

**TITRATION CURVES
AND BUFFERING CAPACITIES
OF HAWAIIAN SOILS**

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ABSTRACT

In the development of a liming program for the acid soils of the Hawaiian Islands, it was found that soils of the various great soil groups varied greatly in their lime requirement for correction of similar degrees of acidity. This variation in lime requirement appeared to be associated with the differences in the buffering capacities of the soils. Titration curves were made on more than a hundred soils selected from the typical profiles of the soil families belonging to the various great soil groups. The results of this study have justified the following conclusion regarding the nature of the titration curves and buffering capacities of the tropical and sub-tropical soils of the Hawaiian Islands:

The buffering capacity of Hawaiian soils was much lower than that found for soils of the temperate regions. The buffering capacity of the soils of the different great soil groups varied greatly; however, there was very little variation in the degree of buffering exhibited by the soils of the different soil families of each group. Each soil group has a typical titration curve. The soils of the low humic latosol and humic ferruginous latosol have the lowest buffering capacity, and the soils of the hydrol humic latosol and brown forest groups exhibit the greatest degree of buffering.

The organic matter fraction of the soil affects the degree of buffering above soil reaction of pH 5.5. It is most "active" in neutral and alkaline portions of the titration curves. However, the organic matter fraction does not influence the nature of the curve. The general character of the titration curve is determined by the nature of the clay minerals. The kaolinite and iron oxide clays give rise to titration curves having a low buffering capacity and montmorillonite and hydrated aluminum oxide clays give titration curves having a high buffering capacity. The silica-sesquioxide ratio of the clay fraction of the soil or the quantity of clay in the soil was not related to the degree of buffering exhibited by the titration curve of the soil. This is probably due to the large amount of "free oxides" found in these soils. There is a direct relationship between the cation exchange capacity of the soil and its buffering capacity. The higher the cation exchange capacity the greater buffering would be exhibited by the titration curve of the soil.

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TITRATION CURVES AND BUFFERING CAPACITIES OF HAWAIIAN SOILS

YOSHITO MATSUSAKA AND G. DONALD SHERMAN

The potentiometric titration of the clay acids of soils has been used to characterize certain properties of soils. Such titration curves provide information regarding the neutralization point of the soil—thus the point of equivalence. Of more practical importance, these curves give the buffering capacity of the soil, which is one of the factors to be considered in the development of a sound liming program for any type of soil. The available information on typical titration curves of tropical soils is very meager and incomplete. The Hawaiian Islands have within their boundaries a wide representation of typical tropical soils, and, therefore, it is the purpose of this article to present the typical and characteristic titration curves of the great soil groups occurring in the islands. This information will be very useful in the management of soils in Hawaii and will also provide information on this important property of tropical soils.

REVIEW OF LITERATURE

Sharp and Hoagland (16) in 1916 used electrometric titration curves to study the lime requirement of soils. They are credited as being the first to apply this method to the study of soils. Since then, the method has been widely used throughout the world for this purpose. Titration curves depict the buffering capacity of soils. Buffering capacity is the capacity of the soil to resist a change in reaction with the addition of a base or acid. A soil with a high buffering capacity does not readily change its pH value. It is generally believed that the buffering of soils is affected by the amount and nature of the clay. Bradfield (4) has shown that soil clays are weak aluminosilicic acids and that buffering is due to their dissociation phenomena. Bradfield's findings have been substantiated by Truog (21). Other workers (1, 14) have found that the buffering capacity of soils varies directly with the amount of clay and the silica-sesquioxide ratio. According to Baver (3) organic matter increases the buffering capacity of soils in the reaction range higher than pH 5.5. He also reported that the removal of free Al_2O_3 , Fe_2O_3 , and SiO_2 did not appreciably affect the buffering capacity. The application of large amounts of phosphate had no effect. Buffering capacity is thus a function of the soil colloids and is primarily affected by the nature of the inorganic colloidal acids. In soils having a high content of organic matter, the organic colloidal acids play an important role in the buffering of the soil in the alkaline reaction range. Anderson and Byers (1) and Runk (14) found that the buffering capacity of soils increased with higher organic matter content.

METHODS OF ANALYSIS

Soil samples are air-dried and passed through a 20-mesh sieve. Exchangeable bases are removed with 0.05 N HCl until the leachate is free from calcium. The chloride is removed by further leaching of the soil with distilled water. The resulting soil is thus hydrogen saturated. Other investigators have prepared a hydrogen-saturated soil by using an electro dialysis cell. There is no detectable difference in the nature of hydrogen-saturated soil prepared by these two methods. The washed soil is air-dried and rescreened through a 20-mesh sieve. Seventeen 5-gm. samples are weighed out on the oven-dry basis and placed in 125-ml. Erlenmeyer flasks. Increments of 0.1 N NaOH ranging from 0 to 50 ml. are added to the soil in the flasks and all volumes are diluted to 50 ml. with distilled water. The flasks are stoppered and allowed to stand for 48 hours, with occasional shaking, to allow an equilibrium to be reached. This step is important as sufficient time must be allowed for the bases to penetrate the soil aggregates. Anderson and Byers (1) and Puri (13) found a period of 48 hours sufficient for the equilibrium to be established. The time for an equilibrium to be established in Hawaiian soils was determined and the data obtained are presented in table 1. The data show that the equilibrium is established in 48 hours.

TABLE 1. The Time Required for an Equilibrium to Be Attained in Hawaiian Soil after Addition of a Standard Base.

Time	Amount of 0.1 N NaOH added to soil				
	0.0 ml.	1.0 ml.	5.0 ml.	25.0 ml.	50.0 ml.
	pH	pH	pH	pH	pH
Immediately	3.7	5.2	8.4	11.7	11.9
1 day	3.7	4.9	7.0	11.4	11.9
2 days	3.7	4.3	6.8	11.3	11.9
3 days	3.7	4.3	6.8	11.3	11.9
6 days	3.7	4.3	6.8	11.2	11.8

After the equilibrium is established the pH of the soil mixtures in each flask is determined by using a Beckman pH meter. The results are plotted with the pH values as the ordinate and milliequivalents of NaOH per 100 gm. of soil as the abscissa.

The soils of the humic latosols and hydrol humic latosols are continually moist or wet under natural conditions, and, therefore, these soils were not

allowed to dry. They were brought into the laboratory in a wet condition and were kept moist throughout the entire procedure. This was done because it is known that certain irreversible changes occur in these soils with drying.

Organic matter was removed from the soil by the addition of 6 percent H_2O_2 and heating to and maintaining a temperature of $60^\circ C$. This treatment is continued until the evolution of gas with additions of H_2O_2 ceases. The soil is then washed several times with distilled water and treated in the same manner as the soil sample. Organic matter content is determined and calculated by the method described by Walkley (22).

The clay was separated by the method of Piper (12) with a few minor modifications. The total cation exchange capacity was determined by the use of neutral normal ammonium acetate as the replacing agent.

DESCRIPTION OF SOILS

Most Hawaiian soils are developed under a humid tropical climate which favors intense chemical weathering. The soil parent materials are derived from the volcanic lavas, cinders, and ashes which have poured out from the volcanoes at various periods in the geological history of the Hawaiian Islands. The intense weathering of these volcanic materials at different periods causes the age of the soil to be very important. This is the reason for the occurrence of many different groups of tropical soils in an area as small as the Hawaiian Islands. The primary minerals of the parent materials have weathered to secondary clay minerals, alumino-silicate minerals, which in turn have, with advancement of soil age, broken down into the free oxides of iron and aluminum. Kaolinite type of clay mineral appears to be the dominant alumino-silicate mineral in Hawaiian soils (6, 20).

Laterization is the dominant soil-forming process in the Hawaiian Islands. Under laterization silica is leached from the soil solum and iron and aluminum are concentrated. In the senile stages of weathering the soil clay minerals break down with one of the sesquioxides, either alumina or iron oxide, becoming stabilized and becoming the dominant oxide of the soil. Under alternating wet and dry conditions kaolinite is decomposed and silica and aluminum are leached from the soil solum with iron being stabilized as goethite and hematite. Titanium will be stabilized as anatase if present in appreciable quantities. The end-product of soil weathering under an alternating wet and dry tropical season is the heavy laterite crust of the humic ferruginous latosol. Under continuously wet conditions kaolinite is decomposed. Under these conditions silica and iron are leached from the soil solum leaving an aluminous clay which probably is bauxite. Tanada (20) found that the SiO_2/Al_2O_3 , SiO_2/Fe_2O_3 , and SiO_2/TiO_2

ratios and the kaolinite content decreases with increase in rainfall. According to Sherman (17) the same thing can happen with age of weathering. Dean (6) and Ayres (2) have reported that the C:N ratio and the organic matter content of the soil increase with rainfall.

Soil samples representing the following ten important great soil groups were studied: low humic latosol, humic ferruginous latosol, humic latosol, hydrol humic latosol, reddish prairie, brown forest, reddish brown, red desert, dark magnesium clays, and gray hydromorphic. These great soil groups have been identified by Cline et al. (5) in the soil survey report for the Hawaiian Islands.

Low humic latosols, the red soils of the Hawaiian Islands, are the best agricultural soils and on them most of the sugar cane and pineapples are grown. These soils have excellent physical properties and respond well to fertilization. The soils of low humic latosols are found at low elevations, usually from sea level to 1,500 feet. They are developed under a rainfall ranging from 15 to 80 inches per year. The A horizon of the soil profile is weak and shallow, usually less than a foot in thickness. The B horizon is from 2 to 3 feet thick and grades gradually into the C horizon. These soils have a high clay content, 50 percent or more, but have the physical properties of a silty clay loam. The dominant clay mineral of this group has been identified as the kaolinite type (6, 20).

