithmetic, the crop responses were geometric. He observed a similar result in the change of soil reaction, pH, by lime. The first addition of lime increases the pH more than does each successive addition applied in multiple additions. The efficiency of lime on a loamy soil was less than on a sandy soil. This he ascribed to the stronger buffer capacity of the loamy soil. Slipher concludes that it appears advisable to use lower rates of liming than have been commonly advised in the past.

Turner (**28**, **29**, **30**) shows that the buffer capacity of humus or its capacity for holding cations per unit weight is about six to seven times that of clay and that the exchange capacity of humus is not greatly affected by the presence of clay. When the ratio of clay to organic matter exceeds 20, the organic matter may be present almost entirely as films on the inorganic or clay particles. The saturation deficits of the good soils can be taken as a guide to the amount of hydrolysis which can take place in them, after they attain equilibrium with calcium carbonate. In the same way, their degree of unsaturation is a measure of the proportion of acidoid material unneutralized under these conditions. Turner shows that the quantities of lime requirements based on the extent of unsaturation of the good soils are equal to the requirements of lime needed to bring the soil into equilibrium with calcium carbonate. The amounts of lime required vary with the degree of unsaturation of the soil. There exists a tendency of the soil reaction to decrease as the soil increases its unsaturation capacity. Magistad, Joffe, and McLean (**29**) have shown that the solubility of iron and aluminum in soils is dependent on soil reaction as well as upon the nature and amount of the anions present. Iron and aluminum do not always come into solution when acid soils are leached with neutral salt solution; the reasons determining their presence or absence are not fully understood. Turner found no replaceable iron, in some instances a trace was visible, in many soils having low pH values but higher saturation deficits. Iron was not found in the filtrates unless the saturation deficit was as high as 10 to 12 milligram equivalents per 100 grams of soil.

McGeorge (**10**) found a close relationship between the exchange capacity and the carbon content of soil. From his work it appears that humus overpowers the effect of clay.

Wilbur, Leighty and Shorey (**32**) observed that the carbon-nitrogen ratio varies considerably in soils. They found that the carbon-nitrogen ratio had a relation to the amount of organic matter present as food for micro-organisms. A ratio of 20:1 was found to indicate a fair amount of decomposable organic matter while a 10:1 ratio, or less, shows an advanced state of degradation of organic matter. They concluded that it was useless to attempt multiplying the total nitrogen by the factor 20 to calculate the organic matter.

Hissink (**6**) noted that in humus soils the buffer capacity increased near the neutral region. He found also that the buffer capacity (lime required to change pH by 0.1) per unit humus content was independent of the actual humus content of soils examined.

Kuchinskii (**7**) found that the buffer capacity of soils was almost zero after the clay particles had been separated from the soil. The humus portion of the soil exhibits a high buffer capacity. The greater the buffer capacity the greater the base exchange capacity. This investigator found some relation between hydrolytic acidity and buffer capacity.

McGeorge (**11**) showed that the exchange capacity of the organic portion increases as the organic matter decomposes. This is due to the fact that the lignin portion of the soil organic matter is most resistant and has the highest exchange capacity.

Morgan (12) observed that soil texture and organic matter content bear a close relationship to the calcium carbonate adsorption factor. It was noted that clay and organic matter each increased the value of the factor.

Myers and Gilligan (**13**) concluded that the acidity of a soil, pH, does not indicate the extent of saturation of the colloidal acids and bases and that the pH values of different soil types do not show the relative buffer capacities of the soils in question. They studied the mechanism of buffer action and explain it as follows: "When acid is added to a soil it reacts with the salts of colloidal acids forming colloidal acids and crystalloidal salts. The resultant reaction of the system is only lightly altered in consequence of the weakness of the colloidal acids. When acid is added in excess of that required to react with the cations of the colloidal salts, the crystalloidal salts formed, having an ion in common with the added acid, tend to repress the ionization of the latter. The net result is a small change in the H-ion concentration of the soil dispersion."

Nemec and Gracanin (**14**) observed that the larger adsorption of potash and phosphoric acid after additions of calcium carbonate was seen only in acid soils (deficient in calcium oxide), but soils containing a fair supply of calcium oxide showed a decrease in the reabsorption of potash and phosphoric acid. These investigators noted that soils containing small amounts of available phosphoric acid respond markedly to calcium carbonate, insofar as the reabsorption of phosphoric acid was concerned, but that in soils with large amounts of available phosphoric acid the calcium carbonate inhibited the reabsorption of the phosphoric acid. The same results were found for potash, but were not as regular.

Pierre, Pohlman, and McIlvaine (**19**) found organic soils to contain low quantities of aluminum even though very acid and that large amounts of organic matter check the harmful effects of soluble aluminum on sensitive crops. These authors showed that there may be less soluble aluminum on acid soils of high percentage base saturation than in soils of low percentage base saturation. The authors showed that the amount of soluble aluminum in different soils of same pH values varied greatly.

Pryanishnikov (**20**) working with a chernozem soil and three types of podzols adjusted to different reactions (from pH 4.5–8.0) grew plants on them. He found that each soil behaved differently. Mustard plants failed to grow at a pH of 4.5 on a sandy soil but grew at the same reaction on a sandy loam. He concluded that soils with high buffer capacity can support plants even at low pH values. This investigator observed that water extracts from acid soils contained large quantities of calcium, which seemingly arrested the deleterious effects of the acids. It was noted that the intake by the plants of this calcium in the acid cultures was obstructed when ammonia was used as a source of nitrogen. He showed that a similar increase of magnesium and potassium in the nutrient solution had an effect much like that of calcium, but not as high. The mobilization of phosphorus and its utilization on limed podzol could be ascribed to the calcium.

This effect of calcium has been noted in the United States, particularly when small applications of limestone have been applied to acid soils with or before superphosphate.

Ganssen (**4**) observed that humus increases the solubility of phosphates in the soil by decreasing the proportion of active alumina.

