

SOIL NITROGEN MINERALIZATION
AS AFFECTED BY DRYING,
LIMING AND SEWAGE SLUDGE ADDITION

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By

Nazir Ahmad

Dissertation Committee:

Yoshinori Kanehiro, Chairman
Robert L. Fox
Chung S. Tang
James A. Silva
Russell S. Yost

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

DISSERTATION COMMITTEE

Yphim Karch

Chairman

Robert L. Fox

Chung-Shik Lee

James A. Silva

Russell Yost

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GENERAL ABSTRACT

This investigation was undertaken to determine the effect of drying and liming on soil nitrogen mineralization, to measure in N-supplying power of soils and to assess the effect of soil type on mineralization of nitrogen from sewage sludge. Laboratory, greenhouse and field experiments were conducted on a number of soils from the Hawaiian Islands.

Air and oven-drying for 12 weeks increased the amount of mineral-N in five soils studied. Oven-drying released about 10-40 times more N than air-drying. Most of the mineral-N was released as $\text{NH}_4\text{-N}$. Cultivation of undisturbed soil in the field resulted in more N being mineralized than from soil which was left undisturbed. Dry matter yield of corn was also affected when grown on air and oven-dried soils. Air-drying was more beneficial to corn yield in the Kaiwiki (Typic Hydrandepts). However, oven-drying had harmful effects on the growth of corn in this soil. Air-drying had little effect on the growth of corn in the Maile 7 (Hydric Dystrendept) soil. But in the oven-dried soil plants were much more healthy and more dry matter yield of corn was produced, compared to the control.

The effect of lime application on N mineralization was studied on the Paaloa (Humoxic Tropohumult) and Wahiawa (Typic Eustrustox) soils in the field. The Paaloa soil had

never previously been cultivated or limed. The Wahiawa soil had been limed twice before. Liming at 2 and 4 tons/ha resulted in greater N mineralization than the control in the Paaloa soil. However, liming from a pH of 4.7 to 7.1 had little effect on the amount of N mineralized in the Wahiawa soil.

An evaluation of the N supplying power of seven soils was made. Two chemical extraction methods as well as aerobic incubation procedures at 25°C and 35°C were used to obtain an index of N availability. Nitrogen mineralized was correlated with N-uptake by corn in the greenhouse. Aerobic incubation at 25°C was significantly correlated ($r=0.96$) with the N-uptake by corn. Incubation at 35°C was also highly correlated ($r=0.92$). The chemical methods employed were, by comparison, unsuitable in evaluating the N status of these soils.

The amount of N mineralized from anaerobically-dried sewage sludge when mixed with two soils was very small, and depended on the soil type and the sludge rate. In the Waimea soil (Typic Eutrandept), 3-4% more N was mineralized than in the Wahiawa soil (Humoxic Tropohumult) when the sludge was applied at 22.4 and 44.8 tons/ha rates. N mineralization potential (N_0) did not adequately predict the actual N mineralized from the soil: sludge mixtures. A two-function equation with two values of N_0 may be necessary to adequately describe N mineralization in sludge

amended soil, because of two different N mineralization rates. One function describes the release of N from a readily-mineralizable fraction in early incubation (0-4 weeks), while the other function describes the later release of N from the more stable fraction in sewage sludge.

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GENERAL INTRODUCTION

Nitrogen (N) is an essential element required by all plants for growth. Although it is present in large quantities in the biosphere, only a small amount is in forms which can be directly utilized by plants. Nitrogen can be supplied to plants from the natural processes of N fixation from soil N mineralization and from rainwater, and from industrial process, such as the manufacture of nitrogenous fertilizers. In the past, relatively inexpensive and abundant supplies of fertilizers were available, so people in developed countries tended to use them indiscriminately. This gave rise in some instances to higher nitrate levels in underground waters. But as the prices of raw materials needed for fertilizer manufacture are increasing and people are showing more concern about the environment, interest is growing in ways to make use of the natural processes of supplying N.

Of the many natural sources, soil nitrogen is one which could contribute towards the N requirement of plants. In soil, most of the N exists in organic forms. The organic forms are subject to transformation to inorganic forms through the microbially-mediated process of mineralization. Similarly, inorganic N may be transformed to organic N by immobilization, which is also a result of microbial action. The accumulation of mineral nitrogen in soil is a net

effect of these opposing processes which occur simultaneously. Net changes occur only when one exceeds the other. The two processes have been collectively referred to as the biological N turnover, or interchange (Hiltbold, et al., 1951; Bartholomew, 1956; Jansson, 1958). Before soil organic N is available to the plant, it usually must be converted to ammonium, nitrite and nitrate forms. Since these conversions are microbial, they are affected by factors such as aeration, pH, presence of essential nutrients, temperature, etc. Factors such as desiccation reduce the activity of the nitrifying bacteria more than that of the ammonifiers (Lawrence, 1956), resulting in an accumulation of NH_4 in drought or dry season. Many of these factors are not independent. A change in pH due to the addition of lime in acid soils might cause a burst of microbial activity which may release inorganic N in soil. Similarly, when added to different soils, the addition of materials like sewage sludge may not release the same amount of N. If we want to make better use of soil N for plants, the effect of these factors must be better understood than it is today.

Soil scientists are also faced with the problem of assessing the nitrogen-supplying power of soils by laboratory examination. The nitrogen system within soil is so dynamic that various forms of N change, even as we try to measure them. The most direct measure of plant-available

N supplied by the soil is the analysis of N content of a plant grown without N fertilizer (Beckwith, 1963).

Less direct methods of estimating the ability of a soil to supply N involve chemical and biological tests in the laboratory. Most of these methods have been tried for temperate soils, but their performance in tropical soils is even more in question. The idea is to find a method which produces consistent results and can be correlated with N uptake by plants grown on tropical soils. A method which will provide significant correlation with N uptake by plants could be used to make an assessment of the amount of N that will be provided by the soil during a growing season of the crop.

Since organic N is a major source of available N for plant use, this study was undertaken with the following four objectives:

1. Study the effect of air-drying and oven-drying on N mineralization in high organic matter soils in the laboratory and obtain preliminary information in the field;
2. Determine the effect of lime on N mineralization in soils of varying organic matter content;
3. Assess the N-supplying power of soil by incubation and chemical methods; and
4. Measure N mineralization of sewage sludge as affected by sludge rate and type of soil.

Each chapter will treat one of the above objectives.

CHAPTER ONE

EFFECT OF DRYING ON,
SOIL NITROGEN MINERALIZATION

ABSTRACT

Laboratory experiments were conducted to determine the effect of air and oven-drying on nitrogen mineralization and its availability to plants. Oven-drying released about 10-40 times more N than air-drying. Most of the mineral-N was released as $\text{NH}_4\text{-N}$.

Cultivating undisturbed soil in field, mineralized more N when compared with the undisturbed soil.

Dry matter yield of corn was also affected, when grown on air and oven-dried soils. Air-drying was more beneficial to corn yield in the Kaiwiki soil (Typic Hydrandepts). However oven-drying had harmful effects on the growth of corn in this soil. Air-drying had little effect on the growth of corn in the Maile 7 (Hydric Dystrandept) soil. But in the oven-dried soil plants were much more healthy and more dry matter yield of corn was produced, compared to the control.

Effect of Drying on Soil Nitrogen Mineralization

INTRODUCTION

As soils dry they undergo a variety of physical, chemical and biological changes. Drying leads to accelerated decomposition of organic matter (Birch, 1958; Chase and Gray, 1957; Cooke and Cunningham, 1958; Stevenson, 1956), which may in turn affect the supply of soil nitrogen. Various investigators have shown that ammonia is liberated from soil organic matter upon drying of soils (Cairns, 1963; Jenkinson, 1966; Solulides and Allison, 1961; Melo and Suzuki, 1976). Birch (1958, 1959, 1960) found a sharp increase in N mineralization after three months of storage at 35°C in several East African soils, which varied in carbon content from 1 to 7% with pH values ranging from 5.8 to 6.4. The amount of N mineralized was greater the longer the soil was kept in an air-dry state, and the higher the temperature at which the soil was dried. He attributed this increased N mineralization to an enlargement of the surface exposed due to fragmentation of organic gels upon drying. He also suggested that enhanced N mineralization may occur as: (a) a result of the high microbial activity associated with a freshly-developing population; and (b) a result of the decomposition of dead micro-organisms killed during the drying.

Cooke and Cunningham (1958) likewise reported a substantial increase in the amount of N mineralized because of air-drying. They attributed this increase to the shattering of soil granules and exposure of new surfaces to bacterial action.

Heating at higher temperatures enhances N mineralization (Cairns, 1963; Birch, 1959; Birch and Friend, 1956). Broadbent, et al. (1964) noted that drying at 100°C and rewetting stimulated N mineralization in both allophanic and non-allophanic soils of New Zealand. Schreven (1967, 1968) incubated calcareous sandy loam soil at 105°C and reported increased N mineralization of humus. He concluded that most of the mineral N produced by the end of the experiment resulted from drying, and not from biological activity. In an effort to determine the effect of room temperature and oven-drying on available N content, Singh and Kanehiro (1970) reported that long-term storage of Akaka (Typic Hydrandept) and Wahiawa (Tropeptic Eutruxtox) soils in an oven at 90°C increased $\text{NH}_4\text{-N}$. The amount of N released was several times higher in the Akaka than in the Wahiawa soil. They associated this higher $\text{NH}_4\text{-N}$ release to the higher organic matter in the Akaka (14.6%) compared to the Wahiawa (1.4%) and speculated that $\text{NH}_4\text{-N}$ came from the splitting of NH_4 from N-bearing organic compounds, especially proteins and amino acids.

Nitrogen Mineralization in the Field

Most of the studies dealing with the effect of drying on N mineralization have been carried out in the laboratory. Of the few field studies reported, Semb, et al. (1969) measured the magnitude of N mineralization under natural field conditions for 13 different soils and climatic environments by sampling soils at weekly intervals over a period extending from the end of the dry season into the following rainy season. They reported a flush of mineral N from sites following rewetting of the soil with the beginning of the rainy season. The magnitude of the observed flush varied from 13 to 183 kg N/ha. They also compared a laboratory measure of potentially available N with corresponding field observations. On three sites, laboratory and field values were similar, but on six sites the observed field values were substantially lower than the laboratory values. Hoogerkamp (1965, 1966) applied four cultivation treatments to plots of permanent pasture, each combined with 0, 100, 200 and 300 kg N/ha. The treatments consisted of: (a) no cultivation; (b) deep digging to 20 cm depth with a 10 to 20 cm soil layer replaced by topsoil; (c) rotovating to 10 cm; and (d) deep digging to 20 cm with the top 10 cm replaced by subsoil. Plots receiving treatments (b), (c) and (d) were resown with mixed grass sward. The fertilizer N applications produced similar increases in dry matter yields from the three cultivation treatments.

They inferred that cultivation mineralized N from organic sources, which was responsible for the high dry matter yield.

Effect of Drying Soil on Plant Growth

Recent studies of the effect of drying on the growth of plants are quite scarce. Birch and Emecheb (1966) grew millet on two tropical soils (A and B) with the following treatments: (a) kept moist under aerobic conditions, (b) air-dried for one week, and (c) dried for 24 hours at 80°C. In both soils, air-drying and oven-drying produced dry matter yield higher than in fresh soil. Dry matter yield for fresh, air-dried and oven-dried soil for A was 4, 12 and 22 mg N/pot, while for soil B these values were 18, 28 and 50 mg N/pot, respectively. However, according to Dawson, et al. (1965), lettuce and tomato growth in soils which had been heated to temperatures above 80°C was often less than in soils heated to 60° to 75°C. They attributed this decrease to an increase in soluble and exchangeable Mn and NO_2 .

Similarly, Boyd (1971) reported that interveinal leaf chlorosis occurring in Argentine peanuts grown in autoclaved soil was the result of Mn toxicity. A foliar analysis showed that Mn level in peanuts grown in autoclaved soil was 66 ppm compared to only 6 ppm in the control.

Sources of Mineralizable N

The soil fraction that responds to mineralization on drying contains high levels of N (Harmsen and Schreven, 1955; Harpstead and Brag, 1958). Stevenson (1956) and Takai and Harada (1959) reported that the degree by which metabolic activity increases in remoistened air-dried soil varied directly with the concentration of free amino acids and other nitrogenous materials released during the air-drying process. Similarly, Paul and Tu (1965) reported that air-drying for one week caused a sharp increase in the quantities of methionine sulfoxide, glutamic acid and lysine, as extracted by 1 N ammonium acetate. Steaming and oven-drying raised the total free amino acid-content of soil by a factor of ten. Soils which were oven-dried contained much greater concentrations of methionine sulfoxide than fresh soils. Simon, et al. (1978) attempted to trace the ammoniacal nitrogen released during steam sterilization. They concluded that steam sterilization leads to the formation of free amino acids that consequently undergo thermal decomposition, thereby releasing $\text{NH}_4\text{-N}$. Marumoto (1977) reported that in addition to amino acids-N, amino sugar-N was also responsible for an increased amount of N mineralization due to air-drying. He showed that the amount of $\text{NH}_4\text{-N}$ coming from amino acid-N was larger than from amino sugars, but amino sugars decomposed more rapidly.

Russell, et al. (1974) studied the effects of heating (200°C) on soil clay-organic complexes and soil organic matter from surface horizons of several agricultural soils. The absorption bands due to peptides decreased at 1550 cm^{-1} and 1650 cm^{-1} , which they interpreted as the result of decomposition of amide linkages of organic components of clay-organic complexes. With the acid-washed complexes, the disappearance of secondary amide absorption bands was accompanied by the appearance of NH_4 absorption near 1410 and 3250 cm^{-1} . From their work, it seems that $\text{NH}_4\text{-N}$ is released by the decomposition of amide linkages of organic components of clay-organic complexes. Watson and Parson (1974) showed that the organic matter extracted by formic acid behaves similarly to the acid-washed clay-organic complexes on heating. Their work supports the observations from infrared spectroscopy that amino acid residues in protein-like structures decompose to yield $\text{NH}_4\text{-N}$ on heating. Kasarda and Black (1968) used mass spectroscopy to identify products of protein pyrolysis. They suggested that the appearance of NH_4^+ is indicative of protein decomposition at 130° to 150°C. Juste and Dureau (1967) showed that thermal stabilities of amino acids were lower when mixed with the clay fraction of a soil than when mixed with quartz. They also found that decomposition of amino acids by heating was accompanied by a large increase in exchangeable NH_4^+ on the clay.

Allen, et al. (1973) showed indirect evidence for non-biological transformation of amino acids in soil. Using ^{15}N , they compared the distribution pattern for the fertilizer-derived N and native humus, and showed that considerably higher proportions of fertilizer N occurred in amino acids (59.0 vs. 36.3%) and amino sugars (9.9 vs. 8.0%). They pointed out that the fertilizer N was initially incorporated into amino acids, amino sugars and other abundant compounds of the soil biomass, and later transformed into more stable humus forms. When conditions are right for N mineralization, the above process reverses.

The increase of $\text{NH}_4\text{-N}$ as a result of drying may be due to: 1) the change in the soil's physical condition, especially that of the gel-like materials in soils; 2) the change in the chemical composition, especially the modification of soil organic matter, increasing its solubility; 3) the destruction of a large number of soil micro-organisms, making their bodies available as sources of energy for surviving micro-organisms; 4) the fact that bacteria use organic nitrogenous substances as well as other carbon compounds as a source of energy and liberate ammonia as a waste product.

Theories Explaining Increased N Mineralization

An excellent account of the theories proposed so far to explain the mechanism of N release following partial

sterilization by drying and heating can be found in Jenkinson (1966), and Schnitzer and Khan (1978). There is general agreement that the mineralization of N following various drying treatments is the result of increased microbial activity.

One group of workers suggested that microbial activity is inhibited in unsterilized soil (Greig, 1911) and that the toxin restraining the microbial growth is destroyed by partial sterilization.

Another group provides theories postulating the stimulation of microbial activity (Birch, 1958; Coleno et al., 1965; Gooding and McCalla, 1945; Kubista, 1966). Yet another group proposes an ecological theory that following partial sterilization a section of population previously kept in check by antagonism between different sections of the population grows, causing an increased release of N (Martin, 1963; McLaren et al., 1962).

Another set of theories emphasizes that otherwise available substrates are physically protected from microbial attack in unsterilized soil and drying and heating removes this protection, allowing attack to proceed until the newly-exposed substrate is consumed. An example of this occurs when drying increases the surface area of organic colloids exposed to microbial attack, either by detaching them from other parts of soil or by increasing their porosity (Birch, 1960; Russell, 1966). Another set

of theories stresses that drying and heating produces available substrates from otherwise unavailable material. These substrates can be provided by killing and autolysis of micro-organisms (Black, 1968) and by chemically altering otherwise nonavailable materials (Waksman and Starkey, 1923; Chase and Gray, 1957). Gooding and McCalla (1945) suggest that air drying converts the microbial forms into inactive spores, and when conditions are favorable for growth by the addition of moisture, the organisms pass into a vegetative highly active form.

Recently Laura (1974, 1975, 1976) proposed a protolytic theory. According to him, "The decomposition of organic matter in soil is affected by the availability of protons in the soil environment. Generally the factors which increase the supply of protons in soil increase mineralization of soil organic matter." He noted that dissociation of water increases as the H_2O content in soil samples decreases. Since dry soil contains residual water it is possible that the supply of protons from this water might cause some chemical changes in humus during drying which could result in the formation of NH_4^+ .

This study was undertaken with the following objectives:

- (1) to measure the effect of air and oven-drying on release of soil N in the laboratory;

- (2) to determine the plant availability of N released by air and oven-drying; and
- (3) to determine if drying of soil in the field could mineralize more N.

MATERIALS AND METHODS

Description of Soils Used

Five soils, Kaiwiki (Typic Hydrandept), Maile 7 (Hydric Dystrandept), Maile 9 (Hydric Dystrandept), Waikaloa (Ustollic Eutrandept), and Waimea (Typic Eutrandept) were collected from the island of Hawaii. The Maile 7 soil has only recently been cultivated while the Maile 9 has been cultivated much longer, and should be near an equilibrium with management practices. A brief description of the soils is as follows.

Kaiwiki Silty Clay is a member of the thixotropic, isomesic family of Typic Hydrandepts. The soil has a dark-brown A horizon with a moderately prismatic structure. It is finely mottled. This soil dehydrates irreversibly into gravel-size aggregates. It was covered with vegetation and was quite moist at the time of sampling. This soil occurs at high elevation, ranging from 240 to 455 m above sea level. The mean annual temperature is 15°C and mean annual rainfall is 375 to 500 cm. This soil has undergone intensive weathering.

Maile Silt Loam is a member of the thixotropic, isomesic family of Hydric Dystrandeps. This soil has a dark reddish-brown A horizon having a moderate subangular blocky structure. It dehydrates irreversibly into sand or silt-size aggregates. This soil occurs under a relatively low

temperature (15°C) and high rainfall (203 cm). The soil has a high clay content.

Waikaloa Fine Sandy Loam is a member of the ashy, isothermic family of Ustollic Eutrandepts. This soil has a dark reddish-brown A horizon that has a weak granular structure, a brown to dark reddish-brown B horizon that has a weak prismatic structure, a Ca horizon at about 75 to 127 cm depth. This soil occurs under arid conditions. The mean annual rainfall is 51 cm and mean annual temperature is 16.5°C. In this environment, organic matter accumulates in the upper part of the solum and bases are maintained at a relatively high level.

Waimea Fine Sandy Loam is a member of the ashy, isothermic family of Typic Eutrandepts. The soil has a dark A₁ horizon with a weak granular structure. The B₂ horizon is very friable and has a silt loam texture. This soil differs from the Waikaloa in that it has no calcium carbonate accumulation in the profile. The soil has developed under a slightly lower temperature and higher rainfall than the Waikaloa soil. The average annual temperature and rainfall are 15.5°C and 92 cm, respectively. Chemical weathering has progressed a little further than in the Waikaloa. Additional properties of these soils are given in Table 1-1.

To measure the effect of drying on N mineralization a series of experiments were conducted in the laboratory,

Table 1-1. Some Properties of the Experimental Soils

Soil	pH (in H ₂ O)	Total N* %	Organic C* %	C:N
Kaiwiki	3.82	0.90	12.40	13.77
Maile 7	5.58	0.80	11.74	14.67
Maile 9	5.88	0.76	10.04	13.21
Waikalua	6.32	0.50	7.13	14.26
Waimea	6.94	0.59	6.63	11.23

*Values expressed on oven-dry basis.

greenhouse and in the field.

Air-Drying and Oven-Drying in the Laboratory

Three hundred grams (O.D.) of these soils was weighed and spread in aluminum trays (20 x 20 x 5 cm). The soils were air-dried (25°C) and oven-dried (105°C) in duplicate for 12 weeks. Samples were taken at 0, 2, 4, 8 and 12 weeks. The soil samples were extracted with 1 N KCl (1:5 soil to solution), shaken for one hour on a wrist-action shaker and filtered. Leachate was saved for the analysis of NH_4 and NO_3 -N. Twenty-five ml of the extract was taken for steam distillation on a micro-Kjeldahl apparatus (Bremner, 1965). Soil moisture was determined at 0, 2, 4, 8 and 12-week intervals.

Effect of Initial Moisture Level on N Mineralization

The effect of initial moisture level of soil on N mineralization was measured by adding various amounts of water to Maile 7 and 9, Waimea and Waikaloa soils. Twenty-five grams (O.D.) of soil were taken in plastic bottles, H_2O equivalent to (1) one-half of field capacity, and (2) field capacity, were added as treatments to all four soils. Soils were dried in oven (105°C) for 48 hours without lids on the plastic bottles. Soil was extracted with 1 N KCl for determination of NH_4 and NO_3 -N.

Air- and Oven-Drying of Bulk Samples

Fifteen kg of Maile 7 and Kaiwiki soils were oven-dried for two weeks at 105°C and air-dried in a greenhouse for 12 weeks. NH_4 - and NO_3 -N were determined as described earlier at the end of each drying period. These samples were later used for growing of corn in the greenhouse.

Plant Availability of Mineralized N

The plant availability of N released as a result of air-drying and oven-drying was measured using corn as a test plant. Two and one-half kg (O.D.) samples of the Maile 7 and Kaiwiki soils, which had been air-dried for 12 weeks and oven-dried (105°C) for two weeks, were limed to give a pH of 6.5. All other nutrients except N were applied as a basal dose at the following rates:

<u>Nutrient</u>	<u>Rate</u>	<u>Form of Application</u>
P	1000 kg/ha	as $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$
K	500 kg/ha	as KCl
Mg	200 kg/ha	as $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
Zn	20 kg/ha	as ZnSO_4
B	2 kg/ha	as H_3BO_3
Cu	3 kg/ha	as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
Fe	50 kg/ha	as $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

Treatments were as follows for both the Maile 7 and Kaiwiki:

1. Fresh soil
2. Soil which had been air-dried for 12 weeks
3. Soil which had been oven-dried for 2 weeks
4. Fresh soil plus an amount of urea equivalent to N released by air-drying
5. Fresh soil plus an amount of urea equivalent to the N released by oven-drying

Corn (Zea mays L.) was planted and thinned to two plants/pot after emergence. Urea was applied after two weeks of emergence. The experiment was harvested after three months. All plants showed N deficiency symptoms at harvest time. Plants were ground and analyzed on a Quantometer.

Field Experiment

The effect of clearing of natural vegetation on N mineralization was determined by selecting two sites in the Helemano area, Oahu. Site 1 was drier, more exposed to sunlight and heat than site 2, which was located in a forest. The sites were cleared of local vegetation and microplots were established using 38-cm diameter metal drums. These drums were buried 15 cm deep into the soil, while 3 cm of the drum was exposed. The main vegetation at site 1 was Melinis minutiflora (molasses grass),

Brachiaria mutica (California grass) and Eucalyptus. Site 2 was covered with Gleichenia linearis (creeping fern) and Acacia koa.

Soil samples were collected at 0, 4, 8 and 12-week intervals and extracted with 1 N KCl; NH_4^- and NO_3^- -N were determined in the extract by the method of Bremner (1965).

RESULTS AND DISCUSSION

The Effect of Air-Drying on Nitrogen Mineralization

When soils were air-dried, the amount of mineralized N increased at 0-12 weeks for the five soils (Table 1-2). The magnitude of $N(NH_4+NO_3)$ which was mineralized upon air-drying in these soils gave the following trend: Maile 7 > Kaiwiki > Waikaloa > Maile 9 > Waimea. The Maile 7 and Kaiwiki soil materials mineralized much greater amounts of N compared to the Waikaloa, Maile 9 and Waimea soils. Prolonged air-drying (12 weeks) resulted in greater N mineralization than short-term air-drying (2 weeks) although the percentage of water lost was negligible after two weeks (Table 1-3).

