

Dept. of Agronomy and Soil Science
2525 Varney Circle
University of Hawaii
Honolulu, Hawaii 96822

**NATIVE FIXED AMMONIUM AND FIXATION OF APPLIED
AMMONIUM IN HAWAIIAN SOILS**

**A THESIS SUBMITTED TO THE GRADUATE SCHOOL OF THE
UNIVERSITY OF HAWAII IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE
IN SOIL SCIENCE
JANUARY 1966**

By

David Takeshi Mikami

Thesis Committee:

**Yoshinori Kaneshiro, Chairman
Donald L. Plucknett
Leslie D. Swindale
Goro Uehara**

We certify that we have read this thesis and that in our opinion it is satisfactory in scope and quality as a thesis for the degree of Master of Science in Soil Science.

THESIS COMMITTEE

Yoshinori Kaneko
Chairman

R. L. Blumhert

Goro Uehara

W. J. Wendale

ACKNOWLEDGMENT

The author wishes to express his sincere gratitude to Dr. Yoshimori Kanehiro for his advice and encouragement throughout the study. He is also grateful to Dr. Goro Uehara for his comments and valuable suggestions, To Mr. Roger T. Watanabe for providing some soil profile samples and data, to Mr. Ramon de la Pena for photographic assistance, and to Mrs. Betty Someda for typing the manuscript. The author is also grateful to the University of Hawaii Agricultural Experiment Station for the assistantship which made this research possible.

TABLE OF CONTENTS

	<u>Page</u>
ACKNOWLEDGMENTS	11
LIST OF TABLES	v
LIST OF FIGURES	vii
INTRODUCTION	1
REVIEW OF LITERATURE	
Native Fixed Ammonium in Soils, Rocks and Minerals	2
Thermal Release of Exchangeable and Native Fixed Ammonium in Soils and Minerals.	4
Ammonium Fixing Capacity of Soils and Minerals	5
Amount and Concentration Dependence of Ammonium Fixation .	7
OBJECTIVES	8
MATERIALS AND METHODS	
I. Native Fixed Ammonium of Some Hawaiian Soils	9
II. Thermal Release of Exchangeable and Native Fixed Am- monium	33
A. Time of Heating	33
B. Temperature of Heating	34
III. Ammonium Fixation in Some Hawaiian Soils	42
IV. Chemical and Mineralogical Studies of Soils.	57
RESULTS AND DISCUSSION	
I. Native Fixed Ammonium of Some Hawaiian Soils	13
A. Range of Native Fixed Ammonium in Hawaiian Soils .	13
B. Native Fixed Ammonium as a Fraction of Total Nitrogen	21
C. Relation Between Native Fixed Ammonium and % K_2O and % Illite	22

TABLE OF CONTENTS (Continued)

	<u>Page</u>
D. Carbon and Nitrogen and the Influence of Native Fixed Ammonium on C/N Ratios	26
II. Thermal Release of Exchangeable and Native Fixed Ammonium	34
A. Time of Heating.	34
B. Temperature of Heating	35
III. Ammonium Fixation in Some Hawaiian Soils	42
A. Mechanical Composition of Soils.	46
B. Fixation of Applied Ammonium	47
C. Concentration Dependent Ammonium Fixation.	52
IV. Chemical and Mineralogical Studies of Soils	57
A. X-ray Diffraction and Petrographic Studies	60
B. Differential Dissolution Analysis.	66
C. Differential Thermal Analysis and Dehydration Curves	67
D. Infrared Absorption Spectra.	71
E. Total Chemical Analysis	74
F. Cation Exchange Capacity	75
G. Discussion and Conclusions	79
SUMMARY	83
LITERATURE CITED.	85

LIST OF TABLES

	<u>Page</u>
TABLE I. CHEMICAL AND MINERALOGICAL PROPERTIES OF SOILS DEVELOPED FROM VOLCANIC ASH	14
II. CHEMICAL AND MINERALOGICAL PROPERTIES OF BASALTIC SOILS	17
III. NATIVE FIXED AMMONIUM (PPM) REMAINING AFTER HEATING AT VARYING LENGTHS OF TIME AT 300° C.	34
IV. NATIVE FIXED AMMONIUM (PPM) REMAINING ON THE SAMPLE AFTER EACH TEMPERATURE OF HEATING	36
V. EFFECT OF HEATING ON THE RELEASE OF AMMONIUM (PPM) OF SOILS DEVELOPED FROM VOLCANIC ASH	38
VI. NATIVE FIXED AMMONIUM REMAINING AFTER EACH TEMPERATURE OF HEATING AFTER KOBr-TREATMENT	41
VII. CATION EXCHANGE CAPACITY AND EXCHANGEABLE BASES OF SOILS	43
VIII. MECHANICAL ANALYSES OF SOILS	45
IX. AMMONIUM FIXATION CAPACITIES OF SOILS SATURATED WITH 10 ME./100 GRAMS AMMONIUM AND OVEN-DRIED AT 110° C. FOR 12 HOURS.	48
X. AMMONIUM FIXATION CAPACITIES OF SOILS SATURATED WITH 50 ME./100 GRAMS AMMONIUM AND OVEN-DRIED AT 110° C. FOR 12 HOURS	49
XI. AMMONIUM FIXATION CAPACITIES OF SEPARATES SATURATED WITH 50 ME./100 GRAMS AMMONIUM AFTER MOISTENING, SUN-DRYING AND OVEN-DRYING AT 110° C.	51
XII. CONCENTRATION DEPENDENT AMMONIUM FIXATION OF A MAALEHU (59-65") SOIL	53
XIII. CONCENTRATION DEPENDENT AMMONIUM FIXATION OF A PAHALA (25-36") SOIL	53
XIV. CONCENTRATION DEPENDENT AMMONIUM FIXATION OF A PAHALA (52-57") SOIL	54
XV. CONCENTRATION DEPENDENT AMMONIUM FIXATION OF A LUALUALAI (1-15") SOIL	54

LIST OF TABLES (Continued)

	<u>Page</u>
TABLE XVI. CONCENTRATION DEPENDENT AMMONIUM FIXATION OF A KOOLAU (4-7") SOIL	55
XVII. CONCENTRATION DEPENDENT AMMONIUM FIXATION OF A MOLOKAI (74") SOIL	55
XVIII. EXTRACTABLE SILICA AND ALUMINA OF SOILS BY DIF- FERENTIAL DISSOLUTION ANALYSIS	68
XIX. ALLOPHANE DETERMINATION OF SOILS BY CATION EXCHANGE CAPACITY DELTA VALUE	69
XX. TOTAL MAGNESIUM CONTENT OF SOILS AND THEIR SIZE FRACTIONS.	75
XXI. CHEMICAL COMPOSITION OF SOILS AND THEIR SIZE FRACTIONS	76
XXII. CATION EXCHANGE CAPACITY OF SOILS AND THEIR SIZE FRACTIONS	77

LIST OF FIGURES

	<u>Page</u>
FIGURE 1. NATIVE FIXED AMMONIUM AS A FRACTION OF THE TOTAL NITROGEN OF SOME YOUNG SOILS FROM VOLCANIC ASH. . .	23
2. NATIVE FIXED AMMONIUM AS A FRACTION OF THE TOTAL NITROGEN OF SOME BASALTIC SOILS	24
3. TOTAL K_2O OR % ILLITE TO NATIVE FIXED AMMONIUM IN SOME VOLCANIC ASH SOILS CONTAINING NO PRIMARY FELDSPARS	27
4. TOTAL K_2O OR % ILLITE TO NATIVE FIXED AMMONIUM IN SOME BASALTIC SOILS.	28
5. TOTAL K_2O OR % ILLITE TO NATIVE FIXED AMMONIUM IN SOME HAWAIIAN SOILS	29
6. RELATIONSHIP OF N ON C OF SOME SOILS DEVELOPED FROM VOLCANIC ASH	30
7. RELATIONSHIP OF N ON C OF SOME BASALTIC SOILS . . .	31
8. THE EFFECT OF AMMONIUM CONCENTRATION ON AMMONIUM FIXATION	36
9. POWDERED X-RAY DIFFRACTION DIAGRAMS OF THE DE-FERBATED, ORGANIC MATTER-FREE MAALEHU PROFILE . . .	61
10. POWDERED X-RAY DIFFRACTION DIAGRAMS OF THE DE-FERBATED, ORGANIC MATTER-FREE PAHALA PROFILE . . .	62
11. X-RAY DIFFRACTION DIAGRAMS OF SOILS	63
12. X-RAY DIFFRACTION DIAGRAMS OF THE 25-36" HORIZON OF THE PAHALA SOIL	64
13. DIFFERENTIAL THERMAL CURVES OF THE SAND, SILT AND CLAY FRACTIONS OF SOILS	70
14. DEHYDRATION CURVES OF SAMPLES REPRESENTING DIFFERENT AMMONIUM FIXING CAPACITIES	72
15. INFRARED ABSORPTION SPECTRA OF THE SIZE FRACTIONS OF SOILS	73

INTRODUCTION

The study of native fixed ammonium in temperate soils has received increasing attention in the past decade. The presence of appreciable amounts of native fixed ammonium has been demonstrated in a variety of temperate soils in the Western and North Central United States and in England. However, a lack of information on native fixed ammonium content of tropical soils exists today. Thus far, only two known investigations, one by Rodrigues (1954) on four soils in the British Caribbean region, and another by Moore and Ayeko (1965) on four Nigerian soils, have been reported. More information on native fixed ammonium distribution in other tropical soils is needed to supplement the meager available data.

Another area of study where little, if any, information is available is in the area of ammonium fixation by the amorphous soil constituents. Much work has already been expended in determining the layered silicate minerals responsible for ammonium fixation and the mechanism of this fixation. Allophane and other amorphous mineraloids have been intensively studied in the past decade. Volcanic ash is accepted to be one of the parent material from which allophane or other reactive amorphous colloidal mineraloids are derived. A large percentage of the soils of Hawaii are derived from volcanic ash. Investigations concerning the genesis and nature of these mineraloids from volcanic ash have been and will be further investigated. This study on the ammonium fixation by these mineraloids is intended to shed further light on the nature and reactivity of amorphous soil mineraloids.

REVIEW OF LITERATURE

Native Fixed Ammonium in Soils, Rocks and Minerals

It was assumed for many years that virtually all soil nitrogen existed in organic combinations and that the only inorganic forms of nitrogen were exchangeable ammonium, nitrite and nitrate. It is now known that some soils contain significant amounts of naturally occurring native fixed ammonium. The existence of native fixed ammonium on four tropical soils from the British Caribbean region was reported by Rodrigues (1954). He reported that 14 to 78% of the total nitrogen in the tropical soils was present in this form after hydrogen fluoride extraction. He concluded that the released ammonium was derived from the clay fraction since it was not removed by methods of cation exchange extraction, hydrogen peroxide oxidation, chromic-sulfuric acid oxidation at 100° C. or boiling with 10% sulfuric acid. He also concluded that the decrease in C/N ratio with increasing depth could be explained by the increase of nitrogen in the form of native fixed ammonium with depth in the profile.

Since then, nitrogen in soils, previously regarded as organic nitrogen, has been reported to occur as native fixed ammonium held within the lattice structure of clay minerals (Brenner, 1959; Brenner and Narada, 1959; Dhariwal and Stevenson, 1958; Hanway and Scott, 1956; Leggett, 1958; Moore and Ayeke, 1965; Stevenson, 1957, 1959a; Stevenson and Dhariwal, 1959; Stevenson, Dhariwal and Choudhri, 1958; Stewart and Porter, 1963; Walsh and Murdock, 1960; Young, 1962). These investigators have indicated that 0.7 to 12.9% of the total nitrogen in the surface soil and 1.2 to 63.0% of the total nitrogen in the subsoil are in the form of native fixed ammonium.

Since the pioneer work by Rodrigues, no work has been reported on tropical soils. Recently, Moora and Ayeke (1965) reported that 2 to 6% of the total nitrogen in the surface layer and 45 to 63% of the total nitrogen in the subsoil of four Nigerian soil profiles existed as HF-extractable ammonium. An increase in HF-extractable ammonium with depth for each profile was demonstrated. This increase in native fixed ammonium with depth in the profile, which accounts for the low C/N ratios, especially of subsoils, has been reported by other investigators (Bremner and Harada, 1959; Dharwal and Stevenson, 1958; Hanway and Scott, 1956; Leighty and Shorey, 1930; Rodrigues, 1954; Stevenson, 1959b; Stevenson, Dharwal and Choudhri, 1958).

The quantity of native fixed ammonium appears to be related to the amount and kind of clay minerals present in the following decreasing order: illite, montmorillonite, kaolinite (Stevenson and Dharwal, 1959; Stevenson, Dharwal and Choudhri, 1958).

The native fixed ammonium in igneous rocks and minerals has been studied by Stevenson (1959a, 1962). He reported that 1/3 to 1/2 of the total nitrogen in some granite rocks occurred as ammonium ions contained within silicate minerals. He later studied the nitrogen in igneous rocks and minerals, and found that 56 to 99% of the total nitrogen in igneous rocks (basalts, granite, peridotite, porphyry, gabbro, dunite); 66 to 99% of the total nitrogen in silicate minerals (illite, muscovite, biotite, vermiculite, orthoclase feldspars); and 77 to 97% of the total nitrogen in some metamorphic rocks (slate, gneiss, granite gneiss) existed as native fixed ammonium.

Thermal Release of Exchangeable and Native Fixed

Ammonium in Soils and Minerals

Thermal release of exchangeable and native fixed ammonium from untreated and ammonium-saturated soils and minerals has been reported by Porter and Stewart (1964) and Scott, Hanway and Stanford (1956). Scott *et al.* (1956) investigated the thermal release in four soil clay minerals: illite, vermiculite, bentonite and kaolinite. The exchangeable ammonium in kaolinite, bentonite and illite started to be released at temperatures below 100° C. and was completely released by heating at 400° C. for 24 hours. Vermiculite, however, released very little exchangeable ammonium and continued to release some ammonium even when the sample was heated at 500° C. Illite and kaolinite contained little, if any, fixed ammonium. Fixed ammonium, in vermiculite and bentonite, did not decompose until the temperature exceeded 400° C. A unique phenomenon for bentonite was noted--ammonium ions which were initially exchangeable became fixed when the clay was heated at 300 to 350° C. From these observations they concluded that fixed ammonium required a higher decomposition temperature than the exchangeable ammonium. In all cases, heating at any one temperature did not result in the segregation of exchangeable ammonium from native fixed ammonium.

Porter and Stewart (1964) measured the amount of exchangeable and fixed ammonium ions remaining in ammonium-treated and non-treated soils after heating at various temperatures (100 to 1000° C.). A 3 to 6-fold increase in exchangeable ammonium was obtained after heating the surface soils at 250 to 300° C. for 5 minutes or longer time intervals. This increase in exchangeable ammonium was caused by the decomposition of

organic matter. In ammonium-treated soils, where large quantities of exchangeable ammonium was present, release of this form of nitrogen began at approximately 200° C. and was completely removed after heating at 500° C. for 5 minutes. An increase in the fixed ammonium content of the ammonium-treated soils was observed until a temperature of 400° C. was attained, above which fixed ammonium was lost.

Ammonium Fixing Capacity by Soils and Minerals

The ability of soils to retain added ammonium in a non-exchangeable (fixed) form has been known for some time. This phenomenon was first demonstrated by McBeth (1917), who found that added ammonium could not be completely recovered by alkaline distillation, extraction with neutral salts, or acid extraction.

Since then, much work has been expended to determine the conditions and the soil minerals responsible for ammonium fixation. Ammonium fixation by montmorillonite, illite, and vermiculite, all of which have a 2:1 (silica-alumina) crystal lattice, and by soils containing these minerals has been shown (Allison, Kafsuver and Roller, 1953; Allison, Roller and Doetsch, 1953; Aomine, 1951; Barshad, 1948; Joffe and Levine, 1947; Page and Bayer, 1940; Stanford and Piarra, 1947; van der Marel, 1954). Soils containing vermiculite were found to fix more ammonium than those containing illite and montmorillonite under moist conditions. Illitic soils fix more ammonium when air-dried or oven-dried than when kept moist after addition of ammonium, but montmorillonitic soils fix little, if any, ammonium unless oven-dried after treatment with ammonium (Axley and Legg, 1960; Barshad, 1951; Hanway and Scott, 1956; Leggett, 1958). Kaolinitic soils are not capable of fixing much ammonium (Joffe

and Levine, 1947)). The ammonium fixing capacity by minerals and rocks has been studied by Adams (1962), Allison and Roller (1955) and Barshad (1954). The feldspars have also been reported to fix ammonium (Nash and Marshall, 1956). Adams (1962) found that all minerals were able to fix some ammonium but the amount fixed was much less than that of soils. The ammonium fixing capacity of the organic fraction of the soil has also been investigated and reported (Burge and Broadbent, 1961; Harmsen and van Schreven, 1955; Mortland, 1958; Sohn and Peech, 1958).

The mechanism of ammonium fixation in soils containing illite, vermiculite and montmorillonite has been suggested by Page and Baver (1940). They postulated that the size of the cation along with its valence and water of hydration is the determining factor in cation fixation. Fixation, according to these workers, occurs by the trapping of ammonium ions in the cavities formed by the hexagonal oxygen rings of the silica sheets of two superimposed layers of a 2:1 type mineral. These cavities have a radius of approximately $1.35 \text{ \AA}$. Potassium ions which have an ionic radius very close to that of ammonium ions are also fixed in this fashion; other cations which have a larger or smaller ionic radii are not fixed by this mechanism. Subsequent works by Barshad (1948, 1950, 1951), Leggett (1958) and van der Marel (1954) lend support to the theory of Page and Baver.

Most of the studies thus far reported have shown that the clay fraction is mostly responsible for ammonium fixation; however, the silt fraction has been reported to fix as much, if not more, ammonium as the clay fraction (Barshad, 1951; Leggett, 1958; Nomsik, 1957).

Amount and Concentration Dependence of Ammonium Fixation

The amount of ammonium fixed increases with an increase in the amount and concentration of ammonium added (McBeth, 1917; Leggett, 1958; McIntosh, 1962; Stanford and Pierre, 1947). The concentration of ammonium necessary to satisfy the ammonium fixing capacity of different soils varies greatly, provided that ample time is allowed for equilibrium to be attained.

OBJECTIVES

This research was concerned with native fixed ammonium and ammonium fixing capacity and the mechanism(s) responsible for fixation. The objectives of this study were:

1. To determine the native fixed ammonium content of a number of representative Hawaiian soils,
2. To study the effect of heating on ammonium release in soils,
3. To study the concentration dependent ammonium fixation of soils,
4. To study the magnitude and significance of ammonium fixation in soils dominated by amorphous minerals, and
5. To identify the amorphous minerals and to determine the mechanism responsible for ammonium fixation.

I. Native Fixed Ammonium of Some Hawaiian Soils

A study was made to determine the native fixed ammonium in some representative agriculturally and non-agriculturally important Hawaiian soils and to supplement the meager available information concerning tropical soils. The soils investigated were separated into two major groups, one derived from volcanic ash and the other from basalt.

Materials and Methods

Materials (Soils):

The soil series profiles from volcanic ash used in this study were Waikaloe (Reddish Brown), Waimea 1* and 2* (Reddish Prairie), Maalehu (Reddish Prairie), Pahala (Reddish Prairie), Hilo (Hydrol Humic Latosol), Akaka (Hydrol Humic Latosol), and Psauhau (Humic Latosol). The soil series profiles from basic igneous rocks were Molokai (Low Humic Latosol), Lahaina (Low Humic Latosol), Wahiawa (Low Humic Latosol), Naiea (Humic Ferruginous Latosol), Kalae (Humic Ferruginous Latosol), Koloale (Humic Ferruginous Latosol), Manana (Humic Ferruginous Latosol), Paaloa (Humic Latosol) and Koolau (Hydrol Humic Latosol).

The soils formed from volcanic ash, with the exception of the Waimea series, were collected and described by Dr. Yoshinori Kanahiro. The Waimea soils were collected and thoroughly described by Hough (1964). The soils from basalt, with the exception of the Kalae series, were collected by Mr. Roger T. Watanabe, the descriptions of which were made available by the Soil Conservation Service. The Kalae series was col-

*Waimea 1 and 2 have also been known as Mahoele and Waikii soils, respectively.

lected and described by the Soil Conservation Service. None of the soil profile descriptions are reproduced in this thesis.

