Structural stability, pore size distribution and surface charge properties of clay soils with varying mineralogy and organic matter content[1]

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ABSTRACT

This study evaluated interactive effects of mineralogy and organic matter content on chemical and physical properties of clay soils. Measurements were taken at different depths in four soil profiles characterized by oxidic, kaolinitic, mixed and montmorillonitic clay mineralogies, respectively. Within a given profile, organic carbon content varied more or less continuously with depth, whereas texture and mineralogy remained relatively constant. Thus in this study the combined effects of organic matter content and clay mineralogy could be evaluated in various combinations while texture remained constant. Resistance of soil aggregates to slaking by water was related primarily to soil organic matter content, with relatively minor differences attributable to mineralogy except in the oxidic soil where oxides seemed to exert an important stabilizing effect. Organic matter was associated with an increase in water-holding capacity both in the inter-aggregate pore space (0 to -0.33 bar moisture retention range) and intra-aggregate porosity (-0.33 to -0.8 bar retention range). The enhancing effect of organic matter on intra-aggregate porosity seemed most prominent in the soils with oxidic and kaolinitic mineralogies, suggesting the importance of organic matter for maximizing plant-available water retention in these soils. For all soils and depths, pore-size distributions within the 0 to -0.33 bar moisture retention range were log-normally distributed, with the geometric mean pore diameter and log standard deviation practically constant. These results implied that although the total 0 to -0.33 bar porosity varied strongly (primarily with organic matter content), the relative pore size distributions were all similar. In agreement with other studies in the

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literature, effective cation exchange capacity (ECEC) increased and the zero point of charge (ZPC) of the variable charge complex decreased as organic matter increased, and as clay mineralogy varied in the order oxidic → kaolinitic → mixed → montmorillonitic. Results of this study highlight the importance of managing organic matter for optimizing physical and chemical properties in soils, particularly those dominated by variable charge minerals.

RESUMEN

Estabilidad estructural, distribucion de tamaño de poros y propiedades electroquímicas de suelos arcillosos de doferemtes mineralogías y contenidos de materia orgánica

En un estudio para evaluar los efectos interactivos de la mineralogía y la materia orgánica sobre las propiedades químicas y físicas de los suelos arcillosos, se tomaron medidas a varias profundidades en cuatro perfiles de suelos de mineralogía oxídica, caolinítica, mixta y montmorilonítica, respectivamente. En cada perfil el contenido de materia orgánica varió con la profundidad; la mineralogía y la textura se mantuvieron constantes. Estas condiciones permitieron evaluar los efectos combinados de la mineralogía y la materia orgánica bajo condiciones de textura constante. Se encontró que la estabilidad de los agregados bajo el agua correlacionó principalmente con el contenido de carbono orgánico del suelo; se observó una influencia relativamente pequeña la mineralogía excepto en el suelo oxídico donde posiblemente hubo cementación por oxidos.

Conjuntante con un aumento en la materia orgánica del suelo, se observó un aumento en la capacidad retención de agua del suelo en los intervalos de potencial matrical entre 0 y -0.33 bares (0 y -33 kPa) y -0.33 y -0.8 bares (-33 y -80 kPa). El efecto de la materia orgánica sobre la retención de agua en el último intervalo fue mas notorio en los suelos de mineralogía oxídica y caolínitica. En todos los suelos y horizontes la distribución de tamaño de poros en la región entre 0 y -0.33 bares de potencial matrical era de tipo logarítmico-normal. Se observó practicamente la misma media geométrica y la misma desviación estádar en cada suelo. Los datos implican una similitud entre suelos, en el sentido que el espacio poroso atribuible a los poros de un tamaño dado, en proporción a la porosidad total entre 0 y -0.33 bares de potencial matrical, siempre fue el mismo. La diferencia principal entre los suelos fue la porosidad total entre 0 y -0.33 bares, lo cual dependió en gran manera del contenido de materia orgánica del suelo. Concorde con otros estudios en la literatura, se observó un aumento en la capacidad efectiva de intercambio catiónico y una disminución del pH correspondiente al punto isoeléctrico, según aumentaba la materia orgánica y según la mineralogía cambiaba en la secuencia oxídica → caolinítica → mixta → montmorilonítica.

Los resultados de estudio destacan la importancia del manejo de la materia orgánica para optimizar las propiedades químicas y físicas de los suelos, particularmente en suelos altamente meteorizados.

INTRODUCTION

Soil characterization work in Puerto Rico and other areas of the tropics has shown a wide variability in the mineralogy of tropical soils (3, 20). These differences in mineralogy are known to have a pronounced effect on soil chemical and physical properties (18, 22). However, mineralogical effects can be masked by differences in soil texture and organic matter content. Thus, studies on effect of mineralogy on soil chemical and physical properties should be conducted under conditions where soil texture and organic matter are controlled, or which allow evaluation of their effects. One possible means of conducting such a study would be to choose several similar-textured soil profiles which vary among themselves in mineralogy, but possess a relatively uniform mineralogical composition of their own over a considerable depth range in any given profile. This method would 1) minimize soil texture as a variable by maintaining relatively constant texture for all soils and depths; 2) treat mineralogy as a constant for any given profile; and 3) treat organic matter content as a depth-related variable in all profiles. Under such a system, soil mineralogy and organic matter content can be treated as independent variables with texture as a constant.

Following this rationale, the present study proposed to evaluate the effects of soil mineralogy and organic matter content on chemical and physical properties of Puerto Rican soils with similar clayey texture.

MATERIALS AND METHODS

Soils studied

Measurements were made in three pedogenic horizons in each of four clay soils. The soils studied were Fraternidad clay (Udic Chromusterts; very fine, montmorillonitic, isohyperthermic); Corozal clay (Aquic tropudults; clayey, mixed, isohyperthermic); Daguey clay (Orthoxic Tropohumults; clayey, kaolinitic, isohyperthermic); and Nipe clay (Typic Acrorthox; clayey, oxidic, isohyperthermic). Table 1 lists the soils and their respective sampled horizons, together with their classifications according to Soil Taxonomy and locations of the sampling areas. Detailed profile descriptions and mineralogical data for the Corozal, Dagüey and Nipe soil profiles have been obtained by Beinroth (4) and Jones et. al. (12). Profile descriptions and mineralogical data for the Fraternidad series can be found in Soil Survey sources (20). Table 2 shows data on bulk density of undisturbed cores, particle density and particle size distribution for the different soils and horizons.

The soils appeared to have been uncultivated for at least several years before sampling. Thus recent mechanical disturbance of the Ap horizon was not a major factor to be taken into account in explaining soil physical properties. All locations were under grass vegetation at the time of sampling.

Field sampling procedures

Undisturbed soil cores 3 cm long and 5.4 cm in diameter were taken from each horizon with a Uhland-type core sampler. In the case of the

TABLE 1.—*Soil samples and their locations*

Soil series	Classification	Horizon	Depth	Location
			cm	
Fraternidad[1]	Udic Chromustert; very	A_1	0-20	Lajas municipality,
	fine, montmorillonitic,	A_2	20-40	Lajas Valley
	isohyperthermic.	C_1	40-60	Agr. Exp. Substation
Corozal	Aquic Tropudults; clayey,	Ap	0-14	Corozal municipality,
	mixed, isohyperthermic.	$B_{21}t$	14-2	Barrio Padilla
		$B_{22}t$	28-55	Agr. Exp. Substation
Daguey	Orthoxic Tropohumults;	A	0-10	Aguas Buenas municipality,
	clayey, kaolinitic,	$B_{21}t$	10-30	Barrio Bayamoncito, Approximately 1 km E of km 3
	isohyperthermic	$B_{22}t$	30-60	on highway PR 791.
Nipe	Typic Acrorthox; clayey,	A_1	0-25	Mayagüez municipality,
	Oxidic, isohyperthermic	B_1	25-40	Barrio Quebrada Grande,
		B_{21}	40-70	40 m S of km 5.45 on highway PR 349.