The review of literature shows that a study of the buffer capacity of soils resolves itself into an individual problem for each soil. No general recommendation as to the amounts of lime or acidic material which must be applied to a given soil to effect a definite change in the reaction of the soil can be predicted accurately except by tests on the soil. Furthermore, the change in the reaction of the soil caused by the use of an amendment or of a basic or acidic fertilizer is of primary practical importance in its effect on the solubility of the nutrient elements in the soil. The solubility of the nutrients will vary according to the buffer capacity and other associated characteristics of the soil. Since the buffer capacity of Toa silt loam has not been extensively studied, it was desirable to investigate its buffer capacity as related to its organic content and changes in the solubilities of the nutrient elements as affected by additions of lime and sulfuric acid.

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EXPERIMENTAL METHODS

The soil used in this work was six different samples of Toa silt loam. The Toa soils occur very extensively on nearly all the streams of the north coast of Puerto Rico (**21**). "The Toa soils have developed from material washed from the shale and limestone hills which has been deposited in the stream-flood plains. They are grayish brown to brown in color, silty in texture, nearly uniform in both color and texture to a depth of several feet. All layers are nearly neutral to slightly alkaline."

"Physically and chemically these soils are among the best sugarcane soils in Puerto Rico. They have a nearly level surface relief, good drainage and are almost ideal for maximum agricultural utilization. These soils permit the cultivation of all the land and the use of any kind of modern machinery. The surface soil is loose and porous and is easily cultivated. Water can penetrate it rapidly and there is enough silt and clay in the subsoil to retain large quantities of moisture. These soils have considerable organic matter and plant food, yet fertilizer and lime bring very good returns. This soil will support a wide diversification of profitable crops, but sugarcane seems to be the most profitable as nearly 100 per cent of the land is planted to cane. Yields vary from 30 to 50 tons but field observation indicates that in many places these yields can be doubled with irrigation, proper handling, good fertilizer rates, and, in some cases, liming."

The six samples of Toa silt loam studied were taken at a depth of six inches in the following location:

1. Central Constancia, 2.5 kilometers north of Toa Baja. Taken at six representative places on March 11, 1931.

II. Central Canóvanas, 0.5 kilometers east of main office. Taken at six representative places on March 5, 1931.

III. Finca Nevares, 1.8 kilometers on Toa Baja road. Taken at six representative places on March 11, 1931.

IV. Finca San Antonio, Bayamón. Taken at six representative places on March 11, 1931.

V. Kilometers 26.6, Río Grande–Mameyes road (left), side-road El Verde, finca Tamarindo. Taken at three representative places on March 5, 1931.

VI. Finca El Naranjal, 1 kilometer north of Carolina. Taken at three representative places on March 5, 1931.

All samples were taken by J. A. Bonnet, Chief of the Division of Soils, Insular Experiment Station, Río Piedras, Puerto Rico, and were air dried and passed through a 2 mm. sieve.*

The buffer effect towards lime was determined by the addition of successive increments of a saturated solution of calcium hydroxide to 50-gram portions of soil at rates beginning with the equivalent of one ton calcium carbonate per acre, 0.05 per cent, and increasing to three tons per acre, 0.15 per cent.

After adding the saturated solution of calcium hydroxide, the samples were stirred for five minutes at thirty-minute intervals for half a day. Percival (**16**) found that by aerating samples after additions of lime had been made, equilibrium was attained during 20 to 24 hours. Since the laboratory equipment did not permit this procedure, intermittent stirring was resorted to and in this way the carbon dioxide was driven off and complete mixing of the soil and lime was obtained. After the addition of the lime increments all the solutions were made up to 73.5 milliliters with water, which was the volume of the largest addition of calcium hydroxide. All samples were evaporated to air-dry condition at room temperature.

Similar procedure was followed in determining the buffer effect towards acid. Tenth normal sulfuric acid was added in increments which were the equivalents of calcium carbonate at the rates of 1, 2, and 3 tons per acre.

The treatments given to each sample of soil were as follows:

1. 50 grams soil plus 30 ml. tenth normal sulfuric acid, equivalent to 2.94 tons sulfuric acid per acre.
2. 50 grams soil plus 20 ml. tenth normal sulfuric acid, equivalent to 1.96 tons sulfuric acid per acre.
3. 50 grams soil plus 10 ml. tenth normal sulfuric acid, equivalent to 0.98 tons sulfuric acid per acre.
4. No treatment. Check.
5. 50 grams soil plus 24.5 ml. limewater, equivalent to 1 ton calcium carbonate per acre.
6. 50 grams soil plus 49 ml. limewater, equivalent to 2 tons calcium carbonate per acre.
7. 50 grams soil plus 73.5 ml. limewater, equivalent to 3 tons calcium carbonate per acre.

The 50-gram portions of air-dried soil were transferred to 500 milliliter Erienmeyer flasks with 250 milliliters of freshly distilled water. The samples were shaken for 5 minutes and filtered through

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* The main purpose in obtaining those samples was to use them in nitrification studies published in Bonnet, J. A. 1935. Nitrification studies with soil types of northern Puerto Rico. Jour. Agric. Univ. P. R. 19(2): 73–103.

neutral quantitative filter paper and the following determinations were made on the filtrate:

1. pH.
2. Soluble Ca and Mg.
3. Soluble P.
4. Soluble K.
5. Soluble Fe and Mn.

Total carbon was determined by the dry combustion method of Winters and Smith (**34**),

Total or protein nitrogen was determined by the Gunning-Hibbard method as modified by Bal (**3**).

The solubility of phosphorus was estimated by the method of Parker (**15**).

Potassium was determined gravimetrically by the sodium cobaltinitrite method as outlined by Van Rysselberge (**31**).

Calcium and magnesium were estimated by the turbidity methods as given by Schreiner and Failyer (**25**).

Iron was measured colorimetrically as proposed in Bulletin 31, U. S. Dept. Agr. Bureau of Soils (**25**).

Manganese was determined by the periodate method of Greathouse as described by Yoe (**35**).

Reaction or pH was determined colorimetrically, using standard indicators and Hellige standard color discs.

