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OF APPLIED AMMONIUM AND NITRATE IN
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ADSORPTION, DENITRIFICATION, AND MOVEMENT OF
APPLIED AMMONIUM AND NITRATE
IN HAWAIIAN SOILS

A DISSERTATION SUBMITTED TO THE GRADUATE DIVISION OF THE
UNIVERSITY OF HAWAII IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN

AGRONOMY AND SOIL SCIENCE

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By

Vethaiya Balasubramanian

Dissertation Committee:

Yoshinori Kanehiro, Chairman
Richard E. Green
Lajpat Rai Ahuja
Tung-Ming Lai
James L. Brewbaker

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DISSERTATION ABSTRACT

The factors influencing adsorption, denitrification, and movement of applied ammonium and nitrate in tropical Hawaiian soils were investigated. Suggestions are incorporated to maximize crop utilization of field-applied fertilizer nitrogen and to minimize loss of mineral nitrogen through leaching and denitrification.

Some oxidic tropical soils, such as the Hydrandepts and Gibbsihumox, in Hawaii were found to adsorb nitrate significantly in pH ranges below 6. Non-specific anion adsorption is believed to be the major mechanism by which nitrate was adsorbed.

The zero point of change (ZPC), which has a close relation with non-specific anion adsorption, is defined as the pH where the net sum of charges is zero. The high ZPC of the subsoil of the Hydrandepts was attributed to the extensive hydration of their iron and aluminum oxides. Hydrolysis and polymerization of the hydrated oxides were suggested as major mechanisms for the decrease of ZPC and pH on drying the Hydrandepts.

Any change in the ZPC was shown to vary the nitrate adsorption. The significant decrease of nitrate adsorption due to dehydration of the Hydrandepts was explained by the change in the ZPC, pH, crystallinity, and surface area on drying. Since this dehydration process is irreversible,

it was concluded that these soils should not be allowed to dry excessively by exposure to direct sun and wind so as to preserve their high exchange capacities, both for anions and cations.

The surface of the Hydrandepts and Gibbsihumox became less positive or more negative on liming, and this was reflected in the (increased) ammonium and (decreased) nitrate adsorption by the limed soils. The finding that raising of soil pH beyond 5.5 with liming produced NO_3^- repulsion in these soils should be taken into consideration in any liming program.

Denitrification loss was found to be important only in soils with large amounts of water-soluble organic matter and nutrients. Available energy source appeared to play a dominant role in denitrification. N_2 and N_2O gases were the prime denitrification products in all the soils studied. Denitrification potential was very low in Oxisols with poor organic carbon (both water-soluble and total) content.

In an infiltration study, it was found that the practically irreversible adsorption of ammonium was responsible for its retention in the Molokai soil. It was further shown that the higher the amount of water infiltrated, the deeper was the position of nitrate peak. An explanation is given on how to take advantage of the

lag of nitrate peak with respect to the wetting front in the initially moist soil during transient water flow. For soils with the same initial moisture content, the depth of nitrate peak was in direct proportion to its wetting front. Thus by controlling the wetting front, one can control the depth of maximum solute concentration, irrespective of the rate of water application.

In short, modified management practices based on the knowledge of nitrogen transformation and transport in soils as well as nitrogen uptake by crops will ensure efficient (nitrogen) fertilizer use in crop production with a minimum chance for the pollution of ground water by nitrate.

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GENERAL INTRODUCTION

Intensive cropping programs, emphasis on high yielding varieties of major crops, and increased industrial production of relatively low cost fertilizer nitrogen have led to the consumption of increasingly large amounts of nitrogen fertilizers during the past two decades. Concurrently with the increased use of nitrogenous fertilizers, research in the areas of soil chemistry, microbiology and fertility has been intensified to determine the fate of the applied fertilizers.

High temperature and moisture conditions favor vigorous microbiological activity in tropical Hawaiian soils. Thus, regardless of the form of nitrogen applied, within a relatively short time nitrate would be expected to be the predominant form of mineral nitrogen present in most cultivated soils. According to Russell (1950), most soils contain 2 to 20 ppm of nitrate. Still higher concentration of nitrate are not unlikely in Hawaiian soils. Nitrate is then recycled as it is consumed by plants and soil microbes. If the consumption rate is less than that of the production, excess nitrate accumulates in the soil. The nitrate, being soluble in water, will be leached down easily when water percolates through the profile. As nitrate is transported through

any moist soil, its movement is generally retarded by sorption processes on surfaces of soil particles, and by microbiological (and chemical) processes of immobilization and denitrification.

The report of Maxcy (1950) which showed that accumulation of nitrate in water can be hazardous to the health of humans and farm animals aroused great concern with the public about the possibility of basal ground water supplies being polluted by nitrate. Agriculture has been charged with contributing to nitrate pollution of our streams and lakes and underground water supplies. Mink (1962) attributed the cause of increased nitrate concentration in certain wells on the island of Oahu to irrigation water which carried nitrogen from adjacent fertilized sugarcane fields. Visher and Mink (1964) reported that waters from wells and springs in irrigated areas contain six to eight times more nitrate than from wells outside the irrigated areas. Similar increases in nitrate and sulfate concentrations in waters from numerous wells of Oahu and Maui were attributed to fertilizer application to sugarcane (Tenorio et al., 1969). As soil scientists, one of our primary responsibilities is to evaluate and to inform the public on the contribution of agriculture to nitrate pollution of basal ground water in Hawaii.

The fate of all fertilizer N applied to major cultivated soils in Hawaii is not completely understood at the present time. Several studies by Takahashi (1964, 1967, 1968, 1969, 1970) with ^{15}N in both lysimeters and field plots have indicated relatively low recovery of applied N in the sugarcane plant (16-47% in several experiments at different locations). Leaching has not appeared to cause major losses, especially when the crop is well established and removes NO_3^- from the soil solution throughout the rooting zone (Takahashi, 1967 & 1968; Ayres and Hagihara, 1960, Ekern, 1970). When O_2 tension is low in soils which are wet for a long period, N loss by volatilization can be large and rapid (Takahashi, 1968). Ayres and Hagihara (1960) attributed the unaccounted for losses of applied N in their lysimeter study to volatilization of N in one form or another. Biological denitrification is considered to be one of the most important processes accounting for gaseous N loss from soils. However, there was no direct study to evaluate the denitrification loss of applied N in Hawaiian soils. Non-specific anion adsorption, which is the major mechanism for chemical retention of nitrate by oxidic tropical soils, has not received as much attention as cation adsorption. Thus, it becomes necessary to study in more detail the

factors influencing nitrogen retention, denitrification, and nitrate leaching in these soils.

The objectives of the studies in this dissertation are grouped into four major parts, each forming a chapter by itself. They are:

1. The zero point of charge (ZPC) of the Hydrandepts and its relation to nitrate adsorption as affected by profile differentiation and dehydration,
2. Effect of two liming materials on the zero point of charge and adsorption of ammonium and nitrate,
3. Denitrification in Hawaiian soils, and
4. Movement of applied ammonium and nitrate during infiltration in a highly aggregated Oxisol.

Each chapter is a complete unit, that is, it has its own Introduction, Materials and Methods, Results and Discussion, and Summary and Conclusions. Similar to this "General Introduction", there is a closing section on "General Summary and Conclusions" for the whole dissertation.

CHAPTER ONE

THE ZERO POINT OF CHARGE (ZPC) OF THE HYDRANDEPTS AND
ITS RELATION TO NITRATE ADSORPTION AS AFFECTED
BY PROFILE DIFFERENTIATION AND DEHYDRATION

Abstract

The ZPC and net surface charge of two Hydrandepts were determined by potentiometric titration as well as by measurement of ion adsorption. The discrepancy in the ZPC values obtained from two different methods is explained by some flaws in the assumptions of potentiometric titration and by differences in the adsorption affinity of ions involved in the two methods. The direct ion adsorption method was considered preferable to ϕ -pH curves because the ion adsorption method gives the magnitude of positive, negative, and net surface charges at the same time.

The decrease of ZPC and pH due to drying was explained by the hydrolysis of oxides on dehydration. Partial drying, high organic matter content, and low Al_2O_3 concentration in the surface soil were responsible for its low ZPC and pH. The high ZPC of the subsoils was attributed to the extensive hydration of their iron and aluminum oxides. The significant decrease of NO_3^- adsorption due to dehydration was discussed in relation to the change in ZPC, pH, crystallinity, and surface area on drying.

THE ZERO POINT OF CHARGE (ZPC) OF THE HYDRANDEPTS AND
ITS RELATION TO NITRATE ADSORPTION AS AFFECTED
BY PROFILE DIFFERENTIATION AND DEHYDRATION

INTRODUCTION

Based on their electrochemical behavior, soils may be conveniently classified, in accordance with two well known types of soil colloids, as (a) those with constant surface charge (variable surface potential) and (b) those with constant surface potential (variable surface charge). The former group covers most temperate zone soils and some tropical soils which display permanent negative surface charge irrespective of the pH of the system. Highly weathered tropical soils like the Hydrandepts, Gibbshu-mox, Tropohumults and Tropudalfs are a few examples of soils with a variable surface charge. The principal criterion of soils in this latter category is that their silica/sesquioxide ratio should be very low (<1.0).

The Hydrandepts are a group of volcanic ash soils which have undergone extreme weathering under a tropical climate with very high rainfall (more than 400 cm annual rainfall). These soils are depleted in silica but enriched with hydrated oxides of Fe, Al, and Ti, and amorphous aluminosilicates. These soils exhibit amphoteric behavior, and thus are capable of adsorbing either anions or cations

depending on the pH of the system. In the pH range under field conditions, these soils have been shown to adsorb considerable amounts of nitrate (Singh and Kaneshiro, 1969).

The Hydrandepts dry irreversibly and in so doing change from an amorphous hydrated state to a more crystalline one (Sherman, 1957). Complete drying was shown to produce a loss of about 70% in both weight and volume of the Akaka subsoil (King, 1961). Surface soils of Hydrandepts are dehydrated when exposed to sun and wind while their subsoils are always highly hydrated. Drying produces changes in surface charge properties among different horizons of these soils.

The purpose of this work is to investigate the effect of dehydration and soil horizonation of the Hydrandepts on ZPC and nitrate adsorption.

THEORY

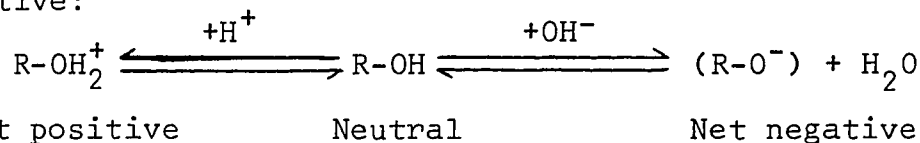
The adsorption of potential determining ions by the solid surface determines the nature of the surface charge in constant potential colloids (Overbeek, 1952; Parks and de Bruyn, 1962; and van Olphen, 1963). H^+ and OH^- are the potential determining ions for the colloidal oxides (Berube and de Bruyn, 1968); the same is probably true for soils rich in such oxides (van Raij and Peech, 1972).

The last two authors analyzed the development and distribution of electric charges in (highly weathered) Oxisols and Alfisols.