[1] The A horizon of Fraternidad soil appeared to be very uniform all the way down to the C horizon. Consequently the sub-division into A_1 and A_2 horizons was only arbitrary.

Faternidad soil, cores 6.25 cm long and 6.0 cm in diameter were taken. About 5 kg of large clods were also obtained from each horizon. We were careful to avoid excessive stresses with the sampling instrument which would cause plastic deformation of the clods. All samples were sealed in plastic bags and stored in a refrigerator at 15° C.

Aggregate analysis

A modification of Yoder's wet sieving method was used (24). Field clods were allowed to dry to the point where they could be fragmented by hand without inducing plastic deformation. The clods were then gently crushed by hand, and the fraction passing through a 4-mesh sieve was kept for analysis. The extreme plasticity of the montmorillonitic Fraternidad soil made it necessary to air-dry the soil completely before it could be fractured without plastic deformation. The resulting clods were so hard that they had to be sharply shattered with a pestle to obtain "aggregates." In this case only the 4- to 10-mesh size fraction was retained for analysis. All samples were placed on a large cloth or sheet of paper and mixed in such a way that a spatially uniform distribution of different sized aggregates was obtained. Six 30-gram samples were weighed out on filter papers and divided into two groups of three, each of which received one of the following treatments; a) air-drying for 3 weeks or b)

TABLE 2.—*General physical data for the soils studied*

Soil	Horizon	Bulk density	Particle density H_2O_2-treated	Particle-size distribution Sand (0.02 mm)	Silt (0.02-0.002 mm)	Clay (<0.002 mm)
		g/cm³	*g/cm³*		%	
Nipe	A	1.01	3.15	5	23	72
	B_1	1.03	3.21	11	25	64
	B_{21}	1.46	3.16	9	24	67
Dagüey	A	0.93	2.85	17	13	70
	$B_{21}t$	1.09	2.89	6	17	77
	B_{22}	1.11	2.87	7	19	74
Corozal	Ap	1.04	2.77	16	20	64
	$B_{21}t$	1.04	2.76	8	16	76
	$B_{22}t$	1.15	2.78	10	17	73
Fraternidad	A_1	1.34	--	27	22	51
	A_2	1.29	2.78	27	25	48
	C_1	1.31	2.78	22	17	61

wetting for 24 hours under 3 cm of tension (H_2O) on a saturated ceramic plate which had an air-entry value of about -1.4 bars. The latter treatment was intended to allow very slow wetting of the aggregates so as to minimize slaking by water. Immediately after these treatments, the aggregate samples were placed on top of a nest of sieves, wet by capillary rise for 10 min and agitated in water for 30 min at a rate of 30 cycles per minute. The sieving system varied from Yoder's method (24) in that the sieve nest was held stationary in a water-filled tank which was mechanically raised and lowered at the desired rate, rather than raising and lowering the sieve nest in a stationary water tank. At the end of the sieving period, the amount of sample retained on each of the 1.7, 0.85, 0.37, 0.25 and 0.15 mm sieves in the nest was oven-dried at 105°C for at least 8 hours and weighed. The oven-dry weight of the initial (unsieved) samples was obtained by drying parallel unsieved samples in an oven at 105°C.

Moisture release characteristics

Moisture desorption in the 0 to -1 bar range was determined on undisturbed soil cores placed in Tempe cells (15). Because of their large size, the Fraternidad cores could not be fitted into Tempe cells so instead were placed on an ordinary pressure plate. Samples were saturated from the bottom at zero tension for at least 24 hours before desorption.

Moisture release in the 0 to -0.1 range was carried out by means of hanging water columns connected to the Tempe cells and pressure plate. A well-regulated air or nitrogen pressure source connected in parallel to a mercury nanometer was used in the -0.1 to -1 bar region. Desorption in the -1 to -15 bar region was carried out on disturbed samples in a pressure plate apparatus (16). However, systematic errors in weighing procedures for the latter samples were discovered after all measurements had been made. As a result all moisture determinations in the -1 to -15 bar range had to be discarded.

Other physical and chemical analysis

Bulk density was determined by measuring the volume and oven-dry weight of the same undisturbed soil cores used for measuring moisture retention in the 0 to -1 bar range.

Particle density was determined by the pycnometer method, in < 10-mesh soil samples which had been treated with $H_2 O_2$ to remove organic matter (21). The method used was similar to that described by Blake (5), except that the solid material in the pycnometer was removed, oven-dried and weighed directly rather than estimating its mass from a parallel sample.

Texture was determined by the pipette method (7). About 15 g of $<$ 10-mesh soil were treated with H_2O_2 to remove organic matter, and 180 ml of a solution containing 0.2 meq of NaOH and 0.4 g of sodium hexametaphosphate $[(NaPO_3)_6]$ was added. Ihe NaOH was included because of its effect of increasing surface potential and thus dispersion of oxide-containing soils. The mixture was dispersed for 14 hours in a reciprocating shaker and taken to 1,000 ml with distilled water in a graduated cylinder for analysis by the pipette method. Sedimentation times were calculated from Stokes' Law using measured particle density values rather than the commonly assumed density of 2.65 g/cm^3.

Organic carbon content was determined by the Walkely-Black wet combustion method (2).

Cation exchange capacity was determined by the 1*N*, pH 7.0 buffered ammonium acetate method (21), and exchangeable Ca^{+2}, Mg^{+2} and K^+ in the leachate were determined by atomic adsorption spectrometry (11). KCl-extractable H^+ and Al^{+3} were determined volumetrically as described by McLean (13).

Zero point of charge (ZPC) determinations were made by a modification of the method of Van Raij and Peech (23). The method used was very similar to that of Van Raij and Peech, except that the soils were not washed with dilute acid before the analysis. All acid or base added to the soil suspension was assumed absorbed to the soil as long as the equilibrium pH lay between 3 and 9. Soils were equilibrated for 4 days at 25° C prior to measuring suspension pH, and were stirred twice daily. The salt concentrations were 0.1, 0.01 and 0.001*N* NaCl.

RESULTS AND DISCUSSION

Aggregate analysis

The different-sized aggregates obtained by wet-sieving were analyzed according to the log-probability method proposed by Gardner (8), in which aggregate diameter is plotted on the log axis of log-probability paper, and the cumulative fraction of aggregates larger than the given diameter is plotted on the Gaussian probability axis. The aggregate diameter corresponding to the 50% cumulative probability is the geometric mean diameter of the aggregate population. The log standard deviation of the population is calculated as the ratio of the diameter at 84.1% cumulative probability to the geometric mean diameter, or the ratio of the geometric mean diameter to the diameter at 15.9% cumulative probability. Table 3 summarizes the geometric mean diameters and log standard deviations obtained by this technique for the air-dried and pre-wet soil samples.

In order to quantify the stability of aggregates under wetting, the

TABLE 3.—*Results of aggregate analysis*

Soil	Horizon	Geometric mean diameter		Log standard deviation		Aggregates retained on 1.7 mm. sieve	
		Pre-wet samples	Air-dried samples	Pre-wet samples	Air-dried samples	Pre-wet samples (a)	Air-dried samples (b)
		mm				%	
Nipe	A	2.15	1.65	0.20	0.44	51.2	45.8
	B_1	1.36	1.21	0.34	0.54	41.6	29.0
	B_{21}	1.15	1.00	0.34	0.50	31.6	18.7
Dagüey	A	1.91	1.55	0.32	0.41	45.4	40.9
	B_{21}t	1.68	0.53	0.37	0.38	43.3	11.7
	b_{22}	1.49	0.31	0.44	0.41	41.2	3.2
Corozal	Ap	2.35	1.48	0.23	0.20	54.1	44.0
	B_{21}t	2.27	0.62	0.33	0.26	54.2	22.1
	B_{22}t	2.55	0.34	0.30	0.32	56.3	7.9
Fraternidad	A_1	1.31	0.65	0.35	0.41	33.7	10.3
	A_2	1.43	0.74	0.36	0.39	36.5	15.3
	C_1	--	--	--	--	92.9	14.3

geometric mean diameters obtained by rapid wetting were divided by the corresponding geometric mean diameters obtained in the slow wetting experiments. This "stability ratio" was considered a better index of aggregate stability than either of the individual geometric mean diameters obtained by rapid or slow wetting, since taking the ratio of geometric mean diameters would cancel out many of the effects of the initial aggregate-size distribution.