EXPERIMENTAL RESULTS AND DISCUSSION

From Table 1 can be seen the changes in the solubilities of the different elements according to the corresponding changes in reaction or pH. Soil I is high in soluble calcium, the check having 384 p.p.m. at a pH of 6.7. In general, Soil I has a high buffer capacity, the lowest pH value attained being 5.0 and the highest being 8.0. The solubility of calcium was doubled from the first two additions of acid. With the third increment, the equivalent of three tons of sulfuric acid per acre, the solubility of calcium increased almost threefold over that in the check. In the alkaline range, the solubility was twice that of the check but the second and third increments, two and three ton equivalents of calcium carbonate, gave the same solubility of calcium. The solubility of magnesium decreased as the pH decreased but increased slightly over that of the check on the alkaline side with the addition of the third increment, the equivalent of three tons of calcium carbonate per acre. Soluble iron was found only as a trace on the acid side. Phosphorus became more soluble as the acidity increased. On the alkaline side its solubility increased as the pH increased but never attained the magnitude of solubility shown on the acid side. Potash was very soluble at low pH values, becoming less soluble as alkalinity increased.

TABLE 1

RELATION OF CHANGE IN SOLUBILITY OF NUTRIENT ELEMENTS TO CHANGE IN REACTION IN TOA SILT LOAM, I

Treatment	Ca p. p. m. *	Mg p. p. m.	Mn p. p. m.	Fe p. p. m.	P p. p. m.	K p. p. m.	pH
1	1040	160	46	trace	3.6	110	5.0
2	680	173	18	trace	3.3	90	6.1
3	671	173	no test	trace	1.8	43	6.2
4	384	208	no test	no test	2.5	15	6.7
5	454	104	no test	no test	1.2	13	7.2
6	769	208	no test	no test	1.7	18	7.8
7	769	346	no test	no test	2.5	18.1	8.0

* On the basis of dry soil.

In general, the solubility of the nutrient elements in this soil decreased with additions of lime. This soil was the second highest in organic carbon content, 2.25 per cent, (Table 7). It ranked second also in total nitrogen, 0.235 per cent. It can be seen from a comparison of the curves showing the buffer capacities of the several samples and from the organic contents shown in Table 7, that an increase in the soil organic matter increases the buffer capacity near neutrality, which is reflected in a flatter curve.

TABLE 2

RELATION OF CHANGE IN SOLUBILITY OF NUTRIENT ELEMENTS TO CHANGE IN REACTION IN TOA SILT LOAM, II

Treatment	Ca p. p. m. *	Mg p. p. m.	Mn p. p. m.	Fe p. p. m.	P p. p. m.	K p. p. m.	pH
1	453	231	59	trace	1.7	40	3.9
2	250	181	48	trace	2.5	30	4.0
3	177	137	25	no test	3.1	30	4.6
4	40	52	9.3	no test	2.8	10	6.0
5	67	119	8	no test	3.6	20	6.9
6	100	133	14	no test	3.1	10	7.2
7	100	166	trace	no test	3.1	none	7.2

* On the basis of dry soil.

Table 2 shows the behavior of Soil II. The check was low in soluble calcium, 40 p.p.m. As in Soil I, lime increased in solubility as the pH became lower. Additions of lime increased the solubility of calcium over that in the check slightly, but on the acid side the solubility of lime increased tenfold with the addition of the three tons equivalent of sulfuric acid per acre. The changes in the solubility of magnesium were like those of calcium except for smaller