The Effect of Oven-Drying on Nitrogen Mineralization

Oven-drying (105°C) enhanced N mineralization in these soils much more than did air-drying (Table 1-2). After 12 weeks of oven-drying, 596.6, 410.1, 391.1, 291.3 and 153.9 $\mu\text{g/g}$ more N were mineralized than the amounts mineralized in fresh soils by the Kaiwiki, Maile 9, Maile 7, Waikaloa and Waimea soils, respectively. The longer the soils were oven-dried, the greater was the amount of N mineralized. Also, drying at 105°C released about 10-40

Table 1-2. Effect of Drying on Nitrogen Mineralization

Soil		<u>Air-Drying</u>				
		Weeks				
		0	2	4	8	12
		----- µg/g -----				
Kaiwiki		100.0	150.3	141.1	151.9	162.1
	Increase due to drying		50.3	41.1	51.9	62.1
Waikaloa		28.5	29.1	33.1	35.4	39.7
	Increase due to drying		0.6	4.6	6.9	11.2
Maile 7		126.3	150.0	140.9	153.5	165.5
	Increase due to drying		23.7	14.6	27.2	39.2
Maile 9		24.2	26.5	27.6	29.2	34.7
	Increase due to drying		2.3	3.4	5.0	10.5
Waimea		22.5	23.5	24.0	30.6	33.6
	Increase due to drying		1.0	1.5	8.1	11.1
		<u>Oven-Drying</u>				
Kaiwiki		100.0	349.3	451.2	579.2	696.6
	Increase due to drying		249.3	351.2	479.2	596.6
Waikaloa		27.8	185.7	248.2	283.8	319.1
	Increase due to drying		157.9	220.4	256.0	291.3
Maile 7		124.3	411.5	463.4	505.2	515.4
	Increase due to drying		287.2	339.1	380.9	391.1
Maile 9		22.4	293.6	412.5	450.8	432.5
	Increase due to drying		271.2	390.1	428.4	410.1
Waimea		27.2	111.0	136.1	150.1	181.1
	Increase due to drying		83.3	108.9	122.9	153.9

Table 1-3. Amount of Water in Air-Dried Soils at
Different Intervals

Soil	<u>Weeks</u>				
	0	2	4	8	12
	----- % -----				
Kaiwiki	228.00	13.37	13.72	12.86	12.86
Waikaloa	54.00	12.48	13.37	13.37	13.37
Maile 7	66.00	18.47	18.48	18.48	18.48
Maile 9	72.00	18.20	19.33	19.33	19.33
Waimea	37.00	11.60	11.60	11.60	11.60

times more N than air-drying for 12 weeks. The increased mineralization of N at high temperatures has been observed by others (Birch, 1959; Birch and Friend, 1956; Cairns, 1963; Singh and Kanehiro, 1970). The effect of drying in relation to N mineralized was cumulative, as was also observed by Birch (1958), Broadbent (1964), Soulides and Allison (1961).

Effect of Air-Drying on $\text{NH}_4\text{-N}$

The amount of $\text{NH}_4\text{-N}$ increased in all soils when air-dried. In the beginning (up to 4 weeks), air-drying (Fig. 1-1) caused less $\text{NH}_4\text{-N}$ to be released from the Waimea, Waikaloa and Maile 9 soil materials. At the end of 12 weeks of drying, N mineralization showed the following trend: Kaiwiki > Maile 7 > Waimea > Maile 9 > Waikaloa.

Nitrate-N as Affected by Air-Drying

The amounts of $\text{NO}_3\text{-N}$ at 0, 2, 4, 8 and 12-week intervals are given in Fig. 1-2. Three soils: Waikaloa, Maile 9 and Waimea had very little change in $\text{NO}_3\text{-N}$ after 12 weeks of air-drying. However, the Kaiwiki and Maile 7 soils behaved quite differently than the other three soils. The Kaiwiki and Maile 7 soils had at the beginning exceptionally high contents of $\text{NO}_3\text{-N}$. Air-drying for two weeks had

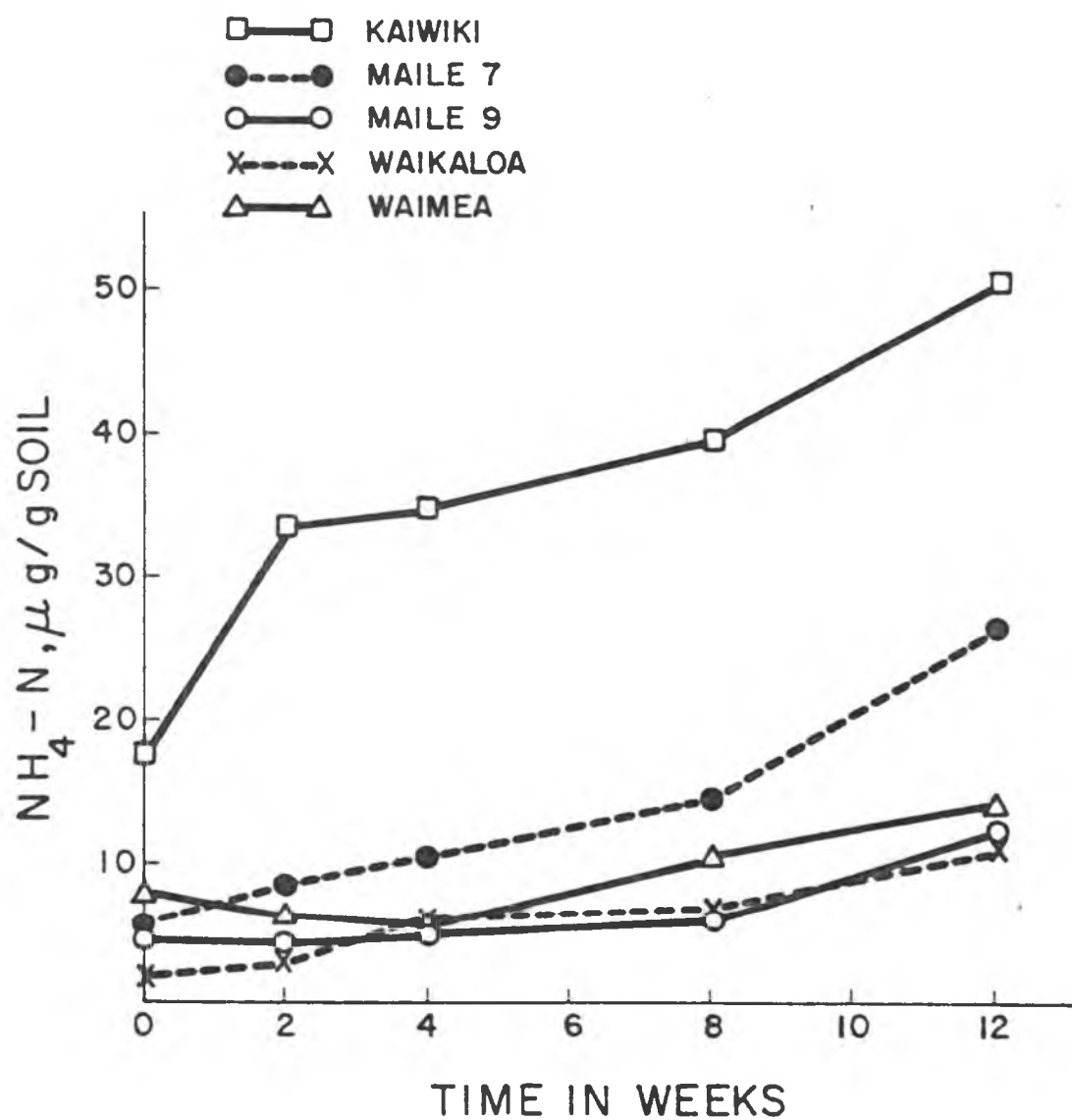


FIG. 1-1. EFFECT OF AIR-DRYING ON $\text{NH}_4\text{-N}$ IN FIVE SOILS.

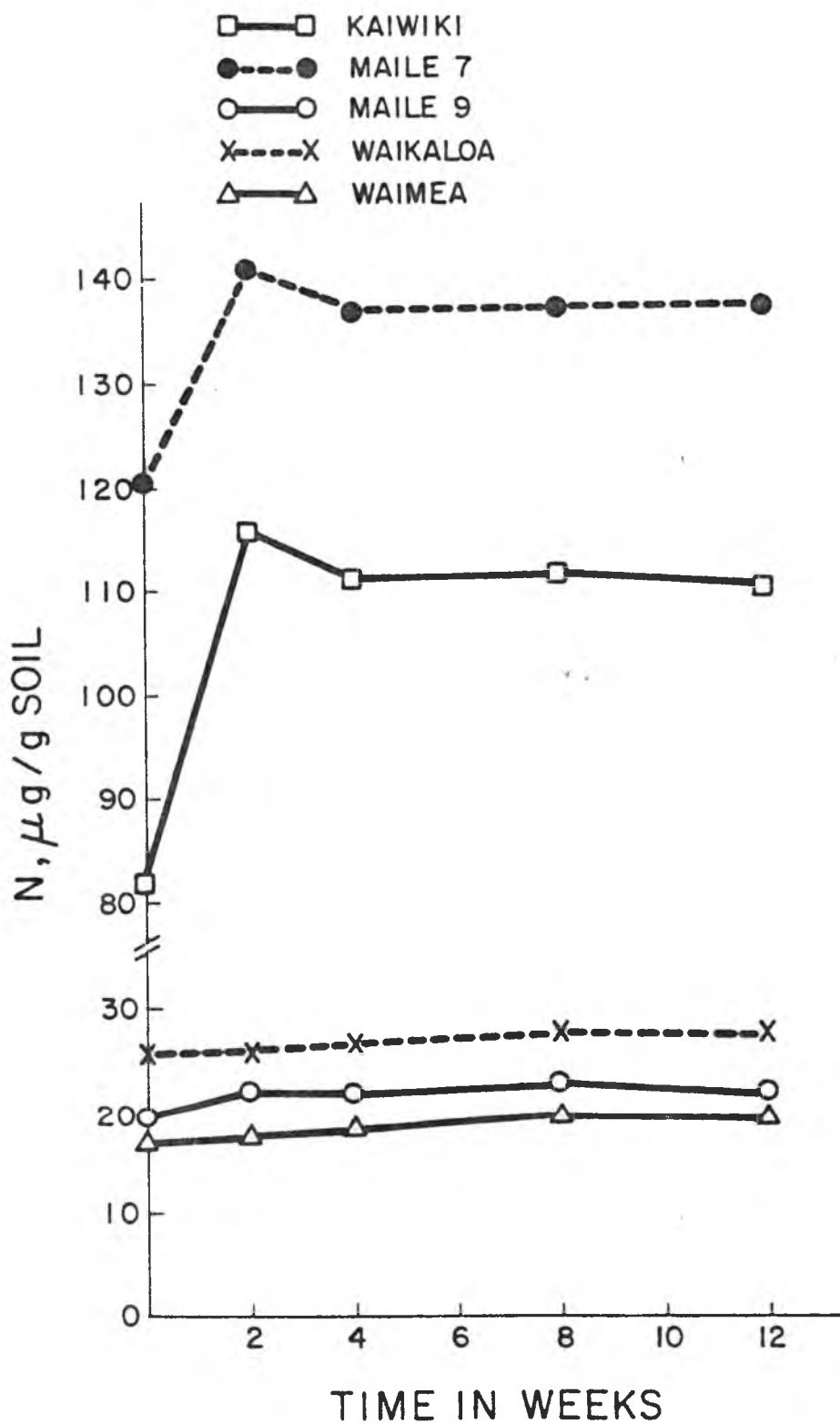


FIG. 1-2. EFFECT OF AIR-DRYING ON $\text{NO}_3\text{-N}$ IN FIVE SOILS.

a tremendous effect in increasing the amount of $\text{NO}_3\text{-N}$ in these two soils. The amount of $\text{NO}_3\text{-N}$ leveled off after two weeks of drying and continued so for 12 weeks. These results are in line with those of Munro and MacKay (1964), who found increased $\text{NO}_3\text{-N}$ production by 15-20 $\mu\text{g/g}$ due to air-drying for 15 weeks.

Effect of Oven-Drying on $\text{NH}_4\text{-N}$

Oven-drying (105°C) gave greater increases in $\text{NH}_4\text{-N}$ than air-drying (Fig. 1-3). The soils gave a very distinct initial flush of $\text{NH}_4\text{-N}$ followed by a more gradual and steady increase. After 12 weeks of drying at 105°C , 19 to 150 times more $\text{NH}_4\text{-N}$ was mineralized for all five soils over the controls. A comparison of Table 1-2 and Fig. 1-3 reveals that most of the mineral N was $\text{NH}_4\text{-N}$ rather than $\text{NO}_3\text{-N}$. One possibility for the low amount of $\text{NO}_3\text{-N}$ is that nitrifiers may have been killed under such severe conditions of low water supply and high temperatures. According to Gibbs (1919) the Nitrosomonas bacteria are killed between 53°C to 55°C but Nitrobacter can withstand such severe conditions. Similarly, Harmsen and Kolenbrander (1965) and Panganban (1925) noted that ammonification proceeded vigorously in the temperature range of 50°C to 70°C . But Nevo and Hagin (1966) found that changes occurring during three months of drying were independent of the presence

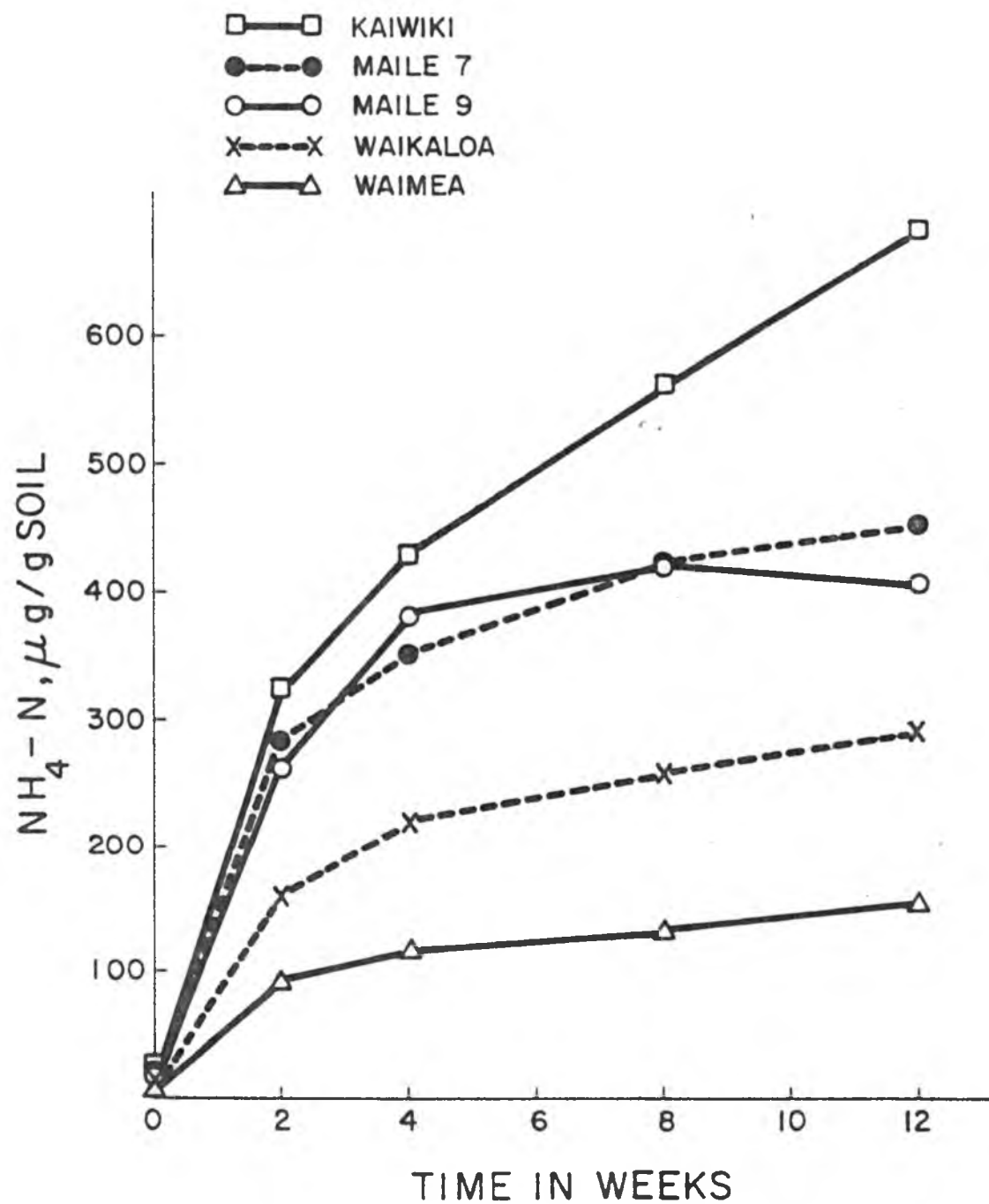


FIG. 1-3. EFFECT OF OVEN-DRYING ON $\text{NH}_4\text{-N}$ IN FIVE SOILS.

of microorganisms and were mainly due to change in the physical structure of the organic matter fraction. It may be possible that drying caused some physical as well as chemical changes in the soils reported in this study. As a result of dehydration these amorphous materials might have changed to crystalline oxides. Thus exposure of new surfaces of soil and increased solubility of organic matter (due to high temperature) may have increased the amount of $\text{NH}_4\text{-N}$ as a result of drying of these soils. Sherman, et al. (1964) reported that amorphous hydrated oxide systems which consist of materials ranging from gels to cryptocrystallines upon dehydration produce crystalline oxides.

The Effect of Oven-Drying on $\text{NO}_3\text{-N}$

Amounts of $\text{NO}_3\text{-N}$ produced as a result of oven-drying for 0, 2, 4, 8 and 12-week periods are given in Fig. 1-4. While $\text{NO}_3\text{-N}$ remained almost unchanged in the Waimea, Maile 9 and Waikalua soils, there was a sharp decrease in $\text{NO}_3\text{-N}$ in the Kaiwiki and Maile 7 soils. After 12 weeks of oven-drying there was a decrease of 72 and 58 $\mu\text{g/g}$ $\text{NO}_3\text{-N}$ in the Kaiwiki and Maile 7 soils, respectively. Similar results were reported by Kelley (1919) who found decomposition of $\text{NO}_3\text{-N}$ in several Hawaiian soils when they were heated at 150°C for two hours. He further reported that there was a total decomposition of $\text{NO}_3\text{-N}$ at 200°C and 250°C . Ekpete

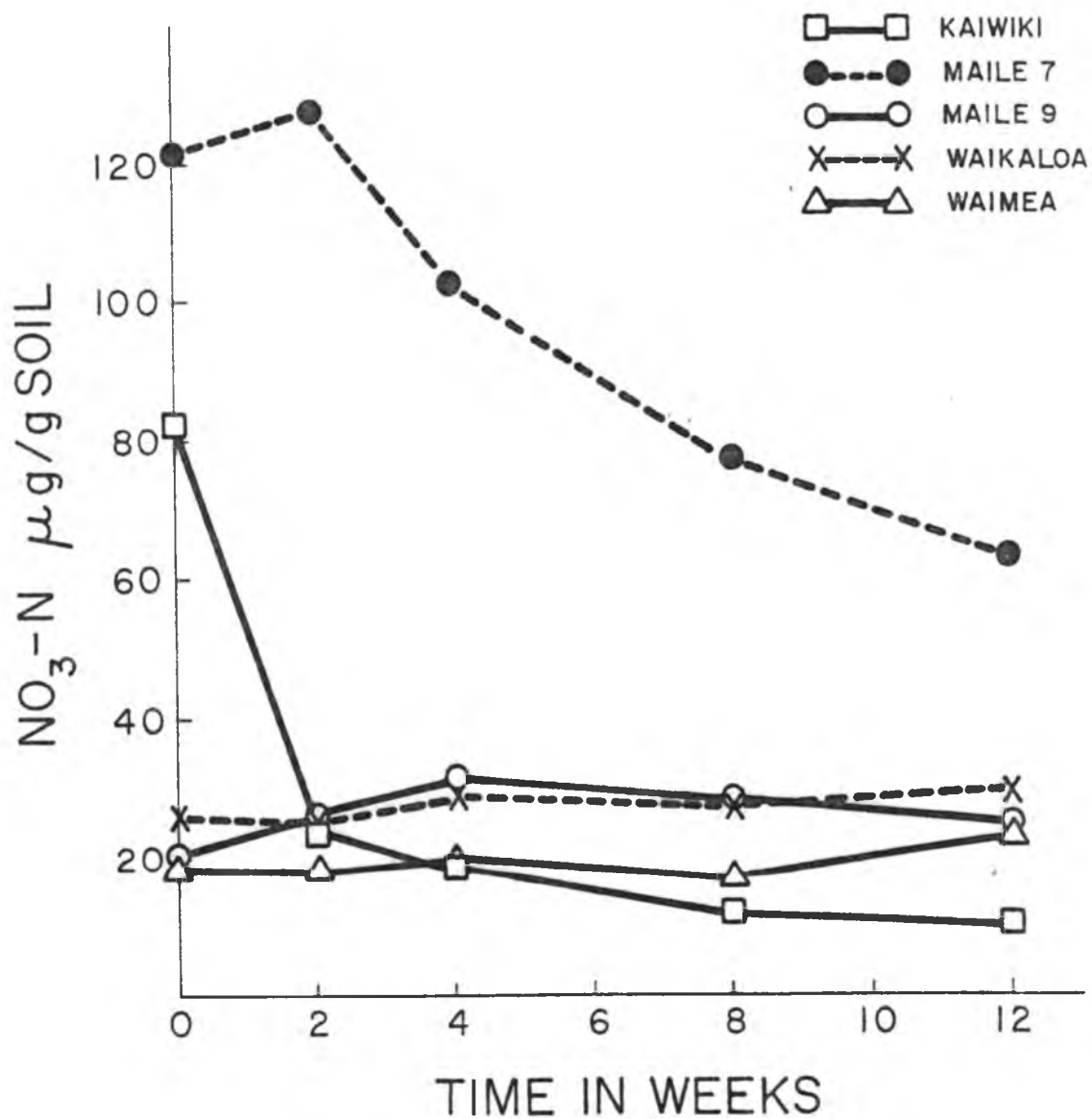


FIG. 1-4. EFFECT OF OVEN-DRYING ON $\text{NO}_3\text{-N}$ IN FIVE SOILS.

and Cornfield (1964) also noted a 10.3 and 21.7 percent loss in $\text{NO}_3\text{-N}$ when an alluvial sandy loam soil with pH 6.5 was incubated at 20 and 50 percent of the maximum water-holding capacity, respectively.

The Effect of Initial Water Content on Nitrogen Mineralized Due to Drying

Amounts of released $\text{NH}_4\text{-N}$ due to air-drying and oven-drying are given in Table 1-4. Oven-drying released approximately 10 times more $\text{NH}_4\text{-N}$ than air-drying. A linear regression between the initial moisture content and the N mineralized upon air-drying, $\text{NH}_4\text{-N}$ released upon air and oven-drying gave significantly high correlation (Table 1-4) coefficients.