Methods:

Native Fixed Ammonium:

The KBr-HF method (procedure A) proposed by Silva (1964) was used to determine the native fixed ammonium in some representative virgin and cultivated soil profiles. Current HF methods proposed by other investigators (Bremner (1959) - Direct method, Bremner (1959) - KOH method, Dharival and Stevenson (1961), Rodrigues (1954), Schachtschabel (1961)) show one or more defects that are possible sources of error. At least two frequent defects were noted in each of the methods cited. Commonly, the pretreatments used in eliminating the interfering organic nitrogen compounds led to the fixation of released ammonium by soil minerals. The procedures used for the release of fixed ammonium were also not quantitative.

The suitability of Silva's method lies in the fact that the soil sample was pretreated with alkaline potassium hypobromite (KBr) to remove exchangeable ammonium and organic nitrogen compounds. A 96 to 100% removal of the interfering organic nitrogen compounds under conditions that did not cause any release of the fixed ammonium in vermiculite was obtained by this pretreatment. Any ammonium formed by the oxidation of the soil organic matter by KBr was immediately converted to N_2 by the following reaction:



The rapid removal of the released ammonium nitrogen and the high concentration of the potassium in solution prevents any fixation of the ammonium from the organic matter by soil minerals during the pretreatment.

Outline of the Method:

A finely ground 1-gram (100 mesh) sample placed in a tall 200 ml. beaker was treated with 20 ml. alkaline potassium hypobromite (KOB_r) solution. The beaker was swirled to mix the soil and hypobromite and then allowed to stand covered with a watch glass. After 2 hours, 60 ml. of distilled water was added and the soil-KOB_r mixture was brought to a vigorous boil for 3 minutes. After allowing the mixture to cool and settle overnight, the clear supernatant solution was decanted and discarded. The residue from this pretreatment was transferred to a 100 ml. polyethylene centrifuge tube using 0.5N KCl as the transferring solution. The tube was centrifuged at 2000 rpm for 10 minutes and the supernatant solution discarded. The residue was washed twice more with 0.5N KCl and centrifuged. To the washed residue, 20 ml. of 5N HF:1N HCl solution was added. The centrifuge tube was stoppered with a rubber stopper and shaken continuously with an end-over-end shaker for 24 hours to decompose the minerals containing the native fixed ammonium.

After completion of the 5N HF:1N HCl treatment, 15 ml. of 10N NaOH was added to a 500 ml. Kjeldahl flask. A long-stem polyethylene funnel with a Tygon tubing extension was placed in the neck of the flask so that the end of the tube was below the surface of the NaOH solution. The contents of the centrifuge tube were transferred into the Kjeldahl flask through the funnel and the transfer was completed by rinsing the centrifuge tube and funnel with distilled water. The ammonium in solution was distilled into 10 ml. of boric acid-methyl red:bromocresol green indicator solution using a modified micro Kjeldahl steam distillation apparatus. The distillation was continued until 90 ml. of the distillate was col-

lected in the receiving flask. The ammonium in the distillate was determined by titration with standard 0.005N H_2SO_4 . The native fixed ammonium was then calculated as the difference between the amount of ammonium liberated in this analysis and the amount of ammonium liberated by steam distillation of 20 ml. of 5N HF:1N HCl solution with 15 ml. of 10N NaOH solution.

Total Nitrogen:

This was determined by the standard Kjeldahl method using 5 grams of a K_2SO_4 : $FeSO_4$: $CuSO_4$ salt mixture in a 10:1:1/2 proportion. The sample was digested with 10 ml. concentrated H_2SO_4 in a 100 ml. Kjeldahl flask for 2 hours, cooled and transferred to a 500 ml. Kjeldahl flask. The ammonium-nitrogen in the digest was determined after distillation with NaOH using a modified micro Kjeldahl steam distillation apparatus.

Organic Carbon:

A rapid titration method proposed by Walkley and Black (1934) was used in this determination. A 0.5 to 1.0 gram sample was treated with $K_2Cr_2O_7$ - H_2SO_4 to digest the organic matter. The organic carbon was calculated after titration with $FeSO_4$ solution.

Total K_2O :

The total K_2O analysis was made on the untreated whole soil. The HF- H_2SO_4 digestion method was used to bring the soil potassium into solution. The flame spectrophotometric method for potassium was used.

pH:

The soil pH was measured with a glass electrode pH meter in a 1:1 soil-water suspension. The sample was allowed to stand for 24 hours with occasional stirring prior to its reading.

Results and Discussion

Soil series, horizon depth, pH values, percent carbon, percent nitrogen, native fixed ammonium and mineralogy are shown in Tables I and II; all other data in the tables were derived from these figures. Exchangeable ammonium, nitrites and nitrates were not determined in this investigation.

Range of Native Fixed Ammonium in Hawaiian Soils:

The results show that virtually all soils investigated contained some native fixed ammonium. Although there were some exceptions, there was a general downward trend in the native fixed ammonium with depth in each profile. This decrease with depth is contrary to the general rule of greater native fixed ammonium in the subsoil than in the surface (Hanway and Scott, 1956; Rodrigues, 1954; Stevenson, Dharwal and Choudhri, 1958).

Native fixed ammonium was found to range from 0.0 to 585.0 ppm, with an average of 93.4 ppm. The soils from volcanic ash generally had a lower native fixed ammonium content (3.8 to 177.8 ppm, with an average of 55.2 ppm) than those from basalt (0.0 to 585.0 ppm, with an average of 121.0 ppm). However, the native fixed ammonium in the soils from volcanic ash did not decrease drastically with depth as did those from basalt.

The native fixed ammonium appears to be related to the K_2O or illite content of the soils. This relationship, however, did not hold whenever potassium bearing feldspars were identified. This relationship will be discussed in a following section.

The amounts of native fixed ammonium in some Hawaiian soils were of similar magnitude with those determined in other areas. Rodrigues (1954)

TABLE I. CHEMICAL AND MINERALOGICAL PROPERTIES OF SOILS DEVELOPED FROM VOLCANIC ASH

Soil Series	Depth in.	pH	Org. C	Tot. N	Tot. K ₂ O	Illite	Native Fixed NH ₄	Native Fixed NH ₄ -N*	Org. C Tot. N	Org. C Org. N	Dominant Minerals
			%	%	%	%	ppm	%			
Waikaloa	0-10	6.6	3.73	0.420	0.83	-	28.6	0.5	8.9	8.9	Amorphous silicates, halloysite, feldspars
	10-19	7.4	1.97	0.188	0.93	-	17.1	0.7	10.5	11.0	
	19-27	7.6	1.08	0.121	0.93	-	25.7	1.6	8.9	9.1	
	27-37	7.8	0.50	0.079	1.72	-	42.8	4.2	6.3	6.6	
	37-46	7.8	0.18	0.042	2.43	-	19.1	3.5	4.3	4.4	
	46-55	8.4	0.21	0.046	2.28	-	12.4	2.1	4.6	4.7	
	55-64	8.5	0.12	0.023	2.41	-	9.5	3.2	5.2	5.4	
Waimea (Mahealani)	0-10	6.9	4.84	0.524	0.85	-	42.8	0.6	9.2	9.3	Amorphous silicates, halloysite, feldspars
	10-22	7.9	2.56	0.295	0.73	-	43.9	1.2	8.7	8.8	
	22-28	7.8	2.98	0.290	0.69	-	47.7	1.3	10.3	10.4	
	28-34	7.7	2.20	0.162	0.63	-	21.4	1.0	13.6	13.7	
	34-54	7.9	1.11	0.059	0.99	-	15.3	2.0	18.8	19.2	
	54+	7.9	1.34	0.021	0.93	-	14.4	5.3	6.4	6.7	
Waimea (Waikiki)	5-11	7.1	5.69	0.572	0.45	-	9.5	0.1	9.9	10.0	Amorphous silicates, feldspars
	11-20	7.1	5.42	0.409	0.42	-	3.8	0.1	13.2	13.3	
	20-23	6.8	3.96	0.275	0.42	-	14.2	0.4	14.4	14.5	
Maalehu	0-11	5.6	3.42	0.378	0.23	-	38.2	0.8	9.0	9.1	Amorphous silicates, feldspars
	11-21	6.7	0.72	0.089	0.12	-	32.4	2.8	8.1	8.3	
	21-54	6.9	0.51	0.051	0.10	-	25.7	3.9	10.0	10.4	
	54-59	7.2	0.29	0.034	0.10	-	26.3	6.0	8.5	9.1	
	59-65	7.0	0.37	0.046	0.09	-	23.4	3.9	8.0	8.4	

*Ionic forms are used without indication of charge throughout this thesis.

TABLE I. CHEMICAL AND MINERALOGICAL PROPERTIES OF SOILS DEVELOPED FROM VOLCANIC ASH (Continued)

Soil Series	Depth	pH	Org. C	Tot. N	Tot. K ₂ O	Illite	Native Fixed NH ₄	Native Fixed NH ₄ -N Tot. N	Org. C Tot. N	Org. C Org. N	Dominant Minerals
	in.		%	%	%	%	ppm	%			
Fehala	0-7	5.9	4.24	0.463	0.38	-	42.8	0.7	9.2	9.2	Amorphous silicates, some feldspars
	7-11	6.6	2.19	0.259	0.34	-	38.2	1.1	8.4	8.5	
	11-18	6.7	1.44	0.169	0.28	-	33.3	1.5	8.5	8.6	
	18-25	6.7	0.87	0.116	0.28	-	31.8	2.1	7.5	8.0	
	25-36	6.9	0.14	0.021	0.22	-	24.8	9.1	6.7	7.3	
	36-39	6.8	0.41	0.054	0.15	-	24.3	3.5	7.6	7.9	
	39-52	6.9	0.43	0.058	0.19	-	23.4	3.1	7.4	7.6	
	52-57	7.1	0.68	0.072	0.17	-	19.1	2.0	9.4	9.6	
Hilo	60-72	6.2	1.77	0.139	0.21	2.9	41.9	2.3	12.7	13.5	Amorphous silicates, amorphous iron and aluminum oxides, gibbsite, quartz
	72-80	6.2	0.93	0.062	0.05	0.7	17.6	2.2	15.0	15.3	
	80-90	6.1	1.54	0.117	0.15	2.1	41.9	2.8	13.2	13.5	
Hilo	12-24	5.8	3.94	0.271	0.37	5.1	76.9	2.2	14.5	14.9	Amorphous silicates, amorphous iron and aluminum oxides, gibbsite, quartz
	45-55	5.9	2.28	0.141	0.13	1.8	35.8	1.9	16.2	16.5	
	60-66	6.0	1.61	0.086	0.12	1.7	41.9	3.7	18.7	19.5	
	72-78	5.8	1.68	0.139	0.53	7.4	105.8	5.9	12.1	12.8	
Akaka	12-34	5.8	4.88	0.309	0.52	7.2	141.1	3.5	15.7	16.4	Amorphous silicates, amorphous iron and aluminum oxides, gibbsite, quartz
	34-40	5.8	4.55	0.231	0.61	8.5	147.4	4.9	19.7	20.7	
	40-50	5.8	4.32	0.246	0.88	12.2	171.7	5.4	17.6	18.6	
	50-74	5.8	3.94	0.243	0.84	11.7	142.2	4.5	16.2	17.0	
	74+	6.0	3.97	0.213	0.13	1.8	49.1	1.8	18.6	19.0	

TABLE I. CHEMICAL AND MINERALOGICAL PROPERTIES OF SOILS DEVELOPED FROM VOLCANIC ASH (Continued)

Soil Series	Depth	pH	Org.	Tot.	Tot. Illite		Native Fixed NH ₄ ppm	Native Fixed NH ₄ -N Tot. N %	Org. C Tot. N	Org. C Org. N	Dominant Minerals
					%	%					
Akaka	0-3	5.1	11.88	0.691	0.22	3.0	61.0	0.7	17.2	17.3	Amorphous silicates, amorphous iron and aluminum oxides, gibbsite, quartz
	3-7	5.1	9.87	0.577	0.25	3.5	72.5	1.0	17.1	17.3	
	7-15	5.6	6.29	0.364	0.42	5.8	101.5	2.1	17.3	17.7	
	15-18	5.9	3.28	0.149	0.13	1.8	52.4	2.7	22.0	22.6	
	18-24	5.8	5.51	0.292	0.46	6.4	105.8	2.8	18.9	19.4	
	24-38	5.6	4.29	0.218	0.34	4.7	108.7	3.8	19.7	20.5	
	38-43	5.7	4.66	0.258	0.33	4.6	107.8	3.2	18.1	18.7	
	57-64	5.9	2.49	0.102	0.04	0.5	5.2	0.4	24.4	24.5	
Pauohau	20-46	6.4	2.80	0.298	0.71	9.9	156.4	6.1	9.4	9.8	Kaolin, illite
	46-60	6.2	2.31	0.270	0.78	10.8	157.3	4.5	8.5	9.0	
	60-74	5.8	1.81	0.212	0.83	11.5	177.8	6.5	8.5	9.1	

TABLE II. CHEMICAL AND MINERALOGICAL PROPERTIES OF BASALTIC SOILS AND STANDARD MINERALS

Soil Series	Depth	pH	Org. C	Tot. N	Tot. K ₂ O	Illite	Native Fixed	Native Fixed NH ₄ -N Tot. N	Org. C Tot. N	Org. C Org. N	Dominant Minerals
	in.		%	%	%	%	ppm	%			
Molokai	0-3	5.8	2.12	0.202	1.17	16.2	215.3	8.2	10.5	11.4	Kaolin, iron oxide
	3-20	6.5	1.04	0.094	0.88	12.2	173.2	14.2	11.1	12.9	
	20-48	6.6	0.59	0.046	0.33	4.6	79.2	13.3	12.8	14.8	
	48-70	6.5	0.65	0.034	0.12	1.7	33.3	7.5	19.1	20.7	
	70+	6.6	0.59	0.024	0.09	1.2	14.2	4.5	24.6	25.8	
Lahaina*	0-21	5.7	2.41	0.239	1.05	14.6	177.8	5.7	10.1	10.7	Kaolin, iron oxide
	21-31	6.5	0.54	0.064	0.93	12.9	145.1	17.5	8.4	10.2	
	31-44	6.7	0.60	0.072	0.61	8.5	93.6	10.0	8.3	9.3	
	44-45	6.9	0.61	0.050	0.24	3.3	28.1	4.3	12.2	12.8	
Wahieva Dry	0-15	5.1	1.19	0.159	1.04	14.4	140.4	6.9	7.5	8.0	Kaolin, iron oxide
	15-25	6.0	0.38	0.073	1.10	15.3	145.1	15.4	5.2	6.2	
	25-35	6.5	0.16	0.058	0.90	12.5	135.7	18.2	2.8	3.4	
	35-60	6.2	-	0.055	0.52	7.2	88.9	12.4	-	-	
Wahieva Wet*	0-4	5.8	3.76	0.378	1.99	27.6	121.7	2.5	9.9	10.2	Kaolin, iron oxide, illite
	4-10	5.6	3.59	0.360	2.05	28.5	112.9	2.4	10.0	10.2	
	10-14	5.5	1.65	0.260	1.86	25.8	84.2	2.5	6.3	6.5	
	14-19	5.8	0.82	0.152	1.85	25.7	154.4	7.8	5.4	5.9	
	19-25	5.9	0.86	0.123	1.44	20.0	243.4	15.2	7.0	8.3	
	25-35	6.2	0.79	0.103	1.36	18.9	210.6	15.7	7.7	9.1	
	35-45	6.2	0.63	0.091	1.33	18.5	238.7	20.2	6.9	8.7	

*Carbon data provided by Mr. Roger Watanabe.

TABLE II. CHEMICAL AND MINERALOGICAL PROPERTIES OF BASALTIC SOILS AND STANDARD MINERALS (Continued)

Soil Series	Depth	pH	Org. C	Tot. N	Tot. K ₂ O	Illite	Native Fixed NH ₄	Native Fixed NH ₄ -N Tot. N	Org. C Tot. N	Org. C Org. N	Dominant Minerals
	in.		%	%	%	%	ppm	%	%	%	
Maiva Exposed*	0-4	4.1	1.44	0.084	0.18	2.5	42.1	3.9	17.1	17.8	Kaolin, iron oxide
	4-7	4.0	1.58	0.075	0.15	2.1	37.4	3.8	21.1	21.9	
	7-11	3.9	1.86	0.074	0.17	2.4	32.8	3.4	25.5	26.4	
	11-13	4.1	2.34	0.080	0.17	2.4	23.4	2.2	29.2	29.9	
	13-14	4.3	4.26	0.140	0.11	1.5	4.7	0.3	30.4	30.5	
	14-21	4.5	13.65	0.320	0.09	1.2	4.7	0.1	42.6	42.7	
	21-25	4.6	6.44	0.178	0.02	0.3	1.8	0.2	36.2	36.2	
	25-29	4.7	5.38	0.134	0.00	0.0	0.0	0.0	40.1	40.1	
Maiva Unexposed*	0-3	4.3	4.95	0.311	0.17	2.4	32.8	0.8	15.9	16.0	Kaolin, iron oxide
	3-4.5	4.3	6.55	0.318	0.15	2.1	37.4	0.9	20.6	20.8	
	4.5-8	4.6	11.99	0.339	0.13	1.8	28.1	0.6	35.4	35.6	
	8-19	4.8	11.05	0.353	0.06	0.8	11.2	0.2	31.3	31.4	
	19-28	4.7	10.86	0.358	0.03	0.4	4.7	0.1	30.3	30.4	
Kala	0-9	5.2	-	0.348	1.23	17.1	196.6	4.3	-	-	Iron oxide, kaolin, illite
	9-15	5.9	-	0.137	1.34	18.6	224.6	12.6	-	-	
	15-26	6.1	-	0.103	1.25	17.4	201.3	15.0	-	-	
	26-41	5.1	-	0.111	0.95	13.2	149.8	10.4	-	-	
	41-53	4.7	-	0.116	0.47	6.7	70.2	4.7	-	-	
	53-62	4.5	-	0.078	0.22	3.0	32.8	3.2	-	-	
	62-67	4.4	-	0.059	0.00	0.0	0.0	0.0	-	-	

*Carbon data provided by Mr. Roger Watanabe.

