STUDIES ON NITROGEN TRANSFORMATION

AND NITRATE ADSORPTION IN SOILS

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By

Budh Ram Singh

Dissertation Committee:

Yoshinori Kanehiro, Chairman
G. Donald Sherman
Wallace G. Sanford
Goro Uehara
Minoru Isobe

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ABSTRACT

Studies on nitrogen transformation and nitrate adsorption were conducted with Hawaiian soils belonging to the Akaka, Wahiawa, Paaloa, Koko, and Lualualei series.

There was no definite or conclusive trend of NH_4- or NO_3-N accumulation with time in the Akaka (virgin), Akaka (cultivated), Wahiawa "A", and Wahiawa "B" soils in situ. However, under laboratory conditions both NH_4- and NO_3-N were affected. The Akaka (virgin), Akaka (cultivated), and Wahiawa "A", stored in polyethylene bags at room temperature, showed a substantial increase in NO_3-N with time but practically no change in NH_4-N. In contrast, when two of the above soils [Akaka (virgin) and Wahiawa "A"] were oven dried at 90°C, NH_4-N increased with time but NO_3-N remained unchanged during the entire course of oven drying. Possibly, increased NH_4-N resulted from the splitting of ammonium from the proteinaceous parts of organic matter.

The Akaka (virgin) and Wahiawa "C" soils were treated with chloride salts. NH_4-N mineralization was generally a direct function of salt concentration and length of incubation. Probably NH_4-N release resulted from microbial cell breakdown and/or chemical processes. Presumably once the NH_4 ions were released from soil organo-inorganic complexes, the subsequent

exchange reaction between cations in soil solution and NH_4 ions on surface was mainly involved with bringing NH_4 ions in the soil solution. A consideration of the overall effect of cations on NH_4-N release in the two soils led to the series, Al > Fe > Ca > Mg > K > Na, in order of decreasing NH_4 replacing power. However, the series was true only to a concentration of 0.1 $\underline{M}$. Beyond this, Al and Fe ions were probably complexed in the soil. The added salts had little or no effect on NO_3-N content of the two soils.

The Akaka (virgin), Wahiawa "C", Paaloa, Koko, and Lualualei soils were subjected to varying dosages of gamma radiation. The release of NH_4-N generally increased with increasing dosages in all soils, while NO_3-N decreased in the first three soils, possibly due to certain chemical reactions rendering the loss of nitrate. The rate of NH_4-N mineralization in irradiated soils was highest during the first seven days and declined during subsequent incubation periods. Irradiation decreased the recovery of added NH_4-N in the Koko and Lualualei soils and NO_3-N in all soils. In another series three acid soils, Akaka (virgin), Wahiawa "C", and Paaloa, were limed before irradiation. Liming decreased the recovery of added NH_4-N and increased the recovery of added NO_3-N. Possibly chemical reactions responsible for nitrate loss were inhibited by liming.

The adsorption of NO_3 was studied with the Akaka (virgin) and Wahiawa "C" soils. Adsorption increased with increasing concentration and decreasing pH of the electrolyte solution. The nitrate adsorption in the two soils followed the Freundlich type of isotherm.

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INTRODUCTION

Nitrogen undergoes a number of transformations in soil which involve organic, inorganic, and volatile compounds. Inter-relationship between organic and inorganic forms is through the processes of mineralization and immobilization. Inorganic forms of N consist mostly of NH_4[1] and NO_3 ions. Nitrite may accumulate in some soils where conditions are conducive to its accumulation. The magnitudes of these forms depend on the physical, chemical, and microbiological conditions of a soil as well as the equilibrium that exists between soil and its environment. Once the soil is removed and brought to the laboratory, the equilibrium is disturbed and a new set of conditions come into play. Laboratory conditions can be further modified by subjecting soil samples to various treatments which in turn will affect the rate, magnitude, and direction of N transformation.

Results on mineralizable soil N in Hawaiian soils have been previously reported by Fukunaga and Dean (1939), Stanford and Ayres (1964), and Stanford et al. (1965). Their interest was primarily to interrelate soil N analyses with N supplying capacities of soils and the response of sugarcane to N fertilization under

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[1] Ionic forms are used without indication of charge in this dissertation except where charge indication is essential to the meaning.

field conditions. This study, however, was concerned with changes in the inorganic nitrogen status of soils, especially those high in organic matter, in the field and in the laboratory under long term storage conditions. Soil samples sent to soil testing laboratories are sometimes air dried or stored for varying lengths of time before they are analyzed by technicians to make recommendations. The problem of Soil N, whose transformation could be greatly modified by methods and techniques of storage, is an important one. The storage part of the present investigation was mainly involved with this problem.

The laboratory studies also included the effect of salts on inorganic N status of soils. The effect of chlorides and sulfates of Na, K, and Ca has been studied by Agarwal (1967) in the Department of Agronomy and Soil Science. He proposed a chemical release of inorganic nitrogen from an organic-inorganic complex brought about by the addition of salts through the action of both cationic and anionic species. Osmotic and cationic effects of other monovalent, divalent, and trivalent chlorides (keeping anion the same) on inorganic soil N were included to test his proposal with respect to cations.

Further extension of imposed artificial condition was to investigate changes in N status under drastic conditions, such as gamma irradiation treatment. Soil nitrogen mineralization as a function of dosages of gamma radiation has been previously

studied by Agarwal (1967). This study included several other aspects of inorganic N relationship in soils as affected by gamma irradiation.

Retention of mineralized or applied NO_3 in a soil is an important consideration in crop husbandry. Therefore, the NO_3 adsorption in experimental soils was also investigated because this aspect has been studied very little in volcanic soils. Thus, the project was involved with the studies on nitrogen transformation and nitrate adsorption in Hawaiian soils belonging to the Akaka, Wahiawa, Paaloa, Koko, and Lualualei series. The specific objectives were to study:

1. changes in soil inorganic nitrogen under natural conditions (in situ);

2. changes in soil inorganic nitrogen under laboratory conditions:

   a. storing soils at room temperature and drying in oven,

   b. treating soils with salts at varying concentrations,

   c. subjecting soils to gamma irradiation; and

3. nitrate adsorption in soils as affected by concentration and pH of the electrolyte solution.

REVIEW OF LITERATURE

Storage Conditions in Relation to Soil Inorganic Nitrogen

The length of time and the environment of storage are known

to cause marked changes in the physical and chemical properties

of soils (Harpstead and Brage, 1963; Munro and MacKay, 1964).

A major change that could occur is in the matter of available

nitrogen, especially nitrate. Ten South Dakota soils were inves-

tigated by Harpstead and Brage (1963) to determine the effect of

prolonged storage under air-drying conditions on the accumulation

of NO_3-N during subsequent laboratory incubation. Fresh as

well as samples stored at room temperature for 3, 6, 9, 18, 34,

and 50 weeks were incubated for 14 days and the rate of nitrifi-

cation was determined. Results showed that the nitrification rate

of freshly collected soil was high compared to that after air drying

and three weeks of storage prior to incubation. Subsequent incu-

bation showed a progressive increase in the level of nitrification.

Similar changes are likely to occur with changes in moisture

status of a soil during storage. Miller and Johnson (1964) incu-

bated soil samples at 30°C for 14 days under soil moisture

conditions varying from zero tension to air-dry after which NH_4-N

and NO_3-N were measured. Maximum nitrification occurred in

the tension range of 0.50 to 0.15 bars. Nitrification proceeded at

tensions above 15 bars but at a very slow rate. Ammonification

took place at a faster rate at both high and low tensions, indicating that NH_4-N can accumulate at high tensions (up to air dry) and low tension (up to zero bar). The action of ammonifying organisms is apparently not affected by air drying (Cornfield, 1952).

Air drying increased nitrate production by 15 to 20 ppm. N over moist samples. Storage at 20% soil moisture caused a 2 to 3 ppm. N decrease compared to 10% (Munro and MacKay, 1964). For a given soil, mineralization of C and N is enhanced both by drying (or heating) and prolongation of these states (Birch, 1959).

<u>Salts in Relation to Soil Inorganic Nitrogen</u>

Apart from storage conditions the effect of various inorganic salts on soil nitrogen has also been studied in the past. Salts which may occur in soils and those applied to them in various operations influence the number, species, and activity of the soil microflora. As early as 1916, Greaves reported that $MgCl_2$ and $FeCl_3$ act as stimulants to ammonifying organisms and gave the series, $CaCl_2$, KCl, $MgCl_2$, NaCl, $FeCl_3$, in the order of decreasing toxicity to ammonifiers. Later Greaves and co-workers (1919) established a similar series, KCl, $MgCl_2$, $FeCl_3$, $CaCl_2$, in order of decreasing toxicity to nitrifiers.

Pathak and Jain (1965) on the basis of laboratory tests involving concentrations of various salts in inoculated liquid medium and soil, reported that nitrification was promoted by $CaCO_3$ even

at high concentrations (up to 1.6%) and by $CaSO_4$ and $MgSO_4$ up to certain concentrations, and was inhibited even at low concentrations of NaCl (0.2%), Na_2SO_4 (1%), Na_2CO_3 (0.2%), and $NaHCO_3$ (0.2%). This supports the earlier findings of Brown and Hitchcock (1917) who recorded that nitrification was stimulated at 0.0005% NaCl, but was depressed at higher concentrations. The toxic point was 0.02% NaCl. Johnson and Guenzi (1963) also reported the depressive effect of NaCl and Na_2SO_4 on nitrification. The effect was less in calcareous than in non-calcareous soils.

Toxicity of salts is due to two factors: (i) the increased osmotic pressure (O.P.) produced by the salts within the soil, and (ii) a probable physiological action of the substance upon the living protoplasm of the microbial cell, changing its chemical and physical properties so that it can no longer function normally. The former factor is probably more far reaching (Greaves and co-workers, 1916, 1919, 1921). Broadbent (1965) stressed the osmotic effect of fertilizer salts on cell breakdown as a contributing factor in the mineralization of soil nitrogen. Greaves and Lund (1921) have given an interesting discussion on the effect of O.P. created by different salts on nitrogen mineralization in soils as follows:

Bacteria produce ammonia in a soil having an osmotic pressure from 8 to 15 atmospheres, due to Na_2CO_3, $Mg(NO_3)_2$, $NaNO_3$, and $Fe(NO_3)_3$. When the O.P. is

due to $Ca(NO_3)_2$, $CaCl_2$, $FeCl_3$, $Fe_2(SO_4)_3$, NaCl,
$MgCO_3$, KCl, and $MgSO_4$, the ammonia production is
reduced to three-fourth normal with an O.P. below 4
atm. It is surprising to find that ammonifying organisms
can function in soils having O.P. as high as 45 atm.
Under these conditions, however, the quantity of
ammonia produced is very small.

Nitrifiers are much more sensitive to osmotic
changes than are ammonifiers. The O.P. at which
nearly all salts become toxic to nitrifying organisms is
between 1 and 2 atm., and it is between 1 and 3 atm.
for ammonifying organisms. No nitrate was produced
in soils having an O.P. of over 8 atm.

Increasing osmotic tensions from 0 to 30 atm. in the soil solution

by addition of Na_2SO_4 or NaCl reduced nitrification of applied

ammonium approximately linearly (Johnson and Guenzi, 1963).

While studying N mineralization in Hawaiian soils as affected

by chlorides and sulfates of Na, K, and Ca under laboratory

conditions, Agarwal (1967) proposed a chemical release of N

from the organo-inorganic complex of soils brought about by salts

through the action of both cationic and anionic species. He gave

the series, $CaCl_2 \cdot 2H_2O$, KCl, NaCl, K_2SO_4, Na_2SO_4,

$CaSO_4 \cdot 2H_2O$, in decreasing order of causing N release.

The effect of salts on the evolution of carbon dioxide from

soils has also been considered by workers in the past. Johnson

and Guenzi (1963) noted that increasing osmotic tension from 0

to 30 bars in the soil solution by additions of NaCl and Na_2SO_4

reduced CO_2 evolution approximately linearly. Carbon dioxide

evolution was less affected by increasing osmotic tension than was

nitrification. Evidently, organisms contributing to CO_2 production showed greater tolerance to salt than nitrifiers. The evolution of CO_2 decreased significantly with increase in amounts of Al ions added to soil, probably due to lowering of soil pH (Mutatkar and Pritchett, 1966).

In addition to the osmotic effect of added salts, the activity of cations in a soil system is also important, especially with respect to exchange reactions. It has already been confirmed that increasing concentrations of an ion in the replacing solution results in greater cationic exchange by the cation involved (Grim, 1962; Kelly, 1948). With increasing concentration, the activity of cations generally increased. This is especially important with respect to exchangeable NH_4 ions present on the clay or soil surface. Among the cations present in soils, Ca shows a decreasing and Na an increasing replaceability with decreasing degree of saturation, while Mg, K, and NH_4 take an intermediate position. Further, NH_4 exchange is easier with diminishing degree of NH_4 saturation when K, Mg, Ca, Ba, and La are the complementary ions, the increase being in the preceding order (Wiklander, 1965).

Some work has been done regarding the effects of individual cation on ammonifiers and nitrifiers responsible for nitrogen transformations in soil. The chlorides of Ca, K, Mg, Na, Fe (Greaves, 1916), and K, Mg, Fe, Na, Ca, (Greaves et al.,

1919) are in the order of decreasing toxicity to ammonifying and nitrifying organisms, respectively. A number of bacteria, actinomycetes, and fungi have been reported to decrease when Al concentration increased; fungi were more tolerant to Al ion than bacteria (Matsuda and Nagada, 1957; Yoshida and Sakai, 1964). The nitrifying bacteria appeared to be sensitive to large concentrations of NH_4 or SO_4 ions (Weber and Gainey, 1962).

Gamma Irradiation in Relation to Soil Inorganic Nitrogen

In addition to treatment with salts, soils have also been subjected to drastic ionizing irradiations. The immediate effect of soil sterilization is to reduce the number of microorganisms (Kubista, 1966; Lawrence et al., 1953; Skou, 1962). It has been shown that the number of viable cells diminishes as a function of irradiation dosages (Stotsky and Mortensen, 1959). Davis et al. (1956) observed that the microbial population decreased rapidly with increased irradiation dosages up to 10 kiloroentgens[2] (Kr.), then leveled off at 10 to 20 Kr. and continued to decrease steadily at dosages greater than 20 Kr. Later, McLaren et al. (1962) reported that at a dosage of 2×10^5 roentgens the microbial population was practically eliminated.

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[2] 1 roentgen = 84 ergs/g. in air and 93 ergs/g. in water or tissue.

Gamma irradiation has been reported to increase nitrogen mineralization in soils (Bowen and Cawse, 1964a; Cawse, 1967; Cummins and McCreery, 1964; Eno and Popenoe, 1963, 1964; Stanovick et al., 1961; Stotsky and Mortensen, 1959). Bowen and Cawse (1964a) noted that the release of NH_4-N was directly related to dosages of gamma radiation. They believed that nitrogen comes from decomposition of organic matter present in soils. Popenoe and Eno (1962) reported that the nitrate production in a 14-day period was progressively reduced by such treatments. Their finding was later supported by Bowen and Cawse (1964b) who observed a decline in the amount of nitrate in the solution of irradiated soils. Cawse (1967) studied the effects of sub-sterilizing dosages of gamma radiation. He noted that nitrification proceeded at a faster rate in soils receiving 200 kilorads[3] radiation. He attributed this to the absence of effect on the oxidation process in non-proliferating cells of the nitrifying bacteria rather than to increased proliferation of survivors. Nitrifiers were greatly reduced in number after irradiation since the nitrification of the irradiated soil was one-third that of the non-irradiated soil at two weeks and about one-half at four weeks (Bowen and Cawse, 1964b).

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[3] 1 rad = 100 ergs/g.

There are three possible ways in which N may be released from soils by irradiation. First, there could be a purely chemical action of irradiation which is known to produce ammonia from nitrogenous organic compounds by a variety of processes, notably deamination of amino acids (Maxwell et al., 1954; Sharpless et al., 1955) and protein (Bennett and Garrison, 1959). Nitrogen release from the fractionation of organic molecules containing N is possible because ionization is thought to split molecules in random locations throughout the organic fraction of a soil (Eno and Popenoe, 1963). Second, MacLaren and co-workers (1957; 1962) have shown that several enzymes, including urease which produce ammonia as a decomposition product, are functional in irradiated soils. Third, some N is thought to be released from dead organisms due to the subsequent lysis of microbial cells (Bowen and Cawse, 1964b; Burgos, 1964; Cummins and McCreery, 1964; Eno and Popenoe, 1963). It is believed that N is, in fact, produced in all of these ways in irradiated soils.

Eno and Popenoe (1963) noticed that the release of N and P was related to soil type. Soils containing the largest amount of organic matter increased the most in extractable N and P after irradiation. The effect of irradiating soil organic matter suggests that only about 4% of the increase in N after 5 Megarads (Mrad) comes from irradiation decomposition of humus; the remainder comes from the lysis of microbial cells killed by the irradiation.

Agarwal (1967) studied N mineralization as a function of gamma radiation dosages in five Hawaiian soils, Akaka, Wahiawa, Paaloa, Koko, and Lualualei. He noted a general increase in NH_4 release in all soils and a decrease in NO_3, at least in some soils.