The surface charge, σ , is defined as

$$\sigma = F (\Gamma_{H^+} - \Gamma_{OH^-}) \quad (1)$$

where F is the Faraday constant and Γ_{H^+} and Γ_{OH^-} are the adsorption densities of H^+ and OH^- , respectively. The zero point of charge (hereafter denoted by ZPC) is the convenient reference point for calculating surface charges of colloids with reversible interfaces. The ZPC is defined as the pH where the net sum of charges is zero. At this point, the adsorption of H^+ is equal to that of OH^- for pure oxides. At the pH values above ZPC, the surface becomes more negative due to deprotonation, whereas on the acidic side of ZPC, protonation makes the surface net positive:



If the surface charge is assumed to originate only from the adsorption of H^+ and OH^- (which is not entirely true in the practical sense), the surface electric potential, ψ_0 , can be calculated using the following Nernst type of relation,

$$\begin{aligned}
 \psi_0 &= (RT/F) \ln (H^+) / (H^+)_{ZPC} \\
 &= 59 (ZPC - pH) \text{ mV at } 25^\circ\text{C} \quad (2)
 \end{aligned}$$

where R is the gas constant and T is the absolute temperature.

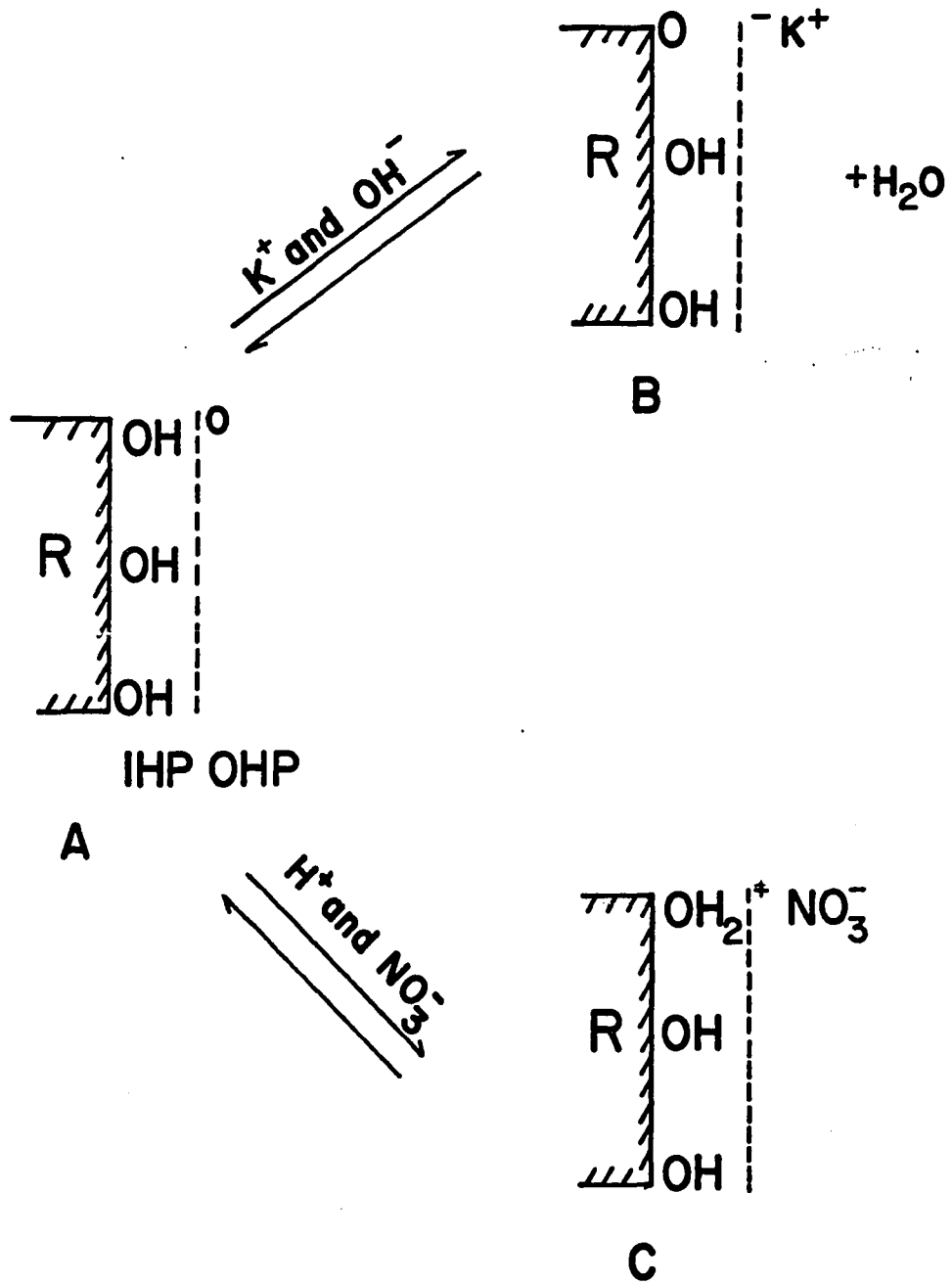
The excess surface charge of soil colloids is satisfied by the adsorption of counter ions (with counter charges). Whether an ion is specifically or non-specifically adsorbed on the surface is determined by the porous or nonporous nature of the surface, electrolyte composition and concentration, and ion affinity to the surface. Ion adsorption in response to Coulombic attraction alone is termed the non-specific adsorption. The amount of ions adsorbed by Coulombic attraction cannot be larger than that equivalent to the original surface charge. On the contrary, specific adsorption is defined as any adsorption for which the adsorption energy differs from the Coulombic one. Specific adsorption can be due to physical forces (e.g. Van der Waals forces) or to chemical ones (e.g. formation of a chemical bond between the ion and the adsorbent as in chemisorption). Specific adsorption of ions produces changes in surface charge (e.g. charge reversal) whereas non-specific ion adsorption does not alter the surface charge.

The plane through the centers of the purely electrostatically (non-specifically) adsorbed ions nearest to the surface is called the outer Helmholtz plane (OHP). The layer between the OHP and the solid surface is the

Stern layer, in which ions are specifically adsorbed. The plane through the center of the specifically adsorbed ions is termed the inner Helmholtz plane (IHP). Protonation and deprotonation of the colloidal oxide take place in the IHP.

Anions such as NO_3^- and Cl^- are believed to be non-specifically adsorbed by soil colloids as contrasted with the strong, specific adsorption of sulfate, phosphate, and silicate (Hingston et al., 1967, 1968, and 1972; Mekar and Uehara, 1972). The scheme in Fig. 1-1 represents non-specific adsorption of ions (K^+ and NO_3^-) on an oxide surface. In this figure, A represents the neutral surface where there is no adsorption in the OHP; B represents the case of non-specific potassium adsorption on the alkaline side of the ZPC, while C denotes the non-specific adsorption of nitrate at pH values lower than ZPC. Note that protonation and deprotonation take place in the IHP.

Figure 1-1. Non-specific adsorption of ions on oxide surface. "R" represents the bulk oxide.



Description and Preparation of Soils: Two soil series (Hilo and Akaka) representing Typic Hydrandepts were chosen for this study. These soils have been subjected to such extreme intensive weathering conditions that they have lost practically all their bases and silica. Thus, the Hydrandepts are dominated by the presence of hydrated oxides of iron, aluminum, and titanium, and amorphous aluminosilicates. According to Uehara et al., (1971), the Al_2O_3 content of the Hilo soil increases with profile depth (about 24% in the surface and 36% in the subsoil) while the Fe_2O_3 and TiO_2 contents are more or less constant throughout the profile (about 27% Fe_2O_3 and 5% TiO_2). The organic carbon in the surface soil is high (about 8.16%) as compared to the subsoil horizons (about 3%).

The two soil profile samples from different depths were collected and stored in double polyethylene bags at 2°C until they were used for the various experiments. The field-moist surface and subsoils were passed through a 6 mm sieve. For the dehydration experiment, subsoils from selected depths were dried as follows: (a) in a room for 15 days (hereafter called "air dry"), in an oven at 110°C (b) for 2 days and (c) for 7 days, which hereafter

will be referred to as "oven dry (2d)" and "oven dry (7d)", respectively. Dried samples were ground and passed through a 20-mesh sieve for ZPC determination and ion adsorption.

General Adsorption Procedure: An equilibrium technique was used to study ammonium and nitrate adsorption. Four gram oven-dry weight equivalent of soil samples were mixed with 15 or 20 ml (depending on the water content of the sample) of KNO_3 or NH_4NO_3 solutions of concentrations ranging from 0.01 N to 0.4 N. To each sample, two drops of toluene were added to arrest microbial activity. The samples were shaken for 1 hour and equilibrated overnight, and then centrifuged at 12,000 rpm for 12 minutes. Supernatant solutions were analyzed for NH_4^+ and/or NO_3^- by the Kjeldahl steam distillation method. The amount of NH_4^+ and NO_3^- adsorbed were calculated from the difference in solution concentration, before and after equilibration. The amounts of NH_4^+ and NO_3^- originally present in the soil were added to the input concentration when calculating adsorbed ions.

Zero Point of Charge (ZPC): Field moist surface and the deepest subsoil samples, and the air dry and oven dry (7d) samples of the subsoil were chosen for the ZPC determination by two methods: (a) potentiometric titration and (b) direct measurement of adsorption of (both positive and negative) ions at different pH values. The original

soil conditions encountered in the field were maintained by avoiding any kind of pre-treatment (e.g. acid washing) to the soil. For the same reason, no special precaution was taken to exclude CO_2 from the titration vessel during the potentiometric titration.

Potentiometric Titration: The procedure was that of Van Raij and Peech (1972). To a 4 g sample of soil in a 50 ml beaker, appropriate amounts of NaCl and 0.1 N HCl or NaOH were added and the final volume was made up to 20 ml with distilled water. The final concentrations of NaCl were 0.1, 0.01, and 0.001 N. The beakers were covered with a piece of parafilm. After 4 days of equilibration, the pH was determined using a Beckman research pH meter.

The amount of H^+ and OH^- adsorbed by the soil sample, at any given pH value, was taken as equal to the amount of HCl or NaOH added to the suspension minus the amount of acid or base required to bring the same volume and the same concentration of NaCl solution, without the soil sample, to the same pH. The intersection point of titration curves in the presence of three concentrations of NaCl was taken as ZPC. The net electric charge was calculated from the amount of H^+ and OH^- adsorbed with respect to ZPC.

Adsorption of NH_4^+ and NO_3^- at Different pH Values:

Positive and negative electric charges of the soil were

also determined by measuring the adsorption of both positive (NH_4^+) and negative (NO_3^-) ions from 0.01 N NH_4NO_3 solution as a function of pH. The procedure was the same as that described in the general adsorption procedure.

The amounts of NH_4^+ and NO_3^- retained represent equivalent amounts of negative and positive charges, respectively. The magnitude of ammonium and nitrate adsorption, and that of net charge were plotted as a function of pH. The intersection point of NH_4^+ and NO_3^- adsorption curves was considered as ZPC.

Delta pH (ΔpH): Delta pH ($\text{pH}_{\text{KCl}} - \text{pH}_{\text{H}_2\text{O}}$) was determined by measuring soil pH in soil suspensions prepared with 1 N KCl and also with distilled water (soil to solution ratio of 1:10 for field moist subsoils and 1:5 for others). As recommended by Peech (1965), the Calomel electrode was immersed in the clear supernatant solution and the glass electrode in the sediments while recording pH. Soil-paste pH was also determined by immersing both electrodes in the paste.