The chemical analysis of a typical soil of the low humic latosol shows that the soil solum has a very high content of both iron and aluminum oxides. The silica-sesquioxide ratio is low, ranging from 1.2 to 1.8. One of the distinguishing characteristics of the low humic latosol is its high manganese content. The cation exchange capacity of these soils is low, ranging from 15 to 30 milliequivalents per 100 gm. The soil reaction of the virgin soils ranges from pH 6.0 to 7.5; but these soils have become very acid, pH 3.5-4.5, under cultivation because of the extensive use of ammonium sulfate as a fertilizer. The base saturation is medium in the virgin soil, but, likewise, under cultivation the base saturation has been greatly reduced. These soils have a low organic matter content as compared to other Hawaiian soils, the usual range being 2.5 to 4.0 percent. A typical chemical analysis of a soil of the low humic latosol group is given in table 2.

Humic ferruginous latosols are developed at somewhat higher elevation and under slightly higher rainfall than the low humic latosols. The annual rainfall ranges from 35 to 150 inches. These soils are usually found on slopes where there is lateral movement of water through the soil solum over an impervious layer. The color of these soils varies from a grayish-purple to a reddish-purple.

These soils are characterized by an abnormally high apparent specific gravity, resulting from an accumulation of heavy minerals in the surface horizon. The lower portion of this horizon (A_2) is hard and cemented and has the properties of the ferruginous laterite crust. The B horizon is yellowish-brown to reddish-brown, structureless, extremely friable, and has the physical properties of a silt loam in nature but contains more than 60 percent clay on mechanical analysis. The C horizon is usually an impervious nonconformity or a very plastic clay.

TABLE 2. The Chemical Analysis of Soil and Clay Fractions of a Typical Low Humic Latosol, Molokai Family.

Horizon	Depth	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	MnO	$\frac{\text{SiO}_2}{\text{R}_2\text{O}_3}$
Soil Analysis	<i>Inches</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	
A	0-8	30.4	33.8	23.8	5.2	0.34	1.05
B ₁	8-18	33.2	32.0	23.2	5.2	0.02	1.20
B ₂	18+	30.9	32.4	26.2	5.8	0.02	1.06
Clay Analysis							
A	0-8	32.2	32.2	22.8	3.2	0.26	1.17
B ₁	8-18	36.5	32.8	21.0	3.4	0.10	1.33
B ₂	18+	32.6	30.2	23.8	4.8	0.10	1.22

The humic ferruginous latosols are the most highly leached soils in Hawaii. Kaolinite has been almost completely decomposed and the silica and alumina have leached from the soil solum. Iron and titanium oxides have accumulated, the former through the entire soil solum and the latter only in the surface horizon. These soils usually contain approximately 50 percent iron oxide and 20 percent titanium oxide. The silica-sesquioxide ratios of these soils range from 0.1 to 1.1. The profound leaching of these soils cannot be entirely attributed to their present medium rainfall but may be due to one or a combination of the following factors: (1) leaching by lateral movement of water through the pervious soil solum over an impervious substratum, (2) age, and (3) higher rainfall in the past. Because of the intense leaching these soils are strongly acid, have a low base content, and a low base saturation. The *pH* of these soils ranges from 4.0 to 6.5 and the cation exchange capacity ranges from 2 to 15 milliequivalents per 100 gm. of soil. Table 3 presents a chemical analysis of a soil profile of the Naiwa family, a very old soil, and shows the composition of a soil approaching the end-point of lateritic weathering (18).

TABLE 3. Chemical Analysis of a Humic Ferruginous Latosol, Naiwa Family, a Typical Ferruginous Laterite Crust of the Hawaiian Islands. (Data from Sherman et al. (18).)

Horizon	Depth	pH	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₃	MnO	Cation Exchange Capacity	Base Saturation	SiO ₂ /R ₂ O ₃
	<i>Inches</i>		<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>m.e./100 gm.</i>	<i>Percent</i>	
A ₁	0-3	4.1	10.8	10.7	38.2	19.4	0.21	31.8	7.0	0.47
A _{2 1}	3-5	4.2	5.5	17.9	48.5	24.7	0.29	7.4	10.7	0.19
A _{2 2}	5-11	4.2	3.8	9.9	47.5	25.0	0.31	2.8	21.1	0.16
A-B	11-13	4.0	5.7	12.6	67.2	9.4	0.17	8.8	10.3	0.18
B	13-27	4.3	5.5	7.6	78.5	7.2	0.08	18.8	3.3	0.16
C	27+	4.3	22.8	21.7	35.4	3.3	0.19	18.6	3.9	0.87

TABLE 4. Chemical Analysis of Colloids of Humic Latosol, Kapoho Family, a Youthful Humic Latosol Profile. (Data from Hough, Gile, and Foster (9).)

Depth	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	MnO	SiO ₂ /R ₂ O ₃
<i>Inches</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	
0-9	22.84	26.06	16.60	2.06	0.37	1.05
9-17	23.26	26.46	17.37	2.51	0.40	1.05
17-25	24.25	27.08	18.24	2.55	0.35	1.05

The soils of humic latosols and hydrol humic latosols are developed under a heavy rainfall. The latter are formed under the heaviest rainfall in the Hawaiian Islands and the former are developed under an annual rainfall of 50 to 150 inches. The rainfall is rather evenly distributed throughout the year and thus supports a heavy vegetative cover over these soils. The organic matter content of the humic latosol ranges from 10 to 15 percent. The soils belonging to the humic latosols are found from sea level to 3,000 feet above sea level, usually on wet mountain slopes. Under the wet condition the kaolinite clay is decomposing, and because of the lack of aeration iron oxides are slowly being reduced and are leaching from the soil solum. The silica content of these soils is very low due to its removal by leaching. Under these conditions the aluminum oxide is the stable oxide of the soil. The silica-sesquioxide ratio of the humic latosol is approximately 0.5. These soils are strongly acid, pH 4.5 to 6.0, and have very low base saturation. However, the cation exchange capacity of the soil is high, approximately 45 milliequivalents per 100 gm. of soil. According to Ayres (2) a large portion of the cation exchange capacity resides in the organic matter fraction of these soils. The volume weight of the soils belonging to humic latosols is about 1.0 for soils developed on lavas and less than 1.0 for soils developed on volcanic ash.

The characteristic physical properties of the humic latosols are a granular structure in the A horizon and a clay which forms a ribbon when pressed between one's fingers. The aggregates of the A horizon are very water stable. The B horizon is made up of a reddish-brown to yellowish-red clay which is quite plastic in some of the profiles.

The soils belonging to the hydrol humic latosols are formed in the regions of the Hawaiian Islands which receive the heaviest annual rainfall, 120 to 300 inches. These soils are found at elevations ranging from 500 to 6,000 feet above sea level. The vegetation is luxuriant and similar to that of the tropical rain forest. Because of the cool, moist climate these soils have a very high organic matter content, 15 to 35 percent. The organic matter content is not detectable from any physical indications as the soil has the appearance of a relatively pure clay. The A horizon is well developed being a dark brown layer of about a foot in thickness. The B horizon is yellowish-red or brown, smeary clay and, in the wetter areas, is usually mottled. The organic matter content is high through the entire soil solum. The C horizon is usually a partially decomposed volcanic ash or explosive volcanic materials; however, many of these soils on the geologically older islands are formed on lavas. One of the peculiar properties of the hydrol humic latosol is its great shrinkage of volume upon complete drying. For this reason the volume weight of these soils is extremely low, rang-

ing from 0.1 to 1.0, and they have a tremendous water holding capacity of about 160 percent of the dry weight. These soils will not swell after complete dehydration, thus the basic crystal structure must be altered on complete dehydration.

The soils of the hydrol humic latosol are considered to be the end-products of laterization under continuously wet conditions. Under a wet climate iron is reduced and leached from the soil solum along with the silica. Aluminum oxide is the stable oxide and thus will be concentrated as bauxite or as one of the other hydrated aluminum oxides. The silica-sesquioxide ratio of these soils usually is approximately 0.4. These soils are leached of their bases and are strongly acid—pH 4.5 to 5.5. According to Ayres (2) the ultimate pH of these soils is high and most of them are at their ultimate pH or approaching it. The cation exchange capacity of these soils is very high, ranging from 50 to 60 milliequivalents per 100 gm. of soil. Again, Ayres (2) has found that as much as 90 percent of the cation exchange capacity resides in the organic matter of these soils. A typical analysis of the clay is given in table 5.

TABLE 5. Chemical Analysis of Clay of Hydrol Humic Latosol, Hilo Family
(Data from McGeorge (11).)

SiO ₂	20.35 percent
Al ₂ O ₃	47.95 percent
Fe ₂ O ₃	12.86 percent
SiO ₂ /R ₂ O ₃	0.61

The soils belonging to reddish prairie and brown forest soil groups are developed on recent volcanic ash materials on the slopes of mountain peaks of the islands of Maui and Hawaii in the regions of rainfall ranging from 25 to 100 inches per year. These soils are generally very friable and support very productive crops wherever rainfall or irrigation water is adequate.

The reddish prairie soils are formed at elevations ranging from 500 to 2,000 feet above sea level and in regions receiving an annual rainfall of 25 to 60 inches. The A horizon, which is a foot deep, is a dark friable silt loam. The B horizon is also a friable silt loam, lighter in color than the A horizon due to a much lower content of organic matter. The calcium content of these soils is high, and is reflected in a near-neutral soil reaction and a base saturation of approximately 90 percent. Calcium is the dominant cation of the exchangeable bases. These soils are peculiar in that their silica-sesquioxide ratio is low, 0.5 to 1.0; the cation exchange capacity is relatively high, 50 to 60 milliequivalents per 100 gm. of soil.

The brown forest soils have developed at high elevations, usually from 2,000 to 8,000 feet, and under higher annual rainfall, 40 to 100 inches. These soils are darker than the reddish prairie soils because of their higher content of

TABLE 6. The Chemical Composition of Typical Profiles of the Reddish Prairie and Brown Forest Soils.

