AGENCY FOR INTERNATIONAL DEVELOPMENT
WASHINGTON, D. C. 20523

BIBLIOGRAPHIC INPUT SHEET

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1. SUBJECT CLASSIFICATION

A. PRIMARY: Agriculture

B. SECONDARY: Soils

2. TITLE AND SUBTITLE

Some exchange adsorption and fixation properties of amorphous volcanic ash soils of Hawaii

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4. DOCUMENT DATE	5. NUMBER OF PAGES	6. ARC NUMBER
1972	34 p.	ARC

7. REFERENCE ORGANIZATION NAME AND ADDRESS

University of Hawaii, Department of Agronomy and Soil Science, College of Tropical Agriculture, Honolulu, Hawaii 98622

8. SUPPLEMENTARY NOTES *(Sponsoring Organization, Publishers, Availability)*

(Presented at Panel on Volcanic Ash Soils of America, Pasto, Colombia, 1972)

9. ABSTRACT

High cation exchange capacity values were obtained in sand, silt, and clay fractions of two dominantly X-ray amorphous volcanic ash soils sampled from an ustic soil moisture regime. The amount of ammonium fixed by selected horizons in these two Typic Eutrandepts was equal to or exceeded that fixed by a montmorillonitic soil. The sand and silt fractions fixed about the same amount of ammonium as did their corresponding clay fraction. A highly significant correlation was found between CEC and ammonium fixation. Soils high in extractive silica and alumina are not always associated with high cation exchange and ammonium fixing capacities. Mineraloids are believed to be involved in ammonium fixation. Cation exchange and anion exchange capacities increased with increasing NH_4Cl concentration in a Typic Hydrandept. a dominantly X-ray amorphous volcanic ash soil sampled from an udic soil moisture regime. CEC increased with increasing pH, with magnitude of increase being greatest between Ph 7 and 9. AEC increased with decreasing pH, with magnitude of increase being greatest between pH 2 and 1. CEC increased with phosphate addition; anion adsorption (as measured by nitrate adsorption) increased with chloride addition and decreased with sulphate and phosphate addition. The use of variable charge model is discussed in relation to Hawaiian soils dominated by oxides of hydrous oxides or iron and aluminum and amorphous aluminosilicates. The Δ pH method for determining net surface charge of a soil also is described.

10. CONTROL NUMBER

PN-AAC-359

11. PRICE OF DOCUMENT

12. DESCRIPTORS

Adsorption
Exchange reactions
Fixation
Hawaii
Volcanic ash

13. PROJECT NUMBER

14. CONTRACT NUMBER

CSD-2833 211(d)

15. TYPE OF DOCUMENT

AID 590-1 (4-74)

Kaneh.
CSD-2833 211(d)
PN-AAC-359

II Panel sobre Suelos Volcánicos de AMERICA

18 a 24 de Junio - 1972

PASTO - COLOMBIA, SA

IICA OEA Universidad de Nariño

Some Exchange Adsorption and Fixation Properties of Amorphous Volcanic Ash Soils of Hawaii 1/

Y. Kanehiro and D. T. Mikami 2/

Introduction

Volcanic ash soils comprise a large percentage of the soils of Hawaii, especially in the younger geological sections of the State. X-ray amorphous material, such as hydrous alumino-silicates and hydrous oxides of aluminium and iron, dominates the mineral make-up in many of these soils. The amorphous material ranges from gels to poorly ordered layer silicate minerals, as well as fresh and weathered remnants of volcanic glass.

The dominant constituent (s) of amorphous material that is found in a volcanic ash soil is determined by the environment in which the soils has formed. In Hawaii the climatic factor, mainly rainfall, largely determines the nature of the amorphous material. The vast majority of the volcanic ash soils are Inceptisols. Four Great Groups of Inceptisols are found: Vitrandepts, Eutrandepts, Dystrandepts and Hydrandepts. Rainfall increases in the direction from the Vitrandepts (dry) to the Hydrandepts (wet). In the dry to subhumid environment weathering has not been as intense as in the wet environment. The soil system is also relatively rich in silica and the bases. In the wet system, weathering is likely to be rapid and intense and occurs in a more acid and silica-poor environment. In the first situation the amorphous material is likely to be volcanic glass,

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which is primarily fresh or slightly weathered, as well as hydrous aluminous silicates, together with remnants of primary minerals, such as feldspars and pyroxenes. Organic matter is likely to be moderately high. In the second situation hydrous oxides of aluminum and iron, as well as hydrous alumino-silicates, will dominate the amorphous fraction. Organic matter will be high and will remain relatively high even in the su soil.

It is generally agreed that volcanic ash soils that contain predominantly amorphous material show great chemical activity. A large part of this is associated with the great surface area that amorphous colloids possess.
Because of this high activity and other unusual chemical properties, means other than conventional methods of interpretation must often be used when working with these soils. The purpose of this study was to obtain further data and to get a better insight on the ion exchange, adsorption, and fixation properties and reactions of these dominantly amorphous Hawaii volcanic ash soils. To better illustrate the properties and behavior of amorphous volcanic ash soils developed under different rainfall conditions, soils from ustic and udic moisture regimes were sampled. The ustic regime is represented by the Naalehu silty clay and Pahala fine sandy loam (both Typic Eutrandepts) while the udic regime is represented by the Akaka silty clay (a typic Hydrandept)

Materials and Methods

Soils Used:

Three Hawaiian soils, Akaka silty clay (Typic Hydrandept), Pahala fine sandy loam (Typic Eutrandept), and the Naalehu silty clay (Typic Eutrandept), sampled from the Island of Hawaii were used for this study. The Akaka soil, chosen to represent an udic moisture regime, has developed from volcanic ash under conditions of over 5000 mm annual rainfall. This soils is a

member of the thixotropic isomesic family of Typic Hydrandepts. It is dominantly amorphous and contains large amounts of hydrate oxides of Fe and Al, hydrous aluminosilicate, and organic matter (organic C= 15%). pH of the surface soils usually ranges from 5.0 to 6.0. Very little exchangeable bases remain in this soil. The Pahala and Naalehu soils represent an ustic moisture regime and have developed from volcanic ash under an annual rainfall of about 900-1500 mm. These soils are members of the medial, isothermic family of the Typic Eutrandepts. They are also dominantly amorphous but because weathering has been less intense in these soils, there is less secondary amorphous material development than in the Akaka soil. Some primary minerals, such as feldspars, olivine, pyroxenes and iron oxides, are found in those soils with appreciable amounts of fresh and weathered glass. In spite of the relatively low rainfall, organic matter in the surface soil is moderately high (organic C=5%) pH of these soils usually rangesfrom 6.5 to 7.5. Base saturation is very high.

Other soils, which are not dominantly amorphous in nature and developed from volcanic basalt rather than ash were included in selected parts of this study for comparative purpose.

Procedures:

X-ray analysis was determined on the less than 2 micron fraction after potassium and magnesium saturation and after orientation on a glass slide, using a Norelco X-ray diffractometer with copper K_α radiation and nickel filter. The sand and silt fractions were run as powder samples in an aluminum holder. These fractions were further run as a smear on a glass slide after differential dissolution analysis (d.d.a.), following the method of Hashimoto and Jackson (12). Extractable silica and alumina of soils and their fractions were also determined by differential dissolution analysis.