RESULTS AND DISCUSSION

Surface Charge-pH Curves in NaCl Solution

The ZPC and net surface charge of field moist surface and subsoils, and the air-dry and oven-dry samples of the latter for the two Hydrandepts are given in Fig. 1-2 and 1-3. The σ -pH curves for 0.1, 0.01, and 0.001 N NaCl solutions intersect at a single point which is termed the ZPC. Net electric charge of the surface was computed with respect to the ZPC. The high concentration of 1 N NaCl was not included in this study because (a) at that high electrolyte concentration, the diffuse double layer is highly compressed and this changes the surface properties; (b) no ionic species is totally devoid of a tendency toward specific adsorption (Parks, 1967) and the chance for specific adsorption of ions from indifferent electrolytes is increased at high concentrations (e.g. specific adsorption of Li on hematite surface at 1 N concentration as reported by Breeuwsma and Lyklema, 1973); and (c) such a high concentration of salts will not be encountered in soils (including the saline ones). Keng (1974) observed that the σ -pH curve for 1 N NaCl solution was shifted toward lower pH values, thereby giving lower ZPC in similar soils.

Figure 1-2. The ZPC and net surface charge of field moist surface and subsoils, and air-dry and oven-dry samples of the latter for the Hilo soil.

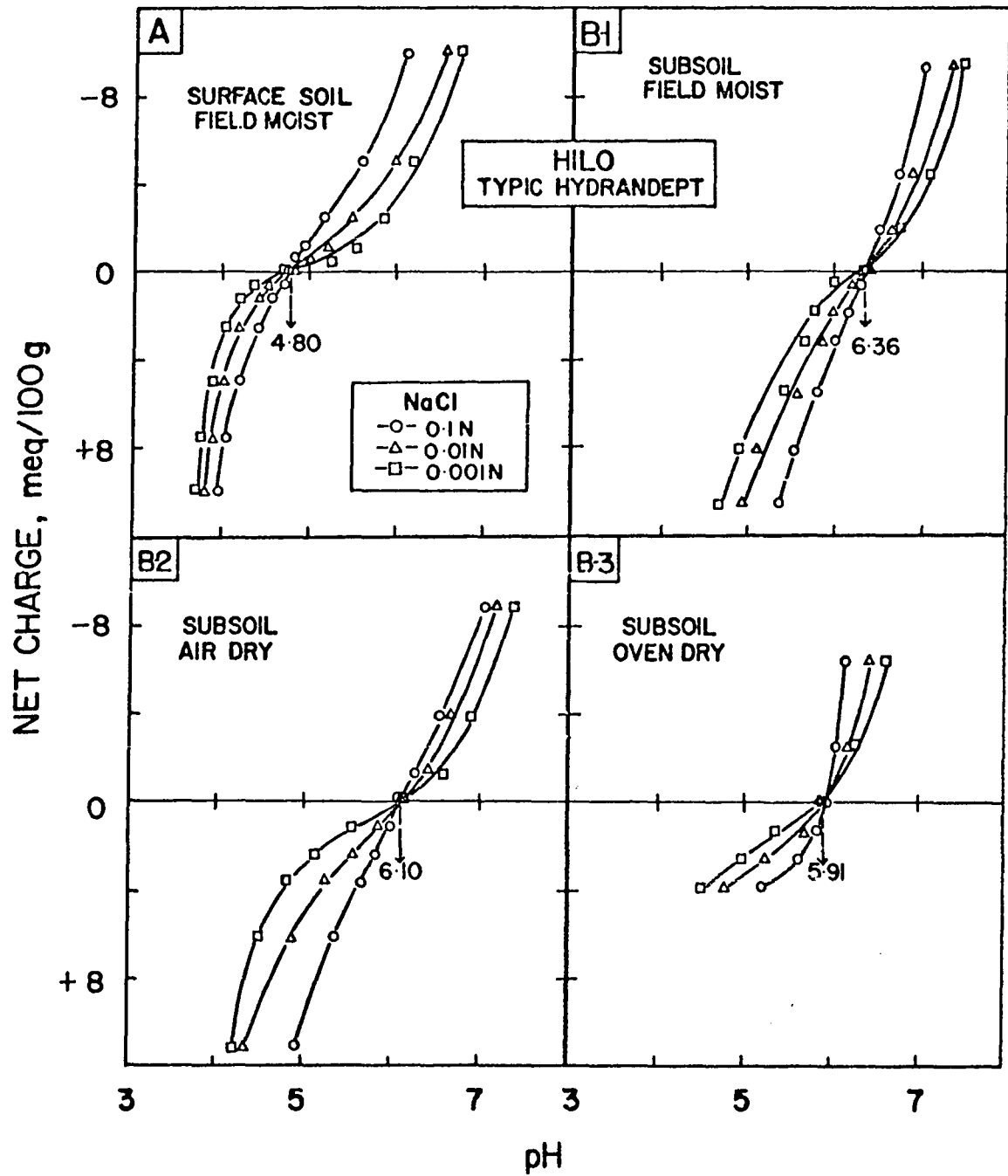
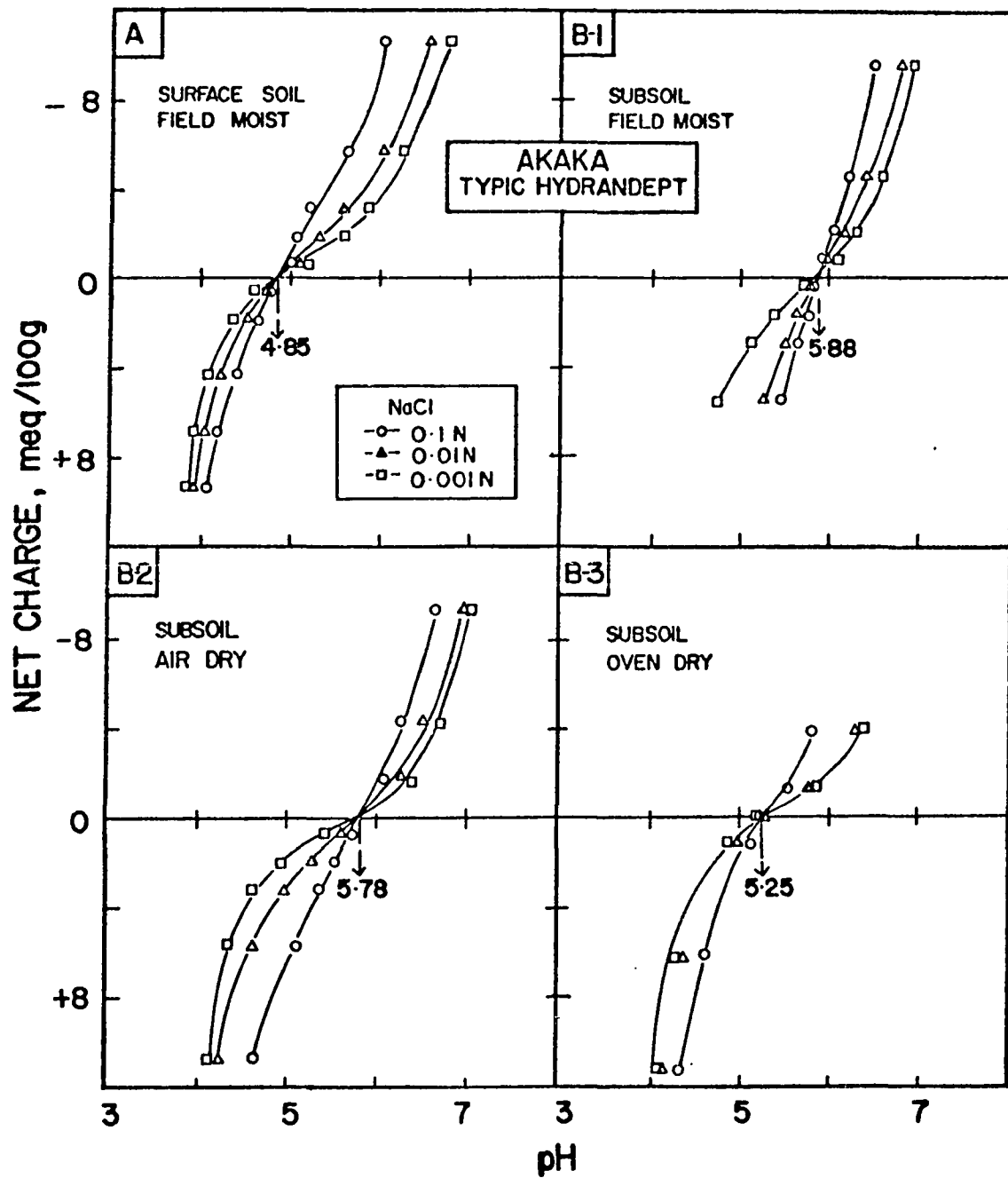


Figure 1-3. The ZPC and net surface charge of field moist surface and subsoils, and air-dry and oven-dry samples of the latter for the Akaka soil.



The ZPC of all samples, except that of the Akaka surface soil, was on the alkaline side of the native soil pH (Table 1-1). In the same way, the Δ pH values were positive for all the samples except for the Akaka surface soil. It can therefore be concluded that Δ pH values measured in soil suspensions (1:5 soil to solution ratio) indicated the nature of the net surface charge of these soil colloids as reported by Mekarū and Uehara, (1972).

The ZPC and pH of field moist surface soils were lower than in the subsoils (Table 1-1 and Fig. 1-2 and 1-3). Partial drying and high organic matter content associated with the surface soils are considered as main factors responsible for their lower pH and ZPC. A similar characteristic effect (decreasing the ZPC) of organic matter in soils is reported by van Raij and Peech (1972). Another factor for the lower ZPC in surface soil may be its lower Al_2O_3 content as compared to the subsoil. O'Connor et. al. (1956) observed that the ZPC of natural aluminum oxides increased with their Al_2O_3 content.