Soil No.	Depth	pH	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	MnO	Cation Exchange Capacity	Base Saturation	$\frac{\text{SiO}_2}{\text{R}_2\text{O}_3}$
	<i>Inches</i>		<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>m.e./100 gm.</i>	<i>Percent</i>	
Brown Forest										
47-507	0-10	6.5	20.2	29.5	14.1	3.22	1.22	66.26	69.0	0.89
47-508	10-26	7.0	28.1	36.0	16.2	3.64	0.85	69.51	76.9	1.03
47-509	26+	6.8	25.8	33.1	21.0	4.84	0.70	63.10	69.4	0.94
Reddish Prairie										
47-510	0-6	6.4	33.72	26.41	15.62	4.41	0.74	56.98	97.2	1.58
47-511	6-12	7.0	23.98	28.63	18.20	4.81	0.48	48.58	97.6	1.02
47-512	12-24	7.4	23.46	31.20	18.20	5.02	0.45	41.59	98.2	0.93
47-513	24-38	7.7	26.00	31.81	18.05	4.84	0.39	47.16	99.8	1.02

TABLE 7. The Chemical Composition of the Soil Clays from Typical Profiles of the Reddish Prairie and Brown Forest Soils.

Soil No.	Depth	pH	Colloid in Soil	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	MnO	$\frac{\text{SiO}_2}{\text{R}_2\text{O}_3}$
	<i>Inches</i>		<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	
Brown Forest									
47-504	0-9	6.2	34.83	7.68	16.80	33.20	3.20	0.18	0.34
47-505	9-17	6.2	32.42	9.58	29.80	27.60	3.40	0.14	0.35
47-506	17+	5.7	40.27	9.54	29.0	33.40	4.40	0.10	0.32
Reddish Prairie									
47-510	0-6	6.4	56.88	15.20	29.00	23.20	3.40	0.33	0.59
47-511	6-12	7.0	43.92	17.00	41.00	21.80	4.60	0.38	0.53
47-512	12-24	7.4	42.22	17.18	32.60	29.40	4.80	0.36	0.57
47-513	24-30	7.7	23.96	17.72	30.80	20.80	4.80	0.30	0.68

organic matter. The physical and chemical properties of the brown forest and reddish prairie soils are very similar as is shown in the data presented in tables 6 and 7. Because of the higher rainfall and greater leaching, the base saturation of the brown forest soils is lower than reddish prairie and ranges from 20 to 60 percent. The brown forest soils are more acid with their soil reaction ranging from pH 4.0 to 6.0. The silica-sesquioxide ratio of the clay fraction of the brown forest soils is extremely low, 0.6, but the cation exchange capacity is very high, usually about 60 to 80 milliequivalents per 100 gm. of soil. This is an anomaly since the two factors, silica-sesquioxide ratio and cation exchange capacity, are usually directly related. This might suggest the presence of a unique type of clay in these soils.

Red desert and reddish-brown soils are found in the arid regions of the Hawaiian Islands. These soils are formed on a wide variety of volcanic materials and have weathered only slightly, thus primary minerals are abundant in these soils. The reddish-brown soils have a deeper profile since they receive a higher annual rainfall than the red desert soils.

The red desert soils have developed at elevations ranging from sea level to 2,000 feet and under a rainfall ranging from 5 to 20 inches per year. The soil is very shallow. Gypsum and calcium carbonate are found as coating on the soil granules. These soils have a neutral to alkaline reaction and a fairly high cation exchange capacity.

The reddish-brown soils are found from sea level to 3,000 feet. They have developed under an annual rainfall ranging from 20 to 50 inches. These soils do have a grass cover and thus have a higher organic matter content than the red desert but lower than the reddish prairie. These soils have a neutral reaction and are base saturated with exchangeable calcium as the dominant cation. The silica-sesquioxide ratio for these soils is approximately 3.0, which is about the highest found in the zonal soils of the islands. The typical chemical analysis is presented in tables 8 and 9.

The gray hydromorphic soils are found in the lowlands such as the floors of the mountain valleys and level lands near the ocean. The level topography, poor drainage, and the accumulation of magnesium salts are dominant factors in their development. The calcium and magnesium salts are brought into this soil in the drainage waters from the higher elevations and are accumulated in these soils. This gives rise to a very heavy plastic clay which is easily dispersed.

The soils of the dark magnesium clays have developed in very arid regions having an annual rainfall of 10 to 30 inches. These soils have a high accumulation of calcium and magnesium salts in which the latter dominates to produce magnesium salinization with the occurrence of dolomitization in small areas

TABLE 8. Chemical Analysis of a Typical Profile of Reddish-Brown Soil. From Cline, M. G. et al. (Soil Survey of the Hawaiian Islands (5).)

Sample No.	Depth	pH	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	MnO	Cation Exchange Capacity	Base Saturation	SiO ₂ /R ₂ O ₃
	<i>Inches</i>		<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>m.e./100 gm.</i>	<i>Percent</i>	
47-515	0-3	6.4	43.52	16.00	13.60	2.80	0.40	49.34	64.1	2.99
47-516	3-6	6.4	51.66	15.80	10.90	2.70	0.37	35.02	87.9	3.86
47-517	6-12	6.2	45.88	20.20	12.10	2.10	0.34	47.49	70.3	2.79
47-518	12+	6.6	38.40	23.40	15.40	3.00	0.46	55.49	94.8	1.97

TABLE 9. Chemical Analysis of Colloidal Fractions of a Typical Reddish-Brown Soil Profile. (From Hough, Gile, and Foster (9).)

Depth	pH	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	SiO ₂ /R ₂ O ₃
<i>Inches</i>		<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	
0-10	6.9	30.54	28.13	13.85	2.93	1.40
10-21	7.4	45.90	24.33	10.61	1.45	2.50
21-40	7.3	35.88	26.81	15.09	2.35	1.67

(19). When wet these soils are plastic clays and as these clays dry, wide and deep cracks will develop. These soils have a very high cation exchange capacity, 60 to 80 milliequivalents per 100 gm. of soil.

EXPERIMENTAL RESULTS

Titration curves were prepared for more than 100 soil samples representing the major great soil groups occurring in the Hawaiian Islands. The curves presented in figures 1, 2, and 3 are the typical titration curves for these soils.

The titration curves of the latosol groups are shown in figure 1. The curves for these soils indicate great variation in buffering capacities. The titration curve for the humic ferruginous latosol was made on the soil from the A₂ horizon—the ferruginous horizon—of the Naiwa family. This horizon is considered to be the ferruginous laterite crust which is the end-product of laterization under a wet-and-dry-season climate. The highly leached condition is reflected in the very low buffering capacity. On the other hand the titration curve of a soil from the Akaka family of the hydrol humic latosol group, a soil developed under 250 to 300 inches annual rainfall, shows a great buffering capacity. This soil is rich in the aluminum oxides which are probably the end-product of laterization under continuously wet conditions. While this soil has a very high organic matter content (17.62 percent) the buffering capacity is due only in part to this factor. The curves of the soils belonging to the low humic latosol and the humic latosol lie between these two extremes. The soils of the low humic latosol are weakly buffered, and the nature of the curve is similar to that found for the soils of the humic ferruginous latosol. The soils of the humic latosols have a much greater buffering capacity and possess a curve which resembles that found for the soils of the hydrol humic latosol. The titration curves for the soils of the humic ferruginous latosols and the low humic latosols show either no break or very small break in their curves, usually between pH 5.5 to 6.5; whereas the curves for the soils of the humic latosols and hydrol humic latosols develop very pronounced breaks between pH 5.0 and 6.5.

The titration curves shown in figure 2 are for soils belonging to the reddish prairie, brown forest, red desert, and reddish-brown soil groups. The curves of the soils of the reddish prairie, red desert, and reddish-brown soil groups are similar in nature and in their degree of buffering. The soils of the brown forest group have a much higher buffering capacity. All of these soils show a break in their titration curves between pH 5.0 and 6.5 and again at pH 9.0 except for the soils of the brown forest group. The clays of these soils are of the montmorillonite type, even in the soils of the reddish prairie and brown forest groups which have a very low silica-sesquioxide ratio.

In figure 3 are shown the titration curves of soils belonging to dark magnesium clays and the gray hydromorphic groups. The curves of these are similar in nature and in degree of buffering. The curves of these soils show buffering between pH 5.0 and 7.0. The soils of the Waimanalo family and the dark-colored soils of the Molokai family of the low humic latosol will exhibit curves similar to these curves. This is probably due to the fact that these soils have montmorillonite type of clay, whereas the majority of the soils belonging to the low humic latosols have a kaolinite type of clay.

The data presented in figure 4 show the titration curve of the clay fraction of certain soils. These data are presented to show if there is a difference in the nature of the titration curves between the soil and its clay fraction. In every case the titration curves are similar for the clay fraction and the whole soil. The curves for the clays show a much greater degree of buffering. The buffering of the titration curve of the clay fraction is initiated at a lower pH than that found for its soil. The greatest buffering capacity was found for the clay fraction of a soil from the dark magnesium clay group, which has the greatest content of clay of the montmorillonite type.

Since many of the soils of the Hawaiian Islands have a high organic matter content (?), it was considered possible that a part of the buffering of the titration curves might be due to the organic matter fraction. In table 10 are given data which show the organic matter content of Hawaiian soils before and after treatment with hydrogen peroxide. These soils represent Hawaiian soils which have a low, medium, and high organic matter content. The titration curves of these soils are shown in figures 5, 6, and 7. The organic matter content of the soil of the dark magnesium clay group (2.77 percent) is too low to have much effect on its buffering capacity. However, in the case of the soil of hydrol humic latosol group the reduction of the organic matter content from 17.62 percent to 1.20 percent greatly decreased the buffering capacity of the soil. The soil belonging to the reddish prairie group showed 5.66 percent organic matter content and a slight decrease in buffering with the removal of the organic matter. The results obtained from these soils have indicated that the effect of organic matter on the buffering of soils is the greatest at a soil reaction higher than pH 5.5. This agrees with the findings of Anderson and Byers (1) and Baver (3). Saeki (15) reported that humus substances in soil are more soluble in the alkaline range and are precipitated in an acid medium. Thus the higher buffering capacity in the neutral to alkaline range may be attributed to a greater dissociation of the organic compounds. However, it is evident from the titration curves in figures 5, 6, and 7 that the type of the soil clay determines the nature of the buffering curve for each soil. The titration curves for any parti-

cular soil, with or without organic matter, are quite similar, while the titration curves of the three different soils after the removal of the organic matter show no similarity to each other. Thus the removal of organic matter does not alter the general nature and character of the titration curve of the Hawaiian soils.