Total chemical analysis was carried out by determining SiO_2, Fe_2O_3, TiO_2, CaO and MgO after Na_2CO_3 fusion; MnO; P_2O_5, Na_2O and K_2O after $HF-H_2SO_4$ digestion. Al_2O_3 was obtained from the difference between R_2O_3 and the oxides of iron, titanium and phosphorus.

The cation exchange capacity (CEC) of the soil and size fractions was determined by the 1N ammonium acetate method at pH 7.0. The ammonium was displaced wiht 4% KCl and the displaced ammonium was determined in a micro-Kjeldahl steam distillation apparatus followed by titration with a standard acid. The CEC delta value of the deferrated whole soil, sand, silt and clay fractions of the Naalehu and Pahala soils was determined by the method of Aomine and Jackson (2). In studies to find out the effects of concentration and pH of exchange ammonium solution on cation exchange capacity (CEC) or anion exchange capacity (AEC), Schofield's procedure (22), as slightly modified by Wada and Ataka (28), was used. Ammonium fixation studies were carried out using the method of Allison et al. (1). Ammonium fixation is defined in this study as that reaction in which adsorbed ammonium is retained against 1N KCl extraction. The influence of various anions on cation and anion exchange/adsorption was determined by treating soil samples with 1M KCl, 0.5M K_2SO_4 and 1M KH_2PO_4. The treated samples were determined for: 1,- CEC by using 1N ammonium acetate at pH 7.0 and; 2.- anion adsorption as measured with 0.01 and 0.1N concentrations of KNO_3. Nitrate determination was carried out by micro-Kjeldahl distillation of amonia after nitrate reduction with Devarda alloy

Results and Discussion

Chemical and mineralogical properties

To characterize the chemical and mineralogical properties of the Naalehu and Pahala soils and to determine the mineral (s)

fixing ammonium, total chemical analysis, extractable silica and alumina analysis (by differential dissolution analysis), X-ray diffraction and petrographic studies were carried out, in addition to cation exchange and ammonium fixation analyses.

Total chemical analysis data on the deferrated, organic matter-free whole soil, sand, silt and clay fractions of the Naalehu (150-165 cm) and Pahala (64-91 cm and 132-145cm) soils are given in Table 1. The data show that no apparent large differences exist among the deferrated, organic matter-free whole soils and sand, silt anda clay fractionas of the three samples analyzed.

They also show that soils are relatively high in silica and bases and low in iron and aluminum, thereby reflecting the development of these soils in an ustic moisture regime.

Table 2 shows data on extractable silica and alumina for these two soils, as well as the montmorillonitic Lualualei, micaceous Alokui and kaolinitic Molokai soils. These chemical data will be discussed in relationship to cation exchange and ammonium fixation in later sections.

X-ray diffraction diagrams of the Pahala soil are presented in Figures 1 and 2. (The diagrams of the Naalehu soil were almost identical to those of the Pahala soil and are not shown). The primary mineral most frequently appearing in the various fractions was plagioclase feldspar. The dominant component of these fractions was generally X-ray amorphous with the exception of halloysite in some horizons of this soil. A relatively prominent 020 (hkl) reflection band near 20° 2θ (4.44 Å) consistently appeared in all fractions, suggesting the presence of some layer silicate mineral. This is in keeping with the belief that amorphous material, such as allophane, precedes the formation of layer silicate minerals, such as halloysite, in the weathering sequence of ash to allophane to halloysite (9,24). Besoain (4) reported finding halloysite associated with allophane, principally in deep older layers of volcanic

ash soils of Chile. In some cases small amounts of montmorillonite and micaceous minerals were also found.

Cation exchange capacity of Naalehu and Pahala soils and their size fractions

The CEC values of the untreated Naalehu and Pahala soils, hydrogen peroxide-treated soils, deferrated soils and size fractions of the two soils are given in Table 3. A general decrease in CEC for the surface horizons occurred after organic matter removal by hydrogen peroxide oxidation. However, a small increase in CEC was noted for the lower horizons.
Aside of the three upper horizons in the Pahala profile, deferration increades CEC. Very high values were obtained for the sand and silt fractions of these soils. This is contrary to the generally accepted idea that CEC is low in the sand fraction of soils.

The clay fractions demonstrated a very high capacity to adsorb cations.
In an earlier work Kelley and Page (15) found two samples from Naalehu and South Point, Hawaii, with CEC of 120 and 88 me/100g respectively (the soil found in the latter location is today classified as an Eutrandepts as are The Naalehu and Pahala soils) They attributed the high CEC to the amorphous mineral in these soils.

CEC delta values are presented in Table 4. The values were largest for the clay fractions. These values were larger for the Pahala 132-145 cm horizon fractions than for the comparable fractions at he 64-91 cm depth.
The delta values for these 64-91 cm fractions were close to the values for the Naalehu 150-165 cm fractions. CEC delta values were not correlated to the CEC of soils and their fractions (Table 3). A highly significant correlation ($r = 0.824^{++}$, $df = 8$) was obtained when the extractable silica and alumina

contents (Table 2) were compared against the CEC delta values of the same horizons. This shows that some relationship exists between two methods of amorphous material determination.

Ammonium fixing capacity of Naalehu and Pahala soils and their size fractions

The ammonium fixing capacity was studied in untreated soils, hydrogen peroxide-treated soils, deferrated soils and size fractions with two rates of ammonium chloride solution (10 and 50 me. ammonium per 100 g. soil.) In the complete soil profile samples of the Naalehu and Pahala soils and in selected horizons of the montmorillonitic Lualualei, micaceous Olokui, and Kaolinitic Molokai soils. The results of Tables 5 and 6 show that as much as a 100% increase in ammonium fixation occurred when the rate of ammonium application was increased from 10 to 50 me. per 100 grams soil.
This was very evident especially in the 64-91 cm. horizon of the Pahala soil. The 50 me. per 100 g. rate was found to be a maximun beyond which fixation decreased.

The results of this study show that the Naalehu and Pahala profiles have some capacity to retain ammonium against N KCl extraction. The amount fixed in selected horizons and treatments was equal to or exceeded that fixed by the montmorillonitic Lualualei and micaceous Olokui soil.

The data in Tables 5 and 6 show that ammonium fixation before and after hydrogen peroxide oxidation of the organic matter was not noticeably different. In fact, only a slight increase or decrease occurred in the capacity of the Naalehu and Pahala soils to fix ammonium into nonexchangeable form. This implies, at least for these soils, that ammonium fixation is not due to the reaction of ammonium with soil organic matter. Free iron removal increased the ammonium fixing capacity to some extend. The most noticeable increase occurred in the 64-91 cm. horizon

of the Pahala soil, demonstrating the high fixing capacity of this particular horizon.
Ammonium fixation by the deferrated sand, silt and clay size fractionas shows that as in the whole soil, the highest fixation occurred in the Pahala (64-91 cm.) horizon. The Naalehu (150-165 cm) horizon also had a high ammonium fixing capacity. In both horizons and with both concentrations, the silt fraction had the highest fixation, followed by the sand and clay fractions, respectively.

In the crystalline soils, the highest fixation occurred in those soil horizons that were predominantly micaceous (Olokui) and montmorillonitic (Lualualei). The kaolin soil (Molokai) fixed little ammonium.