Figure 1 shows the stability ratio plotted as a function of soil organic carbon content. A strong linear relationship exists for the Fraternidad, Corozal and Dagüey soils, showing an increase of about 0.2 in the aggregate stability ratio for every 1% increase in organic carbon. In contrast, the stability ratio for the Nipe soil remained relatively constant, suggesting that organic carbon content in this soil played a relatively small role in determining aggregate stability in water. These results suggest that,

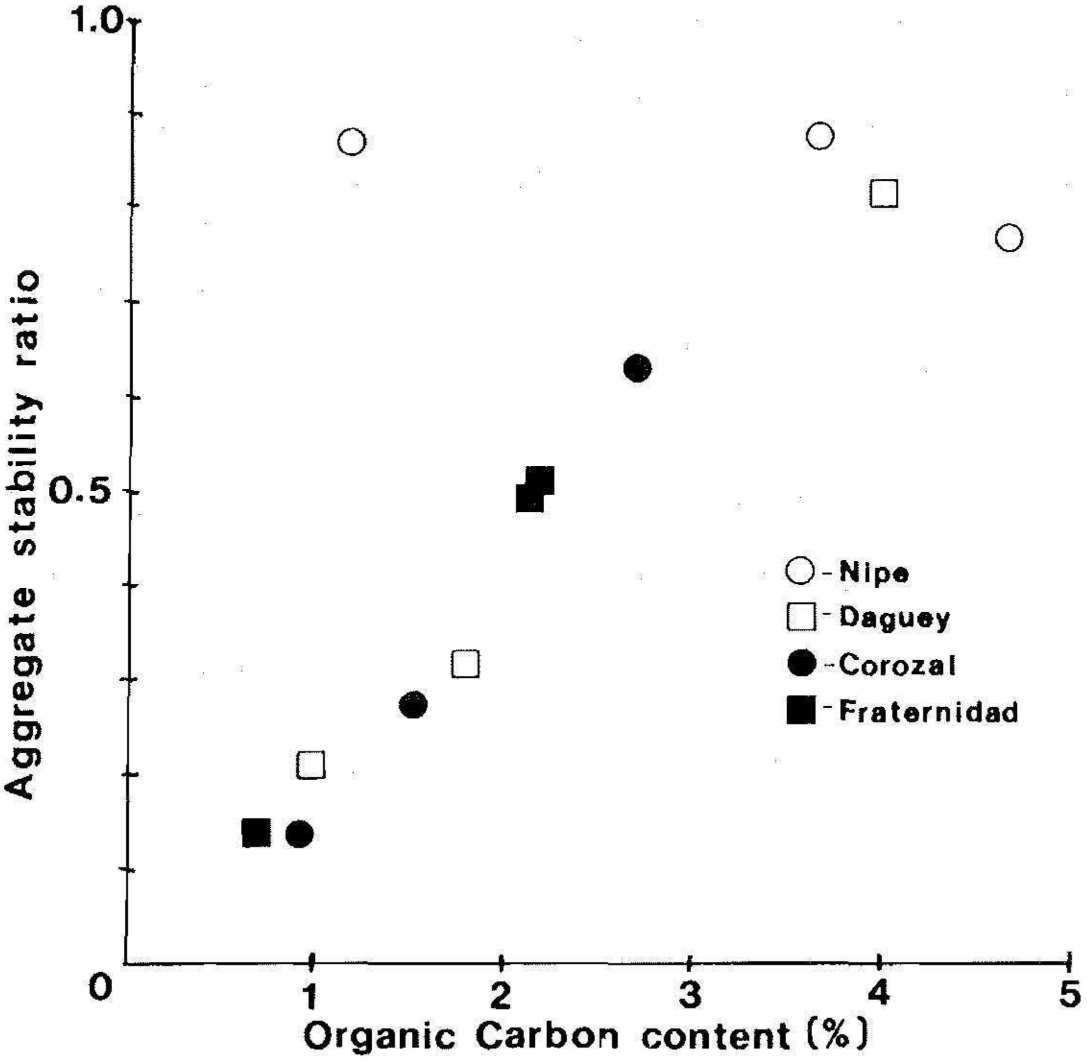

FIG. 1.—Aggregate stability ratio in relation to soil organic carbon content.

with the exception of highly oxidic soils such as Nipe, the stability of aggregates in clay soils with a non-dispersive (low sodium) exchange complex is primarily determined by soil organic matter content.

Moisture release characteristics

Figure 2 shows soil moisture release curves corresponding to 0 to -1 bar extraction pressures for undisturbed cores of the soils studied.

The amount of water (v/v) released in the 0 to -0.33 and -0.33 to -0.8 bar pressure ranges is plotted as function of soil organic carbon content

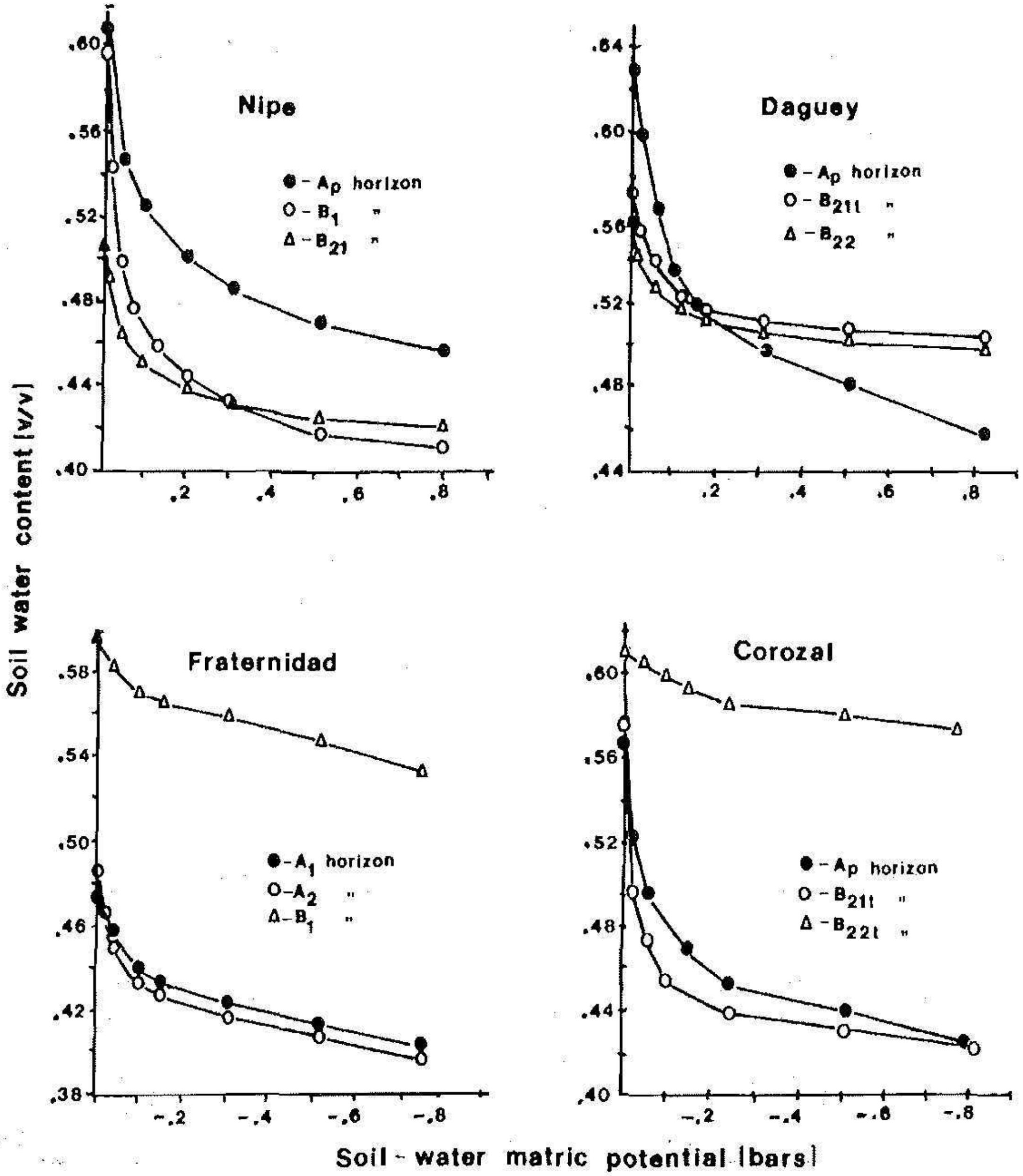

FIG. 2.—Moisture release characteristics for the soil studied.

