Pertanika 11(1), 15–23 (1988)

Acidity and Charge Characteristics of Marine Alluvial Soils from Carey Islands, Selangor.

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Key Words: **Acidity; aluminium, buffering; negative.**

ABSTRAK

Enam siri tanah dari Pulau Carey telah dikaji untuk menentukan ciri keasidan dan cas tanah. Kajian ini telah menunjukkan tanah di Pulau Carey mengandungi kandungan bes kation, A1 dan SO_4^{2-} yang tinggi. *Ini ditunjukkan oleh rendahnya kandungan pH dan tingginya konduksian elektrik. Tanah-tanah itu menampan dengan kuat ke bawah pH 5.5 dan didapati berkorelasi dengan baik kepada kandungan A1. Di samping itu juga, cas negatif di atas permukaan lempung didapati bertambah dengan naiknya pH tanah. Pemerhatian ini bercanggah dengan fakta bahawa mineral lempung dalam tanah-tanah ini adalah jenis cas tetap.*

ABSTRACT

Six soil series from Carey Island were investigated to determine their acidity and charge characteristics. The study showed that the soils contained high amounts of basic cations, Al and So_4^{2-}*, which were reflected by their low pH and high electrical conductiviy. The soils were highly buffered below pH 5.5 and this was found to be highly correlated to Al content. Further, it was found that negative charges on the clay surfaces increased with increase in soil pH. These observations are contrary to the fact that the clay minerals in these soils are of the permanent charge type.*

INTRODUCTION

Carey Island is located on the west coast of Peninsular Malaysia in the Straits of Melaka. It is situated between 2°0′ and 3° 0′N latitude and between 101°15′ and 101°30′E longitudes *(Figure 1)*. The island is located in the estuaries of the Kelang River and the Langat River and consists of marine, estuarine and brackish water deposits of recent origin. The island is flat with an elevation that is below mean high tide level. Thus, the island has been reclaimed by the construction of a coastal bund and a network of drainage canals and water control structures.

Carey Island with an estimated area of 11,667 ha is almost exclusively owned by Harrison Malaysian Plantations. The island is divided into four estates totaling 10,942 ha. Oil palm is by far the dominant crop (9222 ha), while cocoa/coconut occupies 1720 ha. A detailed soil survey of the four estates has been recently carried out (Manoharan, 1985; Pathumanathan, 1985; Rajasekharam, 1985; Yeoh, 1985). Nine soil series were identified on the island. The classification and extent of these soils is shown in Table 1. Some of the soils on the island are acid sulfate in nature and hence are agronomically less suited for agriculture unless some corrective measures are carried out. Depending on the soils, they are limited by low pH, high aluminium content and high electrical conductivity.

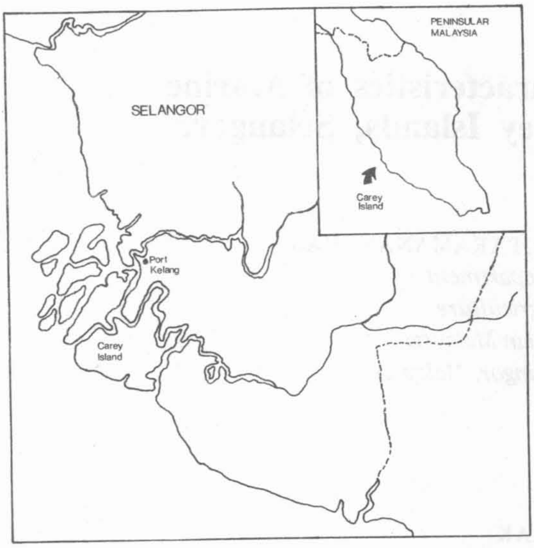

Fig. 1: A map showing the position of Carey Island in Selangor, Peninsular Malaysia.

TABLE 1
Classification and extent of soils in Carey Island.

Soil Series	Classification (Soil Survey Staff 1975)	Extent (ha)
Merbok*	Typic Sulfaquent	638
Parit Botak*	Typic Sulfaquept	254
Tongkang*	Sulfic Tropaquept	810
Bernam*	Typic Tropaquept	492
Linau*	Typic Sulfaquent	881
Sedu	Typic Sulfaquept	722
Jawa	Sulfic Tropaquept	5609
Selangor*	Aeric Tropaquept	1115
Carey	Sulfic Tropaquept	49
Miscellaneous Land Units		362

*Soils sampled for study

Soils developed on marine, estuarine and brackish water deposits, especially acid sulfate soils, are highly buffered at low pH. The high buffering capacity at that pH is attributed to the presence of aluminium in the soils (Shamshuddin *et al.*, 1986) and jarosite (Carson *et al.*, 1982). These soils contain mainly smectite, mica-mixed layers, mica and kaolinite (Shamshuddin *et al.*, 1986). All these minerals are considered to be permanent charge minerals (Uehara and Gillman, 1980; 1981).