Concentration and pH of the Electrolyte Solution
in Relation to Nitrate Adsorption in Soils

Insufficient literature is available on the retention of nitrate ions in soils especially those derived from volcanic materials. Some Japanese workers (Iimura, 1961; Wada and Ataka, 1958) have used allophanic soils derived from volcanic ash to study Cl adsorption. Most of the investigations on anion adsorption and exchange have included H_2PO_4 (Hsu, 1964), SO_4 (Chang and Thomas, 1963; Chao, 1964; Chao et al., 1962a, 1962b, 1964; Kamprath et al., 1956), Cl (Quirk, 1960; Schofield, 1949; Schofield and Samson, 1953, 1954; Sumner and Reeve, 1966), and to some extent NO_3 (Overstreet and Dean, 1951).

Proposed mechanisms for anion adsorption by clay minerals include replacement of OH^- by anions from the clay surface, especially around the flake edges (McAuliffe et al., 1947), and adsorption via anion exchange sites created due to several causes (Schofield, 1949). The replacement of OH^- by SO_4 is the mechanism proposed by Chang and Thomas (1963) for sulfate

adsorption. The mechanism for NO_3 is also the same (Chang and Thomas, 1963; Overstreet and Dean, 1951).

Various theoretical principles of anion exchange have been considered in the study of adsorption of anions in soils. DeHaan and Bolt (1963) have advocated that in the interpretation of experimentally observed interactions between anions and clays, two aspects should be recognized, viz., (i) negative adsorption of anions by negatively charged sites, and (ii) positive adsorption of anions by positively charged sites on the surfaces, probably at the edges. Bolt and Warkentin (1956) postulated that the presence of positively charged sites on clay diminishes the negative adsorption by the quantity equal to the total amount of positive charges.

Positive and negative adsorption are seriously affected by the environmental conditions surrounding the soil particles. It has been pointed out in the literature that the amount of positive adsorption decreases with decrease in the electrolyte concentration. This decrease is due to an increase in the thickness of the diffuse ion layer which renders a partial neutralization of positively charged sites by negatively charged sites (Bolt and Warkentin, 1956; 1958). A similar interpretation has been given by Russell (1963) who attributed the neutralization of positive charges at low concentration to interpenetration of double layers around positive and negative spots.

The effect of soil solution pH is another important factor that significantly affects the quantity of anion retained. Earlier investigators (Kamprath et al., 1956; Mattson, 1931; Toth, 1937) have reported an approximately linear increase in anion retained as the pH of the system was lowered. At pH values above 7, essentially no anions are retained. Lowering of pH has been ascribed to neutralize hydroxyl groups replaced by added anions (Mattson, 1931), and to form anion retention sites by proton adsorption (Schofield and Samson, 1954). The development of pH-dependent positive charge is commonly through the dissociation of OH^- probably from Al-OH groups (Wada and Ataka, 1958). Schofield (1949), and Thomas and Swoboda (1963), however, reported that positive charges developed at low pH belong to ferric oxide rather than to alumina. The dissociation of OH^- groups would be favored with the rise in soil acidity due to suppressed activity of OH^- ions in the solution. The converse is true with rise in pH where negative charges develop probably by the dissociation of H^+ from Si-OH groups (Wada and Ataka, 1958). Thus, iron oxides have a marked effect on anion adsorption. Sumner (1962) has comprehensively studied the effect of iron oxide on positive and negative charges in clays. He advocated:

> The charge on the iron oxide is pH-dependent, being positive at low and negative at high pH values. The higher the content of iron oxide the greater is the positive charge on the surface. With the increasing pH the positive charge decreases until a point is reached where

negative adsorption of anion takes place. The reduction
in negative charge caused by iron oxide at low pH
values is probably due to (i) the iron oxide being bound
to kaolinite by the mutual neutralization of positive charges
on the iron oxide and negative charges on the clays,
and/or (ii) the negative charge on clay being physically
blocked by an iron oxide covering.

Schofield and Samson (1954) have indicated that the edge

face of kaolinite crystals should, under acidic conditions, adsorb

one chloride ion for each 33 $\overset{\circ}{A}^2$. Kaolinite under acidic condi-

tions takes up Cl from the solution indicating that positive

adsorption of chloride exceeds negative adsorption (Schofield,

1949; Schofield and Samson, 1953, 1954; Sumner and Reeve,

1966).

MATERIALS AND METHODS

Description of the Soils

The study was involved with Hawaiian soils belonging to the
Akaka, Wahiawa, Paaloa, Koko, and Lualualei series.   The
soils differ widely in physical, chemical, and mineralogical prop-
erties due to differences in their parent material and the environ-
ment, especially climate, under which they developed.   Although
a detailed description of these soils is given by Cline et al.
(1955), some important properties are included in the following
sections.   The information on mineralogy and cation exchange
capacity (C.E.C.) are based on the reports of Tamura et al.
(1953) and Kanehiro and Chang (1956), respectively.

Akaka Silty Clay (Typic Hydrandept) was collected from
the Hilo Coast on the island of Hawaii.   It is derived from
volcanic ash and has developed under extremely high rainfall
conditions.   The water holding capacity of this soil is very high.
The clay fraction contains large amounts of allophane and iron-
aluminum oxides but no kaolin minerals.   In the hydrated state,
the surface soil has a C.E.C. of 80 me. per 100 g. and base
saturation of about 2%.   The soil possesses a very high buffer-
ing capacity (Matsusaka and Sherman, 1950).

Wahiawa Silty Clay (Tropeptic Eutrorthox) was collected
from two locations of Wahiawa, Oahu.   The Wahiawa "A" and

Wahiawa "B" from Upper Wahiawa (near Hawaii National Guard Armory) were developed under 50 inches of mean annual rainfall, and Wahiawa "C" from the University of Hawaii Agricultural Experiment Station Farm at Poamoho under 40 inches. The site for the Wahiawa "B" was about two miles away from that of the Wahiawa "A". Although developed under different rainfall conditions, these soils are derived from basalt and are predominantly kaolinitic in mineralogy. They have a lower buffering capacity than the other experimental soils.

Paaloa Silty Clay (Humoxic Tropohumult) is a member of the Honolua Family and was obtained from Helemano, Oahu. It is developed from basalt that has weathered in place. The C.E.C. is about 35 me. per 100 g. and base saturation is 5%.

Koko Silty Clay Loam (Ustollic Eutrandept) was collected from the slope of the Koko Crater, Oahu. The parent material is volcanic ash, and due to sparse rainfall, is weathered slightly. It has a C.E.C. of 40 me. per 100 g. and a high base saturation.

Lualualei Clay (Typic Chromustert) was collected from Lualualei Valley, Oahu. Developed from alluvium parent material, it is dominantly montmorillonite and exhibits sticky, plastic, swelling, and shrinking characteristics of such a clay. It is almost 100% base saturated and has a C.E.C. of 50 me. per 100 g. It has a very high buffering capacity.

Some additional properties of the experimental soils are given in Table 1.

Preparation of the Soil Sample

Soil samples from the surface of the aforementioned soils were collected and placed in double polyethylene bags and brought to the laboratory. All the soils were passed through a 20-mesh sieve, except the Akaka which was passed through an 8-mesh sieve because of its high water content. The prepared samples were stored in polyethylene bags for use throughout the experimental period. Sub-samples were oven dried and ground to pass through a 60-mesh sieve for total nitrogen and organic carbon determination.

Experiment I.   Changes in Soil Inorganic Nitrogen In situ

This experiment was conducted with the Akaka and Wahiawa "A" (later Wahiawa "B") soils. An area in the field was marked and samples were collected at two-month intervals for the determination of moisture content, pH and available N (NH_4- and NO_3-N). Samples were prepared as above and 25 g. of homogeneous sub sample was extracted with 150 ml. of a 2 $\underline{N}$ KCl solution for available N determination. The Akaka designated as Akaka (virgin) was collected from the Kaiwiki Forest Reserve; that designated as Akaka (cultivated) came from the Fertilizer House area of the same site of Hilo, Hawaii.

Table 1. Some Properties of the Experimental Soils

Soil Type	Great Soil Group	Elevation (ft.)	Rainfall (in.)	pH	Total N (%)	Organic C (%)	Origin and Mineralogy
Akaka silty clay Virgin	Hydrol Humic Latosol	1500	225	4.7	0.81	14.60	Developed from vol-
Cultivated	(Hydrandept)	1500	225	4.7	0.55	8.00	canic ash. Allophane, hydrated Fe and Al oxides.
Wahiawa silty clay "A" and "B"	Low Humic Latosol (Eutrorthox)	700	50	5.0	0.18	1.50	Developed from basalt. Kaolin, Fe oxides.
"C"		500	40	4.9	0.17	1.44	Developed from basalt. Kaolin, Fe oxides.
Paaloa silty clay	Humic Latosol (Tropohumult)	1000	75	4.5	0.25	3.26	Developed from basalt. Kaolin, Fe and Al oxides, mica.
Koko silty clay loam	Red Desert (Eutrandept)	50	25	7.2	0.29	3.12	Developed from vol- canic ash. Kaolin, montmorillonite.
Lualualei clay	Dark Magnesium Clay (Chromustert)	25	20	7.6	0.10	1.06	Developed from alluvium. Montmorillonite.

The former was undisturbed but the latter was disturbed, being adjacent to a sugarcane field. The vegetation was cleared from both areas at each sampling time. The Wahiawa "A" and Wahiawa "B" were collected from Upper Wahiawa on Oahu.

Experiment II. Changes in Inorganic Nitrogen in Soils Stored at Room Temperature and Dried in Oven

The Akaka (virgin), Akaka (cultivated), and Wahiawa "A" soils were stored in polyethylene bags at room temperature. The Akaka (virgin) and Wahiawa "A" were placed in an oven at 90°C. Storage at room temperature and oven drying continued for 10 months. Changes in NH_4- and NO_3-N were estimated at the same interval as in Experiment I. Soil pH was also determined at each interval.

Experiment III. Changes in Soil Inorganic Nitrogen as Affected by Chloride Salts

The Akaka and Wahiawa soils[4] containing 14.6 and 1.4% organic carbon were used for this experiment. The chlorides of Na, K, Ca, Mg, Al, and Fe were chosen for this study. Concentration of salts ranged from 0.001 to 1 molar (M).

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[4]Except in Experiments I and II, the Akaka (virgin) and Wahiawa "C" are designated as Akaka and Wahiawa throughout the dissertation.

The calculated amount of the respective salt was added to the soil in the flask, depending upon the treatment and was mixed well. The mouth of the flask was covered with a piece of polyethylene which was tied to the neck of the flask by a rubber band. Samples were incubated for periods of 7, 14, 21, and 28 days. At the end of each period, samples were analyzed for NH_4- and NO_3-N.

The measurement of evolved CO_2 was made in another set of flasks with the Akaka soil receiving similar treatments as above. The evolved CO_2 was determined by the method of Moodie (1961)[5] at intervals corresponding to the foregoing periods.

The osmotic pressure of the strong electrolyte is calculated by the van't Hoff equation (Moore, 1962):

$$\pi = i \, c \, R \, T$$

where, π = osmotic pressure in atmosphere

i = van't Hoff factor (2 for NaCl, KCl; 3 for $CaCl_2$, $MgCl_2$; and 4 for $AlCl_3$, $FeCl_3$)

c = solute concentration in moles

T = absolute temperature

R = molar gas constant = 0.0820 liter atm./deg. mole.

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[5]Moodie, C. D. 1961. Washington State University, W-31 Annual Progress Report.

Experiment IV.   Changes in Soil Inorganic Nitrogen

as Affected by Gamma Irradiation

Three experiments were conducted with the Akaka, Wahiawa, Paaloa, Koko, and Lualualei soils.

1.   Effect of Varying Irradiation Dosages

Soil samples (25 g. for Akaka and 50 g. for other soils on the oven-dry basis) were placed in polyethylene bags (4x3x8 in.). The soil in the bag was brought to moisture equivalent and mixed well.   The bags were sealed with an electric sealer and irradiated with a ^{60}Co gamma radiation source at 0, 0.5, 1, 3, and 5 Megarads (Mrads).   Available nitrogen determination was carried out immediately following irradiation.

2.   Effect of Irradiation on Soil Inorganic Nitrogen Release After Periods of Incubation

The soils were irradiated at 0, 0.5, 1, and 3 Megarads as above and were subsequently incubated in the laboratory for 0, 7, 14, 21, and 28 days.   Available N was determined at the end of each period.

3.   Recovery of Added Nitrogen from Gamma Irradiated Soils

Soil samples were placed in polyethylene bags (4x3x8 in.), and 200 ppm. N of $(NH_4)_2SO_4$ or $NaNO_3$ solution was added to the soil in the bag.   The soil was brought to moisture equivalent and mixed well.   The bags were sealed with an electric sealer and irradiated with 3 Mrads.

In another experiment the three acid soils, Akaka (pH 4.7),
Wahiawa (pH 4.9), and Paaloa (pH 4.5), were limed with
$Ca(OH)_2$ together with the addition of 200 ppm. N before being
irradiated at a dosage of 3 Mrads. The lime rates were 0, 2,
10, and 20 tons per acre for the Akaka soil with very high
buffering capacity, and 0, 2, 5, and 10 tons per acre for the
Wahiawa and Paaloa soils with comparatively low buffering
capacities. A control series (without irradiation) was also in-
cluded where soil samples receiving similar treatments were incu-
bated in the laboratory for the same length of time as needed for
irradiating soil samples at 3 Mrads. Available nitrogen (NH_4 +
NO_3) determination was carried out on irradiated as well as
control samples. The recoveries of added NH_4- and NO_3-N
were obtained by subtracting the quantities of NH_4- or NO_3-N in
the control from that in the irradiated samples.

Experiment V. Nitrate Adsorption in Soils
as Affected by Concentration and pH of the Electrolyte Solution

The Akaka and Wahiawa soils were used for this study.
The concentrations of the equilibrating KNO_3 solution were 0,
0.005, 0.01, 0.05, 0.10, 0.30, and 0.50 $\underline{N}$. The pHs of a
0.1 $\underline{N}$ KNO_3 solution in different containers were adjusted to 3.5,
5, 7, and 9 by using sodium hydroxide or acetic acid.

Duplicate soil samples of 2 g. each (on oven-dry basis) were placed in preweighed 50 ml. plastic centrifuge tubes. Twenty-five ml. saturating solution was poured in each tube. The tubes were agitated on an end-to-end shaker for half an hour and allowed to stand for about 10 hours. After another half hour of agitation, the tubes were centrifuged at 2,000 rpm. for ten minutes and the supernatant was discarded. Fresh saturating solutions were poured in and the process of saturation and centrifugation was repeated until "apparent equilibrium" was attained, i.e., until the concentration of NO_3 in the supernatant was the same as that in the input solution. All samples attained equilibrium after four cycles of saturation and centrifugation in the present investigation. Therefore, the time for equilibration was the same for all samples. Following the last centrifugation the tubes were weighed and the amount of solution held in soil pores was calculated by subtracting the initial weight of tube plus soil from this weight. The concentration of nitrate in the entrapped solution was assumed to be the same as when added.

In a preliminary experiment, six cycles of extraction were adequate for complete removal of NO_3 from the soil because the last extract gave no response to the diphenylamine test for NO_3. Nitrate was extracted with a normal solution of KCl or K_2SO_4 following the saturation and centrifugation procedure for six times as above, except that the supernatant was saved and made to a

volume of 200 ml. for NO_3 determination. This extract contained NO_3 from the entrapped solution as well as that adsorbed on the surface. Nitrate was determined by the distillation procedure of Bremner (1965) using Devarda's alloy after distilling NH_4-N with MgO. The amount of nitrate in the entrapped solution as calculated above was subtracted from the quantity in the 200 ml. extract and the remainder was assumed to be adsorbed on the soil surface.

The linear form of the Freundlich equation given below was employed to test the fitness of the isotherm in case of adsorption in the Akaka and Wahiawa "A" soils.

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log C$$

where, x/m = amount adsorbed per unit weight of adsorbent

K, n = constants

C = concentration of the electrolyte.

Analytical Procedures

Determination of Exchangeable Nitrogen

Exchangeable ammonium and nitrate were determined by the method of Bremner (1965) with minor modifications. The details of the method are given in the Methods of Soil Analysis, Part 2 edited by Black et al. (1965). A brief description is presented in the following paragraphs.

Duplicate soil samples were extracted with a 2 $\underline{N}$ KCl solution by shaking for one hour on an end-to-end shaker and filtering through a Whatman No. 2^V folded filter paper. Since the system was equilibrated by shaking, only a desired quantity of the filtrate was collected and used for the determination of NH_4- and NO_3-N. According to this method, the NO_2-N is also included with NO_3-N. Since the magnitude of NO_2-N was very small in experimental soils, no effort was made to determine it separately and the results are reported as NO_3-N.

Twenty-five ml. extract was taken in a 500 ml. Kjeldahl flask and NH_4-N was first distilled by adding 0.5 g. ignited heavy MgO. The distillate was collected in 10 ml. boric acid-mixed indicator prepared according to the method of Bremner (1965). About 35 ml. of the distillate was collected at the rate of 7 ml. per minute. One gram of less than 100-mesh Devarda's alloy was added to the same aliquot in the Kjeldahl flask to reduce NO_3 to NH_4 and the contents were redistilled into a separate receiving flask containing boric acid-mixed indicator. The distillate was titrated with standard sulfuric acid.

Determination of Carbon Dioxide

The carbon dioxide determination in Experiment III at intervals over a period of 28 days was carried out by the method of Moodie (1961). Similar methods with minor differences have been used by Allison and Cover (1960) and Popenoe and Eno

(1962).