Statistical examination of the data showed that a highly significant correlation ($r = 0.627^{++}$, df = 73) existed between CEC and ammonium fixation obtained with the 50 me. ammonium per 100 g. rate. A better correlation could have been obtained if the obvious non-relationshp of the clay fraction to ammonium fixation was not included in the statistical analysis. A correlation coefficient of 0.832, highly significant at the 1% level, was shown when CEC of only untreated whole soil was analyzed against ammonium fixation.

There was no obvius relationship between the chemical composition of the samples (Table 1) and their capacity to fix ammonium. Table 2 shows that considerable amounst of silica and alumina were dissolved in the horizons studied. Some relationship between ammoniun fixation and amorphous material constant is shown the lower the extractable silica and alumina content. the greater the ammonium fixing capacity.

Effect of concentration of salt solution on cation and anion exchange capacities of Akaka soil.

Figure 3 shows that cation exchange capacity (CEC) increased from 10 to 68 me/100 g. as concentration of NH_4Cl increased

from 0.25 to 1 0N, respectively, in the Akaka (20-40 cm.) soil. This increase was especially pronounced from 0.75 to 1. 5N. Beyond 1. 5N, CEC appears to be leveling off. Wada and Ataka (28) also noted increased CEC with increasing NH_4Cl concentrations in allophane samples prepared from Japanese volcanic ash soils.
These workers also found this concentration effect on CEC in halloysite but not for montmorillonite-illite. They discussed two different mechanism of ion adsorption by these clay minerals. The first type depends on Coulombic forces between the ions and the clay particles and is applicable to adsorption by the montmorillonite-illite clay, although this type was noted to be found also with allophane and halloysite. The second type depends on non-Coulombic attraction which is not pH-dependent on concentrations of the exchange solution. Such attraction accounts for mucho of the CEC, in allophane and halloysite colloids.

New Zealand soils containing allophane, "palagonite", and amorphous oxides were found to give CEC values which depend markedly upon concentration of ammonium solution (5). Adsorption of cations by these soils was noted to closely resemble the behavior of hydranted alumina prepared by precipitation. Physical adsorption of cations in these soils was proposed as being responsible to a greater or less extend for increases in CEC values as concentration of the ammonium solution was increased.

Figure 4 shows that anion exchange capacity (AEC) increased from 10 to 73 me./100 g. as concentration of NH_4Cl increased from 0.25 to 2. 0N, respectively, in the Akaka (20-40 cm.) soil. The data of Table 8 also show that nitrate adsorption was higher when 0.1N rather than 0.01N KNO_3 was used as the exchange solution in this same soil.

Singh and Kanehiro (23) reported that nitrate adsorption in the abovementioned Akaka soil and in the Kaolinitic Wahiawa

soil follows a Freundlich type of adsorption isotherm. A highly significant correlation existed between the electrolyte concentration and the amount of NO_3 adsorbed in these two soils. The adsorption increased consistently with each increment in electrolyte concentration. They found that the magnitude of adsorption was greater in the dominantly amorphous Akaka soil than in the Kaolinitic Wahiawa soil.

Adsorption of anionic organic matter in the Akaka soil was observed to increase exponentially with increasing addition of carbon to he system by Briones (7). The adsorption isotherm followed a Freundlich type of isotherm.
She reporter that adsorption was greater in the gibbsite-rich subsoil than in the surface horizon of this Akaka soil.

Japanese investigators (26) have also observed increased AEC with increasing concentration of the exchange NH_4Cl solution in allophanic colloids.
They proposed that non-Coulombic attraction between ions and clay particles plays a large role in increasing AEC under such conditions.

The adsorption of NO_3 was also reported to be concentration-dependent and was describe by a Langmuir type isotherm by Kinjo and Pratt (16) in their work on Andepts, Oxisols, and Alfisols from Mexico, Colombia and Brazil. Hassan et al. (13) showed that adsorption of sulfate fits the linear form of the Langmuir equation over a limited range of concentration in Hawaii volcanic ash soils.

Effect of pH of salt solution on cation and anion exchange capacities of Akaka soil.

Amorphous soils derived from volcanic ash and containing large amounts of allophane, hydrated iron and aluminum oxides

and organic matter are known to be made up of colloids with variable charge or pH-dependent charge.
Figure 5 shows that the magnitude of increase in CEC was much greater per unit rise in pH above than below neutrality in the Akaka (20-40 cm.) soil.
CEC rose from 65 (at pH 7.0) to 105 me./100 g. at pH 9.0. It took a 4-unit change in pH (from pH 3.0 to 7.0) to effect this same magnitude of increase in the acid range. Lai and Swindale (17) also noted that change in CEC between pH 4.0 and 7.0 was much less than between 7.0 and 8.5 in four Hawaiian allophanic soils.

Wada and Atka (28) reported increase in CEC between pH 5 and 7 in two samples of allophane prepared from two Japanese volcanic ash soils. This increase was attributed to an acquisition of negative charges probably due to dissociation of H^+ ions from Si-OH groups with rise in pH. Fieldes (10) and Tan (26) similary reported increasing negative charge as pH increased above 5 in allophanic soils from New Zealand and Indonesia, respectively.

AEC in the Akaka soil increased from 21 to 37 me./100 g. as pH was decreased from 9.0 to 2.0 (see Figure 6). There is pronounced increase of 24 me./100 g. with only a unit decrease in pH from 2.0 to 1.0. Singh and Kanehiro (23) showed increasing NO_3 adsorption with decreasing pH in this Akaka subsoil. They reported greater magnitudes of adsorbed nitrate in this dominantly amorphous Akaka soil than in the Kaolinitic Wahaiwa soil under comparable pH conditions. They attributed the greater adsorption in the former soil to the greater number of reative OH groups in the allophane and hydrated iron and aluminum oxide fractions which give rise to positive adsorption sites. The fact that positive adsorption of nitrate took place at pH above 7 led them to conclude that positive charges in these

soils exist even under alkaline conditions. The AEC data in Figure 6 substantiate this conclusion.

Briones (7) observed that amounts of humic and fulvic acids adsorbed by the Akaka soil was highest at low values and as the pH was increased adsorption decreased. Adsorption of these organic compounds was attributed to a chemical interaction betweeathe soil colloids and carboxyllic acids of organic matter.

Kinjo and Pratt (16) reported a sharp rise in NO_3 adsorption as the pH of the equilibrium solution dropped to 3.5 from 6.0 and then adsorption leveled off in Andepts from Mexico and Colombia. Other investigators working with allophanic ash soils have reported similar increases in anion adsorption with decrea sin pH. Wada and Ataka (28) reported appreciable increase in AEC when pH of the equilibrium solution of NH_4Cl was decreased from 7.0 to 5.0 in allophanic clays, while there was very little change in halloysite and montmorillonite-illite clays at a comparable change in pH.
Fieldes (10) also demonstrated increased anion retention with decreasing pH in allophane.

Effect of ions on cation exchange capacity and nitrate adsorption in Akaka soil.

Table 7 shows that CEC was approximately tripled with the addition of phosphate. Mekaru and Uehara (18) similary showed increased CEC of phosphated soils in the Hilo silty clay which is also a Typic Hydrandept. They calculated that each millimole of adsorbed phosphate increases CEC by approximately 0.8 me. at pH 7.0

The other anions, chloride and sulfate, did not increase CEC. It was thought that sulfate would also displace hydroxyls and thereby increase CEC but this apparently did not happen. The reason for this failure of sulfate addition to increase CEC

most probably must be due to the fact that the untreated Akaka soil was already very high in native sulfate content. Hassan et al. (13) and Mokaru and Uehara (18) noted that Hydrandepts of Hawaii possess a high sulfate adsorption capacity and native sulfate content.