TABLE II. CHEMICAL AND MINERALOGICAL PROPERTIES OF BASALTIC SOILS AND STANDARD MINERALS (Continued)

Soil Series	Depth	pH	Org. C	Tot. N	Tot. K ₂ O	Illite	Native Fixed NH ₄ -N ppm	Native Fixed NH ₄ -N Tot. N %	Org. C Tot. N	Org. C Org. N	Dominant Minerals
	in.		%	%	%	%		%		%	
Kolekole	0-4	5.0	4.76	0.342	0.57	7.9	88.9	2.0	13.9	14.2	Kaolin, iron oxide
	4-8	4.88	4.41	0.197	0.60	8.3	117.0	4.6	22.4	23.5	
	8-13	4.7	3.37	0.264	0.65	9.0	140.4	4.1	12.8	13.3	
	13-18	4.6	3.79	0.288	0.63	8.7	103.0	2.7	13.2	13.5	
	18-23	4.7	3.45	0.253	0.63	8.7	145.1	4.4	13.6	14.3	
	23-27	4.7	3.51	0.206	0.63	8.7	103.0	3.8	17.0	17.7	
	27-33	4.5	2.03	0.124	0.41	5.7	70.2	4.4	16.4	17.1	
	33-36	4.6	1.95	0.118	0.42	5.8	72.0	4.7	16.5	17.3	
	36-40	4.7	2.40	0.138	0.26	3.6	51.5	2.9	17.4	17.9	
	40+	4.8	3.35	0.154	0.23	3.2	42.1	2.1	21.7	22.2	
	below 40+	4.8	1.68	0.080	0.14	1.9	28.1	2.7	21.0	21.6	
	80-90	4.1	0.80	-	0.05	0.7	4.7	-	-	-	
Manana	0-12	3.9	2.44	0.244	1.96	27.2	355.7	11.2	10.0	11.3	Kaolin, illite, iron oxide
	12-21	4.2	0.99	0.128	1.96	27.2	358.6	21.6	7.7	9.9	
	21-34	4.2	0.81	0.128	1.47	20.4	307.1	18.5	6.3	7.8	
	34-46	4.3	0.45	0.058	1.33	18.5	248.1	32.9	7.8	11.6	
Paaloo	0-4	4.5	2.68	0.184	1.42	19.7	271.4	11.4	14.6	16.4	Kaolin, illite oxide quartz
	4-9	4.5	1.78	0.146	1.40	19.4	266.8	14.1	12.2	14.2	
	9-17	4.3	2.38	0.132	1.34	18.6	248.0	14.5	18.0	21.1	
	17-25	4.5	2.19	0.102	0.91	12.6	176.0	13.3	21.4	24.8	
	25-26	-	-	-	0.66	9.2	98.3	-	-	-	
	26+	4.6	-	-	0.52	7.2	70.2	-	-	-	
	illite pocket	-	-	-	0.78	10.8	121.7	-	-	-	

TABLE II. CHEMICAL AND MINERALOGICAL PROPERTIES OF BASALTIC SOILS AND STANDARD MINERALS (Continued)

Soil Series	Depth <u>in.</u>	pH	Org. C <u>g</u>	Tot. N <u>g</u>	Tot. K ₂ O <u>g</u>	Illite <u>g</u>	Native Fixed NH ₄ <u>ppm</u>	Native Fixed NH ₄ -N Tot. N <u>g</u>	Org. C Tot. N	Org. C Org. N	Dominant Minerals
Koolau	0-4	4.3	48.47	2.440	0.14	1.9	28.6	0.1	19.9	19.9	Illite, kaolin, quartz, titanium oxides
	4-7	6.3	2.04	0.110	2.29	31.8	388.4	27.2	18.5	25.6	
	7-10	4.3	3.01	0.144	0.60	8.3	149.2	8.0	20.9	22.7	
	10-14	4.5	1.97	0.076	0.52	7.2	109.6	11.1	25.9	29.2	
	14-20	4.9	1.56	0.066	0.34	4.7	55.3	6.4	23.6	25.3	
	20-30	5.0	0.95	0.043	0.20	2.8	21.1	3.8	22.1	22.9	
	30+	5.0	0.84	0.042	0.20	2.8	23.8	4.4	20.0	20.9	
Koolau	3-6.5	-	-	-	3.19	44.3	585.0	-	-	-	
Lualaba	0-1	7.6	1.18	0.042	0.67	-	60.1	11.1	28.1	31.6	Montmoril- lonite
	1-15	7.8	0.75	0.031	0.46	-	41.0	10.3	24.2	27.0	
	15-24	7.7	0.63	0.027	0.47	-	63.9	18.4	23.3	28.6	
	24-35	7.8	0.48	0.020	0.47	-	33.3	12.9	24.0	27.6	
	35-44	7.7	0.28	0.007	0.51	-	23.8	26.4	40.0	53.8	
Koolau clay	4-7	-	-	0.152	3.91	54.3	748.8	37.9	-	-	Illite
Molokai clay	3-20	-	-	-	0.97	13.5	196.6	-	-	-	Kaolin
Illite No. 35	-	-	-	0.121	4.96	-	1039.0	66.1	-	-	Illite
Illite No. 36	-	-	-	0.093	5.07	-	725.4	60.1	-	-	Illite
Biotite	-	-	-	0.022	5.79	-	84.2	29.5	-	-	Biotite + feldspars
Biotite	-	-	-	0.021	9.31	-	79.6	29.2	-	-	Biotite
Muscovite	-	-	-	0.020	5.50	-	88.9	34.2	-	-	Muscovite + feldspars

showed that tropical soils in the British Caribbean region contained between 281.6 to 1920.0 ppm. His reported values are thought to be too high because of certain weaknesses in methodology. Some of the possible defects that are possible sources of error have been presented earlier. Recently, 30 to 220 ppm., with an average of 75.6 ppm., was reported by Moore and Ayeke (1963) in four Nigerian soils. Nine to 366 ppm., with an average of approximately 135 ppm., have been reported in a variety of temperate soils in the North Central regions of the United States (Dhariwal and Stevenson, 1958; Hamway and Scott, 1956; Leggett, 1958; Stevenson, 1957, 1959a; Stevenson and Dhariwal, 1958, 1959; Stewart and Porter, 1963; Walsh and Murdock, 1960). Stevenson and Dhariwal (1958) and Young (1962) reported between 31 to 432 ppm. with an average of 133 ppm. in the soils of the Western region of the United States. A range of 52 to 252 ppm. was reported by Bremner (1959) and Bremner and Harada (1959) in a variety of temperate soils from England.

The data, when compared to those reported by others in different areas, show that the average native fixed ammonium content of Hawaiian soils is generally lower than those from other areas. Since only two other tropical areas, namely, those from the British Caribbean region and Nigeria, have been reported, comparisons among those tropical soils cannot give a complete picture of the native fixed ammonium content of the tropics.

Native Fixed Ammonium as a Fraction of Total Nitrogen:

Native fixed ammonium as a fraction of total nitrogen in the individual horizons varied from 0.00% (Maui exposed, 25-29"; Kala, 62-67") to 32.93% (Maui, 34-46"). Since exchangeable ammonium, nitrite and nitrate nitrogen were not determined, inorganic nitrogen as a function of total nitrogen for each horizon could not be calculated.

According to Stevenson (1959b) and Young (1962), the relative amount of nitrogen present as native fixed ammonium increased with increasing depth. This increase was due to the increase of native fixed ammonium with depth in the profile. The same relationship was observed by Rodrigues (1954) and Moore and Ayeke (1965) in tropical soils. The soils studied in this investigation are unique in that they do not follow any of the patterns reported in the literature.

The ratio of native fixed ammonium to total nitrogen varied among soils. For example, the Waikalae, Pahala, Molokai, Lahaina, Naiea exposed and Kalae soil profiles were characterized by having the highest percentage of nitrogen in the fixed form somewhere within the profile.

A highly significant relationship ($r = 0.740^{**}$, $df = 21$) was obtained when the native fixed ammonium was compared with the percent of total nitrogen of the young, weathered volcanic ash soils (Figure 1). A similar relationship ($r = 0.820^{**}$, $df = 70$) was obtained for the soils derived from basalt (Figure 2). However, this was not the case for the soils derived from young, partially weathered volcanic ash soils (Figure 1).

Relation Between Native Fixed Ammonium and % K_2O and % Illite:

Since native fixed ammonium is usually considered to be associated with the clay fraction of the soil, a study was made to determine the clay minerals responsible for the native fixed ammonium. Kaolinite and illite were found to be the most predominant clay minerals in the soils containing a large quantity of native fixed ammonium. Since it is generally accepted that kaolinite has a low capacity to ammonium, the native fixed ammonium of the soils must be attributed to the mineral illite.

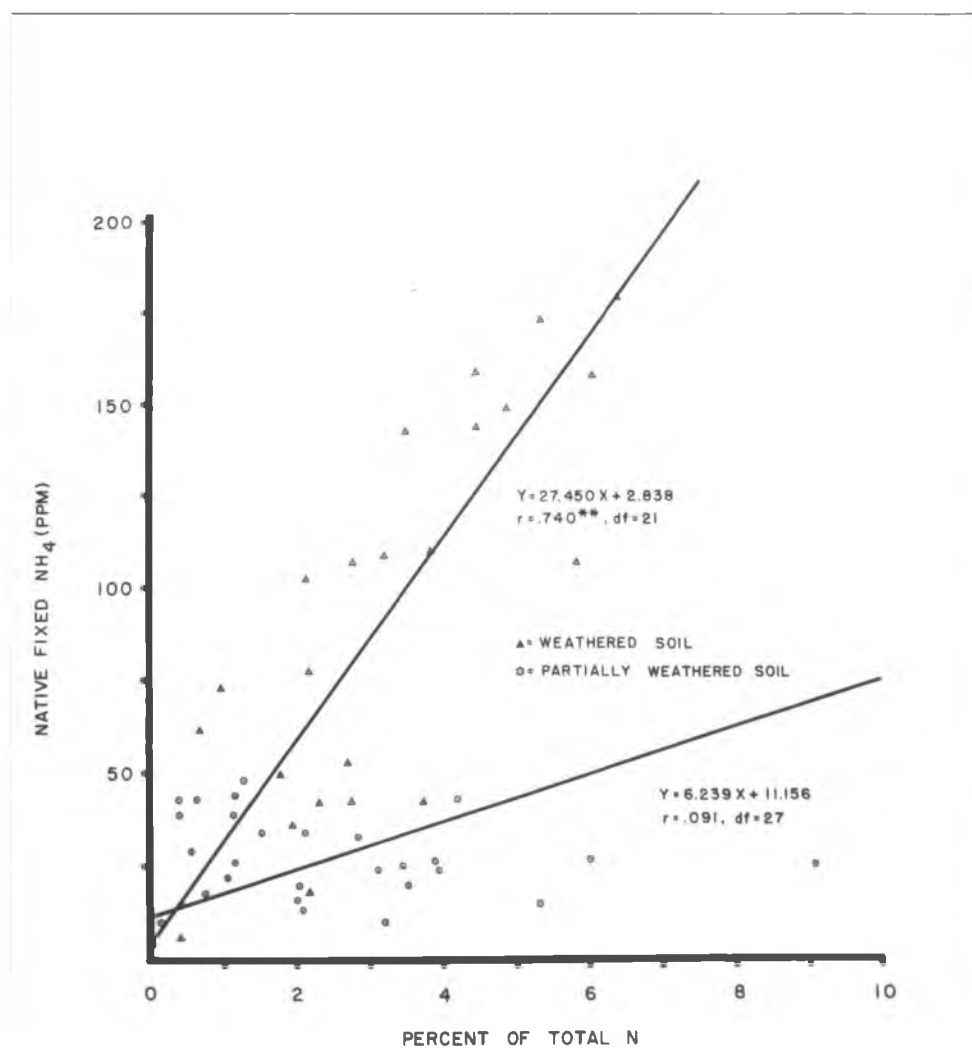


FIGURE 1. NATIVE FIXED AMMONIUM AS A FRACTION OF THE TOTAL NITROGEN OF SOME YOUNG SOILS FROM VOLCANIC ASH

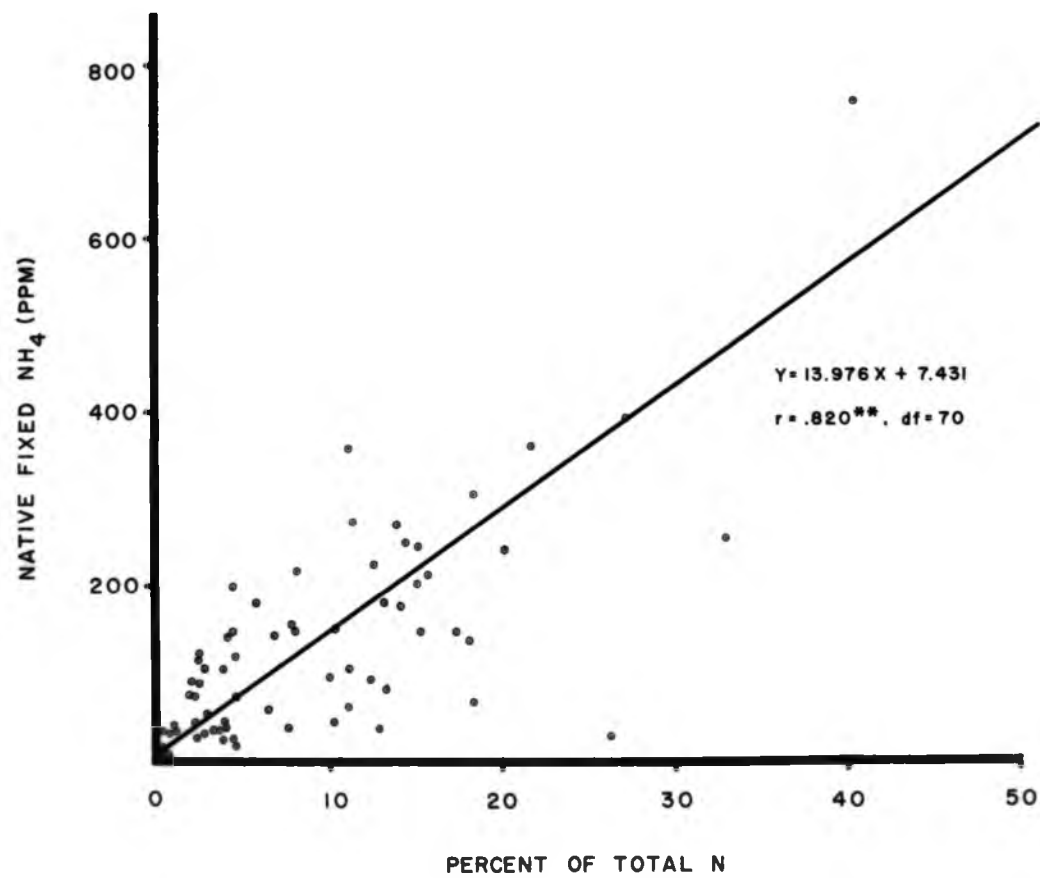


FIGURE 2. NATIVE FIXED AMMONIUM AS A FRACTION OF THE TOTAL NITROGEN OF SOME BASALTIC SOILS

A study on the distribution, polymorphic form and origin of mica minerals in some Hawaiian soils was recently investigated by Juang (1964). His X-ray data established two points: (1) Mica content increased with an increase in soil elevation and rainfall, and (2) mica content was at a maximum at the surface. Juang's results were not in agreement with most published data in other areas. He also characterized the Koolau (3-6.5") horizon, containing the largest amount of illite, by chemical methods and determined that a 100% oven-dried Hawaiian mica mineral contained 7.20% K_2O . In order for this assumption to be true, he assumed that all the exchangeable sites were saturated by cations other than potassium and that all soil micas in Hawaiian soils are identical. He also showed the applicability of allocating the total K_2O content to the mica mineral, at least for weathered Hawaiian soils. This, however, does not hold true for young, partially weathered soils which contain potassium minerals other than micaceous minerals and high amounts of exchangeable potassium. Some of the volcanic ash soils studied in this investigation fall in this category.

The total K_2O content and percent illite of the soils studied are presented in Tables I and II. Percent illite was calculated from the percent K_2O , but soils containing extraneous sources of potassium, especially feldspars, were not calculated.

As far as is known, no one has yet found a relationship between total K_2O or percent illite to native fixed ammonium. This is because allocation of the total K_2O to illite would not be justified for most soils throughout the world. When the data for the total K_2O or percent illite and native fixed ammonium in Tables I and II, excluding those

soils containing feldspars, were statistically analyzed, a correlation coefficient of 0.956, highly significant at the 1 percent level (Figure 3), was obtained for the volcanic ash soils. Analysis of the soils from basalt produced a correlation coefficient of 0.908, also highly significant at the 1 percent level (Figure 4). Combining the two groups of soils (Figure 5), a correlation coefficient of 0.910 was obtained, which was again highly significant at the 1 percent level.

The results above indicate explicitly that native fixed ammonium is in combination with the clay mineral illite, at least in the Hawaiian soils.

Carbon and Nitrogen and the Influence of Native Fixed Ammonium on C/N Ratios:

The results of the analyses for carbon and nitrogen along with the calculated carbon/nitrogen ratios in 116 soil samples are shown in Tables I and II. Carbon content generally decreases with depth, except for the Hilo, Akaka, Maui and Kolskole soil profiles, where irregular distribution is shown. This phenomenon may be due to the mobilization of humus from the surface to the subsoil or to buried soil horizons.

Total nitrogen varied closely with the carbon content in the soils investigated. A correlation of N on C (Figure 6) of the soils from volcanic ash was highly significant ($r = 0.894^{**}$, $df = 30$). The results compare very favorably with the results obtained by Hwang (1964) on similar volcanic ash soils. A significant correlation ($r = 0.748^{**}$, $df = 61$) of C on N was also obtained for the soils from basalt (Figure 7).

The organic C/total N and organic C/organic N* relationships of the soils studied are given in Tables I and II. Organic C/total N ratios

*For this thesis, "organic N" refers to total N minus native fixed ammonium.