TABLE 10. Organic Matter Content of Soil before and after H₂O₂ Treatment.

Soil No.	Soil Type	Before H ₂ O ₂ Treatment		After H ₂ O ₂ Treatment
		Natural Soil	Washed with 0.05N HCl	
		<i>Percent</i>	<i>Percent</i>	<i>Percent</i>
49-256	Hydrol Humic Latosol	17.30	17.62	1.20
48-569	Reddish Prairie	4.99	5.66	1.27
48-571	Dark Magnesium Clay	2.78	2.77	0.74

The experimental results show that the buffering capacities of Hawaiian soils are much lower than those found for soils developed under a temperate climate. The work of Anderson and Byers (1) has shown that the soils of the podsol, gray brown podsol, chernozems, and prairie groups are highly buffered and that the titration curves of these soils exhibit a level break in the curve—a point where the clay acids are neutralized by the added base. The Hawaiian soils do not exhibit this break in their titration curves. The only Hawaiian soils having a pronounced break are those of the dark magnesium clay, gray hydromorphic, and the Waimanalo family of the low humic latosol groups. The clays of these soils are of the montmorillonite type.

The difference in the degree of buffering between the tropical and temperate zone soils is probably due to the nature of the soil clays. In general the montmorillonite type of clays is dominant in the soils of the temperate zone and kaolinite type of clay is dominant in tropical soils. The high negative charge of the montmorillonite type of clays causes greater adsorption of cations and bases, thus giving a higher buffering capacity to the soil. On the other hand, the kaolinite type of clay has a low negative charge which results in a low adsorptive capacity for cations and a low buffering capacity.

Although titration curves of Hawaiian soils vary greatly, each soil group has its own characteristic curve which appears to be as much an inherent property as cation exchange capacity, chemical composition, profile characteristics, or textural composition. Soils developed under similar environmental conditions have similar types of clay acids, and since buffering capacity is determined

by the type of clay, it is logical to believe that similar soils will have similar titration curves. For instance, soils of the low humic latosols collected from the islands of Kauai, Hawaii, and Oahu have very similar curves. The titration curves of six soil families (Molokai, Lahaina, Wahiawa, Kahana, Kohala, and Waialua) of the low humic latosol group are presented in figure 8. The buffering capacities and the general shape of the curves are similar. The titration curve of the soils of the Waimanalo family of the low humic latosol is not included in figure 8, since this soil is of minor importance and does not possess properties usually associated with the low humic latosol. The Waimanalo soils, in the authors' opinion, should be classified as a dark magnesium clay since they possess every property of that soil group.

The soils of the humic ferruginous latosols are the one exception in that their titration curves show, in most cases, a weak buffering but in a few youthful soils exhibit considerable buffering. This variation may be explained thus: the soils of this group represent the end-product of laterization under a wet and dry season climate, and hence the relative degree of decomposition of the kaolinite clay and the resulting free oxide accumulation may be the important factor responsible for this variation. The soils of this group showing the greatest iron and titanium oxide contents have the lowest degree of buffering in their titration curves.

Titration curves can be considered as a relatively definite property of the various great soil groups, and they are used as a tool for classifying and identification of soils. Puri (13), Runk (14), and Baver (3) also believe that each soil has its own characteristic titration curve. Anderson and Byers (1) have stated: "Further attention should be given to the usefulness of titration curves as a means of detecting similarities and differences in soil colloids. Perhaps no criteria thus far utilized are more satisfactory as a means for comparing the acid character of soil colloids than are titration data over a wide range of hydrogen-ion concentration. Some colloids may be similar at one pH and widely different in another range."

In Hawaiian soils, the buffering capacity does not seem to be related to either the silica-sesquioxide ratio or amount of clay in the soil. A close relationship between these factors has been reported for soils of the temperate regions (1, 3). The silica-sesquioxide ratio is generally low in Hawaiian soils because of the occurrence of lateritic weathering and low quartz content of the soil parent material, basalt. In table 11 are given the silica-sesquioxide ratios of soils of the humic ferruginous latosol and low humic latosol, two of the weakest buffered soils, as 0.7 and 1.5, respectively, and soils of the hydrol humic latosol and brown forest, the strongest buffered soils, as 0.4 and 0.3, respective-

ly. The soils of the reddish-brown group which have a medium buffering capacity have a silica-sesquioxide ratio of 3.0. Individual members of these groups vary greatly in their silica-sesquioxide ratio, but again there does not appear to be any relationship between this ratio and buffering capacity.

TABLE 11. Average Silica-Sesquioxide Ratios of Hawaiian Soils.

Soil	$\frac{\text{SiO}_2}{\text{R}_2\text{O}_3}$
Low Humic Latosol	1.5
Ferruginous Humic Latosol	0.7
Humic Latosol	0.5
Hydrol Humic Latosol	0.4
Reddish Prairie	0.5
Brown Forest	0.3
Reddish Brown	3.0
Dark Magnesium Clays	3.0
Gray Hydromorphic	2.0

In figure 9 is shown graphically the lack of a relationship between the clay content and buffering capacity of the soil. The clay content of soils 47-249 and 47-504 is approximately the same, but the former is the least buffered while the latter is strongly buffered. Soil 48-456 has the highest clay content, 60 percent, and yet its buffering capacity is about the same as that of 47-249, which has 34 percent clay.

The abnormally high Fe_2O_3 content of Hawaiian soils, ranging from 20 to 50 percent of the soil with a few as high as 75 percent, may be responsible for the lack of a relationship between the buffering capacity and the silica-sesquioxide ratio and also the clay content of the soil. Bradfield (4) has shown that the colloids of $\text{Al}(\text{OH})_3$ have a greater buffering capacity than the colloids of $\text{Fe}(\text{OH})_3$ and SiO_2 . The chemical composition of Hawaiian soils varies greatly, ranging from the extremely high Fe_2O_3 content and low SiO_2 and Al_2O_3 content of the soils of the humic ferruginous latosols to the high Al_2O_3 content and low SiO_2 and Fe_2O_3 content of the soils of the hydrol humic latosol group. Thus, it is probable that soil having a high clay content and a low silica-sesquioxide ratio may be very high in relatively inert Fe_2O_3 , as hematite, and low in Al_2O_3 , and as a result the titration curves may only show weak buffering. This would explain the weak buffering of the soils of the humic ferruginous latosol and low humic latosol groups.

Another important factor to be considered is the high content of "free oxides" in Hawaiian soils. Fujimoto et al. (8) have reported the "free oxide" content of a humic ferruginous latosol soil to be 65 percent and a "free iron oxide"

content of 52 percent. Bayer (3) has found that removal of the "free oxides" does not materially affect the titration curves. Kelley et al. (10) have found that presence of "free iron oxide" makes the silica-sesquioxide ratio less significant. It is then reasonable to assume that with such a high content of "free iron oxide" in Hawaiian soils, the silica-sesquioxide ratio would not be a significant factor.

In figure 10 is shown graphically the relationship which exists between the cation exchange capacity of the soil and the degree of buffering shown in the titration curve. There appears to be a direct relationship between the degree of buffering in the titration curve and the cation exchange capacity of the soil. The evidence gathered from the titration curves of a large number of soil samples would indicate a very positive relationship between cation exchange capacity and buffering capacity of the soil.

It is reasonable to believe that new clay types exist in Hawaii judging from the variations in buffering capacity and in the nature of the titration curves of the soils, and from the nonconformities which exist with generally accepted relationships of buffering capacity with the silica-sesquioxide ratios, and clay content. Further studies such as chemical analysis, dehydration curves, differential thermal analysis, and X-ray diffraction methods may help to identify the nature of the type of clay minerals occurring in Hawaiian soils.

SUMMARY

As a result of studying the titration curves of over 100 Hawaiian soil samples the following conclusions appear to be justified:

1. The buffering capacity of Hawaiian soils is much lower than that of soils of the temperate climate regions.
2. The buffering capacity of the great soil groups varies greatly between each group. The soils of the low humic latosols and humic ferruginous latosols are the least buffered, and the soils of the hydrol humic latosol and brown forest groups exhibit the greatest buffering.
3. The organic matter of the soil affects the degree of buffering in a soil reaction above pH 5.5. It is most "active" in neutral and alkaline portions of the titration curves. However, the nature of the soil clay determines the character of the titration curve.
4. The silica-sesquioxide ratio of the soil and clay fraction is not related to the buffering capacity of the soil.
5. The clay content of the soil does not influence the degree of buffering of the soil.
6. Neither the silica-sesquioxide ratio nor the clay content of the soil has the same significance in Hawaiian soils that it does in soils of temperate regions.

This may be due to the high content of Fe_2O_3 and "free oxides" found in Hawaiian soils.

7. There is a direct relationship between the cation exchange capacity of the soil and its buffering capacity. The higher the cation exchange capacity the greater will be the buffering capacity of the soil.

8. Each soil group has a characteristic titration curve. Thus the nature of the clay minerals determines the nature of the titration curve and the degree of buffering exhibited by the soil.