Mikami and Kimura (19) reported appreciable reduction in CEC after lime addition in the Akaka soil and in two Hawaiian Tropohumults. CEC measured 58.7 me. in the no-lime as compared to 52.0 me./100g. in the limed Akaka soil, five months after application. The comparable values for the two Tropohumults were 17.6 reduced to 9.7 and 23.3 to 16.7 me./100 g. These two soils are also known to be high in oxides of iron and aluminum.

Table 8 shows that sulfate and phosphate additions decreased nitrate adsorption. This decrease was especially pronounced with the phosphatetreated sample at both KNO_3 concentrations. The reduction in nitrate adsorption with sulface addition was more effective at the 0.01N than at the 0.1N KNO_3 concentration. The chloride treatment increased nitrate adsorption and the increase was greater at the 0.1N than at the 0.01N KNO_3 concentration. Mekaru and Uehara (18) reported negative adsorption of nitrate and chloride ions when sulfate ions were added to a soil colloidal suspension of a Hawaiian Hydrandept which was initially net-positively charged. In their anion-exchange equilibria studies with two Andepts and one Oxisol from Mexico and South America, Kinjo and Pratt (16) reported that chloride was slightly preferred over nitrate, and sulfate and phosphate were greatly preferred over nitrate. They found that negative adsorption of nitrate occurred when sulfate or phosphate exceeded certain concentrations.

Additional Discussion and Conclusions

Adsorption and fixation mechanisms

Some explanation describing the source and mechanism of the high cation exchange capacity of the clay fraction and their obvius

non-relationship to ammonium fixation is needed in the Naalehu and Pahala soils. The data (Table 2) show that the extractable silica and alumina of the Molokai clay (kaolinite) and the sand, silt and clay fractionas of the Naalehu and Pahala soils are extremely high. However, their cation exchange capacities and ammonium fixing capacities range from low to very high. Soils high in extractable silica and alumina are not always associated with high cation exchange and ammonium fixing capacities. This can be explained by the origin of their aluminum. Aluminum in halloysite is held in its structure in octahedral coordination. However, mineraloids or allophane differ from other clay minerals with respect to its aluminium which is held in its structure in tetrahedral co-ordination. This is supposed to be the main cause for its many unusual actities, one of them being its cation holding mechanism (10). Egawa (8) in describing the mechanism of ion adsorption of allophane described the shift of the coordination number of the octahedral aluminium to tetrahedral as being considered one mechanism by which the acidic nature originates

The foregoing results with Naalehu and Pahala soils showed the definite capability of certain mineraloids to adsorb and fix large quantities of ammonium. It should be pointed out that adsorption and fixation reactions are not irreversible reactions and that these two reactions overlap each other. Tamimi et al. (25) have shown that fixation of ammonium in the presence of phosphate can occur by the formation of taranakite in amorphous soils of Hawaii. Fox et al. (11) reported that phosphorus adsorption/fixation is much higher in soils dominated by amorphous colloids than in those dominated by layer silicate minerals. Our data have shown that not all amorphous materials with CEC have a high capacity to fix ammonium. Furthermore, it is generally believed that the adsorbing and fixing intensities of humus and amorphous material are generally weaker than those of crystalline clays.

Birrell (5) has stated that retention of cations by amorphous

alumino-silicates requires an alkaline medium; therefore, there is no mechanism for an effective fixation of cations like potassium in some volcanic ash soils within the normal soil pH range. The Naalahu and Pahala soils apparently do have enough of an alkaline medium to effectively fix ammonium. Their pH is generally about 7 and base saturation is high. SiO_2/Al_2O_3 molecular ratios ranged between 3.10 and 4.00 in the sand. silt and clay fractions of the two high ammonium fixing horizons of the two soils (Table 1). Van Reeuwijk and de Villiers (27) have in fact demonstrated that synthetic aluminosilica gels fixed potassium against replacement by common alkali and alkaline earth cations. They further reported that amounts of K fixed against exchange by a particular ion increased with total CEC and with the pH value at which K-saturation originally took place.

To add to the mineralogical information, the silt and sand fractions of the high ammonium fixing Naalehu (150-165cm.) and Pahala (64-91 cm.) soils were examined by the petrographic microscope. Some feldspars, olivine, pyroxenes, and iron oxides were present in all samples but the most important single mineral relative to fixation was glass or its weathered equivalent. Weathered glass can be distinguished from fresh glass by a progressive increase in birefingence as the glass weathers. The non-crystalline and yet birefrigente character of this material fits the definition of Wentworth's (29) palagonite. This amorphous material also fits the description of the Birrell's (5) "palangonite". He reported this material as being formed from the weathering of basaltic glass and noted its presence in a soil from Aitutaki Island and also speculated on its presence in Pahala Ash soil. The ion exchange capacity of these samples can be largely attributed to this weathered glass and this value must be near 200 me. per 100 grams considering the sample is about 30-50% fresh glass, plant opal, feldspar, pryroxenes and iron oxide.

The difference in capacity to fix ammonium among mineraloids must arise through some fundamental mechanism. It appears that the origin of the charge on the colloid surface may be an important factor. Aluminium in volcanic glass is most probably tetrahedrally co-ornidated along with silicon. In this condition the charge unbalance created by the trivalent aluminum is satisfied by sodium, calcium and magnesium. These cations cannot undergo ion exchange and the cation exchange capacity of fresh glass would be low.

In soils, however, weathering of glass by hydration, hydrolysis and carbonation results in loss of the soluble cations leaving an open network of silica and alumina. This material is still amorphous, has a high charge density and now can, due to its openness, permit ion exchange.

It is further proposed that with further leaching and increased acidity, the aliminum alters to the more stable octahedrally co-ordinated hydroxide (gibbsite) or alumino-silicate (kaolin) and loses its capacity to fix ammonium. The 132-145 cm. horizon of the Pahala soil may represent weathering in this direction.

If, on the other hand, leaching is not too intense and the pH is favorable, a large fraction of the aluminum atoms may remain in the four-co-ordinated state and give rise to a material similar to the Naalehu (150-165 cm.) and Pahala (64-91 cm.) soil. These two samples in some ways behave chemically like montmorillonite. Birrel (5) also noted that an amorphous colloid that formed under conditions of restrited leaching, wich he called "palagonite", resembled montmorillonite chemically.

It is importante to stress again the wide differences noted in the reactivity of amorphous material to ammonium. A mere identification of large quantities of amorphous material in a soil does not necessarily imply that it will fix ammonium.

Variable charge colloidal system

Mekaru and Uehara (18) have recently proposed the use of a theory of constant potential colloids in describing soil colloidal systems in Hawaii which are dominated by oxides or hydrous oxides of iron and aluminum and amorphous aluminosilicates. In such colloids charges arise at exterior lattice sources. These constant potential colloids types are more commonly called variable charge colloids or pH-dependent charge colloids. In such a system potential-determining ions, such as H^+, OH^-, F^- and PO_4^{---}, can alter surface charges. With this type of colloids, anion adsorption can occur either by way of non-specific anion adsorption or by specific ion adsorption (14). Anions are retained as counter ions in the diffuse layer or can enter into coordination with the oxide metal ion which involves displacement of one anion by another.