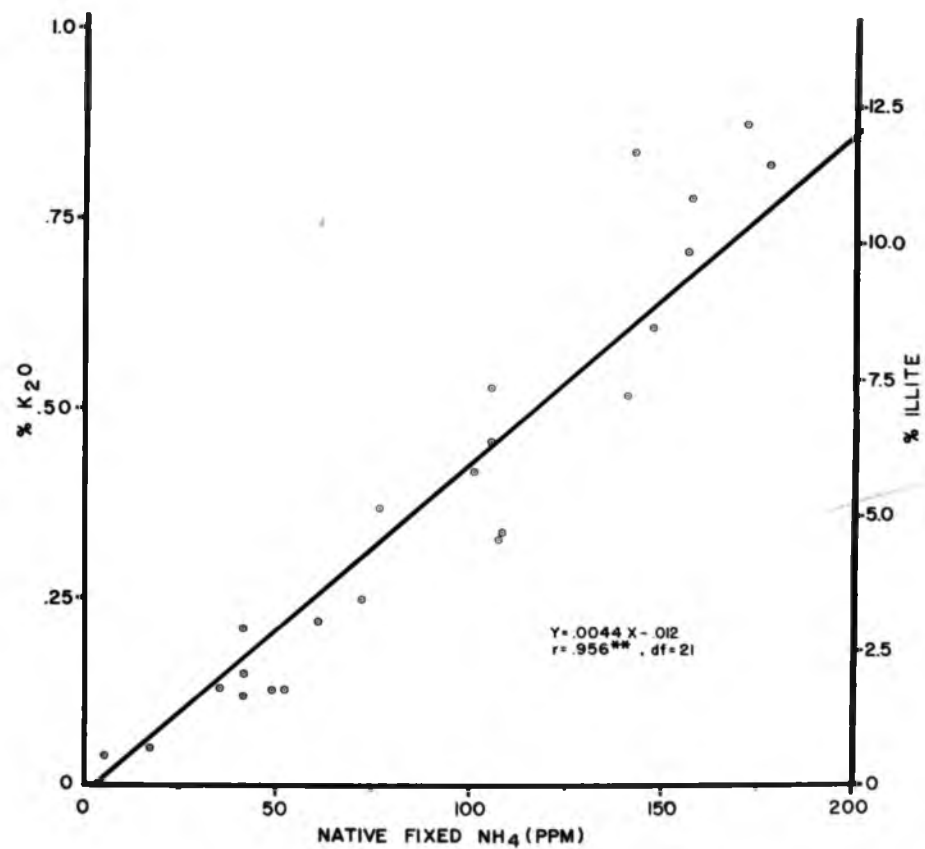


FIGURE 3. TOTAL K₂O OR % ILLITE TO NATIVE FIXED AMMONIUM IN SOME VOLCANIC ASH SOILS CONTAINING NO PRIMARY FELDSPARS

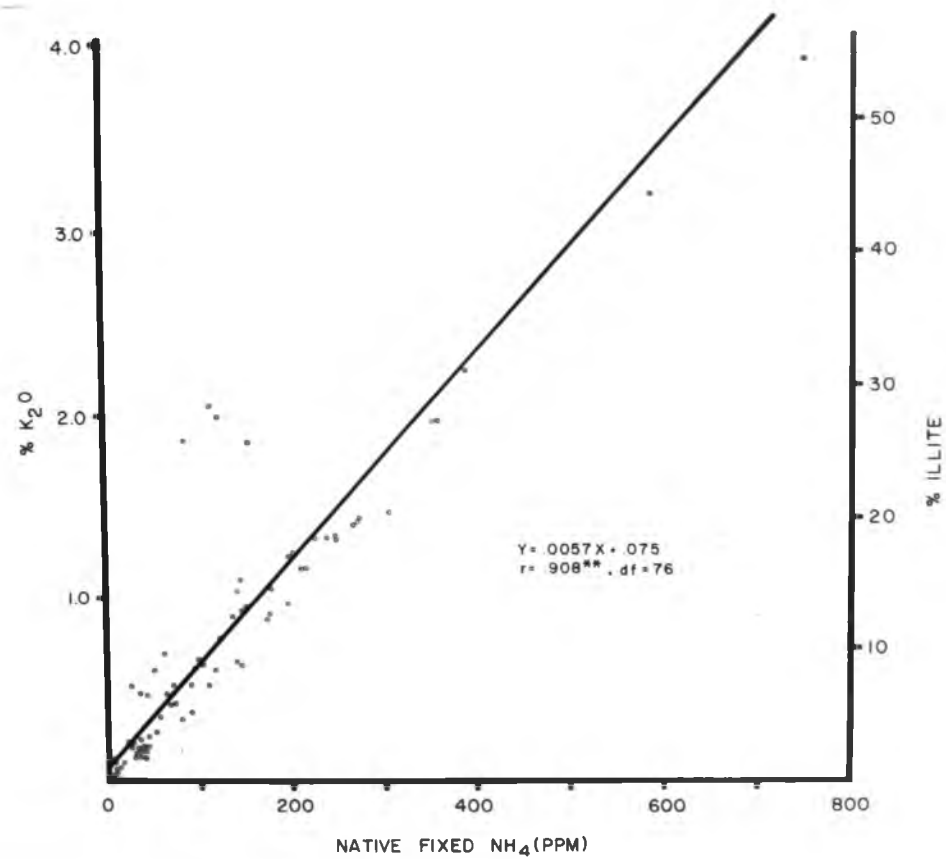


FIGURE 4. TOTAL K₂O OR % ILLITE TO NATIVE FIXED AMMONIUM
IN SOME BASALTIC SOILS

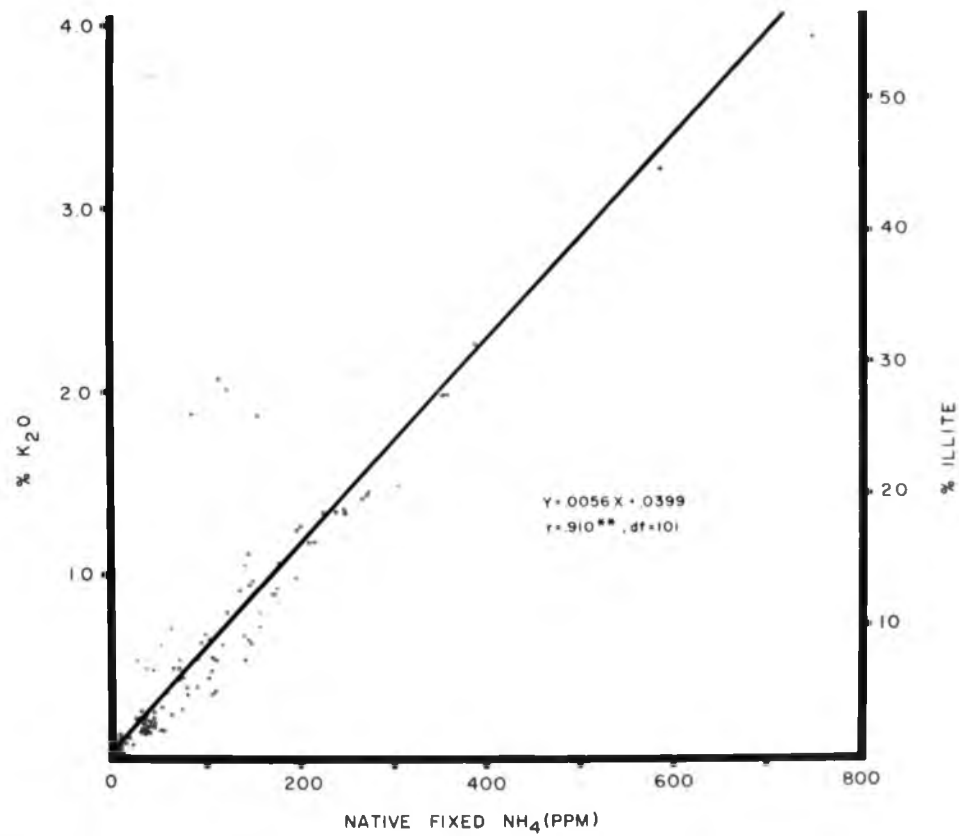


FIGURE 5. TOTAL K₂O OR % ILLITE TO NATIVE FIXED AMMONIUM
IN SOME HAWAIIAN SOILS

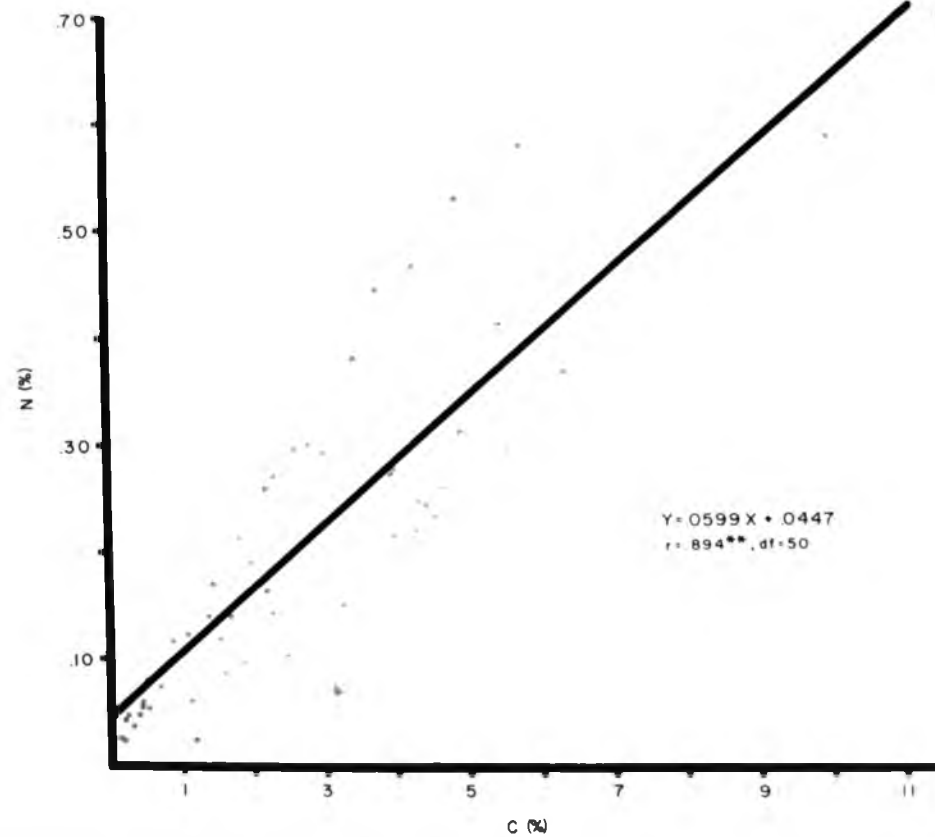


FIGURE 6. RELATIONSHIP OF N ON C OF SOME SOILS
DEVELOPED FROM VOLCANIC ASH

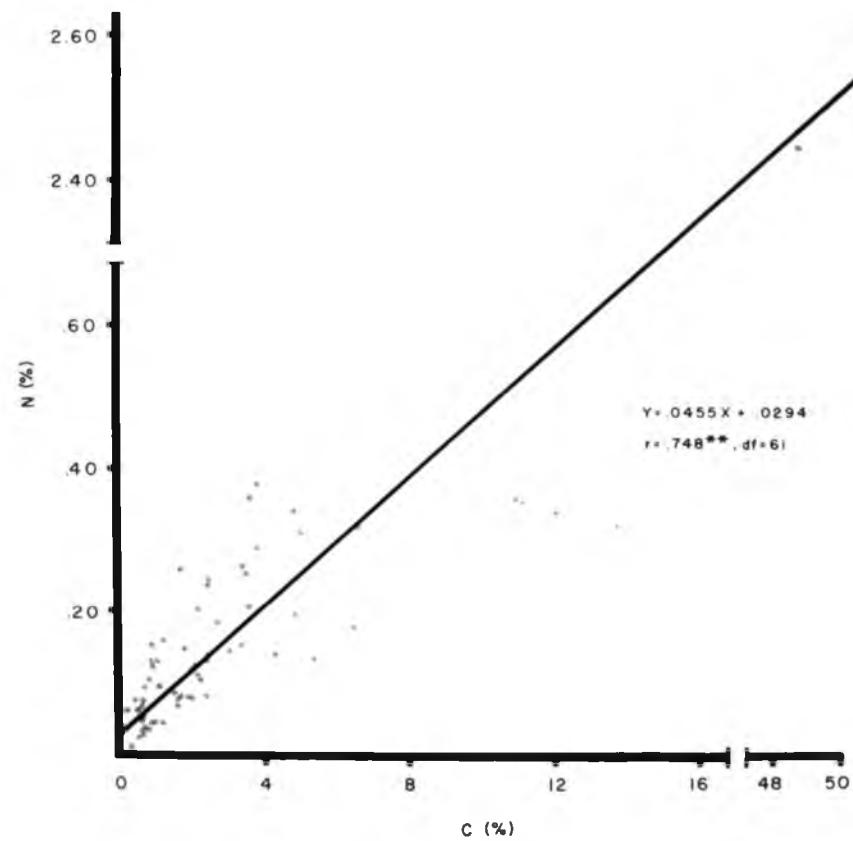


FIGURE 7. RELATIONSHIP OF N ON C OF SOME BASALTIC SOILS

varied from 4.2 to 24.4 in the volcanic ash soils. No obvious relationships within soil profiles were evident. Organic C/organic N, after correcting for native fixed ammonium-N from total N, was not significantly different from the organic C/total N ratios. At best only a 1.02 increase in organic C/organic N ratio was obtained in the Akaka (34-40") horizon over that of the organic C/total N ratio. This implies that the native fixed ammonium plays only a small part in the total nitrogen in Hawaii volcanic ash soils. This is contrary to other areas (Hanway and Scott, 1956; Leighty and Shorey, 1930; Rodrigues, 1954; Stevenson, 1959b), where the native fixed ammonium plays a significant role in determining the carbon/nitrogen ratios of subsoils.

Organic C/total N relationships for the soils from basalt were higher; they varied from a low of 2.7 (Wahiawa dry, 23-35") to a high of 42.6 (Maie exposed, 14-21"). Here, too, the ratio did not change much within the profile or show any significant trends. The values reported here are much higher than those reported previously by Blomberg and Holmes (1959) for other Hawaiian soils.

II. Thermal Release of Exchangeable and Native Fixed Ammonium

A. Time of Heating

A study was made to determine the length of time a sample containing native fixed ammonium should be heated at any one temperature for maximum recovery of ammonium released. This was determined by measuring the amount of native fixed ammonium remaining after each time interval of heating. There is no report in the literature indicating the stability of the native fixed ammonium held by tropical clay minerals subjected to prolonged heating. It is possible, therefore, that prolonged heating at a very low temperature is sufficient to release all or some of the native fixed ammonium.

Materials and Method

Since the native fixed ammonium has been found to be related to the soil mineral illite in Hawaiian soils, two samples with differing illite content were selected. Standard Illite No. 35, obtained from Ward's Natural Science Establishment Incorporated, was also included for purposes of comparison.

To determine the effect of time of heating on release of ammonium, 1-gram untreated whole soils were placed in Vycor crucibles and heated in a Mu-55 muffle furnace at 300° C. for 1, 2, 4, 8, 12 and 24 hours. The 300° C. temperature was selected for this study since evidence thus far reported (Scott et al., 1956) indicated that the native fixed ammonium remains unaffected up to a maximum temperature of 400° C. The native fixed ammonium remaining after each heating period was determined by the KBr-HF method described in the previous section on the native fixed ammonium in Hawaiian soils.

Results and Discussion

The effect of heating samples containing native fixed ammonium at 300° C. for varying lengths of time is shown in Table III. The results demonstrate that time of heating has a marked effect on the release of native fixed ammonium. A gain in native fixed ammonium occurred in the two soil samples, the maximum occurring after heating for 4 hours. A decrease was observed when the time of heating was extended. Native fixed ammonium of Illite No. 35 gradually decreased with increasing time of heating. From these results, 4 hours is used as the time of heating in the following section on temperature of heating.

TABLE III. NATIVE FIXED AMMONIUM (PPM) REMAINING AFTER HEATING AT VARYING LENGTHS OF TIME AT 300° C.

Sample	Time of Heating (hours)					
	1	2	4	8	12	24
Illite No. 35	1020.2	1001.5	992.2	978.1	968.7	959.4
Molokai clay 3-20"	172.8	191.9	215.3	201.2	187.2	187.2
Manana soil 12-21"	337.0	449.3	468.0	454.0	430.6	454.0

B. Temperature of Heating

A study was made to determine the magnitude of the thermal release of native fixed ammonium by illite with increasing temperature of heating. From the literature, native fixed ammonium held as fixed ammonium on bentonite and vermiculite was found to be stable until the temperature exceeded 400° C. (Scott et al., 1956). Whether the same conditions hold true for tropical illite or not was investigated.

Materials and Method

Soil horizons containing the largest quantity of native fixed ammonium determined previously were selected for the study of the thermal release of the native fixed ammonium. The soil horizons in almost all cases were surface horizons representing the highest content of native fixed ammonium in their respective profiles. Illite No. 36, obtained from Werd's National Science Establishment Incorporated, was also included.

One-gram untreated soil samples were placed in Vycor crucibles and were heated to 110, 200, 300, 400, 500, 600 and 700° C. for 4 hours in a Mu-55 electric muffle furnace. This time of heating was selected because the maximum recovery of native fixed ammonium was demonstrated to be 4 hours in the previous section. The total amount of native fixed ammonium remaining in the soil samples after each temperature of heating was determined by the KBr-H₂O method.

Results and Discussion

The native fixed ammonium remaining after each temperature of heating is given in Table IV. The data show that the native fixed ammonium content of most of the samples increased with increasing temperature of heating with the maximum occurring between 200 and 300° C. The values obtained after heating at 400° C. were lower than that measured at either 200 or 300° C. and were approximately the same as those when measured at 110° C. for most soils. The native fixed ammonium content decreased drastically after 400° C., demonstrating the partial thermal decomposition of the illite mineral. Complete removal of the native fixed ammonium occurred after heating at 600° C.; however, temperatures of 600° C. or

TABLE IV. NATIVE FIXED AMMONIUM (PPM) REMAINING ON THE SAMPLE
AFTER EACH TEMPERATURE OF HEATING

Soil series	Depth in.	Temperature-degrees centigrade						
		110	200	300	400	500	600	700
Molokai	0-3	215.3	257.4	280.8	210.6	65.5	0.0	0.0
	3-20	173.2	196.6	182.5	159.1	28.1	0.0	0.0
Lahaina	0-12	177.8	238.7	238.7	187.2	56.2	0.0	0.0
	12-21	145.1	168.5	168.5	140.4	37.4	0.0	0.0
Wahiawa Dry	0-15	140.4	163.8	107.6	98.3	14.0	0.0	0.0
	15-25	145.1	163.8	149.8	135.7	18.7	0.0	0.0
	25-35	135.7	187.2	163.8	117.0	28.1	0.0	0.0
Paaloa	0-4	271.4	374.4	388.4	290.2	65.5	0.0	0.0
	4-9	266.8	360.4	374.4	332.3	74.9	0.0	0.0
	9-17	248.0	337.0	355.7	266.8	42.1	0.0	0.0
	17-25	176.0	234.0	234.0	173.2	18.7	0.0	0.0
Kolekole	4-8	117.0	163.8	163.8	112.3	9.4	0.0	0.0
	8-13	140.0	177.8	205.9	168.5	18.7	0.0	0.0
	18-23	145.1	187.2	220.0	163.8	20.5	0.0	0.0
Manana	0-12	355.7	402.5	510.1	393.1	56.2	0.0	0.0
	12-21	358.6	397.8	468.0	304.2	51.5	0.0	0.0
	21-34	307.1	327.6	379.1	252.7	37.4	0.0	0.0
	34-46	248.0	271.4	304.2	210.6	34.6	0.0	0.0
Koolau	3-6.5	585.0	673.9	702.0	673.9	248.0	46.8	0.0
Koolau	4-7	388.4	449.3	477.4	458.6	163.8	32.8	0.0
Koolau clay	4-7	748.8	776.9	814.3	762.8	280.8	26.3	0.0
Illite No. 35		1039.0	1039.0	996.8	725.4	154.4	46.8	0.0
Illite No. 36		725.4	725.4	702.0	556.9	84.2	28.1	0.0

higher was required for samples predominantly illitic. Porter and Stewart (1964) also reported an increase of native fixed ammonium in some NH_4Cl -treated soils until a temperature of 400°C . was reached. Above this temperature the native fixed ammonium was lost. Since their study has not been published, their explanation for the increase in fixed ammonium with increase in temperature is not available.

Illite No. 35 and 36 did not gain in their native fixed ammonium content with increasing temperature of heating as did the other soil samples investigated. A decrease in fixed ammonium started above 200°C . with a drastic decrease occurring above 400°C ., due to the thermal decomposition of the illite mineral.

The increase in native fixed ammonium with increasing temperature of heating cannot be explained from the results obtained in this investigation. However, an attempt will be made to speculate on the mechanism of the increase. Scott et al. (1956) suggested the fixation of exchangeable ammonium by bentonite after heating at 300 to 350°C . It may be that this type of mechanism is one possible explanation for the increase in native fixed ammonium with increasing temperature of heating.

Table V shows the results of the effect of heating on the thermal release of exchangeable ammonium in some untreated volcanic ash soils. The results show that heating at 300°C . for 12 hours greatly increased the exchangeable ammonium content. This increase was as much as a hundred-fold in some samples. Porter and Stewart (1964) reported a 3 to 6-fold increase in exchangeable ammonium after heating at 250 to 300°C . for 5 minutes or longer time intervals. The increase in exchangeable ammonium could have come from the thermal decomposition of the organic matter

TABLE V. EFFECT OF HEATING ON THE RELEASE OF AMMONIUM (PPM)
OF SOILS DEVELOPED FROM VOLCANIC ASH SOILS

Soil series	Depth in.	Temperature-degrees centigrade		
		Room temp. (25)	110	300
Maalehu	0-11	100.8	189.0	306.6
	11-21	7.0	25.2	170.8
	21-34	5.6	21.0	231.0
	34-59	1.4	12.6	121.8
	59-65	1.4	9.8	134.4
Pahala	0-7	37.8	74.2	154.0
	7-11	-	-	112.0
	11-18	7.0	25.2	113.4
	18-25	4.2	19.6	110.6
	25-36	2.8	4.2	40.6
	36-39	1.4	4.2	86.8
	39-52	0.0	4.2	154.0
	52-57	0.0	4.2	119.0
Waikaloe	0-10	33.6	98.0	112.0
	10-19	4.2	58.8	86.8
	19-27	4.2	35.0	81.2
	27-37	4.2	5.6	96.6
	37-46	2.8	4.2	77.0
	46-55	4.2	5.6	81.2
	55-64	2.8	5.6	77.0
Mahoeia	0-10	-	-	86.8
	10-22	-	-	85.4
	22-28	-	-	113.4
	28-34	-	-	93.8
	34-34	-	-	74.2
	34+	-	-	68.6
Waiki	5-11	-	-	145.6
	11-20	-	-	152.6
	20-23	-	-	121.8
Pauhanu	20-46	8.4	57.4	89.6
	46-60	7.0	36.4	54.6
	60-74	5.6	84.0	60.2
Akaka	12-34	21.7	-	306.6
	34-40	13.4	-	172.2
	40-50	10.9	-	166.6
	50-74	8.7	-	182.0
	74+	8.7	-	191.8

TABLE V. EFFECT OF HEATING ON THE RELEASE OF AMMONIUM (PPM) OF SOILS DEVELOPED FROM VOLCANIC ASH SOILS (Continued)

Soil series	Depth in.	Temperature-degrees centigrade		
		Room temp. (25)	110	300
Akaka	0-3	8.1	-	139.6
	3-7	7.4	-	256.2
	7-15	5.9	-	365.4
	15-18	2.5	-	246.4
	18-24	4.5	-	411.6
	24-38	2.5	-	373.8
	38-43	3.9	-	352.8
	57-60	2.5	-	120.4
Hilo	60-72	1.1	-	161.0
	72-80	0.0	-	89.6
	80-90	0.0	-	107.8
Hilo	12-24	2.1	-	245.0
	45-55	2.1	-	134.4
	60-66	1.8	-	67.2
	72-78	5.3	-	218.4
Koolau	0-4	-	-	91.0
	4-7	-	-	232.4
	7-10	-	-	123.2
	10-14	-	-	126.0
	14-20	-	-	149.8
	20-30	-	-	142.8
	30+	-	-	154.0

residue, or from the thermally released native fixed ammonium. But from the data in Table IV, it appears that only a negligible amount, if any, of the native fixed ammonium is released at temperatures below 300° C. In fact, an increase in native fixed ammonium may have resulted from the fixation of the exchangeable ammonium released by the organic fraction on heating. Whether such a phenomenon actually occurs cannot be concluded from the results obtained thus far. This is further handicapped by the fact that the loss of ammonium due to heating at any one temperature cannot be positively attributed to only the exchangeable ammonium. Any ammonium released either from the organic nitrogen or illite mineral at temperatures of 400° C. or higher could not be measured as exchangeable ammonium due to gaseous ammonia loss. This makes it almost impossible to measure the loss of organic nitrogen in the form of ammonium and of native fixed ammonium by the method used.