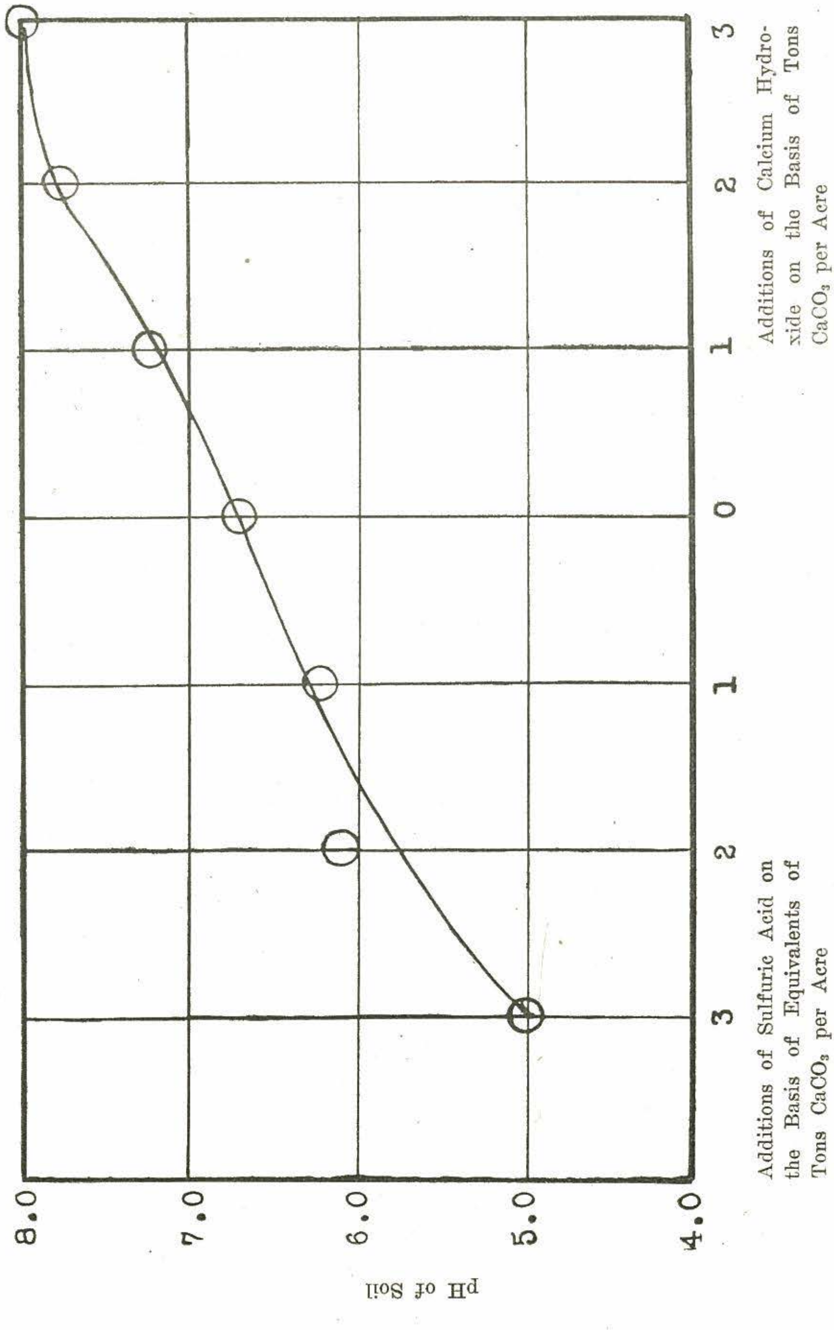

FIG. 1. Buffer Curve for Toa silt loam, I

differences. The soil seemed to maintain about a 1:1 ratio of Ca:Mg at neutrality. Soil II, like Soil I, was high in soluble manganese. This nutrient element was more soluble on the acid range, increasing its solubility as the pH decreased. Manganese was present in the check, (pH 6.0), and in the treatments with the first two increments of lime. There was no appreciable increase in the pH from the addition of the third increment of lime, yet, only a trace of manganese was present as compared to 14 p.p.m. present in the two ton treatment or second increment. There was only a trace of iron at a pH of 3.9 and 4.0. These correspond to the additions of three and two tons of sulfuric acid per acre, respectively. No test for soluble iron was obtained at other pH values in Soil II. The solubility of phosphorus increased with the one ton per acre application of sulfuric acid but in the successive applications the solubility decreased and was less than that of the check. With the addition of one ton of calcium carbonate the solubility of phosphorus was the highest of all, 3.6 p.p.m., this being 0.8 p.p.m. over the check. However, the two and three ton applications of lime decreased the solubility from 3.6 p.p.m. to 3.1 p.p.m. for each application. (It should be mentioned here that the greater solubility of phosphorus on the alkaline range may have been due to the colloidal state of the filtrates since it was impossible to get clear filtrates in the alkaline range.) Potash increased in solubility as the pH decreased. The solubility on the alkaline side was twice that of the check from the one ton treatment of calcium carbonate but decreased thereafter.

Soil II was the lowest in organic carbon content, 1.19 per cent, (Table 7) and it also ranked last in total nitrogen, 0.126 per cent. It is very obvious from the buffer curves of Soils I and II and from Table 7 that Soil I which has a relatively high organic content is highly buffered near neutrality, while Soil II which has a low organic content is lightly buffered near neutrality but is highly buffered at the extreme ranges.

TABLE 3

RELATION OF CHANGE IN SOLUBILITY OF NUTRIENT ELEMENTS TO CHANGE IN REACTION IN TOA SILT LOAM, III

Treatment	Ca p. p. m. *	Mg p. p. m.	Mn p. p. m.	Fe p. p. m.	P p. p. m.	K p. p. m.	pH
1.............	625	92	6.3	no test....	1.4	60	4.0
2.............	525	87	7.8	no test....	1.2	80	4.3
3.............	500	106	trace......	no test....	1.1	50	4.7
4.............	145	55	no test....	no test....	1.5	10	6.0
5.............	165	81	no test....	no test....	1.4	10	6.5
6.............	190	87	no test....	no test....	1.6	10	6.8
7.............	275	100	no test....	no test....	1.6	30	6.9

* On the basis of dry soil.