The positive surface charge and high ZPC of subsoils in the Hydrandepts may be due to the extensive state of hydration of their sesquioxides. The ferric iron or its

Table 1-1

Moisture Content, Organic C, pH, Delta pH (Δ pH), and Zero Point of Charge (ZPC) of the Hydrandepts

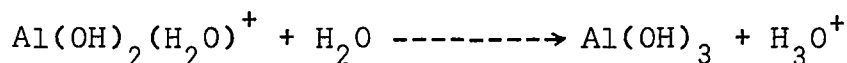
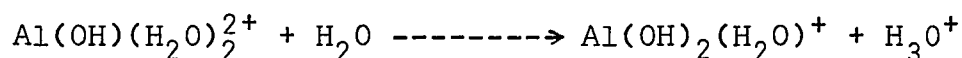
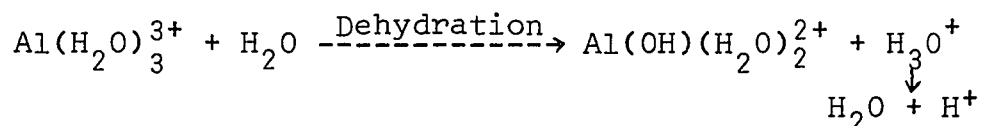
Soil series	Depth cm	Condition of the soil	Moisture (θ_g) %	Organic C %	pH (Soil paste)	Δ pH*	ZPC	
							Pot. Titr.	Ion Adsorp.
Hilo	0-13	Field moist	69.6	8.01	4.61	0.03	4.80	4.33
	62-114	Field moist	211.1	3.17	6.00	0.39	6.36	5.80
	62-114	Air dry	21.9	--	5.26	0.50	6.10	5.44
	62-114	Oven dry	10.2	--	4.98	0.38	5.91	4.67
Akaka	0-13	Field moist	114.4	9.44	5.01	-0.27	4.85	4.32
	61-91	Field moist	367.2	4.98	5.84	0.23	5.88	5.31
	61-91	Air dry	26.2	--	5.22	0.27	5.78	4.70
	61-91	Oven dry	10.2	--	4.79	0.26	5.25	4.28

*The pH was measured by immersing the glass electrode in the sediment and the calomel electrode on the clear supernatant solution. (1:5 soil to solution ratio).

oxide, when hydrolyzed, forms hydroxy species like $\text{Fe}(\text{H}_2\text{O})_3^{3+}$, $\text{Fe}(\text{OH})(\text{H}_2\text{O})_2^{2+}$, $\text{Fe}(\text{OH})_2(\text{H}_2\text{O})^+$, and $\text{Fe}(\text{OH})_3$ as reported by Langdon *et. al.*, 1973. These species have a tendency to polymerize as is shown by the formation of dimeric and trimeric cations: $\text{Fe}(\text{OH})_2(\text{H}_2\text{O})_8^{4+}$ (Mulay and Selwood, 1956) and $\text{Fe}_3(\text{OH})_4^{5+}$ (Schlyter, 1965). Aluminum or its oxide may form similar hydroxy species on hydration (Hsu and Bates, 1964; Hunt, 1963; Frink and Peech, 1963 a,b). High ZPC of the subsoils may be attributed to the presence of these positively charged hydrated oxide gels of Fe and Al. Using a spot technique, Langdon *et. al.*, (1973) found that the adsorption of sulfate and phosphate on the freshly-cleaved 001 face of muscovite mica was enhanced only when the surfaces were covered with the colloidal hydrolysis products of ferric iron. They also indicated that this surface-active hydrous oxide gel of high water content collapses when dried in air. Similarly, soil minerals were shown to be coated with a thin gelatinous film (Jones and Uehara, 1973), but the effect of such a mineral coating on the surface properties of soils is not fully established. It should be noted here that much of soil material in the subsoil of Hydrandepts is made up of amorphous materials and colloidal hydrous oxide gels of high water content. The highly positive nature of their soil colloidal surface

is derived from such a composition.

The ZPC and pH of the subsoils shifted to lower values as the samples were progressively dried (Fig. 1-2 and 1-3; Table 1-1). The following mechanism is suggested to account for the changes in the ZPC and pH due to drying:



The stepwise hydrolysis of the hydrated aluminum and its oxides is enhanced by drying. The lower pH of the partially dehydrated surface soils, and the decrease of pH upon drying the subsoil (Table 1-1) can be explained by this reaction. Apart from the effect on the foregoing hydrolysis of oxides, drying may also induce the polymerization of hydroxy aluminum. This mechanism would reduce positive charges available per aluminum atom as shown below (after Hsu and Bates, 1964):

Hydroxy aluminum polymer ---	Positive charge per aluminum ---
$\text{Al}_6(\text{OH})_{12}^{6+} \cdot 12 \text{H}_2\text{O}$	1.00
$\text{Al}_{10}(\text{OH})_{22}^{8+} \cdot 16 \text{H}_2\text{O}$	0.80
$\text{Al}_{24}(\text{OH})_{60}^{12+} \cdot 24 \text{H}_2\text{O}$	0.50
$\text{Al}_{54}(\text{OH})_{144}^{18+} \cdot 36 \text{H}_2\text{O}$	0.33
$\text{Al}(\text{OH})_3$	0.00

Since the positive surface sites are neutralized by drying, the surface of dried samples become less positive with the resultant decrease in the ZPC. Ignition of hydrated oxides and natural α - Al_2O_3 changed an originally positive surface to a negative one (O'Connor et. al., 1956; Johansen and Buchanan, 1957; Berube and De Bruyn, 1968). The ZPC of soils relates to the isoelectric point of solid, IEP(s), for pure oxides. In the absence of specific adsorption, ZPC is same as IEP(s). An examination of the work of Parks (1965) will reveal that the IEP(s) for pure oxides increases with hydration. For instance the values of IEP(s) for anhydrous and hydrous oxides are

Fe_2O_3	6.7 and 8.6,
Al_2O_3	6.7 and 9.2,
TiO_2	4.7 and 6.2,

respectively. Since oxide gels in Hawaiian Hydrandepts contain high amounts of Al, Fe, and Ti, the ZPC of such soils will likely decrease with drying.

On drying, the amorphous, hydrated oxides may have been converted to crystalline ones. Sherman et. al., (1964) reported that the aluminum oxide gel in the Hydrandepts will differentially crystallize to gibbsite on complete dehydration. The earlier hydrolysis mechanism also suggests the formation of gibbsite upon

drying the hydrated aluminum oxide species. Increasing crystallinity shifts the IEP(s) of pure oxide in the acid direction (Parks, 1967).

Surface Charges as Determined by the Direct Measurement of Ammonium and Nitrate Adsorption.

The measurement of adsorption of NH_4^+ and NO_3^- , under specified pH and electrolyte concentration, facilitates the direct determination of positive (by NO_3^- adsorption) and negative (by NH_4^+ adsorption) surface charges as well as the net charge. The adsorption densities of the soil for NH_4^+ and NO_3^- at 0.01 N concentration as a function of pH are given in Fig. 1-4 and 1-5. The concentration of 0.01 N NH_4NO_3 was chosen for this experiment with the assumption that the electrolyte concentration of soil solution for many soils will be around this value.

The intersection point of NH_4^+ and NO_3^- adsorption curves in Fig. 1-4 and 1-5 was considered as the ZPC. These figures also depict the characteristic behavior of amphoteric soils with changing pH, i.e., these soils behave like mixed bed exchangers with more of one charge than another on either side of the ZPC. At the ZPC, there are equal densities of NH_4^+ and NO_3^- adsorption, thereby indicating the coexistence of low but equal amounts of positive and negative charges (with the resultant zero net charge) at this point. The co-

Figure 1-4. The adsorption densities of the field moist and dried samples of the Hilo soil for NH_4^+ and NO_3^- at 0.01 N NH_4NO_3 concentration as a function of pH.

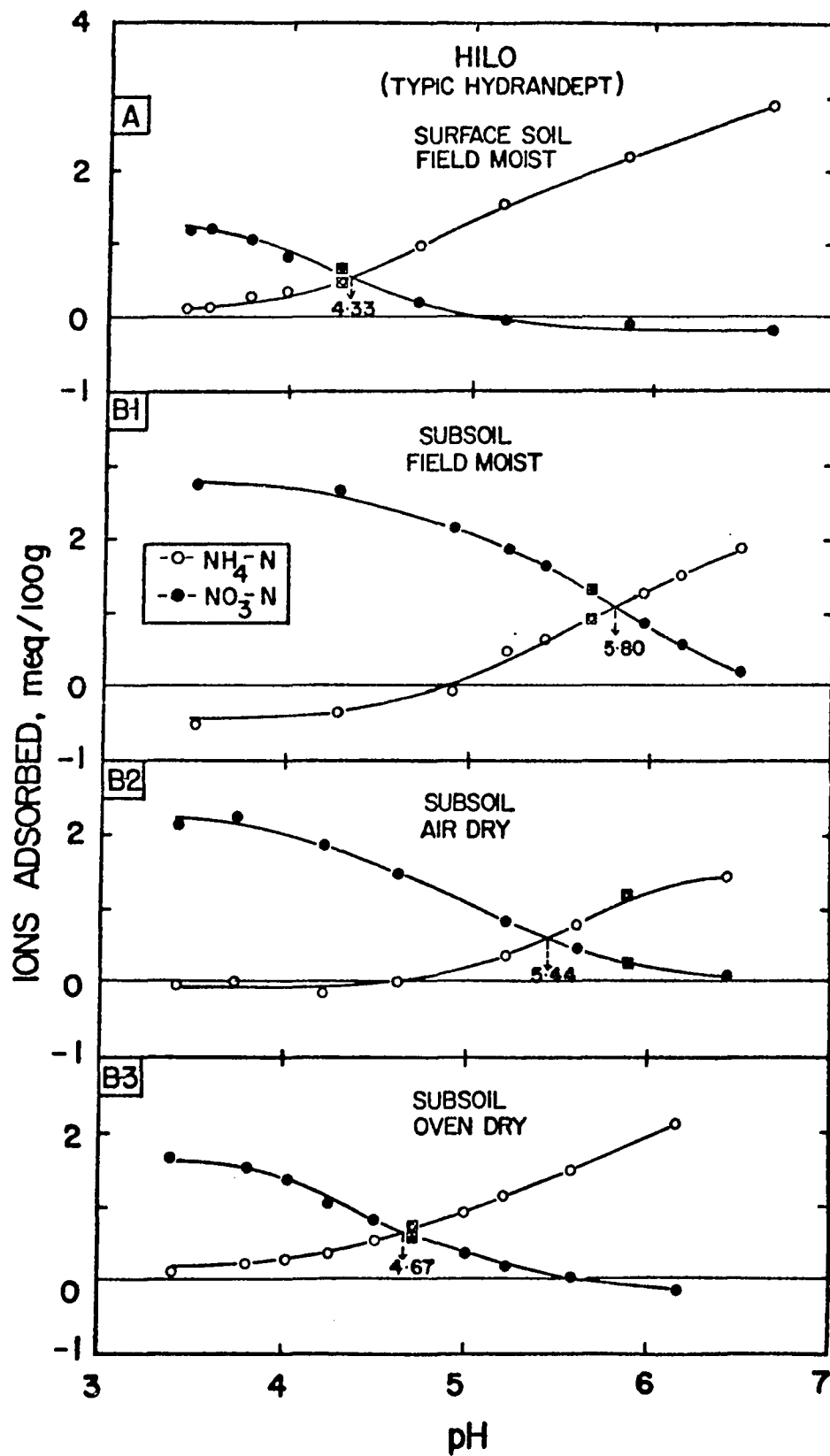
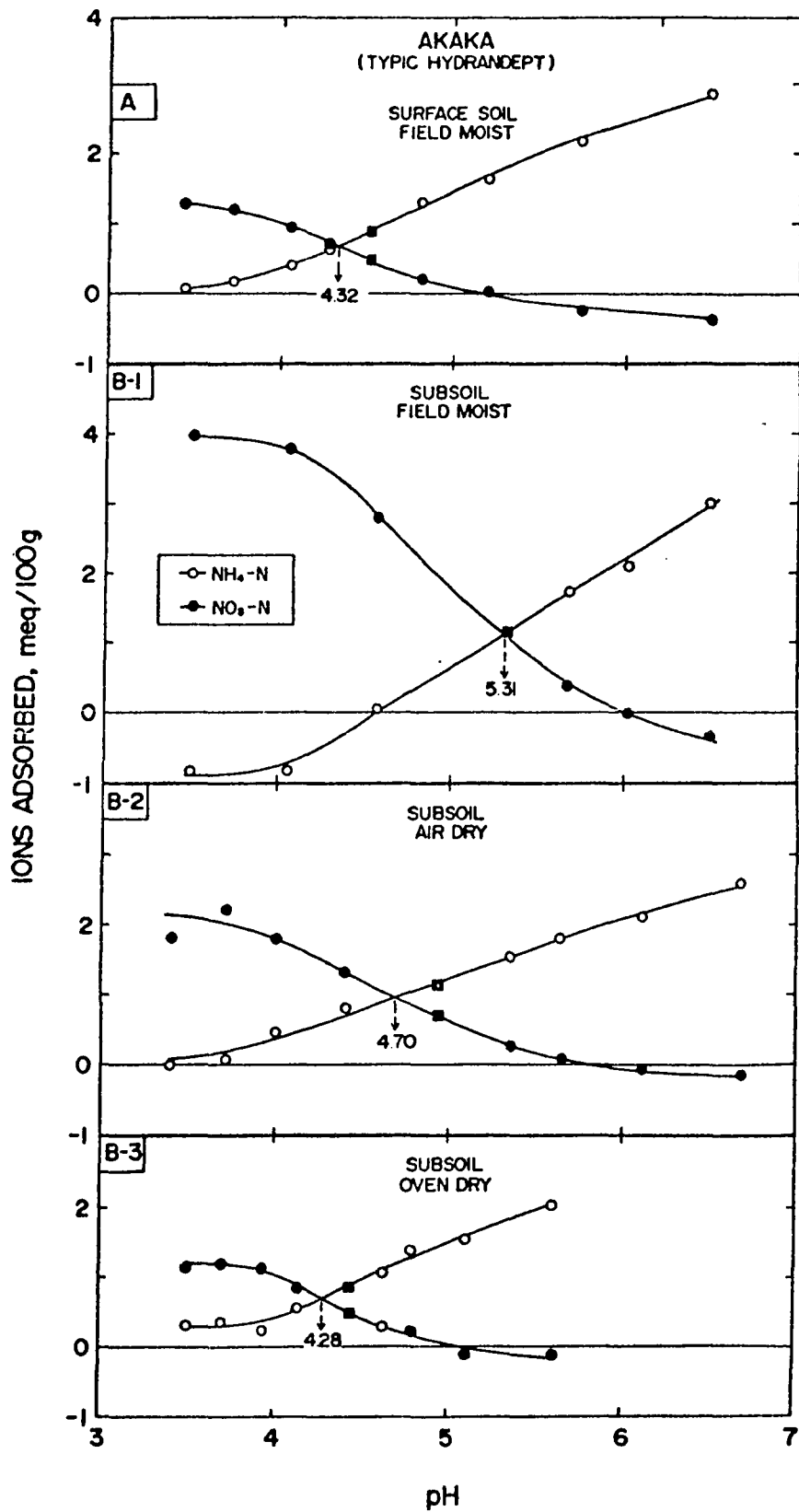