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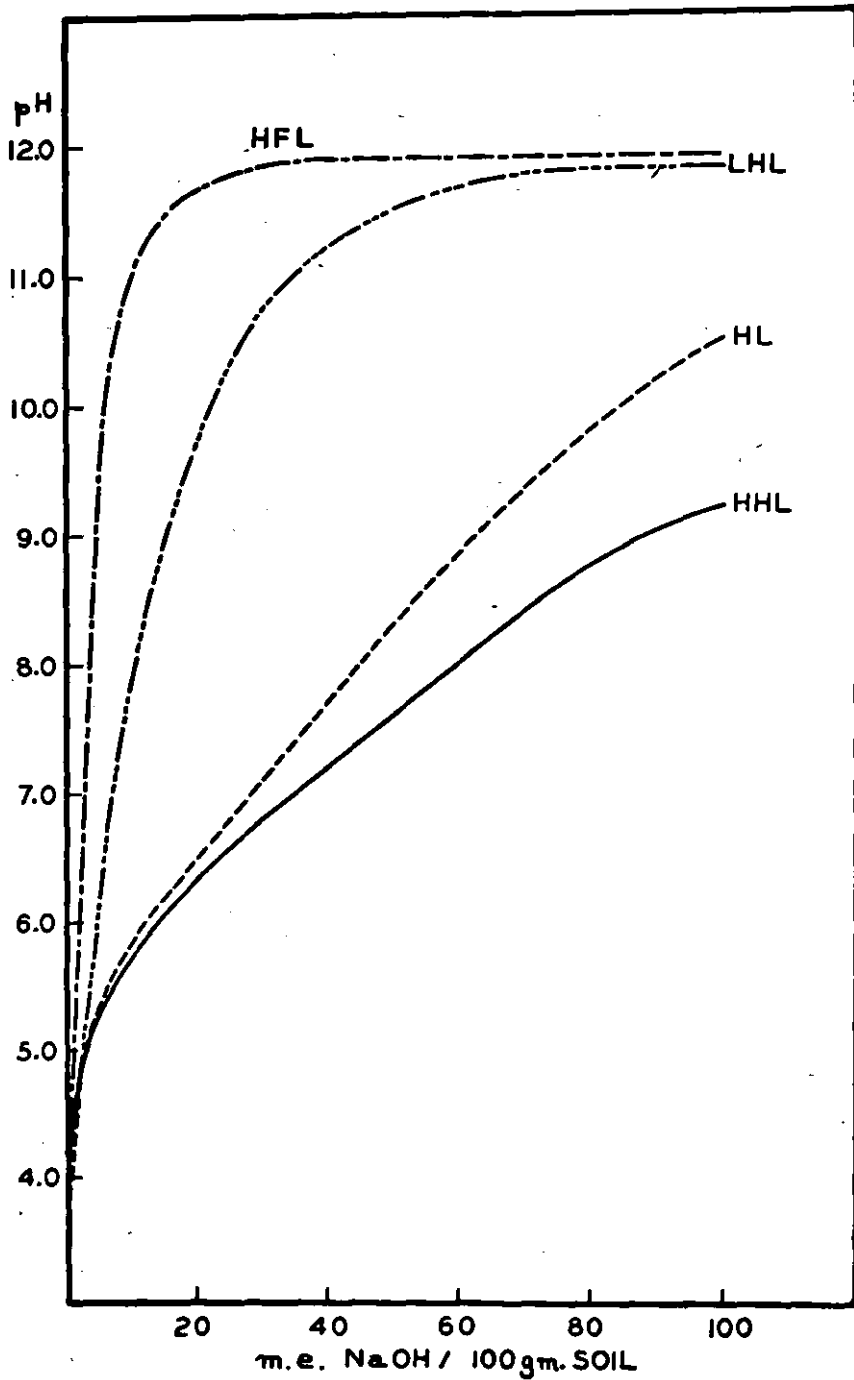


FIG. 1. Typical titration curves of soils belonging to the latosol group: HFL=humic ferruginous latosol; LHL=low humic latosol; HL=humic latosol; and HHL=hydrol humic latosol.

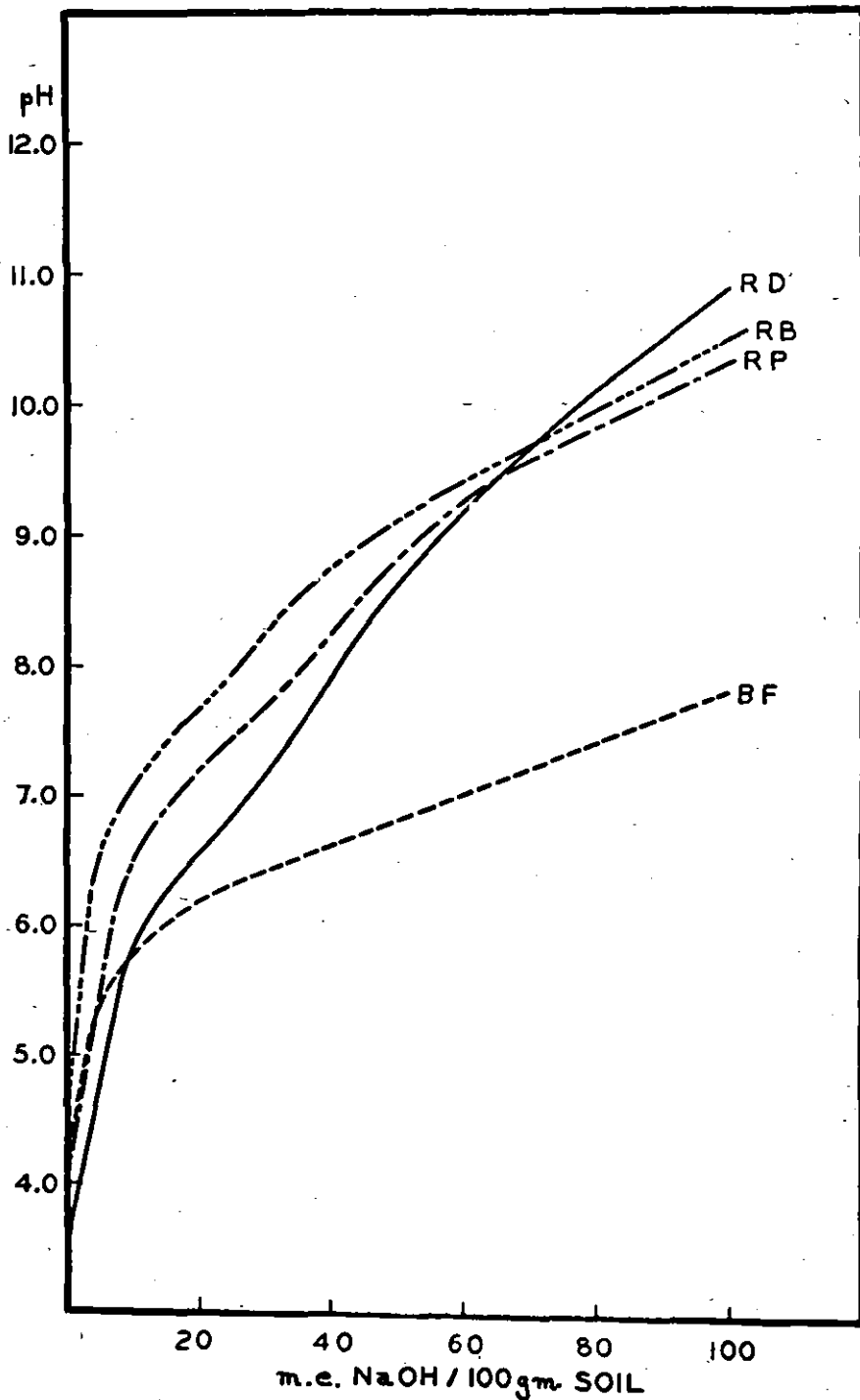


FIG. 2. Typical titration curves of soils belonging to the younger zonal soils: RD=red desert; RB=reddish-brown; RP=reddish prairie; and BF=brown forest.