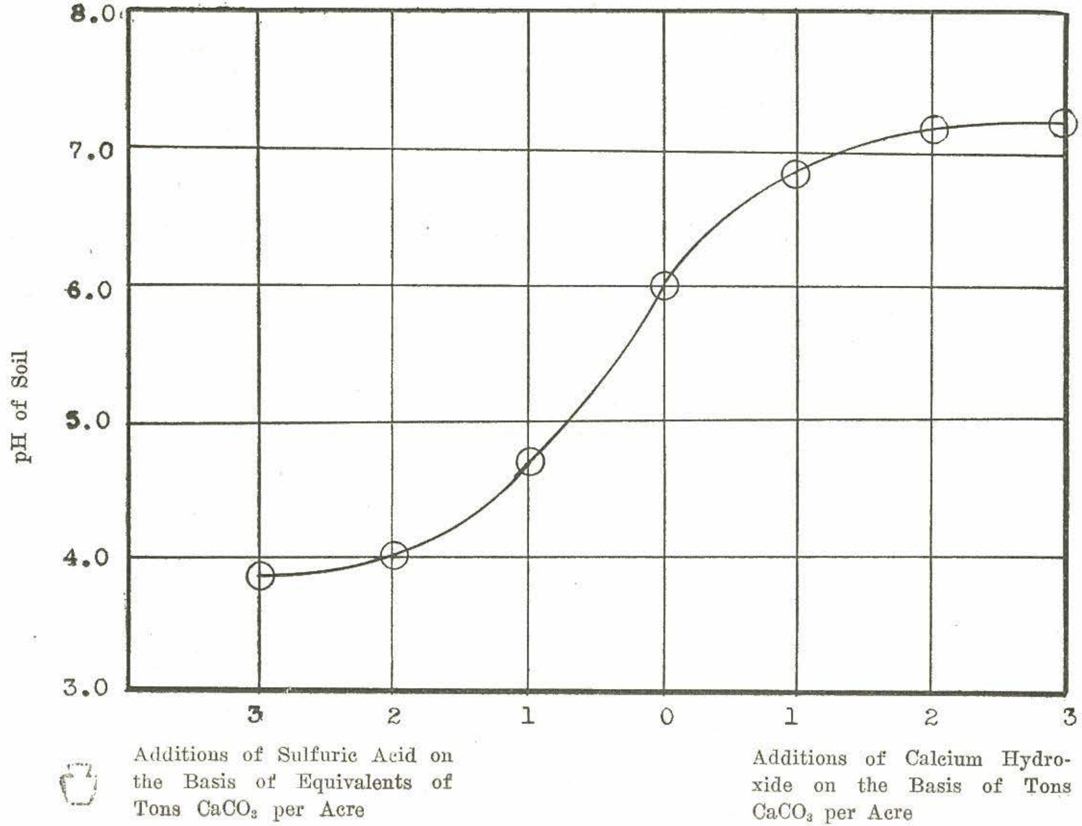

FIG. 2. **Buffer Curve for Toa silt loam, II**

Table 3 shows that Soil III was high in calcium which became more soluble as the acidity increased. The additions of lime also increased the solubility of calcium over that of the check, but to a lesser degree than the increase from the additions of sulfuric acid. Magnesium showed relatively less changes in solubility from additions of either acid or base. There was not much soluble manganese in this soil. At pH 4.3, after the addition of two tons of sulfuric acid per acre, there was 7.8 p.p.m. of soluble manganese, present. The solubility of manganese was too low to be measured above a pH of 4.7 in Soil III. No test for soluble iron was obtained for this soil. Phosphorus was slightly more soluble on the alkaline side than on the acid side. As in Soil II, this may be ascribed to the colloidal state of the alkaline filtrates, it being impossible to get clear filtrates. Potash was six times more soluble at a pH of 4.0, three tons of sulfuric acid per acre, than the check. The highest solubility was attained at pH 4.3, two tons of sulfuric acid per acre. The three ton addition of lime increased the solubility of potash over that of the check.

Soil III, like Soil II, is low in organic matter, (Table 7), and shows the same peculiar property in buffering the effects of acid and base; that is, the soil is much more highly buffered at the extreme ranges than near neutrality.

TABLE 4

RELATION OF CHANGE IN SOLUBILITY OF NUTRIENT ELEMENTS TO CHANGE IN REACTION IN TOA SILT LOAM, IV

Treatment	Ca p. p. m. *	Mg p. p. m.	Mn p. p. m.	Fe p. p. m.	P p. p. m.	K p. p. m.	pH
1.	555	104	44	no test....	0.8	50	4.0
2.	417	173	26	no test....	0.8	10	4.3
3.	345	148	9	no test....	1.1	10	5.0
4.	83	139	no test....	no test....	1.9	10	6.1
5.	167	173	no test....	no test....	1.7	none......	6.9
6.	167	104	no test....	no test....	1.7	none......	7.2
7.	227	130	no test....	no test....	2.0	none......	7.3

* On the basis of dry soil.

Table 4 shows the data for Soil IV. This soil was low in lime content but the solubility of lime increased sixfold at the lowest pH, 4.0, (three tons sulfuric acid per acre), over that of the check. Lime additions caused a slight increase in the solubility of calcium. The solubility of magnesium was slightly altered on the acid side but it decreased with the second and third applications of lime. Soil IV was as high as Soils I and II in its manganese content but in this particular soil manganese was soluble up to a pH of 5.0 only. No test for soluble iron was obtained for this soil. Phosphorus was ap-

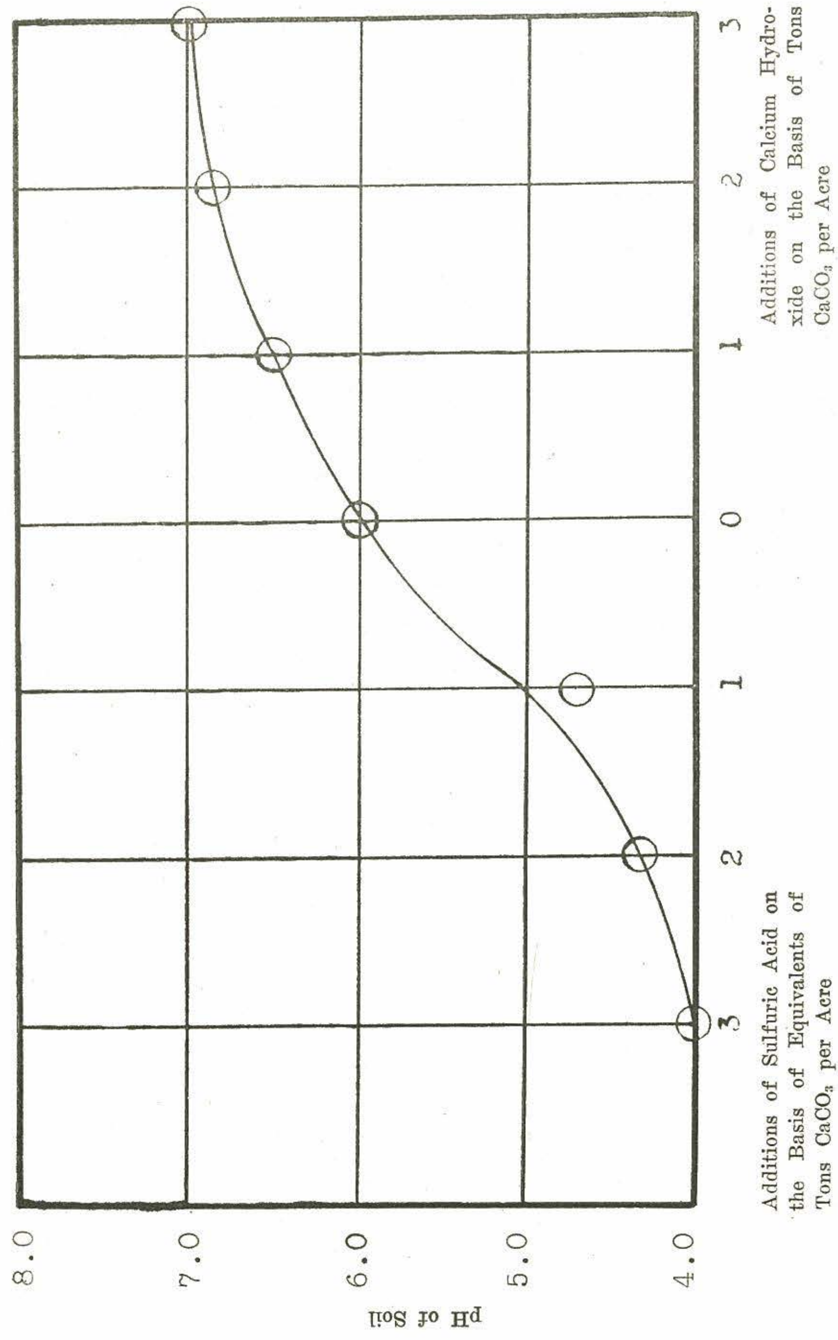

FIG. 3. Buffer Curve for Toa silt loam, III

parently less soluble on the acid side. The turbidity of the filtrates, as explained before, may account for this. This soil was low in potash content 10 p.p.m. The first two additions of sulfuric acid, (one and two tons per acre, respectively), failed to affect the solubility of potash but the third increment increased the solubility five times over that of the check. On the alkaline range the solubility was too little to be measurable.