Figure 1-5. The adsorption densities of the field moist and dried samples of the Akaka soil for NH_4^+ and NO_3^- at 0.01 N NH_4NO_3 concentration as a function of pH.



existence of small amounts of positive and negative sites at the ZPC has been reported for ZrO_2 , ThO_2 , and SnO_2 (Kraus et. al., 1958; Amphlett et. al., 1958).

The ZPC values obtained by the measurement of NH_4^+ and NO_3^- adsorption are lower than those obtained from the potentiometric titration curves (Table 1-1). The discrepancy may be due to:

- (a) some flaws in the assumption that added H^+ and OH^- in the potentiometric titration are solely adsorbed on the surface as potential determining ions. Although this might be the major reaction occurring during the addition of NaOH and HCl to the soil, one cannot deny that there might be other reactions like dissolution of aluminum at low pH values and precipitation of complex metal hydroxides at high pH in which the added H^+ and OH^- may participate, and
- (b) the difference in adsorption affinities of ions involved in the two methods (NH_4^+ and NO_3^- vs. H^+ and OH^-).

The direct determination of surface charge by ion adsorption is preferable to potentiometric titration because (a) the former method gives the magnitude of

positive, negative, and net charges developed in the soil at different pH values; (b) it indicates the point in the pH scale where negative adsorption of positive and negative ions begin (See Fig. 1-4 and 1-5); and (c) it shows the coexistence of small but equal amounts of positive and negative charges at the ZPC which is not observed in the plot of the net charges vs. pH. Similar discrepancy in the ZPC values of soils obtained through potentiometric titration and ion adsorption method was recorded by van Raij and Peech (1972). The low ZPC values attained through adsorption of ions from indifferent electrolytes as shown in Table 1-1 closely compared with the ZPC values measured by potentiometric titration in CaCl_2 solution by Keng (1974).

The net charges measured by ion adsorption were plotted as a function of pH in Fig. 1-6 and 1-7. The ZPC of the surface soil was lower than that of the subsoil in the moist condition. Progressive dehydration of the field moist subsoil shifted the ZPC to more acid pH values. Thus a similar pattern was observed in the change of ZPC due to drying and soil horizonation when both potentiometric titration and ion adsorption methods were compared (Fig. 1-2 and 1-3 vs. Fig. 1-6 and 1-7).

Figure 1-6. The net electric charge of field moist and dried samples of the Hilo soil.

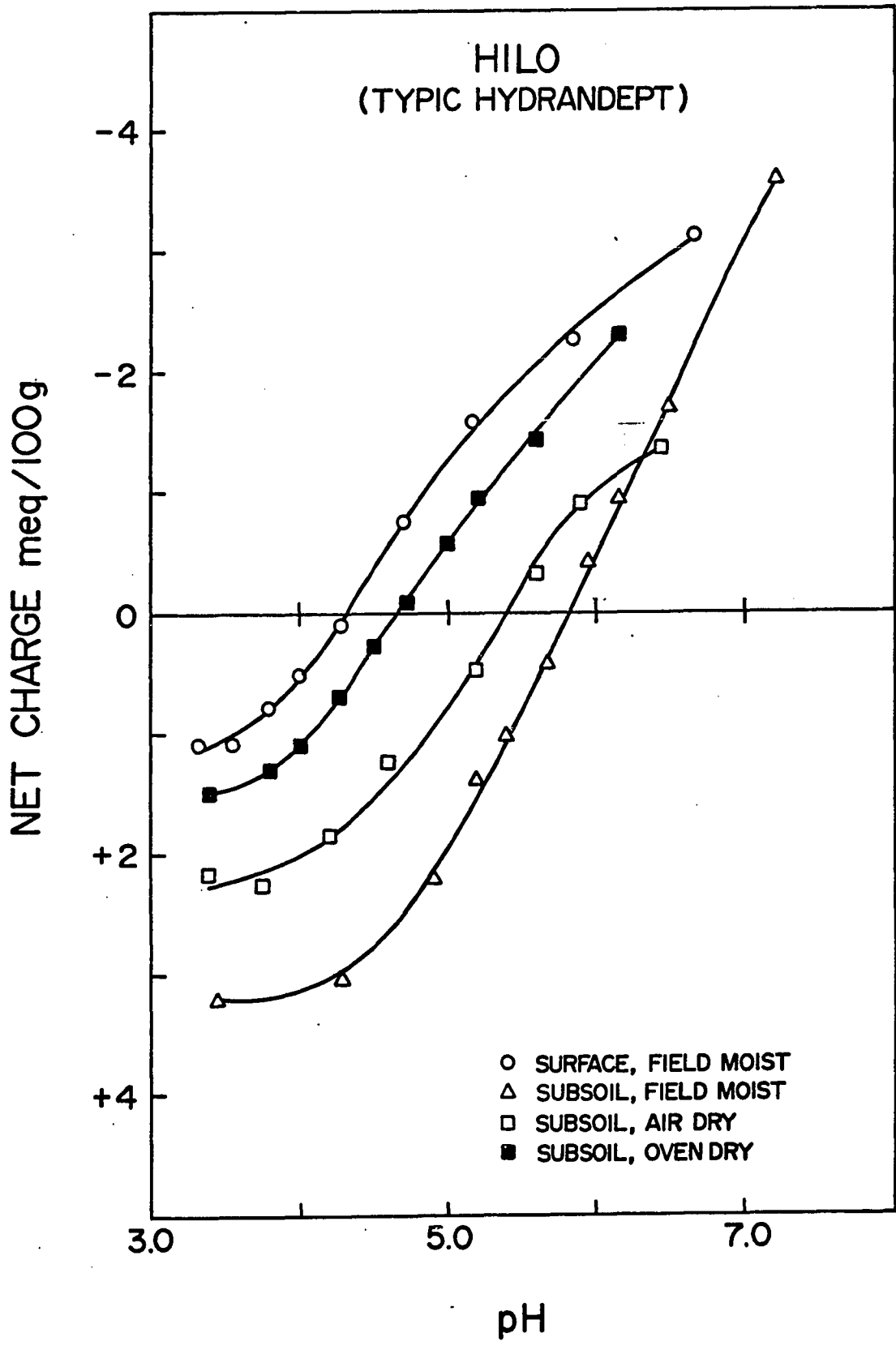
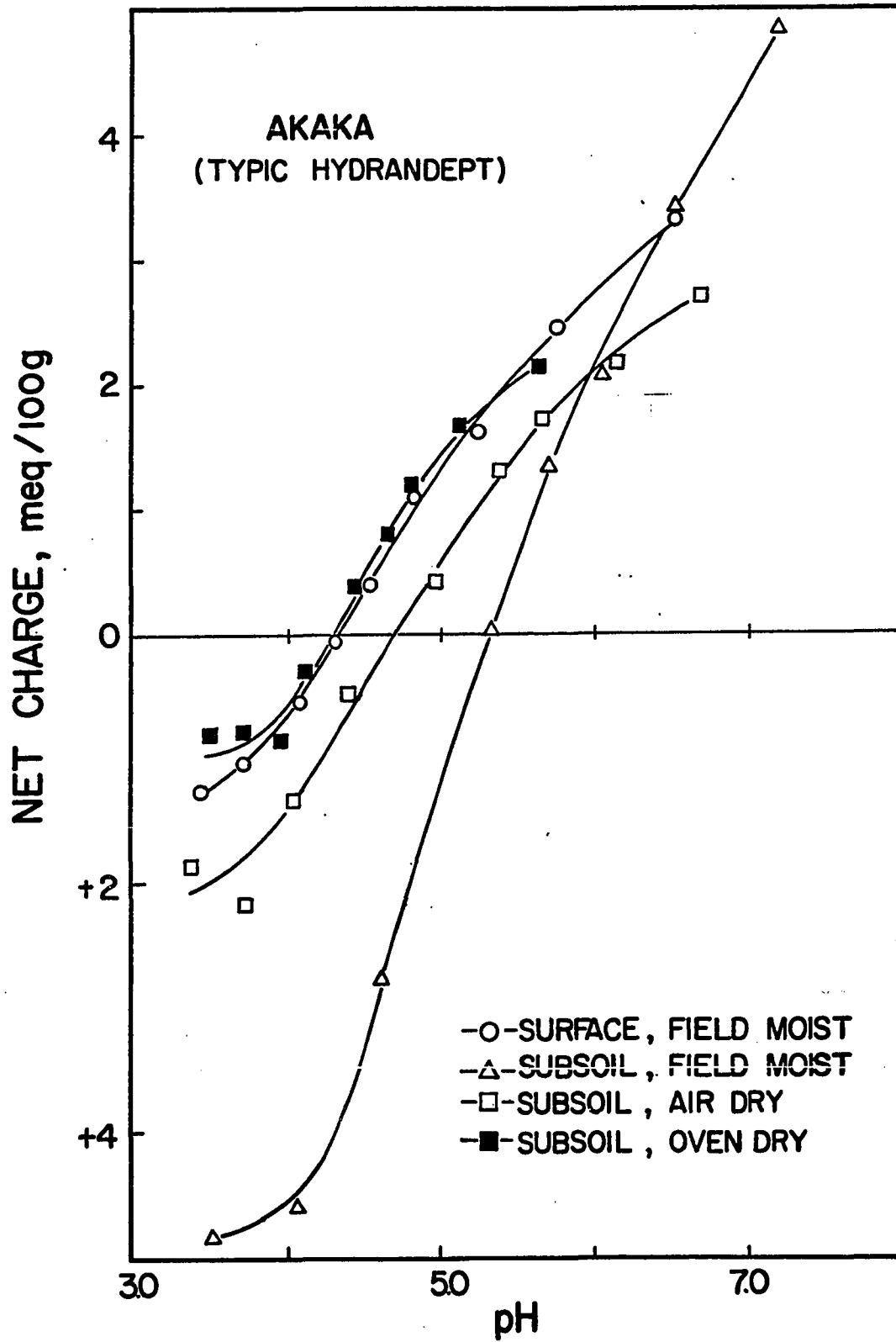


Figure 1-7. The net electric charge of field moist and dried samples of the Akaka soil.