A method was described by Mekaru and Uehara (18) for determining net surface charge of a soil by taking soil pH measurement in water and in 1N KCl solution. They proposed the term ΔpH as the pH difference between the pastes prepared with 1N KCl and water. Much of this concept on pH is based on Parks and DeBruyn's (20) work on the measurement of surface charge density of hematite as a function of pH in suspensions containing varying concentrations of KNO_3. These workers showed that when the hematite surface possess a net positive charge, pH increased with increasing KNO_3 (an indifferent electrolyte) concentration. Conversely, pH decreased with increasing concentration when surface charge was net negative. At the zero point of charge pH was independent of concentration. Others (3,30) have made similar studies for goethite and α-alumina.

Mekaru and Uehara (18) emphasized that an indifferent electrolyte ion, such as chloride, be used to properly interpret pH

values for net surface charge determination. A specifically adsorbed ion, such as sulfate, displaces hydroxylis coordinated to the metal oxide and will increase suspension pH. The phosphate ion is also known to behave similarly. The consequence of such displacement is an increase in negative charges which in turn will mean increased CEC. These two investigators, reported that each millimole of adsorbed phosphate increased CEC by approximately 0.8 me./100 g. soil at pH. 7.0 in the Hilo silty clay loam, a Typic Hydrandept that has many similar properties as the Akaka silty clay. The foregoing discussion does much to explain the increased CEC that was obtained with phosphate addition (Table 7).
The failure of sulfate to increase CEC was most probably due to the fact that the soil surface was negatively charged. In a previous study it was shown that the Akaka subsoil horizons possess a negative Δ pH (18). Sulfate has been shown to affect zeta potential of a mineral only when the surface is positively charged (21). Furthermore, it has been dosmonstrated by other Hawaiian workers that the Akaka soil contains a high amount of native adsorbed sulfate content (13).

This approach also helps to explain the reduction in CEC obtained after lime application and "fixation" of calcium in the Akaka soil and two oxisols in Hawaii (19). Purcell and Sun (21) reported that when the colloidal surface was negatively charged calcium ions rapidily reduced zeta potential, and at a concentration of 10^{-3} moles per l. the potential was positive for all pH values. Calcium ions were attracted to the negative surface by both electrostatic and covalent forces.

Hawaiian soils that possess Δ pH values near zero or even positive values are those that are high in oxides or hydrous oxides of iron and aluminum and other amorphous colloids (18) Such soils fall in the variable charge type and can best be described by a constant potential model.

On the other hand, soils high in mica, montmorillonite, and vermiculite possess relatively high negative pH values and should be treated by a constant charge model. The Akaka soil fits in very well with the variable charge type model. The Pahala and Naalehu soils, although showing some chemical properties of a 2:1 layer silicate mineral, such as the ability to fix ammonium still are dominantly X-ray amorphous and should also be treated as a variable charge rather than a constant charge model.

Abstract

High cation exchange capacity values were obtained in sand, silt and clay fractions of two dominantly X-ray amorphous volcanic ash soils sampled from an ustic soil moisture regime. The amount of ammonium fixed by selected horizons in these two Typic Eutrandepts was equal to or exceeded that fixed by a montmorillonitic soil. The sand and silt fractions fixed about the same amount of ammonium as did their corresponding clay fraction. A highly significant correlation was found between CEC and ammonium fixation. Soils high in extractable silica and alumina are not always associated with high cation exchange and ammonium fixing capacities. Mineraloids are believed to be involved in ammonium fixation.

Cation exchange and anion exchange capacities increased with increasing NH_4Cl concentration in a Typic Hydrandept, a dominantly X-ray amorphous volcanic ash soil sampled from an udic soil moisture regime. CEC increased with increasing pH, with magnitude of increase being greatest between pH 7 and 9. AEC increased with decreasing pH, with magnitude of increase being greatest between pH 2 and 1. CEC increased with phosphate addition; anion adsorption (as measured by nitrate adsorption) increased with chloride addition an decreased with sulfate and

phosphate addition.

The use of variable charge model is discussed in relation to Hawaiian soils dominated by oxides of hydrous oxides or iron and aluminum and amorphous aluminosilicates. The ΔpH method for determining net surface charge of a soil is also described.

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Acknowledgements.

Presentation of this paper by the author at the "II Panel on Volcanis Soils of America" conference held at the University of Nariño, Pasto, Colombia was made possible by the funds a 211(d) Grant AID/osd-2833, "To strengthen the capabilities of the University of Hawaii in Special Problems of Tropical Soils". This work was supported in part by the Western Regional Research Project No. W-31

Table 1. Chemical Composition of Naalehu and Pahala Soils and their Size Fractions.

SOIL	Naalehu 150-165 cm.				Pahala 64-91 cm				Pahala 132-145 cm.			
	Def	Sand	silt	clay	Def.	sand	silt	clay	def.	sand	silt	clay
SiO_2	45.59	45.89	46.99	43.03	44.40	42.37	44.89	41.30	45.07	45.45	46.89	41.66
Fe_2O_3	11.01	10.65	11.89	10.76	13.24	14.42	11.18	14.47	8.02	8.80	8.32	6.62
Al_2O_3	21.72	19.49	22.72	21.03	18.92	21.19	24.59	22.35	22.84	21.28	23.20	26.22
TiO_2	2.04	2.42	2.24	2.59	2.15	3.37	3.62	4.21	2.28	2.21	2.34	2.66
CaO	1.87	2.65	1.67	.58	2.27	3.15	2.02	.91	3.23	3.65	3.92	.45
MgO	3.64	6.24	1.90	.90	2.74	3.15	2.60	1.21	4.16	6.59	3.42	.68
K_2O	.15	.15	.18	.17	.26	.24	.20	.11	.14	.17	.17	.12
Na_2O	3.54	3.40	2.83	6.94	3.02	2.85	2.39	4.34	2.97	2.71	2.51	5.92
P_2O_5	.17	.11	.02	.09	.18	.11	.17	.05	.36	.23	.20	.37
MnO_2	.03	.04	.03	.05	.04	.07	.06	.12	.04	.08	.09	.03
H_2O+	10.70	8.80	9.76	12.90	11.23	9.30	9.77	12.25	11.18	9.24	9.52	14.91
Total	100.46	99.82	100.23	99.04	98.45	100.22	101.49	101.32	100.29	100.41	100.58	99.64
$\frac{SiO_2}{Al_2O_3}$	3.56	4.00	3.51	3.47	3.97	3.39	3.10	3.13	3.35	3.62	3.43	2.70

Table 2. Extractable Silica and Alumina of Soils and their Size Fractions by Differential Dissolution Analysis.

SOIL	Dpth cm.	SiO_2	Al_2O_3	$SiO_2 + Al_2O_3$
		%		
Naalehu	150-165			
Def.		24.6	20.4	45.0
sand		19.2	14.4	33.6
silt		23.6	20.0	42.0
clay		23.7	18.3	42.0
Pahala	64-91			
def.		20.8	18.7	39.5
sand		17.1	15.1	32.2
silt		16.0	18.3	34.3
clay		20.5	18.5	39.0
Pahala	132-145			
def.		29.2	28.1	57.3
sand		28.3	22.3	50.6
silt		27.8	26.4	54.2
clay		35.6	20.4	56.0
Lualualei	3-38			
clay		9.9	4.2	14.1
Olokui	10-18			
clay		2.6	6.8	9.4
Molokai	188+			
clay		17.8	22.3	40.1

Table 3. Cation Exchange Capacity of Naalehu and Pahala Soils and their Size Fractions.