Effect of Changing Initial Moisture Content on Nitrogen Mineralization

High amounts of $\text{NH}_4\text{-N}$ being released as a result of air and oven-drying may either be due to water loss or the effect of temperature to which soils were exposed upon oven-drying. Since effects of both these parameters were confounded, this experiment was conducted to determine how a change in initial moisture content of soil would affect the amount of $\text{NH}_4\text{-N}$ released. Fig. 1-5 gives the amounts of $\text{NH}_4\text{-N}$ when the Waikalua, Waimea, Maile 7 and Maile 9 were oven-dried for 48 hours after adding varying amounts of water (control, soil + water equivalent to one-half field capacity, and soil + water equivalent to field

Table 1-4. Initial Moisture Content and Various Forms of N Released Due to Drying,

Soil	Moisture %	NH ₄ +NO ₃ -N Air-dried	NH ₄ -N Air-dried	NH ₄ -N Oven-dried
		----- μg/g -----		
Kaiwiki	228.00	162.13	51.28	686.46
Waikalua	54.00	39.69	11.79	228.57
Maile 7	66.00	165.50	26.90	452.21
Maile 9	72.00	34.67	12.52	407.40
Waimea	37.00	33.64	14.60	157.52
Equation	$y=34.06 + 0.58x$		$y=5+0.2x$	$y=181.24+2.28x$
r		0.64	0.93	0.89

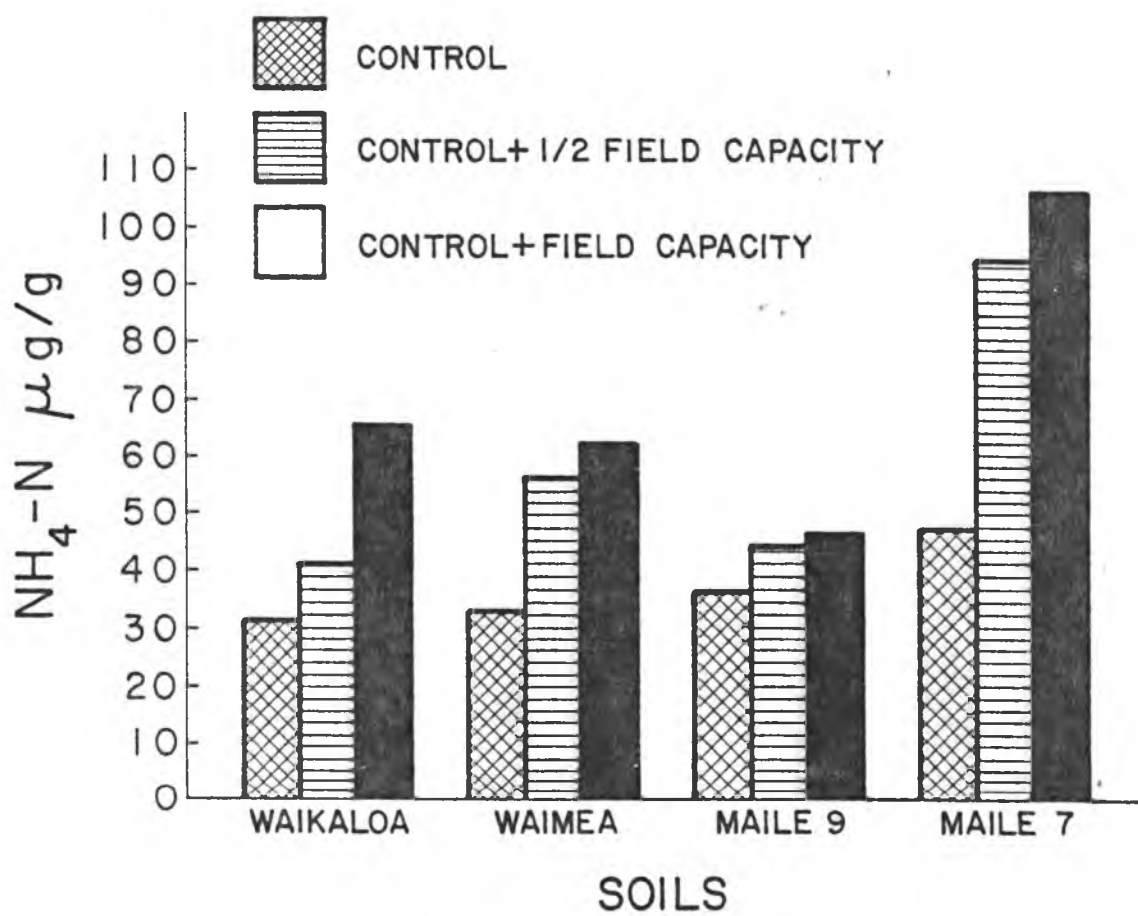


FIG. 1-5. AMMONIUM-N RELEASED DUE TO DRYING AFTER ADDING DIFFERENT AMOUNTS OF WATER.

capacity). All four soils released greater amounts of $\text{NH}_4\text{-N}$ at both added water levels, indicating that initial moisture content does affect the amount of $\text{NH}_4\text{-N}$ released upon drying. However, no clear trend was found in $\text{NO}_3\text{-N}$ (Fig. 1-6).

Reasons for Increased Nitrogen Mineralization

There are several reasons which have been given for the increase in mineral N. All of these may be involved to some extent in this flushing phenomenon, and are as follows.

(1) Microbial Stimulation: The increased amount of $\text{NH}_4\text{-N}$ on drying has often been attributed to microbial stimulation (Birch, 1958; Singh and Kanehiro, 1970; Wooldridge and Glass, 1937). On the other hand, Cornfield (1963) reported that this increase in $\text{NH}_4\text{-N}$ and decrease in $\text{NO}_3\text{-N}$ was due to a partial sterilization effect. Ammonifiers, being spore formers (while nitrifiers are not), can withstand longer periods of drying than nitrifiers. However, Nevo and Hagin (1965) and Schreven (1967) claim that changes occurring in N due to drying are independent of microorganisms. They feel the major factor involved was a change in the physical structure of organic matter.

(2) Increased Solubility of Organic Matter Due to Chemical Alterations: It is possible that drying of soil might lead to the increased solubility of organic matter.

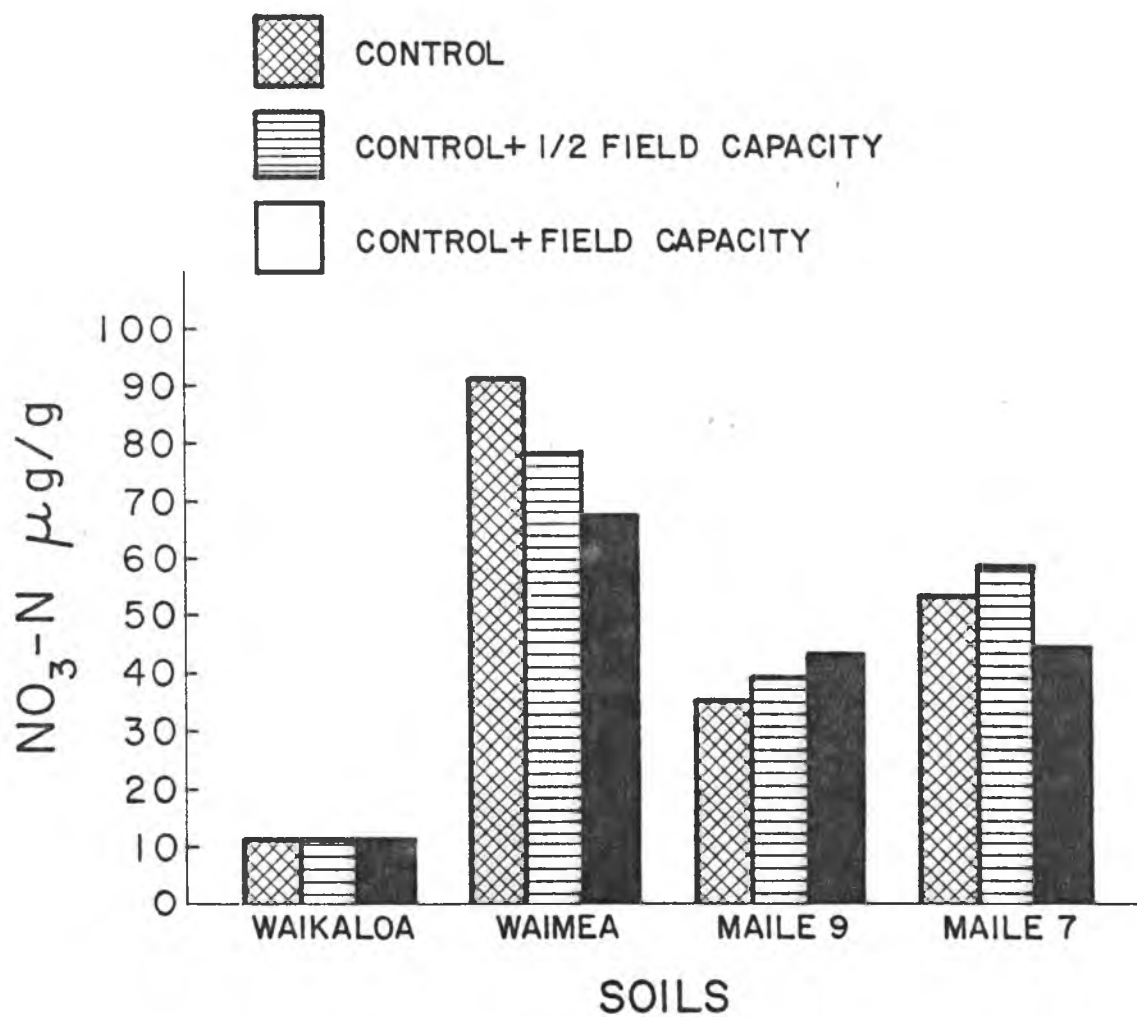


FIG. 1-6. NITRATE-N RELEASED DUE TO DRYING AFTER ADDING DIFFERENT AMOUNTS OF WATER.

When a dry soil is moistened organic matter goes into solution and rapidly decomposes. The magnitude of this flush of decomposition depends on the percentage of carbon in the soil (Birch, 1958) and length of the drying period. The drying effect may bring about changes in organic fraction, especially organic colloids. Boutaric and Thevenet (1937) showed that solutions of humus colloids decline in viscosity with time and that decline is hastened at higher temperatures. This idea has been supported by Birch (1959) and Chase and Gray (1957).

(3) Killing of Microorganisms and Autolysis: It may also be possible that under such severe conditions of air and oven-drying, part of the biomass is killed, which on subsequent autolysis may be a source of $\text{NH}_4\text{-N}$. Although the biomass and its decaying products appear to constitute a small proportion of total N in the system, the fast turnover time of this fraction makes it a very important constituent in terms of mineral N released (Clark and Paul, 1970; Schreven, 1967; Soulides and Allison, 1961). Jenkinson (1966), using the tracer technique, indicated the biomass of the soil organic matter is the fraction of soil organic matter which is most influenced by drying. This idea has also been supported by Swaby and Ladd (1962), Birch (1959) and Black (1968). In support of this theory are the findings of Stevenson (1956), Takai and Harada (1959) that drying increased the amino acid concentration

in water extracts.

The killed microorganisms are partly mineralized and partly used for the synthesis of new microbial materials and contributes to the formation of humus (Jager, 1968). Jensen (1932) observed that 19 to 60 percent of the killed and air-dried fungal mycelia and bacterial cells were mineralized during a 60-day incubation period. Jenkinson (1966) observed a 30 percent decomposition of bacterial cells (Nitrosomonas) in ten days.

(4) Exposure of New Surfaces Due to Drying: Prolonged drying may affect the physical conditions of soil (shrinking of colloids, etc.), leading to greater exposure of new organic surfaces. Jones and Uehara (1973) have confirmed the presence of gel-like material on the crystalline particles in Andepts from Hawaii. These gels become porous on drying (Lykov, 1947). Vold, et al. (1952) found that on drying and aging the structure of the cells disintegrates, giving rise to more surface area. As these surfaces were previously protected by the coatings, they are not exposed because of disintegration and more mineral N could be a result of these newly-exposed surfaces. Sherman, et al. (1964), working with Akaka and Waimea soils, reported that when these soils are exposed to dehydration, crystallization occurs, causing an increase both in bulk density and particle density. On crystallization the material will not rehydrate to its former amorphous state.

(5) Splitting off of $\text{NH}_4\text{-N}$ from Nitrogen-Bearing Organic Compounds: Drying changes the soil both physically and chemically. The chemical fractions of organic matter which are influenced most by drying seem to be the amino acids, amino sugars and amides (Cheng and Kurtz, 1963; Chu and Knowles, 1966; Freeney and Simpson, 1969; McGill, et al. 1973). Sowden, et al. (1976) reported that volcanic tropical soils contained higher amounts of acidic amino acids (glutamic and aspartic acid) than non-volcanic tropical soils. They speculated that accumulation of the amino acids was a result of the interaction between allophane and these acids. But Carle and Decaue (1960) reported that in tropical soils basic amino acids accounted for one-half the total amino acids. They also suggested that high amounts of amino acids may be due to the interaction of amino acids with the amorphous hydrous aluminum and iron oxides. It is possible that peptides containing amino acids are selectively, physically adsorbed on or interact chemically with amorphous allophanic materials and thus are protected against further degradation. Perhaps upon drying these nitrogenous materials are split apart, giving rise to free amino acids in soil systems.

Various methods of drying (air, oven, steam) alter the concentration of free amino acids in ammonium acetate extracts (Paul and Tu, 1965 ; Invarson and Sowden, 1966). Table 1-5 indicates the free amino acid content of soils

Table 1-5. Free Amino Acid Content ($\mu\text{g/g}$) of the Summer Fallow Hoey Soil Sample Before and After Physical Treatments (after Paul and Tu, 1965)

<u>Amino Acid</u>	<u>Untreated</u>	<u>Air-Dried</u>		<u>Oven-Dried</u>	<u>Steamed</u>
		1 week	24 weeks	2 hours	2 hours
Methionine Sulfoxide	0.57	1.89	1.12	7.73	2.74
Aspartic Acid	0.38	0.57	0.25	2.84	3.14
Glutamic Acid	0.94	3.31	2.39	9.76	9.80
Lysine	*	1.74	0.80	3.20	4.42
All Others	3.54	6.09	3.35	34.91	44.47
TOTAL	5.43	13.60	7.91	58.44	64.57
Free Amino Acid N	0.10	1.70	1.00	7.00	7.70
Ammonium N	6.60	10.20	4.60	25.00	29.80
Soluble Amino N	3.00	3.40	3.20	11.70	11.90

* Not present in measurable concentrations.

before and after different drying treatments of other studies (Paul and Tu, 1965). In general, air-drying for one week caused a sharp increase in the quantities of methionine sulfoxide, glutamic acid and lysine. With extended drying, the concentration of these amino acids decreased somewhat but were still above those found in the untreated sample. Twenty-four weeks of air-drying increased the amino acid concentration slightly. Steaming and oven-drying raised the total free amino acid content of the soils by a factor of ten. It is also possible that free peptides or proteins (released by drying treatments) may also be present in soil. Paul and Tu (1965) reported the presence of peptides in ammonium acetate extracts in some soils.

(6) Increased Supply of Protons: Another hypothesis has been recently proposed by Laura (1974, 1975, 1976) who suggests that the decomposition of organic matter in soil is affected by the availability of protons in the soil environment, and that drying increases the availability of protons due to the increased dissociation of water. The dissociation of water increases as the water content decreases. However, Laura's protolytic theory seems to be more chemically oriented and too simple to explain such complex changes taking place when soils are dried. If his theory on supply of protons as a result of residual water is accepted, then addition of dilute acid (which also supplies protons) should also result in release of $\text{NH}_4\text{-N}$ from

soil. But there is no evidence in the literature suggesting that the addition of acid increases NH_4 -N mineralization from soil. Another reason for rejecting Laura's protolytic theory is that experiments in which four soils with three different moisture levels were dried in an oven for 48 hours gave different results that what would be expected from the proton-supply theory. According to Laura, soils in which no water was added should have had less residual water than those in which additional water was added, and thus should have provided more protons in the system and hence more mineralization. But soils in which additional amounts of water were added released more NH_4 -N than the controls (Fig. 1-5).

This investigation indicates that there is no single simple reaction to explain the results from drying of these soils. Drying affects both the soil microbial population and the soil organic matter. Microorganisms are affected by autolysis of their cells and the production of microbial intermediates such as free amino acids, peptides and proteins.

Effect of Drying in the Field

The changes in mineral N (NH_4 and NO_3) due to drying soils in the field are presented in Fig. 1-7. It is clear that drying (exposure to sunlight) mineralized considerably more N as compared with the undisturbed area. The effects

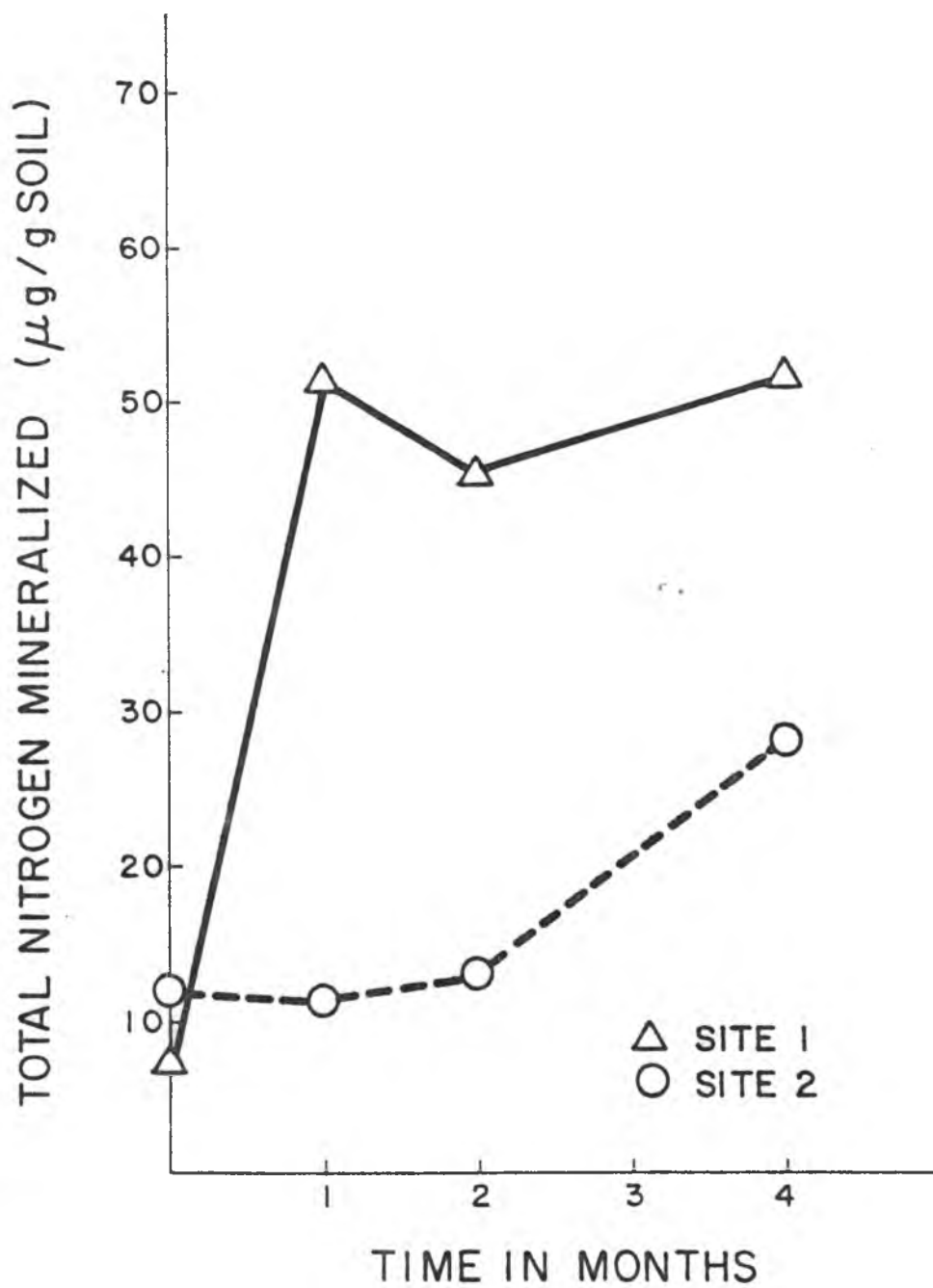


FIG. 1-7. NITROGEN MINERALIZATION AS AFFECTED BY DRYING OF PAALOA SOIL IN THE FIELD.

of drying appeared much more quickly at location 1 than at location 2. This may be attributed to more exposure of site 1 to sunlight and drying. Also, location 2 was wetter than site 1 at all times, whenever samples were taken (Table 1-6). There could be several possibilities for increased N at both sites because of removal of vegetation. These are:

1. Improved aeration and drying that might directly increase microbial activity or indirectly affect microflora by removal of volatile toxic substances or may increase chemical oxidation of the soil organic matter;
2. Break-up of clumps of bacteria and fungal hyphae to give better distribution throughout the soil; and
3. Exposure of organic matter previously protected from microbial attack by its location in inaccessible sites.

Effect of Soil Drying on Corn Growth

The effect of drying soil on corn growth was determined in a greenhouse experiment. Corn was grown on two soils which received five treatments: fresh, air-drying, oven-drying; fresh plus urea applied equivalent to N mineralized upon air- and oven-drying (Fig. 1.8). The Maile 7 soil produced higher dry matter yield of corn in all

Table 1-6. Percentage of Water at Time of Sampling.

<u>Sample Number</u>	<u>Location 1</u>	<u>Location 2</u>
	FIRST MONTH	
1	18.4	35.9
2	21.8	38.2
3	20.6	46.9
4	22.2	33.3
Average	20.7	38.6
	SECOND MONTH	
1	37.7	64.3
2	52.4	59.7
3	39.1	73.6
4	41.1	74.2
Average	42.6	67.9
	FOURTH MONTH	
1	37.7	46.2
2	23.9	43.7
3	26.6	52.9
4	19.0	54.3
Average	26.8	49.3

Table 1-7. Effect on Drying on Growth of Corn in Two Soils

<u>Treatment</u>	<u>Kaiwiki</u>			<u>Maile 7</u>		
	Days after Germination			Days after Germination		
	10	20	37	10	20	37
	Plant height (cm)					
Fresh	26.5	41.2	61.5	31.5	40.5	79.0
Air-Dried	14.7	24.7	55.0	27.7	43.7	76.2
Oven-Dried	11.7	15.3	plants died	22.7	37.7	68.2

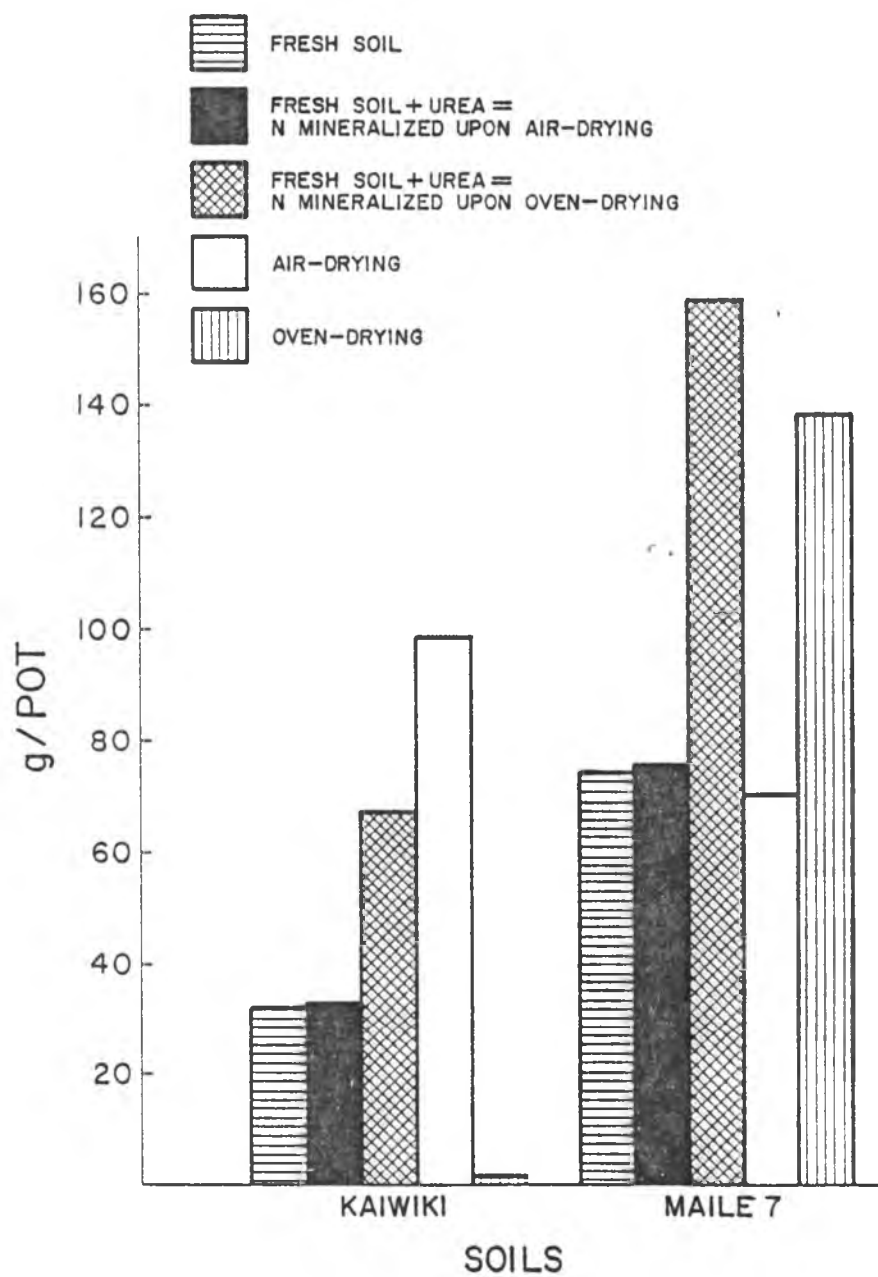


FIG. 1-8. DRY MATTER YIELD OF CORN AS AFFECTED BY DRYING AND FERTILIZER N.

treatments except the air-dry treatment; i.e. air-drying was more beneficial to corn growth in the Kaiwiki soil than in the Maile 7. King (1961), working on Akaka subsoils, also reported significantly higher yields with dry than moist Akaka soils. However, the reverse was true for the oven-dry treatment. Oven-drying had a detrimental effect on the growth of corn in the Kaiwiki soil. Plants that were growing in the oven-dried Kaiwiki soil never recovered from the injurious effects of drying this soil. In the oven-dried Maile 7 soil, plants grew to a larger size than in the fresh and air-dried soils. It is possible that both beneficial and harmful compounds are produced by drying the soil. Schreiner and Lathrop (1912) reported that beneficial compounds included nucleic acid, hypoxanthine, xanthine, guanine, histidine, arginine and cretinine. All of these compounds were shown to be decidedly beneficial to the growth of wheat seedlings. They also reported that dihydroxystearic acid was responsible for reducing growth of wheat seedlings in dried soils. The effect on plant growth is the combination of these two influences and thus beneficial effects may not be fully apparent unless the harmful compounds have been eliminated by oxidation, reduction, cultural or other means. Similarly, the full harmful effect of a compound is not attained in the presence of a beneficial compound.