It can be noted that Soil IV, like Soil II and III, was low in organic matter content. Like Soils II and III, this soil shows a low buffer capacity near neutrality and a high resistance to change in reaction at the extreme ranges. The solubilities of phosphorus and potassium are very low in this soil. This may be due to the high buffering power shown at the extreme ranges.

TABLE 5

RELATION OF CHANGE IN SOLUBILITY OF NUTRIENT ELEMENTS TO CHANGE IN REACTION IN TOA SILT LOAM, V

Treatment	Ca p. p. m. *	Mg p. p. m.	Mn p. p. m.	Fe p. p. m.	P p. p. m.	K p. p. m.	pH
1.	555	187	trace	no test	1.6	7	4.2
2.	450	148	trace	no test	1.2	10	4.9
3.	450	148	no test	no test	1.3	20	5.4
4.	710	173	no test	no test	1.3	7	6.5
5.	710	187	no test	no test	1.6	10	6.5
6.	500	104	no test	no test	1.9	7	7.2
7.	355	159	no test	no test	1.6	10	7.1

* On the basis of dry soil.

The differences in solubilities of the nutrient elements at varying pH values for Soil V can be seen in Table 5. This soil is the highest in soluble lime content, 710 p.p.m. The additions of acid did not increase the solubility of calcium. The same was evident with the additions of lime but to a larger extent. The solubility of magnesium did not vary appreciably on either range. Only a trace of manganese was seen at pH values of 4.2, (three tons of sulfuric acid per acre), and 4.9, (two tons of sulfuric acid per acre). No test for soluble iron was obtained. Phosphorus was slightly more soluble at a pH of 4.2 than at any other except at pH 7.2 which, as mentioned before, may be due to the lack of a clear filtrate. This soil was very low in potash. The check contained 7 p.p.m. Potash became most soluble with the addition of the first increment of sulfuric acid. Successive increments had little effect on the solubility of potash. Lime additions did not increase the solubility of potash.

Soil V is the highest soil of the six samples in organic carbon content, 2.35 per cent, (Table 7) and in total nitrogen content, 0.270

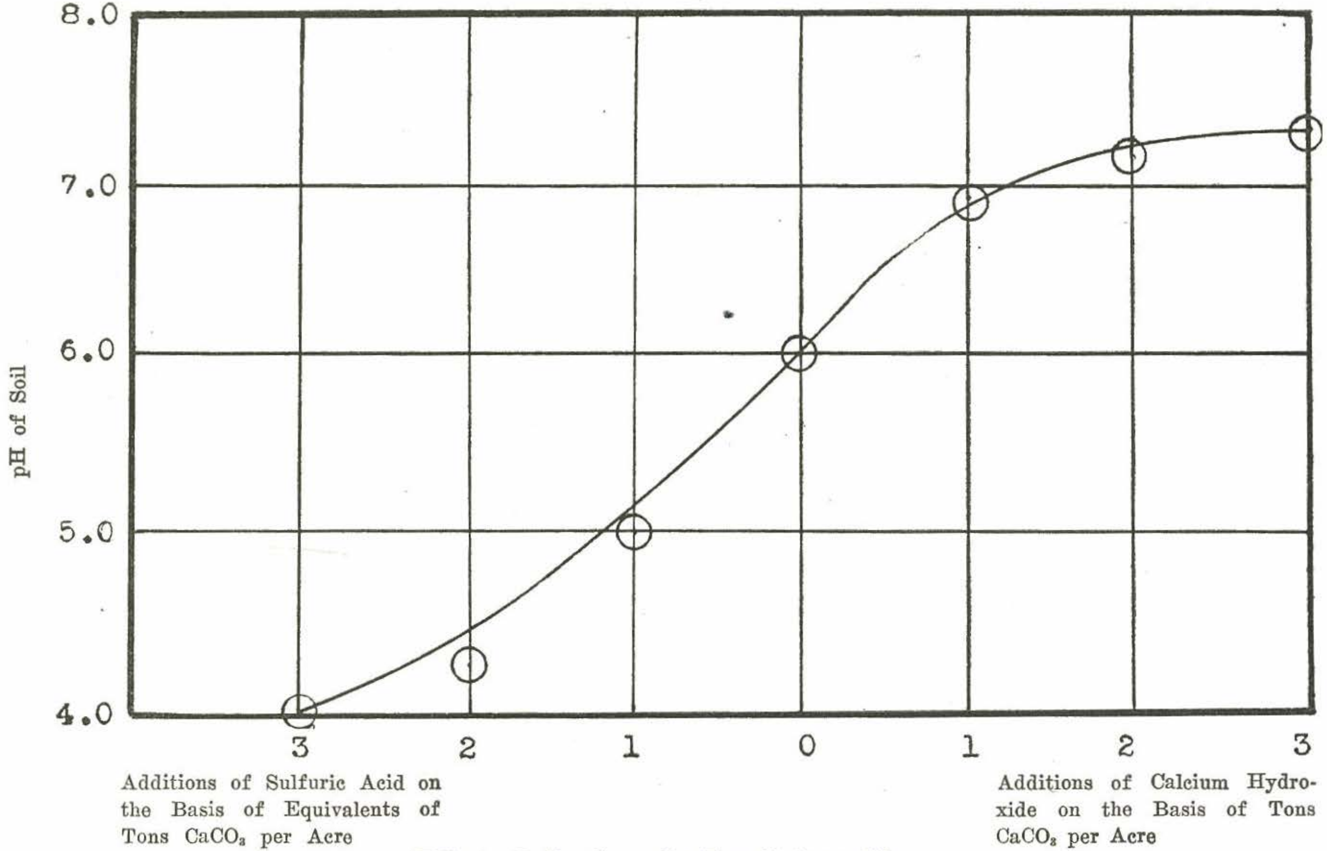

FIG. 4. Buffer Curve for Toa silt loam, IV

per cent. It is a highly buffered soil, being resistant to changes in reaction near neutrality. Although very low in potash the solubility of this nutrient element increased somewhat with the addition of one ton of sulfuric acid per acre. Lime additions did not affect the solubility of potash. The solubility of phosphorus was not increased markedly on either side and was comparatively low in this soil.