The purpose of this investigation is to characterise the acidity and charge characteristics of six of the soils found on Carey Island. It is hoped that the information obtained will supplement other measures in the amelioration of the soils for agricultural production.

MATERIALS AND METHODS

The soils were described and sampled according to pedogenetic horizons and air-dried, ground and passed through a 2 mm sieve. pH was determined in water (1:2.5) after 24 hrs. of equilibration. Basic cations were extracted using 1M NH_4OAC at pH 7; Na^+ and K^+ were determined by flame photometer, while Ca^{2+} and Mg^{2+} were determined by atomic absorption spectrophotometer.

Aluminium was extracted by 1M KCl and was determined colorimetrically. Water soluble sulfate was determined by turbidimetry after extracting 5 g soils with 100 ml H_2O. Electrical conductivity was measured in water at the soil: water ratio of 1:5 after equilibration for 24 hours. Free iron was determined by the method of Mehra and Jackson (1960), while organic carbon was determined by the Walkley-Black Method.

Potentiometric titration curves were obtained by titrating the soil and soil extracts with 0.1M KOH using an autotitrator. 5 g of soils was equilibrated overnight in 50 ml 1M KCl. Negative and positive charges at pH 3, 4, 5, 6 and 7 were measured by the method of Gillman and Uehara (1980). Nuclear activation analysis (NAA) was employed to determine the total elemental composition of the soils.

RESULTS AND DISCUSSION

Morphological Characteristics of the Soils

Six of nine soils mapped on Carey Island were used in this study viz. Merbok, Parit Botak, Tongkang, Bernam, Linau and Selangor Series. The main morphological properties of these soils are summarised in Table 2. From this table it can be seen that both the Merbok and Linau Series have sulfidic materials close to the surface, while in all the other soils sulfidic materials occur at varying depths depending on the soil type. Buried wood is common in the C horizon of the Linau Series indicating its brackish water origin. Soils developed over the marine alluvium are light gray in colour, have jarosite mottles at varying depths and coarse angular blocky structures with sticky consistence. On the other hand, the Selangor Series which is developed on brackish water deposits, has moderate, subangular blocky structures and friable consistence. The differences in the soils developed over marine and brackish water deposits are consistent with those reported by Paramananthan and Noordin (1986).

Chemical Characteristics of the Soils

The chemical characteristics of six soils in the study are given in Table 3. A number of differences can be ascertained from this table. The C

TABLE 2
Morphological properties of the soils studied

Soil Series	Parent Material	Horizonation	Diagnostic Subsurface Horizon/Property	Brief Description
Merbok	Marine alluvium	A/C	Sulfidic Material	Bluish gray clay, sticky and massive, value low in upper but high in lower horizons. Black material oozes out in the lower horizons
Parit Botak	Marine alluvium	A/Bw/C	Sulfuric horizon over sulfidic Material	Light gray, clay, wet sticky, dry hard with coarse angular blocky structures. Yellow Jarosite mottles 0–50 cm depth
Tongkang	Marine alluvium	A/Bw/C	Sulfuric horizon over sulfidic material	Light gray, clay, wet sticky, coarse angular blocky structures. Yellow jarosite mottles 50–100 cm depth.
Bernam	Marine alluvium	A/Bw/C	Cambic horizon	Light gray, clay, wet sticky, coarse angular blocky structures. No jarosite mottles to 100 cm
Linau	Brackish water deposits	O/AC/C	Sulfidic	Sapric material to depth less than 50 cm overlying wet, sticky blush gray structureless clay. Many pieces of wood.
Selangor	Brackish water deposits	A/Bw/C	Cambic horizon	Brown, silty clay, moderate medium subangular blocky, friable, No jarosite mottles to 100 cm depth.