Soil	Depth, cm.	Untrt. soil	H_2O_2-trt. soil	Def. soil	Def. sand	Def. silt	Def. clay
		me./100 g.					
Naahelu	0- 28	52.2	43.9	57.0	26.0	34.7	106.3
	28- 53	60.9	63.5	89.9	76.7	71.0	111.6
	53-137	67.0	70.4	102.4	78.5	87.6	111.2
	137-150	73.6	77.4	97.4	75.3	85.4	105.9
	150-165	75.1	77.5	104.7	91.0	95.4	116.1
Pahala	0- 18	36.8	24.9	22.3	8.4	17.4	92.3
	18- 28	31.7	26.3	27.8	11.3	22.6	102.5
	28- 46	32.9	31.4	33.4	15.6	—	108.2
	46- 64	39.3	42.3	49.2	29.5	37.9	105.1
	64- 91	72.7	80.4	96.6	88.9	87.7	102.3
	91- 99	53.4	58.5	68.4	61.6	58.8	91.9
	99-132	41.2	46.0	61.9	47.0	48.4	106.9
	132-145	56.4	64.7	91.4	81.0	77.8	124.2

Table 4. Delta cation exchange capacity of Naalehu and Pahala soils and their size fractions.

SOIL	Dept, cm.	Cation Exchange capacity, me./100 g. 2% Na_2CO_3 treated (B)	$NaOA_c$ pH. 3.5 treated (A)	Value (B-A)
Naalehu	150-165			
def.		92.6	77.1	15.5
sand		90.8	73.8	17.0
silt		100.6	84.8	15.8
clay		116.4	92.3	24.1
Pahala	64-91			
def.		97.7	83.4	14.3
sand		—	—	—
silt		95.5	78.7	16.8
clay		106.5	82.8	23.7
Pahala	132-145			
def.		99.4	63.0	36.4
sand		—	—	—
silt		85.5	55.1	30.4
clay		130.4	80.8	49.6

Table 5. Ammonium fixation capacities of soils saturated with 10 me./ 100 g. ammonium and oven-dried at 105 C. for 12 hours.

S O I L	Depth, cm.	Untrt. soil	H_2O_2 trt soil	Def. soil	Def. sand	Def. silt	Def. clay
		me. /100 g.					
Naalehu	0- 28	.42	.36	1.37	8 .48	.59	.83
	28- 53	1.19	1.96	1.96	1.25	1.93	1.58
	53-137	1.49	1.61	2.08	1.55	2.14	1.19
	137-150	2.30	2.26	2.98	.60	1.60	1.58
	150-165	1.90	2.20	2.65	1.67	3.00	1.42
Pahala	0-18	.30	.36	.48	.18	.30	.77
	18-28	.41	.54	.63	.21	.36	.83
	28-46	.59	.71	.74	.42	.77	.95
	46-64	1.43	1.43	1.81	1.25	1.37	.60
	64-91	2.97	3.15	4.19	3.09	3.98	2.50
	91-99	.71	.50	.83	.71	.62	.71
	99-132	1.07	.87	.89	1.01	1.07	1.31
	132-145						
Lualualei	3-38	2.32	1.37	--	--	--	--
Olokui	10-18	2.50	2.91	3.93	--	--	6.90
Molokai	188+	.30	--	--	--	--	.21

Table 6. Ammonium Fixation Capacities of Soils Saturated With 50 me./100 g. Ammonium and Oven-Dried at 105° C. for 12 hours.

SOIL	Depth, cm.	Untrt soil	H_2O_2 trt. soil	Def. soil	Def sand	Def silt	Def clay
		me. / 100 g.					
Naalehu	0- 28	1.19	.71	1.55	1.01	1.19	3.75
	28- 53	1.96	2.50	2.86	2.74	2.91	3.15
	53-137	2.44	2.44	3.51	3.15	3.69	3.33
	137-150	5.47	4.94	5.95	1.17	3.15	4.46
	150-165	4.10	4.11	4.88	4.94	5.56	4.16
Pahala	0- 18	.42	.45	.65	.42	.59	2.26
	18- 28	.49	.65	.89	.59	.60	1.90
	28- 46	.74	.83	1.43	.83	1.13	1.90
	46- 64	1.78	1.61	2.44	1.96	2.06	2.02
	64- 91	6.48	5.71	7.91	6.84	7.38	5.59
	91- 99	3.27	3.15	3.57	2.26	3.03	2.97
	99-132	.95	1.13	1.55	.95	1.31	1.67
	132-145	1.31	1.05	1.61	1.13	1.31	1.78
Lualualei	3- 38	5.71	—	—	—	—	6.78
Olokui	10-18	2.76	2.44	3.03	—	—	9.93
Molokai	188+	.65	—	—	—	—	.39

TABLE 7. Effect of chloride, sulfate and phosphate on the cation exchange capacity (CEC) of the Akaka soil (Data of W. Y. Shiroma)

Treatment	CEC, me./100 g.
Control	66.7
Chloride (KCl)	61.2
Sulfate (K_2SO_4)	65.6
Phosphate (KH_2PO_4)	183.6

TABLE 8. Effect of chloride, sulfate and phosphate on nitrate adsorption at 0.01 and 0.1N KNO_3 concentrations in the Akaka Soil (Data of W. Y. Shorima)

Treatment	NO_3^- adsorbed me./100 g.
0.01N KNO_3	
Control	3.89
Chloride (KCl)	5.61
Sulfate (K_2SO_4)	1.73
Phosphate (KH_2PO_4)	1.51
0.1N KNO_3	
Control	9.84
Chloride (KCl)	32.50
Sulfate (K_2SO_4)	8.12
Phosphate (KH_2PO_4)	1.31