in figures 3 and 4, respectively. A fairly noticeable relation between organic carbon content and moisture release was observed in both pressure ranges. In the 0 to -0.33 bar range, the amount of water released increased approximately 3-fold from about 0.05 to 0.15 as soil organic carbon content increased from 1.0 to 4.5%. In the -0.33 to -0.8 bar range, an approximately 3-fold increase in water release was again observed in the Nipe, Dagüey and Corozal soils, with water release varying from about 0.01 at 1.0% organic carbon content to 0.03 at 4.5% carbon. A negative relation between -0.33 to -0.8 bar moisture release and organic carbon seemed apparent in the montmorillonitic Fraternidad soil. However, this trend was very possibly not significant as it was observed on only three data points.

These results show the importance of soil organic matter content in maximizing porosity in the 0 to -0.8 bar moisture retention region. This is particularly relevant to highly weathered soils where most of the plant-available soil water is held in the 0 to -1 bar matric potential range (19). Porosity in the 0 to -0.33 bar moisture retention range is important from

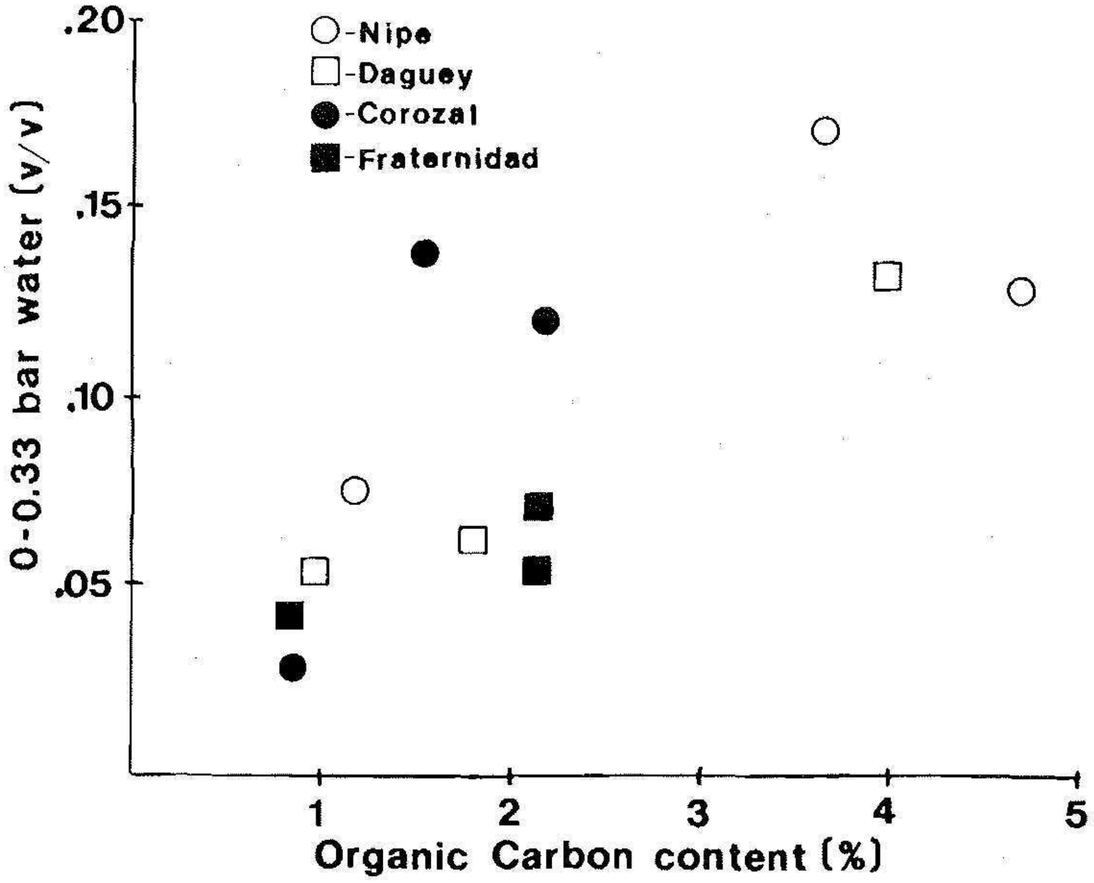

FIG. 3.—Total soil porosity corresponding to the 0-0.33 bar moisture retention range as a function of soil organic carbon content.

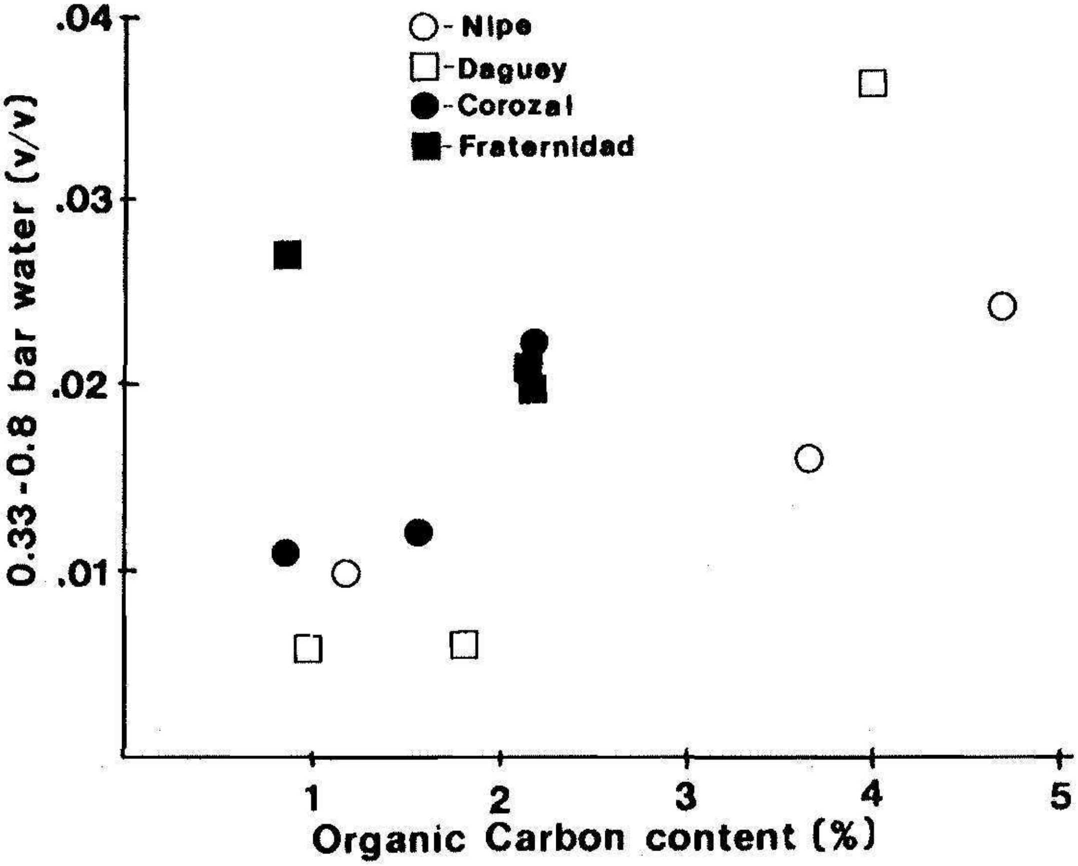

FIG. 4.—Total soil porosity corresponding to the 0.33-0.8 bar moisture retention range as a function of soil organic carbon content.

the point of view of water movement. Ahuja et. al. (1) and others have related it to hydraulic conductivity functions, which in turn determine drainage properties and the point at which field capacity is reached (6, 10). Research on Oxisols, Vertisols and Mollisols has shown that soil pores in the 0 to -0.33 bar range are primarily associated with spaces between soil aggregates (9, 19, 25). Thus they are readily modified by processes such as organic matter changes which influence aggregate size.