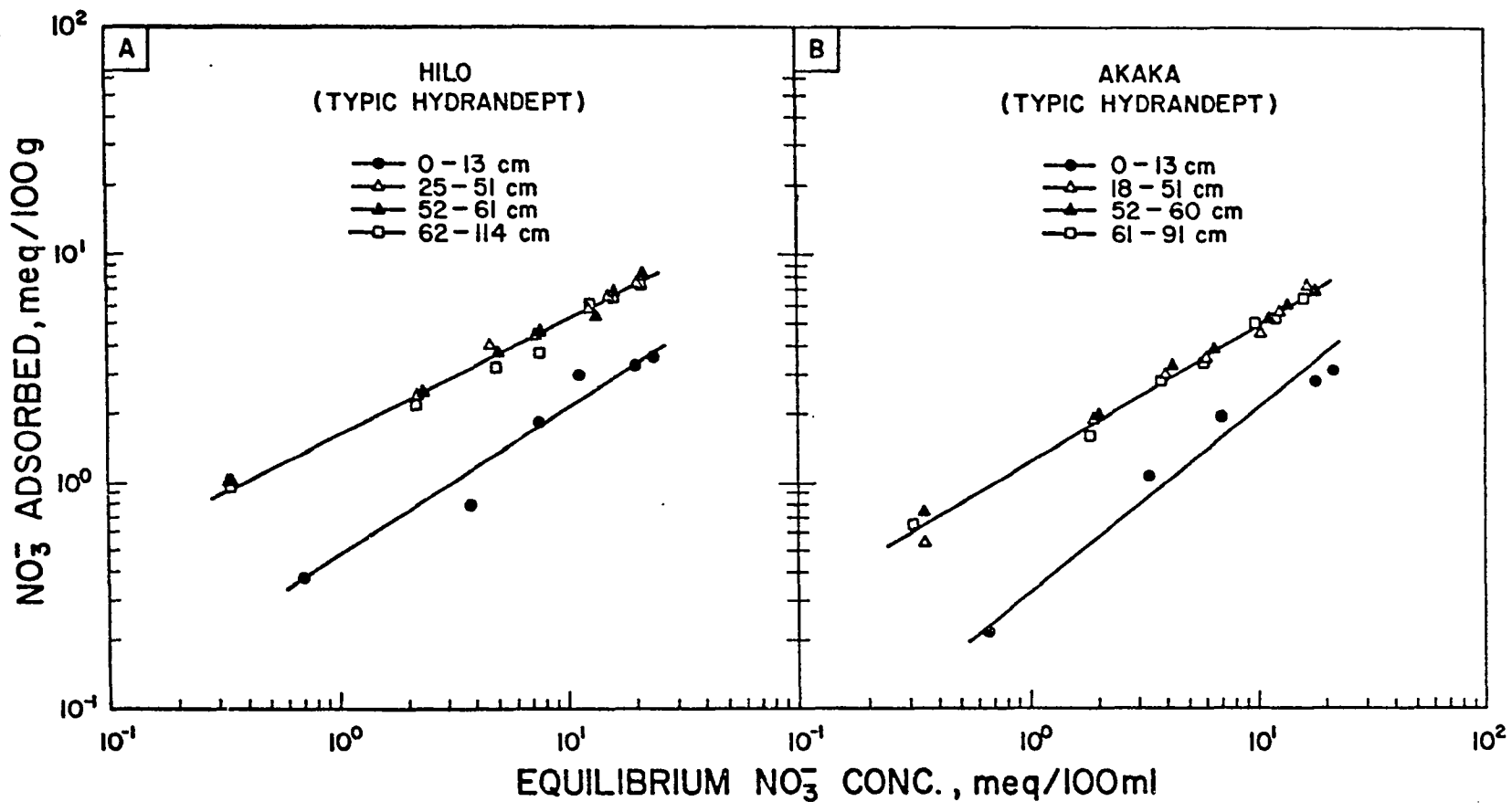


The decrease in NO_3^- adsorption due to drying was very much pronounced as compared to the change in NH_4^+ adsorption due to drying (Fig. 1-4 and 1-5). As earlier explained, drying neutralizes most of the positive surface sites while the effect of drying on negative surface sites is negligible. Thus NO_3^- adsorption is decreased significantly by dehydration, while leaving NH_4^+ adsorption more or less unaffected at this low electrolyte concentration (0.01 N NH_4NO_3).

Nitrate Adsorption Isotherm

Surface horizons (0-13 cm) of the two Hydrandepts adsorbed less NO_3^- than subsoil horizons (Fig. 1-8), although all the horizons showed affinity for NO_3^- . NO_3^- adsorption capacity of different subsoil horizons was approximately equal. The surface soil was less hydrated than the unexposed subsoil (see moisture content in Table 1-1). This natural drying in the surface soil was associated with decreased NO_3^- adsorption (Fig. 1-8). Other factors, such as a high percentage saturation of exchange sites by soil organic matter, low ZPC, and the closeness of the pH value to zero are also believed to be associated with low NO_3^- adsorption by the surface soil.

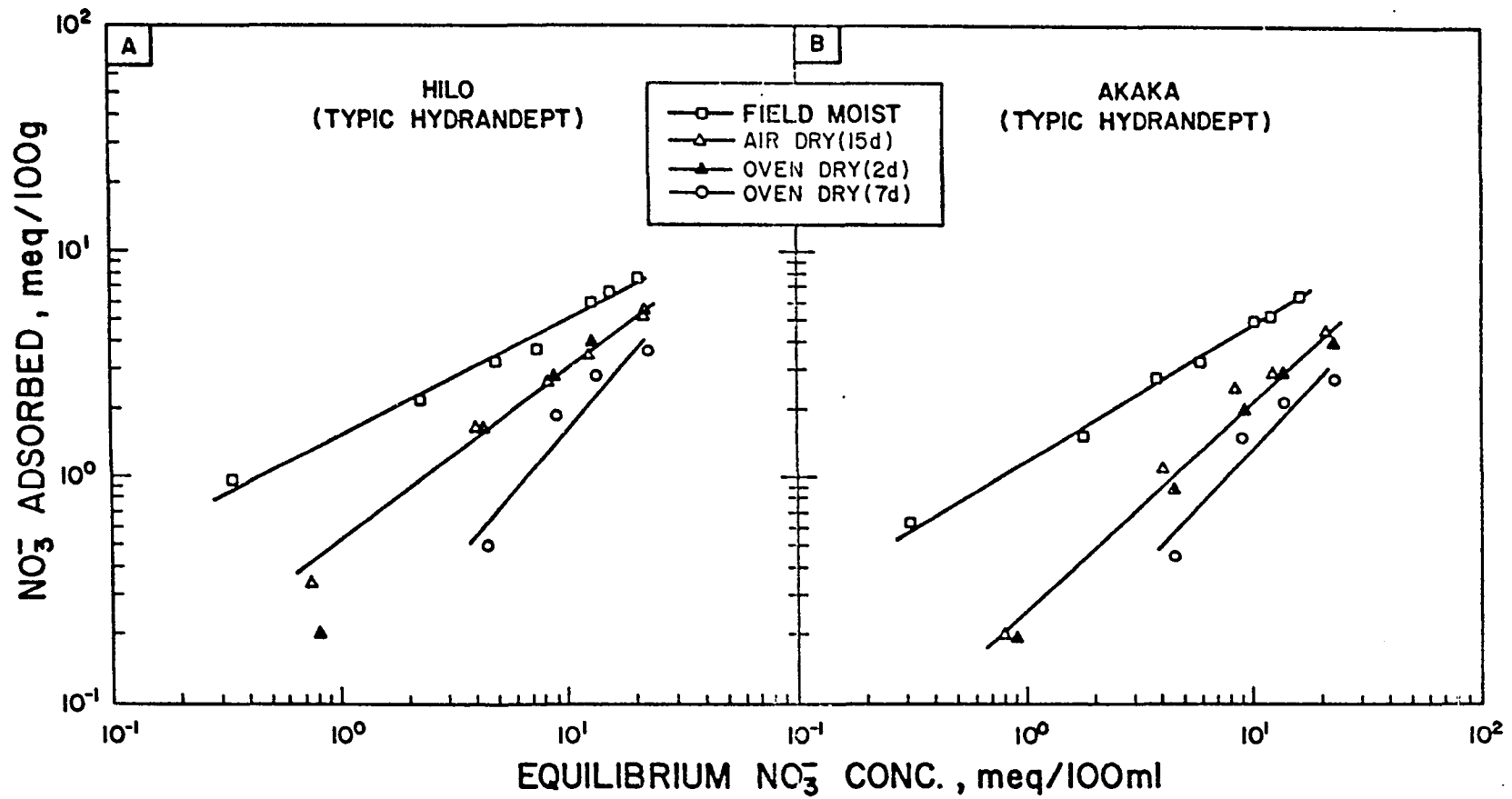
Figure 1-8. Nitrate adsorption isotherm as a function of profile depth in two Hydrandepts.



The data in Fig. 1-9 indicate that complete drying reduced NO_3^- adsorption by almost 50% in two Hydrandepts. The decrease in NO_3^- adsorption was similar in the 2-day oven dried and 15-day air dried samples. However, continued oven drying at 110°C (for 7-days) further decreased NO_3^- adsorption. Since the drying process mainly decreased the positive surface sites, the significant reduction in NO_3^- adsorption due to dehydration was not unexpected. Moreover, the acid shift of the ZPC due to drying (Table 1-1) narrows down the pH range over which NO_3^- will be adsorbed. Crystallization and perfection of structure due to drying of the amorphous, hydrated oxide gel (Sherman et. al., 1964) will result in less surface charges and hence will decrease NO_3^- adsorption.