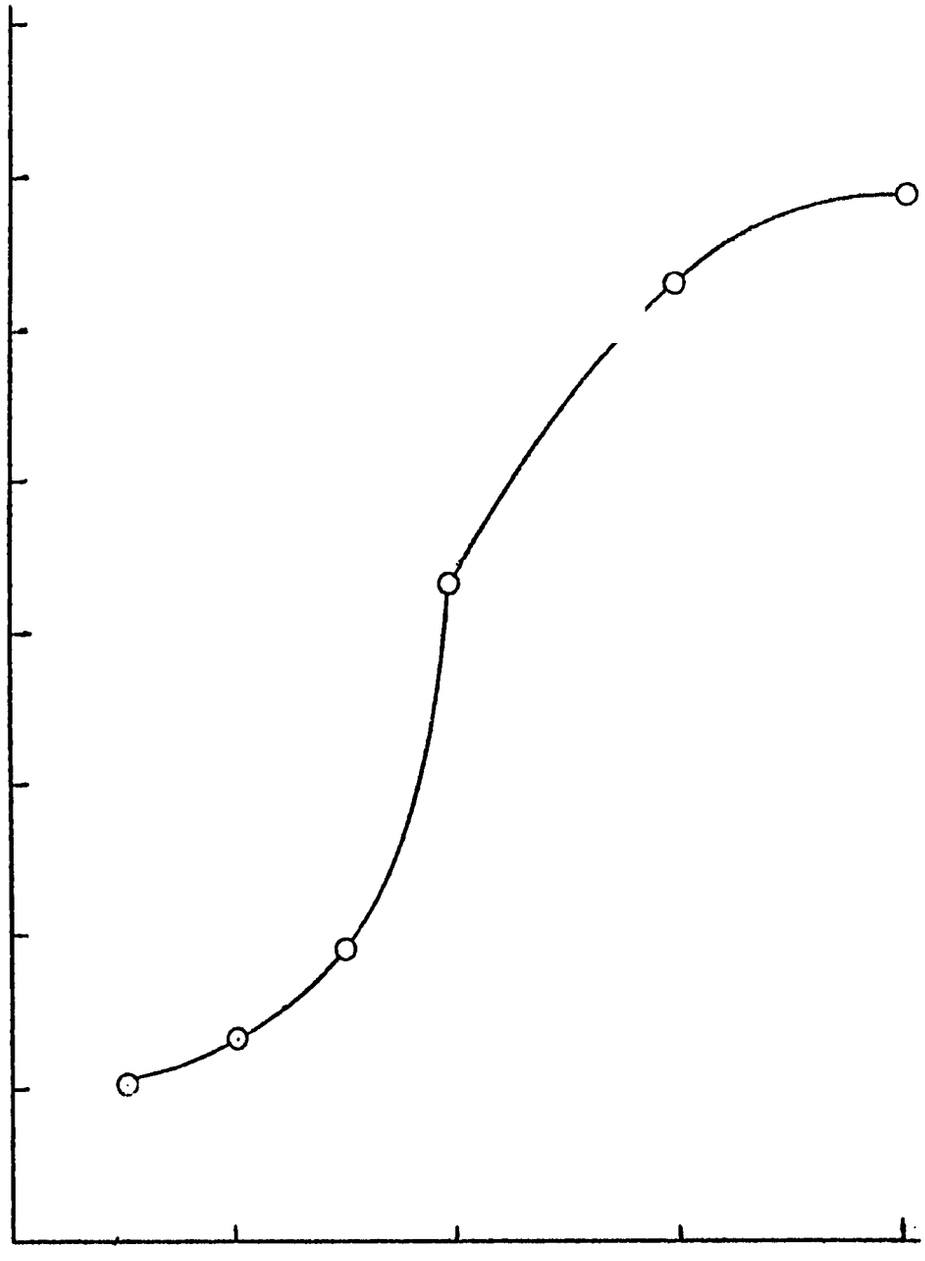

Fig. 3 Effect of NH_4Cl concentration on cation exchange capacity of the Akaka soil.

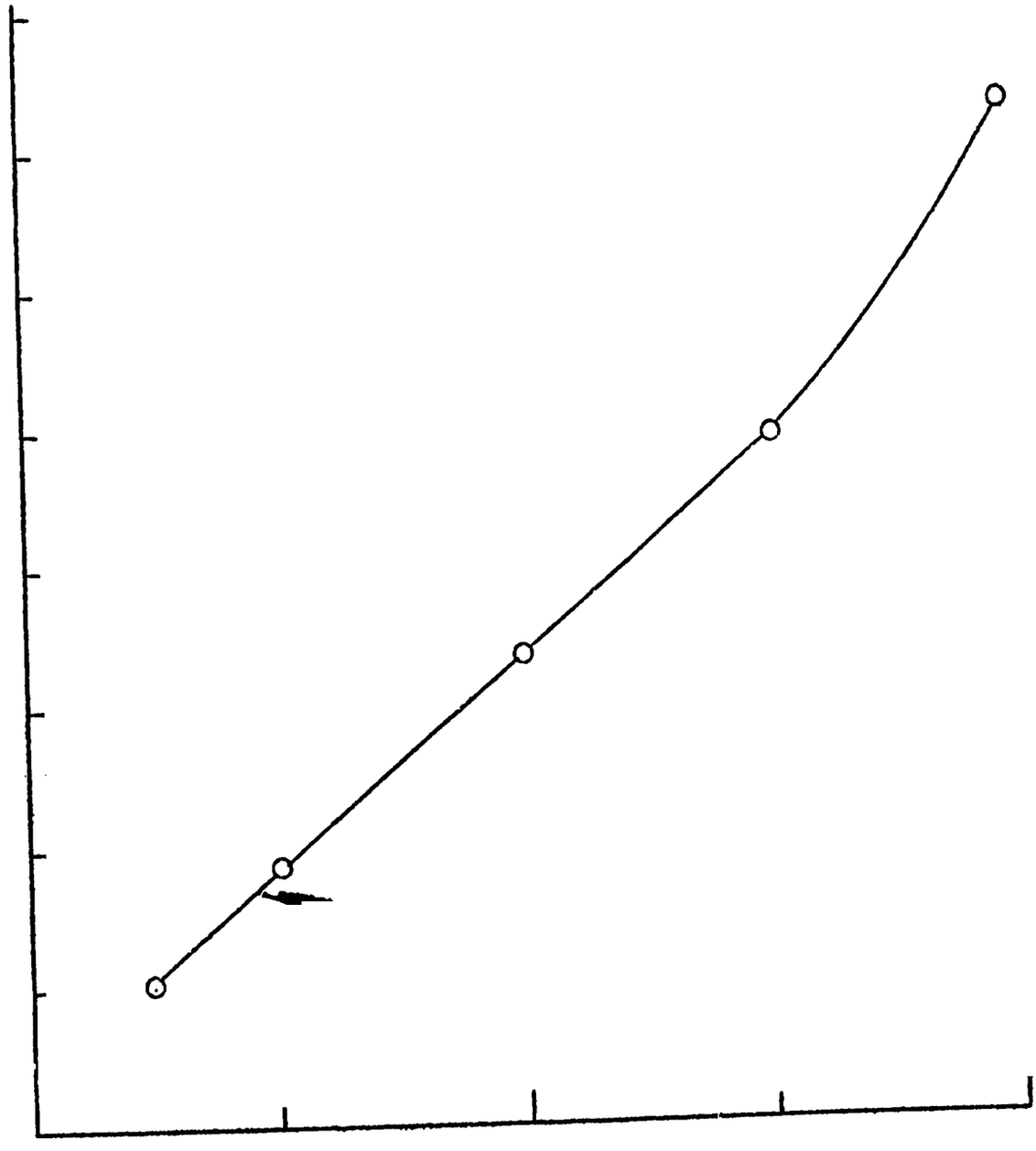

Fig. 4 Effect of NH_4Cl concentration on anion exchange capacity of the Akaka soil.