The results of this study may be explainable by hypothesis that both harmful and beneficial compounds have been produced. The Kaiwiki soil contains beneficial compounds as well as harmful compounds. In the Maile 7 soil, harmful compounds were either absent or at a minimum. Consequently, the beneficial compounds exert their full effect. In the case of the Kaiwiki soil, oven-drying brings about such a rapid and sudden change that even though beneficial compounds are liberated, the effects of harmful compounds which are also produced more than overbalances them. The result was that corn seedlings were killed.

Corn plant height at various intervals shows that seedlings in dried soils grew less rapidly than in fresh soils (Table 1-7). This possible toxic effect became less apparent after 37 days in the case of the air-dried Kaiwiki but was most severe in the oven-dried soils. However, in the case of the Maile 7 soil, plants in the air-dried and oven-dried soils recovered after 20 days. Dawson, et al. (1965) attributed such decreased growth to chemical toxicities of Mn and NO_2 released because of drying, but in this case enough lime was applied at the start of the experiment that Mn toxicity should not have been a problem. Plant analysis (Table 1-8) also did not indicate large amounts of Mn, even in plants grown in the oven-dried Kaiwiki soil which died after 37 days. The percentage of N in the

Table 1-8. Concentration of Various Elements in Corn Plants

<u>Treatment</u>	<u>Kaiwiki</u>						
	N	P	K	Ca	Mg	Al	Mn
	%			µg/g			
Fresh	0.80	1.19	1.13	0.21	0.17	98.50	119.50
Fresh + Urea = Air-dry	0.88	0.15	1.18	0.21	0.15	102.00	96.50
Fresh + Urea = Oven-dry	0.87	0.10	0.40	0.28	0.22	103.50	95.00
Air-dried	0.83	0.10	0.55	0.22	0.22	104.00	165.00
Oven-dried	2.78	0.15	0.54	0.82	0.59	795.00	34.00
	<u>Maile 7</u>						
Fresh	0.80	0.14	1.13	0.18	0.15	105.50	56.50
Fresh + Urea = Air-dry	0.89	0.13	1.22	0.19	0.12	117.50	72.60
Fresh + Urea = Oven-dry	0.86	0.10	0.49	0.22	0.23	78.50	55.50
Air-dry	0.83	0.13	0.86	0.18	0.16	94.50	88.00
Oven-dry	1.18	0.09	0.98	0.32	0.26	232.00	205.50

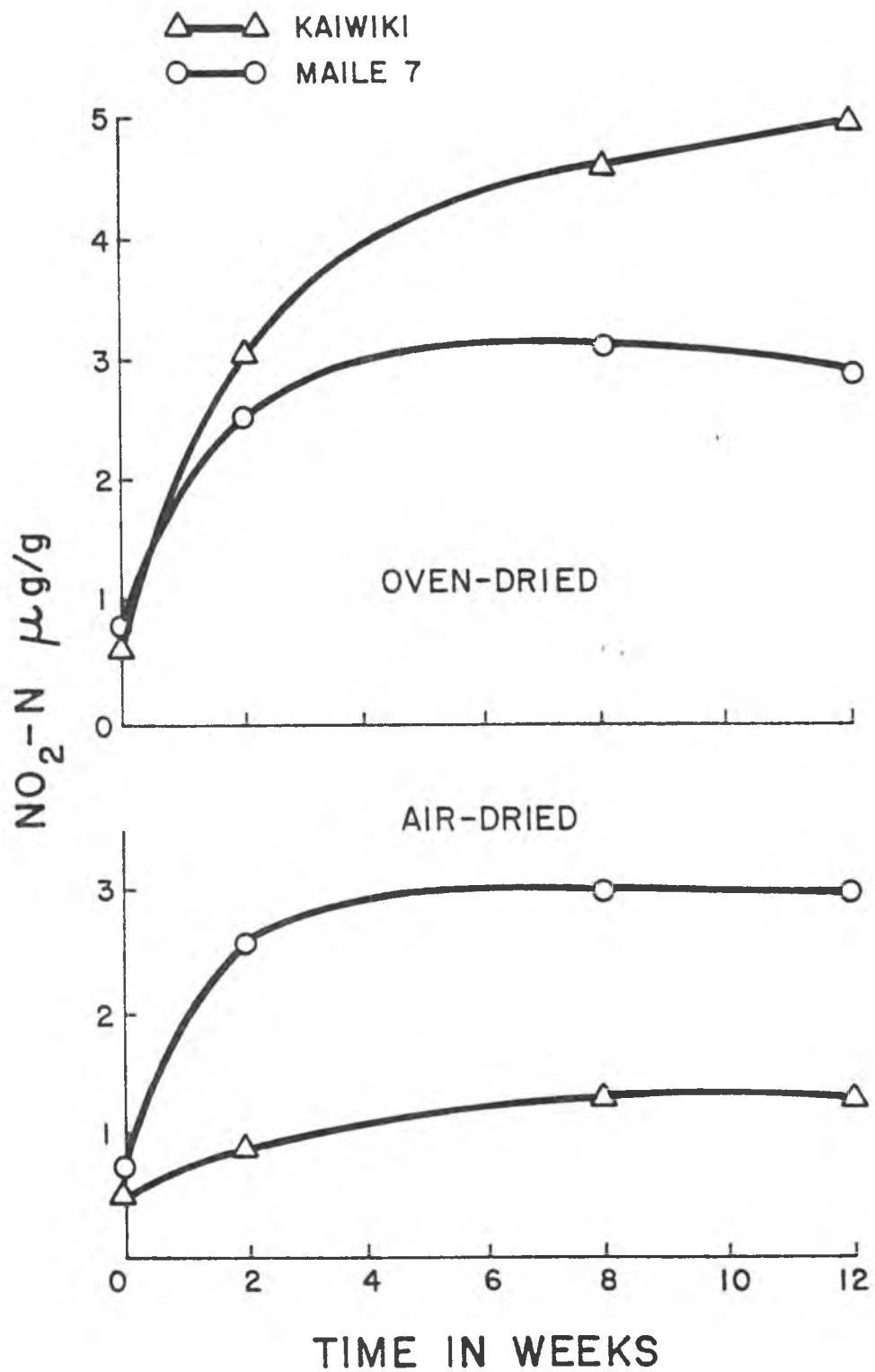
plants which died was extremely high compared to the rest of the treatments. The decreased growth of corn may either be due to a high concentration of $\text{NH}_4\text{-N}$ and free ammonia in the soil or $\text{NO}_2\text{-N}$ (Fig. 1-9). It is evident that the concentration of $\text{NO}_2\text{-N}$ in oven-dried Kaiwiki soil was 5 ppm after 12 weeks of oven-drying.

Oven-drying of the Maile 7 soil (Fig. 1-8) had a beneficial effect on corn growth. Birch (1964) attributed this beneficial effect to the greater N availability due to drying.

The Effect of Fertilizer on Dry Matter Yield of Corn

The dry matter yield of corn was not different from the control when urea was applied in amounts equivalent to those amounts of N released by air-drying Kaiwiki and Maile 7 soils (90 kg/ha in the Kaiwiki and 11 kg/ha in the Maile soil) (Fig. 1-10).

Possibly, such small amounts of N were insufficient to give a growth response. Fertilizer N applied equivalent to air-drying in the Kaiwiki soils gave a dry matter yield of corn 3.4 times lower than the air-dried treatment. However, in the Maile 7 soil there was no significant difference in the yield of these two treatments. It is possible that upon air-drying of the Kaiwiki soil, in addition to mineral N many other organic compounds beneficial to corn growth were produced.

FIG. 1-9. EFFECT OF DRYING ON $\text{NO}_2\text{-N}$.

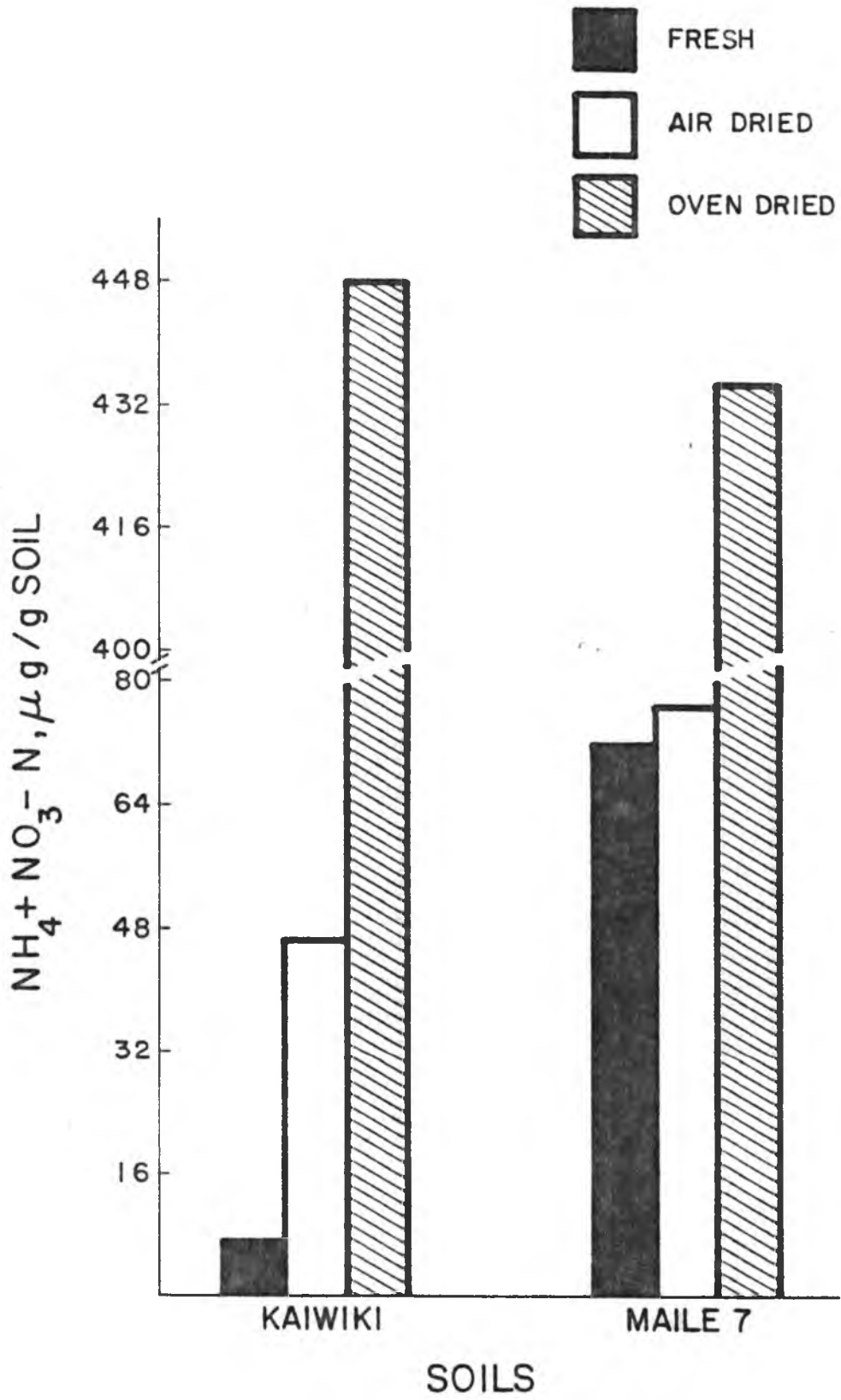


FIG. 1-10. EFFECT OF DRYING ON N MINERALIZATION IN A BULK SAMPLE.

Dry matter yield of corn was significantly affected when fertilizer N was applied in amounts equivalent to those released upon oven-drying of these two soils (Fig. 1-8). In the Kaiwika soil the fertilizer N treatment gave a yield 2.1 times higher than the control and 67 times higher than the oven-dried treatment. It is possible that oven-drying this soil at 105°C produced many organic compounds detrimental to corn growth. In the Maile 7 soil, both oven-dried and fertilizer N treatments produced significantly higher yields of corn. Fertilizer N treatment out-performed the oven-dried treatment by 1.1 times. This may again be explained as the retarding effect of harmful organic compounds produced upon oven-drying.

Practical Implications

A change in the available N content of soil upon natural drying at normal temperatures in the field suggests that prolonged high temperatures will have a great effect on the availability of N to agronomic crops. Maximum N will be available at the start of rains after a long dry spell. Farmers should therefore aim at having their crops planted when rains begin, so that the crop gets the maximum amount of N produced during the flush of decomposition of organic matter.

Intentional burning of crop trash (e.g. sugarcane and pineapple trash in Hawaii) in the field also might have a

drying effect on the soil and likewise may release some N for crop use.

Results of oven-drying show that a large amount of $\text{NH}_4\text{-N}$ is released. Thus, unintentional occurrences such as forest fires in many parts of the world would be expected to increase the exchangeable NH_4^+ at the soil surface. This increased supply of $\text{NH}_4\text{-N}$ may or may not be beneficial for plant growth, depending upon the soil type and the amounts of other beneficial and harmful compounds being produced.

CHAPTER TWO

THE EFFECT OF LIME ON
SOIL NITROGEN MINERALIZATION

ABSTRACT

A field study was undertaken to determine the effect of liming on N mineralization on the Paaloo (Humoxic Tropo-humult) and Wahiawa (Typic Eutruxox) soils. The Paaloo soil had never been disturbed and limed. The Wahiawa soil had been limed twice before. Liming at 0, 2 and 4 tons/ha mineralized more N than the control in the Paaloo soil. However, liming from a pH of 4.7 - 7.1 had little effect on the amount of N mineralized in the Wahiawa soil.

The Effect of Lime on Soil Nitrogen Mineralization

INTRODUCTION

Lime is usually added to correct soil acidity. Liming increases the pH of the soil, influences the microbial population and may affect the availability of many nutrients. As a result, the availability of N to plants may also be affected. The effect of lime on N mineralization has been the source of conflicting reports. Liming of acid soils has often been reported to increase N mineralization (Broadbent, 1962; Halvorson and Caldwell, 1948; Ogata and Caldwell, 1960; Noyes and Conner, 1919; Dean and Smith, 1933; Choudhury and Cornfield, 1979; El-Shakweer, 1976). An elaborate discussion of the effect of liming upon the mineralization of N has been given by Kappen, et al. (1949), and Schachtschabel (1953). The latter reported carefully-conducted laboratory experiments on the effect of liming. He obtained an increase in N mineralization varying between 100-150 kg N/ha when acid sandy soils with high humus content were limed.

Commenting on why lime increases N mineralization, Broadbent (1962) stated that changes in the soil microbial population caused by changes in soil pH may result in increased mineralization of soil N. Many other investigators have reported that increased N mineralization by liming of

acid soils may be because of direct stimulation of the activity or to an increase in bacterial population (Stevenson and Chase, 1953; Allison and Sterling, 1949; Walker, et al., 1937). On the other hand, in some cases negative effects on the N mineralization have been demonstrated (Kaila and Soini, 1957; Kivekas and Kivinen, 1959; Zottl, 1960, 1963; Viro, 1963). Nommik (1968) limed raw humus at 0, 1, 2.5, 5 and 10 percent rates. He reported a decrease in the amount of $\text{NH}_4\text{-N}$ in limed soils. The rate of NH_4 accumulation was very little affected because of liming in the initial stages. During continued incubation of up to 127 days, the CaCO_3 additions resulted in marked decreases in the net mineralization of N. He attributed this depression to increased microbial activity.

Most of the studies dealing with the effect of lime on N mineralization have been done on acid soils of temperate regions. Information on this subject in the tropics is quite limited. Cornforth (1971) reported that mineralization of N in several West Indian soils was related to the supply of exchangeable bases in the base-deficient soils. Thompson, et al. (1954) reported a positive effect of liming in the laboratory, but found no significant change in N mineralization with varying pH in the field. They suggested that the absence of pH effect in the field may be explained on the basis that the effect of liming found in laboratory experiments is only temporary.

MATERIALS AND METHODS

Two field experiments were conducted for assessing the effect of lime application on mineralization of organic N. One experiment was on a Paaloo silty clay soil (Humoxic Tropohumult) in the Helemano area. The area had not been disturbed of natural vegetation, nor had it been previously limed.

The second experiment was conducted at the University of Hawaii Poamoho Experimental Farm, which has a history of lime application. Both sites are located on the island of Oahu. Some of the properties of soils used are given in Table 2-1.

Experiment One

The Paaloo soil is formed from basalt; the annual rainfall is 2000 mm and the elevation is 400 m. The dominant minerals present in the soil are kaolinite, iron oxide and gibbsite. The soil has a cation exchange capacity of 35 m eq/100 g as determined by NH_4OAc (pH 7).

Two sites (1 and 2) were selected on this soil. The soil in site 1 was covered with a closed 100 percent ground cover of two dominant grasses--Melinis minutiflora (molasses grass) and Brachiaria mutica (California grass)--but the tree canopy layer was relatively open (40 percent

Table 2-1. Some Properties of the Experimental Soils

<u>Soil</u>	<u>pH</u> (in H ₂ O)	<u>Total N*</u> %	<u>Total C*</u> %	<u>C:N</u>
Wahiawa	5.40	0.16	1.70	10.62
Paaloa Site 1	5.35	0.27	3.26	12.07
Paaloa Site 2	4.94	0.29	3.30	11.37

* Values expressed on oven-dried basis.

cover) and was dominated by planted Eucalyptus. Other trees present were native Acacia koa and Meterosideros collina. Site 2 was one mile away and covered with a closed ground cover of Gleichenia linearis (creeping fern). Andropogon virginicus (broom sedge) was also present. The tree canopy layer was closed (100 percent) and was dominated by Acacia koa. Other trees present were Araucaria excelsa (Norfolk Island pine) and Psidium cattleianum (purple strawberry guava). Site 1 was relatively drier and warmer than site 2. Both sites were previously uncultivated. On November of 1978 microplots of 0.114 m² were established by removing saplings, shrubs and other vegetation. The area was cleared without burning and with minimum disturbance of the surrounding area. Metallic drums cut 20 cm high were buried 15 cm into the soil at both sites. The soil inside the microplots was disturbed with a small hoe up to a depth of 15 cm. Lime (CaCO₃) was applied at 0, 2 and 4 tons/ha and mixed in the surface 15 cm; soil samples were taken at 0, 1, 2 and 4-month intervals; NH₄ and NO₃-N were determined by the method of Bremner (1965) after extracting with 1 N KCl (1:5 solution ratio). pH was determined in saturated paste on the samples collected at 0, 1, 2 and 4-month intervals.

Experiment Two

The second experimental site was on the University of Hawaii Poamoho Experimental Farm. Elevation is 250 m above sea level. Mean annual rainfall is 1200-1300 mm, most of which falls between October and May. Soil temperature at 7.5 cm depth at this location is typically about 20°C during the rainy season. The soil, a Wahiawa silty clay (Typic Eutruxox), is generally believed to have developed in residuum from basalt, but volcanic ash deposits can be recognized in the area and it seems probable that volcanic ash has influenced soils of the area to some degree. The dominant soil mineral is kaolinite, but there is also some hematite, goethite, gibbsite, mica and manganese oxide.

The field layout was a continuous function design (Fox, 1973). It was comprised of 4 blocks, each block having 16 plots 1 meter wide by 16 meters long (Fig. 2-1). In each block lime was applied to systematically increase pH on one axis. The plots were first limed in 1973 and then relimed in 1976. For this experiment plots were again limed (or acidulated) to produce a desired gradient of pH ranging from 4.7 to 7.1. After the lime or acid was added, the plots were rototilled to a depth of 15 cm across the lime strips, K was applied as K_2SO_4 (130 kg per ha) and P as triple super phosphate (0.2 ppm) as the basal dose. Three rows of corn were planted in each block. The rest

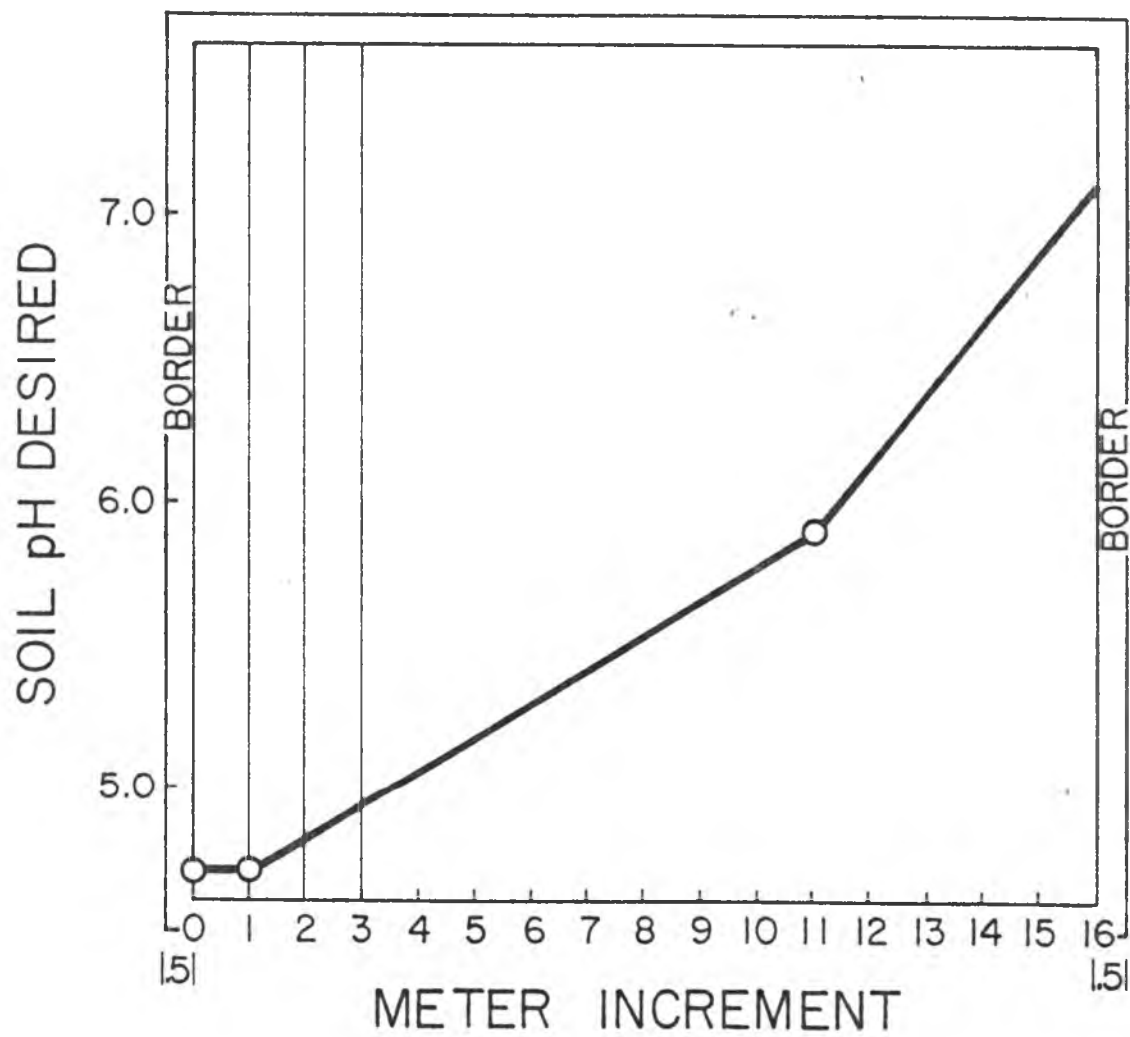


FIG. 2-1. LAYOUT OF ONE BLOCK AT POAMOHO FIELD.

of the area was used for another experiment. One block was heavily damaged by birds and was therefore not reported in the study. Ear-leaf samples were taken after two months and corn was harvested after 2½ months. Soil samples were collected one month after the lime application, NH_4^- and NO_3^- -N in soil were determined by steam distillation by the method of Bremner (1965) after extraction with 1 N KCl. pH of soil samples was determined in saturated water paste. Total N in ear leaves and corn plants was determined by a semi-automated method using sodium thiosulfate, sodium sulphate, and H_2SO_4 containing selenium and salicylic acid for digestion, and then steam distilled using NaOH. The distillate was absorbed in 4 percent boric acid and titrated by standard H_2SO_4 .