TABLE 6

RELATION OF CHANGE IN SOLUBILITY OF NUTRIENT ELEMENTS TO CHANGE IN REACTION IN TOA SILT LOAM, VI

Treatment	Ca p. p. m. *	Mg p. p. m.	Mn p. p. m.	Fe p. p. m.	P p. p. m.	K p. p. m.	pH
1	625	115	4	no test	1.1	100	4.3
2	555	135	no test	no test	1.2	30	4.8
3	370	135	no test	no test	1.5	30	6.1
4	190	148	no test	no test	1.9	10	6.9
5	355	115	no test	no test	1.9	60	7.2
6	355	148	no test	no test	1.9	none	7.4
7	500	135	no test	no test	2.0	none	7.8

* On the basis of dry soil.

Table 6 shows that Soil VI responded markedly to both additions of sulfuric acid and lime, as shown by the increase in solubility of the lime content. The solubility of magnesium was changed only slightly from additions of sulfuric acid and lime. Soil VI is low in manganese. Manganese was insoluble above pH 4.8. Phosphorus was less soluble on the acid side. Additions of lime did not increase the solubility of phosphorus. Soil VI is low in soluble potash, but the additions of acid brought a marked increase in its solubility. The addition of one ton of lime per acre increased the solubility of potash but with the two and three ton increments the solubility of potash became too small to be measured. The reason for the increase from the first increment of lime may have been due to the stimulation of extra organic decomposition during the period of one week between the treatment and drying of the soil.

The organic carbon and nitrogen contents, 1.66 and 0.205 per cent respectively, show that this soil is intermediate in organic matter content and the buffer curves show that the soil is not so well buffered near neutrality as Soils I and V which contain more organic matter. However, Soil VI is more highly buffered near neutrality than Soils II and III whose buffer curves are of the sigmoid type which is characteristic of the soils low in organic matter.

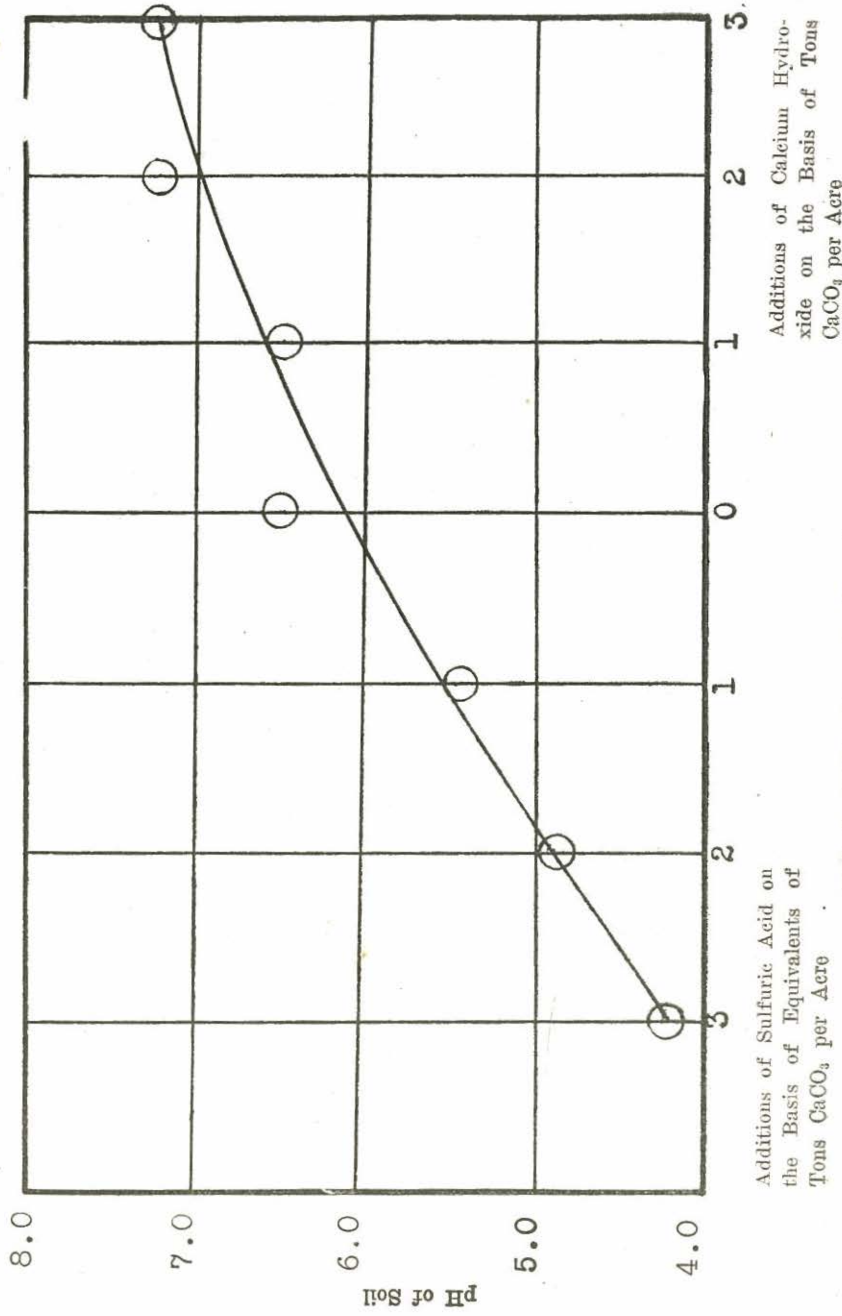

FIG. 5. **Buffer Curve for Toa silt loam, V**

TABLE 7

THE ORGANIC CARBON AND NITROGEN CONTENTS AND RATIOS IN THE SIX SAMPLES OF TOA SILT LOAM STUDIED

No. of Soil	% Moisture	% Organic carbon	% Total N	C/N
I	1.55	2.25	0.235	9.5
II	0.79	1.19	0.126	9.4
III	1.15	1.44	0.150	9.6
IV	1.31	1.61	0.199	8.1
V	1.03	2.35	0.270	8.7
VI	0.69	1.66	0.205	8.1