In essence the procedure consists of trapping the evolved CO_2 in a 5 ml. standard NaOH solution placed in a glass vial and hanging it from a wooden cork used to stopper the flask in a 500 ml. Erlenmeyer flask containing soil sample. The cork was then covered with a piece of polyethylene which was tied to the neck of the flask to prevent any loss of CO_2. At regular intervals the alkali was quantitatively transferred (using CO_2-free distilled water) to a 250 ml. Erlenmeyer flask. Fresh 5 ml. NaOH solution was placed in the vial for the next interval. Ten ml. of 1 $\underline{N}$ $BaCl_2$ was added to the 250 ml. flask to precipitate the carbonate formed by reaction of CO_2 with NaOH in the vial.

$$2 \text{ NaOH} + CO_2 = Na_2CO_3 + H_2O$$

$$Na_2CO_3 + BaCl_2 = BaCO_3 + 2 \text{ NaCl}$$
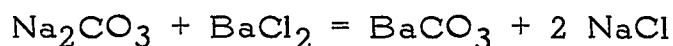
The excess of alkali was titrated against standard HCl using 6 drops of 1% phenolphthlein indicator (prepared in 95% ethyl alcohol). The amount of evolved CO_2 was calculated by the difference:

$$\text{me. NaOH} - \text{me. HCl} = \text{me. } CO_2$$

Determination of Total Nitrogen

A 5 g. soil sample was placed in an 800 ml. Kjeldahl flask. Ten grams of a $K_2SO_4:FeSO_4:CuSO_4$ salt mixture in a $10:1:\frac{1}{2}$ proportion and 30 ml. of concentrated technical grade H_2SO_4 were added to the flask. The content was digested until the

color changed to light yellow or gray. To the cooled flask were added 300 ml. distilled water, 10 ml. 50% NaOH, and a few pieces of mossy zinc and the content was distilled into a 4% boric acid solution which was subsequently titrated with standard H_2SO_4 solution.

Determination of Organic Carbon

The organic carbon was estimated by the Walkley-Black wet combustion method (Walkley, 1935). A soil sample containing 10-20 mg. C was placed in a 500 ml. Erlenmeyer flask and 10 ml. of $\underline{N}$ $K_2Cr_2O_7$ and 20 ml. concentrated H_2SO_4 were added. After letting it stand for 30 minutes with occasional shaking, 200 ml. distilled water was added to the flask and the content was filtered through a White Ribbon No. 589 paper. Ten ml. of 85% phosphoric acid and 15 drops of 0.16% barium diphenylamine sulfonate indicator were added and the excess of $K_2Cr_2O_7$ was titrated with standard $FeSO_4$. The quantity of C was calculated from the amount of $K_2Cr_2O_7$ used up.

Determination of Soil pH

The soil pH was measured using an Expandomatic Beckman pH meter in a 1:2.5 soil-water mixture that was allowed to stand for almost 12 hours.

Statistical Analysis

Correlation given by Snedecor (1956) was used as an aid in interpretation of the data. Throughout this dissertation * and

** indicate significance at the 5% and 1% level of probability, respectively.

RESULTS AND DISCUSSION

Experiment I.   Changes in Soil Inorganic Nitrogen In situ

Variations in rainfall and temperature significantly affect the physical, chemical, and biological properties of a soil. These properties in turn have a vital influence on many useful transformations, the most practical being the transformation of native nitrogen to readily available NH_4 and NO_3 ions. Nitrite may also accumulate in some soils where conditions are conducive to its accumulation. The magnitude of these forms in any soil will depend largely on the quantity and frequency of rainfall. This experiment was involved with the study of changes in inorganic N in the Akaka (virgin), Akaka (cultivated), Wahiawa "A", and Wahiawa "B" soils in situ. The two Akaka soils were sampled from September 1967 through May 1968. The Wahiawa "A" was sampled from September 1967 through March 1968, and Wahiawa "B" from March to July 1968 because the former site was bulldozed. The former two soils were collected from an area with an annual rainfall of 250 inches and the latter two soils from an area with 50 inches.

Data in Table 2 reveal that there was no definite or conclusive trend of NH_4- or NO_3-N accumulation with time in these soils. However, the magnitude of available nitrogen (NH_4 + NO_3) was higher in the Wahiawa "A" and Wahiawa "B" than in

Table 2. Changes in Soil Inorganic Nitrogen With Time In situ

Soil	Month	Soil Moisture %	Soil pH	Changes in Nitrogen		
				NH$_4$	NO$_3$	NH$_4$+NO$_3$
					ppm. N	
Akaka (virgin)	Sept. 1967	168	4.3	12	7	19
	Nov. 1967	244	4.7	3	1	4
	Jan. 1968	168	4.4	0	0	0
	Mar. 1968	–	–	–	–	–
	May 1968	103	4.8	21	0	21
Akaka (cultivated)	Sept. 1967	90	4.7	3	21	24
	Nov. 1967	92	4.8	4	0	4
	Jan. 1968	85	4.8	9	2	11
	Mar. 1968	–	–	–	–	–
	May 1968	86	5.2	4	3	7
Wahiawa "A"	Sept. 1967	30	5.8	0	20	20
	Nov. 1967	29	5.5	16	46	62
	Jan. 1968	48	6.3	7	10	17
	Mar. 1968	41	5.7	17	52	69
Wahiawa "B"	Mar. 1968	41	4.7	12	4	16
	May 1968	35	4.6	11	2	13
	July 1968	28	4.9	43	5	48

the other two soils. Similarly, no relationship was observed

between soil moisture and available N content of the soils. The

soil pH did not follow any definite trend either.

Discussion

The inconsistent pattern of NH_4- and NO_3-N accumulation

in these soils during the experimental period could be attributed to

variations in the quantity and frequency of rainfall. There was

no relationship between the moisture content and the available N

in each of these soils, possibly because N accumulation was

dependent on the quantity and frequency of rainfall preceding the

sampling.

Experiment II. Changes in Inorganic Nitrogen
in Soils Stored at Room Temperature and Dried in Oven

The previous experiment was concerned with the study of

changes in inorganic N in situ, where soils are in equilibrium

with their environment. Once they are removed and brought to

the laboratory the equilibrium is disturbed. The laboratory con-

ditions are modified further by subjecting the soils to various

treatments such as addition of salts or gamma irradiation. These

will be discussed in later experiments. Apart from these treat-

ments the methods and techniques of storage in the laboratory also

affect the rate, magnitude, and direction of N transformation.

Samples of the Akaka (virgin), Akaka (cultivated), and Wahiawa

"A" were stored in polyethylene bags at room temperature, and samples of the Akaka (virgin) and Wahiawa "A" were placed in an oven at 90°C. The temperature was even in the room and oven at all times. The available N was determined at two-month intervals for 10 months. The data are given in Table 3.

1.   Changes in Inorganic Nitrogen in Soils Stored at Room Temperature

The data in Table 3 show a four-month lag period during which the NH_4- and NO_3-N contents of the Akaka (virgin) soil were practically unchanged at room temperature. While the NH_4-N remained the same even after this period, the NO_3-N increased linearly up to eight months, then leveled off (Fig. 1, solid line). A consistent increase with the length of storage was noted in the release of NO_3-N in the Akaka (cultivated) (Fig. 2) and Wahiawa "A" (Fig. 3, solid line). With respect to their available N content, these soils can be arranged in the series, Wahiawa "A" > Akaka (virgin) > Akaka (cultivated), in order of decreasing magnitudes of N release with the length of storage. However, the available N was more in the Akaka (cultivated) than in Akaka (virgin) during the first four months.

2.   Changes in Inorganic Nitrogen in Soils Dried in Oven

Oven drying at 90°C resulted in an increase in the magnitude of NH_4-N in the Akaka (virgin) soil (Fig. 1, broken line). The mineralization increased linearly up to eight months with a

Table 3. Changes in Inorganic Nitrogen With Time
in Soils Stored at Room Temperature and Dried in Oven

| Soil | Months | Soil pH | | Changes in Nitrogen | | | | | |
| | | | | NH$_4$ | | NO$_3$ | | NH$_4$+NO$_3$ | |
		Room temp.	Oven 90°C	Room temp.	Oven 90°C	Room temp.	Oven 90°C	Room temp.	Oven 90°C
						ppm. N			
Akaka	0	4.3	4.3	12	12	7	7	19	19
(virgin)	2	4.3	3.7	11	718	7	9	18	727
	4	4.3	3.8	12	1030	16	13	28	1043
	6	3.8	4.0	18	1148	164	11	182	1159
	8	3.9	4.2	15	1238	225	12	240	1250
	10	3.9	4.3	15	1246	243	10	258	1256
Akaka	0	4.7	–	3	–	21	–	24	–
(cultivated)	2	4.7	–	2	–	45	–	47	–
	4	4.7	–	4	–	80	–	84	–
	6	4.6	–	24	–	100	–	124	–
	8	4.7	–	13	–	141	–	154	–
	10	4.7	–	2	–	175	–	177	–
Wahiawa "A"	0	5.8	5.8	0	0	20	20	20	20
	2	5.8	6.2	4	380	97	22	101	402
	4	5.7	6.2	1	435	155	23	156	458
	6	5.7	6.2	9	443	190	25	199	468
	8	5.7	6.3	9	457	249	31	258	488
	10	5.7	6.2	16	484	322	33	338	517
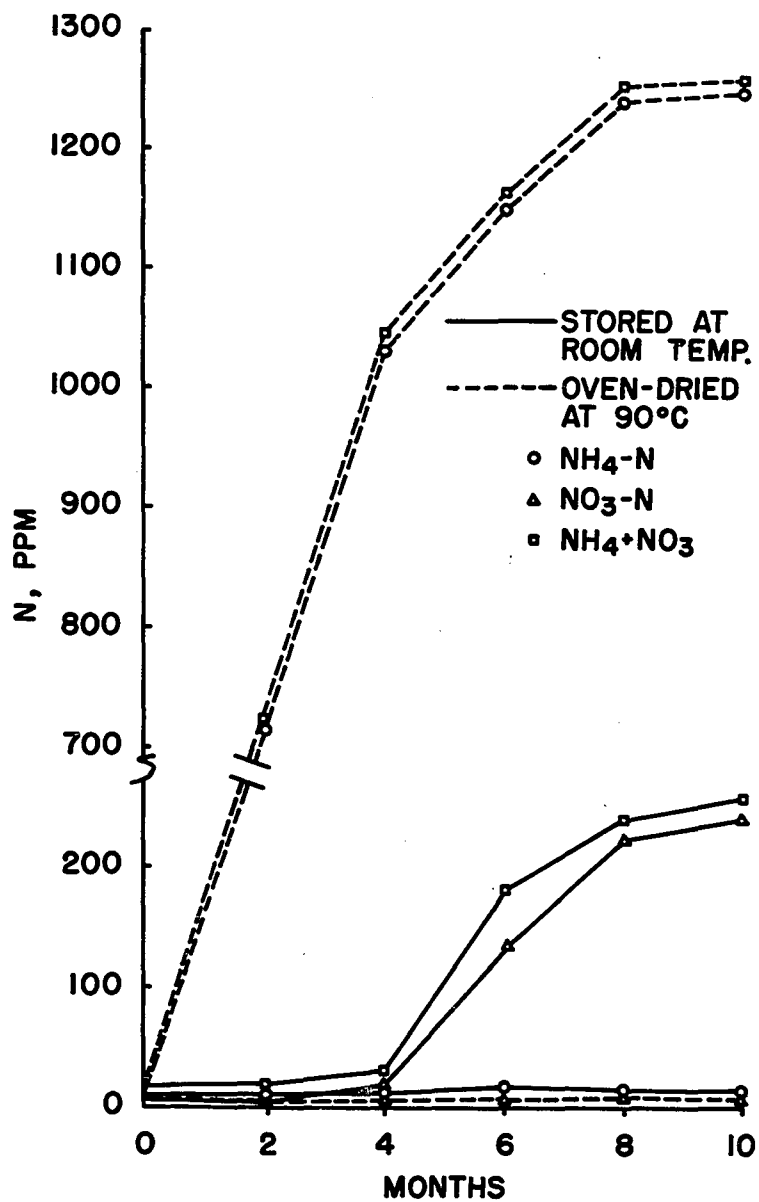
Fig. 1. Changes in Inorganic Nitrogen in the
Akaka (Virgin) Soil Stored at Room Temperature
and Dried in Oven at 90°C.
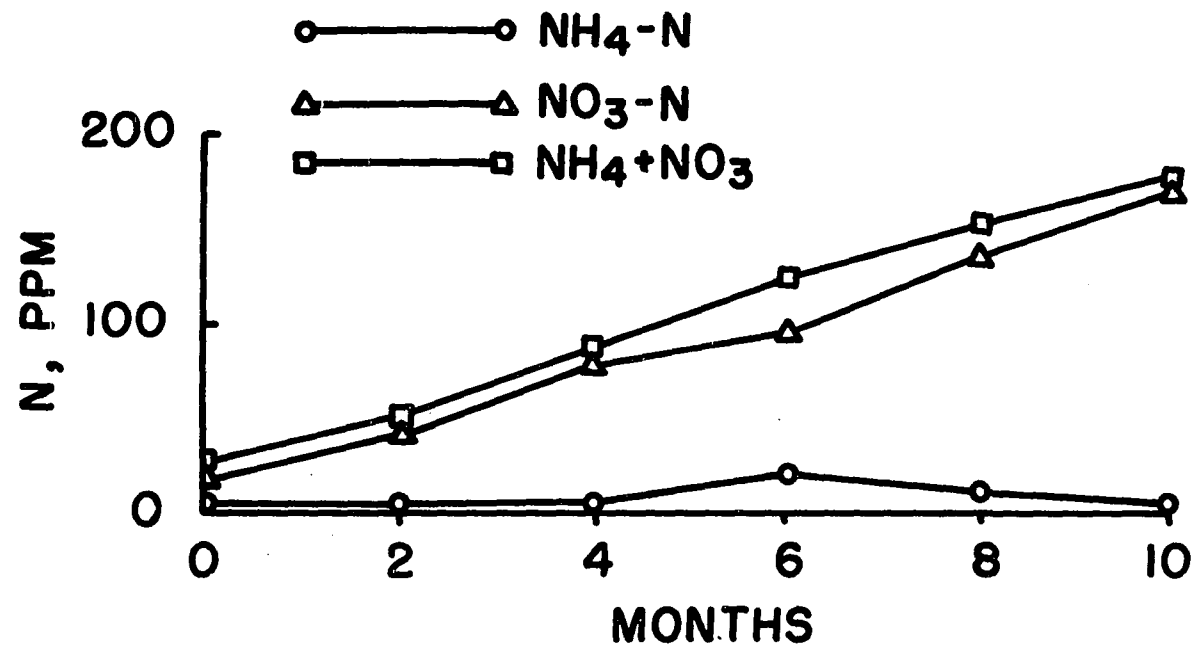
Fig. 2. Changes in Inorganic Nitrogen in the Akaka (Cultivated) Soil Stored at Room Temperature.
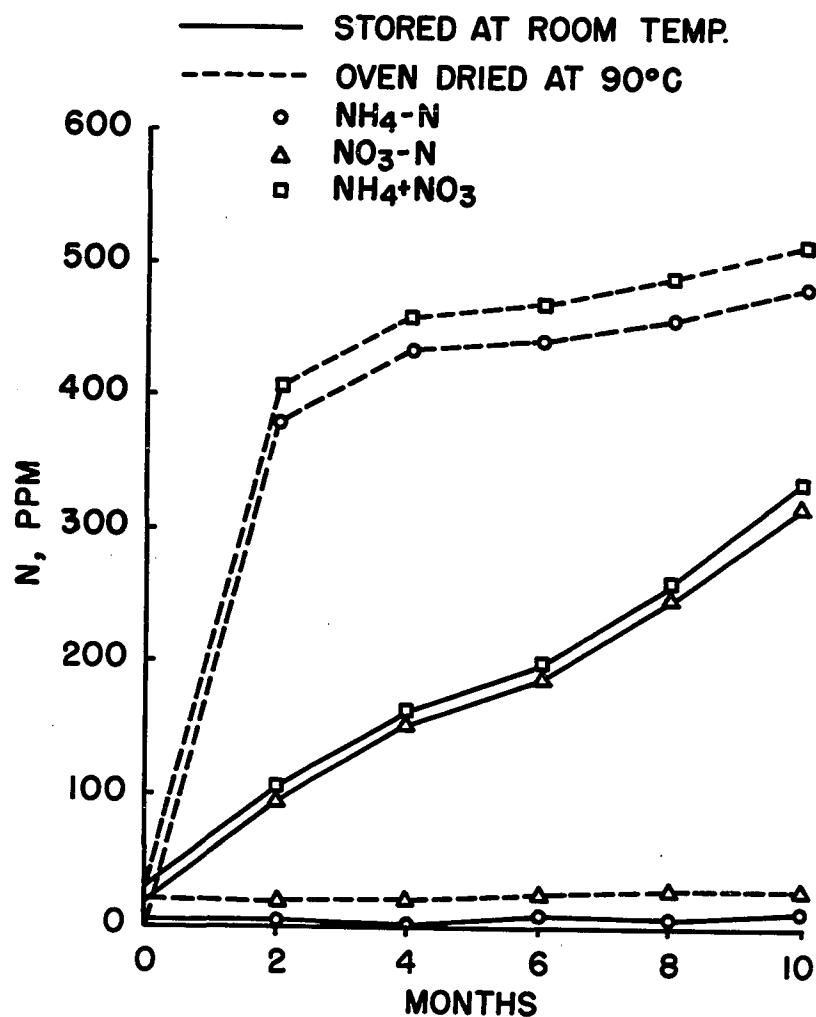
Fig. 3. Changes in Inorganic Nitrogen in the
Wahiawa "A" Soil Stored at Room Temperature and
Dried in Oven at 90°C.

faster rate during the first four months than the following months, then leveled off. A similar increase in NH_4-N mineralization was observed in the Wahiawa "A" soil except the linear increase was only up to two months (Fig. 3, broken line). Beyond this period the mineralization proceeded at a relatively slower rate. There was very little change in NO_3-N content of these two soils during the entire course of oven drying.