RESULTS AND DISCUSSION

Experiment One

Effect of Liming on Release of $\text{NH}_4\text{-N}$

Liming released significantly larger amounts of $\text{NH}_4\text{-N}$ at both the two and four tons/ha lime rates compared with the control at both sites. Changes in the $\text{NH}_4\text{-N}$ content during four months is shown in Table 2-2. At site 2 the amount of $\text{NH}_4\text{-N}$ released at two and four ton/ha lime rates was much greater than site 1. This may be due to the higher pH of soil at site 2, especially at four months/ha rates (Fig. 2-2). In both the two and four ton/ha rates, the maximum accumulation of NH_4^+ was two months after the lime application at both the sites. This may be due to the time taken by microbes to build up their population. Extractable NH_4^+ decreased by four months after lime application at site 1, with a particularly marked loss at the four ton/ha rate. The NH_4^+ level was even less (51%) where four tons of lime/ha had been applied, than in the control. This may have been due to a volatilization loss of N because the pH of the soil at both sites was close to 7. At site 2, there was only a small decrease in the NH_4^+ at two and four ton/ha rates after four months of equilibration.

Table 2-2. Changes in Various Forms of Inorganic Nitrogen (NH_4^- and NO_3^- -N) in the Paaloa Soil Due to Lime

Lime Rates tons/ha	Incubation Time			
	months			
	0	1	2	4
	<u>Site 1</u>			
	NH_4^- -N $\mu\text{g/g}$			
0	3.7	44.7	36.4	38.7
2	3.2	54.2	58.8	53.6
	% Increase over Control	21.0	61.0	39.0
4	3.2	69.7	70.0	18.9
	% Increase over Control	56.0	94.0	-51.0
	NO_3^- -N			
0	4.4	6.7	8.6	7.8
2	4.3	4.8	6.3	11.8
4	4.3	6.2	8.2	25.4
	$\text{NH}_4^- + \text{NO}_3^-$ -N			
0	8.0	51.4	45.0	46.5
2	7.5	58.9	65.2	65.4
	% Increase over Control	14.8	44.8	40.6
4	7.5	75.8	78.3	44.3
	% Increase over Control	47.6	73.9	-4.8
	<u>Site 2</u>			
	NH_4^- -N			
0	4.7	5.9	6.2	9.3
2	4.8	25.6	30.0	23.7
	% Increase over Control	334.0	383.0	155.0
4	4.8	32.9	36.0	36.3
	% Increase over Control	457.9	479.7	289.7
	NO_3^- -N			
0	7.1	5.3	12.8	18.4
2	7.2	6.7	5.2	18.1
4	7.2	4.6	4.8	21.4
	$\text{NH}_4^- + \text{NO}_3^-$ -N			
0	11.8	11.2	19.0	27.7
2	12.0	32.3	35.2	41.8
	% Increase over Control	189.3	84.8	51.0
4	12.0	37.6	40.8	57.6
	% Increase over Control	236.4	114.5	107.9

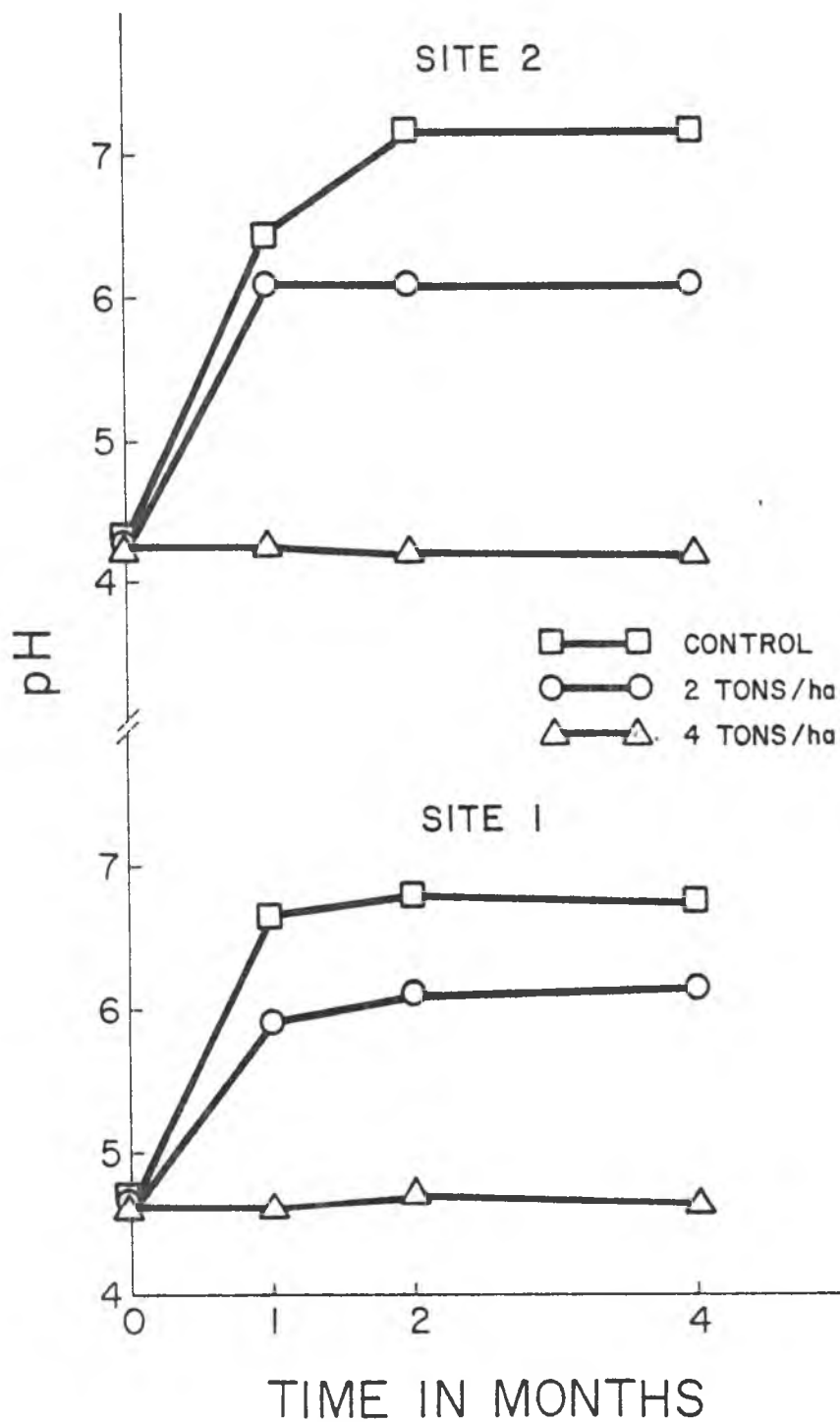


FIG. 2-2. CHANGES IN pH WITH VARYING AMOUNTS OF LIME APPLICATION.

Changes in NO₃-N

The NO₃-N content was little affected by lime application during the two months after liming (Table 2-2). However, by the fourth month nitrate values had increased. The percent increase over control was 50 and 225 for site 1 at both the two and four ton/ha rates, respectively. The corresponding value for site 2 at four ton/ha rate was 16%. This difference between the two sites may be due to a higher leaching loss at site 2 (this site received more rainfall than site 1).

Changes in Total Nitrogen Mineralized

The beneficial effect of lime in increasing the amount of N mineralized ($\text{NH}_4^+ + \text{NO}_3^-$) was apparent the first month after liming (Table 2-2). The maximum values were attained in the second month in site 1. These values were 45, 65 and 78 $\mu\text{g/g}$ for site 1. For location 2 maximum N mineralization occurred in the fourth month (Table 2-2). These values were 27.7, 51.0 and 107.9 $\mu\text{g/g}$ for 0, 2 and 4 ton/ha rates at site 2, respectively.

Correlation Studies

A regression analysis of various forms of N as affected by time was prepared for both sites. These results are presented in Fig. 2-3 through Fig. 2-6. The prediction equations for these curves are also given on the graphs. Each point on the curve represents values obtained from

samples taken at monthly intervals.

Ammonium Nitrogen Content of Soil as Affected by Liming

The amount of $\text{NH}_4\text{-N}$ released increased with increasing rate of lime at both sites (Fig. 2-3 and 2-4). The statistical analysis of the data showed significant differences among lime rates. The amount released was much higher at site 1 than at site 2. A possible reason for this higher NH_4 level at site 1 may be that more $\text{NH}_4\text{-N}$ was released even in the control at site 1, since this site was more open to drying, which might have caused this difference.

Nitrate Nitrogen Content of Soil as Affected by Liming

There was no clear-cut difference in the $\text{NO}_3\text{-N}$ due to lime at either site (Fig. 2-5). At site 1 $\text{NO}_3\text{-N}$ released in the control treatment was higher than at two and four-ton lime rates for all months. These differences were not so pronounced at site 2.

Nitrogen Mineralization as Affected by Liming

The amount of N mineralized increased two months after lime application at site 1 (Fig. 2-6) followed by a decrease at all rates. The decrease was most noticeable at the four ton/ha rate. This may be due to the reason that microbial population at this rate was so much stimulated that they exhausted the mineralizable N reserve of the soil at a faster rate than at the other two rates. At site

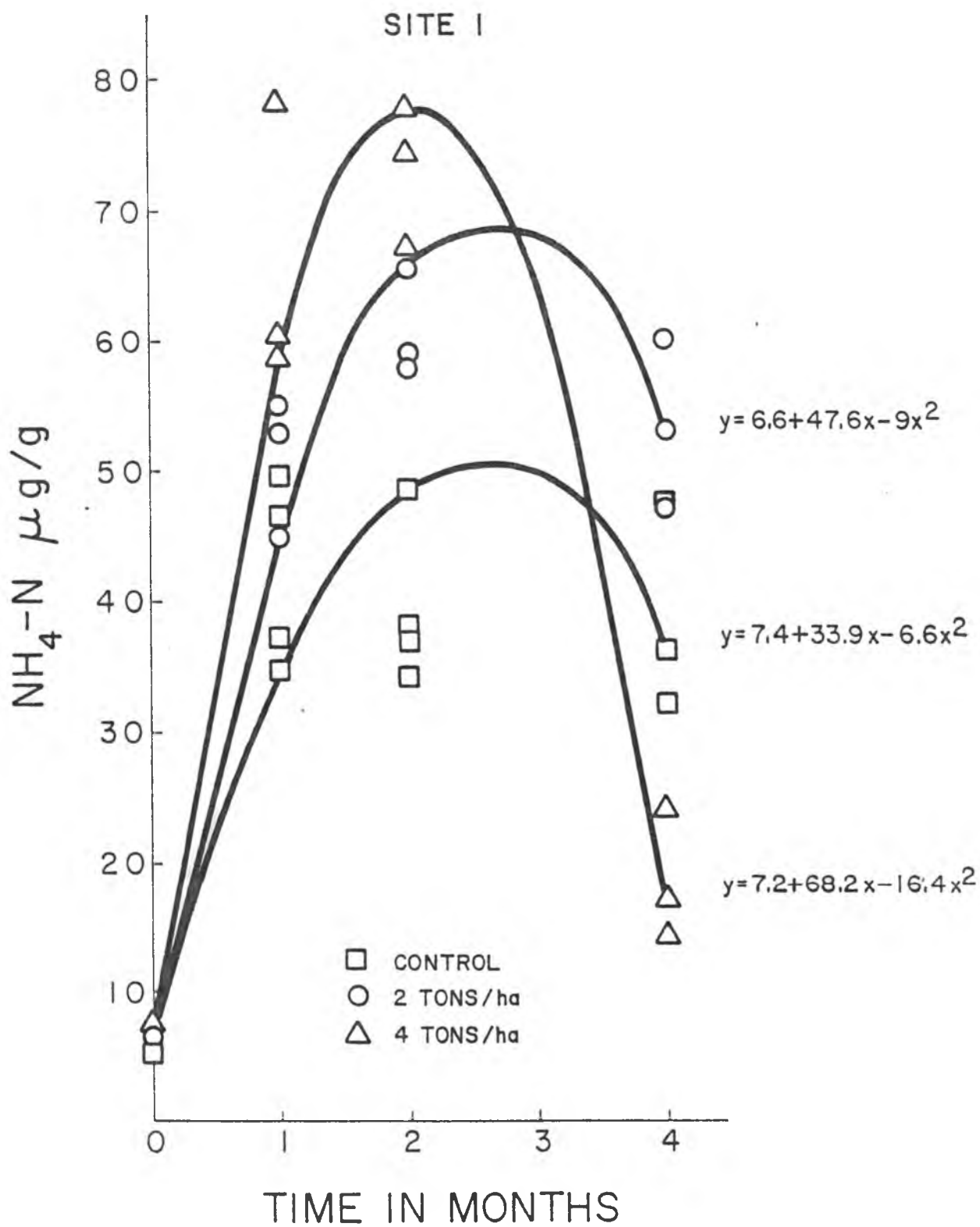


FIG. 2-3. CHANGES IN EXCHANGEABLE NH₄-N DUE TO LIMING AT SITE 1.

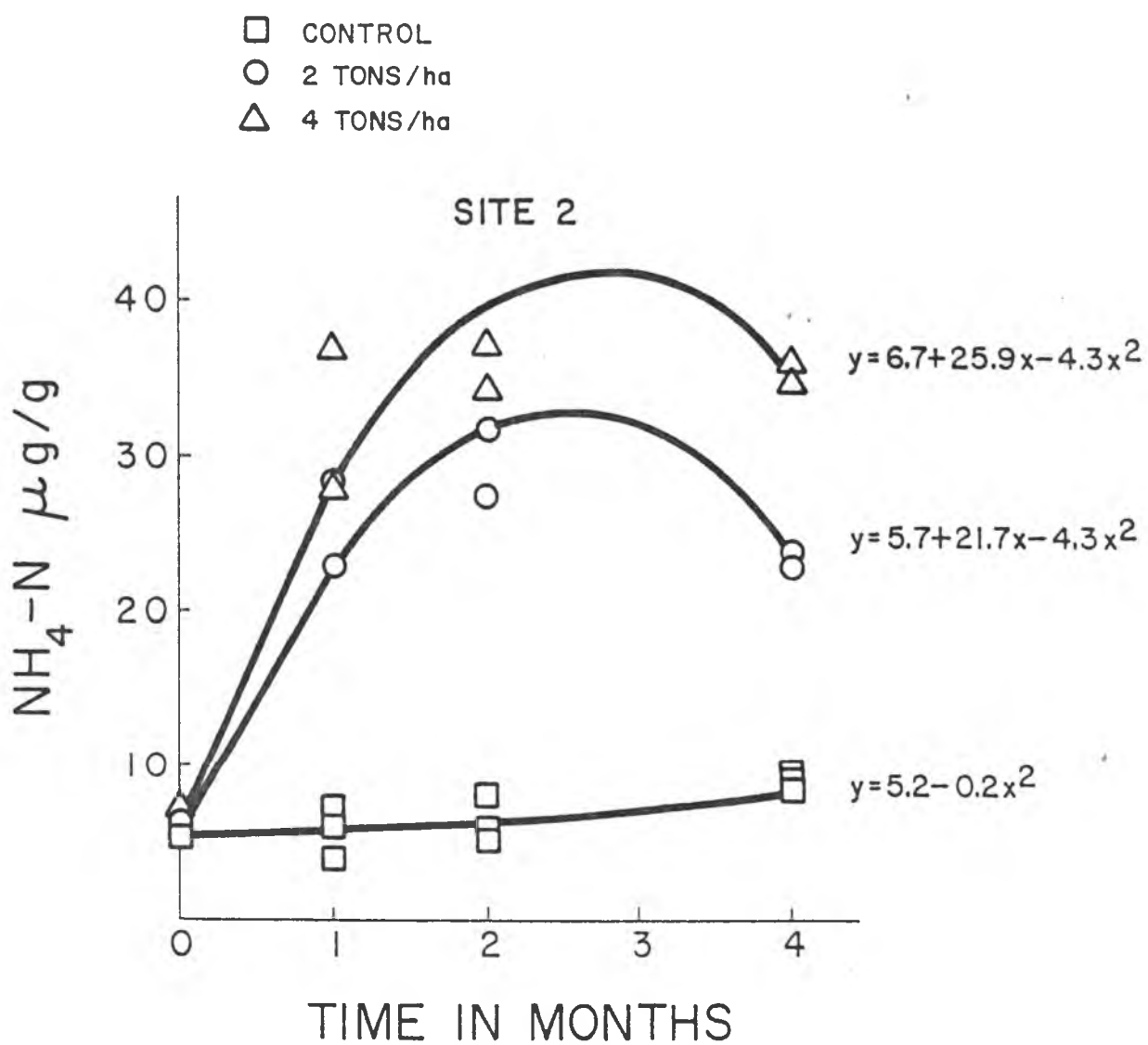


FIG. 2-4. CHANGES IN EXCHANGEABLE $\text{NH}_4\text{-N}$ DUE TO LIMING AT SITE 2.

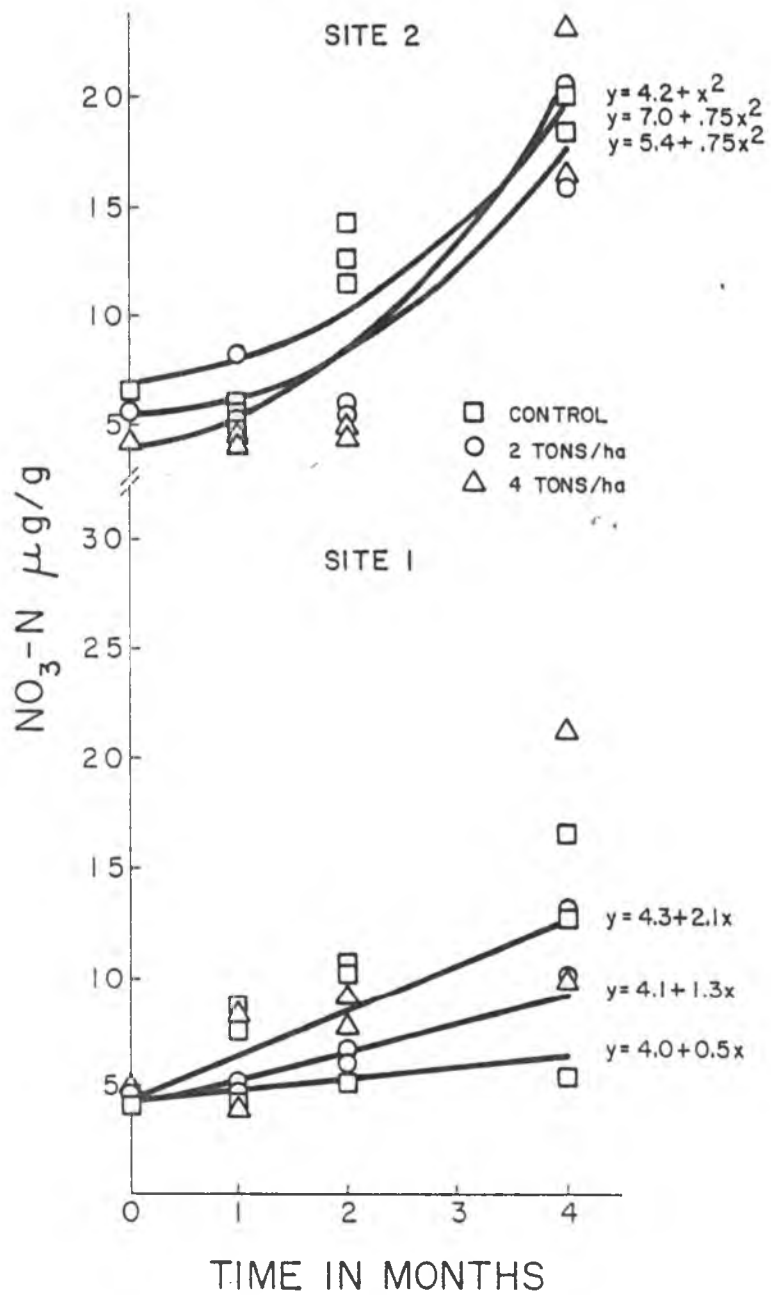


FIG. 2-5. CHANGES IN $\text{NO}_3\text{-N}$ DUE TO LIMING.

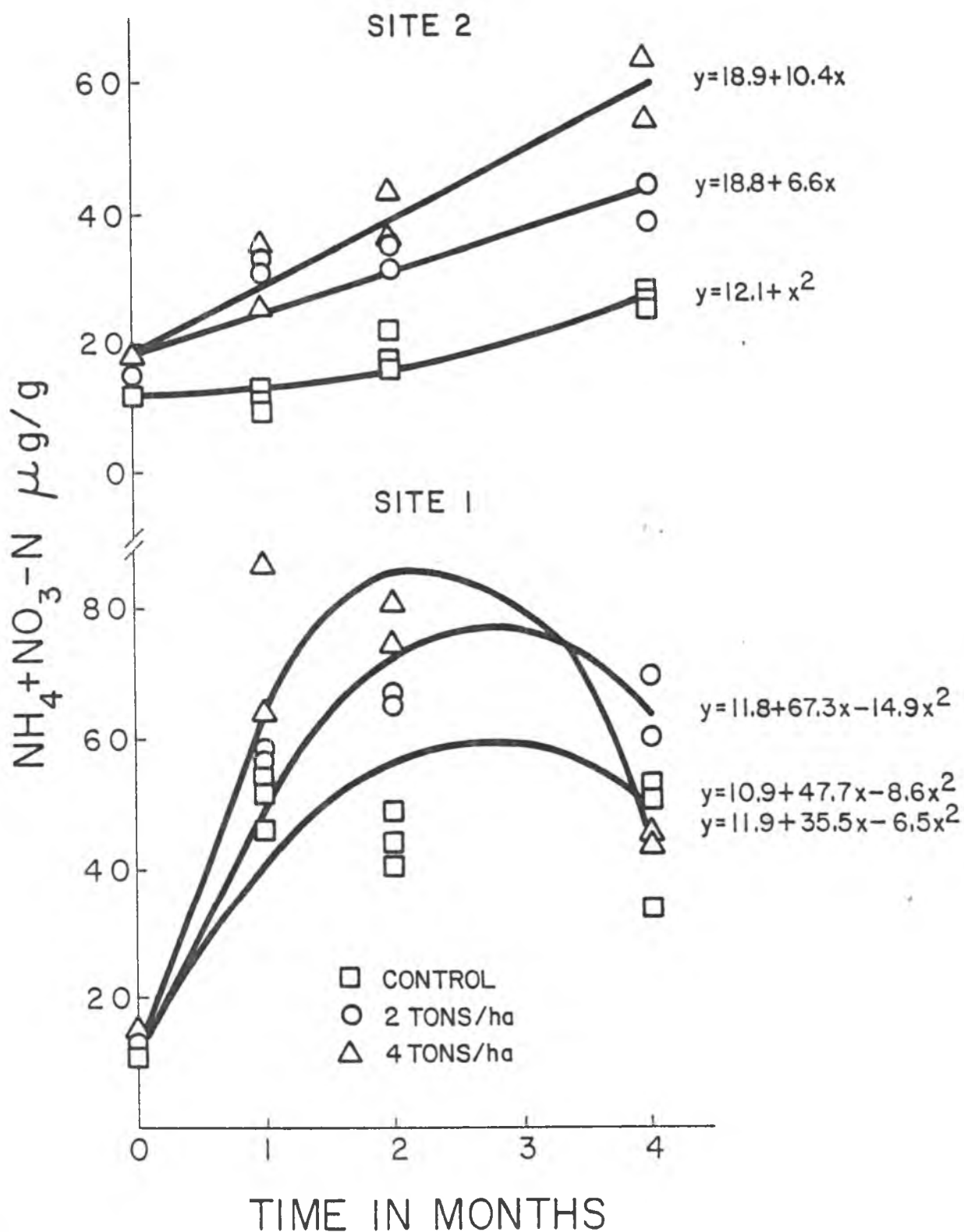


FIG. 2-6. CHANGES IN MINERAL-N DUE TO LIMING.

2 there was an increase in the amount of mineral N up to four months after lime application.

The beneficial effects of lime in increasing the amount of N mineralized may be due to a more favorable environment for the microorganisms provided by neutralizing the excess acidity and supplying calcium. It has been hypothesized (Stevenson and Chase, 1953; Allison and Sterling, 1949; Walker et al., 1937) that lime stimulates microorganisms involved in N transformation by bringing about a favorable change in soil conditions. This suggestion agrees with the results of many investigators who have reported that adding lime to acid soils markedly increases N mineralization (Halvorson and Caldwell, 1948; Ayers, 1961; Bornemisza, 1967; Stevenson and Chase, 1953; Allison and Sterling, 1949; and Walker et al., 1937). Chaudhury and Cornfield (1979) suggested that increase in mineral N may be attributed either to a direct stimulation of the microbial population or to a decreased level of Al in the soil due to lime. Matsuda and Nagata (1957) and Yoshida and Sakai (1964) reported that numbers of bacteria, actinomycetes and fungi decreased when Al concentration in soil increased.

Agarwal, et al. (1972), working with the Paaloo soil, reported N availability was increased when the soil was treated with $\text{Ca}(\text{OH})_2$ and CaCl_2 . They proposed the increased N is derived from the breaking down of microbial

cells and N-containing organic/inorganic complexes. Waksman and Starkey (1923) argued that marked evolution of CO_2 due to addition of CaCO_3 may not be due to biological action, but to a result of chemical reactions taking place between CaCO_3 and acid-producing material in the soil. They also reported a limited increase in bacterial numbers. Recently, Laura (1974) put forward the hypothesis of chemical decomposition of organic matter in soil due to protolytic action of H_2O . Water, being amphoteric in nature, may lose or gain protons depending on the pH of the medium: in an acid medium, it acts as a base; in a basic medium, it acts as an acid, readily giving its protons to other bases. Therefore, an increase in pH might increase the supply of protons from water. This might explain the increased mineralization of organic matter with increased pH due to liming.