In order to further elucidate the increase in fixed ammonium, the native fixed ammonium remaining after each temperature of heating was determined on a sample free of organic nitrogen and exchangeable ammonium. The 4-7" horizon of the Koolau soil was selected for this study because of its high native fixed ammonium content. The sample was KBr-treated and subjected to the same temperature treatment as those reported previously. The data of Table VI show that an increase in native fixed ammonium still occurs between 200 to 300° C. The sample behaved similarly to that observed in the original fresh soils except for one distinct feature--the illite mineral appears to be able to withstand a higher temperature of heating before complete decomposition occurs. This is evident at temperatures above 400° C. where a larger amount of native

TABLE VI. NATIVE FIXED AMMONIUM REMAINING AFTER EACH
TEMPERATURE OF HEATING AFTER KBr-TREATMENT

Soil	110	200	300	400	500	600	700	800
Koolau def.	645.8	697.3	673.9	622.4	439.9	154.4	65.5	0.0

fixed ammonium was measured. This may be due to the addition of potassium ions during the KBr pretreatment, making the illite mineral more resistant to thermal decomposition.

As previously reported, a substantial quantity of ammonium is apparently released from the organic nitrogen until a temperature of 300° C. is attained. Above this temperature any ammonium released either from the organic nitrogen or native fixed form is lost by volatilization. From the results of the experiment reported above, it is uncertain as to whether the thermally released organic ammonium is actually being fixed by the illite mineral at temperatures up to approximately 300° C. or is being lost in the form of ammonia. Since this observation is based on only one sample, the results of a few more organic matter and exchangeable ammonium-free soils are desirable before any conclusions can be drawn.

III. Ammonium Fixation in Some Hawaiian Soils

Materials and Methods

Material (Soils):

Two Reddish Prairie soil profiles, the Maalehu and Pahala soils, were selected for ammonium fixation studies after preliminary investigations showed that an appreciable amount of the added ammonium was being retained against extraction with N KCl after oven drying at 110°C . X-ray analysis of these soils did not give any indication of occurrence of any layered silicate clay minerals. Similar soils that fixed little, if any, ammonium were not included in this investigation. A typical montmorillonite soil (Lualualai, 1-15"), illite soil (Koolau, 4-7") and a kaolinite soil (Molokai, 74+"") were also included in this study for comparative purpose. Cation exchange capacity and exchangeable base data of these soils are given in Table VII. Other chemical and physical properties are given in other sections of this thesis.

Pretreatment of the Sample and Separation into Size Fractions:

Soil samples after being brought back to the laboratory in polyethylene bags were air dried and passed through a 20 mesh screen. Each sample was thoroughly mixed and stored in gallon bottles or in polyethylene bags. Approximately 300 grams of each sample was then treated with N NaOAc buffer adjusted to pH 5.0 to remove soluble calcium and magnesium carbonates, soluble salts and exchangeable cations. The sample was next treated with H_2O_2 for approximately 1 week to destroy organic matter. The H_2O_2 -treated sample was filtered, washed with distilled water, air-dried and passed through a 60 mesh screen before being stored in air tight bottles. The bulk of the organic matter-removed sample was

TABLE VII. CATION EXCHANGE CAPACITY AND EXCHANGEABLE
BASES OF SOILS

Soil series	Depth in.	C.E.C.	Ca	Mg	Na	K
mg./100 g.						
Maalehu	0-11	52.24	31.10	18.00	1.29	1.22
	11-21	60.91	39.82	20.34	2.19	.37
	21-54	67.09	47.94	21.81	2.79	.24
	54-59	73.61	50.21	26.10	3.33	.39
	59-65	75.18	48.36	28.49	3.81	.30
Pahala	0-7	36.87	27.15	13.30	.61	3.08
	7-11	31.76	16.29	8.99	.65	3.04
	11-18	32.96	18.86	11.00	1.17	2.26
	18-25	39.39	23.38	13.05	1.51	1.84
	25-36	72.74	45.89	23.80	1.80	2.29
	36-39	53.40	33.75	16.27	2.08	1.51
	39-52	41.22	25.37	10.79	2.00	1.08
	52-57	56.42	37.00	16.83	2.13	1.05
Lualualei	1-15	70.23	45.18	17.05	2.64	1.44
Koolau	4-7	11.00	.48	.33	.24	.16
Molokai	3-20	8.10	3.67	2.51	.42	.14

separated into their size fractions. The sample was treated with sodium dithionate-citrate to remove free iron oxide following the method of Jackson (1958). The sample was then dispersed with 2% Na_2CO_3 and the silt and clay fractions were separated by sedimentation after removal of the sand by wet sieving through a 325 mesh screen. The sedimentation process was continued with repeated washing with water until a well-separated sample was obtained (Jackson, 1956). The deferrated, organic-matter-free soil and their size fractions were air dried and used for the subsequent experiments.

A mechanical analysis of the sand, silt and clay contents of the soils was determined on another sample under the same conditions given above. All fractions separated were weighed, and percent yield on the oven-dried weight basis were calculated. The results are listed in Table VIII.

Ammonium Fixing Capacity:

The procedure used for determining the ammonium fixing capacity of the soils was that developed by Allison, Doetsch and Roller (1951) with some modifications. A 2-gram sample, treated with a known amount of NH_4Cl in 5 ml. of solution, was shaken for 1 hour on a reciprocating shaker and left to stand at room temperature for 12 hours. The samples were either kept moist, air-dried or placed in an oven at 110°C . to dry for 12 hours. Fifty ml. of N KCl was added to the sample which was then agitated for 1 hour. The sample was filtered under suction using a Buchner funnel on a 125 ml. filtering flask. The soluble and readily exchangeable ammonium was removed by washing with N KCl and methyl alcohol. The soil plus filter paper was transferred to a 100 ml. Kjeldahl

TABLE VIII. MECHANICAL ANALYSES OF SOILS (THE VALUES ARE ON THE ORGANIC MATTER-FREE SAMPLES)

Soil series	Depth	Sand	Silt	Clay	Total	Dithionite-soluble materials
	in.	%	%	%	%	%
Waialeale	0-11	19.1	40.5	25.9	85.5	14.5
	11-21	16.9	40.3	24.5	81.7	18.3
	21-54	16.4	43.3	21.2	80.9	19.1
	54-59	27.9	44.6	15.9	88.4	11.6
	59-65	28.3	42.4	15.1	85.8	14.2
Pahala	0-7	37.4	36.2	12.1	85.7	14.3
	7-11	39.7	39.3	11.8	90.8	9.2
	11-18	30.6	44.6	13.4	88.6	11.4
	18-25	27.3	45.2	15.5	88.0	12.0
	25-36	36.6	44.5	9.5	90.6	9.4
	36-39	33.4	41.6	11.1	86.1	13.9
	39-52	26.1	48.3	13.7	88.0	12.0
	52-59	29.4	41.1	11.1	81.6	18.4
Lualualei	1-15	2.8	19.4	72.1	94.3	5.7
Koolau	4-7	1.1	58.9	35.8	95.8	4.2
Molokai	74+	-	49.8	41.4	91.2	8.8

flask and digested with 5 grams $K_2SO_4:FeSO_4:CuSO_4$ salt mixture in a ratio of 10:1:1/2 for 2 hours. The digested sample was transferred quantitatively to a 500 ml. Kjeldahl flask and diluted to a volume of approximately 200 ml. The total nitrogen of the ammonium-treated sample was measured by collection using a modified micro-Kjeldahl steam distillation apparatus. The ammonium released by steam distillation with NaOH was determined by titration with 0.01N H_2SO_4 standard solution. A non-treated soil sample (blank) was also analyzed under the same conditions as the ammonium-treated sample. The difference between the total nitrogen in the ammonium-treated sample and of the total nitrogen in the untreated blank represented the quantity of ammonium fixed.

Results and Discussion

Mechanical Composition of Soils:

As shown in Table VIII, the Raddish Preirie soils, namely the Maalehu and Pahale soils, have a very low clay content. The values are less than those reported by other investigators on similar Hawaiian soils (Houng, 1964; Matsusaka, 1952; Tenma, 1965). The bulk of the sample is in the sand and silt fractions.

Questions may arise at this point as to whether complete dispersion was obtained for these soils. The samples were dispersed in an alkaline solution (2% Na_2CO_3) at pH 9.5. Complete separation was obtained after repeated extraction with water. This method of separation was used instead of the conventional mechanical analysis methods because of better dispersibility.

In these soils it was found that after apparent dispersion, there still remained aggregates in the sand and silt fractions. Petrographic

examination revealed some birefringent non-dispersible aggregates in the sand and silt fractions. Whether this is the result of unsuccessful dispersion is not known. The aggregates may have been destroyed if ultrasonic treatment prior to dispersion was attempted as has been reported by Kobo (1964).

Fixation of Applied Ammonium:

The results of ammonium fixation of the untreated soil samples, organic matter-free samples, deferrated samples and size fractions are presented in Tables IX and X. The rates of NH_4Cl applications were 10 and 50 me. ammonium per 100 grams soil, respectively. The results 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 is very evident especially in the 25-36" horizon of the Pahala soil. A more detailed concentration-dependent ammonium fixation study is given in a following section.

The results of this study show that the Naalehu and Pahala profiles have some capacity to retain ammonium against $\frac{1}{2}$ M KCl extraction. The amount fixed was equal to or exceeded that fixed by the montmorillonitic Lualualei soil. These soils, whose mineralogical make-up has been reported to be allophane and halloysite (Houng, 1964), fixed more ammonium than other similar volcanic ash soils investigated during the preliminary studies.

The data in Tables IX and X 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 nonexchange-

TABLE IX. AMMONIUM FIXATION CAPACITIES OF SOILS SATURATED
WITH 10 ME./100 GRAMS AMMONIUM AND OVEN-DRIED
AT 110° C. FOR 12 HOURS

Soil series	Depth	Untrt. soil	H ₂ O ₂ trt. soil	Def. soil	Def. sand	Def. silt	Def. clay
	in	me./100 g.					
Waelehu	0-11	.42	.36	1.37	.48	.59	.83
	11-21	1.19	1.96	1.96	1.25	1.93	1.58
	21-54	1.49	1.61	2.08	1.55	2.14	1.19
	54-59	2.30	2.26	2.98	.60	1.60	1.58
	59-63	1.90	2.20	2.65	1.67	3.00	1.42
Pahala	0-7	.30	.36	.48	.18	.30	.77
	7-11	.41	.54	.63	.21	.36	.83
	11-18	.59	.71	.74	.42	.77	.95
	18-25	1.43	1.43	1.81	1.25	1.37	.60
	25-36	2.97	3.15	4.19	3.09	3.98	2.50
	36-39	1.84	2.26	2.08	1.07	1.55	1.55
	39-52	.71	.60	.83	.71	.62	.71
	52-57	1.07	.87	.89	1.01	1.07	1.31
Lualualei	1-15	2.32	1.37	-	-	-	-
Koolau	4-7	2.50	2.91	3.93	-	-	6.90
Molokai	74+	.30	-	-	-	-	.21

TABLE X. AMMONIUM FIXATION CAPACITIES OF SOILS SATURATED
WITH 50 mg./100 GRAMS AMMONIUM AND OVEN-DRIED
AT 100° C. FOR 12 HOURS

Soil series	Depth in	Untrt. soil	H ₂ O ₂ trt. soil	Def. soil	Def. sand	Def. silt	Def. clay
mg./100 g.							
Naalehu	0-11	1.19	.71	1.55	1.01	1.19	3.75
	11-21	1.96	2.50	2.86	2.74	2.91	3.15
	21-54	2.44	2.44	3.51	3.15	3.69	3.33
	54-59	5.47	4.94	5.95	1.17	3.15	4.46
	59-65	4.10	4.11	4.88	4.94	5.56	4.16
Pahala	0-7	.42	.45	.65	.42	.59	2.26
	7-11	.49	.65	.89	.59	.60	1.90
	11-18	.74	.83	1.43	.83	1.13	1.90
	18-25	1.78	1.61	2.44	1.96	2.06	2.02
	25-36	6.48	5.71	7.91	6.84	7.38	5.59
	36-39	3.27	3.15	3.57	2.26	3.03	2.97
	39-52	.95	1.13	1.55	.95	1.31	1.67
	52-57	1.31	1.05	1.61	1.13	1.31	1.78
Lualualei	1-15	5.71	-	-	-	-	6.78
Koolau	4-7	2.76	2.44	3.03	-	-	9.93
Molokai	74+	.65	-	-	-	-	.39

able 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 extent. The most noticeable increase occurred again in the 25-36" horizon of the Pahala soil, once again demonstrating the high fixing capacity of this particular horizon.

The ammonium fixing capacity of the deferrated size fractions of the Naalehu and Pahala profiles are given in Tables IX and X. In each case, ammonium fixation by the sand, silt and clay size fractions is shown. Here, too, the highest fixation occurred in the Pahala (25-36") horizon. The Naalehu (59-65") horizon also had a high ammonium fixing capacity. In both cases, the silt fraction had the highest fixation, followed by the sand and clay fractions, respectively. The nature of the mineral(s) fixing ammonium in the Naalehu and Pahala profiles will be determined and discussed in a following section.

In the crystalline soils, the highest fixation occurred in those soil horizons that were predominantly illitic (Koolau) and montmorillonitic (Lualualei). The kaolin soil (Molokai) did not fix much ammonium.

Ammonium Fixation of Soil Separates after Moistening, Sun-Drying and Oven-Drying at 110° C.:

Since only the ammonium fixation of the soil samples after oven drying at 110° C. for 12 hours was determined, a short study was made to determine the amount of fixation under moistening and sun-drying conditions. The sand and silt fractions of the Naalehu (59-65") and Pahala (25-36") horizons were selected. The clay fractions, though desirable, could not be determined due to insufficient amount of the sample. A

montmorillonitic (Lualualei, 1-15") clay sample was also studied. The results of the laboratory analysis (Table XI) show that the Naalehu and Pahala soils fixed 1.49 and 1.58 me. per 100 grams soil for the sand fractions and 0.79 and 0.54 me. per 100 grams for the silt fractions, respectively, under moist conditions. Ammonium fixation was further increased after sun-drying and oven-drying.

Table XI also shows the ammonium fixing capacity of the samples after differential dissolution analysis (d.d.a.). The highest values were observed in the silt fractions of both soils and after d.d.a. treatment.

TABLE XI. AMMONIUM FIXATION CAPACITIES OF SEPARATES SATURATED WITH 50 ME./100 G. AMMONIUM AFTER MOISTENING, SUN-DRYING AND OVEN-DRYING AT 110° C.

Soil Series	Depth in.	Moist	Sun-dried	Oven-dried	
				1*	2†
		me./100 g.			
Naalehu	59-65				
sand		1.49	3.21	4.94	5.82
silt		.79	2.20	5.65	8.44
Pahala	25-36				
sand		1.58	2.97	6.84	8.92
silt		.54	2.02	7.38	9.16
Lualualei	1-15				
clay		.43	-	8.78	-

*before differential dissolution analysis

†after differential dissolution analysis

Concentration Dependent Ammonium Fixation:

The ammonium fixing capacity of some of the soil horizons (Tables IX and X) were of sufficient magnitude to warrant further study. The Naalehu (59-65"), Pahala (25-36" and 52-57"), Lualualei (1-15"), Koolau (4-7") and Molokai (74") horizons were selected to study their concentration dependent ammonium fixation. The ammonium fixation determinations involving applications of NH_4Cl at various amounts in 5 ml. of solution per 2 grams soil were made on the untreated whole soil, organic matter-free soil, free iron oxide-removed soil, and their size fractions. The results of these determinations are listed in Tables XII to XVII. The data show that the soil horizons, with the exception of the kaolinite (Molokai) horizon, have a high ammonium fixing capacity. It will be noted that a large percentage of ammonium applied at the lower rates was fixed but that the fixation capacity was not satisfied when the NH_4Cl was applied at the rate of 10 me. per 100 grams of soil which has been the amount used by Bower (1950). Fixation capacity for the Naalehu and Pahala horizons was virtually satisfied after addition of 50 to 100 me. ammonium per 100 grams soil. Data on the amounts of ammonium fixed by the other soil samples are also given in Tables XV to XVII. At higher rates of NH_4Cl addition, fixation capacity gradually decreased. This phenomenon, shown graphically in Figure 8, reveals that a significant decrease in fixed ammonium occurred in virtually every soil horizon and separate investigated after the 50 me. rate was exceeded. Possibly the fixing sites on the soil mineraloids are somehow being blocked, presumably by some salts being formed at high ammonium concentrations. Other explanation(s) are warranted, but further work is needed before any conclusions can be made.

TABLE XII. CONCENTRATION DEPENDENT AMMONIUM FIXATION
OF A MAALEHU (59-65") SOIL

Conc. NH_4 added	Untrt. soil	H_2O_2 -trt. soil	Def. soil	Def. sand	Def. silt	Def. clay
mg./100 g.	mg./100 g.					
5	1.25	1.43	1.55	1.01	2.02	1.07
10	1.90	2.20	2.65	1.67	3.00	1.42
20	2.97	3.33	4.10	3.39	4.58	2.02
50	4.10	4.11	4.88	4.94	5.65	4.16
100	4.05	4.40	5.35	5.00	6.01	5.12
150	3.81	3.99	5.29	4.94	5.77	5.07
200	-	3.45	5.00	4.46	5.30	5.19

TABLE XIII. CONCENTRATION DEPENDENT AMMONIUM FIXATION
OF A PAHALA (25-36") SOIL

Conc. NH_4 added	Untrt. soil	H_2O_2 -trt. soil	Def. soil	Def. soil	Def. soil	Def. soil
mg./100 g.	mg./100 g.					
5	1.78	2.26	2.32	1.72	2.26	-
10	2.97	3.15	4.19	3.09	3.98	2.50
20	4.82	4.70	6.19	5.12	5.83	4.64
50	6.48	5.71	7.91	6.84	7.38	5.59
100	5.95	5.53	7.79	6.96	7.62	6.66
150	5.18	4.94	7.38	6.60	7.32	-
200	4.46	4.34	6.66	5.53	6.07	6.54

TABLE XIV. CONCENTRATION DEPENDENT AMMONIUM FIXATION
OF A PAHALA (52-57") SOIL

Conc. NH_4 added	Untrt. soil	H_2O_2 -trt. soil	Def. soil	Def. sand	Def. silt	Def. clay
mg./100 g.						
5	.65	.65	.83	.77	.83	1.19
10	1.07	.87	.89	1.01	1.07	1.31
20	1.13	.95	1.25	1.07	1.13	1.42
50	1.31	1.05	1.61	1.13	1.31	1.78
100	1.01	1.01	1.43	1.25	1.25	2.14
150	.95	.95	1.31	1.19	1.19	2.02
200	.77	.89	1.36	1.17	1.13	1.90

TABLE XV. CONCENTRATION DEPENDENT AMMONIUM FIXATION
OF A LUALUALEI (1-15") SOIL

Conc. NH_4 added	Untr. soil	H_2O_2 -trt. soil	Def. clay
mg./100 g.			
5	.95	.95	-
10	2.32	1.37	-
20	3.69	1.84	-
50	5.71	-	6.78
100	5.65	2.85	10.23
150	5.53	2.91	11.90
200	5.41	3.21	11.84

TABLE XVI. CONCENTRATION DEPENDENT AMMONIUM FIXATION
OF A KOOLAU (4-7") SOIL.