3. Effect of Storage at Room Temperature and Oven Drying on Soil pH

The Akaka (virgin) soil stored at room temperature showed a decreasing trend of pH with time whereas the oven-dried samples showed an increasing trend (Table 3). The pH of the Wahiawa "A" soil did not change with time, but was slightly higher in the oven-dried sample than that stored at room temperature.

Discussion

The length of time and the environment in which soil samples are stored are known to cause marked changes in the physical and chemical properties of a soil (Harpstead and Brage, 1963; Munro and MacKay, 1964). The four-month lag period in the Akaka (virgin) soil (Fig. 1, solid line) shows that the soil microorganisms are also disturbed and take a long time to adjust to their new environment.

Little or no increase in the NH_4-N content of these soils stored at room temperature does not mean that there was no ammonium release; in fact the mineralized NH_4-N was rapidly nitrified. This is strongly evidenced by a rapid increase in NO_3-N in the Akaka (virgin) soil after four months, and in the Akaka (cultivated) and Wahiawa "A" soils from the very beginning of the storage period. Air-drying of soils has been reported to increase nitrification (Harpstead and Brage, 1963; Munro and MacKay, 1964). A consistent increase in the magnitude of NO_3-N in the experimental soils except the Akaka (virgin) until four months suggests that nitrate production is also enhanced by laboratory storage in polyethylene bags where soils suffer no moisture loss. It is worth mentioning that the polyethylene bags are permeable to air but almost impermeable to moisture (Eno, 1960). Enhanced nitrification during storage at room temperature could be attributed to increased microbial population.

The moisture contents of the Akaka (virgin), Akaka (cultivated), and Wahiawa "A" soils during storage were 168, 90, and 30%, and their organic carbon contents were 14.6, 8.0, and 1.5%, respectively. Despite their high organic matter content, the nitrate production was lower in the two Akaka soils than in the Wahiawa "A".

An increase in the magnitude of NH_4-N in the Akaka (virgin) soil placed in the oven at 90°C could be attributed to its

high organic matter content. This is substantiated by reports of Agarwal (1967), Birch (1959), Birch and Friend (1956), and Cairns (1963). The NH_4-N increase in the Wahiawa "A" was not as high as in the Akaka (virgin) under similar oven drying conditions. The broken lines in Figs. 1 and 3 show that the rate of ammonium release in the two soils was essentially the same during the first two months of oven drying. The rate declined in the Wahiawa "A" soil after two months. In the Akaka (virgin) soil the rate declined slightly after four months and leveled off after eight months.

There are several reasons which could account for the substantial increase in NH_4-N in these soils during oven drying. Initially, samples placed in the oven underwent partial sterilization. Greig-Smith (1911) suggested that the toxin restraining the microbial growth is destroyed by partial sterilization. Another group of researchers (Birch, 1958; Coleno et al., 1965; Gooding and McCalla, 1945; Kubista, 1966) has mentioned the stimulation in microbial vigor following partial sterilization which renders decomposition of organic matter. A third group (Martin, 1963; McLaren et al., 1962) believed that under such treatments a section of microbial population, previously kept in check by opposition from a different group of microbes, grows to cause an increase in release of nitrogen and carbon. Other theories have been proposed by Birch (1960) and Jenkinson (1966).

According to Gibbs (1919), nitrosomonas and nitrobacters are killed at 53-55°C and 56-58°C, respectively. Later, Lawrence (1956) reported that while nitrifiers are killed by partial sterilization, ammonifiers survive sterilization in fair numbers. Unlike nitrifying bacteria which exist as thin-walled cells that are very susceptible to heat, the ammonifying bacteria produce thick-walled cells, or spores, which can survive 212°F (100°C). Almost no change in NO_3-N in the Akaka (virgin) and Wahiawa "A" soils could be due to killing of the nitrifying bacteria. Increased NH_4-N on heating could be partly due to survival of ammonifiers on heating. In addition, the heat treatment has been reported to increase NH_4-N release due to chemical transformation of organic matter. Birch (1959) noted that the solubility of organic matter in the aqueous solution increased with heating. He thought this could be due to some chemical alteration. Jenkinson (1966) attributed it to the killing of microorganisms because the death and subsequent lysis of microorganisms will be accompanied by an increase in water soluble organic matter. Cairns (1963) reported that the effect of heat on NH_4-N release could be due to either the chemical oxidation of humus or the release of difficultly exchangeable ammonium fraction. It is speculated that the splitting of ammonium from the proteinaceous parts of organic matter could be largely responsible for increased NH_4-N in the two soils. Presumably this is the reason for a

greater NH_4-N release in the Akaka (virgin), a soil with high organic matter content, than in the Wahiawa "A".

The decreased soil pH of Akaka (virgin) during storage at room temperature could be due to release of certain acids from decomposing organic matter. The Akaka soil dries irreversibly on heating (Kanehiro and Sherman, 1956). Probably the increased pH on oven drying of the Akaka (virgin) is due to inaccessibility of H ions. For similar reasons, the pH of the oven-dried Wahiawa "A" was slightly higher than that stored at room temperature.

Experiment III. Changes in Soil Inorganic Nitrogen
as Affected by Chloride Salts

To elucidate the changes in soil inorganic nitrogen, the Akaka silty clay (organic carbon content of 14.6%) and Wahiawa silty clay (organic carbon content of 1.4%) were treated with chlorides of Na, K, Ca, Mg, Al, Fe, and K, Ca, Al, respectively. Samples of both soils were subsequently incubated in the laboratory and NH_4- and NO_3-N were determined at intervals over a period of four weeks. It is pertinent to mention here that the anion (Cl^-) was kept constant to avoid complications due to anionic effect and to get insight of the cationic effect on NH_4-N release. These soils with such a wide difference in their organic C contents were chosen to study the interaction of salts

and the initial organic matter content on N mineralization. Also, the effect of the above salts on CO_2 production in the Akaka soil was studied.

1. Changes in Carbon Dioxide

The cumulative carbon dioxide data as affected by different concentration of salts are given in Table 4. The CO_2 measurement was extended to a period of 28 days. The CO_2 evolution was less in salt-treated samples than in the control. The production declined gradually with successive increments of salts, i.e., with increasing osmotic pressure. The results also showed no definite or conclusive change in CO_2 production by the respective salts.

2. Changes in Ammonium Nitrogen

The data on this phase of the study for the Akaka soil are included in Table 5 and illustrated in Figs. 4, 5, and 6, and that for the Wahiawa soil in Table 6 and Fig. 7.

Chemical and/or biological processes involved in the NH_4-N release were enhanced by addition of salts in the Akaka soil. The N mineralization was generally a direct function of salt concentration and the length of incubation. There was appreciable increase in the amount of NH_4-N released in this soil by salt treatment.

Increasing concentration of the monovalent cations in the soil solution enhanced NH_4-N release in the Akaka soil. Although

Table 4. Effect of Chloride Salts on the Production of Carbon Dioxide (Cumulative) in the Akaka Soil

Salt	Molar Concentration	Osmotic Pressure (atm.)	Days			
			7	14	21	28
			mg. C/25 g. Soil			
No Salt	0.0	0.0	5	10	15	20
NaCl	0.001	0.05	6	10	14	18
	0.01	0.49	5	9	13	17
	0.10	4.92	5	8	12	16
	1.00	49.20	4	8	11	13
KCl	0.001	0.05	4	9	13	18
	0.01	0.49	5	9	13	16
	0.10	4.92	5	9	12	16
	1.00	49.20	4	9	12	15
$CaCl_2$	0.001	0.07	6	10	15	18
	0.01	0.74	4	8	11	14
	0.10	7.38	6	9	12	15
	1.00	73.80	3	5	9	11
$MgCl_2 \cdot 6H_2O$	0.001	0.07	5	9	13	17
	0.01	0.74	5	9	12	16
	0.10	7.38	6	9	12	14
	1.00	73.80	3	5	8	10
$AlCl_3 \cdot 6H_2O$	0.001	0.09	5	9	13	17
	0.01	0.98	5	8	12	16
	0.10	9.84	7	10	11	14
	1.00	98.40	3	3	4	5
$FeCl_3$	0.001	0.09	6	10	13	17
	0.01	0.98	6	9	14	17
	0.10	9.84	7	11	15	18
	1.00	98.40	6	9	11	14

Table 5. Effect of Chloride Salts on the Release
of NH_4-N in the Akaka Soil

Salt	Molar Concentration	Days			
		7	14	21	28
		ppm. N			
NaCl	0.001	2	19	20	15
	0.01	15	44	52	48
	0.10	35	72	82	93
	1.00	69	157	166	182
KCl	0.001	0	18	13	12
	0.01	14	47	48	57
	0.10	60	100	118	133
	1.00	98	159	234	257
$CaCl_2$	0.001	4	11	18	12
	0.01	23	50	64	68
	0.10	75	112	134	151
	1.00	26	99	178	207
$MgCl_2 \cdot 6H_2O$	0.001	5	15	29	22
	0.01	21	54	69	72
	0.10	64	101	119	140
	1.00	30	91	139	168
$AlCl_3 \cdot 6H_2O$	0.001	14	19	42	53
	0.01	47	84	99	109
	0.10	156	229	247	273
	1.00	13	14	13	5
$FeCl_3$	0.001	13	20	27	15
	0.01	53	72	95	76
	0.10	102	185	226	273
	1.00	0	2	36	24
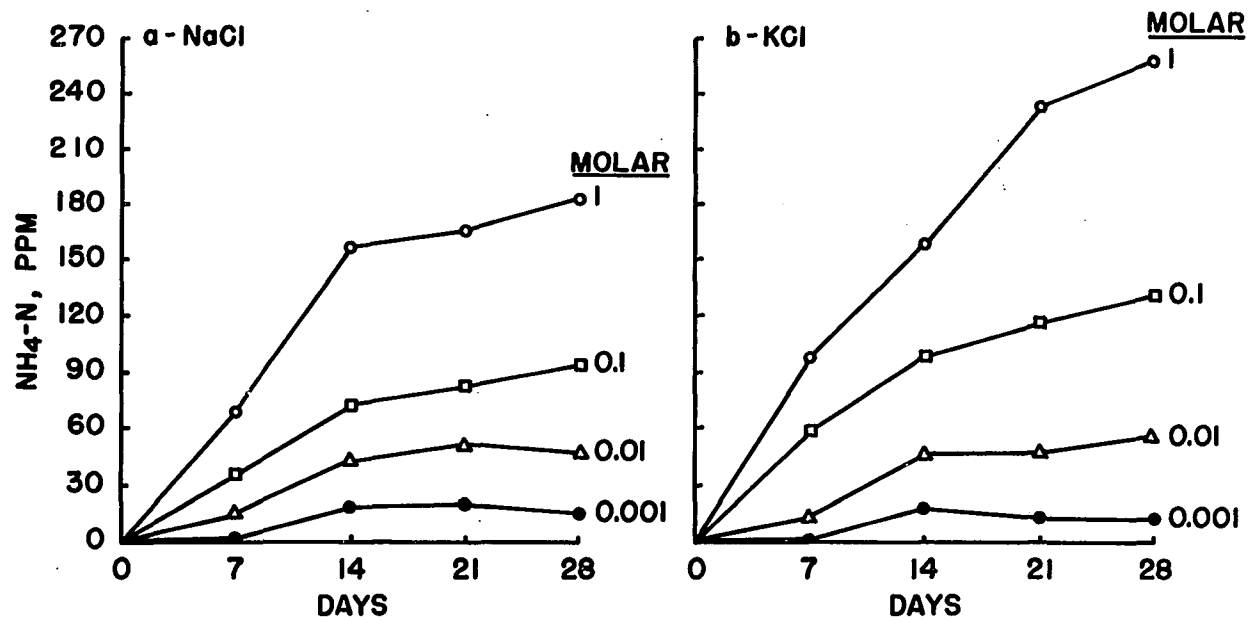
Fig. 4. Changes in NH$_4$-N as Affected by Concentrations of NaCl and KCl in the Akaka Soil.
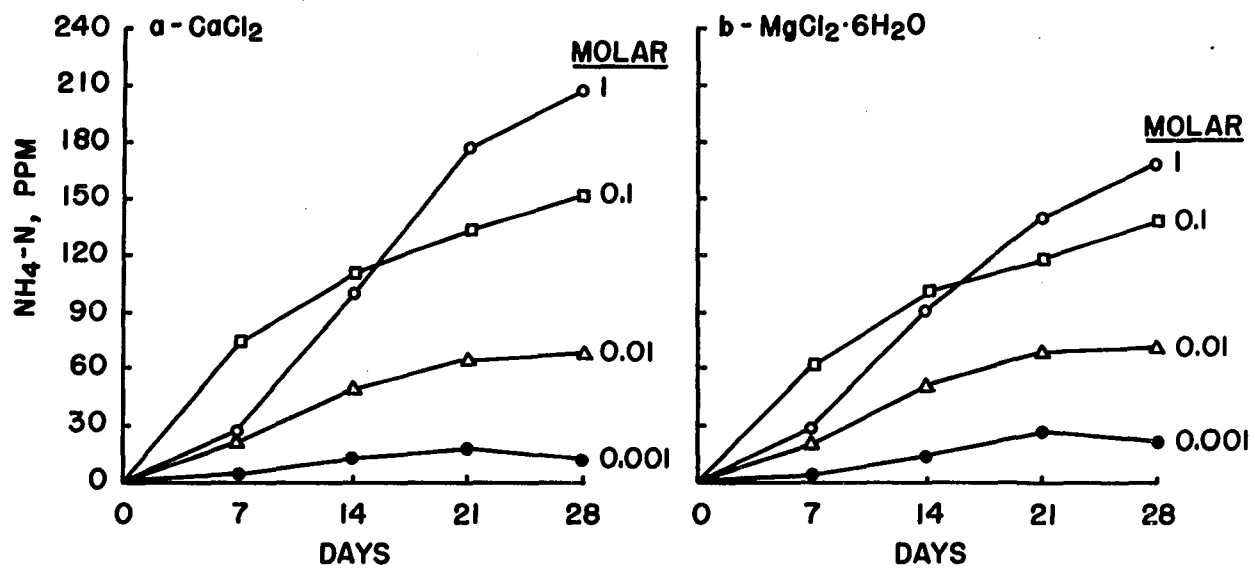
Fig. 5. Changes in NH_4-N as Affected by Concentrations of $CaCl_2$ and $MgCl_2 \cdot 6H_2O$ in the Akaka Soil.
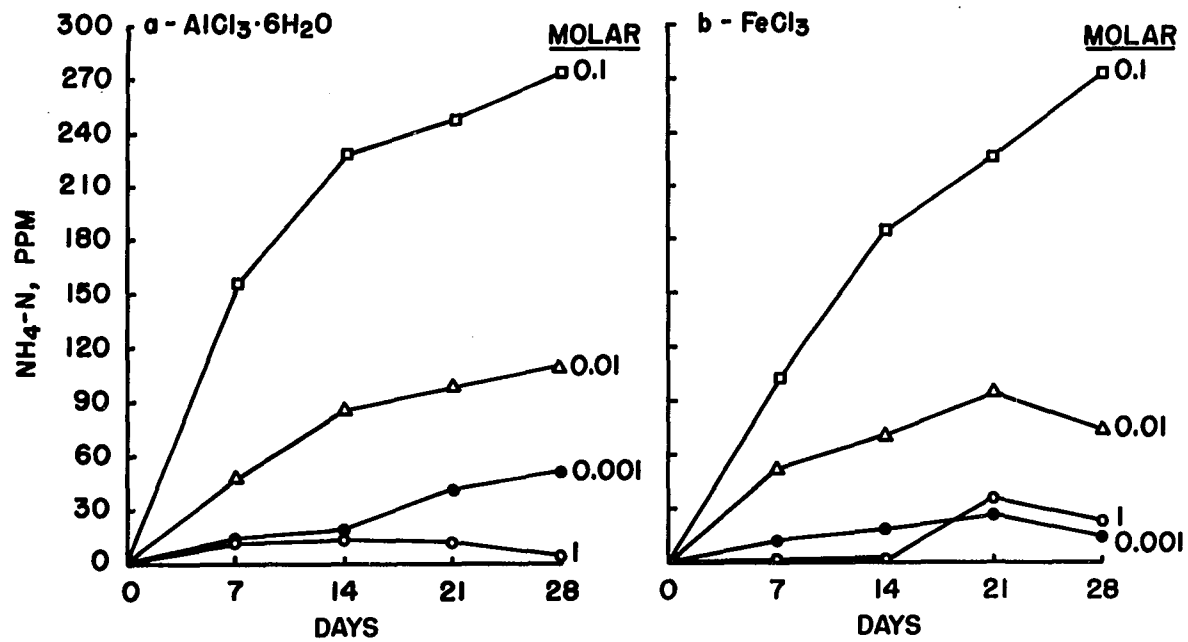
Fig. 6. Changes in NH_4-N as Affected by Concentrations
of $AlCl_3 \cdot 6H_2O$ and $FeCl_3$ in the Akaka Soil.