During dehydration, the hydrated, amorphous colloids formed sand-sized aggregates. This increase in aggregate size upon drying will decrease the surface area (at least the external surface area) significantly. The reduction in surface area (no experimental data on surface area were given because of the lack of suitable method to determine surface area in field moist Hydrandepts) may also contribute to decreased NO_3^- adsorption by the dried samples. King (1961) observed that complete drying produced a loss of about 70% in both weight and volume of the Akaka subsoil. The work of Kanehiro and Sherman (1956) shows that the

Figure 1-9. Effect of drying on nitrate
adsorption by two Hydrandepts.



cation exchange capacity of the Hydrandepts decreased by as much as 50% on drying. Thus, the simultaneous decrease of anion and cation adsorption at high concentrations because of drying could likely be due to reduction in surface area in the dried Hydrandepts. Any or all of the above factors are believed to be responsible for the change in NO_3^- adsorption due to drying and soil horizonation.

Nitrate adsorption in these soils (Fig. 1-8 and 1-9) can be described by the Freundlich type of isotherm,

$$\log (x/m) = \log K + (1/n) \log C$$

where $x/m = \text{NO}_3^-$ adsorbed, meq/100 g

$K, n = \text{constants}$

$C = \text{Equilibrium concentration, meq/100 ml}$

The calculated Freundlich constants, K (the intercept at unit concentration) and $1/n$ (the slope of the isotherm), are presented in Table 1-2. The decrease of K value with progressive drying indicates decreased NO_3^- adsorption in the dehydrated samples.

Since the drying process in Hydrandepts is practically irreversible (Kanehiro and Sherman, 1956), the ion exchange capacity lost in dehydration cannot be regained by wetting the dried samples. Therefore, these soils should not be allowed to dry excessively by

Table 1-2

Calculated Freundlich constants for nitrate adsorption isotherms obtained with field moist and dried samples of two Hydrandepts.

Sample	Hilo		Akaka	
	K	1/n	K	1/n
Field-moist surface soil	0.48	0.65	0.32	0.82
Field-moist subsoil	1.54	0.52	1.20	0.61
Air-dry (15d) or O. D. (2d) sample of subsoil	0.53	0.76	0.26	0.93
O. D. (7d) sample of subsoil	0.11	1.19	0.11	0.93

exposure to direct sun and wind if their high exchange capacities are to be preserved. A constant ground cover and minimum tillage will help to keep these soils from drying.

SUMMARY AND CONCLUSIONS

The ZPC of the field moist surface soil was lower than that of the subsoil because the former was partially dried, high in organic matter, and low in Al_2O_3 content. The subsoils of the Hydrandepts contain hydrous oxide gels of high water content. The positive sites associated with these hydrous oxides contributed to the high ZPC of the subsoils. The decrease of the ZPC and pH due to drying was explained by the hydrolysis of oxides on dehydration.

The ZPC values determined by the direct measurement of adsorption of ions from an indifferent electrolyte (NH_4NO_3) were lower than those obtained from ϕ -pH curves in NaCl solutions. The reason for this inconsistency in the ZPC values obtained from two different methods may be due to the failure of the assumption that added H^+ and OH^- in the potentiometric titration are solely adsorbed on the surface as potential determining ions; the involvement of added H^+ and OH^- in side reactions like dissolution of aluminum at very low pH values and precipitation of complex metal hydroxides at alkaline pH is highly possible in complex mixtures like soils. The direct ion adsorption method is preferable to the potentiometric titration procedure for the ZPC determination of soils, because the former gives the magnitude of positive, negative, and net

surface charges at the same time.

The significant decrease of NO_3^- adsorption due to dehydration was discussed in relation to the change in the ZPC, pH, crystallinity, and surface area on drying. Since this dehydration process is irreversible, it was concluded that these soils should not be allowed to dry excessively by exposure to direct sun and wind so as to preserve their high exchange capacity both for anions and cations.

CHAPTER TWO

EFFECT OF TWO LIMING MATERIALS ON THE ZERO
POINT OF CHARGE AND ADSORPTION OF
AMMONIUM AND NITRATE

ABSTRACT

The effect of two liming materials, CaCO_3 and CaSiO_3 , on the zero point of charge (ZPC) and NH_4^+ and NO_3^- adsorption capacities of two Hydrandepts and one Gibbsihumox was studied. The pH increased and the ZPC decreased due to liming of acid soils. The surface of soils became less positive or more negative, and this was reflected in the (increased) NH_4^+ and (decreased) NO_3^- adsorption by the limed soils. Raising of soil pH beyond 5.5 with liming produced NO_3^- repulsion in these soils. Although pure CaCO_3 has been shown by others to develop positive surface charge and to adsorb NO_3^- , CaCO_3 applied to these soils as a liming material did not increase NO_3^- adsorption.

EFFECT OF TWO LIMING MATERIALS ON THE ZERO POINT OF CHARGE
AND ADSORPTION OF AMMONIUM AND NITRATE

INTRODUCTION

Soils high in hydrated sesquioxides and amorphous aluminosilicates have very high anion adsorption capacity (Singh and Kanehiro, 1969; Mekar and Uehara, 1972). Liming of such acid soils increases the pH and surface negative charges, and decreases the surface positive charges. An increase in cation exchange capacity following calcium silicate or carbonate applications was reported by Monteith and Sherman, 1963. The increase of net negative charge due to liming would be expected to result in a lowered retention of weakly adsorbed anions like NO_3^- and Cl^- which are bound mainly by electrostatic forces.

The study of Somasundaran and Agar (1967) showing that CaCO_3 , under certain conditions, develops a positively-charged surface suggests that NO_3^- interaction with CaCO_3 is a distinct possibility. Jurinak and Griffin (1972) corroborated the interaction of NO_3^- and CaCO_3 in equilibrium NO_3^- adsorption studies with pure CaCO_3 and NO_3^- elution experiments in columns packed with CaCO_3 treated sand. However, they also indicated that naturally occurring carbonates in calcareous soils did not increase

NO_3^- retention significantly in the column elution study.

The purpose of this investigation is to study the effect of two liming materials, CaCO_3 and CaSiO_3 , on the zero point of charge (ZPC) and NH_4^+ and NO_3^- adsorption capacities of two Hydrandepths and one Gibbsihumox.

MATERIALS AND METHODS

Soils: Two Hydrandepts (Hilo and Akaka) and one Gibbshumox (Halii) were used in this study. The description and pertinent properties of the two Hydrandepts are included in Chapter One. The Halii soil, developed from olivine basalt, is extremely weathered under very high rainfall (~400 cm annual rainfall) with the consequent depletion of silica and enrichment of sesquioxides. Principal secondary minerals in this soil are gibbsite, goethite, and kaolinite in the order of decreasing importance (Uehara et. al., 1971).

Liming: Three levels of CaSiO_3 (0, 20, and 40 meq Ca^{2+} /100 g of soil) and two levels of CaCO_3 (0 and 40 meq of Ca^{2+} /100 g of soil) were employed for liming. Calculated amounts of the lime were mixed with the surface soils and allowed to react for about five months.

Experimental Procedures: The equilibrium adsorption technique as described in the general adsorption procedure in Chapter One was used to study NH_4^+ and NO_3^- adsorption in these soils. The ZPC was determined by potentiometric titration in NaCl solutions as well as by

ion adsorption from NH_4NO_3 solution (detailed procedures are given in Chapter One).

RESULTS AND DISCUSSION

Zero Point of Charge (ZPC): The surface charge-pH curves from 0.001, 0.01, and 0.1 N NaCl solutions did not intersect at a distinct point in the limed soils, thereby making the potentiometric titration procedure unsuitable for the ZPC determination in limed soils. Therefore for limed soils only those ZPC values obtained from the ion adsorption method are included in this report. The pH, Δ pH and ZPC of the treated soils are listed in Table 2-1. It can be noted that the ZPC of the limed soils was lower than that of the control in both silicate- and carbonate- treated soils. The pH and ZPC values showed opposite trends in response to liming. Parks (1967) reported that in general anionic impurities shifted the ZPC to more acid values and cationic impurities to more basic values. Hingston et. al., (1972) corroborated a part of Park's statement by showing that the presence of silicate in goethite system shifted its ZPC to more acid values. Thus, the specific adsorption of silicate and carbonate could probably have decreased the ZPC values in the limed soils. However, other reports in the literature indicated that the ZPC values obtained from measurements in CaCl_2

Table 2-1

Moisture Content, pH, Delta pH (Δ pH), and Zero Point of Charge (ZPC) of
Soils Included in the Liming Experiment.

Soil series	Treatment*	Moisture (θ_g) %	pH (Soil paste)	Δ pH [†]	ZPC	
					Pot. Titr.	Ion Adsorp.
Hilo	Control	77.0	4.94	-0.38	4.91	4.31
	CaSiO ₃ (40)	74.5	5.60	-0.50	--	3.65
	CaCO ₃ (40)	77.0	6.65	-0.44	--	3.67
Akaka	Control	175.0	4.01	+0.25	4.48	4.15
	CaSiO ₃ (20)	179.4	4.36	-0.15	--	N.D.
	CaSiO ₃ (40)	175.2	4.60	-0.23	--	3.50
	CaCO ₃ (40)	173.0	5.77	-0.25	--	3.75
Halii	Control	8.9	4.06	+0.22	4.51	4.28
	CaSiO ₃ (20)	9.0	4.88	-0.29	--	N.D.
	CaSiO ₃ (40)	9.0	5.36	-0.37	--	3.40
	CaCO ₃ (40)	8.9	6.85	-0.11	--	3.35

*Numbers within the parentheses indicate the amount in milliequivalents of Ca²⁺ added per 100g of oven dry soil.

†The pH was measured by immersing the glass electrode in the sediment and calomel electrode in the clear supernatant solution (1:5 soil to solution ratio).

N.D. = Not determined.

solutions were always lower than those obtained from NaCl or NaNO₃ solutions (Breeuwsma and Lyklema, 1971; van Raij and Peech, 1972; and Keng, 1974). The above works also showed that the adsorption of sulfate from Na₂SO₄ or MgSO₄ shifted the ZPC to higher pH values. Thus, the reports on the effect of specifically adsorbed ions on the ZPC are highly contradictory.

Ammonium and Nitrate Adsorption: Liming in general increased NH₄⁺ adsorption (Fig. 2-1) and decreased NO₃⁻ adsorption (Fig. 2-2). The magnitude of these changes were higher in CaCO₃-treated than in CaSiO₃-treated soils. This is because of the dependence of surface charge on soil pH which was higher in the former than in the latter (Table 2-1). CaSiO₃ is reported to have about 80% of the liming potential of CaCO₃ (Silva, 1971); thus CaCO₃ was more effective in raising soil pH than CaSiO₃ in the limed soils.

When the pH increased beyond 5.5 because of liming, the soils started to repel added NO₃⁻ (Fig. 2-3). The negative ΔpH values in the limed soils (Table 2-1) indicate that the surface charge became more negative with liming. This is the likely reason for the repulsion of NO₃⁻ by the limed soils. Although solid phase CaCO₃ has been shown to develop a positively-charged surface under certain

Figure 2-1. Effect of two liming materials on ammonium adsorption isotherms in two Hydrandepts and a Gibbsiumox.