Conc. NH_4 added	Untrt. soil	H_2O_2 -trt. soil	Def. clay
		mg./100 g.	
5	.95	2.79	3.15
10	2.50	2.91	6.90
20	3.03	2.85	10.23
50	2.76	2.44	9.93
100	2.67	2.14	8.98
150	2.50	2.08	8.27
200	2.38	1.96	8.21

TABLE XVII. CONCENTRATION DEPENDENT AMMONIUM FIXATION
OF A MOLOKAI (74+") SOIL.

Conc. NH_4 added	Untrt. soil	H_2O_2 -trt. soil	Def. clay
mg./100 g.		mg./100 g.	
5	.30	-	.15
10	.30	-	.21
20	.41	-	.33
50	.65	-	.39
100	.83	-	.34
150	.55	-	-
200	.30	-	.33

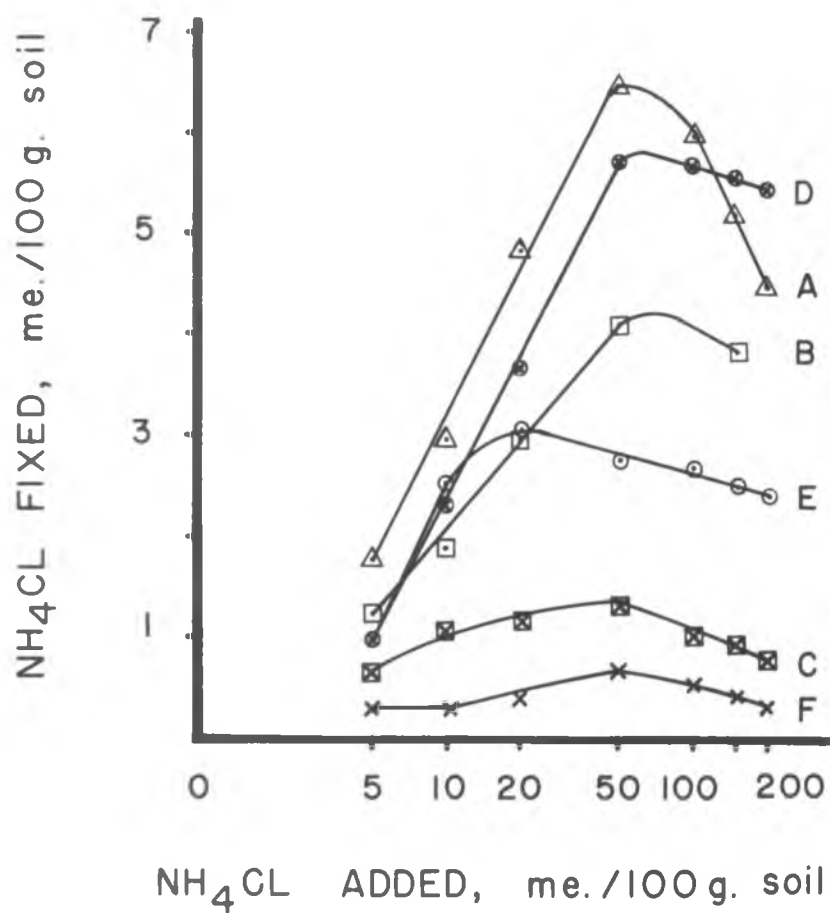


FIGURE 8. THE EFFECT OF AMMONIUM CONCENTRATION ON AMMONIUM FIXATION. THE SAMPLES ARE: A, PAHALA 25-36"; B, MAALENU 59-65"; C, PAHALA 52-57"; D, LUALUALEI 1-15"; E, KOOLAU 4-7"; F, MOLOKAI 74+"

IV. Chemical and Mineralogical Studies of Soils

This study was made to determine the chemical and mineralogical properties of the Maalehu and Pahala soils and to determine the mineral(s) fixing ammonium. Three soil horizons, Pahala (25-36"), Maalehu (59-65") and Pahala (52-57"), representing high, intermediate and low ammonium fixing capacities, respectively, were thoroughly investigated.

Methods

Total Chemical Analysis:

The procedure used by Dr. Takeshi Katsura of the Institute of Technology, Tokyo, Japan during his stay at the Department of Agronomy and Soil Science, University of Hawaii, in 1961 was followed. SiO_2 , TiO_2 , Fe_2O_3 , CaO and MgO were determined after Na_2CO_3 fusion; MnO , P_2O_5 , Na_2O and K_2O after $\text{HF-H}_2\text{SO}_4$ digestion. Al_2O_3 was obtained from the difference between R_2O_3 and the oxides of iron, titanium and phosphorous.

Silica was determined gravimetrically after dehydration with HCl . R_2O_3 was precipitated with ammonia in excess of ammonium chloride from which Fe_2O_3 and TiO_2 were determined by the orthophenanthroline and hydrogen peroxide methods, respectively. Calcium was precipitated as calcium oxalate and titrated with standard solution of potassium permanganate. Magnesium was precipitated as magnesium phosphate, ignited and weighed as magnesium pyrophosphate. The vanadomolybdic acid method for phosphorous, periodate method for manganese and the flame spectrophotometric method for potassium and sodium were also used.

Prior to Na_2CO_3 fusion, the sample was ignited after oven-drying to obtain the loss on ignition (LOI). The sample prior to $\text{HF-H}_2\text{SO}_4$ digestion was also ignited to decompose organic matter.

Cation Exchange Capacity and Exchangeable Bases:

The cation exchange capacity of the soils and size fractions was determined by the standard $\text{N NH}_4\text{OAc}$ method. The ammonium was displaced with 4% KCl . The displaced ammonium was determined by distillation with NaOH using a micro steam distillation apparatus and subsequent titration with standard H_2SO_4 solution.

Only the exchangeable bases of the untreated soil were determined. Calcium was determined as calcium oxalate and titrated with standard potassium permanganate. Magnesium was determined as the ignited magnesium pyrophosphate. The flame spectrophotometer was used to determine sodium and potassium.

Cation Exchange Capacity Delta Value:

The cation exchange capacity delta values of the deferrated whole soil, sand, silt and clay fractions of the Maalehu and Pahala profiles were determined by the method proposed by Aomine and Jackson (1959) with some modifications. Cation exchange capacity was determined by the standard $\text{N NH}_4\text{OAc}$ method instead of the N Ca(OAc)_2 method suggested. The ammonium released was collected using a modified micro Kjeldahl steam distillation apparatus. The ammonium was then determined by titration with a standard acid solution.

Differential Dissolution Analysis (d.d.a.):

The procedure described by Hashimoto and Jackson (1958) was used as a means of determining the amorphous content and of purifying the soil separates. Only the deferrated, organic matter-free soil, sand, silt and clay fractions were analyzed.

An oven-dried 100 mg. sample was boiled for 2½ minutes in a nickel crucible containing 100 ml. 0.5% NaOH . The solution was immediately

cooled and centrifuged in a 100 ml. polyethylene tube. Fifty ml. of the solution was transferred to a 100 ml. volumetric flask from which aliquots were taken for determination of aluminum and silica. Silica was determined by the ammonium-molybdate method (Jackson, 1958); the aluminum was determined by the aluminum-acetate method (Hsu, 1963). The Klett-Summerson photocolormeter was used for both analyses. The residue unaffected by this treatment was smeared on a glass slide and analyzed by X-ray diffraction.

X-ray Diffraction Analysis:

X-ray analysis was used to determine the soil minerals responsible for ammonium fixation using a Norelco X-ray diffractometer with copper K_{α} radiation and nickel filter. X-ray analysis was determined on the less than 2 micron fraction after potassium and magnesium saturation. The potassium-saturated sample was oriented on a glass slide and heated to 110, 350 and 550° C. The magnesium-saturated slide was glycolated by permitting the slide to equilibrate in an ethylene-saturated atmosphere at 70° C. for 2 hours.

The sand and silt fractions were run as a powder in an aluminum holder. The size fractions were further run as a smear on a glass slide after differential dissolution analysis.

Differential Thermal Analysis:

Differential thermal analysis was run on the defarreted, organic matter-free sand, silt and clay fractions of the Naalahu (59-65") and Pahala (25-36" and 52-57") horizons. The samples were ground to pass through a 100 mesh sieve and oven-dried overnight at 110° C. prior to this analysis.

A 0.4 gram sample and a thermally inert aluminum oxide were subjected to a temperature increase of approximately 15° per minute, from room temperature to 990° C., during which time the galvanomic readings were recorded at 1 minute intervals.

Dehydration Curves:

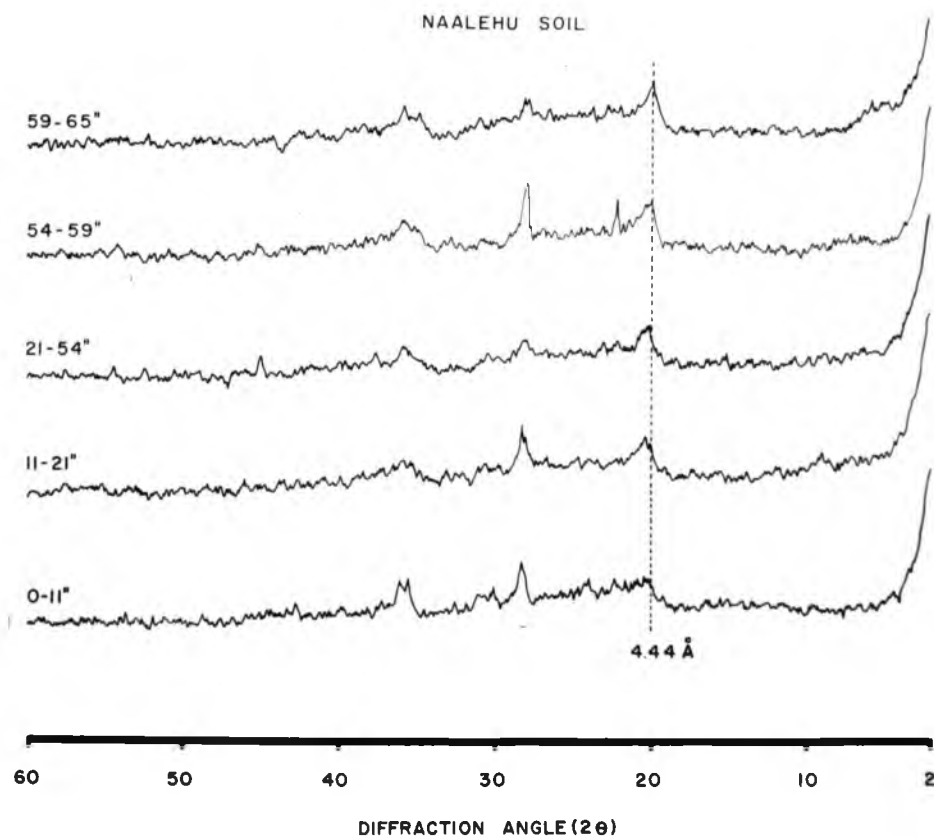
Organic matter-free, deferrated whole soils of the Naalehu and Pahala profiles were heated to 110, 200, 300, 400, 500, 600 and 800° C. in platinum crucibles for periods of 24 hours in a Mu-33 muffle furnace. The samples were heated to a final temperature of 1000° C. for 4 hours. The percent weight loss was calculated on the basis of the oven-dried sample (110° C.).

Results and Discussion

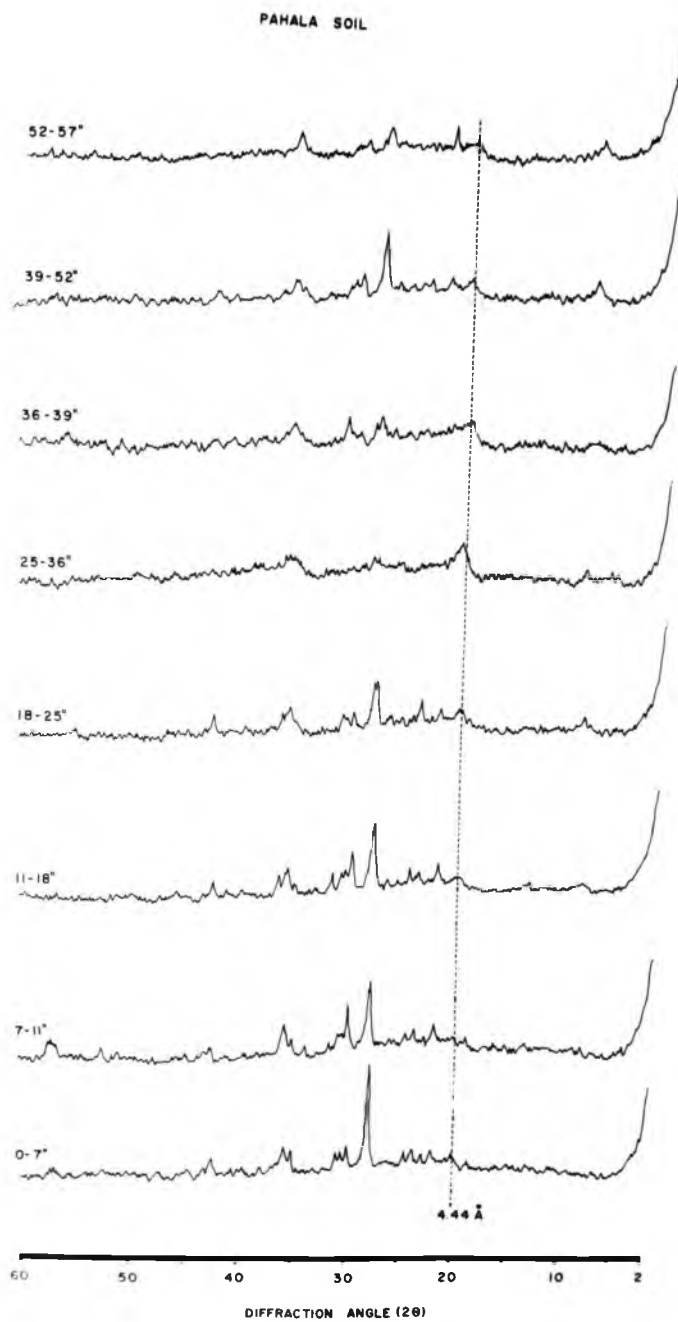
X-ray Diffraction and Petrographic Studies:

Sand and Silt:

The Naalehu and Pahala soils were analyzed by X-ray diffraction to determine the mineral(s) responsible for ammonium fixation. X-ray diffraction diagrams are given in Figures 9 to 12. The primary mineral most frequently appearing in the sand and silt fractions was the feldspars. No existence of any layered silicate minerals was evidenced in the sand and silt fractions. However, a (020) (hkl) reflection band near 20° θ consistently appeared in every horizon examined. The intensity of this line appeared to be related to ammonium fixation. This is most evident in the Pahala profile where great changes in ammonium fixation within the profile exist. This relationship does not apply to horizons where layered silicate minerals can be identified.



**FIGURE 9. POWDERED X-RAY DIFFRACTION DIAGRAMS OF THE DEFERRATED,
ORGANIC MATTER-FREE NAALEHU PROFILE**



**FIGURE 10. POWDERED X-RAY DIFFRACTION DIAGRAMS
OF THE DEFERRATED, ORGANIC MATTER-
FREE PAHALA PROFILE**

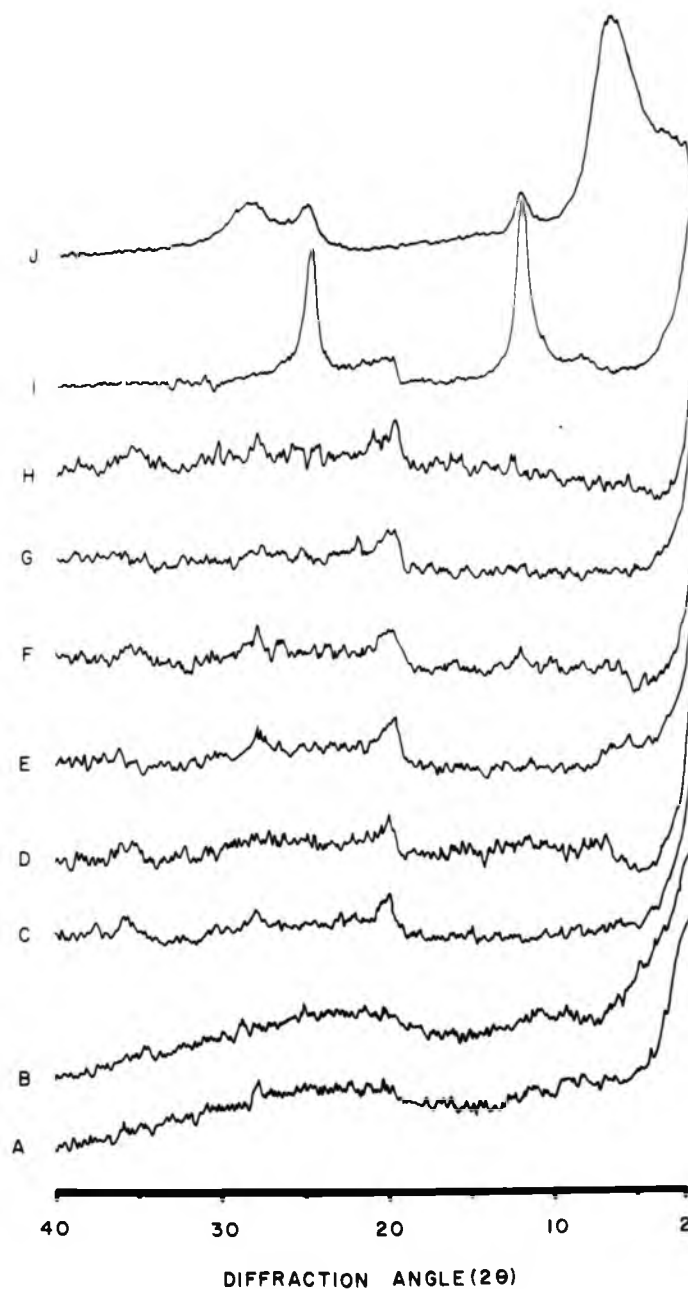


FIGURE 11. X-RAY DIFFRACTION DIAGRAMS OF SOILS. DIAGRAMS A TO H ARE THOSE OF THE NAALHEU 59-65" HORIZON (SCALE FACTOR: 2-1-8): A, POTASSIUM-SATURATED, ROOM TEMPERATURE; B, MAGNESIUM-SATURATED, GLYCOLATED; C, CLAY, BEFORE D.D.A.; D, CLAY, AFTER D.D.A.; E, SILT, BEFORE D.D.A.; F, SILT, AFTER D.D.A.; G, SAND, BEFORE D.D.A.; H, SAND AFTER D.D.A. I REPRESENTS A KAOLINITE CLAY (SCALE FACTOR: 4-1-8); J, A MONTMORILLONITE CLAY (SCALE FACTOR: 8-1-8)

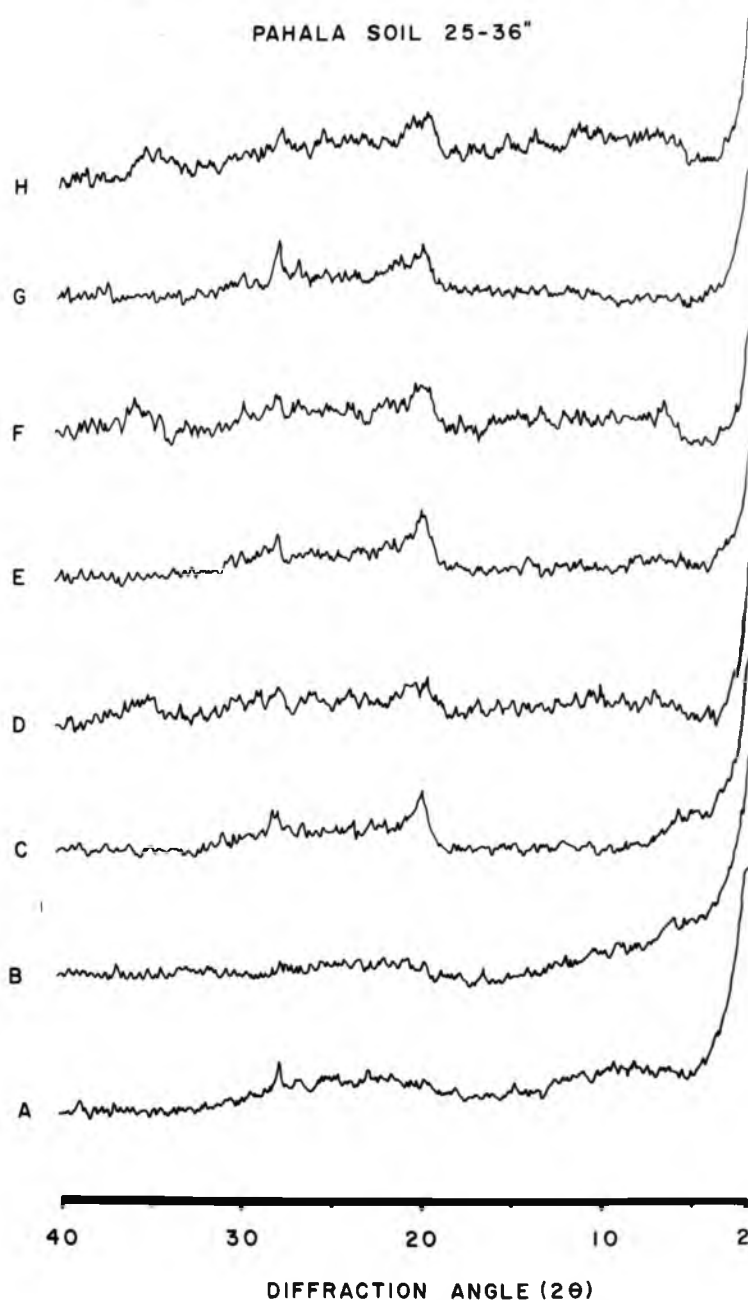


FIGURE 12. X-RAY DIFFRACTION DIAGRAMS OF THE 25-36" HORIZON OF THE PAHALA SOIL. THE DIAGRAMS ARE: A, POTASSIUM-SATURATED, ROOM TEMPERATURE; B, MAGNESIUM-SATURATED, GLYCOLATED; C, CLAY, BEFORE D.D.A.; D, CLAY, AFTER D.D.A.; E, SILT, BEFORE D.D.A.; F, SILT, AFTER, D.D.A.; G, SAND, BEFORE D.D.A.; H, SAND, AFTER D.D.A.