Table 6. Effect of Chloride Salts on the Release
of NH_4-N in the Wahiawa Soil

Salt	Molar Concentration	Days			
		7	14	21	28
		ppm. N			
KCl	0.001	4	2	2	0
	0.01	4	2	1	2
	0.10	3	18	21	20
	1.00	0	22	28	36
$CaCl_2$	0.001	-4	3	4	-4
	0.01	-6	3	2	-1
	0.10	2	15	15	22
	1.00	6	31	18	27
$AlCl_3 \cdot 6H_2O$	0.001	-6	5	0	2
	0.01	1	5	6	14
	0.10	2	17	22	39
	1.00	-6	4	2	11
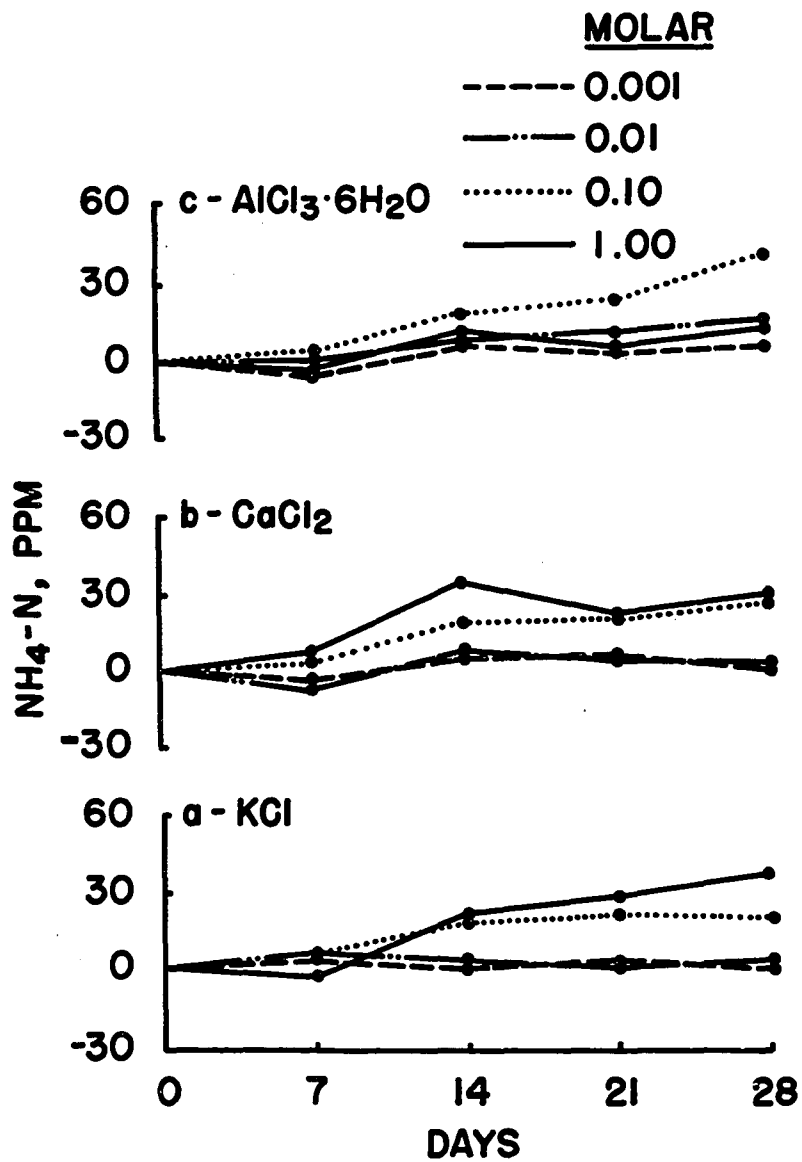
Fig. 7. Changes in NH_4-N as Affected by
Concentrations of KCl, $CaCl_2$, and $AlCl_3 \cdot 6H_2O$
in the Wahiawa Soil.

their effect was similar, the quantity of mineralized NH_4-N at any particular concentration was substantially more in the presence of K (Fig. 4b) than Na (Fig. 4a). However, this did not apply at lower concentrations to 0.01 $\underline{M}$ where NaCl was equal or better than KCl.

The patterns of NH_4-N release in samples treated with $CaCl_2$ (Fig. 5a) and $MgCl_2 \cdot 6H_2O$ (Fig. 5b) were similar to those treated with the chlorides of monovalent cations. In general, Ca rendered greater NH_4-N mineralization than Mg. It is interesting to note in Figs. 5a and 5b that the 1 $\underline{M}$ concentration of $CaCl_2$ and $MgCl_2 \cdot 6H_2O$ exhibited less influence on N mineralization than 0.1 $\underline{M}$ until 14 days of incubation. Beyond this period, however, the 1 $\underline{M}$ concentration effected high NH_4-N release. This was not the case with Na and K chlorides. The divalent cations resulted in greater release than the monovalents at all concentrations with the exception at 1 $\underline{M}$ where K superseded the effect of Ca, Mg, and Na.

At low concentrations, the trivalent Al and Fe effected relatively large release of NH_4-N in the Akaka soil throughout the period of incubation. At a concentration of 0.1 $\underline{M}$ both of these cations caused considerably greater release than the rest of the cations. It can be easily comprehended from Figs. 6a and 6b that the magnitude of released NH_4-N is higher when Al rather than Fe was added to the soil. Although a release of

273 ppm. NH_4-N at 0.1 $\underline{M}$ concentration was obtained for both cations, the slopes of the two curves over the entire range are not the same. The curve is flatter for Fe than Al. However, additions of $AlCl_3 \cdot 6H_2O$ and $FeCl_3$ at the highest concentration of 1 $\underline{M}$ showed considerably less release of NH_4-N than that obtained at 0.001 $\underline{M}$.

The effect of the chlorides of K, Ca, and Al (Table 6, Fig. 7) on NH_4-N release in the Wahiawa soil was similar to that in the Akaka soil, except that the magnitude was considerably lower.

3.   Changes in Nitrate Nitrogen

Table 7 and 8 include data on mineralized NO_3-N in the Akaka and Wahiawa soils, respectively. Negative figures correspond to treatments where nitrate production was less than that in the control. The added salts had little effect on the NO_3-N content of the Akaka soil. However, the positive figures for samples incubated for seven days and the negative figures at all other periods suggest that these salts become toxic to nitrifiers over a period of time. No definite trend was noticed among concentrations, salts, and periods. The results were similar in the Wahiawa soil. In this soil, however, the higher negative values for NO_3-N at 0.1 $\underline{M}$ and 1 $\underline{M}$ concentrations of KCl and $CaCl_2$, and 0.1 $\underline{M}$ concentration of $AlCl_3 \cdot 6H_2O$ corresponded to the greater NH_4-N release (Table 6) at these concentrations.

Table 7. Effect of Chloride Salts on the Release
of NO_3-N in the Akaka Soil

Salt	Molar Concentration	Days			
		7	14	21	28
		ppm. N			
NaCl	0.001	3	3	0	4
	0.01	4	1	0	0
	0.10	4	2	-2	-1
	1.00	3	-1	-2	0
KCl	0.001	3	2	1	1
	0.01	4	0	-1	-2
	0.10	4	-2	-1	-4
	1.00	5	1	-3	-4
$CaCl_2$	0.001	4	-2	1	-1
	0.01	3	-1	2	0
	0.10	3	-1	0	-1
	1.00	4	1	0	-2
$MgCl_2 \cdot 6H_2O$	0.001	3	1	1	0
	0.01	3	2	0	-1
	0.10	1	-2	0	-4
	1.00	0	-4	1	-3
$AlCl_3 \cdot 6H_2O$	0.001	6	-1	0	0
	0.01	3	0	-1	0
	0.10	1	0	0	-4
	1.00	2	-3	-4	0
$FeCl_3$	0.001	3	1	2	0
	0.01	4	-2	1	-1
	0.10	1	0	0	-1
	1.00	4	-2	4	-1

Table 8. Effect of Chloride Salts on the Release
of NO_3-N in the Wahiawa Soil

Salt	Molar Concentration	Days			
		7	14	21	28
		ppm. N			
KCl	0.001	-1	1	3	-3
	0.01	-2	3	6	-7
	0.10	-6	-2	-7	-18
	1.00	-4	-5	-8	-30
$CaCl_2$	0.001	2	4	7	-2
	0.01	0	0	1	-1
	0.10	-7	-6	-13	-25
	1.00	-6	-2	-13	-29
$AlCl_3 \cdot 6H_2O$	0.001	-4	0	1	-9
	0.01	-4	0	-9	-13
	0.10	-6	-4	-13	-27
	1.00	-7	-7	-14	-30

Discussion

From the results presented herein, it can be concluded that the addition of salts had no stimulative effect on the microbial activity in the Akaka soil. In fact CO_2 production in the salt-treated samples was less than CO_2 production in the control. This agrees with the earlier finding of Johnson and Guenzi (1963). They concluded that increasing osmotic pressure from 0 to 30 bars in soil solution reduced CO_2 evolution approximately linearly. That the high O.P. causes cellular breakdown with subsequent N release (Broadbent, 1965) is well evidenced by the data in the Table 4 where CO_2 evolution declined, and Table 5 where NH_4-N release increased with successive increments of salts in the soil.

In the mineralization of NH_4-N in salt-treated soils two types of processes, biological and chemical, may be involved. Several investigators (Lipman, 1909; Greaves, 1916; Greaves and Lund, 1921) have reported that salts stimulate ammonifiers. Greaves (1916) gave a series, $CaCl_2$, KCl, $MgCl_2$, $NaCl$, $FeCl_3$, in the order of decreasing toxicity to ammonifying organisms. However, if CO_2 is indicative of microbial activity, its production should increase with increasing salt concentration in a soil due to the stimulative effect of salts on soil population. Evidence presented herein shows that the CO_2 production was less in salt-treated samples than the control. Further, the evolution

decreased with increased osmotic pressure. Therefore, the stimulative effect of salts reported by these investigators as being responsible for increased NH_4-N mineralization in soils appears to be of less significance.

The deleterious effect of increasing osmotic pressure due to salts on the physiological action of the microbial cell protoplasm was considered by Greaves and Lund (1921). They mentioned that increasing O.P. changes the physical and chemical properties of protoplasm so that it can no longer function normally. Consequently, soil microbes will no longer mineralize NH_4-N. Contrary to this observation, from Tables 5 and 6 it is quite evident that NH_4-N production in experimental soils was generally a direct function of increasing concentration or O.P. of salts except at the 1 $\underline{M}$ concentration of $AlCl_3 \cdot 6H_2O$ and $FeCl_3$. Consequently, the osmotic effect in inhibiting microbial functioning seems to be unlikely. A consistent increase in NH_4-N release with increasing concentration of salts or O.P. in the experimental soils may be due in part to cellular breakdown and subsequent lysis of dead cells as was advanced by Broadbent (1965).

However, O.P. is not the sole factor contributing to NH_4-N release. If this was the only factor then the magnitudes of released NH_4-N by monovalent, divalent, and trivalent cations at the same osmotic pressure should have been the same. Results of this experiment show that the release of NH_4-N by monovalent,

divalent, and trivalent cations increased in the order named.

In addition to the osmotic effect, possibly certain chemical reactions and/or processes also contribute to the NH_4-N release from the organo-inorganic complexes of the soil as was speculated by Agarwal (1967). Once the ammonium ions are released from the soil complex, they are subsequently exchanged with the cations in the surrounding soil solution. This exchange reaction will depend to a great extent on the nature and valence of cations and their concentration in the soil solution.

The differences in the magnitudes of NH_4-N in presence of Na, K, Ca, Mg, Al, and Fe ions in the experimental soils could be due to the differences in the nature and capacities of these cations to participate in exchange reactions. The author strongly feels that once the NH_4 ions are released from the soil complex through microbial cell breakdown due to O.P. (Broadbent, 1965) and/or through the chemical release (Agarwal, 1967), the subsequent exchange reactions become highly important. The longer the time of reaction, i.e., longer incubation period, the more exchange will take place. The idea that the exchange reactions are involved in NH_4-N release agrees with Chu and Knowles (1966) but contradicts Broadbent (1965), who, by using N^{15}, showed that ionic exchange is not involved.

The increase in the magnitude of released NH_4-N with successive increment of salts could be explained on the basis of

their effect on the electric double layer. Schofield and Taylor (1955) reported that increasing cationic activity by increasing the electrolyte concentration in the surrounding solution compresses the electric double layer towards the surface. Consequently, the exchange reaction between cations on the surface and in solution is greatly enhanced.

Appreciably higher release of NH_4-N at 1 $\underline{M}$ concentration of KCl than chlorides of Na, Ca, and Mg can be attributed to the similarity in the ionic sizes of K and NH_4 ions. At lower concentrations, divalents are better replacers of NH_4 ions than monovalents. The influence of trivalent Al and Fe on NH_4-N release was very pronounced. The magnitude of release at 0.1 $\underline{M}$ was even higher than that at 1 $\underline{M}$ for the rest of the cations. But additions of $AlCl_3 \cdot 6H_2O$ and $FeCl_3$ at the highest concentration of 1 $\underline{M}$ decreased the ammonium production considerably less than that obtained at 0.001 $\underline{M}$. Probably, Al and Fe ions were complexed in the soil at such a high concentration. The complexing of these ions has been reported by several investigators in the past (Hsu and Bates, 1964; Kaddah and Coleman, 1967; Rich, 1960; Schwertmann and Jackson, 1964; Shen and Rich, 1962). Kawaguchi and Kyume (1967) reported that humic and fulvic acids in the soil form complex compounds (probably chelate) with Al^{3+} and/or Fe^{3+}, but not with Ca^{2+}. The fulvic acid fraction has a higher chelation capacity than the humic acid.

A consideration of the overall picture leads to the series, Al > Fe > Ca > Mg > K > Na, in order of decreasing NH_4 replacing power. However, this series holds only to a concentration of 0.1 $\underline{M}$; beyond this, Al and Fe ions were ineffective in enhancing NH_4-N release. It is strongly suggested that the processes involved in the NH_4 release are more chemical than biological in nature.

Agarwal (1967), while studying the effect of chlorides and sulfates of Na, K, and Ca, speculated that anions are also involved in the N mineralization in the Akaka soil. He noted differences in magnitudes of NO_3-N due to differences in the accompanying anions with a specific cation. In the present investigation, when the anion was kept constant there was very little difference in the nitrate production in the soil due to different salts. This substantiates his finding that both cationic and anionic species are involved in N release from soils.

Appreciably little or no change in nitrate content of these two soils also suggests that the salts are toxic to nitrifiers even at low concentrations. The toxic effects of salts to nitrifiers have also been reported in the past (Brown and Hitchcock, 1917; Greaves et al., 1919; Johnson and Guenzi, 1963; Pathak and Jain, 1965).

The results on the available nitrogen (NH_4 + NO_3) for the Akaka and Wahiawa soils can be seen in Appendix Table I.

Experiment IV.   Changes in Soil Inorganic Nitrogen

as Affected by Gamma Irradiation

To further the study of changes in soil inorganic nitrogen under laboratory conditions, the Akaka, Wahiawa, Paaloa, Koko, and Lualualei soils were subjected to varying dosages of gamma radiation.   In another experiment irradiated Akaka, Wahiawa, and Lualualei soils were incubated for different periods prior to N determination.   In addition the recoveries of added NH_4-N and NO_3-N from gamma-irradiated soils were investigated also.

1.   Effect of Varying Irradiation Dosages

The five aforementioned soils were irradiated at dosages ranging from 0 to 5 Megarads (Mrad).   Available N was determined immediately following irradiation.

(a).   Effect on NH_4-N

The data of Table 9 show that NH_4-N content generally increased with increasing dosages of irradiation in all soils.   The greatest release was in the Akaka followed by Lualualei and Koko.   The differences in the magnitudes of mineralized NH_4-N between 0 and 5 Mrads in these three soils were 32, 17, and 14 ppm. N, respectively.   Although there was an increasing trend in the Wahiawa and Paaloa soils, the differences in the magnitudes of mineralized NH_4-N due to successive dosages were not appreciable.   On the whole the increase in NH_4-N content in these soils with irradiation followed the series,

Table 9. Effect of Gamma Irradiation on Soil Inorganic Nitrogen

Soil	Dosage (Mrad)	NH_4	NO_3	$NH_4 + NO_3$
			ppm. N	
Akaka	0.0	3	308	311
	0.5	8	307	315
	1.0	16	291	307
	3.0	24	247	271
	5.0	35	210	245
Wahiawa	0.0	21	25	46
	0.5	21	28	49
	1.0	24	28	52
	3.0	26	25	51
	5.0	28	20	48
Paaloa	0.0	98	112	210
	0.5	111	113	224
	1.0	101	111	212
	3.0	104	99	203
	5.0	104	87	191
Koko	0.0	50	97	147
	0.5	52	95	147
	1.0	57	107	164
	3.0	64	105	169
	5.0	64	108	172
Lualualei	0.0	19	9	28
	0.5	24	11	35
	1.0	26	14	40
	3.0	34	13	47
	5.0	36	12	48

Akaka, Lualualei, Koko, Wahiawa, Paaloa, in order of decreasing magnitude. Aside from an 11 ppm. increase in the Akaka soil, no difference was recorded in the NH_4-N content of the other soils irradiated at 3 and 5 Mrads.