The relative size distribution of soil pores in the 0 to -0.33 bar range is shown in figure 5, where the water-filled fraction of the total drainable 0 to -0.33 bar porosity is plotted as a function of soil water matric potential. A single curve closely represents the data for all soils and horizons. The sole exception is the B_{22t} horizon of the Corozal soil, which is not included in figure 5 (see figure 6 for data on this horizon). These results imply pore space similarity for all horizons, in that the fraction of total (0 to -0.033 bar) drainable pores corresponding to a given pore size was always constant. The major difference among soils resided in the *total* number of drainable pores, i.e. the total drainable 0 to -0.33 bar porosity. As discussed within the context of figures 3 and 4, this porosity was primarily a function of soil organic content in the mechanically undisturbed soils studied here.

The same data were plotted on a log-probability scale (fig. 6) in terms of the log of equivalent pore-radius vs. percentage oversize. Equivalent pore radius was calculated from the capillary equation

$$r = 2\,S/P \qquad (1)$$

where r is pore radius in centimeters, S is surface tension of the air-water interface in dynes/cm and P is matric potential in dynes/cm^2. A surface tension of 70 dynes/cm was assumed. Figure 6 shows that all data fit a log-normal distribution very well. Table 4 gives respective geometric mean pore radii and log standard deviations. It can be seen that the

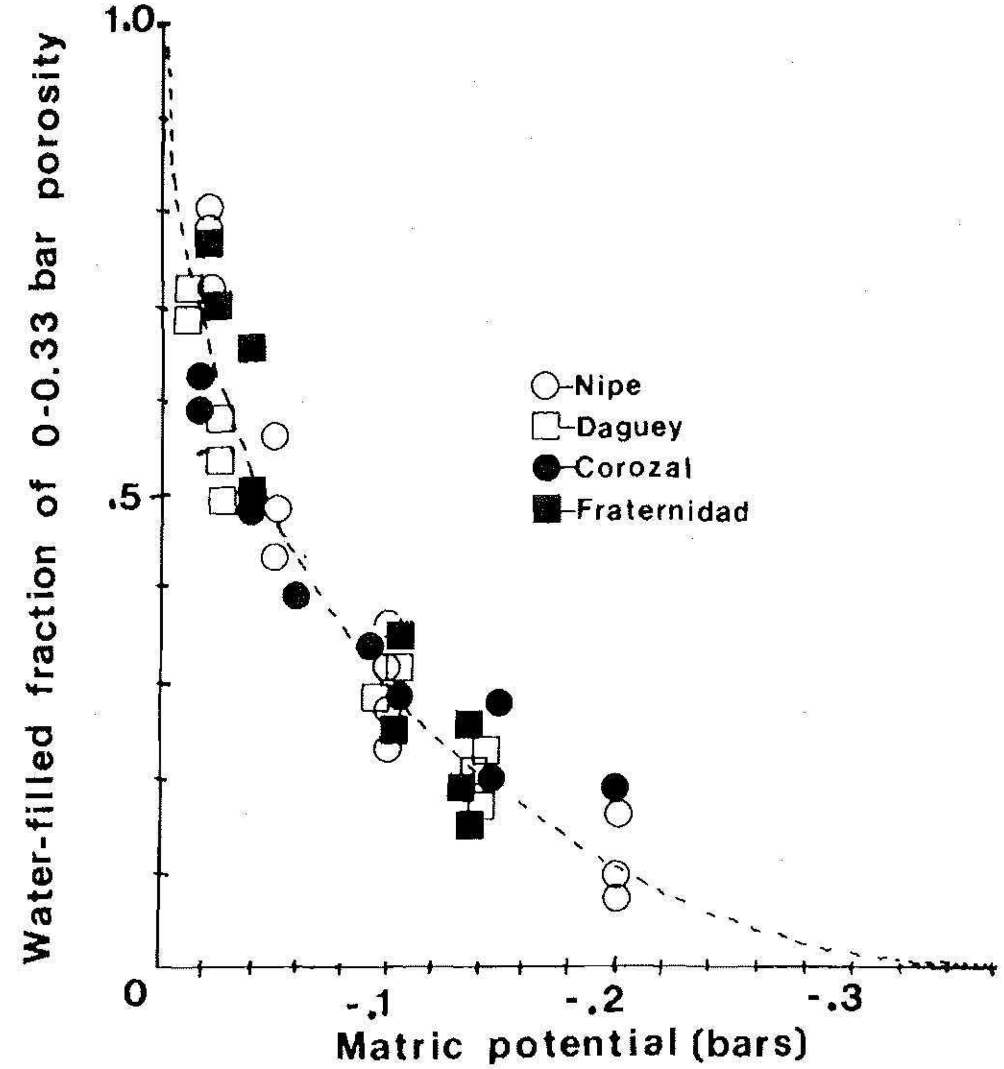

FIG. 5.—Water-filled fraction of 0-0.33 bar porosity as a function of soil water matric potential.