Experiment Two

Dry Matter Yield of Corn

Table 2-3 gives dry matter yield data on mature corn plants grown on plots limed from pH 4.7 to 7.5. Above pH 5.6, a small increase in yield occurred. The dry matter yield of corn ranged from 3.5 to 6.5 kg/plot, indicating that the "best" plot had a dry matter yield only 1.85 times higher than the "poorest" plot. Calculation of a simple

Table 2-3. Dry Matter Yield of Corn

<u>Meter Number</u>	<u>pH</u>	<u>Yield</u> kg/m
1	4.7	3.9
2	4.8	3.5
3	4.9	4.4
4	5.0	4.4
5	5.1	4.9
6	5.2	4.4
7	5.3	4.7
8	5.4	4.2
9	5.6	5.4
10	5.7	4.6
11	5.9	5.6
12	6.1	5.1
13	6.4	6.3
14	6.7	5.7
15	7.0	6.5
16	7.5	5.3

linear correlation (Fig. 2-7) between pH and dry matter yield for 16 plots showed a significant correlation (0.79). These increased yields may not necessarily be due to higher N mineralization; increased Ca supply and reduced Mn toxicity may also be responsible for the increased yield.

Similar observations were made by Soares, et al. (1974), who found a yield increase (15-40%) of corn when 5 t/ha of lime was applied to dark red Latosols in four locations in central Brazil. Soil pH in unlimed plots was less than 5.0. Also, in Brazil, Freitas, et al. (1960) reported a strong response by corn to liming from two Humic Latosols with initial pH values of 4.3 and 4.5, and only traces of exchangeable Ca. They suspected that the increased supply of Ca was responsible for this increase. The amount of N-uptake by corn from limed plots was very poorly correlated with pH of the plots.

Nitrogen-Supplying Power of Soil

Table 2-4 gives values of mineral N determined in soil samples taken one month after lime application. The data indicates quite a narrow range of values, from 12.8 to 19.4 $\mu\text{g/g}$, with a pH change from 4.7 to 7.5. A linear regression between soil N mineralized and plant N was very poor (0.27). The possible reasons for such results from a soil with a history of three years of liming may be: (1) whatever temporary stimulating effect lime had on native

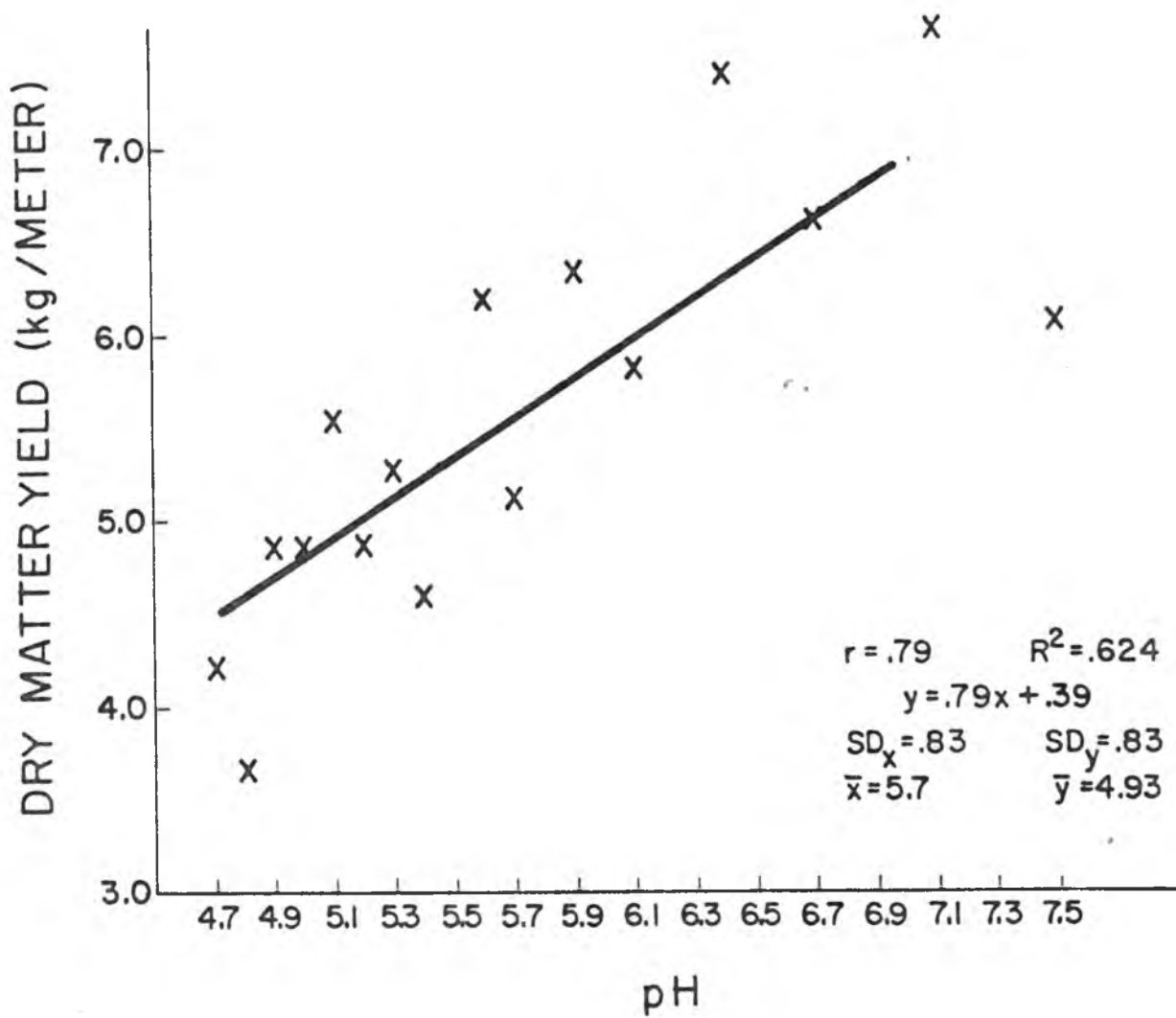


FIG. 2-7. EFFECT OF LIME ON DRY MATTER YIELD OF CORN.

Table 2-4. Effect of Lime on Nitrogen Mineralization and Nitrogen Uptake by Corn

<u>Plot number</u>	<u>Soil N</u> µg/g	<u>N Uptake</u> g
1	14.7	43.9
2	13.6	35.9
3	19.4	51.1
4	15.5	44.5
5	13.9	47.6
6	12.8	44.0
7	14.7	63.2
8	13.9	34.1
9	13.4	64.2
10	16.1	46.6
11	13.1	52.9
12	13.6	55.2
13	16.4	74.0
14	15.8	64.6
15	16.6	68.9
16	17.7	51.2

$$y = 26.04 + 1.76x$$

soil N mineralization might have already occurred during the first years of liming of these plots in 1973; and (2) the Wahiawa soil did not contain as much organic matter or total N as the Paaloa soil. Thus, less N was available for mineralization (Table 2-1).

It can be concluded from this study that accelerated release of N as a result of liming could increase the N supply to the crops. Nitrogen mineralization during the first season might well prove desirable. Release of substantial amounts of N however may also result in leaching and denitrification losses. Thus, if heavy liming is to be practiced in soils high in organic N, some modification in the N fertilizer application may be desirable to take into account additional N being made available from native source.

CHAPTER THREE

NITROGEN-SUPPLYING POWER OF SOILS

ABSTRACT

An evaluation of the N supplying power of seven soils was made. Two chemical extraction methods as well as aerobic incubation procedures at 25°C and 35°C were used to obtain an index of N availability. Nitrogen mineralized was correlated with N-uptake by corn in the greenhouse. Aerobic incubation at 25°C was significantly correlated ($r=0.96$) with the N-uptake by corn. Incubation at 35°C also gave high correlation ($r=0.92$). Chemical methods are a poor index of N availability for these soils.

Nitrogen-Supplying Power of Soils

INTRODUCTION

For efficient use of nitrogenous fertilizers, it is important that their indiscriminate use be avoided. To accomplish such a purpose, it is necessary that rates and timing or fertilization be controlled so that the farmer gets the maximum benefit out of every dollar invested. The quantity that needs to be supplied through fertilizers is the difference between that required for a specified yield and the quantity supplied by the soil. Of the many methods of determining the quantity of fertilizer needed for a specific yield, one has to take into account the internal N requirement of various crops (Stanford et al., 1970). For example, the internal N requirement for corn is 1.2% N in the total dry matter, 1 to 1.3% for small grain crops, and 0.2% for sugarcane. But determining the N-supplying power of soils is still a problem because so many factors affect mineralization and the immobilization processes in soil. Biological N availability indices are considered by many to be the most reliable because the same organisms (*Nitrosomonas*, *Nitrobacter*) which mineralize N in the field are involved (Dahnke and Vasey, 1973). The procedures most widely used are based upon the aerobic incubation technique developed by Stanford and Hanway (1955).

This technique was later modified by Stanford and Smith (1972), and Stanford, et al. (1973). They determined potentially mineralizable N (N_0) from aerobic incubation at 35°C for 30 successive weeks. They concluded that cumulative N mineralized over time conformed to the first order equation:

$$\log (N_0 - N_t) = \log N_0 - kt/2.303$$

N_0 = potentially mineralizable N

N_t = N mineralized in time (t)

k = the mineralization constant

Later Stanford, et al. (1974) showed that reasonable estimates of the potentially mineralizable N could be made from short term (3 to 4 week) incubations. In subsequent studies, Stanford, et al. (1977) found a highly significant (>0.80) correlation between N-uptake by sugar beets and the potentially mineralizable N in southern Idaho soils.

Biological methods, however, are time consuming and may not be convenient for large-scale soil testing. In search of a reliable chemical method for a measure of N availability, Stanford and Demar (1970), and Smith and Stanford (1971) recommended autoclaving the soil with 0.01 M CaCl_2 for 16 hours. Stanford and Smith (1976) reported that N mineralized under aerobic and anaerobic incubation, correlated well ($r=0.93$) with the amount of NH_4 -N extracted by autoclaving in 0.01 M CaCl_2 for 16 hours at 121°C for 212 surface soils. Smith, et al. (1977) compared

autoclaving, aerobic, and anerobic incubation to field incubation studies. For the latter study they put eight soil samples in polyethylene bags and filter tubes, and buried them in the field for two seasons. They reported a significant correlation between calculated values from the incubation method and autoclaving.

Another chemical method being widely used as an index of N availability is extraction of soil with 0.01 M NaHCO_3 (MacLean, 1964). MacLean found a correlation coefficient of 0.85 between N extracted with 0.01 M NaHCO_3 and N uptake by oat plants in 24 soils. Fox and Piekielek (1978a) using corn as a measure of N uptake, compared 0.01 M NaHCO_3 with four other methods (0.025 M $\text{Al}_2(\text{SO}_4)_3$, 1 N KCl, boiling with 0.01 M CaCl_2 , and autoclave-extractable $\text{NH}_4\text{-N}$), and reported a high correlation coefficient ($r=0.94$) for MacLean's extractant. Later (1978b) they reported the UV absorbance of the soil extracts with NaHCO_3 to be a measure of concentration of organic matter in a particular soil. They suggested absorbance at 260 nm was proportional to soil organic matter. If the soil is rich in $\text{NO}_3\text{-N}$, then UV absorbance at 205 nm should be a better measure of $\text{NO}_3\text{-N}$ and of mineralizable organic matter. The obvious advantage of this method is that no reagents or color forming complexes are required for the determination.

Considerable effort has been expended to evaluate the N-supplying power of temperate region soils. But little

is known about the N-supplying power of tropical soils or applicability of the above methods to tropical soils.

Lathwell, et al. (1972), working with ten soils from Puerto Rico, compared the aerobic incubation method with four chemical extractants (1 N KCl, 1 N K_2SO_4 , boiling with 0.01 M $CaCl_2$, and sodium pyrophosphate) to predict N availability for corn. Mineralizable N which was (1) produced during incubation, (2) extracted with 0.01 N $CaCl_2$, and (3) extracted with 1 N K_2SO_4 , was highly correlated with N uptake by corn.

The present study was undertaken to (1) compare various incubation methods of measuring available N released from tropical soils at 25°C and 35°C; (2) determine whether chemical methods can provide reasonable indices of N availability; (3) correlation of these methods with N-uptake by corn grown in the greenhouse.

MATERIALS AND METHODS

Description of Soils Used

Seven soils were used for this study: the Kaiwiki (Typic Hydrandept), Waikaloa (Ustollic Eutrandept), Waimea (Typic Eutrandept), Maile 7 and Maile 9 (Hydric Dystrandept), Lualualei (Typic Chromustert) and Halii (Typic Gibbsihumox) soils. The Kaiwiki, Waikaloa, Waimea, Maile 7 and Maile 9 were described in Chapter 1. The Lualualei and Halii soils are described as follows.

The Lualualei is a member of the very fine, montmorillonitic isohyperthermic family, and is formed from deep alluvium with an annual rainfall of 500 mm at an elevation of 5 m. The average air temperature for this soil site for the months of January and July is about 21.7°C and 26.6°C, respectively. Mean annual temperature is about 23.9°C. The dominant clay mineral is montmorillonite.

The Halii consists of well-drained and moderately-drained soils from the uplands of the island of Kauai. It is highly weathered and developed from igneous rock. It is rich in iron and aluminum oxides and also contains titanium oxide concretions. Important properties of the Lualualei and Halii are given in Table 3-1.

Table 3-1. Some Properties of Experimental Soils

<u>Soil</u>	<u>pH</u>	<u>Total N</u> %	<u>Organic C</u> %	<u>C:N</u>
Lualualei	7.7	0.09	1.06	10.7
Halii	5.2	0.31	4.31	14.0

Incubation Studies

The seven soils (40 g O.D.) were mixed with perlite (7 g) and placed in leaching tubes. The tubes were leached with 100 ml of 0.01 M CaCl_2 solution followed by N-free nutrient solution (Stanford et al., 1974) to remove inorganic N initially present in the soil. The leaching tubes were then subjected to a uniform suction (60 cm Hg) to remove excessive liquid. The tubes were covered and incubated at 25°C and 35°C. The tubes were extracted weekly for eight weeks with CaCl_2 and N-free nutrient solution. NH_4^- and NO_3^- -N were determined in the weekly extracts by the micro-Kjeldahl distillation procedure of Bremner (1965).

Autoclave-Extractable NH_4^- -N

Ammonium-N was determined by the method of Stanford and Demar (1970). Ten grams (O.D.) of soil were placed in 50 ml centrifuge tubes with 25 ml of 0.01 M CaCl_2 and autoclaved at 15 lbs pressure for 16 hours at 121°C. The suspension was centrifuged and the supernatant decanted. The soil sediment was resuspended twice in 25 ml of 0.01 M CaCl_2 , recentrifuged, and the supernatant was combined with that from the prior centrifugation. The extract plus two rinses were placed in a steam distillation flask, 1 ml of 10 N NaOH was added, and the NH_3 present was steam distilled into boric acid and titrated with standard H_2SO_4 .

NaHCO₃-Extractable Nitrogen

NaHCO₃-extractable N was extracted by the method of MacLean (1964). Five-gram soil sample was shaken in 100 ml of 0.01 M NaHCO₃ for 15 minutes in 250-ml Erlenmeyer flasks. The suspension was suction-filtered through Whatman #42 filter paper. The UV absorption was measured with a model Unicam SP 1800 ultraviolet spectrophotometer. When UV measurements were made at 205 nm to estimate the NO₃-N content of the extract, two drops of concentrated HCl were added to eliminate HCO₃⁻ (which also absorbs in this range).

Five soils: The Kaiwiki, Waikalua, Waimea, Maile 7 and Maile 9 soils were used to obtain an index of N availability. A greenhouse experiment was conducted using Zea mays (corn) as the indicator plant. Four kg/pot of soil was used for the Waikalua, Waimea, Maile 7 and Maile 9 soils. The Kaiwiki was taken on a volume basis to the equivalent of 4 kg/pot. All nutrients except N were applied at optimum rates as follows:

<u>Nutrient</u>	<u>Rate</u>	<u>Form of Application</u>
P	800 kg/ha	Ca(H ₂ PO ₄)H ₂ O
K	500 kg/ha	KCl
Mg	200 kg/ha	MgSO ₄ · 7H ₂ O
Fe	50 kg/ha	FeSO ₄ · 7H ₂ O
Zn	20 kg/ha	ZnSO ₄
B	2 kg/ha	H ₃ BO ₃
Cu	3 kg/ha	CuSO ₄

RESULTS AND DISCUSSION

Effect of Incubation Temperature on Nitrogen Mineralization

The amounts of N (NH_4^+ + NO_3^-) mineralized weekly in seven soils at two temperatures is shown in Table 3-2. Cumulative N mineralized (N_c) after eight weeks at 25°C showed the following increasing trend: Kaiwiki < Lualualei < Waimea < Maile 9 < Maile 7 < Waikaloa < Halii.

These soils when incubated at a higher temperature (35°C) gave the following trend in N mineralization: Lualualei < Maile 9 < Waimea < Kaiwiki < Maile 7 < Waikaloa < Halii. These values were higher than those at 25°C for all soils. The Q_{10} values for N mineralization over the temperature from 25°C to 35°C were: 1.2, 1.3, 1.4, 1.7, 2.0, 2.0 and 1.3 for the Lualualei, Halii, Maile 9, Waikaloa, Waimea, Maile 7 and Kaiwiki soils, respectively. Some of these Q_{10} values are not in agreement with the commonly-held notion that the "temperature coefficient" of N mineralization is approximately 2 (Bray and White, 1957; Stanford et al., 1973). However, Meyer and Anderson (1963) suggested that the range of Q_{10} values for most enzymatic reactions falls between 1.4 and 2.0. In this case only Q_{10} for the Kaiwiki soil was higher than this range, which may be due to the unique properties of this soil, being thixotropic, and that it dries irreversibly.

Table 3-2. Soil Nitrogen Mineralized from Seven Soils When Incubated at Two Temperatures

<u>Soil</u>	25°C									Total
	<u>Incubation Time (Weeks)</u>									
	0	1	2	3	4	5	6	7	8	
	----- μg/g -----									
Kaiwiki	4.0	4.3	6.1	7.2	7.4	5.5	6.1	6.1	5.5	51.6
Waikaloa	13.4	29.7	30.8	14.8	11.4	11.7	10.4	10.0	9.9	142.1
Maile 7	28.4	14.4	9.5	9.3	8.1	9.1	8.6	9.3	9.3	106.0
Maile 9	10.4	8.0	5.5	6.6	8.0	7.4	8.3	5.1	5.1	64.4
Waimea	6.1	6.4	6.4	5.9	5.5	7.6	8.3	6.3	6.3	58.8
Halii	86.8	60.8	34.5	23.2	14.7	11.3	8.9	8.8	8.8	257.6
Lualualei	4.2	12.4	7.6	6.0	6.2	4.7	5.1	3.8	3.8	53.8

	35°C									
Kaiwiki	3.4	7.8	14.6	14.0	16.3	20.3	19.5	21.6	20.3	137.9
Waikaloa	14.6	51.3	40.9	22.9	26.3	22.7	21.0	18.6	18.6	236.9
Maile 7	28.4	28.9	26.5	21.2	25.9	24.2	18.4	20.6	18.4	212.4
Maile 9	10.8	11.9	11.7	9.7	7.6	11.2	9.4	11.0	9.4	92.8
Waimea	4.2	20.8	16.1	16.5	15.1	12.7	10.6	11.9	10.6	118.5
Halii	95.4	69.7	38.3	28.4	30.2	22.6	15.3	11.4	11.4	322.7
Lualualei	4.5	10.5	7.6	6.8	7.2	6.6	6.2	7.8	6.2	63.4

Nitrogen Mineralization Potential

Values in Table 3-2 were used to calculate N mineralization potential (N_0) using the approach of Stanford and Smith (1972). First estimates of N_0 were obtained from the following expression:

$$1/N_t = 1/N_0 + b/t$$

where N_t = ppm N mineralized (cumulative); t = time (weeks); and b = the slope of regression line between $1/N_t$ vs $1/t$. Estimates of N_0 are given in Table 3-3. These N_0 values were derived from regression analysis based on cumulative N mineralized (N_t) from one to eight weeks of incubation. Coefficients of determinations for soils were at least 0.98 for all soils.

The hypothesis that the rate of mineralization is proportional to the amount of potentially-mineralizable N is expressed by the first order reaction equation: $dN/dt = -kN$ (Stevenson, 1965). Integration of this expression gives:

$$\log (N_0 - N_t) = \log N_0 - k(t)/2.303$$

where the terms are as described before.

This equation was employed to calculate N_0 giving the best linear fit for the regression of $\log (N_0 - N_t)$ on t (Table 3-4). N_0 values for this equation were used from estimates based on the $1/N_0$ vs $1/t$ regression. It is clear from Table 3-4 that N_0 values at 35°C were higher for all soils except the Waimea, where N_0 at 25°C is very high

Table 3-3. Estimates of Soil Nitrogen Mineralization Potential Based on $1/N_t$ vs $1/t$

<u>Soil</u>	<u>Regression Equation</u>	<u>r</u>	<u>N_0</u>
Kaiwiki	$y = 0.224x - 0.160$	0.99	60.6
Waikalua	$y = 0.025x + 0.004$	0.99	221.8
Maile 7	$y = 0.064x + 0.006$	0.99	155.9
Maile 9	$y = 0.123x + 0.004$	0.99	215.2
Waimea	$y = 0.157x - 0.0003$	0.99	3062.1
Halii	$y = 0.012x + 0.003$	0.99	255.2
Lualualei	$y = 0.068x + 0.013$	0.99	76.6

Table 3-4. Estimates of Nitrogen Mineralization Potential at Two Temperatures

Soil	25°C		
	N_t	N_0 1/t vs 1/ N_t	N_0 log ($N_0 - N_t$) vs t
Kaiwiki	47.6	60.6	76.3
Waikalua	128.6	221.8	201.2
Maile 7	77.6	155.9	157.2
Maile 9	53.9	215.8	214.8
Waimea	52.7	3062.1	3062.0
Halii	170.8	255.2	201.5
Lualualei	49.6	76.6	71.9
		35°C	
Kaiwiki	134.5	70.9	79.3
Waikalua	222.3	434.9	409.5
Maile 7	183.9	967.8	960.7
Maile 9	82.0	386.0	385.3
Waimea	114.3	369.7	362.2
Halii	227.3	371.2	323.2
Lualualei	58.5	131.7	131.8

(3062), which shows that this approach may not be a good criterion for calculating N-supplying power of this soil because it is based upon the reciprocal of the intercept of the regression line. In case the intercept value is extremely small, its reciprocal values tend to be large, giving rise to erroneous N_0 values.

Stanford, et al. (1974) suggested that estimates of N_0 from short-term incubation could be made from the equation:

$$\log (N_0 - N_t) = \log N_0 - kt/2.303$$

Solving for N_0 :

$$N_0 = \frac{N_t}{1 - 10^{-kt/2.303}}$$

Hence, for the one-week period of incubation at 35°C ($k = .054$), $N_0 = 19.05 N_t$.

For an eight-week period of incubation it will be $2.85 N_t$.

Values of N_0 calculated are given in Table 3-5.

All these approaches were used to calculate N_0 in this study, and will be related to plant estimates of N availability later in this chapter.

The following example will illustrate how N_0 , soil temperature and soil water content may be used to calculate field N mineralization. Suppose that N_0 measured in the laboratory is 100 $\mu\text{g/g}$, and the first week average soil temperature and water content in the field are 25°C and 75%

Table 3-5. Nitrogen Mineralization Potential of Seven
Soils Using $N_0 = \frac{N_t}{1 - 10^{-kt/2.303}}$

<u>Soil</u>	----- N_0 ($\mu\text{g/g}$) -----	
	<u>25°C</u>	<u>35°C</u>
Kaiwiki	257.7	383.4
Waikalua	695.8	633.6
Maile 7	419.9	524.3
Maile 9	292.1	233.6
Waimea	283.6	325.6
Halii	924.0	647.9
Lualualei	265.1	167.7

field capacity, respectively. Then the amount of N mineralized for the week would be:

$$100 \times 0.0270 \times 0.75 = 2.01 \text{ } \mu\text{g/g,}$$

where 0.027 is the rate constant/month for 25°C (Stanford and Smith, 1972).

Autoclaving with 0.01 M CaCl₂

Autoclaving soil with 0.01 M CaCl₂ for 16 hours gave values of N released ranging from 27.6 to 338.8 $\mu\text{g N/g}$ soil. The values of N released by 16 hours autoclaving in the Lualualei, Waimea, Waikalua, Maile 9, Halii, Maile 7 and Kaiwiki were 27.6, 92.0, 161.3, 253.5, 293.8, 338.8 and 386.0, respectively. A comparison with Table 1-2 in Chapter One shows that the amounts of N released due to oven drying and autoclaving are quite comparable. Thus it can be inferred that approximately similar changes in N are taking place due to both these treatments.