(b). Effect on NO_3-N

Table 9 further shows a consistent NO_3-N decrease with increasing dosages in the Akaka and Paaloa soils and a slight decrease at 5 Mrads in the Wahiawa soil. A small increase was noticed in the Koko and Lualualei soils.

Discussion

The effect of varying irradiation dosages on soil N has been considered in great detail by Agarwal (1967) and it will be discussed here only briefly. The finding of this experiment on the mineralization of NH_4-N is consistent with Bowen and Cawse (1964a) who noted that the release of NH_4-N was directly related to dosages of gamma radiation.

There are three possible ways in which N may be released from soils by irradiation. First, a chemical action of irradiation could produce ammonia from nitrogenous organic compounds by a variety of processes, notably deamination of amino acids (Maxwell et al., 1954; Sharpless et al., 1955) and protein (Bennett and Garrison, 1959). Nitrogen release from the fractionation of organic molecules containing N is possible because ionization is

thought to split molecules in random locations throughout the organic fraction of a soil (Eno and Popenoe, 1963). Second, McLaren and co-workers (1957, 1962) have shown that several enzymes, including urease which produces ammonia as a decomposition product, are functional in irradiated soils. Third, some N is thought to be released from dead organisms due to the subsequent lysis of microbial cells (Bowen and Cawse, 1964b; Burgos, 1964; Cummins and McCreery, 1964; Eno and Popenoe, 1963). Relative to the theories mentioned above, the greatest release of NH_4-N in the Akaka soil could be attributed to its high organic matter content (organic carbon = 14.6%).

On the basis of their NO_3-N content following irradiation, the experimental soils can be grouped in two categories, (i) soils exhibiting NO_3 loss - Akaka, Paaloa, Wahiawa, and (ii) soils exhibiting NO_3 gain - Koko, Lualualei. Bowen and Cawse (1964b) reported that the nitrifiers in soil were greatly reduced and the nitrification in the irradiated soils was one-third that in the non-irradiated soils at two weeks and about one-half at four weeks. However, their observations were based on incubated samples. In the present experiment a consistent decrease with increasing irradiation dosages in the NO_3-N content of the Akaka, Paaloa, and Wahiawa soils was noted immediately following irradiation. In other words, there was a loss of the initial NO_3-N in these soils during irradiation. The immediate loss

cannot be attributed to reduced bacterial population. Possibly certain chemical reactions rendering NO_3-N loss are enhanced by gamma irradiation. No explanation could be furnished for a small NO_3-N gain in the Koko and Lualualei soils.

2.   Effect of Irradiation on Soil Inorganic Nitrogen Release After Periods of Incubation

Data pertaining to this aspect of gamma irradiation study are given in Table 10 and illustrated in Figs. 8, 9, and 10 for the Akaka, Wahiawa, and Lualualei soils, respectively. Negative values for NH_4- or NO_3-N indicate less N content in incubated samples than at zero time following irradiation.

(a).   Effect on the Akaka Soil

Figure 8 shows that NH_4-N release was much higher in irradiated than unirradiated Akaka soil. The rate of NH_4-N mineralization was highest for the first seven days. Irradiation at 0.5 Mrads was very effective, giving a maximum ammonification rate of 8.2 ppm. per day during the first seven days. This was followed by treatments at 1 and 3 Mrads where the rates were 7.0 and 5.9 ppm. per day, respectively, during the same period. The ammonification rate declined during subsequent incubations in all cases.

It is interesting to note from Fig. 8 that the pattern of nitrification was the reverse of the ammonification at respective dosages of gamma radiation. In other words, the maximum

Table 10. Rate of Ammonification (Amm.), Nitrification (Nit.), and Mineralization (Min.) of Nitrogen in Gamma-Irradiated Soils

Soil	Dosage (Mrad)	7			14			21			28		
		Amm.	Nit.	Min.	Amm.	Nit.	Min.	Amm.	Nit.	Min.	Amm.	Nit.	Min.
							ppm. N						
Akaka	0.0	0.3	2.9	3.2	0.0	1.9	1.9	0.2	1.9	2.1	0.1	1.8	1.9
	0.5	8.2	-5.0	3.2	6.4	-4.6	1.8	6.0	-4.0	2.0	5.4	-3.6	1.8
	1.0	7.0	-5.5	1.5	5.1	-4.2	0.9	4.4	-3.7	0.7	4.2	-3.1	1.1
	3.0	5.9	-2.4	3.5	3.5	-1.8	1.7	3.2	-1.2	2.0	2.8	-1.0	1.8
Wahiawa	0.0	0.4	0.8	1.2	0.2	0.1	0.3	0.3	0.1	0.4	0.1	0.1	0.2
	0.5	0.6	-0.4	0.2	0.3	-0.1	0.2	0.4	0.0	0.4	0.3	0.0	0.3
	1.0	0.1	-0.2	-0.1	0.2	-0.1	0.1	0.2	0.0	0.2	0.3	-0.1	0.2
	3.0	0.5	-0.4	0.1	0.4	-0.4	0.0	0.4	-0.1	0.3	0.2	-0.1	0.1
Lualualei	0.0	-2.8	3.5	0.7	-1.3	2.2	0.9	-0.8	1.8	1.0	-0.7	1.3	0.6
	0.5	0.1	3.2	3.3	0.0	2.4	2.4	-0.2	2.4	2.2	-0.3	1.9	1.6
	1.0	2.5	3.2	5.7	1.5	1.5	3.0	1.1	1.4	2.5	0.7	1.2	1.9
	3.0	2.9	0.3	3.2	2.0	0.1	2.1	1.9	0.1	2.0	1.6	0.1	1.7
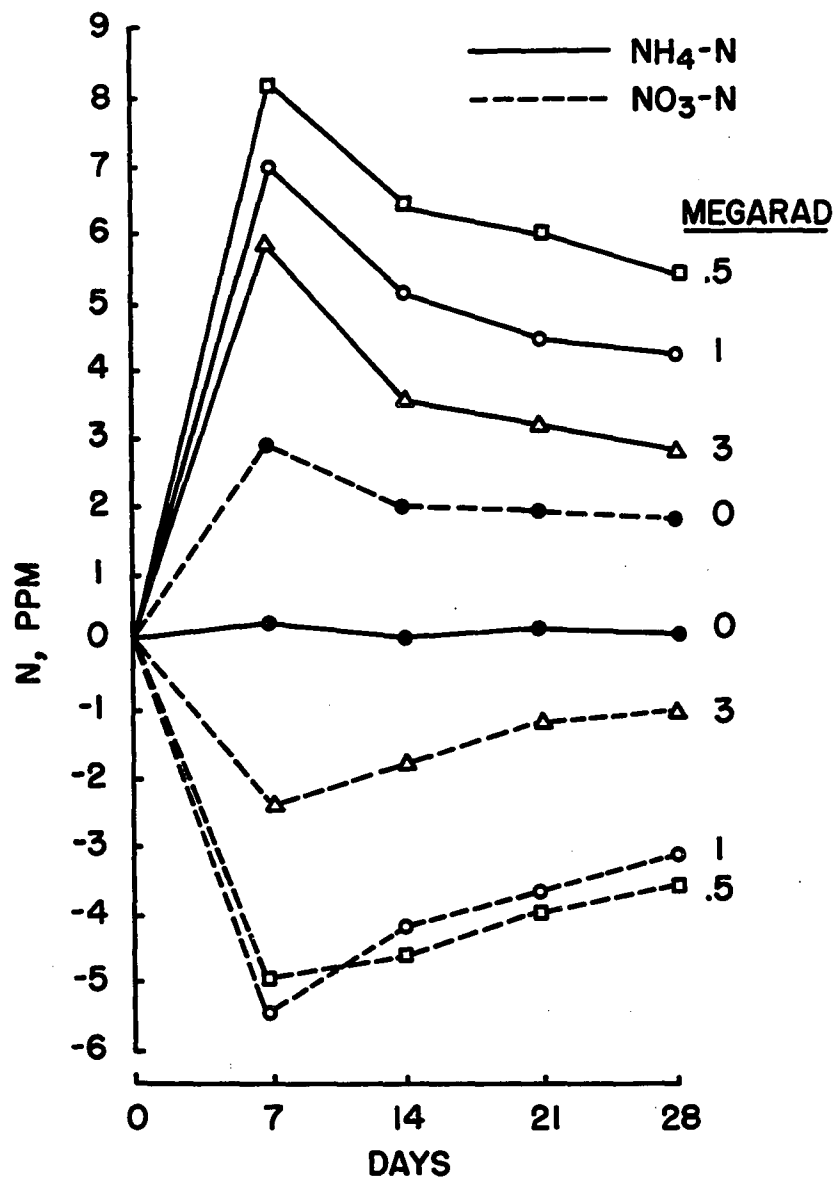
Fig. 8. Rate of Ammonium and Nitrate Release in the
Akaka Soil as Affected by Different Dosages of
Gamma Irradiation After Different Periods of Incubation.
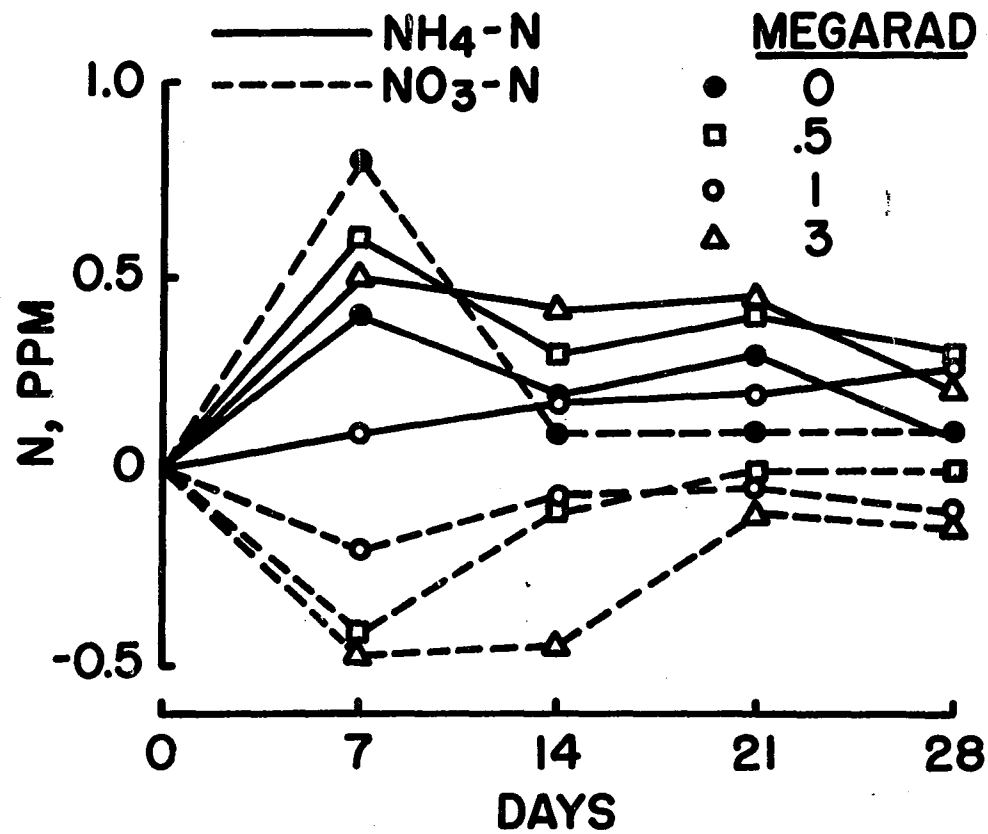
Fig. 9. Rate of Ammonium and Nitrate Release in the Wahiawa Soil
as Affected by Different Dosages of Gamma Irradiation
After Different Periods of Incubation.
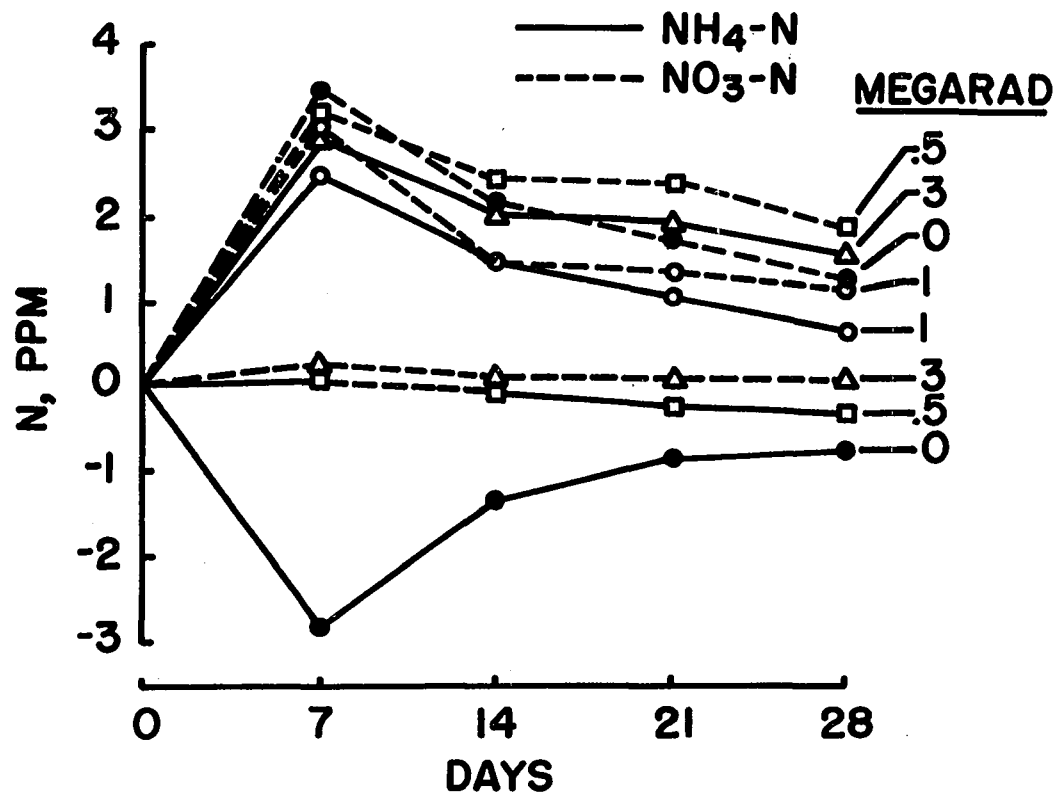
Fig. 10. Rate of Ammonium and Nitrate Release in the Lualualei Soil
as Affected by Different Dosages of Gamma Irradiation
After Different Periods of Incubation.

ammonification rate corresponded to the minimum nitrification rate. The nitrification was much higher in the control than in irradiated soil.

(b). Effect on the Wahiawa Soil

The overall magnitude of mineralized N in this soil (Fig. 9) was very low compared to that in the Akaka. The irradiated soil followed the same trend as the Akaka with few exceptions, but the rate of ammonification or nitrification was too small to draw any plausible conclusion.

(c). Effect on the Lualualei Soil

The negative values for NH_4 and positive values for NO_3 in the unirradiated soil are indicative of the high nitrifying capacity of organisms in the Lualualei soil (Fig. 10). The maximum ammonification rate during the first seven days was in samples irradiated at 3 Mrads followed by those at 1 Mrad. The nitrification rate was almost zero at the former, and a little higher than the ammonification rate at the latter dosage. Almost all released NH_4-N was nitrified in samples that were either unirradiated or irradiated at 0.5 Mrads. The latter dosage showed even a greater nitrification rate than the control. The nitrification in this soil was seriously affected at 3 Mrads.

Discussion

The maximum rate of ammonification during the first seven

days following irradiation could be attributed to the rapid ammonium release from nitrogenous organic compounds due to deamination of amino acids (Maxwell et al., 1954; Sharpless et al., 1955) and protein (Bennett and Garrison, 1959). This rate could also be due to fractionation of N-containing organic molecules (Eno and Popenoe, 1963). The most contributory source could be dead organisms that release N during their subsequent lysis (Bowen and Cawse, 1964b; Burgos, 1964; Cummins and McCreery, 1964; Eno and Popenoe, 1963). In the light of the above discussion, the high ammonification rate in the Akaka compared to the other two soils could be attributed to its high organic matter content.

The reduction in ammonification rate during successive incubations after seven days in the Akaka and Wahiawa soils (Figs. 8 and 9) was due to the corresponding increase in the nitrification rate by recovering nitrifiers.

Reduction in the native nitrate content of irradiated Akaka, Paaloa, and Wahiawa soils was pointed out in Experiment IV (1). Similar results with irradiated Akaka and Wahiawa soils were also observed in this experiment. The maximum negative values at seven days following irradiation show further that the loss of nitrate from irradiated soils continued even after several days of irradiation. Later improvement in nitrification rate may be due to the recovery of nitrifiers. Still, the magnitudes were less

than the initial NO_3-N content of these two soils. The loss of nitrate from these soils could be attributed to chemical reactions enhanced by irradiation, as mentioned earlier.