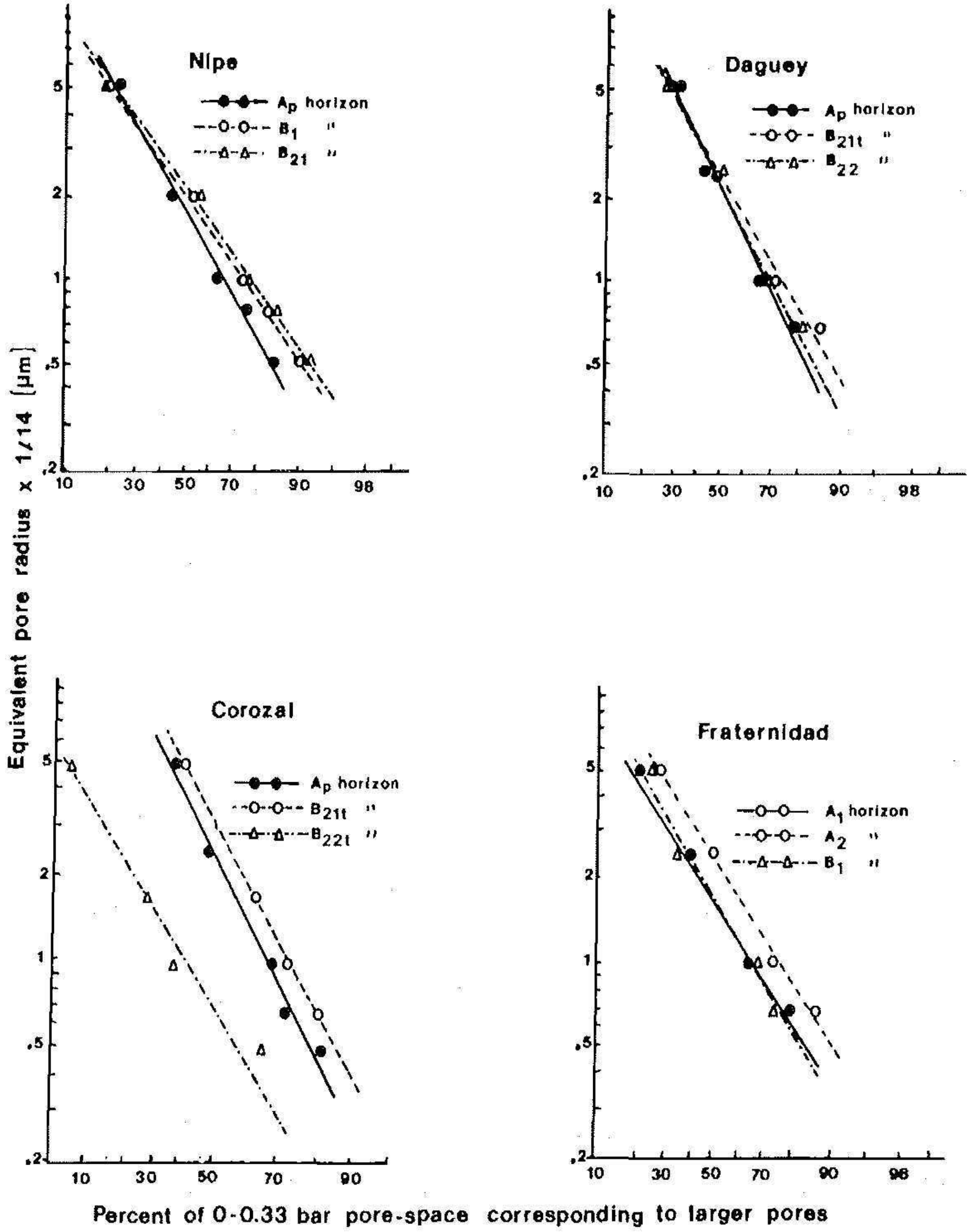

FIG. 6.—Log-probability plots of equivalent pore radius vs. percent oversize in the 0-0.33 bar matric potential range.

values are very similar among all soils, with the sole exception of the Corozal B_{22t} horizon. The average geometric mean pore radius for the 12 soil horizons was 31 μm (corresponding to a matric potential of -0.045 bars), with a coefficient of variation of 0.31. The average value for the

TABLE 4.—*Geometric mean radii and log standard deviations for pore-size distributions in the 0-0.33 bar moisture retention range of undisturbed soil cores*

Soil	Horizon	Geometric mean pore radius	Log standard deviation
		-μm-	
Nipe	A	25.2	25.7×10^{-3}
	B$_1$	30.8	24.4×10^{-3}
	B$_{21}$	32.2	2.19×10^{-3}
Dagüey	Ap	30.8	2.95×10^{-3}
	B$_{21}$t	33.6	2.75×10^{-3}
	B$_{22}$	32.2	$3.39\ z\ 10^{-3}$
Corozal	A$_p$	40.6	2.88×10^{-3}
	B$_{21}$t	51.8	2.75×10^{-3}
	B$_{22}$*	12.6	2.09×10^{-3}
Fraternidad	A$_1$	25.2	2.29×10^{-3}
	A$_2$	33.6	2.29×10^{-3}
	C$_1$	23.8	2.63×10^{-3}
Mean (arithmetric) of values		31.03	2.59×10^{-3}
Standard deviation		±9.53	±0.38
Coefficient of variation		±0.31	±0.15

log standard deviation of pore radii was 2.50×10^{-3} with a coefficient of variation of 0.15.

A relation such as that represented by figure 6 provides a straightforward way of estimating the 0 to -0.33 bar moisture release characteristic. The only measurements required are the volumetric water content at saturation and -0.33 bars matric potential. That is providing figure 6 adequately represents a large number of soils. All soils in this study were clayey in texture, had been uncultivated for a long time and were under similar vegetation when sampled. The effects of texture changes, mechanical disturbance and differences in vegetation on relative pore size distribution would have to be studied before generalizing the results obtained here.

Surface charge characteristics

Potentiometric titration curves for the Nipe, Carreras and Dagüey soils are given in figures 7 through 9. Titration curves for the montmorillonitic Fraternidad soil are not given since a zero point of change was

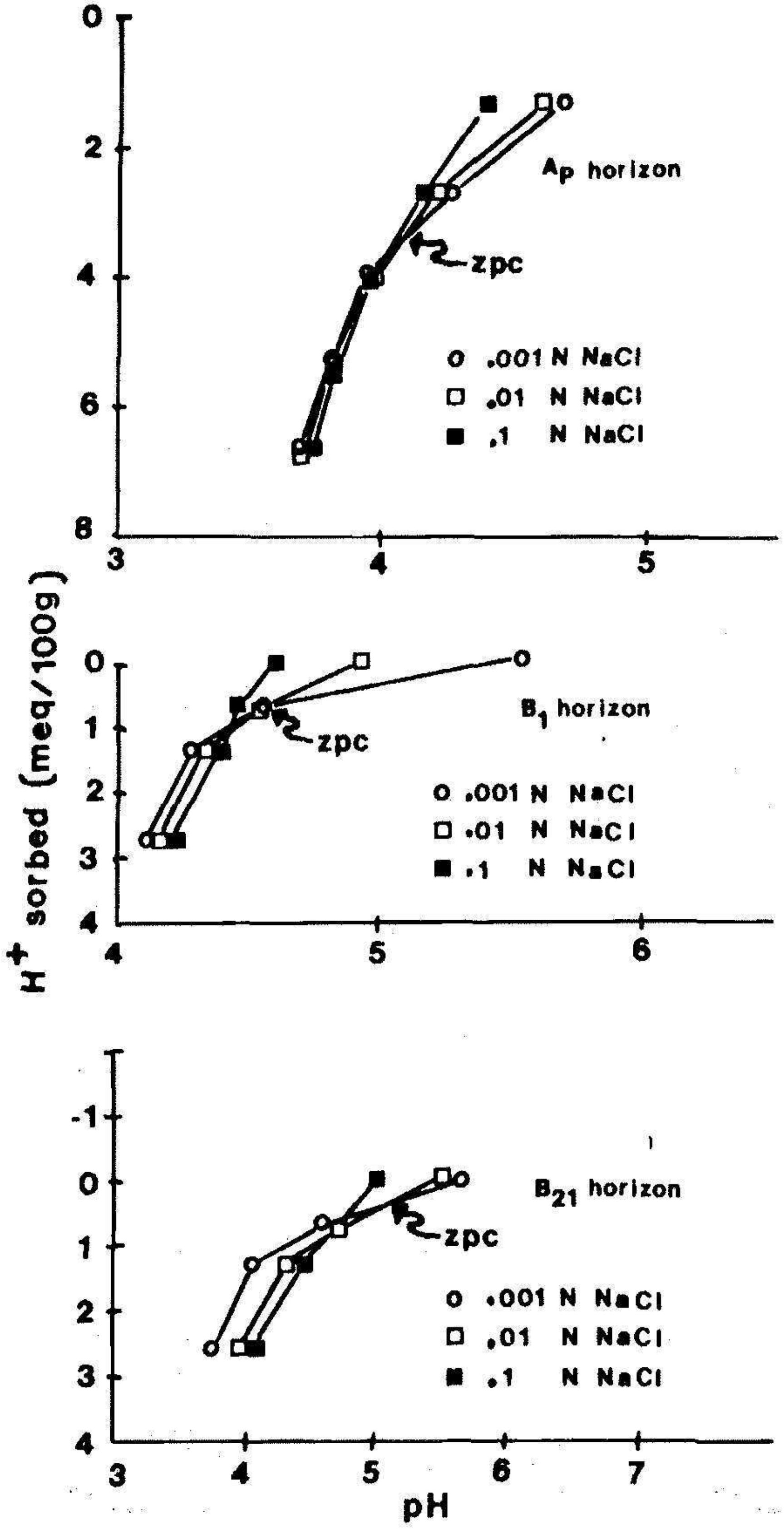

FIG7.—Potentiometric titration curves for the Nipe soil.