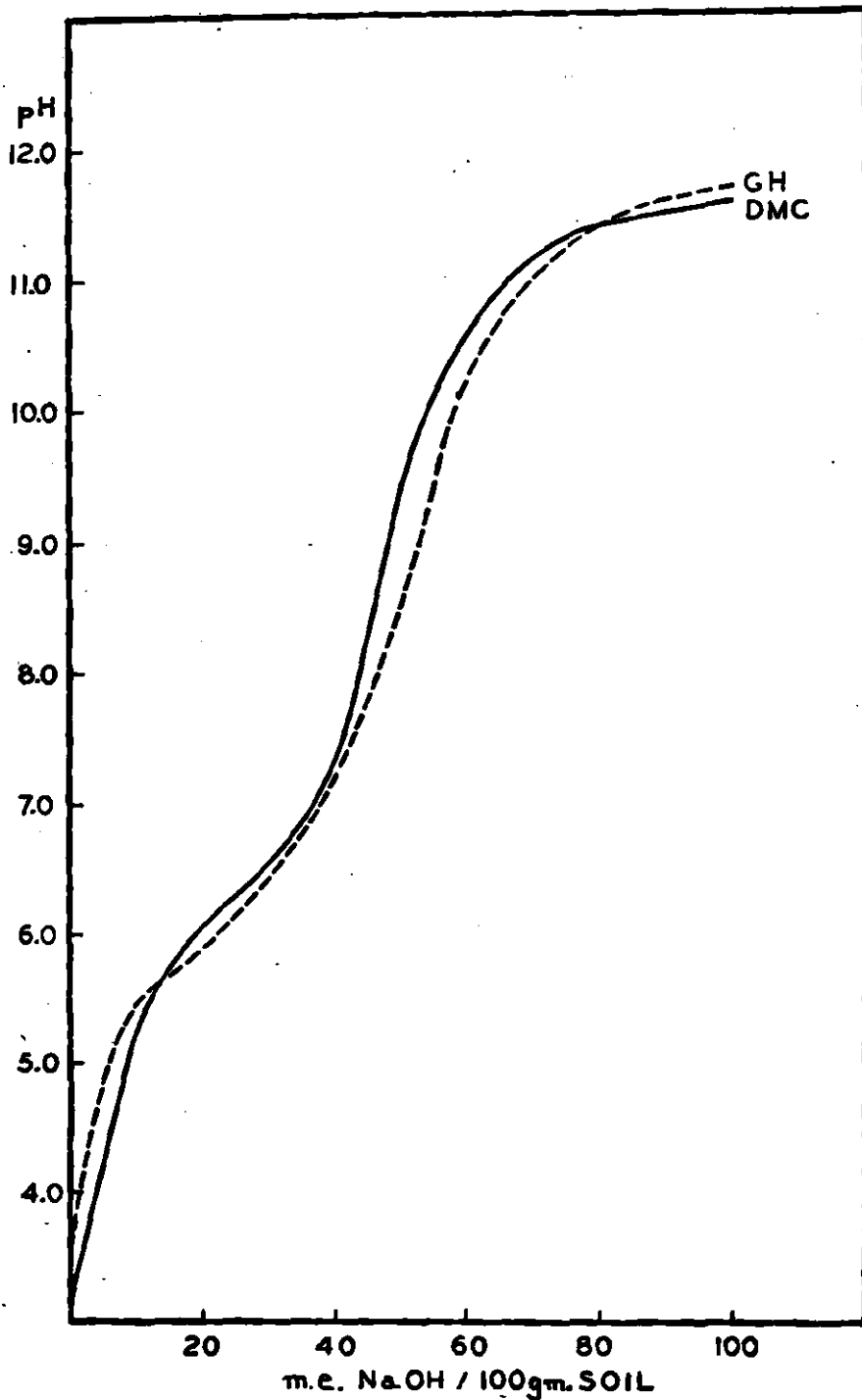


FIG 3. Typical titration curves of soils belonging to the intrazonal magnesium groups: GH=gray hydromorphic and DMC=dark magnesium clays.

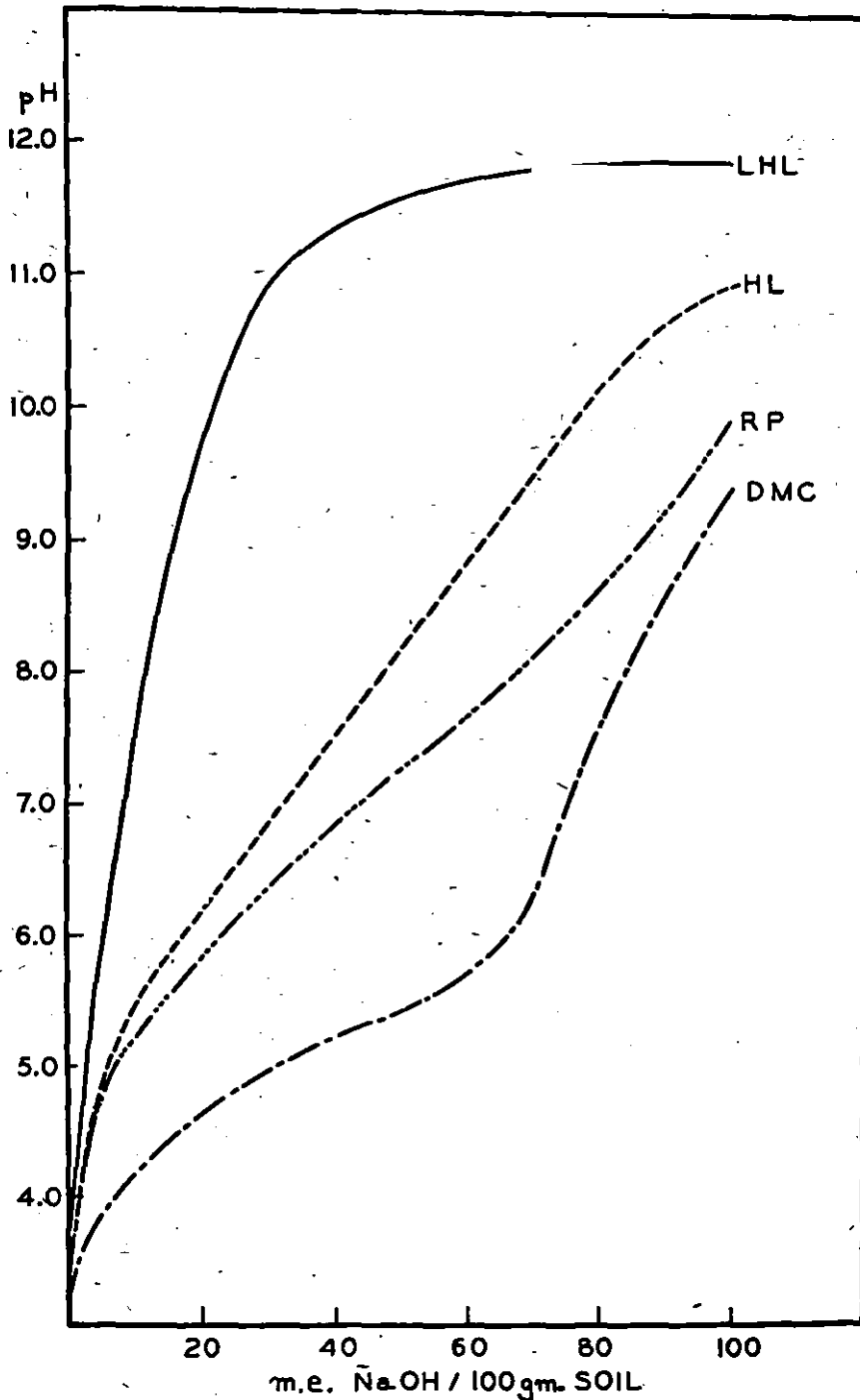


FIG. 4. Typical titration curves of soil clays: LHL=low humic latosol; HL=humic latosol; RP=reddish prairie; and DMC=dark magnesium clays.

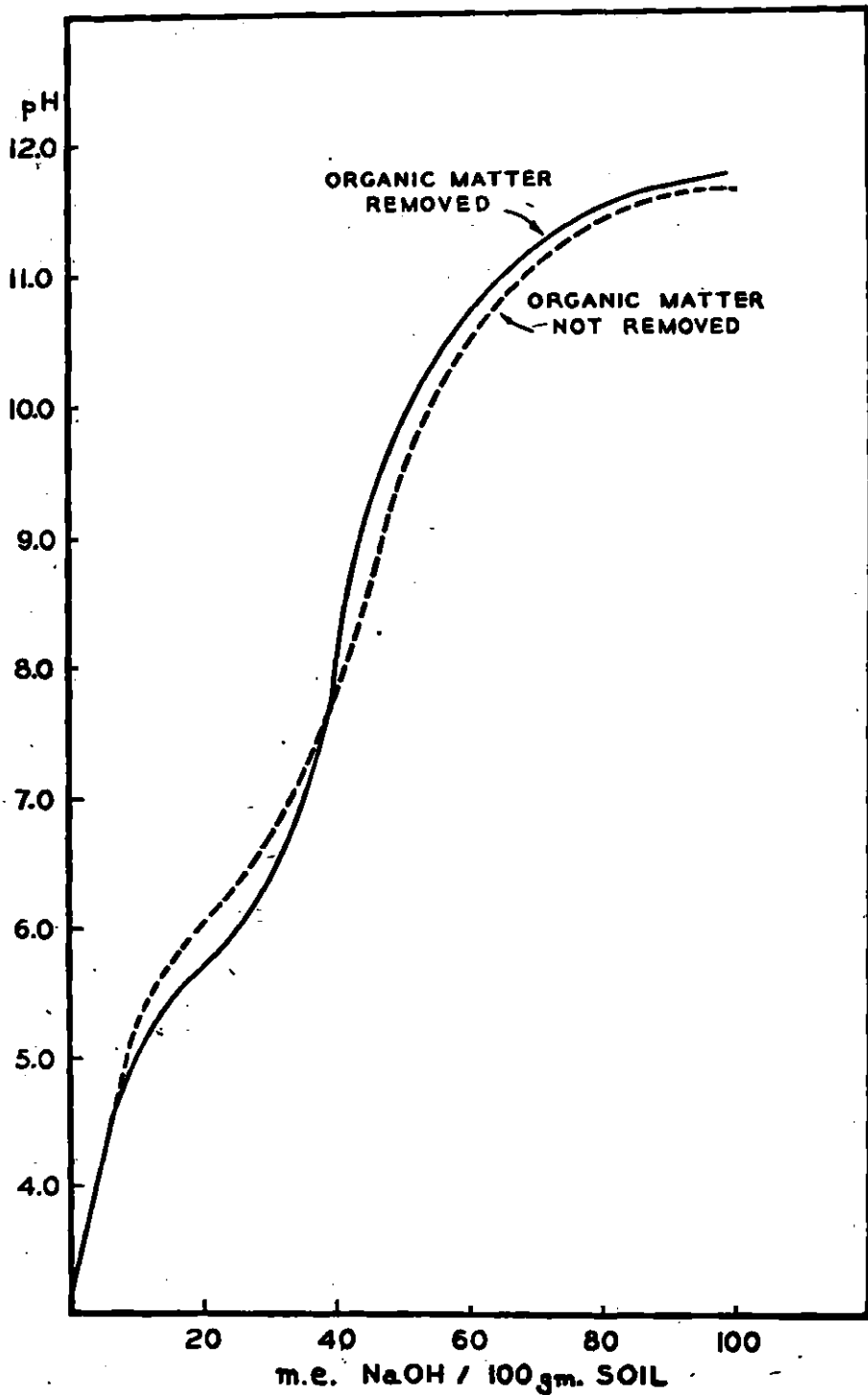


FIG. 5. Titration curves of a soil of the dark magnesium clay group, showing no effect of organic matter on the buffering capacity.