The Lualualei soil has been reported to possess a very high nitrifying capacity (Tamimi and Kanehiro, 1962). This property explains the complete nitrification of NH_4-N in unirradiated and irradiated samples at 0.5 Mrads. Cawse (1967) reported that nitrification proceeded at a fast rate in soils irradiated at 0.2 Mrads, probably due to the absence of effects on the oxidation process in non-proliferating cells of the nitrifying bacteria, rather than to increased proliferation of survivors. Greater nitrification at 0.5 Mrads than the control (Fig. 10) shows the stimulative effect of irradiation to nitrifiers in the Lualualei soil at a dosage even higher than that reported by Cawse (1967). However, this was not the case in the Akaka and Wahiawa soils. A dosage of 3 Mrads certainly inhibited nitrifiers because nitrification was almost completely arrested at this rate.

3. Recovery of Added Nitrogen from Gamma-Irradiated Soils

This experiment was undertaken to study the recovery of added nitrogen from irradiated Akaka, Wahiawa, Paaloa, Koko, and Lualualei soils. In addition, the effect of the interaction of lime and gamma irradiation on N recovery was also investigated.

(a). Gamma irradiation affecting the added N recovery

The data in Table 11 show that the added NH_4-N

was recovered in the unirradiated series except in the Lualualei clay. With irradiation, substantially decreased recoveries of 89.5% and 88.5% of the added 200 ppm. NH_4-N were obtained in the Koko and Lualualei soils, respectively. There was no corresponding change in the NO_3-N status (Appendix Table II) in all these soils following irradiation. This means that there was no nitrification of added NH_4-N during the treatment.

Table 11. Net Recovery of Added Nitrogen (200 ppm. N) from Five Hawaiian Soils as Affected by Gamma Irradiation

| Soil | Recovery of added: | | | |
| | NH_4-N (ppm.) | | NO_3-N (ppm.) | |
	Unirradiated	Irradiated	Unirradiated	Irradiated
Akaka	200	197	193	163
Wahiawa	200	194	200	192
Paaloa	200	199	200	181
Koko	200	179	200	155
Lualualei	192	177	200	119

Recovery of added NO_3-N was practically complete in all unirradiated soils. A decrease in the native NO_3-N of the Akaka, Wahiawa, and Paaloa soils with increasing dosages of gamma radiation was observed in Experiment IV (1). The data presented in Table 11 show that such irradiation treatment is responsible for decreased recovery of added nitrate as well. Like the NH_4-N recovery discussed earlier, the recovery was lowest in the Lualualei (59.5%), followed by that in Koko (77.5%), Akaka (81.5%), Paaloa (90.5%), and Wahiawa (96.0%).

(b). Interaction of gamma irradiation and lime affecting the added N recovery

In the previous discussion it was pointed out that the added NH_4-N recovery in irradiated Koko and Lualualei (high pH soils) decreased appreciably. To test if the soil pH is involved in affecting NH_4-N recovery, three acid soils, Akaka, Wahiawa, and Paaloa, were limed with $Ca(OH)_2$ together with the addition of 200 ppm. N before irradiation with 3 Mrads. The effect of lime on the recovery of NO_3-N from irradiated soils was also investigated. The data are included in Table 12.

The NH_4-N results are presented in Fig. 11. The heavy line indicates 100% recovery of added NH_4-N in unirradiated soils, although recovery decreased slightly in the Paaloa soil. Following irradiation the Akaka showed a steady decrease in recovery with increasing amounts of lime after the 2-ton rate. In the Paaloa soil recovery decreased only with the 10-ton rate. The Wahiawa soil showed the greatest decrease, recovery being only 84.4% at the 10-ton rate.

Similarly, the heavy line in Fig. 12 shows nitrate recovery in the three unirradiated soils. Aside from a decrease of 11 ppm. for the 20-ton rate in the Akaka soil, recovery was 100% for all unirradiated soils. Contrary to the foregoing ammonium recovery pattern in irradiated soils, nitrate recovery increased consistently with increasing liming rates in the irradiated

Table 12. Effect of Lime on the Net Recovery
of Added Nitrogen (200 ppm. N) from Three Hawaiian Soils
as Affected by Gamma Irradiation

Soil	Amount of Lime (T/A)	Recovery of added:			
		NH_4-N (ppm.)		NO_3-N (ppm.)	
		Unirradiated	Irradiated	Unirradiated	Irradiated
Akaka	0	200	194	193	163
	2	200	200	200	190
	10	200	192	200	192
	20	— 200	186	189	199
Wahiawa	0	200	194	200	192
	2	200	193	200	197
	5	200	188	200	198
	10	200	169	200	198
Paaloa	0	200	199	200	181
	2	200	200	200	192
	5	200	200	200	200
	10	195	187	200	200
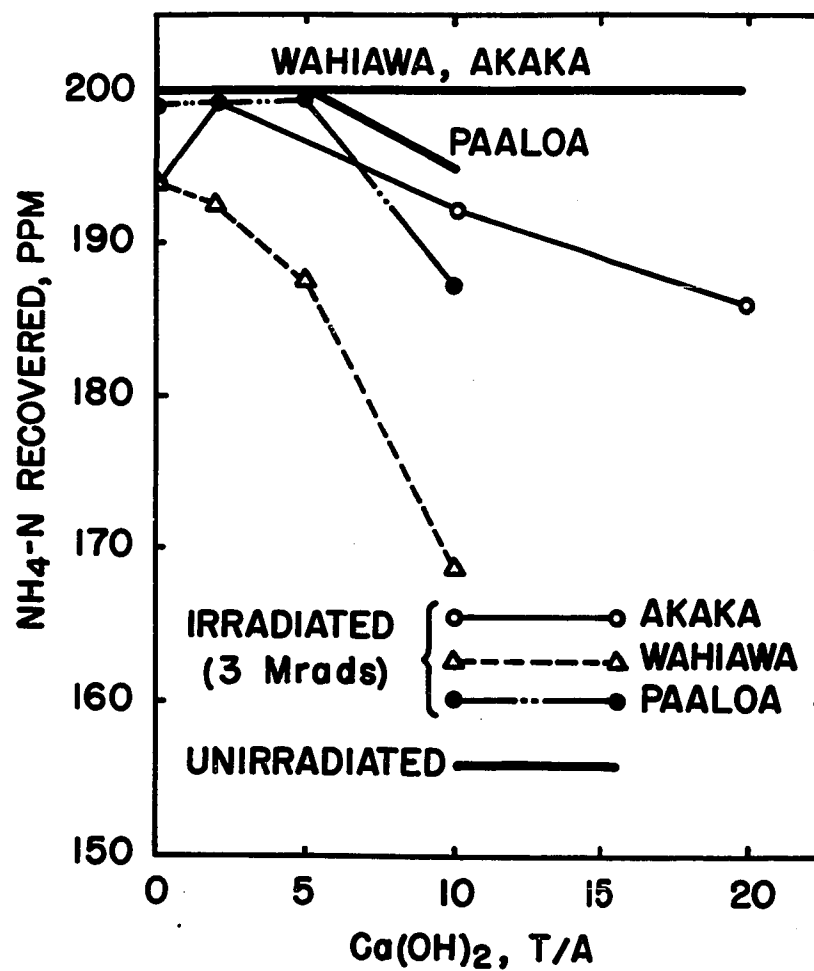
Fig. 11. Interaction of Gamma Irradiation and Lime
in Relation to the Recovery
of Added NH$_4$-N (200 ppm.) from Soils.
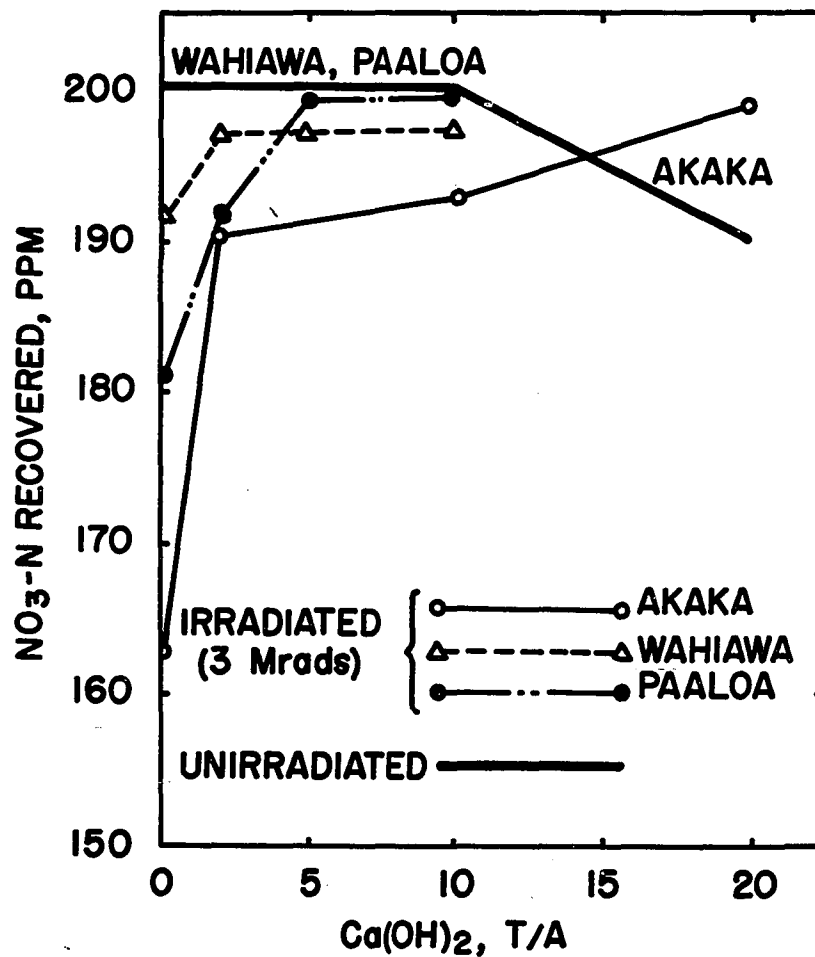
Fig. 12. Interaction of Gamma Irradiation and Lime
in Relation to the Recovery
of Added NO_3-N (200 ppm.) from Soils.

Akaka and Paaloa soils. The effect of lime was very small in the Wahiawa soil because recovery was already high with no lime.

Discussion

The loss of added NH_4-N in the Koko and Lualualei soils could be partly attributed to fixation of NH_4 ions by the clay fraction. The Lualualei soil is dominantly montmorillonite, while the Koko contains some montmorillonite (Table 1). The loss could be also partly due to volatilization to NH_3 gas at the relatively high pH of these two soils. Ammonia loss of added nitrogen from surfaces of neutral or alkaline (Jewitt, 1942; Martin and Chapman, 1951) and calcareous soil (Gasser, 1964; Larsen and Gunary, 1962; Terman and Hunt, 1964) have been reported. The extent to which the mineralogy and/or pH per se were responsible for such losses should be indicated by the results on the unirradiated samples as well. From the data of Table 11, it is apparent that the large loss of NH_4-N is only from irradiated Koko and Lualualei soils. The high pH, therefore, can be responsible for added NH_4-N loss in this experiment only in conjunction with gamma irradiation and not alone. The liming part of the present investigation, which will be considered in a subsequent section, further substantiates the above conclusion.

Davis et al. (1956) observed that the microbial population decreased rapidly with increasing irradiation dosages up to 10 kiloroentgens (Kr.), then leveled off at 10 to 20 Kr. and continued to decrease steadily at dosages greater than 20 Kr. Later, McLaren et al. (1962) reported that at a dosage of 2×10^5 roentgens the microbial population was practically eliminated. Thus, the soil microbial population may be killed at the 3 Mrads[6] used in these experiments, and biological denitrification presumably will be completely arrested. Therefore, the loss of added nitrate in irradiated samples is through avenues other than biological denitrification. On the basis of results of Experiment IV (1), the experimental soils were placed in two categories, (i) soils exhibiting loss of native NO_3 - Akaka, Paaloa, Wahiawa, and (ii) soils exhibiting gain of NO_3 - Koko, Lualualei. From Table 1, it can be seen that the former group of soils has a lower pH while the latter has higher pH. The decreased recovery of added NO_3 from these five irradiated soils shows that the soil pH is presumably not involved in increasing native or added nitrate loss. As mentioned earlier, it is possible that chemical reactions enhanced by gamma irradiation are responsible.

Substantially decreased recovery of added NH_4-N by liming was noted in the Wahiawa soil. The appreciable effect of liming

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[6]One rad is approximately equal to one roentgen.

in this soil may be due to its poor buffering capacity; the increase in pH with successive additions of lime was presumably enough to effect gaseous loss in the irradiated soil. There was no corresponding increase in the amount of nitrate in these soils to an appreciable extent to account for all the loss (Appendix Table III). Evidently the loss of added NH_4-N from irradiated soils is due in part to the high pH of the soils as discussed in the previous section.

According to the data in Table 11, the losses of 22.5% and 40.5% in nitrate recovery were noted in irradiated Koko and Lualualei soils, although their pH is above neutral. The increased NO_3-N recovery in irradiated Akaka, Wahiawa, and Paaloa soils, therefore, cannot be attributed to the effect of increasing pH due to liming. Presumably gaseous or other losses of added nitrate due to certain chemical reactions in irradiated soils are inhibited in the presence of lime.

Experiment V. Nitrate Adsorption in Soils as Affected by Concentration and pH of the Electrolyte Solution

It was felt necessary to evaluate the experimental soils with respect to their capacities to retain NO_3 mineralized under different storage and imposed treatment conditions in the laboratory. With this intent, the nitrate adsorption as a function of concentration and pH of the electrolyte solution was studied in the Akaka

and Wahiawa soils.

Discussions presented herein are based entirely on the following considerations:

The "adsorbed nitrate" is that amount of nitrate retained by a soil at "apparent equilibrium" which is extractable with a replacing anion such as Cl or SO_4. The "apparent equilibrium" refers to the situation when the concentration of NO_3 in a supernatant is the same as that in the input solution; at this stage the soil is assumed to be in equilibrium with the electrolyte.

1. Adsorption of Nitrate as a Function of the Electrolyte Concentration

The behavior of the Akaka and Wahiawa soils was quite similar as far as adsorption of NO_3 was concerned. A highly significant correlation existed between the electrolyte concentration and the amount of NO_3 adsorbed by these two soils (Fig. 13). The positive adsorption was very small at low concentration and increased consistently with each increment in the electrolyte concentration (Table 13). The magnitude of adsorption was comparatively smaller in the Wahiawa than in the Akaka soil.

From the data presented in Table 13, it is also evident that the amount of adsorbed nitrate is higher when SO_4 rather than Cl was used as the replacing anion. It was observed that the nitrate adsorption in the experimental soils can be described approximately by the Freundlich type of isotherm (Fig. 14).
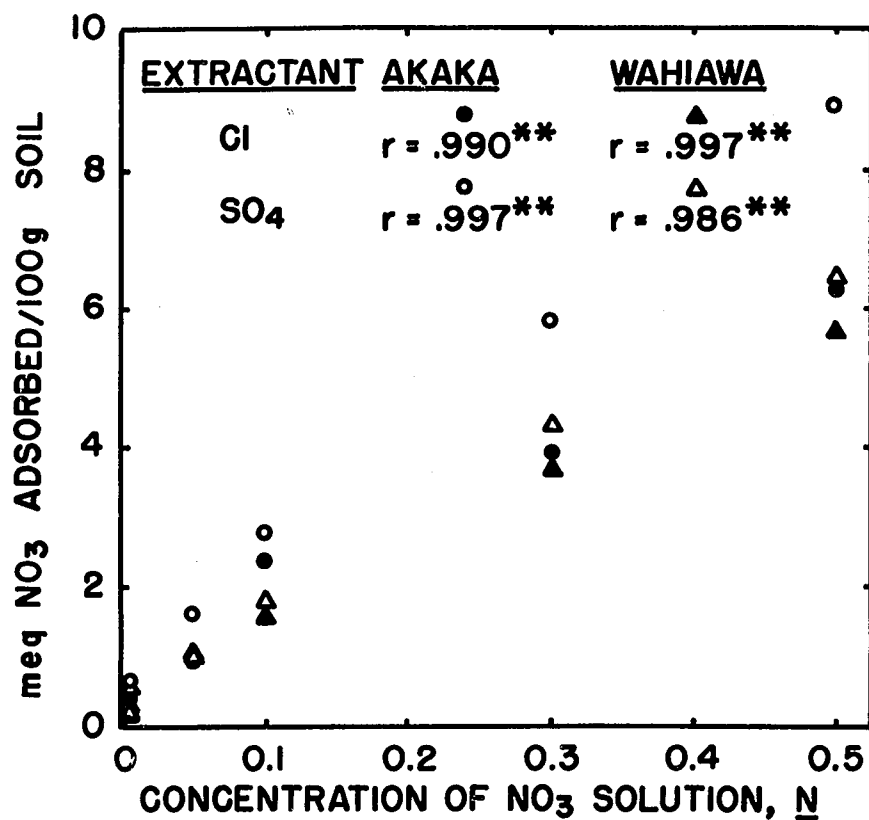
Fig. 13. Scattered Diagram Showing Correlation
Between the Electrolyte Concentration
and NO_3 Adsorbed in the Akaka and Wahiawa Soils.