TABLE 3
Chemical properties of soils on Carey Island

Soil Series	Horizon Symbol	Depth (cm)	pH–H_2O (1:2.5)	Basic Cations (meq/100g.soil)				Al^{3+}	SO_4^{2-}	E.C.	Fe_2O_3	Organic Carbon (%)
				Na	K	Ca	Mg	meq/100g.soil		m siemen/ cm		
Merbok	AD	0–11	6.3	13.70	1.80	44.63	10.71	tr	2.50	2.28	0.37	3.87
	AC	11–50	3.6	21.64	2.34	32.16	11.19	1 11111	11.60	6.58	tr	4.18
	C	50–90+	2.7	20.76	2.29	19.27	10.91	16.68	21.25	9.04	tr	2.77
Parit Botak	Ap	0–15	3.5	0.31	0.17	tr	0.51	13.52	1.38	9.49	1.16	2.66
	Bw_1	15–40	3.3	0.20	0.23	tr	1.18	15.94	1.04	0.61	2.72	1.30
	Bw_2	40–70	3.2	0.24	0.27	0.71	1.63	15.36	1.25	0.75	2.91	0.75
	BC	70^+	3.2	0.41	0.23	0.93	1.95	13.60	1.33	0.95	1.56	0.93
Tongkang	Ap	0–10	4.0	0.09	0.21	4.57	1.11	10.04	1.10	0.10	0.31	2.59
	Bw_1	10–40	4.0	0.06	0.26	0.61	2.20	15.38	1.00	0.10	0.91	0.85
	Bw_2	40–70	3.3	0.23	0.23	0.54	1.90	15.38	0.81	0.32	0.96	1.23
	Bw_3	70–105	3.3	0.44	0.23	0.73	1.48	13.78	0.90	0.33	1.99	1.54
Bernam	Ap	0–7	4.2	0.20	0.23	4.49	2.24	12.74	1.10	0.07	0.53	1.28
	Bw_1	7–40	4.0	0.19	0.30	1.25	1.98	15.80	0.50	0.12	0.98	0.88
	Bw_2	40–105	3.9	0.28	0.07	tr	0.46	4.35	0.40	0.09	tr	1.89
Linau	Ap	0–20	3.3	0.69	0.23	1.80	1.27	8.04	0.88	0.77	0.77	1.28
	AC	20–35	2.6	2.28	0.17	17.88	1.87	12.06	10.42	4.01	4.01	0.81
	C	354	3.7	3.25	0.19	23.98	4.72	12.28	9.58	5.25	5.25	1.89
Selangor	Ap	0–16	3.9	0.12	0.10	tr	0.10	3.44	0.21	0.11	0.11	1.28
	Bw_1	16–45	3.5	0.10	0.12	tr	0.11	6.08	0.38	0.26	0.26	0.81
	Bw_2	45–104	3.2	0.32	0.12	tr	0.91	10.28	0.67	0.71	0.71	1.88

horizons of the poorly drained soils are marine clays which are very juvenile as indicated by the high calcium, magnesium, sodium and sulfate content, eg. Merbok and Linau Series. Some of the Ca in these soils may be present in the form of gypsum ($CaSO_4.2H_2O$). The drained soils which are developed on marine clays. For example: Parit Botak, Tongkangand Berham, have higher magnesium and calcium values as compared to Selangor Series which is developed on brackish water deposits. This is possibly due to the higher leaching. Note that we do not have Mg and Ca data on the C horizons of Parit Botak, Tongkang and Bernam series to conclusively prove its marine origin. But from past experience we know that these soils are usually found in marine alluvial areas. Selangor Series has a pH of less than 3.5 but no jarosite was observed in the field to a depth of 100 cm. However, brownish yellow mottles were present. It is possible that these mottles were in fact jarosite but have browner hues due to the presence of organic acids. The organic carbon content values may not be a true reflection of the carbon content as these soils also contain pyrite which may also be oxidised during the determination of organic carbon.

Total Elemental Composition

Table 4 gives the total content of Na, K, Mn, Al and Fe in the soils under investigation. The most important determined cation in the soils is Al, with values ranging from 2.44% (Selangor, Ap) to 10.4% (Parit Botak, BC). This is followed by Fe and K. The amount of Mn in the soil is also quite substantial which could be toxic to crops.

The high amounts of Al and K in the soils is due to the fact that these elements form important constituents of silicates. Mica and smectite are the dominant minerals in soils developed on marine deposits (Shamshuddin *et al.*, 1986). The presence of high acidity in the soils, as shown by the low pH (Table 3), may result in the clay minerals being attacked by the acid, and as a result, Al is released into the solution in large amounts. Similarly, K will be released into the solution as the mineral weathers, but subsequently taken up by the formation of jarosite ($KFe_3(SO_4)_2(OH)_6$) particularly in acid sulfate soils.