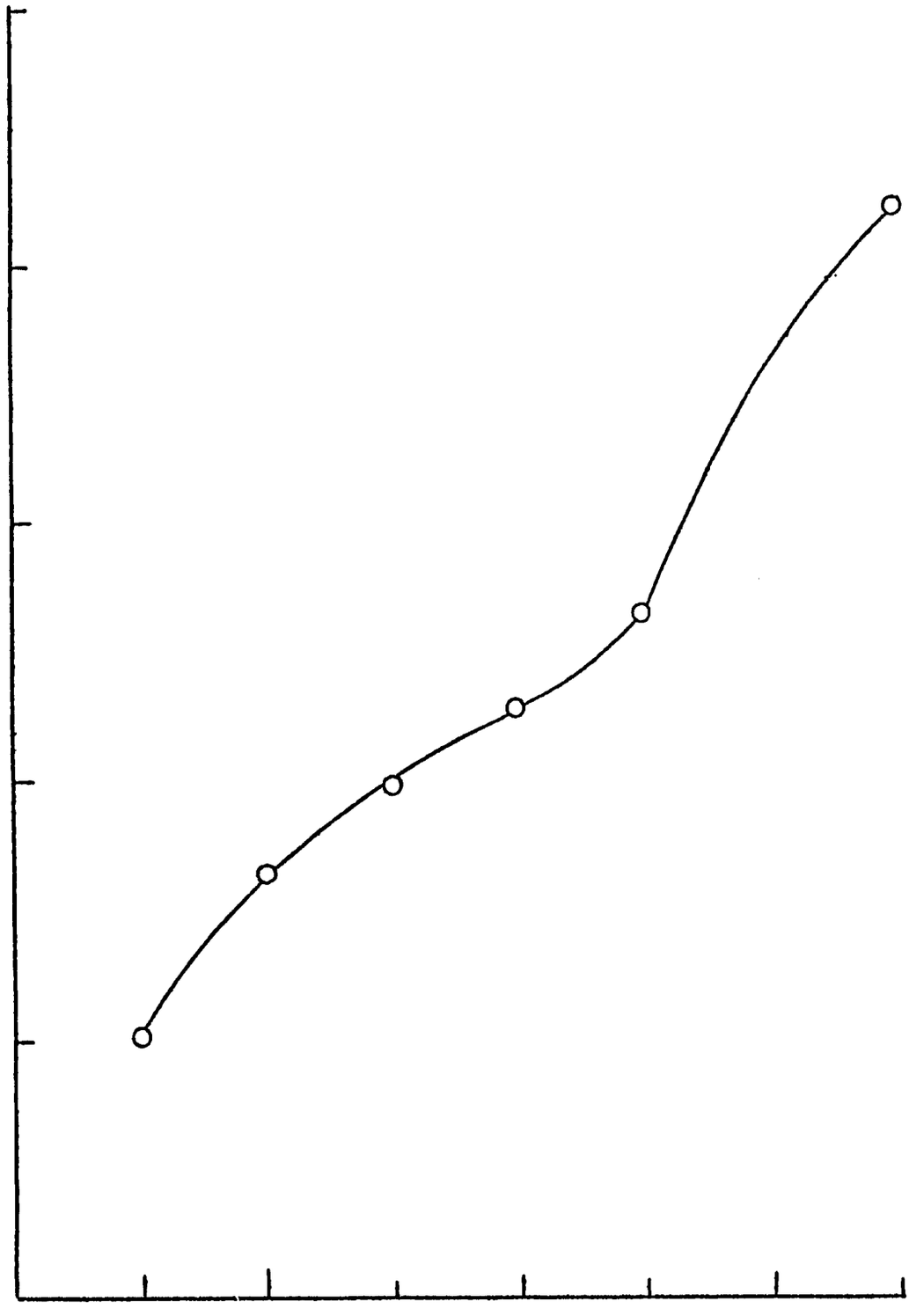

Fig. 5 Effect of pH of NH_4Cl solution on the cation exchange capacity of the Akaka soil.

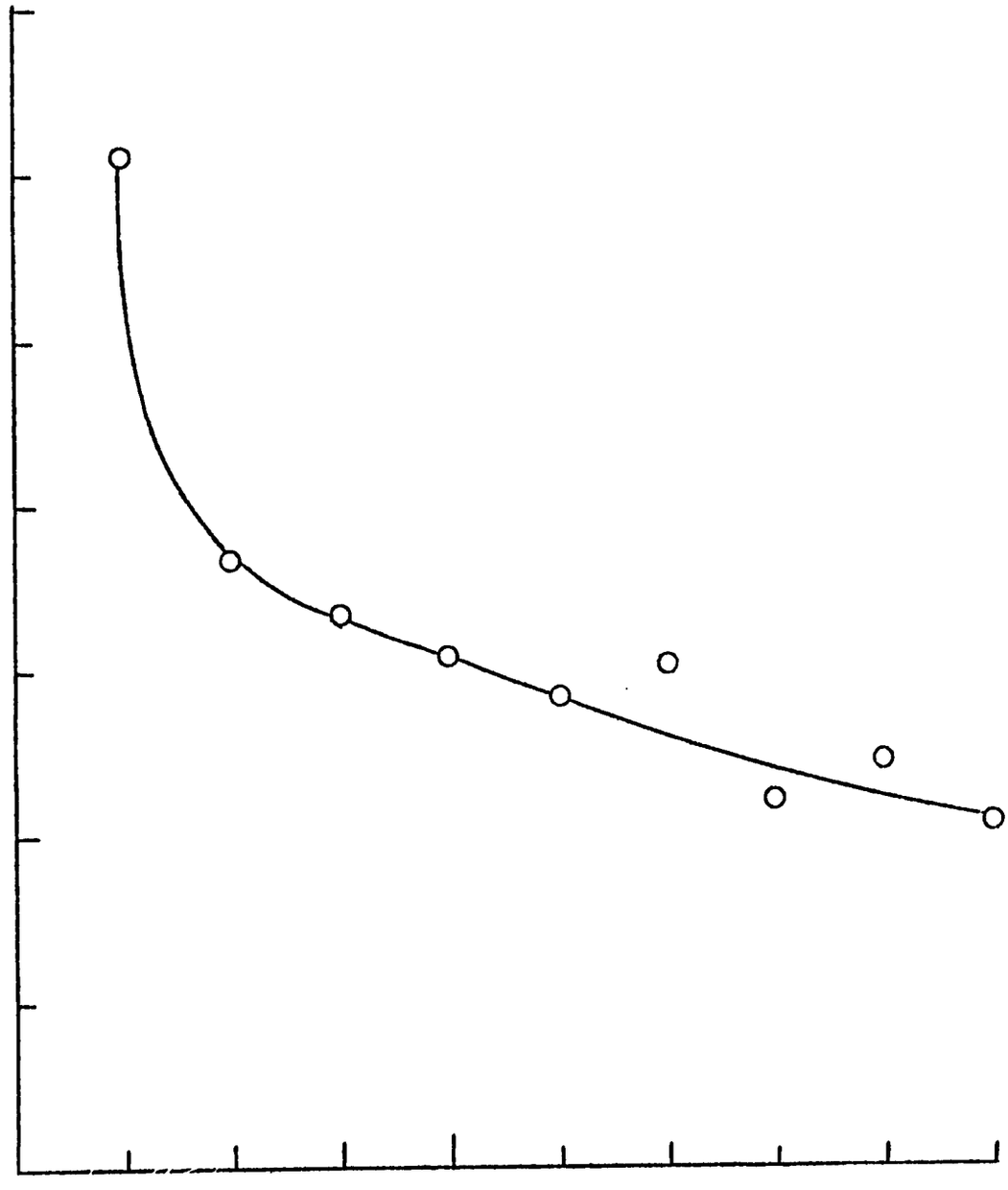

Fig. 6 Effect of pH of NH_4Cl solution on the anion exchange capacity of the Akaka soil.