Table 13. Adsorption of Nitrate as a Function
of Electrolyte Concentration

Normality of KNO_3	Soil used:			
	Akaka		Wahiawa	
	KCl Extractable	K_2SO_4 Extractable	KCl Extractable	K_2SO_4 Extractable
	me. NO_3/100 g. soil			
0.00	0.00	0.00	0.00	0.00
0.005	0.45	0.56	0.12	0.18
0.01	0.60	0.62	0.35	0.56
0.05	1.02	1.63	1.05	1.04
0.10	2.40	2.77	1.60	1.86
0.30	3.87	5.84	3.70	4.31
0.50	6.27	8.90	5.65	6.42
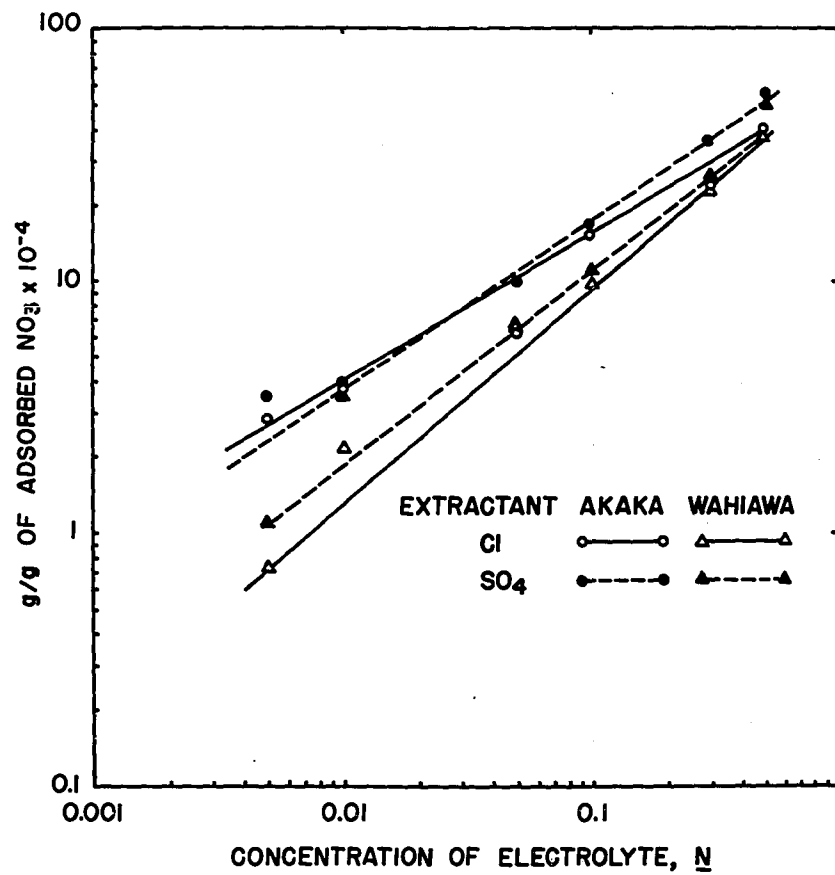
Fig. 14. Linear Form of Freundlich Isotherm for NO_3 Adsorption in the Akaka and Wahiawa Soils.

2. Adsorption of Nitrate as a Function of the pH of the Electrolyte Solution

Adsorption of nitrate as a function of pHs of 0.1 $\underline{N}$ KNO$_3$ solution was studied in the same two soils. The data are given in Table 14.

Table 14. Adsorption of Nitrate as a Function
of the pH of Electrolyte Solution

pH of KNO$_3$	Soil used:			
	Akaka		Wahiawa	
	KCl Extractable	K$_2$SO$_4$ Extractable	KCl Extractable	K$_2$SO$_4$ Extractable
	me. NO$_3$/100 g. soil			
3.5	3.93	2.77	2.25	2.10
5.0	2.27	2.56	1.30	1.73
7.0	1.67	2.31	1.22	1.54
9.0	1.28	1.91	0.90	1.23

Both soils exhibited the same trend of decreasing positive adsorption of nitrate with increasing pH values. The magnitude, however, was greater in the Akaka than in the Wahiawa soil. Some adsorption was noted even at pH above 7. As mentioned earlier, at any pH the magnitude of adsorbed nitrate was higher when SO$_4$ rather than Cl was replacing NO$_3$ except at pH 3.5 where it was the reverse.

Discussion

As the electrolyte concentration decreases, the thickness of the diffuse ion layer increases and the partial neutralization of

positively charged sites by negatively charged sites causes a decrease in the magnitude of the anion adsorbed (Bolt and Warkentin, 1956, 1958). A similar interpretation has been given by Russell (1963) who attributed the neutralization of positive charges at low concentrations to interpenetration of double layers around positive and negative spots.

The trend of increased NO_3 adsorption with increasing concentration is in agreement with the findings of Japanese workers (Iimura, 1961; Wada and Ataka, 1958). They reported a similar trend for Cl adsorption in volcanic ash soils. The greater adsorption in the Akaka rather than Wahiawa soil can be attributed to their differences in mineralogy. The amorphous Akaka soil containing high amounts of organic matter, allophane, and hydrated iron and aluminum oxides has more positive sites for nitrate adsorption than the kaolinitic Wahiawa soil. The concentration-dependent nitrate adsorption is presumable due to electrostatic (coulombic) attraction between NO_3 ions and positively charged sites as well as to van der Waal forces. Some adsorption at low concentrations in these two soils could be due to insufficiency of the electrolyte concentration to compress the double layer to prevent interpenetration or neutralization of positively charged sites responsible for anion adsorption by negatively charged sites. The adsorption at lower electrolyte concentrations may be more of a van der Waal type than electrostatic.

The finding that the amount of adsorbed nitrate was higher when SO_4 rather than Cl was used as replacing anion is not surprising because a divalent ion is a better replacer than a monovalent one from the surfaces of exchanger complex.

The development of pH-dependent positive charges commonly occurs through the dissociation of OH^-, probably from Al-OH groups (Wada and Ataka, 1958). However, Schofield (1949) and Thomas and Swoboda (1963) reported that positive charges developed at low pH values belong to ferric oxide rather than to alumina. The dissociation of OH^- groups would be favored with the rise in soil acidity due to suppressed activity of OH^- ions in solution. The converse is true with rise in pH where negative charges develop probably through the dissociation of H^+ from Si-OH groups (Schofield, 1949; Wada and Ataka, 1958). Other investigators (Coleman and Thomas, 1964; Schwertmann and Jackson, 1964; Volk and Jackson, 1964) reported that the major source of the pH-dependent negative charge is the layer silicate-sesquioxide complex. Although the Wahiawa soil contains kaolin minerals which are reported to develop net positive charge under acidic conditions (Schofield and Samson, 1953, 1954), the positive adsorption is proportionately more in the allophanic Akaka soil. The Akaka soil has a comparatively greater number of reactive groups than the Wahiawa soil in the allophane and hydrated ion and aluminum oxide fractions which give rise to

positive adsorption sites. This means that the allophane and hydrated oxides of iron and aluminum are more responsible for anion adsorption in the Hawaiian soils than are kaolin minerals.

From the foregoing discussions it can be deduced that while the concentration-dependent NO_3 adsorption is due to electrostatic and van der Waal forces, the pH-dependent adsorption is largely due to electrostatic forces.

It is pertinent to mention that while discussing the anion adsorption as a function of pH of the electrolyte solution, the competition between anions in question and those added through solution used to adjust the pH should not be overlooked. These anions may compete for the exchange sites and may reduce the adsorption of the anion in question.

SUMMARY AND CONCLUSIONS

Studies on nitrogen transformation and nitrate adsorption were conducted with Hawaiian soils belonging to the Akaka, Wahiawa, Paaloa, Koko, and Lualualei series.

There was no definite or conclusive trend of NH_4- or NO_3-N accumulation with time in the Akaka (virgin), Akaka (cultivated), Wahiawa "A", and Wahiawa "B" soils in situ. The magnitude of available N was higher in the latter two than the former two soils. However, under laboratory conditions, both NH_4- and NO_3-N were affected. The Akaka (virgin), Akaka (cultivated), and Wahiawa "A", stored in polyethylene bags at room temperature, showed a substantial increase in NO_3-N with time but practically no change in NH_4-N. Little or no change in NH_4-N was due to the fact that the released NH_4-N was rapidly nitrified during storage. With respect to their available N content, these soils can be arranged in the series, Wahiawa "A" > Akaka (virgin) > Akaka (cultivated) in order of decreasing magnitudes of N release. Contrary to the results obtained at room temperature, when two of the above soils [Akaka (virgin) and Wahiawa "A"] were oven dried at 90°C NH_4-N increased with time but NO_3-N remained unchanged during the entire period. Possibly, increased NH_4-N resulted from the splitting of ammonium from the proteinaceous parts of organic matter. The higher amount of

mineralized NH_4-N in the Akaka (virgin) than in the Wahiawa "A" was due to the high organic matter content of the former soil.

The decreased pH of the Akaka (virgin) with time at room temperature was attributed to the release of acids from decomposing organic matter. The increased pH of this soil on oven drying was probably due to inaccessibility of H^+ ions since the Akaka soil dries irreversibly. For similar reasons, the pH of the oven-dried Wahiawa "A" was slightly higher than that stored at room temperature.

The Akaka soil was treated with chlorides of Na, K, Ca, Mg, Al, and Fe, while the Wahiawa soil was treated with chlorides of K, Ca, and Al. The NH_4-N mineralization was generally a direct function of salt concentration and length of incubation. Released NH_4-N was considerably higher in the Akaka than in the Wahiawa soil. NH_4-N release probably resulted from microbial cell breakdown due to increased osmotic pressure and/or chemical processes. Presumably, once the NH_4 ions were released from soil organo-inorganic complexes, the subsequent exchange reactions between cations in the surrounding solution and NH_4 ions on soil surface was mainly involved with bringing NH_4 ions in the soil solution. The exchange reaction was dependent to a great extent on the nature, valence, and activity of cations in the soil solution as well as the length of

reaction. A consideration of the overall effect of cations on NH_4-N release in the two soils led to the series, Al > Fe > Ca > Mg > K > Na, in order of decreasing NH_4 replacing power. However, this series was true only to a concentration of 0.1 $\underline{M}$. Beyond this, Al and Fe ions were ineffective probably due to complex formation in the soil. The added salts had little effect on the NO_3-N content of the Akaka and Wahiawa soils, and no definite trend was noticed among concentrations, salts, and periods.

To further study changes in soil inorganic N, the experimental soils were subjected to varying dosages of gamma radiation. Increasing dosages of irradiation generally increased the NH_4-N mineralization. On the whole the increase in NH_4-N content in these soils with irradiation followed the series, Akaka > Lualualei > Koko > Wahiawa > Paaloa, in order of decreasing magnitude. The NO_3-N decreased with increasing irradiation dosages in the Akaka, Paaloa, and Wahiawa, and increased slightly in the Koko and Lualualei soils. In another experiment irradiated Akaka, Wahiawa, and Lualualei soils were incubated for different periods. The rate of NH_4-N mineralization in the Akaka soil was highest for the first seven days and declined during subsequent incubation periods. The pattern of nitrification was the reverse of ammonification at respective irradiation dosages. The irradiated Wahiawa soil followed the same trend as the Akaka but the rates of ammonification and nitrification were very slow. The Akaka and

Wahiawa irradiated at 0.5 Mrads and Lualualei at 3 Mrads exhibited maximum ammonification rate. The maximum rate during the first seven days following irradiation was attributed to the rapid NH_4-N release from nitrogenous organic compounds and dead organisms. The loss of NO_3-N in some soils was attributed to certain chemical reactions enhanced by irradiation.

The recoveries of added NH_4- and NO_3-N from irradiated soils were also investigated. With irradiation, substantially decreased recoveries of 89.5% and 88.5% of the added 200 ppm. NH_4-N were obtained in the Koko and Lualualei soils, respectively. As in the NH_4-N recovery, the NO_3-N recovery was lowest in the Lualualei (59.5%), followed by that in Koko (77.5%), Akaka (81.5%), Paaloa (90.5%), and Wahiawa (96.0%). Liming of the three acid soils, Akaka, Paaloa, and Wahiawa, decreased NH_4-N and increased NO_3-N recoveries in the irradiated soils. It was speculated that gaseous or other losses of added nitrate due to certain chemical reactions in irradiated soils are inhibited in the presence of lime.

The adsorption of nitrate was studied with the Akaka and Wahiawa soils. Adsorption increased with increasing concentration and decreasing pH of the electrolyte solution. The magnitude of adsorbed NO_3 was higher in the amorphous Akaka than in the kaolinitic Wahiawa soil. Sulfate was a better extractant of NO_3 than chloride. It was deduced that while the concentration-

dependent NO_3 adsorption is due to electrostatic and van der Waal forces, the pH-dependent adsorption is largely due to electrostatic forces. Nitrate adsorption followed the Freundlich type of isotherm.

The results obtained in the storage and oven-drying experiments suggest that soil samples sent to soil testing laboratories for the determination of available N status and for making fertilizer recommendations should be analyzed immediately. Apparently, storage or drying changes the NH_4- and NO_3-N status of soils.

Salts which may occur in or are applied to soils in various operations may have a significant influence on N availability to agronomic crops. Results on gamma irradiation are of academic interest at present.

Retension of mineralized or applied NO_3 in a soil is an important practical consideration in crop husbandry. Results show that the allophanic Hawaiian soils containing large amounts of organic matter have greater NO_3 adsorption capacity than kaolinitic soils.

Appendix Table I
Effect of Chloride Salts on the Release of Available (NH4 + NO3) Nitrogen in the Akaka and Wahiawa Soils

Salt	Molar Concentration	Osmotic Pressure (atm.)	Akaka soil 7	14	21	28	Wahiawa soil 7	14	21	28
						ppm. N				
NaCl	0.001	0.05	5	22	20	19				
	0.01	0.49	19	45	52	48				
	0.10	4.92	39	74	80	92				
	1.00	49 20	72	156	164	182				
KCl	0.001	0 05	3	20	12	13	3	3	5	-3
	0.01	0.49	18	47	47	55	2	5	7	-5
	0.10	4.92	64	98	117	129	-3	16	28	2
	1.00	49.20	104	160	231	253	-4	17	20	6
CaCl$_2$	0.001	0.07	8	9	19	11	-2	7	11	-6
	0.01	0.74	26	49	66	68	-6	3	3	-2
	0.10	7.38	78	111	134	150	-5	9	6	-2
	1.00	73 80	30	100	178	205	0	29	6	-2
MgCl$_2 \cdot$6H$_2$O	0.001	0.07	8	16	30	22				
	0.01	0.74	24	56	69	71				
	0.10	7.38	65	99	119	136				
	1.00	73.80	30	87	140	165				
AlCl$_3 \cdot$6H$_2$O	0.001	0.09	20	18	42	53	-10	5	1	-7
	0.01	0.98	50	84	98	109	-3	5	-3	1
	0.10	9.84	157	229	247	269	-4	13	9	12
	1.00	98.40	15	11	9	5	-1	-13	-11	-19

Appendix Table I (Continued)
Effect of Chloride Salts on the Release of Available $(NH_4 + NO_3)$ Nitrogen
in the Akaka and Wahiawa Soils

Salt	Molar Concentration	Osmotic Pressure (atm.)	Days of incubation							
			Akaka soil				Wahiawa soil			
			7	14	21	28	7	14	21	28
			ppm. N							
FeCl$_3$	0.001	0.09	16	21	29	15				
	0.01	0.98	57	70	96	75				
	0.10	9.84	103	185	226	272				
	1.00	98.40	4	0	40	23				

Appendix Table II
Changes in Available N in Gamma Irradiated Soils
Treated With 200 ppm. N

Soil	Treatment	Available N		
		NH_4	NO_3	$NH_4 + NO_3$
			ppm. N	
Akaka	Control	18	249	267
	NH_4 added	211	250	461
	NO_3 added	18	343	361
Wahiawa	Control	28	24	52
	NH_4 added	222	23	245
	NO_3 added	26	216	242
Paaloa	Control	116	102	218
	NH_4 added	315	102	417
	NO_3 added	110	283	393
Koko	Control	59	114	173
	NH_4 added	235	113	348
	NO_3 added	62	257	319
Lualualei	Control	30	14	44
	NH_4 added	206	13	219
	NO_3 added	28	113	161

Appendix Table III
Changes in Available N in Gamma Irradiated Soils
Treated With Lime and 200 ppm. NH$_4$-N

Soil	Treatment	Available N		
		NH$_4$	NO$_3$	NH$_4$ + NO$_3$
		ppm. N		
Akaka	0 T/A lime	18	249	267
	0 T/A lime + NH$_4$	211	250	461
	2 T/A lime	19	255	274
	2 T/A lime + NH$_4$	221	256	477
	10 T/A lime	29	283	312
	10 T/A lime + NH$_4$	221	286	507
	20 T/A lime	32	308	340
	20 T/A lime + NH$_4$	218	310	528
Wahiawa	0 T/A lime	28	24	52
	0 T/A lime + NH$_4$	222	23	245
	2 T/A lime	29	28	57
	2 T/A lime + NH$_4$	222	27	249
	5 T/A lime	29	28	57
	5 T/A lime + NH$_4$	217	30	247
	10 T/A lime	31	30	61
	10 T/A lime + NH$_4$	119	30	249
Paaloa	0 T/A lime	116	102	218
	0 T/A lime + NH$_4$	315	102	417
	2 T/A lime	112	107	219
	2 T/A lime + NH$_4$	317	109	426
	5 T/A lime	112	112	224
	5 T/A lime + NH$_4$	314	114	428
	10 T/A lime	105	117	222
	10 T/A lime + NH$_4$	292	118	410

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