TABLE 4
Total elemental composition of soils on Carey Island

Soil Series	Horizon	Depth (cm)	Total Elemental Composition				
			Na(%)	K(%)	Al(%)	Fe(%)	Mn(ppm)
Merbok	Ap	0–11	0.42	1.31	8.04	1.73	100
	C	50–90	0.80	1.70	7.39	–	240
Parit Botak	Ap	0–15	0.11	0.16	3.52	2.83	32
	BC	70⁺	0.11	1.43	10.41	2.73	77
Tongkang	Bw_3	70–105	0.15	1.47	7.73	–	119
Bernam	Ap	0–7	0.10	1.31	9.43	2.30	88
	Bw_2	40–105	0.14	1.00	3.92	0.93	49
Limau	Ap	0–20	0.17	1.07	4.98	2.26	47
	C	354	0.24	1.06	4.90	1.45	57
Selangor	Ap	0–16	0.10	0.87	2.44	–	53
	Bw_2	45–104	0.10	1.15	4.25	0.94	38

Jarosite was indentified in the soils of the Parit Botak dan Tongkang Series as mottles on ped faces. The high K values may also be due to illite in these soils.

Soil pH

The pH values for the soils of Carey Island vary from 2.66 to 6.28 (Table 3). It appears that pH values depend on the amount of Al in the soil. The higher the amount of Al in the soil, the lower the pH. For instance when pH is 3.9, the Al content is 3.44 meq/100g soil (Selangor, Ap). When the pH goes to 2.7, the amount of Al is 16.68 meq/100g soil (Merbok, C). On the contrary when Al content was plotted against pH, the correlation between pH and Al content was found to be poor. This may be partly due to the presence of organic acids in these soils. However, we cannot disregard the role of Fe^{3+} (pka 3) in the buffering action of soil although iron is low except in Linau Series. Iron in these soils could exist in the form of $(Fe)_2(SO_4)3$. At low pH, the iron goes into the solution as Fe^{3+} and this causes soil buffering below pH_4.

Electrical Conductivity

The soils in Carey Island are derived from marine clays and thus salt is an important component of the soils. Under such conditions, high electrical conductivity could be a serious limitation to crop growth. However, salt can be leached out under a proper system of management. More recent soils such as Merbok and Linau Series (Sulfaquents) contain more salt (Table 3) than the drained soils, such as Tongkang and Parit Botak Series, which are classified as Sulfic Tropaquept and Typic Sulfaquept respectively.

This study shows that there exists a good correlation between electrical conductivity, basic cations and sulfate. This is shown by the equation:-

$$EC = 0.01 + 0.02 \text{ basic cation} + 0.38\, SO_4{}^{2-}$$

$$R^2 = 0.98, \; F_{2;17} = 392.92^{**}$$

The relationship between EC and $SO_4{}^{2-}$ is given by the equation:-

$$EC = -0.06 + 2.11 SO_4{}^{2-}$$

$$R^2 = 0.96, \; F_{1;18} = 386.30^{**}$$

EC and basic cations are somewhat less correlated as shown by the equation:-

$$EC = 2.43 + 7.21 \text{ basic cations}$$

$$R^2 = 0.64, \; F_{1;18} = 32.06^{**}$$

This study suggests that in order to lower EC to an acceptable level, sulfate has to be removed. For instance, the sulfate in the soils of Linau and Merbok Series, whose EC is rather high in the lower horizons, have to be leached by fresh water. Plant growth is affected when EC is more than 4 m siemens/cm (Wong, 1974).

Soil Buffering

Soils developed over marine and brackish water deposits along the coastal plains of the west coast of Peninsular Malaysia, are known to be highly buffered at a low pH. As a consequence, a high amount of lime is needed to raise the soil pH to the level suitable for plant growth. According to Bloomfield and Powlson (1977) some of these soils need about 200 tonnes of $CaCo_3$ to neutralize the potential acidity in 1 ha of the soil to a depth of 1 m. This point can be studied in some detail by using buffer curves.

Some titration curves of selected horizons for both soil and soil extract are given in *Fig. 2*. Other curves are not presented as they show a similar trend. It appears here that similar curves were produced when OH was added to soil or to soil extract. But on closer examination, we found that more OH^- was needed to raise the pH of soil to pH 5.5 than the soil extract. T-test on paired observations yielded the equation:-

$$t_{W0.001;18} = 3.92 < 7.34$$

This shows that there is real difference between titration curves of soil and soil extract. This indicates that when using the curves for interpreting lime requirement, it is better to use the buffer curves obtained from the soil rather than those obtained from the soil extract because it will reflect the true reaction taking place in the soil.