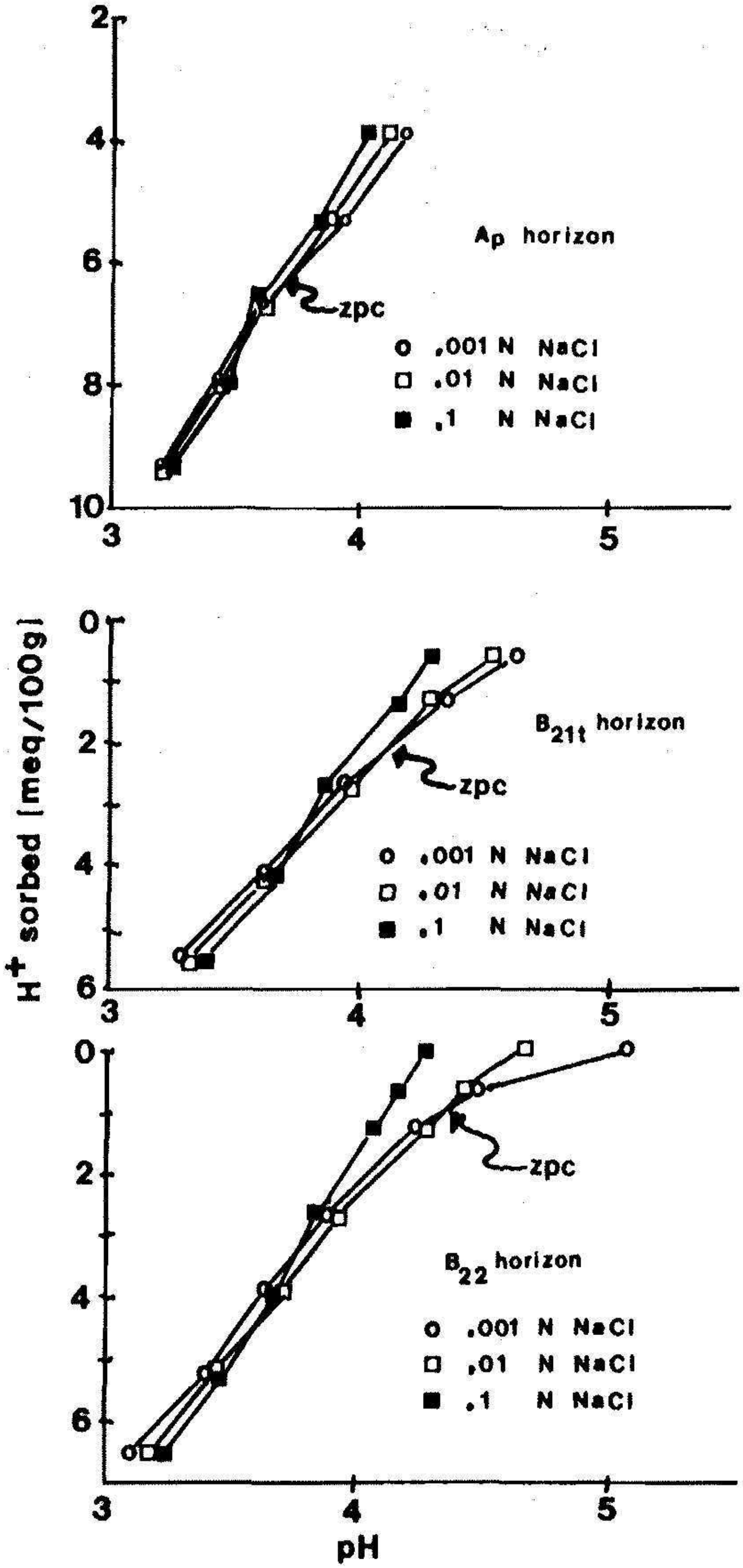

FIG. 8.—Potentiometric titration curves for the Dagüey soil.

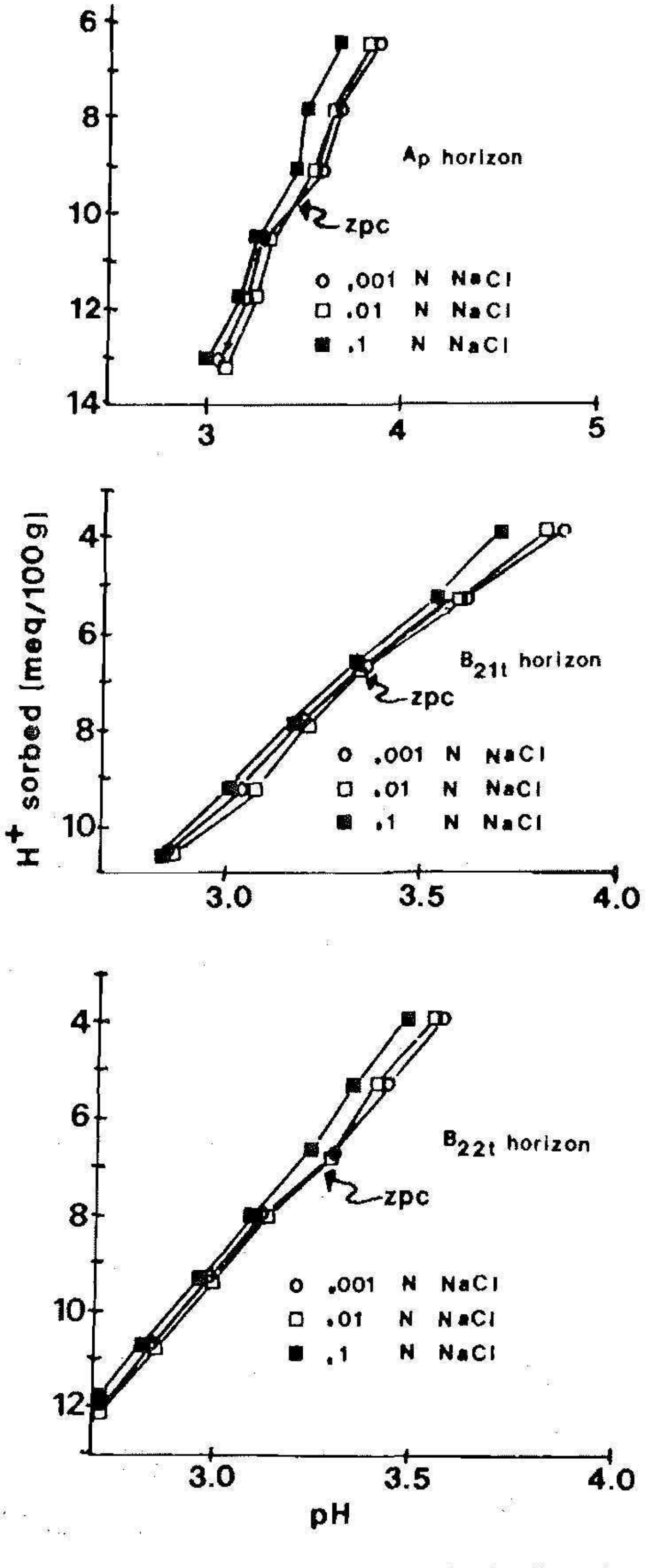

FIG. 9.—Potentiometric titration curves for the Corozal soil.