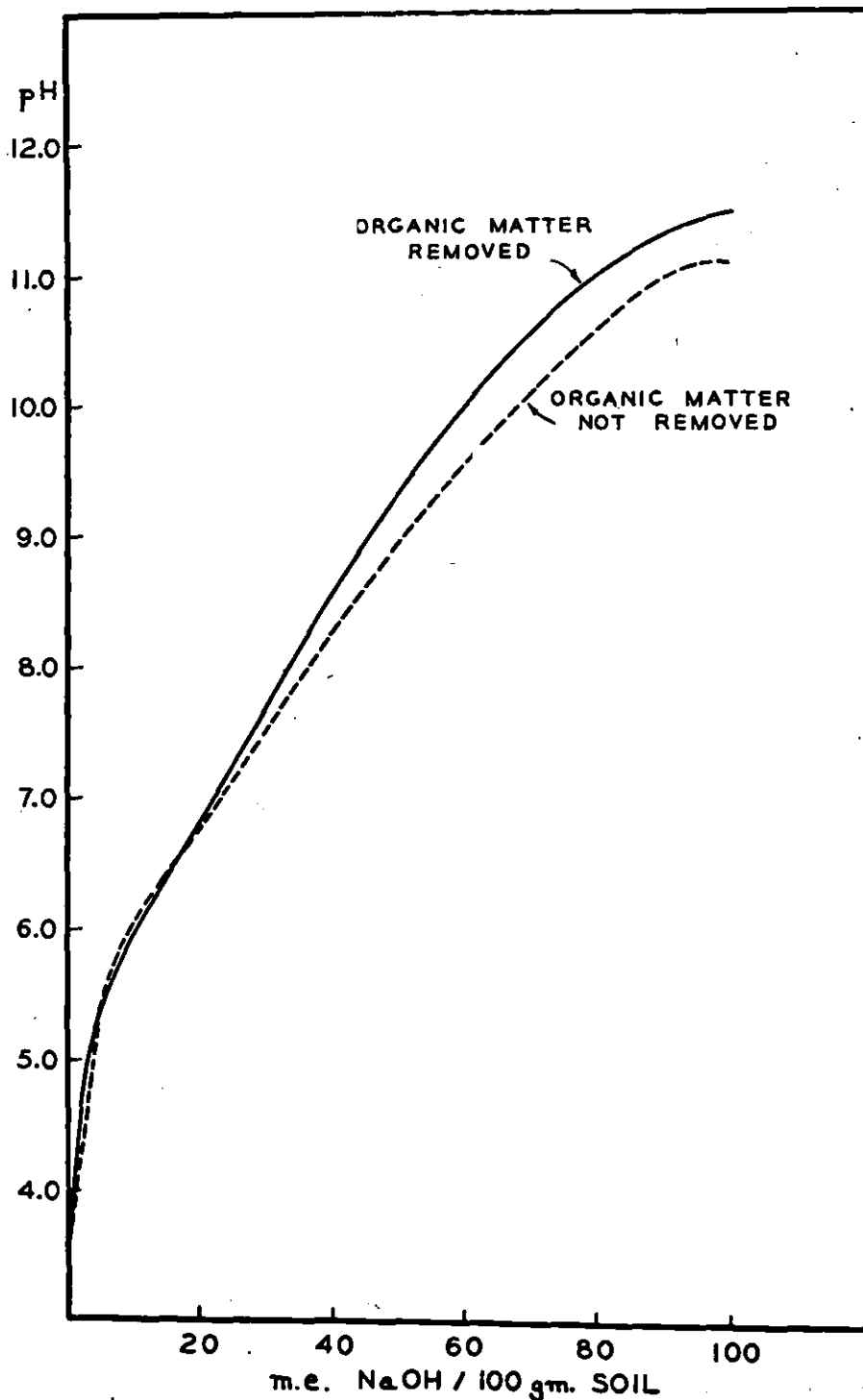


FIG. 6. Titration curves of a soil of the reddish prairie group, showing slight effect of organic matter on the buffering capacity.

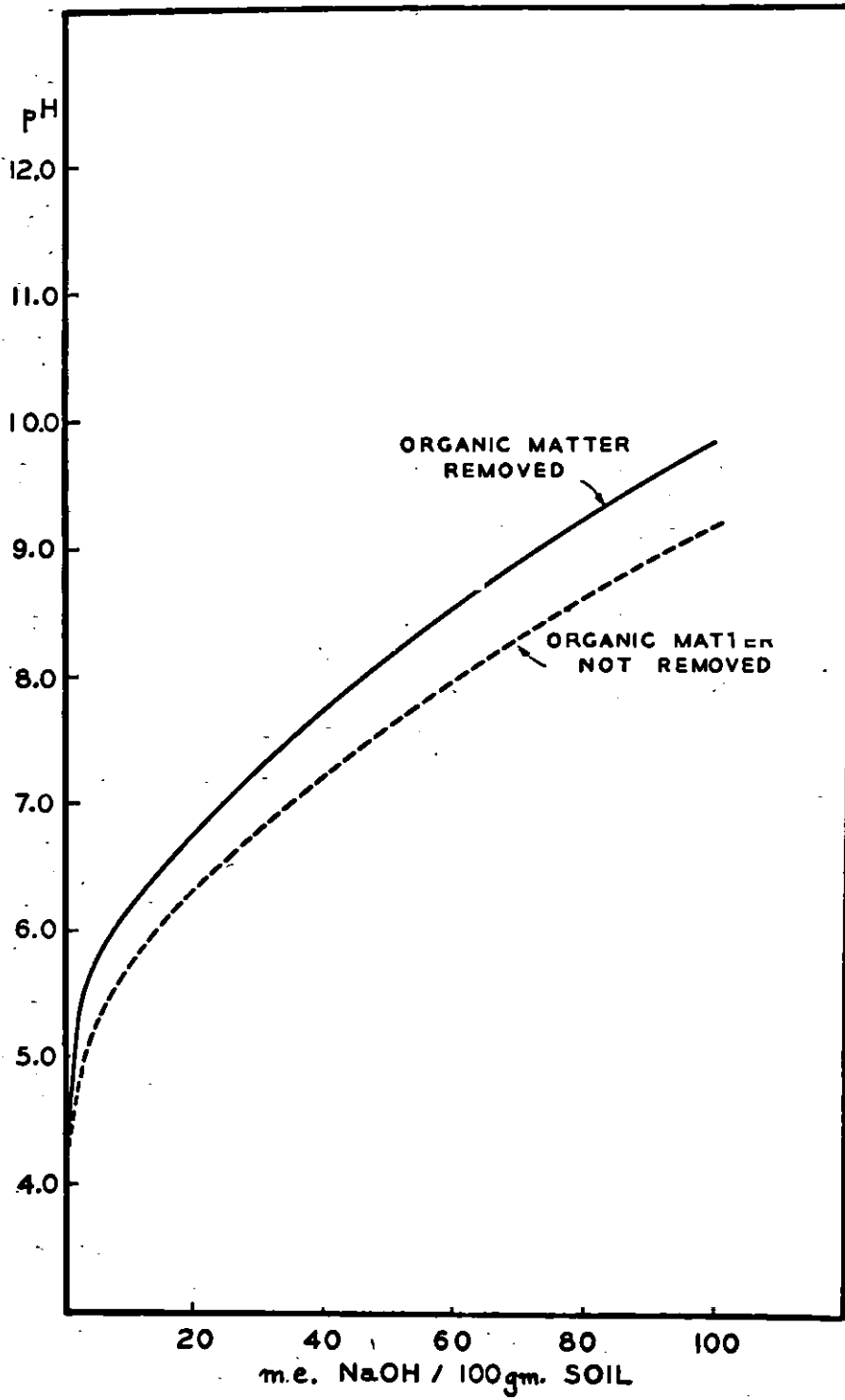


FIG. 7. Titration curves of a soil of the hydrol humic latosol group, showing the effect of organic matter on the buffering capacity.