Nitrogen Extractable with 0.01 M NaHCO₃

Typical ultraviolet (UV) absorption of the 0.01 M NaHCO₃ extracts from soils are shown in Fig. 3-1. The UV absorbance of the soil extract is a measure of the concentration of organic matter (Rao, 1967). As the wavelength increases from 230 to 310 nm, there is a parallel linear decrease in the absorbance of extracts.

For the determination of NO₃ in the soil, the absorption at 204 nm was taken as a measure of NO₃ and organic

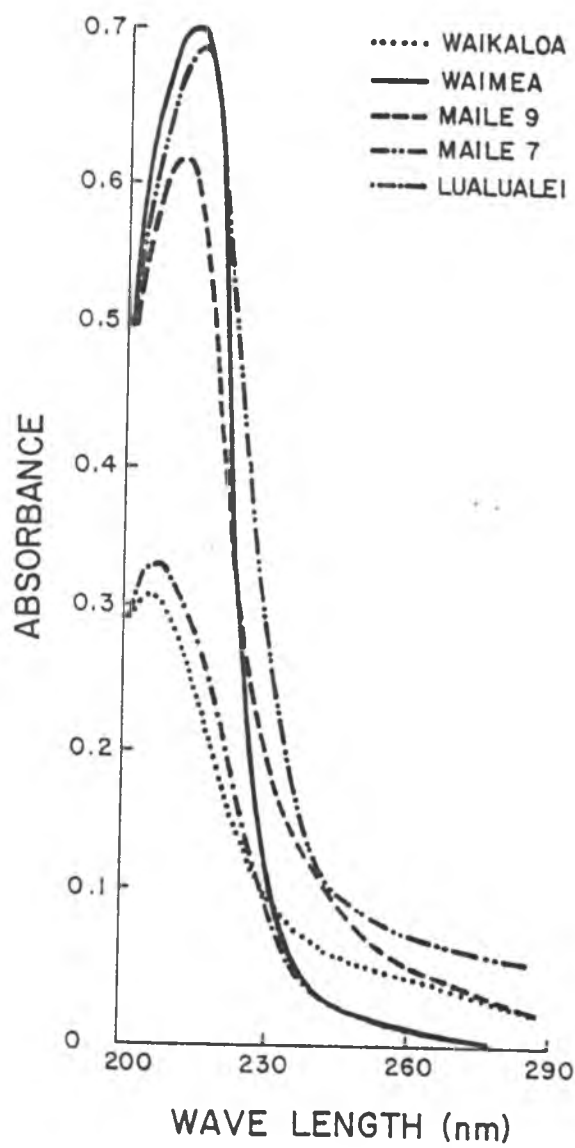


FIG. 3-1. THE ULTRA VIOLET ABSORPTION OF 0.01 M NaHCO_3 EXTRACTS FROM FIVE SOILS.

matter content of the extract.

Nitrogen-Uptake by Corn

All corn plants showed N deficiency symptoms at harvest time, i.e. yellowing of older leaves of plants. The N-supplying power of each soil was therefore under stress, and may have been reflected by plant yield and N uptake.

The highest dry matter yield of corn (Waikaloa) was 13 times higher than the lowest (Kaiwiki) yield (Fig. 3-2). Similarly there was a wide range in the ability of the five soils to provide N for corn growth. Uptake of N from soils without any N fertilizer ranged from 22.3 to 362.9 mg/pot, indicating that the best soil had a N-supplying capacity of 16 times greater than the poorest soil. This may serve as a good criterion for comparing the N-supplying capabilities of these soils obtained from incubation studies. As is clear from Fig. 3-2, the Waikaloa soil provided the most N that the plants could actually use, followed by Maile 7, Maile 9, Waimea and Kaiwiki.

Correlation Between N-Uptake by Corn and N Measured by Chemical and Incubation Methods

Simple linear correlations between the soil N test values and N uptake by corn in the greenhouse are given in Table 3-6.

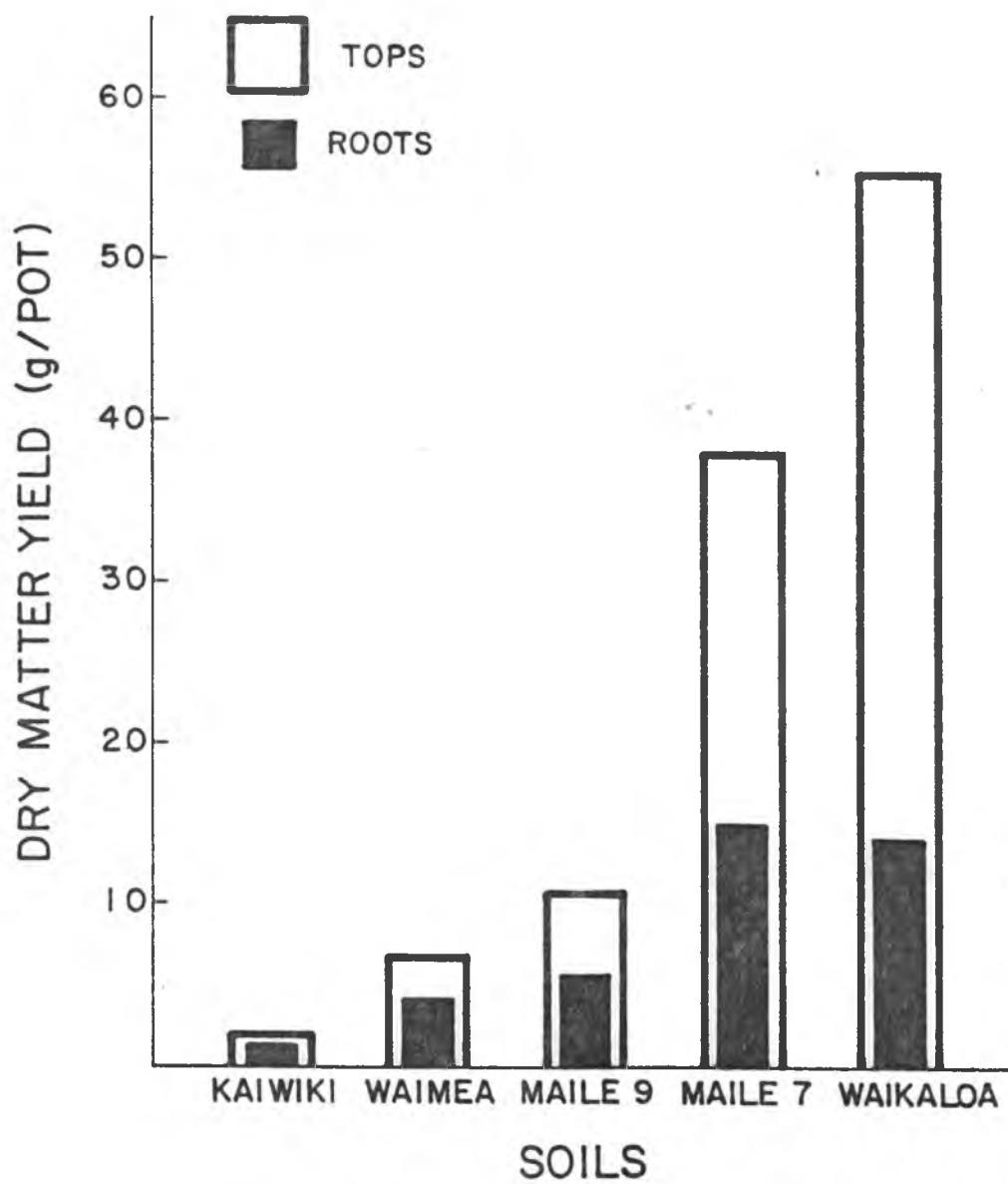


FIG. 3-2. DRY MATTER YIELD OF CORN GROWN ON FIVE SOILS IN GREENHOUSE.

Table 3-6. Linear Correlation Co-efficients of N-Uptake
by Corn for Several N Availability Methods

	<u>25°C</u>	<u>35°C</u>
Initial N	0.76	--
N Released	0.96	0.92
Initial + Released	0.96	0.92
$1/N_t$ vs $1/t$	-0.21	0.07
$\log (N_0 - N_t)$ vs t	0.57	0.68
$N_0 = \frac{N_t}{1 - 10^{-kt/2.303}}$	0.88	0.88
Autoclaving	0.43	--
UV Absorbance	0.40	--

Aerobic Incubation at 25°C: Nitrogen released during eight weeks incubation at 25°C was significantly correlated ($r = 0.96$) with the capacity of the various soils to supply N to plants. The initial amount of inorganic N in the soils gave $r = 0.76$. When the initial amount of N in the soil and N released during eight weeks incubation were added together a very high correlation (0.96) was obtained with N uptake by corn.

Aerobic Incubation at 35°C: The correlation values for N released during eight weeks of incubation, and initial plus N released, are given in Table 3-6. These N release values were highly correlated (0.92 for both incubation and initial plus N released) with N uptake by corn.

Correlations Between N_0 and N-Uptake: Nitrogen mineralization potentials (N_0) did not correlate well with plant uptake of N (Table 3-6) and thus do not seem to be good N-availability indices. These observations are not in agreement with those of Stanford and Smith (1972), Stanford, et al. (1977), and Stanford, et al. (1974) who found the N_0 approach to be quite satisfactory for estimating the N-supplying capacity of soils. It may be significant that none of their 39 soils were Andepts as were the soils in this study.

Autoclaving with 0.01 M CaCl₂: N released when the soils were autoclaved with 0.01 M CaCl₂ gave a low correlation of 0.43 with N uptake by corn and may not be a good criterion for estimating the N-supplying power of soils studied. Autoclaving, in addition to speeding up the mineralization of N, should have killed microorganisms in the soil and perhaps solubilized more organic matter than would have been under normal conditions of N mineralization.

These results are not in agreement with those of Ryan et al. (1971), who found significant correlation between the method of autoclaving the soil with 0.01 M CaCl₂ and the third harvest of sorghum from pot experiments with 15 soils from Kentucky, and Lathwell, et al. (1972) also found a significant correlation between autoclaving and N uptake by maize and sorghum grown in pots in ten different soils from Puerto Rico.

0.01 M NaHCO₃ Extractable N: Ultraviolet absorption of 0.01 M NaHCO₃ extracts gave a low correlation ($r = 0.40$) with N-uptake by corn. These results are not in line with those of Fox and Piekielek (1978) who got high correlation with N-uptake by field grown corn on eight soils from Pennsylvania.

CHAPTER FOUR

SOIL INFLUENCES ON THE MINERALIZATION
OF NITROGEN IN SEWAGE SLUDGE

ABSTRACT

A laboratory incubation study showed that soils with varying characteristics mineralize significantly different amounts of N.

The amount of N mineralized from anaerobically-dried sewage sludge when mixed with two soils was very small, and depended on the soil type and the sludge rate. In the Waimea soil (Typic Eutrandept), 3-4 percent more N was mineralized than in the Wahiawa soil (Humoxic Tropohumult) when the sludge was applied at 22.4 and 44.8 tons/ha rates. N mineralization potential (N_0) did not adequately predict the N-supplying power of the sewage sludge. A two-function equation with two values of N_0 may be necessary to adequately describe N mineralization in sludge-amended soil because of two different N mineralization rates. One function describes the release of N from a readily-mineralizable fraction in early incubation (0-4 weeks), while the other function describes the release of N from the more stable fraction which is mineralized later in sewage sludge.

Soil Influences on the Mineralization of Nitrogen in Sewage Sludge

INTRODUCTION

With an ever-increasing urban population, the disposition of large amounts of sewage sludge is a major concern. In large amounts, sewage sludge can be a pollution hazard. However, if properly used it can be an energy-efficient source of many nutrients required by crops.

Several methods of disposing of wastes have been tried; e.g. application to agricultural lands, incineration, composting and recycling (Morgan, 1971). Application of sewage sludge to soil is considered one of the most ecologically and economically viable methods (Seabrook, 1973; Thomas and Law, 1968).

Among many nutrients contained in sludge, N is the one found in largest quantity. However, this N is mostly in organic forms which must mineralize before being used by plants. Mineralized N, when oxidized to nitrate, is not only available to plants but may leach out of the soil profile with water. Therefore, the mineralization rate of sludge is an important factor in determining the amount of N that will be available for a crop under different soil conditions.

Chemical and physical properties of a soil determine the loading rates of sewage sludge which are appropriate

for a particular soil. The soil environment affects the composition of the soil microbial population both quantitatively and qualitatively (Alexander, 1961). The rate of decomposition of an organic waste depends primarily on those factors which affect the microbial population. Thus, soil properties having the greatest effect on microbial growth and activity will have the greatest potential for altering the rate of sludge decomposition.

It has been estimated that from two per cent to greater than 50 per cent of the organic N in sewage sludge becomes available in one growing season (Sabey, 1977). While determining the effect of sewage sludge addition on nitrification of the added $\text{NH}_4\text{-N}$ (as sewage sludge), Ryan, et al. (1973) reported that 48, 20, 11, 11 and 4 per cent of the N added as NH_4 was mineralized for 47, 94, 141, 188 and 235 $\mu\text{g/g}$ rates of sewage sludge, respectively. The per cent of organic N mineralized was inversely related to the quantity of organic N added. Relatively little information is available on the effects of soil pH, soil N and sludge rates on decomposition of sewage sludge. Some investigators have found that the percentage of organic C evolved as CO_2 decreased with increasing sludge rates (Abgim et al., 1977). Similar results were reported by Premi and Cornfield (1969), who mixed 10 g of soil with 0.25, 0.5, 1 and 2 ml of digested sewage sludge slurry, providing 25.5, 51, 102 and 204 ppm $\text{NH}_4\text{-N}$ rates,

respectively. They reported that the addition of sewage sludge stimulated the mineralization of native soil organic N by 14 and 17 ppm (NH_4 and $\text{NO}_3\text{-N}$) at 0.25 and 0.5 ml/10 g soil rates, respectively. Nitrification of $\text{NH}_4\text{-N}$ from the sewage sludge was also rapid at these two rates, while at higher rates there was a lag phase before nitrification started. The apparent stimulating effect of the two lower levels on the mineralization of native soil organic N was attributed to trace elements (Zn and Cu) in the sludge. But reasons for inhibiting mineralization and nitrification at higher levels were not clear. These workers suggested that higher levels of heavy metals associated with the high rates of sludge probably did not cause the inhibition of nitrification. In 1971, they also found that per cent N mineralized decreased with increasing rates of sewage sludge application (Premi and Cornfield, 1971). The delay in nitrification at 2%, the highest application rate of sewage sludge, was attributed to some organic material in sludge and a relatively high content of $\text{NH}_4\text{-N}$ at this rate, which resulted in a high pH (>7.3), which in turn might have caused a temporary inhibition of the activity of nitrifying bacteria. In another study, Wilson (1977) tested domestic and industrial sludges. Dried sewage sludge from both sources was incorporated into soil at 0, 1, 4 and 16 mg/g rates. These mixtures were incubated with or without the addition of 100 $\mu\text{g/g}$ $\text{NH}_4\text{-N}$ (as NH_4Cl) for six weeks.

Reduction in nitrification was reported at 4 and 16 mg/g rates of industrial sewage sludge for the first three to four weeks. Domestic sewage sludge reduced nitrification only at the highest application rate (16 mg/g). He associated this inhibition with higher levels of Zn, Cd and Pb. However, other researchers have observed the same degree of mineralization at various sludge loading rates (Tester et al., 1977). Similar observations were made by Milne and Graveland (1972), who suggested that nitrification was only slightly affected by the rate of air-dried sludge. Likewise, Madgoff and Chromec (1977) mixed two different sludges with soil to obtain application rates of 0, 150, 300 and 900 ppm N. They reported no significant difference in the amount of N mineralized for the 150 and 300 ppm treatments for either sludge.

While there are many studies dealing with rate of sewage sludge loading, why various soils will affect the nitrogen mineralization of sewage sludge differently is seldom known. Terry, et al. (1979) reported that soil factors such as texture, pH and moisture content had little effect on sludge decomposition rate.

The present study was undertaken to measure:

1. the effect of sewage sludge rate on N mineralization,
2. the effect of incubation time on N mineralization,
- and 3. the effect of soil type on N mineralization.

MATERIALS AND METHODS

Two Hawaiian surface soils, the Wahiawa and Waimea, were used for this study. These soils have developed under two very different climatic conditions and have different physical, chemical and mineralogical properties.

The Wahiawa silty clay, a member of the clayey, kaolinitic, isohyperthermic family of Tropeptic Eutruxtox, is derived from basalt and developed under an annual rainfall of 250 cm. The average air temperature for this soil site for the months of January and July is about 20.6°C and 22.8°C, respectively. Mean annual temperature is about 21.7°C. The clays are predominantly kaolin with some iron oxide; buffering capacity is low.

The Waimea soil, fine sandy loam, a member of the ashy, isothermic family of Typic Eutrandedpts, has a dark A horizon with a weak granular structure. This soil has an average annual temperature of 15.5°C and average annual rainfall of 102 cm.

The sewage sludge, which was obtained from the Wahiawa Wastewater Treatment Plant had been processed anaerobically. The sludge was oven-dried at 60°C and finely ground to pass through a 4 mm sieve. It was stored in polyethylene bags for two months before use.

The important properties of soils and sludge are also described in Table 4-1.

Table 4-1. Some Properties of Soils and Sewage Sludge Studied

<u>Soil</u>	<u>pH</u>	<u>Total N</u> %	<u>Organic C</u> %	<u>C:N</u>
Wahiawa	5.55	0.18	1.70	9.44
Waimea	6.94	0.59	6.63	11.23
Sewage Sludge	5.81	4.00	29.50	7.37

Concentrations of Cu, Ni, Cd and Zn in Sewage Sludge*

<u>Cu</u>	<u>Ni</u>	<u>Cd</u>	<u>Zn</u>
----- $\mu\text{g/g}$ -----			
191.00	56.90	9.40	1731.00

* Sewage sludge digested by 70% perchloric acid, conc. Nitric acid digestion (1:2) and determined for heavy metals by Perkin Elmer model 103 atomic absorption spectrophotometer.

Total N in the soils and sludge was determined by the semi-micro Kjeldahl method (Bremner, 1965), organic C by the Walkley and Black method (1934), pH in a saturated water paste and NH_4 and NO_3 -N by the micro-Kjeldahl methods (Bremner, 1965) after extraction with 1 N KCl (1:5 ratio soil to solution).

Incubation of Soils and Sludge

The soils (40 g OD) were mixed with perlite (7 g) and various amounts of sludge to provide the equivalent of 0, 22.4 and 44.8 tons/ha rates. The total amount of N added in the form of sewage sludge was 0, 400 and 800 $\mu\text{g/g}$ for 0, 22.4 and 44.8 tons/ha rates, respectively. The soil and sludge mixtures were put into leaching tubes. The tubes were leached with 100 ml of a 0.01 M CaCl_2 solution followed by 25 ml of N-free nutrient solution (Stanford, 1974) to remove inorganic N initially present in the soil sludge mixture. The leaching tubes were then subjected to a uniform suction (60 cm Hg) to remove excess liquid. The tubes were covered and incubated at 25°C. The soil and sludge mixtures were extracted weekly with CaCl_2 and N-free nutrient solution for eight weeks and NH_4 and NO_3 -N were determined in the extracts by steam distillation.

RESULTS AND DISCUSSION

Effect of Sludge Rate on Nitrogen Mineralization

Nitrogen mineralization in sludge mixed soils was affected by the rate of sludge application. More N was mineralized with increasing rates of sludge (Table 4-2). In the Wahiawa soil, 75 and 154 $\mu\text{g/g}$ more N was mineralized compared to the control, when the soil was mixed with sludge at 22.4 and 44.8 tons/ha rates, respectively (Fig. 4-1). The corresponding values for the Waimea soil were 90 and 179 $\mu\text{g/g}$ for 22.4 and 44.8 tons/ha rates, respectively.

After eight weeks incubation, approximately 19% of the total N applied in the form of sewage sludge was mineralized in the Wahiawa soil at both sludge rates. In the Waimea soil over 22% of the total N applied was mineralized at both the 22.4 and 44.8 tons/ha rates. Thus total net mineralization data in Table 4-2 shows that, irrespective of the rate of sludge application, the per cent of added N mineralized remained essentially the same for individual soils.

Weekly N mineralization data in Table 4-2 also reveals that after four weeks of incubation, most of the easily-mineralizable N had been released at both sludge rates. From five to eight weeks a steady state was reached, and N was coming from a fraction which apparently is not

Table 4-2. Nitrogen Mineralization as Affected by Sewage Sludge Rate of Application and Soil Type

Soil	Sludge Rate	N mineralized from Soil and Sewage Sludge								Total	%* of added N Mineralized
		-- Incubation Time (weeks) --									
		1	2	3	4	5	6	7	8		
	tons/ha	----- µg N/g soil -----									
Wahiawa	0	17	13	9	7	8	8	8	8	78	---
	(0)**										
	22.4	31	37	19	14	13	13	13	13	153	18.70
	(400)										
Waimea	44.8	50	59	34	20	17	17	18	17	232	19.21
	(800)										
	0	13	14	7	7	7	9	9	8	74	---
	(0)										
Waimea	22.4	50	23	16	13	15	16	16	16	164	22.5
	(400)										
	44.8	83	41	23	20	21	21	22	22	253	22.41
	(800)										

* Percent of N mineralized calculated as follows:

$$\frac{100 \times \text{total N mineralized} - \text{soil mineralized}}{\text{N added initially (rate) as } \mu\text{g N/g soil}}$$

** Values in parentheses are amounts of total N added as sewage sludge ($\mu\text{g N/g}$ of sludge).

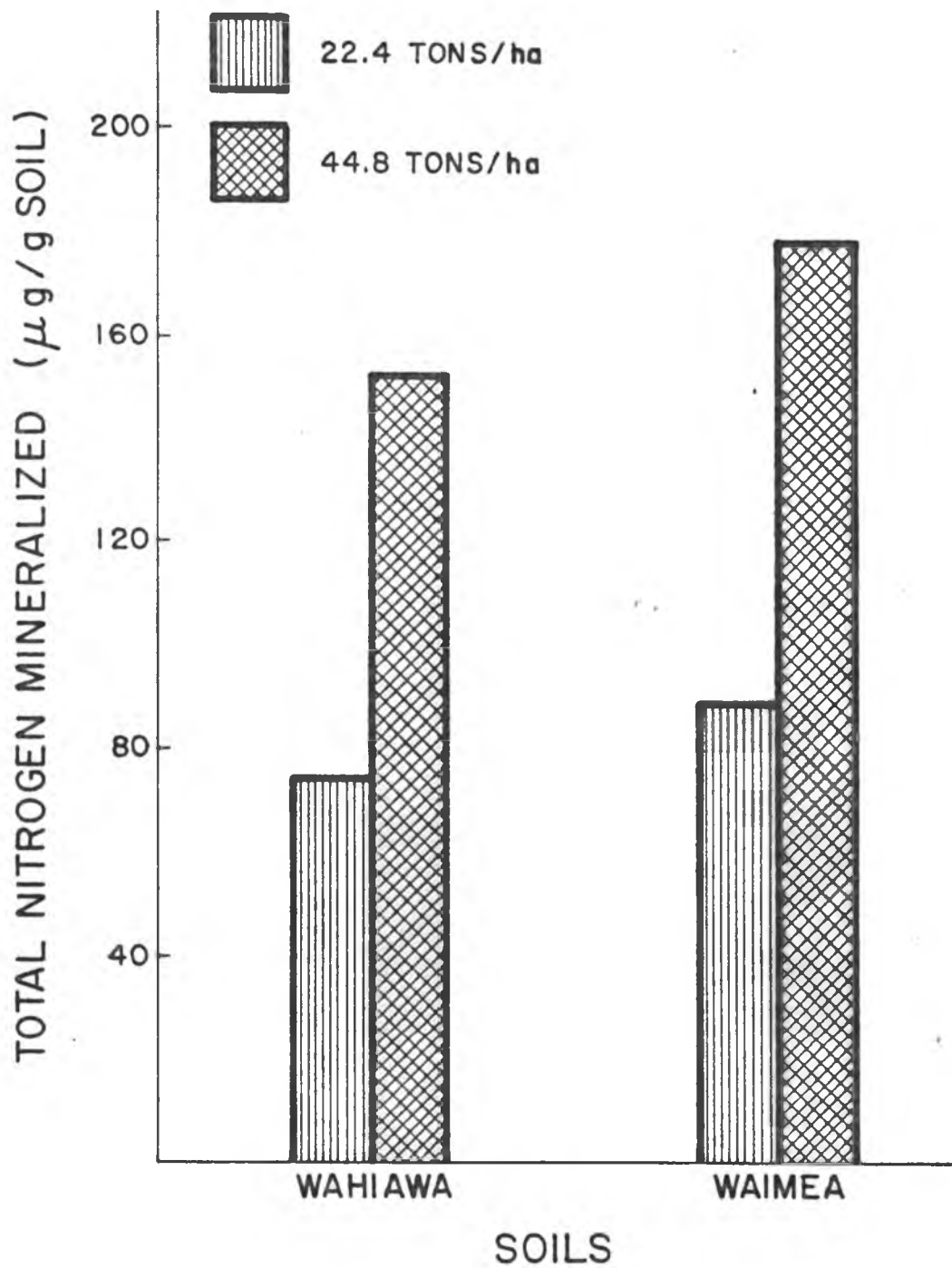


FIG. 4-1. NET NITROGEN MINERALIZED FROM SEWAGE SLUDGE DURING EIGHT WEEKS.

readily mineralizeable.