It can be seen from Table 7 that the organic matter in the six samples of soil is well decomposed or largely in the humic state. This is indicated from the relatively narrow carbon-nitrogen ratios. From this it can be inferred that the changes in the buffering effect as related to the different amounts of organic matter in the samples is largely controlled by the lignin-humus fraction of the organic matter (10, 11) which makes up the major part of it.

SUMMARY

1. Organic matter, buffer capacity, and the relation of changes in reaction to the solubilities of the mineral nutrient elements in six samples of Toa silt loam were studied.

2. The buffer characteristics may vary rather widely within a given soil type. The buffer curves for different samples of Toa silt loam show that the presence of larger amounts of organic matter markedly increases the buffer capacity near neutrality. This is reflected in the flatter buffer curves. The samples which contained lower quantities of organic matter are most highly buffered at the extreme ranges of high acidity and basicity. This is indicated by typical sigmoid buffer curves.

3. The state of the decomposition of the organic matter in these samples indicates as has been shown by previous work that the buffering effect of the organic matter is associated with the lignin-humus fraction.

4. Additions of acid to the soil increased the solubility of the nutrient mineral elements. The increases in the solubilities were greatest in the samples that were low in organic matter.

5. Although liming increased the amount of soluble calcium in the soil, it did not decrease the solubility of phosphorus. The additions of lime decreased the solubility of potassium. The solubilities of iron and manganese were too low to be easily measured above pH 7.2 and in only one case above pH 5.0.

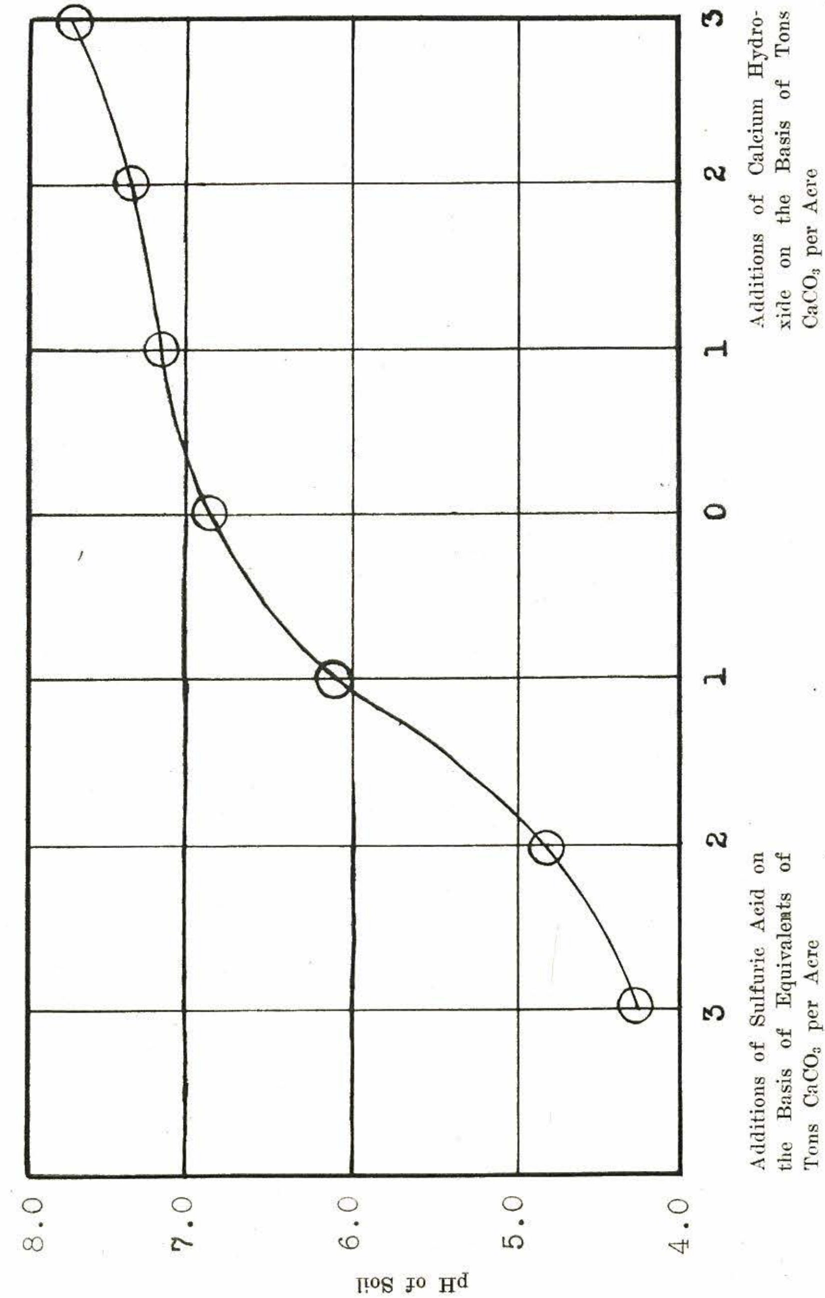

FIG. 6. Buffer Curve for Toa silt loam, VI

6. Additions of acid to the soil increased the solubility of potassium when the reaction was forced lower than pH 5.0. There was a greater increase in the solubility of potassium from the acid treatments in the samples that were lower in organic matter.

7. The solubilities of iron and manganese were increased from additions of acid. Manganese became much more soluble than iron from increased acidity and its solubility was more affected in the samples that were low in organic matter.

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