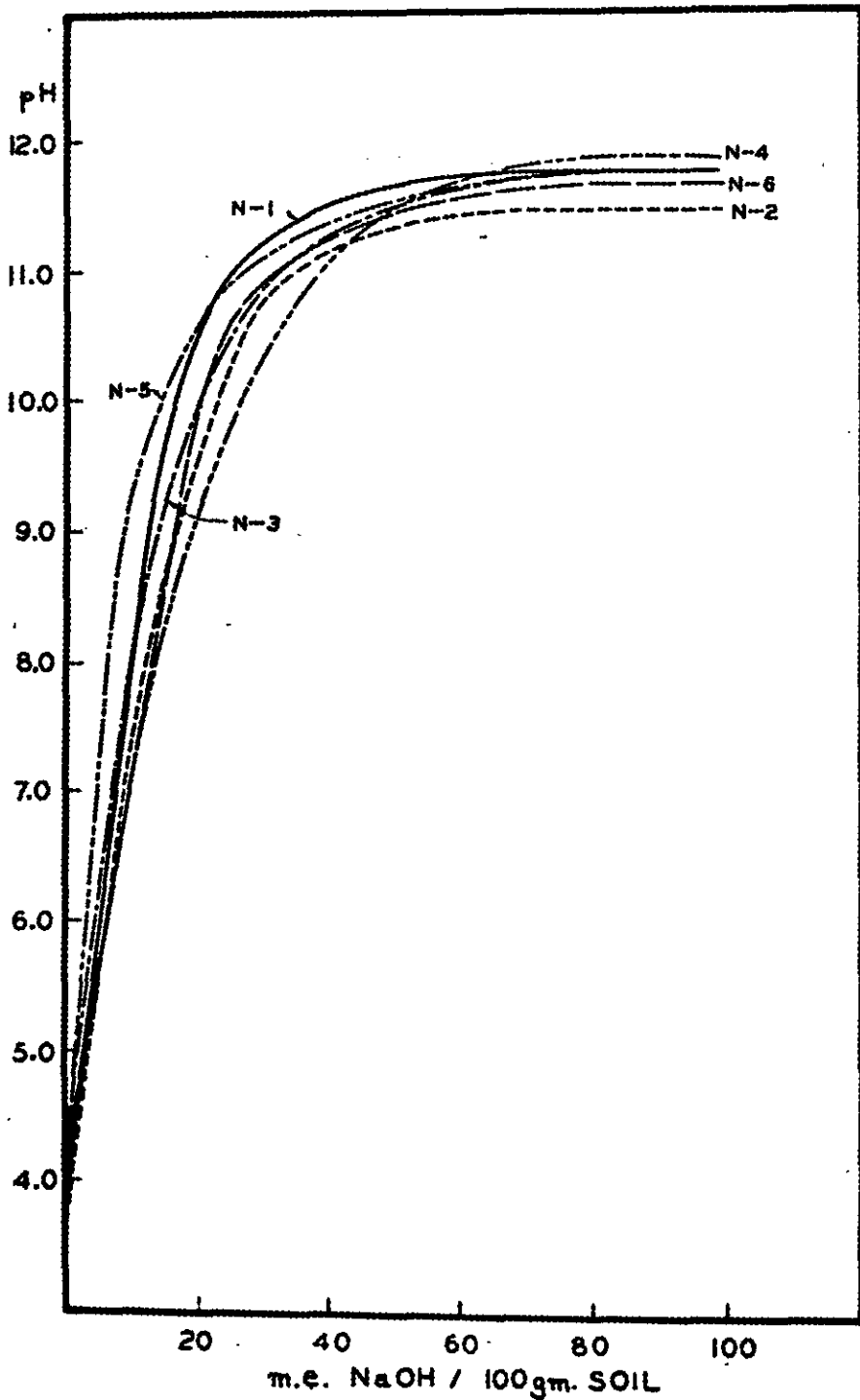


FIG. 8. Typical titration curves of soils from soil families of the low humic latosol group: N-1=Molokai family; N-2=Lahaina family; N-3=Wahiawa family; N-4=Kahana family; N-5=Kohala family; and N-6=Waialua family.

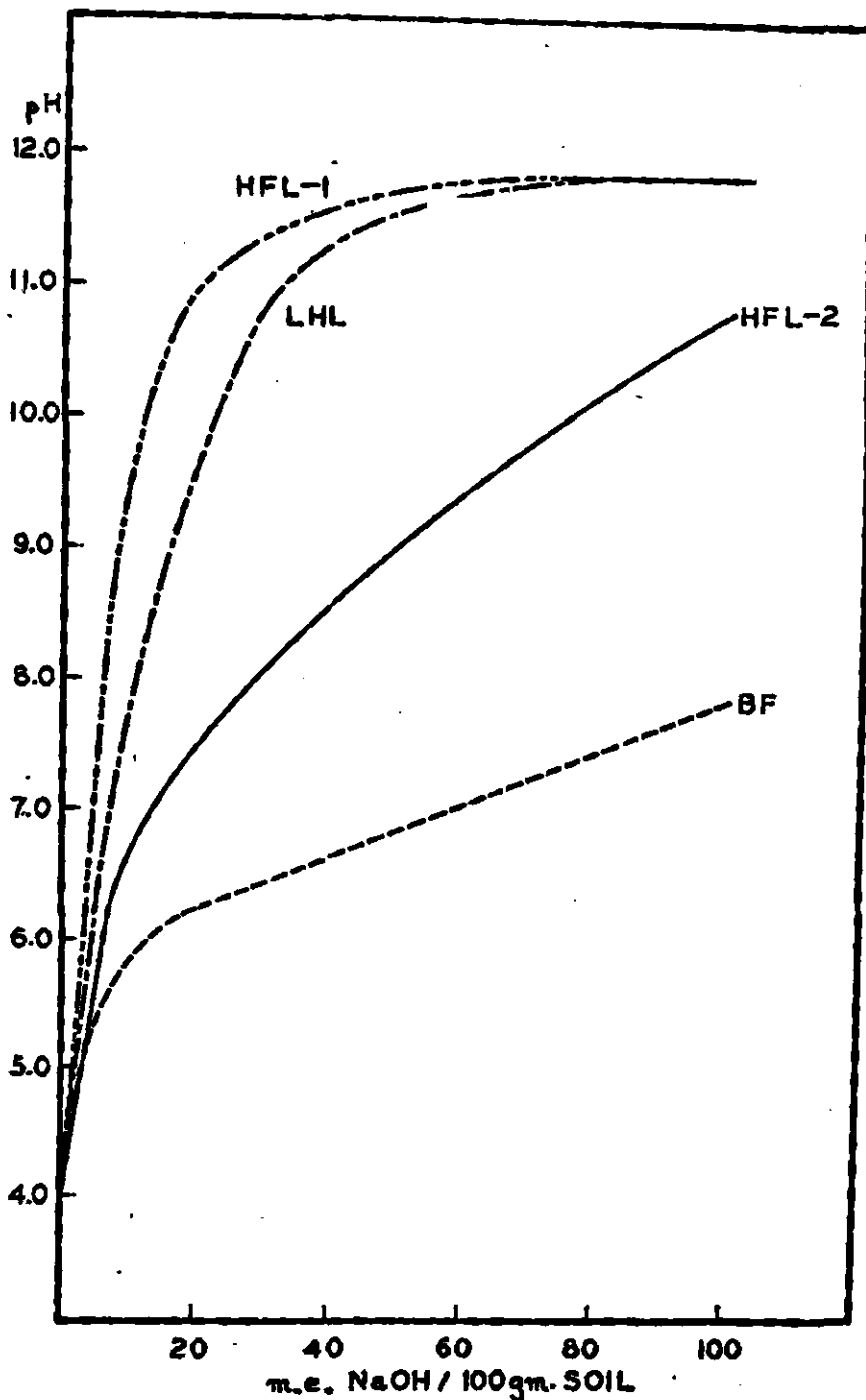


FIG. 9. Titration curves of soils showing lack of relationship between clay content and buffering capacity: HFL-1=humic ferruginous latosol, soil no. 47-249, 34.34 percent clay content; LHL=low humic latosol, soil no. 48-456, 60.00 percent clay content; HFL-2=humic ferruginous latosol, soil no. 47-251, 53.34 percent clay content; and BF=brown forest, soil no. 47-504, 34.83 percent clay content.

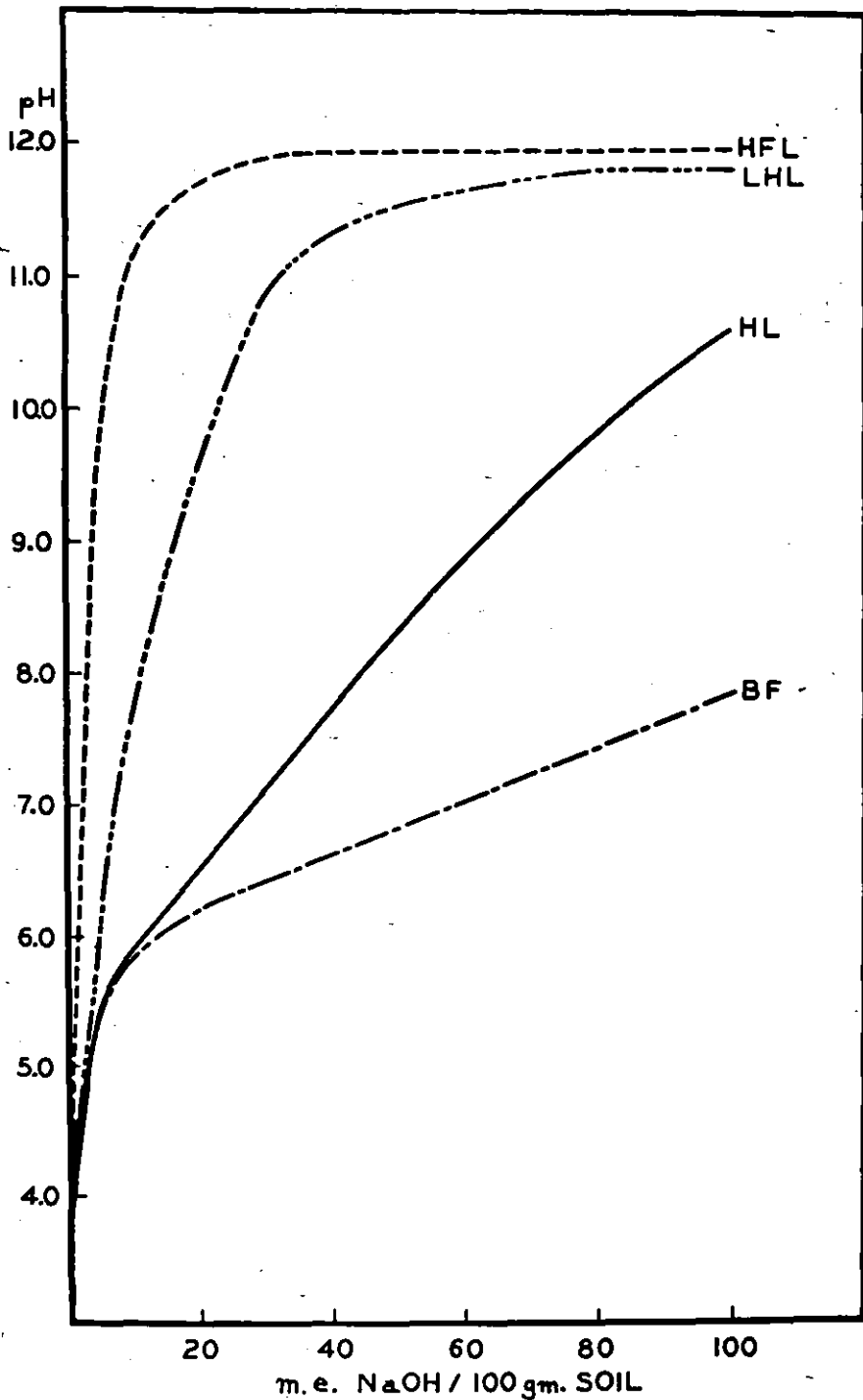


FIG. 10. Titration curves of soils showing close relationship between cation exchange capacity and buffering capacity: HFL=humic ferruginous latosol, 2.89 m.e./100 gm.; LHL=low humic latosol, 14.18 m.e./100 gm.; HL=humic latosol, 45.08 m.e./100 gm.; and BF=brown forest, 89.21 m.e./100 gm.

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