These results are in agreement with those of Sommers, et al. (1976), who reported that 20 to 25% of sludge N was mineralized during a 168-day incubation study. Similarly, Pratt, et al. (1973) developed decay series as predictive models which can be used for determining loading rates of organic wastes. They suggest a decay series of 0.35, 0.10 and 0.05 for the first three years.

The fact that only small amounts (19 to 22%) of added sludge N were mineralized suggests that the rest of the added sludge N may not be easily mineralizeable in this short-term incubation.

There was no extended lag period for N mineralization at high rates of sludge application. This was in contrast to the findings of Premi and Cornfield (1969), who found a lag period at higher levels (> 114 kg/ha) of sludge application. Miller (1974) also reported a similar inhibition at higher rates of sludge application. It has been hypothesized that the inhibition is caused by an organic or inorganic toxin in the sludge which decomposes or adapts to the soil microbes (Ryan et al., 1973).

Effect of Incubation Time on Nitrogen Mineralization

The amount of N mineralized was a function of incubation time. Following initially high rates of N mineralization in the first two weeks in the Wahiawa soil

and the first week in the Waimea soil, there was a rapid decrease until after four weeks, when a near steady state was reached. The maximum amount of N mineralized occurred during the second week of incubation in the Wahiawa soil at both sludge rates (first week in the control), and during the first week in the Waimea soil (Table 4-3). It is also clear from the table that the Waimea soil, when mixed with sludge, had a much higher steady-state mineralization rate compared to the Wahiawa soil.

Effect of Soil on Nitrogen Mineralization

The amount of N mineralized also depended on soil type. As indicated in Table 4-2, more N was mineralized when sewage sludge was mixed with the Waimea soil than with the Wahiawa soil. At the end of an eight-week incubation, the amount of N mineralized was 78, 153 and 232 $\mu\text{g N/g soil}$ for the Wahiawa soil and 74, 164 and 253 $\mu\text{g N/g soil}$ for the Waimea soil at 0, 400 and 800 $\mu\text{g N/g sludge application rates}$. Although the amount of N mineralized from the Wahiawa soil (eight week total) without any sludge addition was more than in the Waimea soil, when these soils were amended with sewage sludge the reverse was true. At 22.4 and 44.8 tons sludge/ha rates, respectively, 11 and 21 $\mu\text{g N per g soil}$ more N was mineralized by the Waimea soil than by the Wahiawa soil.

Table 4-3. Percent* Nitrogen Mineralized at Weekly Intervals in Sludge-Amended Soils at Varying Rates

<u>Sludge Rates</u> tons/ha	<u>Incubation Time</u> Weeks							
	1	2	3	4	5	6	7	8
	<u>Wahiawa Soil</u>							
22.4	3.50	6.00	2.50	1.75	1.25	1.25	1.25	1.25
44.8	4.12	5.75	3.12	1.62	1.12	1.12	1.12	1.12
	<u>Waimea Soil</u>							
22.4	9.25	2.25	2.25	1.50	2.00	1.75	1.75	2.00
44.8	8.75	3.37	2.00	1.62	1.75	1.50	1.62	1.70

$$* \frac{\text{Sludge N Mineralized}}{\text{Total N added as sludge}} \times 100$$

	<u>Wahiawa Soil</u>							
22.4	3.50	6.40	2.80	1.90	1.45	1.47	1.49	1.51
44.8	4.12	5.99	3.46	1.86	1.31	1.33	1.35	1.37
	<u>Waimea Soil</u>							
22.4	9.25	2.47	2.54	1.73	2.35	2.11	2.16	2.52
44.8	8.75	3.69	2.27	1.89	2.07	1.81	2.00	2.20

$$* \frac{\text{Sludge N mineralized}}{\text{Total N left at the start of the week}} \times 100$$

Thus, in the Waimea soil conditions were more conducive for the mineralization of sewage sludge-N than in the Wahiawa soil. It may be possible that some portions of the sludge organic material which was readily decomposable when mixed with the Waimea soil was somewhat resistant to decomposition when mixed with the Wahiawa soil.

Another possible reason may be that microorganisms present in the Waimea soil may be more efficient in mineralizing N from sewage sludge than those in the Wahiawa soil.

Changes in $\text{NH}_4\text{-N}$

Ammonium concentrations were generally a function of sludge rate (Table 4-4). There was a rapid increase in the concentration of $\text{NH}_4\text{-N}$ during the first week in the Wahiawa soil, followed by a gradual decrease up to the fourth week. After the fifth week a steady state was reached in this soil at 22.4 and 44.8 tons/ha sludge rates. In the sludge-amended Waimea soil, $\text{NH}_4\text{-N}$ concentrations were not as high as in the Wahiawa soil. There was a small increase up to the first three weeks. After the fourth week the concentration of $\text{NH}_4\text{-N}$ was almost the same as in the control treatment.

Nitrate-N

Increasing rates of sludge resulted in higher concentrations of $\text{NO}_3\text{-N}$ up to the first three weeks, followed by

Table 4-4. Extractable NH_4 and NO_3 -N Content of the Wahiawa and Waimea Soils with Varying Rates of Sewage Sludge

Sludge Rate tons/ha	Incubation Period							
	Weeks							
	1	2	3	4	5	6	7	8
----- NH_4 -N -----								
$\mu\text{g/g}$								
<u>Wahiawa Soil</u>								
0	3.7	2.5	2.7	2.4	2.5	2.5	2.5	2.5
22.4	11.0	2.9	2.7	2.8	2.5	2.5	2.5	2.5
44.8	31.5	12.0	4.3	2.6	2.5	2.5	2.5	2.5
<u>Waimea Soil</u>								
0	2.8	2.4	3.0	2.4	2.5	2.5	2.5	2.5
22.4	3.9	2.8	3.4	2.2	2.5	2.5	2.5	2.5
44.8	4.0	2.8	2.6	2.5	2.5	2.5	2.5	2.5
----- NO_3 -N -----								
<u>Wahiawa Soil</u>								
0	13.3	10.6	6.0	5.1	8.5	5.6	8.4	7.6
22.4	20.3	34.4	16.0	10.8	13.0	10.4	13.4	13.4
44.8	18.5	46.8	29.6	17.4	17.0	14.4	17.7	17.4
<u>Waimea Soil</u>								
0	10.4	12.0	4.2	4.3	7.3	6.2	8.7	8.5
22.4	46.3	19.7	12.6	10.8	15.1	13.4	16.0	15.5
44.8	79.3	38.0	20.0	19.5	21.4	19.0	22.3	22.0

a steady state after the fourth week in the Wahiawa sludge mixture. The maximum concentration was in the second week at both sludge rates in the Wahiawa soil. Nitrate concentrations in the case of the Waimea sludge mixture were significantly higher compared to the Wahiawa soil. Maximum concentration of $\text{NO}_3\text{-N}$ was found in the first week in the sludge-amended soil. Most of the N coming into mineral form was $\text{NO}_3\text{-N}$ in both the sludge-amended and the control soils, possibly suggesting that whatever $\text{NH}_4\text{-N}$ was being formed from organic N was rapidly being nitrified to $\text{NO}_3\text{-N}$. It was assumed that denitrification losses were negligible during the incubation.

The greater mineralizations of N in the Waimea soil versus the Wahiawa soil possibly includes the following effects.

(1) The higher pH of the Waimea soil (6.94 before incubation) compared to the Wahiawa soil (pH 5.5 before incubation) may have favored the growth of ammonifying and nitrifying bacteria in the Waimea soil (Alexander, 1965). The optimum pH for many of the ammonifying organisms is between 7 and 9, and between pH 7 and 8 for the nitrifiers (Alexander, 1965). The post-incubation pH values are given in Table 4-5.

The pH values of the Waimea soil treatments were higher by approximately 0.6 units than for the Wahiawa soil at all rates of sludge application. These results

Table 4-5. pH Values of Soil and Sludge Mixtures.

<u>Sludge Rate (t/ha)</u>	<u>Wahiawa</u>	<u>Waimea</u>
0	6.14	6.70
22.4	6.17	6.76
44.8	6.15	6.73

are not in agreement with those of Terry, et al. (1979), who reported no significant difference in the mineralization of N in soils having initial pH values of 5.3, 6.0 and 7.5. But these workers also admit that they failed to show the effect of pH on sludge-N mineralization because the soil acidity may have been neutralized by CaCO_3 in the synthetic sludge, which is not the case in the results reported here.

(2) The sludge and its decomposition products may have accelerated the breakdown of native organic N in the soil (priming effect). Possible explanations for the priming effect are: 1) As many microorganisms develop due to addition of sewage sludge, the easily decomposable portion of sewage sludge is first consumed after which the microorganisms are forced to feed on native soil organic matter. 2) Sludge addition may introduce more varied microorganisms, which helps in speedy breakdown of soil organic matter. 3) Sewage sludge provides an energy source for the development of a new population, which once established, accomplishes greater utilization of soil organic

matter. 4) Sludge addition may promote the development of numerous new microbial cells, which possess great physiological vigour and are able to decompose soil organic matter more rapidly.

The Waimea soil had a higher natural percentage of total N (0.59) than the Wahiawa soil (0.18%). Sommers (1976) and Terry (1976) reported a priming effect in the mineralization-decomposition of native organic N when several soils were amended with samples of sewage sludge, from sewage treatment plants in 11 Indiana cities.

Calculation of Nitrogen Mineralization Potential

Cumulative N mineralization data are presented in Fig. 4-2 for the Wahiawa soil and Fig. 4-3 for the Waimea soil. First estimates of N mineralization potential (N_0) were derived from regression analysis based on cumulative N mineralized (N_t) during eight weeks of incubation, using the expression:

$$\frac{1}{N_t} = \frac{1}{N_0} + \frac{b}{t}$$

This procedure was already discussed in detail in Chapter Three. Table 4-6 gives the N_0 values obtained by this approach. Actual values of N_0 were obtained from regression analysis based on the expression:

$$\log (N_0 - N_t) = \log N_0 - \frac{kt}{2.303}$$

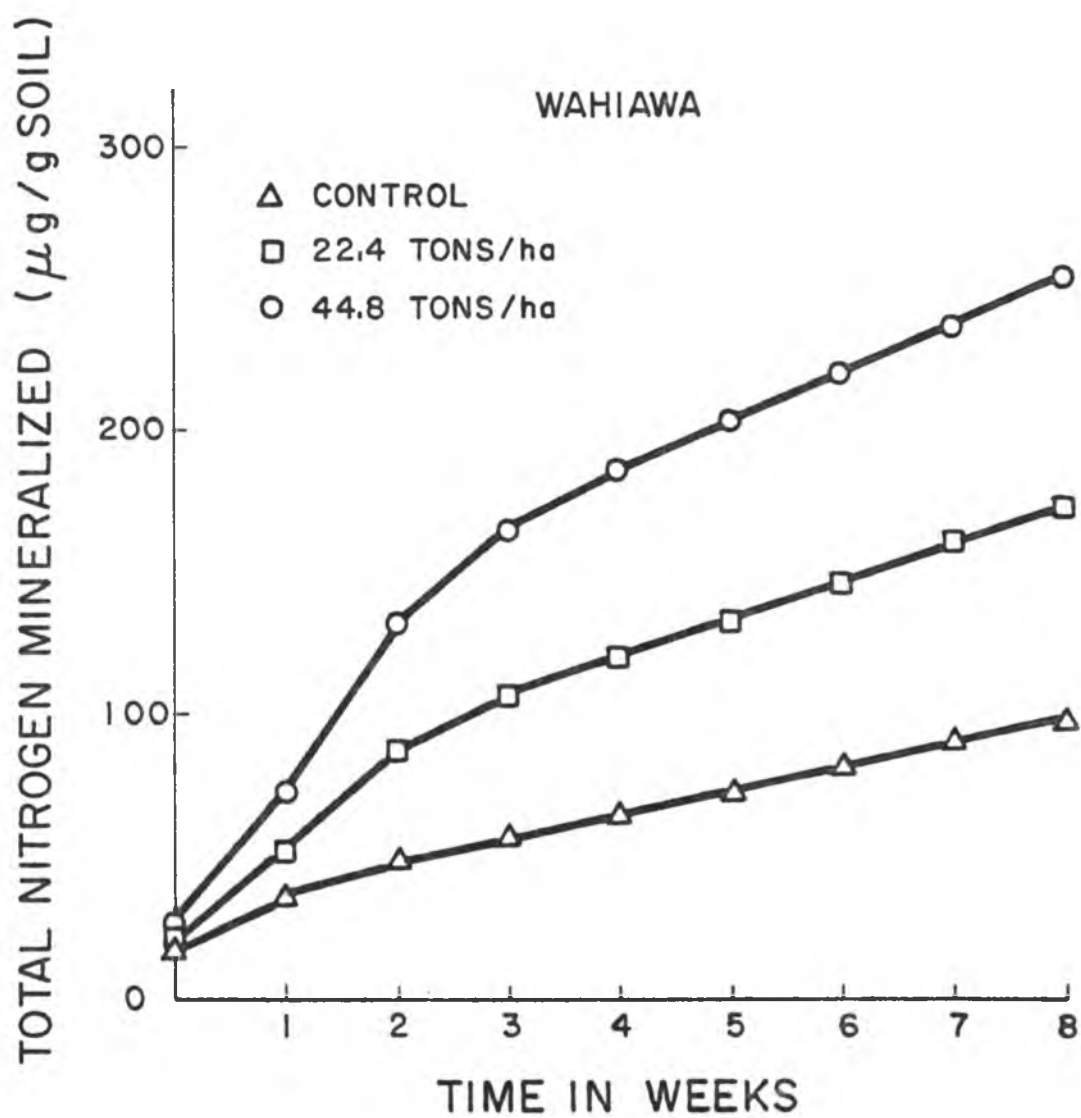


FIG. 4-2. CUMULATIVE TOTAL N MINERALIZED AT VARYING SEWAGE SLUDGE RATES IN THE WAHIAWA SOIL.

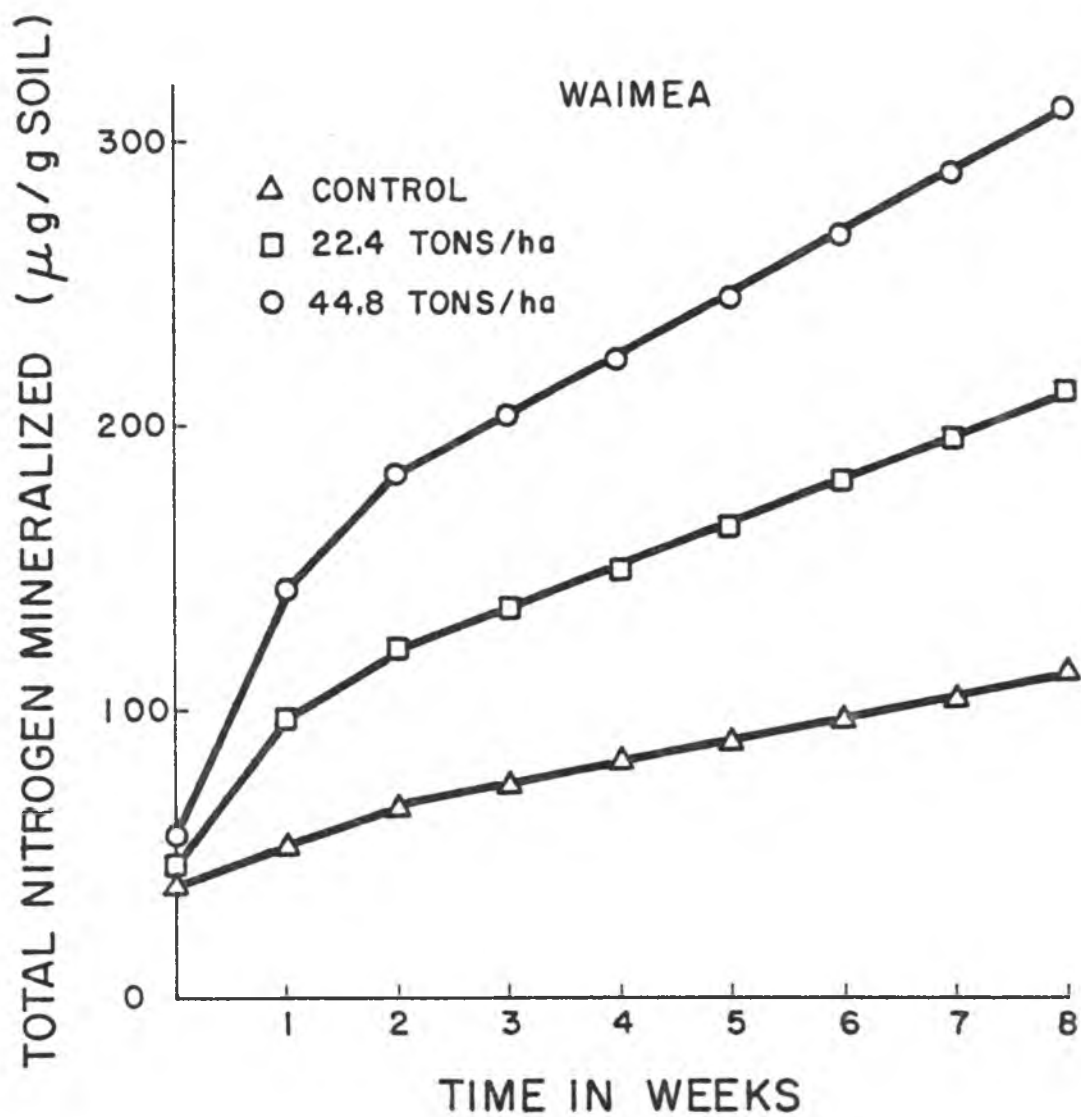


FIG. 4-3. CUMULATIVE TOTAL N MINERALIZED AT VARYING SEWAGE SLUDGE RATES IN THE WAIMEA SOIL.

Table 4-6. Regression of Nitrogen Mineralization Potential (N_0)
for Two Soils at Varying Sludge Rates

<u>Wahiawa</u>					
First Estimates Based on $1/N_t$ vs $1/t$					
<u>Sludge Rate</u> tons/ha	<u>Equations</u>	<u>r</u>	<u>Slope(m)</u>	<u>Intercept</u>	<u>N_0</u>
0	$y = 0.007 + 5x$	0.998	0.500	0.007	134.658
22.4	$y = 0.002 + .030x$	0.991	0.028	0.002	494.500
44.8	$y = 0.001 + .017x$	0.988	0.017	0.001	747.580
Second Estimates Based on $\log(N_0 - N_t)$ vs t					
0	$y = 2.114 - 0.043x$	-0.997	-0.043	2.114	130.230
22.4	$y = 2.670 - 0.017x$	-0.987	-0.017	2.670	467.770
44.8	$y = 2.843 - 0.017x$	-0.978	-0.170	2.843	697.256
<u>Waimea</u>					
First Estimates Based on $1/N_t$ vs $1/t$					
0	$y = 0.005 + 0.069x$	0.997	0.069	0.005	186.600
22.4	$y = 0.004 + 0.015x$	0.990	0.015	0.004	214.900
44.8	$y = 0.002 + 0.009x$	0.980	0.009	0.002	385.000
Second Estimates Based on $\log(N_0 - N_t)$ vs t					
0	$y = 2.260 - 0.250x$	-0.996	-0.025	2.260	182.000
22.4	$y = 2.309 - 0.070x$	-0.987	-0.070	2.309	203.970
44.8	$y = 2.520 - 0.048x$	-0.996	-0.048	2.526	336.317

Based on this approach N_0 values of the sludge-Wahiawa mixture were 130, 468 and 697, and 182, 204 and 335 $\mu\text{g/g}$ for the sludge-Waimea soil mixture of 0, 22.4 and 44.8 ton/ha rates, respectively (Table 4-6). A closer look at Table 4-2 and N_0 values in Table 4-6 indicates that this method of estimating N_0 did not adequately predict the actual values of N mineralization for sludge-amended soils. Although the sludge-Waimea soil mixture had larger number of N mineralized (164 and 253 $\mu\text{g N/g}$) at the end of the eight-week study than the sludge-Wahiawa soil mixture (153 and 232), the sludge-Waimea mixture had lower values of N_0 than the sludge-Wahiawa soil at both rates of sludge application.

A plot of weekly N mineralized (Fig. 4-4) shows that: (1) nitrogen mineralization in sludge-amended soils proceeds vigorously during the first four to five weeks while a more stable fraction is mineralized later, from five to eight weeks; and (2) the N_0 approach based on the regression of $\log(N_0 - N_t)$ versus time gives erroneous values of N-supplying power of nitrogen-rich materials. This approach might also result in large errors in N_0 when N_t approaches the value of N_0 toward the end of incubation.

Amounts of N mineralized over a prescribed time period and that present before the start of incubation may be considered available for plant growth. This quantity could roughly be equivalent to inorganic fertilizer N. Thus, after taking into account the amount of N that will be

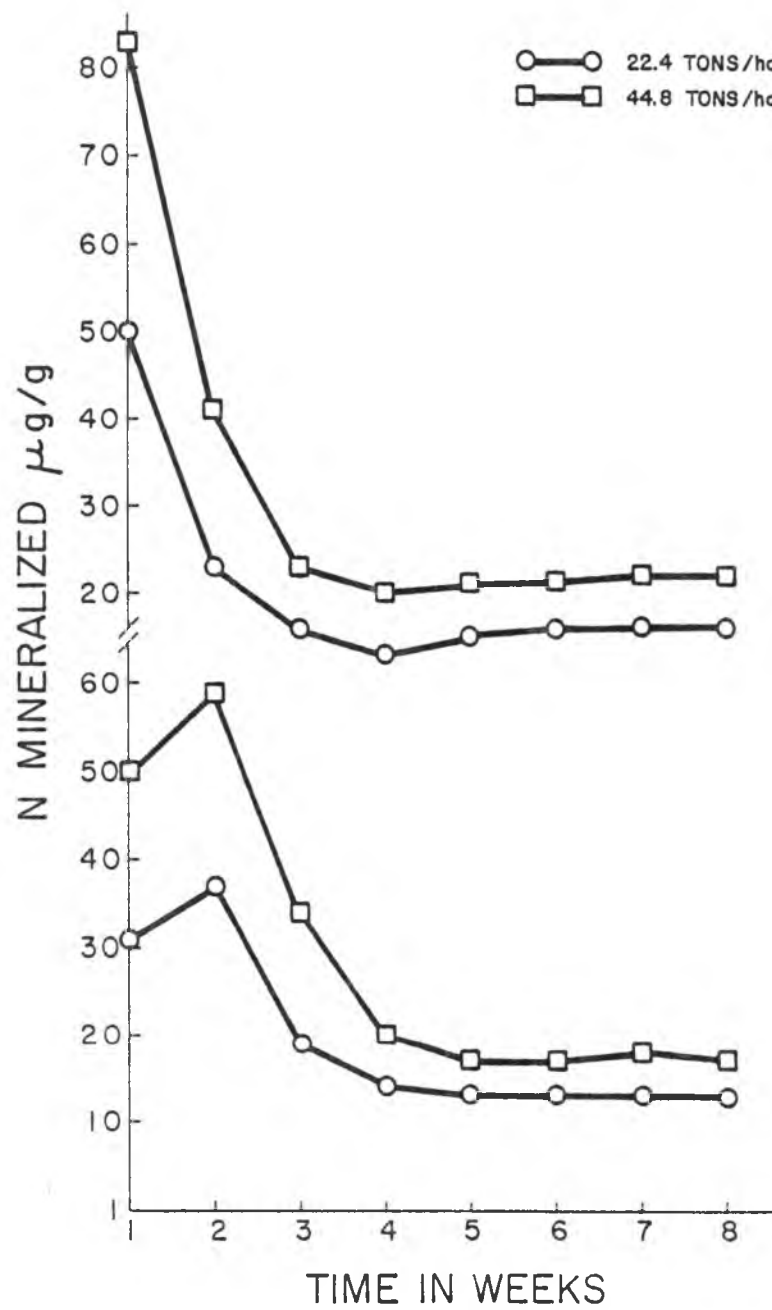


FIG. 4-4. WEEKLY TOTAL N MINERALIZED AT VARYING SLUDGE RATES.

provided by the sewage sludge during the growing season of the crop, reasonable estimates of additional amounts of N to be supplied in the form of N fertilizer may be made.

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