For both types of titration curves, the amount of OH^- needed to raise the pH to 5.5 and from 5.5 to 9.0 were estimated. The limit was set at 5.5

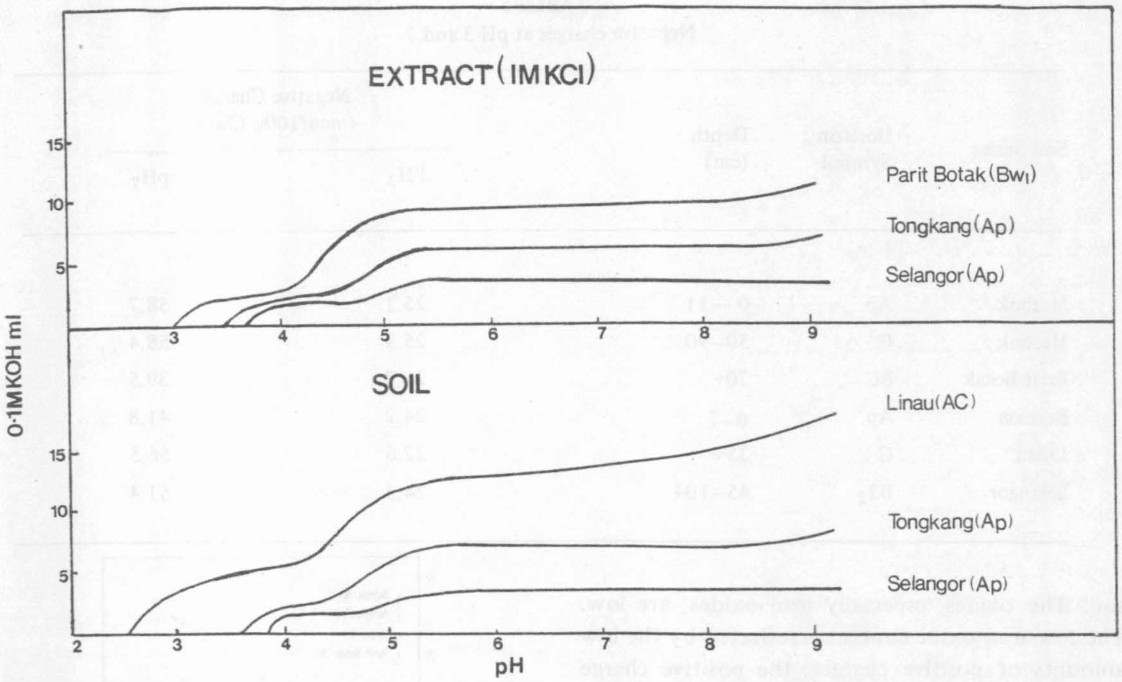

Fig. 2: Potentiometric titration curves of soil extract and soil.

because it is known that the end point of Al titration is around that pH (Cabrera and Talibudeen, 1979) and that the soil is usually limed to that pH (Sanchez, 1976).

Multiple linear regression analysis was carried out to relate bases, Al and clay content. There is a good correlation between bases (pH 5.5), Al and clay, as shown by the equations:-

$$OH^- = 2.44 + 1.33\,Al + 0.01\,clay\ (soil)$$
$$R^2 = 0.81,\ F_{2;16} = 34.80^{**}$$

and

$$OH^- = 3.36 + 0.94\,Al + 0.01\,clay\ (soil\ extract)$$
$$R^2 = 0.83,\ Fe_{2;16} = 38.24^{**}$$

The relationship between OH^- and Al alone for the soil is given by the equation:-

$$OH^- = 0.63 + 0.61\,Al$$
$$R^2 = 0.81,\ F_{1;17} = 73.95^{**}$$

For soil extract, the relationship between OH^- and Al is given by the equation:-

$$OH^- = 0.99 + 0.85\,Al$$
$$R^2 = 0.83,\ F_{1;17} = 80.21^{**}$$

Above pH 5.5, there is no correlation between OH^-, Al and clay either for the soil or for the extract.