TABLE 5.—*Chemical data for the soils studied*

Soil	Horizon	pH (*in* 0.001*N* Nacl)	Organic Carbon	ZPC	Exchangeable cations				CEC		Variable charge[1]
					Ca	Mg	K	Al	(NH_4OAc)	(Sum cations)	
			%		meq./100g						
Nipe	A	5.39	4.68	4.10	2.5	0.9	0.1	1.0	27.4	4.5	–3.4
	B_1	5.55	3.65	4.50	0.6	--	--	1.2	28.2	1.8	–0.8
	B_{21}	5.66	1.18	5.05	0.4	--	--	0.2	11.0	0.6	–0.4
Dagüey	A	5.74	3.99	3.60	6.9	2.0	0.4	0.3	29.9	9.6	–6.6
	$B_{21}t$	5.21	1.80	4.10	3.3	1.1	0.1	2.5	18.2	7.0	–2.2
	B_{22}	5.06	0.98	4.35	2.0	0.8	--	4.4	19.0	7.2	–1.0
Corozal	Ap	6.00	2.19	3.45	15.7	0.7	1.3	0.7	29.6	18.4	–9.7
	$B_{21}t$	4.91	1.54	3.35	8.3	0.2	0.7	9.4	27.6	18.6	–6.6
	$B_{22}t$	4.35	0.86	3.30	3.3	--	0.7	23.2	34.3	27.2	–6.7
Fraternidad	A[1]	7.49	2.11	--	48.1	10.3	0.4	--	56.1	58.8	--
	A_2	7.50	2.11	--	50.5	9.3	0.3	--	56.1	60.1	--
	C_1	7.80	0.83	--	47.8	17.0	0.4	--	59.2	65.2	--

[1] Defined as the negative value of the amount of added acid necessary to bring a soil to its zero point of charge.

not reached even after adding acid in excess of 25 meq/100 g of soil. The zero point of change (ZPC) and net negative charge of the variable-charge soil components were calculated from these curves and summarized in table 5 along with other chemical data.

The ZPC was taken as the pH at the intercept of the titration curves in 0.001 and 0.01N NaCl. The intercepts for the 0.1N and 0.01N salt solutions were not used because they shifted toward lower pH values than the intercepts with 0.01 and 0.001N salt solutions. The shift possibly occurred because of displacement and hydrolysis of exchangeable aluminum in the presence of the more concentrated 0.1*N* NaCl solution (17).

The negative charge of the variable-change complex was calculated as the amount of acid required to bring the soil from its natural pH to the ZPC in the potentiometric titrations.

Table 5 shows that the ZPC in a given soil shifted toward lower pH values, and the negative variable charge increased, with greater amounts of soil organic matter. This effect of organic matter has been reported elsewhere (14, 22).

As mineralology varied in the sequence oxidic → kaolinitic → mixed (corresponding to the Nipe, Dagüey and Corozal soils, respectively), the contribution of the variable negative charge to the effective cation exchange capacity (CEC) (or the sum of exchangeable bases and aluminum) became successively smaller in proportion. In the oxidic Nipe soil the effective CEC was only slightly greater than the negative variable charge component, with the difference almost exactly equal to the amount of exchangeable Al present. This agrees with results of Sakurai (17), who found that the exchangeable Al present in four oxidic soils occupied the permanent charge sites and the exchangeable bases occupied the variable charge sites. The difference between effective CEC and the negative variable charge component became successively larger as mineralogy changed to kaolinitic (Dagüey soil), then to mixed (Corozal soil) and finally to montmorillonitic (Fraternidad) where no variable charge could be measured. This again agrees with the results expected from the particular mineralogical sequence studied.

REFERENCES

1. Ahuja, L. R., J. W. Naney, R. E. Green and D. R. Nielsen. 1984. Macroporosity to characterize variability of hydraulic conductivity and effects of land management. *Soil Sci. Soc. Am. J.* 48:699-70.
2. Allison, F. E. 1965. Organic carbon. *In*: Black, C. A. (ed.), Methods of Soil Analysis II. Agronomy Monograph No. 9. American Society of Agronomy. Madison, WI.
3. Aubert, G. and R. Tavernier. 1972. Soil survey. *In*: Drosdoff, M. (chairman), Soils of the Humid Tropics. National Academy of Sciences.
4. Beinroth, F. H. 1982. Some highly weathered soils of Puerto Rico. 1. Morphology, formation and classification. *Geoderma* 27:1-73.

5. Blake, G. R. 1965. Particle density. *In*: Black, C. A. (ed.), Methods of Soil Analysis I. Agronomy Monograph No. 9. American Society of Agronomy. Madison, WI.
6. Campbell, G. S. 1985. Soil Physics with Basic. Elsevier, Amsterdam.
7. Day, P. R. 1965. Particle fractionation and particle size analysis. *In*: Black, C. A. (ed.), Methods of Soil Analysis I. Agronomy Monograph No. 9. American Society of Agronomy. Madison, WI.
8. Gardner, W. R. 1956. Representation of soil aggregate size distribution by a logarithmic-normal distribution. *Soil Sci. Soc. Am. Proc.* 20:151153.
9. Gupta, S. C. and W. E. Larson. 1982. Modeling soil mechanical behavior during tillage. *In*: Unger, P. W., D. M. Van Doren, F. D. Whisler and E. L. Skidmore (eds.), Predicting Tillage Effects on Soil Physical Properties and Processes. ASA Spec. Pub. No. 44. American Society of Agronomy, Madison, WI.
10. Hillel, D. 1971. Soil and Water: Physical Principles and Processes. Academic Press, New York.
11. Isaac, R. A. and J. D. Kerber. 1971. Atomic absorption and flame photometry: techniques and uses in soil, plant and water analysis. *In*: Walsh, L. M. (ed.), Instrumental Method for Analysis of Soils and Plant Tissue. Soil Science Society of America. Madison, WI.
12. Jones, R. C., W. H. Hudnall and W. S. Sakai. 1982. Some highly weathered soils of Puerto Rico. 2. Mineralogy. *Geoderma* 27:75-137.
13. McLean, E. O. 1965. Aluminum. *In*: Black, C. A. (ed.), Methods of Soil Analysis II. Agronomy Monograph No. 9. American Society of Agronomy. Madison, WI.
14. Parfitt, R. L. 1980. Chemical properties of variable charge soils. *In*: Theng, B. K. G. (ed.), Soils with Variable Charge. New Zealand Society for Soil Science. Private Bag, Lower Hutt.
15. Reginato, R. J. and C. H. M. Van Bavel. 1962. Pressure cell for soil cores. *Soil Sci. Soc. Am. Proc.* 26:1-3.
16. Richards, L. A. 1965. Physical condition of water in soil. *In*: Black, C. A. (ed.), Methods of Soil Analysis I. Agronomy Monograph No. 9. American Society of Agronomy. Madison, WI.
17. Sakurai, K., A. Nakayama, T. Watanabe and K. Kyuma. 1989. Influences of aluminum ions on the determination of ZPC (zero point of charge) of variable charge soils. *Soil Sci. Plant Nut.* 35:623-633.
18. Sánchez, P. A. 1976. Properties and Management of Soils in the Tropics. Wiley.
19. Sharma, M. L. and G. Uehara. 1968. Influence of soil structure in low humic latosols: I. Water retention. *Soil Sci. Soc. Am. Proc.* 32:765-770.
20. Soil Survey Staff. 1967. Soil Survey Laboratory Data and Descriptions for Some Soils of Puerto Rico and the Virgin Islands. USDA- Soil Conservation Service in coop. with UPR Agric. Exp. Sta.; Soil Survey Invest. Rep. No. 12.
21. Soil Survey Staff. 1972. Soil Survey Laboratory Methods and Procedures for Collecting Soil Samples. USDA- Soil Conservation Service; Soil Survey Invest. Rep. No. 12.
22. Uehara, G. and Gillman, 1981. The Mineralogy, Chemistry, and Physics of Tropical Soils with Variable Charge clays. Westview. Boulder, CO.
23. Van Raij, B. and M. Peech. 1972. Electrochemical properties of some Oxisols and Alfisols of the tropics. *Soil Sci. Soc. Am. Proc.* 36:587-593.
24. Yoder, R. E. 1936. A direct method of aggregate analysis of soils and a study of the physical nature of erosion losses. *J. Am. Soc. Agron.* 28:337-351.
25. Yule, D. F. and J. T. Ritchie. 1980. Soil shrinkage relationships of Texas Vertisols: small cores. *Soil Sci. Soc. Am. J.* 44:1285-1291.