Other minerals present in the sand and silt fractions were further identified under the petrographic microscope. The principle minerals present in these soils were feldspars, with inclusions of apatite and magnetites, volcanic glass, plant opal, olivine, pyroxenes and birefringent non-dispersible aggregates of weathered glass. Combinations of these minerals varied from horizon to horizon. The silt fraction of these soils appears to be quite similar to its corresponding sand fraction. After careful examination of each horizon, it became evident that the ammonium fixation in the sand and silt fraction was related to the amount and intensity of the birefringence of the non-dispersible aggregates of weathered glass. The identity of this material, however, is yet unknown. It is this material that is believed responsible for the (020) (hkl) reflection band determined by X-ray diffraction. The intensity of this line also is closely related to the amount and intensity of the birefringent material. The greatest amount of the highly birefringent aggregates occurred in the 25-36" horizon of the Pahala soil where ammonium fixation was also the greatest. Only a few glass shards, feldspars, plant opal and pyroxenes were present in either the sand or silt fractions. Greatest fixation occurred in the silt fraction of every horizon. This appears to be related more to particle size than to composition since the composition of the sand and silt fractions is similar.

Horizons intermediate in their capacity to fix ammonium contained more feldspar, volcanic glass, plant opal and lesser amounts of the birefringent material than the 25-36" horizon of the Pahala soil.

The 0-11" Horizon of the Naalehu soil representing a horizon where fixation was extremely low was studied under the petrographic microscope.

The sample consisted primarily of plant opal which constituted more than half of the sample, volcanic glass and feldspars. The amount of birefringent material in the sand and silt fractions was extremely low. This accounts for the low ammonium fixation in this horizon. The sequence of weathering of the volcanic glass was clearly seen in these young, partially weathered horizons. Closer examination revealed that the birefringent material could be seen as patchy spots within the glass grains, the amount varying from particle to particle.

X-ray diffraction and petrographic microscopic investigations revealed that ammonium fixation in the sand and silt fractions was dependent on the amount and birefringence of the weathered glass which gives an indication of the degree of weathering of each soil horizon. These observations suggest the existence of buried horizons, particularly in the Pahala profile where a wide variation in mineral weathering exists.

Less Than Two Microns:

The dominant component of the clay fraction was generally amorphous to X-ray diffraction with the exception of halloysite in some horizons of the Pahala soil. Neither the glycolated, magnesium-saturated sample nor the potassium-saturated, thermally-treated samples gave any indication of minerals capable of fixing ammonium. Powdered samples of the clay fraction also revealed a (020) (hkl) reflection band (Figures 11 and 12). This tends to indicate that the sand, silt and clay fractions of these soils have about the same composition.

Differential Dissolution Analysis (d.d.a.):

Due to the high ammonium fixation capacity of some of the horizons of the Naalehu and Pahala soils, differential dissolution analyses were

conducted on three selected horizons representing different ammonium fixing capacities. The Pahala (25-36"), Maalehu (59-65") and Pahala (52-57") horizons, representing high, intermediate and low ammonium fixing capacities, respectively, were selected for this study. It was anticipated that the identity of the highly birefringent non-dispersible aggregates responsible for the fixation could be determined by X-ray analysis after mineral purification. The X-ray diffraction patterns after the differential dissolution analyses are given in Figures 11 and 12. The (020) (hkl) reflection line remained prominent demonstrating the stability of the ammonium fixing soil material. Petrographic examination of the sand and silt fractions after this treatment was not different from that determined earlier on the untreated sample.

Table XVIII shows that considerable amounts of silica and alumina are dissolved in the horizons studied. Some relationship between ammonium fixation and amorphous material content is shown--the lower the extractable silica and alumina content, the greater the ammonium fixing capacity.

A highly significant correlation ($r = 0.824^{**}$, $df = 8$) was obtained when the extractable silica and alumina content (Table XVIII) was compared against the cation exchange capacity delta values of the same horizons (Table XIX). This shows that some relationship exists between these two methods of amorphous material determination.

Differential Thermal Analysis and Dehydration Curves:

Differential thermal analyses were determined on the sand, silt and clay fractions to further characterize the mineral(s) fixing ammonium. Differential thermal curves for three horizons are shown in Figure 13.

TABLE XVIII. EXTRACTABLE SILICA AND ALUMINA OF SOILS
BY DIFFERENTIAL DISSOLUTION ANALYSIS

Soil series	Depth in.	SiO ₂	Al ₂ O ₃ %	SiO ₂ + Al ₂ O ₃
Maalehu	59-65			
def.		24.6	20.4	45.0
sand		19.2	14.4	33.6
silt		23.6	20.6	44.2
clay		23.7	18.3	42.0
Pahala	25-36			
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	52-57			
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	1-15			
clay		9.9	4.2	14.1
Koolau	4-7			
clay		2.6	6.8	9.4
Molokai	74+			
clay		17.8	22.3	40.1

TABLE XIX. ALLOPHANE DETERMINATION OF SOILS
BY CATION EXCHANGE CAPACITY DELTA VALUE

Soil series	Depth in.	Cation exchange capacity, me./100 g.		
		2% Na ₂ CO ₃ treated (B)	NaOAc pH 3.5 treated (A)	Δvalue (B-A)
Nasichu	59-65			
def.		92.6	77.1	15.5
sand		90.8	73.8	17.0
silt		100.6	84.8	20.8
clay		116.4	92.3	24.1
Pahala	25-36			
def.		97.7	83.4	14.3
sand		-	-	-
silt		95.5	78.7	16.8
clay		106.5	82.8	23.7
Pahala	52-57			
def.		99.4	63.0	36.4
sand		-	-	-
silt		85.5	55.1	30.6
clay		130.4	80.8	49.6

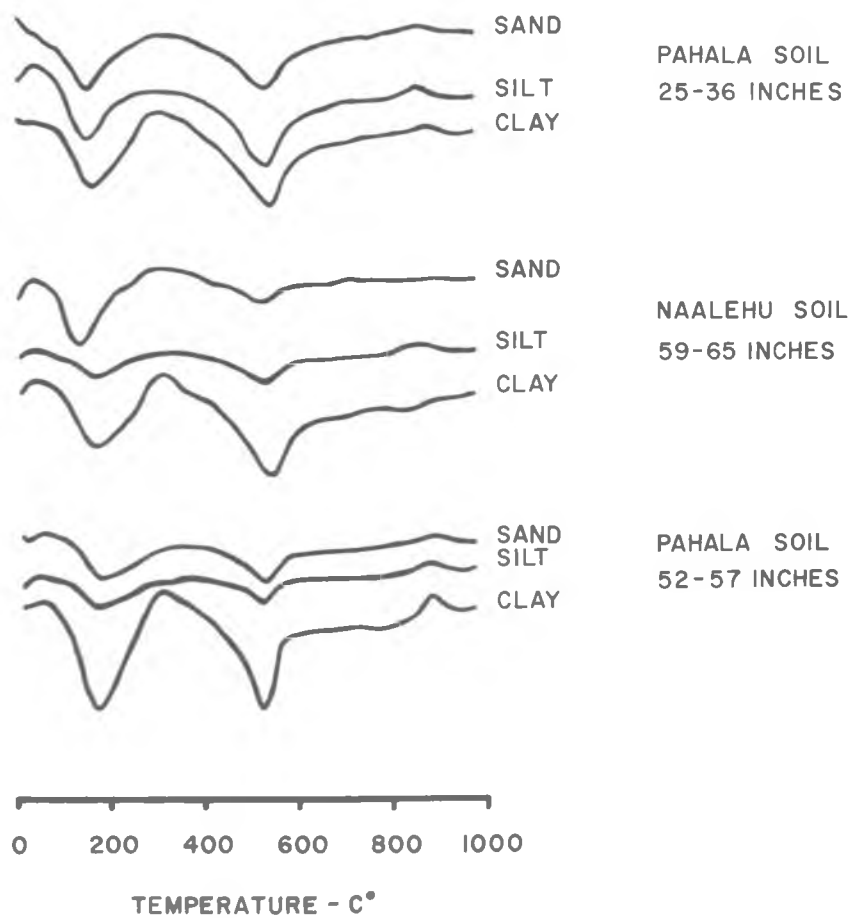


FIGURE 13. DIFFERENTIAL THERMAL CURVES OF THE SAND, SILT AND CLAY FRACTIONS OF SOILS

The broad endothermic peak between 100 to 200° C. is characteristic of sillophane and adsorbed water. The effect of adsorbed water was eliminated by oven drying the sample at 110° C. for 24 hours before the analysis. An endothermic peak between 535 to 550° C. was observed for all the soil fractions. The asymmetric endothermic peak at 535° C. of the clay fraction of the 52-57" horizon of the Pahala soil is that of halloysite. This was confirmed by X-ray analysis. The endothermic peak at 535° C. for the silt and sand fractions of the same sample most probably is halloysite.

The identity of the mineral responsible for the broad, round endothermic peak at 535 to 550° C. is questionable. The peak does not have the features characteristic of the kaolinite mineral. However, characteristic endothermic peaks of very small amounts of halloysite, if present, could have been masked by the effect of other endothermic reactions occurring at about the same temperature. The endothermic peak does not correspond to any silicate minerals capable of fixing ammonium. Apparently, the mineral is of such fine particles that thermal decomposition occur at a considerably lower temperature.

Figure 14 shows the dehydration curves of the deferrated, organic matter-free whole soil of three samples. A montmorillonite and kaolinite dehydration curve are included for purposes of comparison. No indication of layered silicate minerals is evident from the dehydration curves.

Infrared Absorption Spectra:

Infrared absorption spectra of the sand, silt and clay fractions of three horizons were obtained with a Beckman IR5 infrared spectrophotometer using pressed KBr discs. They are shown in Figure 15. The peaks

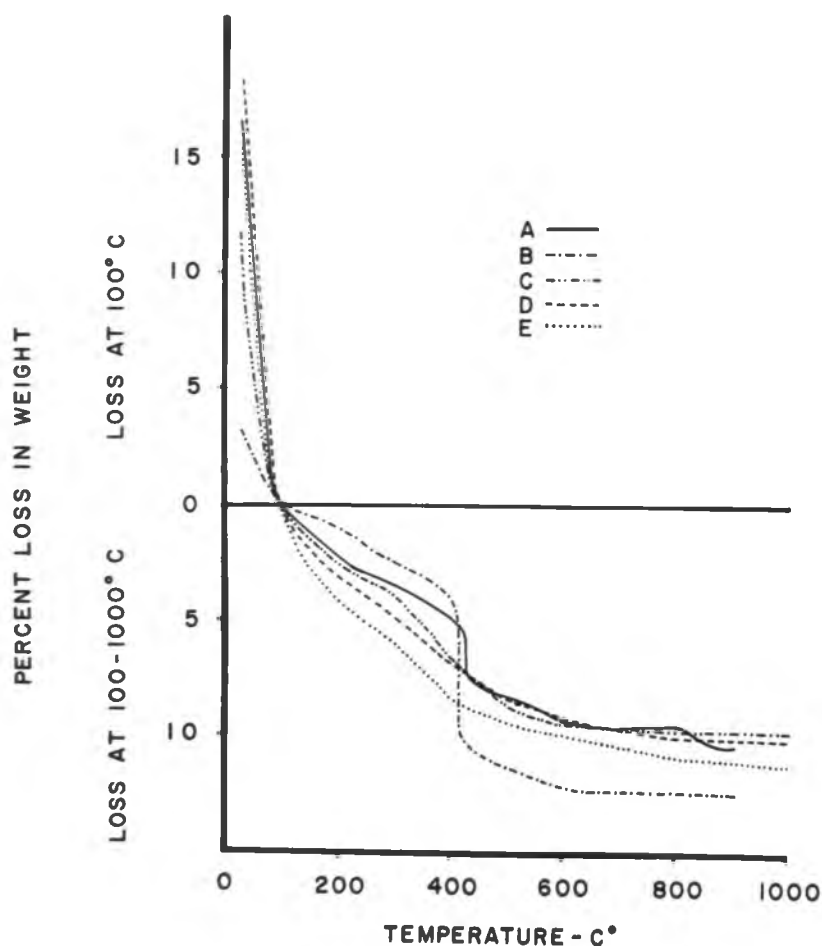


FIGURE 14. DEHYDRATION CURVES OF SAMPLES REPRESENTING DIFFERENT AMMONIUM FIXING CAPACITIES. ALL SAMPLES ARE DEFERRATED, ORGANIC MATTER-FREE WITH THE EXCEPTION OF A AND B, WHICH ARE CLAY FRACTIONS. THE SAMPLES ARE A, LUALUALI CLAY; B, KAOLIN CLAY; C, PAHALA 25-36"; D, MAALENU 59-65"; E, PAHALA 52-57". (DATA FOR A AND B WERE OBTAINED FROM MATSUSAKA (1952))

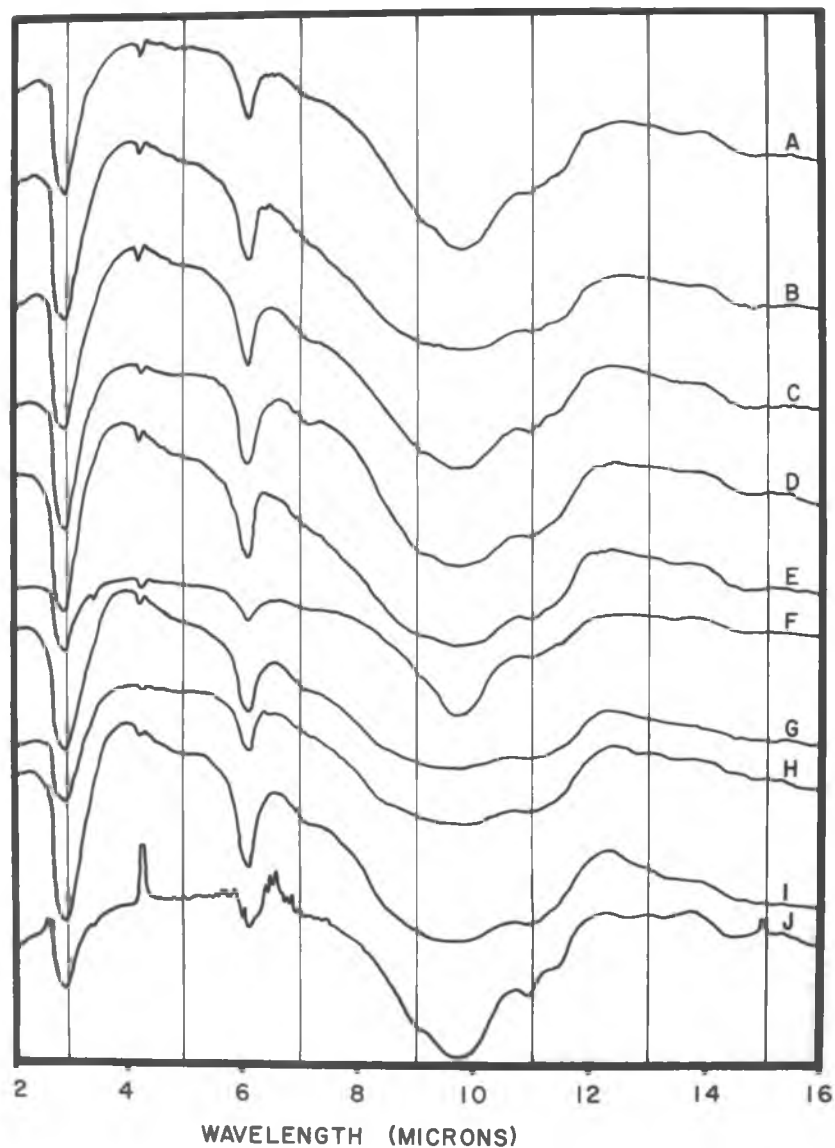


FIGURE 15. INFRARED ABSORPTION SPECTRA OF THE SIZE FRACTIONS OF SOILS. THE SAMPLES ARE THE SAND, SILT AND CLAY FRACTION, RESPECTIVELY, FOR THE FOLLOWING HORIZONS: A, B, AND C, PAHALA 25-36"; D, E AND F, NAALEHU 59-65"; G, H and I, PAHALA 52-57". J REPRESENTS A LUALUALI CLAY, 1-15" HORIZON

appearing at 2.9 and 6.2 microns are due to OH groups, the broad peak between 8.5 to 10.5 microns is mainly due to Si-O bonding and peak at 11.0 microns is the Al-OH bonding, a peak characteristic of montmorillonite, kaolinite and illite. Assuming that the infrared absorption spectra of the sand, silt and clay fractions of the 52-57" horizon of the Pahala soil are that of halloysite, as determined by X-ray diffraction and differential thermal analyses, it is difficult to observe any differences when these spectra are compared against those of the silt fractions of the other two soil horizons. Some of these spectra are similar to the allophane patterns reported by Roung (1964) and Tanma (1965).

Total Chemical Analysis:

Total chemical analyses were carried out on the deferrated, organic matter-free whole soil, sand, silt and clay fractions of three soil horizons and the results expressed on the oven dried basis are listed in Table XXI. The data show that no apparent differences exist among the deferrated, organic matter-free whole soils of the three samples analyzed. This observation also applied to the sand, silt and clay fractions. However, wide variation in magnesium and calcium contents were observed between the deferrated, organic matter-free whole soil and their size fractions. The results of the magnesium content are listed in Table XX.

The data show that most of the magnesium is in the sand fraction, with the exception of the 25-36" horizon of the Pahala soil. The magnesium content of the clay fraction decreased with decreasing ammonium fixation. This was the reverse from the results obtained in the sand fraction, where ammonium fixation decreased with increasing magnesium.

TABLE XX. TOTAL MAGNESIUM CONTENT OF SOILS
AND THEIR SIZE FRACTIONS

	Soil Series	Depth	Def. Whole Soil	Def. Sand	Def. Silt	Def. Clay
		in.				
Increasing NH ₄ fixation	Pahala	25-36	2.74	3.19	3.60	1.21
	Naalehu	59-65	3.64	6.24	1.90	.90
	Pahala	52-57	4.16	6.59	3.42	.68

No attempt was made to calculate the structural formula of the material fixing ammonium from the chemical data because mineral purification was not done prior to the analysis. However, the data show at least one point: no obvious relationship is shown between the chemical composition of the samples and their capacity to fix ammonium.