This study shows that it is difficult to raise the pH to 5.5 due to the action of Al, which exists in the solution or on the clay surfaces. Once the pH goes up beyond 5.5, it needs only a small amount of OH^- to bring up the soil to pH 9.0. A similar conclusion has been reached by Shamshuddin *et. al.* (1986) who studied acid sulfate soils from Perak, Peninsular Malaysia. The effect of clay minerals, in soil buffering is not significant, either below or above pH 5.5. This is somewhat different from the results obtained for riverine alluvial soils, where OH^- is well correlated to clay content (mainly kaolinite) above pH 5.5 (Shamshuddin and Tessens, 1983). This difference is probably due to the interference of Al, SO_4^{2-} and basic cations which are present in large amounts in the soils on marine deposits.

Charge Characteristics

The soils in Carey Island are poorly drained. The impeded drainage condition reduces soil weathering, resulting in the dominance of silicates in the

TABLE 5
Negative charges at pH 3 and 7

Soil Series	Horizon Symbol	Depth (cm)	Negative Charge (meq/100g Clay)	
			PH_3	pH_7
Merbok	Ap	0 – 11	25.1	58.7
Merbok	C	50–90	25.9	58.4
Parit Botak	BC	70+	21.7	39.5
Bernam	Ap	0–7	24.2	41.8
Linau	C	35+	22.6	56.5
Selangor	$B2_2$	45–104	24.3	51.4

soil. The oxides, especially iron oxides, are low. The low iron oxide content is reflected by the low amounts of positive charges; the positive charge in the soil is about 1 meq/100g soil (not shown in table). On the other hand, the negative charge was found to be quite high with values exceeding 50 meq/100g clay (Table 5) indicating the presence of substantial amounts of smectite and/or mica-mixed layers. Thus we expect the soils under study to contain dominantly mica, mica-mixed layers, smectite and kaolinite, similar to the marine derived soils from Perak studied by Shamshuddin *et al.* (1986).

Mica, mica-mixed layers and smectite are, by definition, permanent charge minerals (Uehara and Gillman, 1980; 1981). Even the charges on kaolinite itself are mostly permanent in nature. It means here the charges in the soils will not change very much with the change in pH. This is not the case when the charges were determined at various pH as clearly shown in *Fig. 3*. At pH 7, the negative charges are rather high, but at pH 3 (around the soil pH under field condition) the values are reduced to about half. For instance, at pH 7, the negative charge of Selangor Series (Bw_2) is 51.4 meq/100g clay, while at pH 3 the value is 24.3 meq/100g clay (Table 5).

This phenomenon is probably due to the charges on mica, mica-mixed layers and smectite which are not completely permanent, as suggested by Hendershot and Lavkulich (1983). Thus, when

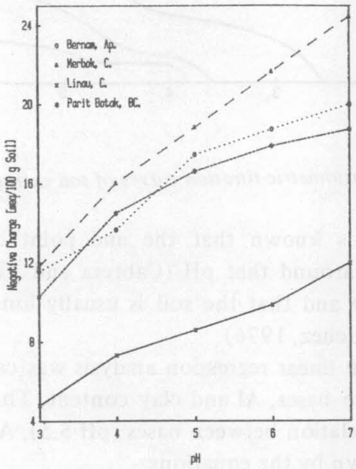

Fig. 3: The change of negative charge with pH for Bernam, Merbok, Linau and Parit Botak Series.

the pH was raised from 3 to 7, some hydrogen from the aluminol group was released into the solution, forming a negative charge. This phenomenon is of relevance to soil management.

Currently the fertilizer applications are based on the CEC determined at pH 7. This study implies that since the CEC of the soils depends on the pH, the fertilizer rates currently used are an over estimate. An oversupply of nutrients will entail higher costs and losses by leaching may result. From the results, it is suggested that the fertilizer rates are better estimated by determining the CEC at the pH of the soil.

CONCLUSION

It was found that the soils in Carey Island contained high amounts of Al, basic cations and sulfate. High amounts of these materials were reflected by the low pH and high electrical conductivity. Electrical conductivity was well correlated to the amounts of basic cations and sulfate (R^2 = 0.98). The soils were highly buffered, especially below pH 5.5, due to the presence of Al. The charges on the clay surfaces were found to increase with an increase in pH. Fertilizer requirements based on CEC at pH 7 is considered to give an overestimated value. This study suggests that the CEC at the soil pH will give a better estimate.

ACKNOWLEDGEMENTS

The authors wish to record their appreciation to UPM for financial support during the conduct of the research and the laboratory staff of Soil Mineralogy Section of the Department of Soil Science for the soil analysis.

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(Received 15 October, 1986)