Cation Exchange Capacity:

The cation exchange capacity of the whole soil, organic matter-free soil, deferrated soil and size fractions of the Naalehu and Pahala profiles are listed in Table XXII. A general decrease in cation exchange capacity for the surface horizons occurred after organic matter removal by hydrogen peroxide oxidation. However, a small increase in cation exchange capacity was noted for the lower horizons. Deferration greatly increased cation exchange capacity, especially in horizons having high cation exchange capacity. Very high values were obtained for the sand and silt fractions of these soils. This is contrary to the accepted idea that cation exchange capacity is very low in the sand fraction of soils. Closer examination revealed that cation exchange capacity was closely

TABLE XXI. CHEMICAL COMPOSITION OF SOILS AND THEIR SIZE FRACTIONS

	Naalehu 59-65"				Pahala 25-36"				Pahala 52-57"			
	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 ₂ O 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 ₂ O 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 ₂ O	.15	.15	.18	.17	.26	.24	.20	.11	.14	.17	.17	.12
Na ₂ O	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 ₂ O 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 ₂ O ⁺	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
<u>SiO₂</u> <u>Al₂O₃</u>	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 XXII. CATION EXCHANGE CAPACITY OF SOILS
AND THEIR SIZE FRACTIONS

Soil series	Depth <u>in.</u>	Untrt. soil	H ₂ O ₂ -trt. soil	Def. soil	Def. sand	Def. silt	Def. clay
me./100 g.							
Waelehu	0-11	52.24	43.98	57.06	26.07	34.74	106.34
	11-21	60.91	63.52	89.93	76.73	71.08	111.67
	21-54	67.09	70.49	102.40	78.50	87.65	111.21
	54-59	73.61	77.41	97.43	75.37	85.43	105.99
	59-65	75.18	77.57	104.77	91.08	95.40	116.10
Pahala	0-7	36.87	24.90	22.33	8.46	17.42	92.35
	7-11	31.76	26.30	27.86	11.34	22.61	102.53
	11-18	32.96	31.46	33.41	15.60	-	108.23
	18-25	39.39	42.37	49.22	29.59	37.97	105.19
	25-36	72.74	80.43	96.61	88.90	87.70	102.34
	36-39	53.40	58.52	68.45	61.64	58.85	91.91
	39-52	41.22	46.01	61.91	47.02	48.43	106.95
	52-57	56.42	64.74	91.44	81.04	77.80	124.27

related to the birefringence of the ammonium fixing material. This, however, holds true only to a limited extent since allophane, which constitutes a good percentage of the samples, also have high cation exchange capacities. The data also verified another point discussed previously, the sand and silt fractions are very similar in their mineral and chemical composition.

The clay fractions demonstrated a tremendous capacity to adsorb cations. This was also observed by Kelley and Page (1942) who used differential thermal analysis and X-ray methods to study the colloids of several Hawaiian soils. They found two samples from Naalehu and South Point, Hawaii, with cation exchange capacities of 120 and 88 me./100 grams soil, respectively. They attributed the cation exchange capacity to the amorphous mineral in these soils. Hwang (1964) working with the clay fractions of some volcanic ash soils reported some high cation exchange capacity values. He observed that cation exchange capacity of the amorphous material was highly pH dependent. This observation had been previously reported by Fialdas (1962).

Statistical examination of the data showed that a highly significant correlation ($r = 0.627^{**}$, $df = 73$) existed between the cation exchange capacity and ammonium fixation after addition of 50 me. ammonium per 100 gram soil. A better correlation could be obtained if the obvious non-relationship 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 cation exchange capacity of only the untreated whole soil was analyzed against ammonium fixation. The interpretation of this relationship is difficult due to the nature of the minerals involved.

Some explanation describing the source and mechanism of the high cation exchange capacity of the clay fraction and their obvious non-relationship to ammonium fixation is needed. The data (Table XVIII) show that the extractable silica and alumina of the Molokai clay (kaolinite) and the sand, silt and clay fractions of the Waialehu 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 co-ordination. However, amorphous mineraloids or allophane differ from other clay minerals with respect to its aluminum which is held in its structure in tetrahedral co-ordination. This is supposed to be the main cause for its many unusual activities, one of them being its cation holding mechanism (Fieldes, 1962).

Discussion and Conclusions:

This investigation was initiated to determine whether non-crystalline material in Hawaiian volcanic ash soils was able to retain ammonium against $\frac{1}{2}$ N KCl extractions. The results showed the definite capability of certain amorphous mineraloids to fix ammonium. It appeared, however, that not all amorphous materials have the same capacity to fix ammonium. Amorphous soil constituents have one major feature in common, namely their noncrystallinity; beyond this they differ not only in composition but in behavior as well.

Failure of most standard mineralogical methods to characterize the material comprising the Pahala (23-36") and Waialehu (59-65") soils prompted

the author to examine the silt and sand fractions of these samples under 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. Fresh glass can be readily identified by its isotropic character and differs from plant opal by its shape, higher refractive index and yellowish-brown color. Weathered glass can be distinguished from fresh glass by a progressive increase in birefringence as the glass weathers. The non-crystalline and yet birefringent character of this material fits the definition of Wentworth's (1938) palagonite. This amorphous material also fits the description of Birrell's (1964) "palagonite". He has reported this material as being formed from the weathering of basaltic glass and has noted its presence in a soil from Aitutaki Island and also has speculated on its presence in Pahala Ash soil. The ion exchange capacity of these samples can be entirely attributed to this weathered glass and this value must be near 200 me. per 100 grams considering the samples are about 30-50% fresh glass, plant opal, feldspar, pyroxenes and iron oxide.

Large quantities of zeolites are found in the weathered tuff cones on Oahu. It appears that ash and tuff near the surface by-pass the zeolite stage and go through a non-crystalline permutitic intermediate stage. Zeolite and weathered glass have high ion exchange capacities but the latter is non-crystalline. Weathered glass of the kind found in the Waialeale (59-65") and Pahala (25-36") horizons may with good justification be called natural permutites.

The weathered glass in the Pahala (52-57") horizon differs from those observed in the Pahala (25-36") and Waialeale (59-65") horizons in

birefringence; weathered glass in the Pahala (52-57") horizon was in all cases less anisotropic than the latter two.

The difference in capacity to fix ammonium among amorphous minerals must arise through some fundamental mechanism. In the absence of any direct evidences some postulations will be suggested at this time. It appears that the origin of the charge on the colloid surface may be an important factor. Aluminum in volcanic glass is most probably tetrahedrally co-ordinated 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. The chemistry of synthetic silica alumina gels with high cation exchange capacities has been reviewed by Iler (1955). It is not unlikely that we are working with a natural system not unlike those considered by Iler.

It is further proposed that with further leaching and increased acidity, the aluminum alters to the more stable octahedrally co-ordinated hydroxide (gibbsite) or aluminosilicate (kaolin) and loses its capacity to fix ammonium. The 52-57" horizon of the Pahala soil 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 Naalahu

(59-65") and Pahala (25-36") soil. These two samples behave chemically like montmorillonite and probably constitute a system which may eventually stabilize as montmorillonite.

The Maalehu (59-65"), Pahala (25-36") and Pahala (52-57") soils are, however, neither kaolin nor montmorillonite by any stretch of the imagination. Although some incipient layered lattice minerals may be in the making they are by no means true clay minerals; they must be considered at this time to be amorphous mineraloids.

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

If the hypothesis of the four and six co-ordinated aluminum is correct, there must exist some correlation between the fraction of aluminum in each form and ammonium fixation. Unfortunately methods to determine the co-ordination number of aluminum has not been developed so that it may be measured routinely. The Japanese (Kagawa, 1964) has used fluorescence technique in determining the co-ordination state of allophane. It remains for others to establish the relationship of ammonium fixation and co-ordination number of aluminum in amorphous mineraloids.

SUMMARY

A wide range in native fixed ammonium content was found in some representative Hawaiian soils. Native fixed ammonium was found to range from 0.0 to 585.0 ppm., with an average of 93.4 ppm. Native fixed ammonium generally decreased with depth in most of the profiles studied. There was a highly significant correlation ($r = 0.910^{**}$, $df = 101$) between total K_2O or percent illite and native fixed ammonium. This correlation indicates that illite is responsible for the native fixed ammonium content of the Hawaiian soils investigated. This relationship, however, does not apply to young, partially weathered soils containing some primary potassium-bearing minerals.

An increase in native fixed ammonium occurred after heating the soil samples containing large amounts of native fixed ammonium to temperatures of 200 to 300° C. The mechanism for the increase could not be elucidated from the results obtained in this study.

The ammonium fixing capacity of the Maalehu and Pahala soils, which were amorphous to X-ray diffraction, was investigated. A typical montmorillonitic soil (Lualualei), illite soil (Koolau) and a kaolinite soil (Molokai) were also investigated. The amount fixed by the Maalehu and Pahala soils was equal to or exceeded that fixed by the montmorillonitic Lualualei soil. The sand and silt fractions of these soils fixed about the same amount of ammonium as did their corresponding clay fractions. Concentration study on selected horizons showed that ammonium fixation was virtually satisfied after addition of 50 to 100 me. ammonium per 100 grams soil. A decrease in ammonium fixation was observed at higher concentrations.

The mineralogical and chemical properties of the Naslaku and Pahala soils were examined by the techniques of petrographic microscope, X-ray diffraction, thermal analyses, infrared absorption and chemical analyses to identify the mineral(s) fixing ammonium. It was concluded from results obtained from these methods of mineral identification that amorphous mineraloids were responsible for the ammonium fixation. The results also showed that not all amorphous materials have the same capacity to fix ammonium. This was most evident in the Pahala soil where great changes in ammonium fixation were observed within the soil profile.

LITERATURE CITED

- Adams, R. S., Jr. 1962. Ammonium sorption and release of soil forming rocks and minerals. Unpublished Ph.D. thesis. Library, University of Illinois, Urbana, Illinois.
- Allison, F. E., Doetsch, J. H., and Roller, E. M. 1951. Ammonium fixation and availability in Harpster clay loam. *Soil Sci.* 72: 187-200.
- Allison, F. E., Kafauver, M., and Roller, E. M. 1953. Ammonium fixation in soils. *Soil Sci. Soc. Am. Proc.* 17:107-110.
- Allison, F. E., and Roller, E. M. 1955. Fixation and release of ammonium ions by clay minerals. *Soil Sci.* 80:431-441.
- Allison, F. E., Roller, E. M., and Doetsch, J. H. 1953. Ammonium fixation and availability in vermiculite. *Soil Sci.* 75:173-180.
- Aomine, S. 1951. Studies on the fixation of ammonium in soils. I. Ammonium fixation of some soils in the southeastern province of Japan. *J. Sci. Soil Manure, Japan* 22:83-87. Abstract in *C. A.* (1952) 46:3692.
- Aomine, S., and Jackson, M. L. 1959. Allophane determination in Ando soils by cation exchange capacity delta value. *Soil Sci. Soc. Am. Proc.* 23:210-214.
- Axloy, J. H., and Legg, J. O. 1960. Ammonium fixation in soils and the influence of potassium on nitrogen availability from nitrate and ammonium sources. *Soil Sci.* 90:151-156.
- Barshad, I. 1948. Vermiculite and its relationship to biotite as revealed by base exchange reactions, x-ray analysis, differential thermal curves and water content. *Am. Mineralogist* 33:655-678.
- Barshad, I. 1951. Cation exchange in soils. I. Ammonium fixation and its relation to potassium fixation and to determination of ammonium exchange capacity. *Soil Sci.* 72:361-371.
- Barshad, I. 1950. The effect of interlayer cations on the expansion of mica type of crystal lattice. *Am. Mineralogist* 35:225-238.
- Barshad, I. 1954. Cation exchange in micaceous minerals. II. Replaceability of ammonium and potassium from vermiculite, biotite and montmorillonite. *Soil Sci.* 78:57-76.
- Birrel, K. S. 1964. Some properties of volcanic ash soils. Report on the "Meeting on the Classification and Correlation of Soils from Volcanic Ash", World Soil Resources Report No. 14, FAO, Tokyo. pp. 74-81.

- Blumberg, W., and Holmes, W. E. 1959. The carbon-nitrogen ratios of some Hawaiian soils. Hawaii Agr. Exp. Sta. Tech. Prog. Rept. No. 122.
- Bower, C. A. 1950. Fixation of ammonium in difficultly exchangeable form under moist conditions by some soils of semiarid regions. Soil Sci. 70:375-383.
- Bremner, J. M. 1959. Determination of fixed ammonium in soils. J. Agr. Sci. 52:147-160.
- Bremner, J. M., and Harada, T. 1959. Release of ammonium and organic matter from soil by hydrofluoric acid and effect of hydrofluoric acid treatment on extraction of soil organic matter by neutral and alkaline reagents. J. Agr. Sci. 52:137-146.
- Burge, W. S., and Broadbent, F. E. 1961. Fixation of ammonia by organic soils. Soil Sci. Soc. Am. Proc. 25:199-204.
- Dharival, A. P. S., and Stevenson, F. J. 1958. Determination of fixed ammonium in soils. Soil Sci. 86:343-349.
- Egawa, T. 1964. Nature and properties of allophane. Report on the "Volcanic Ash Soils of Japan", Ministry of Agr. and Forestry, Japanese Government. pp. 38-43.
- Fieldes, M. 1962. The nature of the active fraction of soils. Trans. Intern. Soil Soc. Conf. New Zealand. pp. 62-78.
- Fieldes, M., and Schofield, R. K. 1960. Mechanism of ion absorption by inorganic soil colloids. New Zealand J. Sci. 3:563-679.
- Hanway, J. J., and Scott, A. D. 1956. Ammonium fixation and release in certain Iowa soils. Soil Sci. 82:379-386.
- Harmeen, G. W., and van Schreven, D. A. 1955. Mineralization of organic nitrogen in soil. Advances in Agronomy 7:299-398.
- Hashimoto, I., and Jackson, M. L. 1958. Rapid dissolution of allophane and kaolinite-halloysite after dehydration. Reprint from Seventh National Conference on Clay and Clay Minerals. Pergamon Press, New York. pp. 102-113.
- Houng, Kum-Huang. 1964. A study of the soils containing amorphous materials in the Island of Hawaii. Unpublished Ph.D. thesis. Library, University of Hawaii, Honolulu, Hawaii.
- Hsu, Fa Ho. 1963. Effect of initial pH, phosphate, and silicate on the determination of aluminum with aluminon. Soil Sci. 96:230-238.
- Ilor, R. K. 1955. The Colloid Chemistry of Silica and Silicates. Cornell University Press, Ithaca, N. Y.

- Jackson, M. L. 1936. Soil Chemical Analysis--Advance Course. University of Wisconsin, Madison, Wisconsin.
- Jackson, M. L. 1958. Soil Chemical Analysis. Prentice-Hall, Inc.
- Joffa, J. S., and Levine, A. K. 1947. Fixation of potassium in relation to exchange capacity of soils. II. Associative fixation of other cations, particularly ammonium. *Soil Sci.* 63:151-158.
- Juang, Tso-chuen. 1964. Genesis of secondary micas from basalt and related rocks in the Hawaiian Islands. Unpublished M.S. thesis. Library, University of Hawaii, Honolulu, Hawaii.
- Kelly, W. P., and Page, J. B. 1942. Criteria for the identification of the constituents of soil colloids. *Soil Sci. Soc. Am. Proc.* 7:175-181.
- Kobo, K. 1964. Properties of volcanic ash soils. Report on the "Meeting on the Classification and Correlation of Soils from Volcanic Ash", World Soil Resources Report No. 14, FAO, Tokyo. pp. 71-73.
- Leggett, G. E. 1958. Ammonium fixation in soils and minerals. Unpublished Ph.D. thesis. Library, State College of Washington, Pullman, Washington.
- Leighty, W. R., and Shorey, E. C. 1930. Some carbon-nitrogen relationships in soils. *Soil Sci.* 30:257-266.
- Matsusaka, Y. 1952. Dehydration curves and differential thermal curves of clays from Hawaiian soils. Unpublished M.S. thesis. Library, University of Hawaii, Honolulu, Hawaii.
- McBeth, I. G. 1917. Fixation of ammonia in soils. *J. Agr. Research* 9:141-155.
- McIntosh, I. H. 1962. Fixation of added ammonium by the clay and organic fractions of soil. Unpublished Ph.D. thesis. Library, Iowa State University of Science and Technology, Ames, Iowa.
- Moore, A. W., and Ayoko, C. A. 1965. HF-extractable ammonium fixation in four Nigerian soils. *Soil Sci.* 99:335-338.
- Mortland, M. M. 1958. Reactions of ammonia in soils. *Advances in Agronomy* 10:325-348.
- Nash, V. E., and Marshall, C. E. 1956. The surface reaction of silicate minerals. Part II. Reactions of feldspars surfaces with salt solutions. *Missouri Agr. Exp. Sta. Res. Bull.* 614. 36 pp.
- Nomik, H. 1957. Fixation and defixation of ammonium in soils. *Acta. Agr. Scand.* 7:395-436.

- Page, J. B., and Baver, L. D. 1940. Ionic size in relation to fixation of cations by colloidal clay. *Soil Sci. Soc. Am. Proc.* 4:150-155.
- Porter, L. K., and Stewart, B. A. 1964. Thermal release of exchangeable and fixed ammonium ions in soils. *Western Society of Soil Science, Program and Abstracts. The University of British Columbia, Vancouver, B. C., Canada.*
- Rodrigues, G. 1954. Fixation of ammonia in tropical soils. *J. Soil Sci.* 5:264-274.
- Schachtschabel, P. 1961. Bestimmung des fixierten Ammoniums in Boden. *Z. Pfl. Ernähr. Dung. Bodenk.* 93:125-136.
- Scott, A. D., Hanway, J. J., and Stanford, G. 1956. Thermal studies of ammonium fixation and release in certain clay minerals. *Am. Mineralogist.* 41:701-721.
- Silve, J. A. 1964. Determination of fixed ammonium in soils. Unpublished Ph.D. thesis. Library, Iowa State University, Ames, Iowa.
- Sohn, J. B., and Peech, M. 1958. Retention and fixation of ammonia by soils. *Soil Sci.* 85:1-9.
- Stanford, G., and Pierre, W. H. 1947. The relation of potassium fixation to ammonium fixation. *Soil Sci. Soc. Am. Proc.* 11:155-160.
- Stewart, B. A., and Porter, L. K. 1963. Inability of the Kjeldahl method to fully measure indigenous fixed ammonium in some soils. *Soil Sci. Soc. Am. Proc.* 27:41-43.
- Stevenson, F. J. 1957. Distribution of the forms of nitrogen in some soil profiles. *Soil Sci. Soc. Am. Proc.* 28:283-287.
- Stevenson, F. J. 1959a. On the presence of fixed ammonium in rocks. *Science* 130:221-222.
- Stevenson, F. J. 1959b. Carbon-nitrogen relationships in soils. *Soil Sci.* 88:201-208.
- Stevenson, F. J. 1962. Chemical state of the nitrogen in rocks. *Geochim. Cosmochim. Acta.* 26:797-809.
- Stevenson, F. J., and Dharwal, A. P. S. 1959. Distribution of fixed ammonium in soils. *Soil Sci. Soc. Am. Proc.* 23:121-125.
- Stevenson, F. J., Dharwal, A. P. S., and Choudhri, M. B. 1958. Further evidence for naturally occurring fixed ammonium in soils. *Soil Sci.* 85:42-46.
- Tenna, H. 1965. Some characteristics of non-crystalline constituents in Hawaiian soils. Unpublished M.S. thesis. Library, University of Hawaii, Honolulu, Hawaii.

- van der Marel, W. W. 1954. Potassium fixation in Dutch soils: Mineralogical analyses. *Soil Sci.* 78:63-179.
- Walkley, A., and Black, T. A. 1934. An examination of the Degtjareff method for determining soil organic matter, and a proposed modification of the chromic and titration method. *Soil Sci.* 37:29-38.
- Walsh, C. M., and Murdock, J. T. 1960. Native fixed ammonium and fixation of applied ammonium in several Wisconsin soils. *Soil Sci.* 89:183-193.
- Wentworth, C. K. 1938. Ash formation of the island of Hawaii. Hawaiian Volcano Observ., 3rd Spec. Rept., Honolulu.
- Young, J. L. 1962. Inorganic soil nitrogen and carbon: Carbon ratios of some Pacific Northwest soils. *Soil Sci.* 93:397-404.