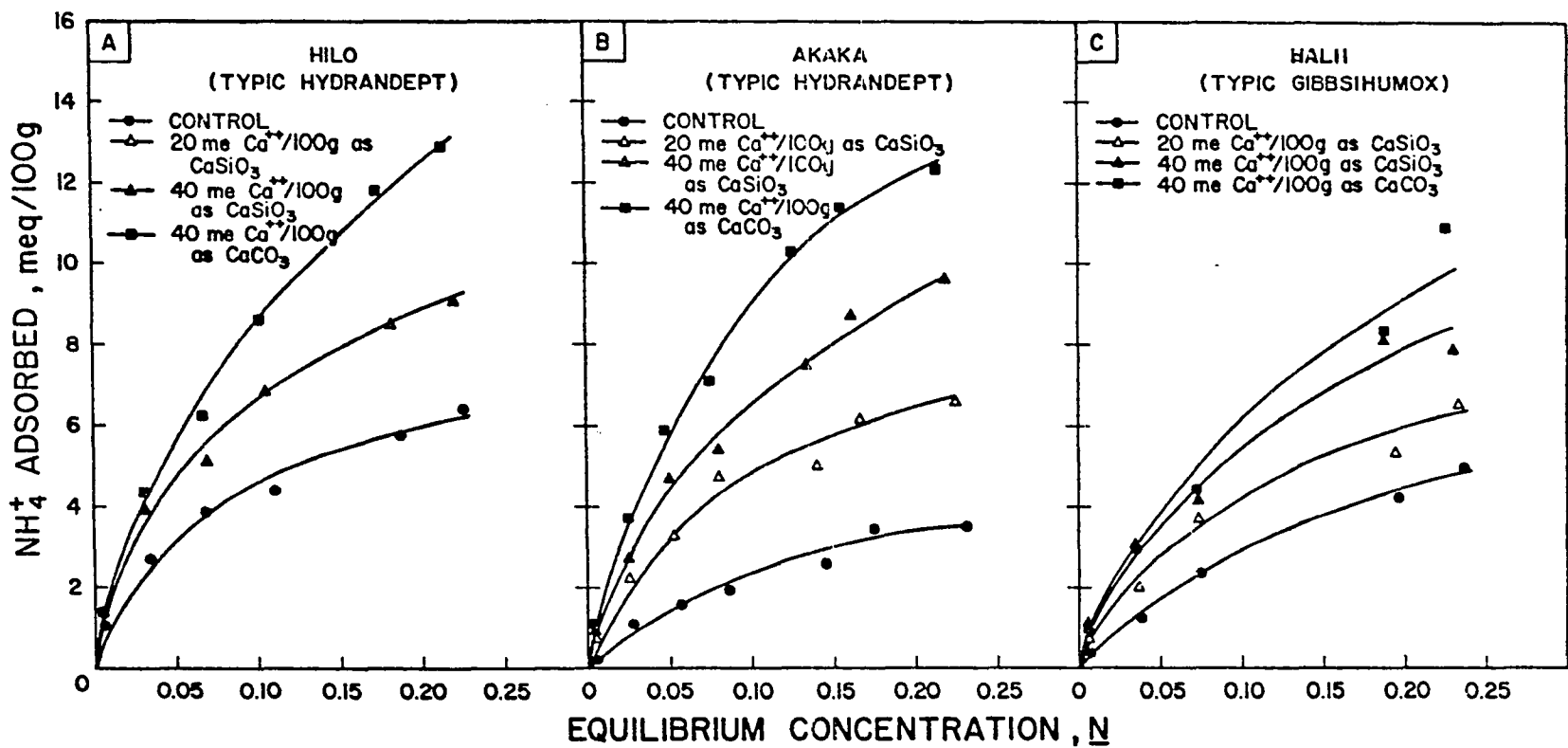


Figure 2-2. Nitrate adsorption isotherm
as affected by liming of the
Hydrandepts and Gibbsihumox.

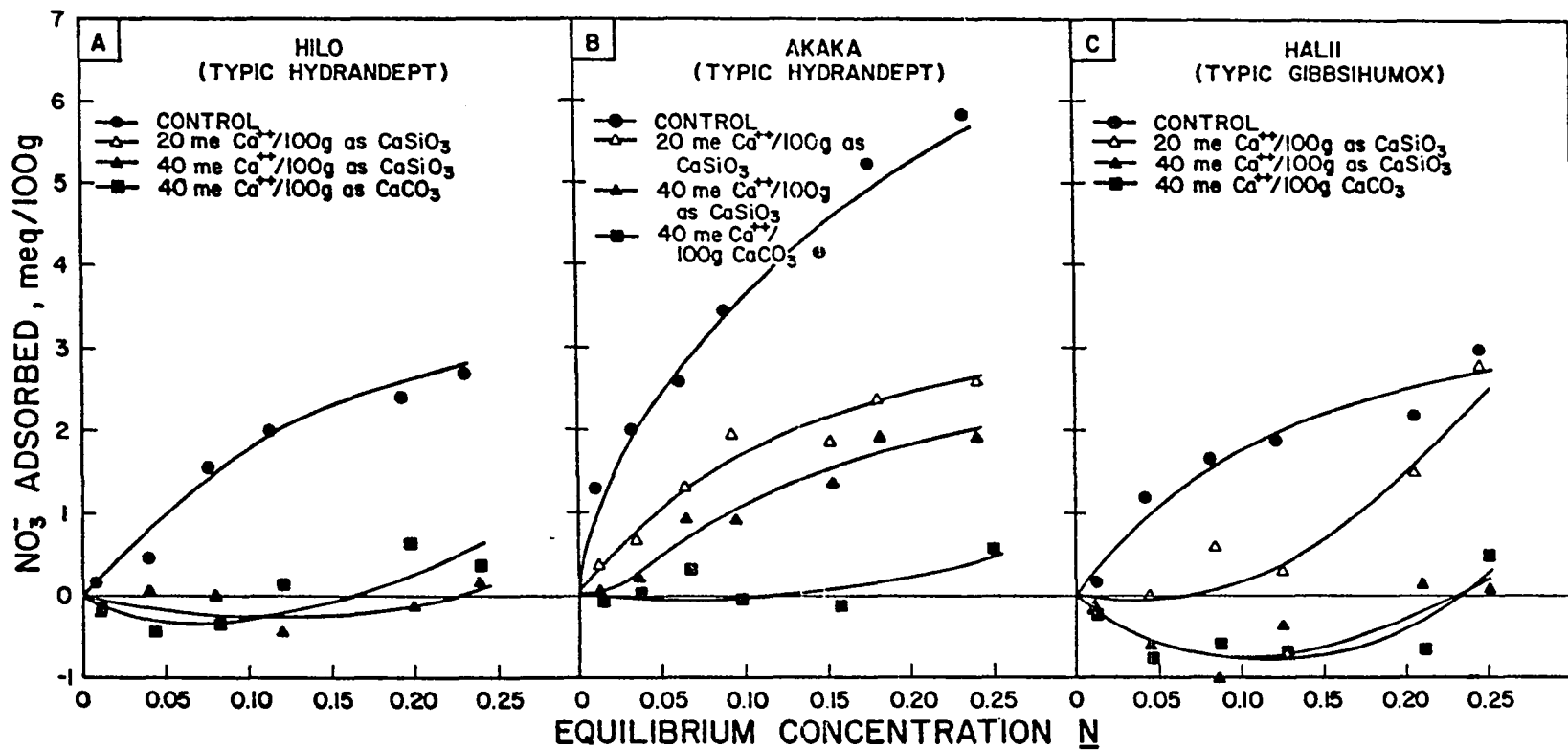
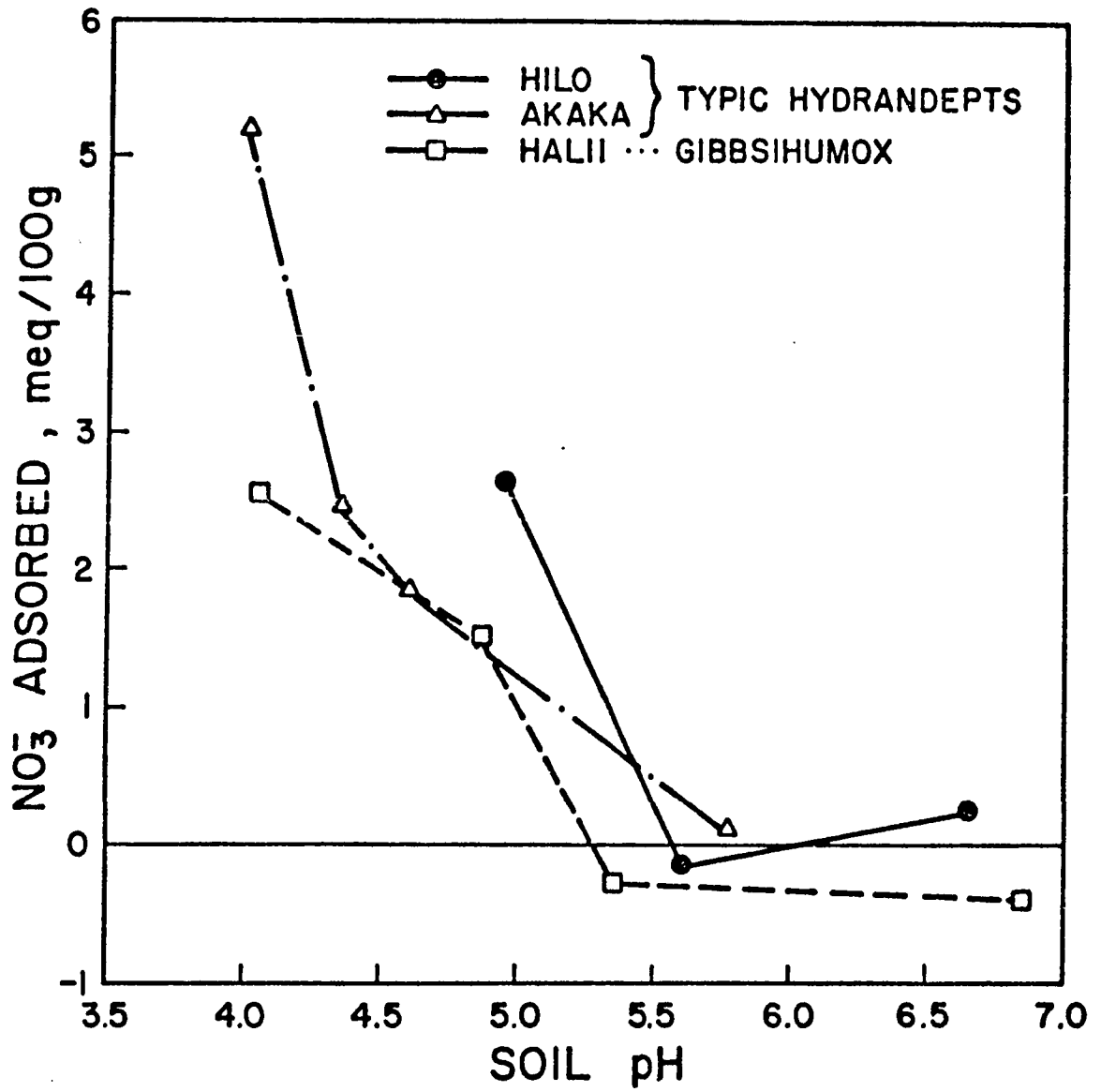


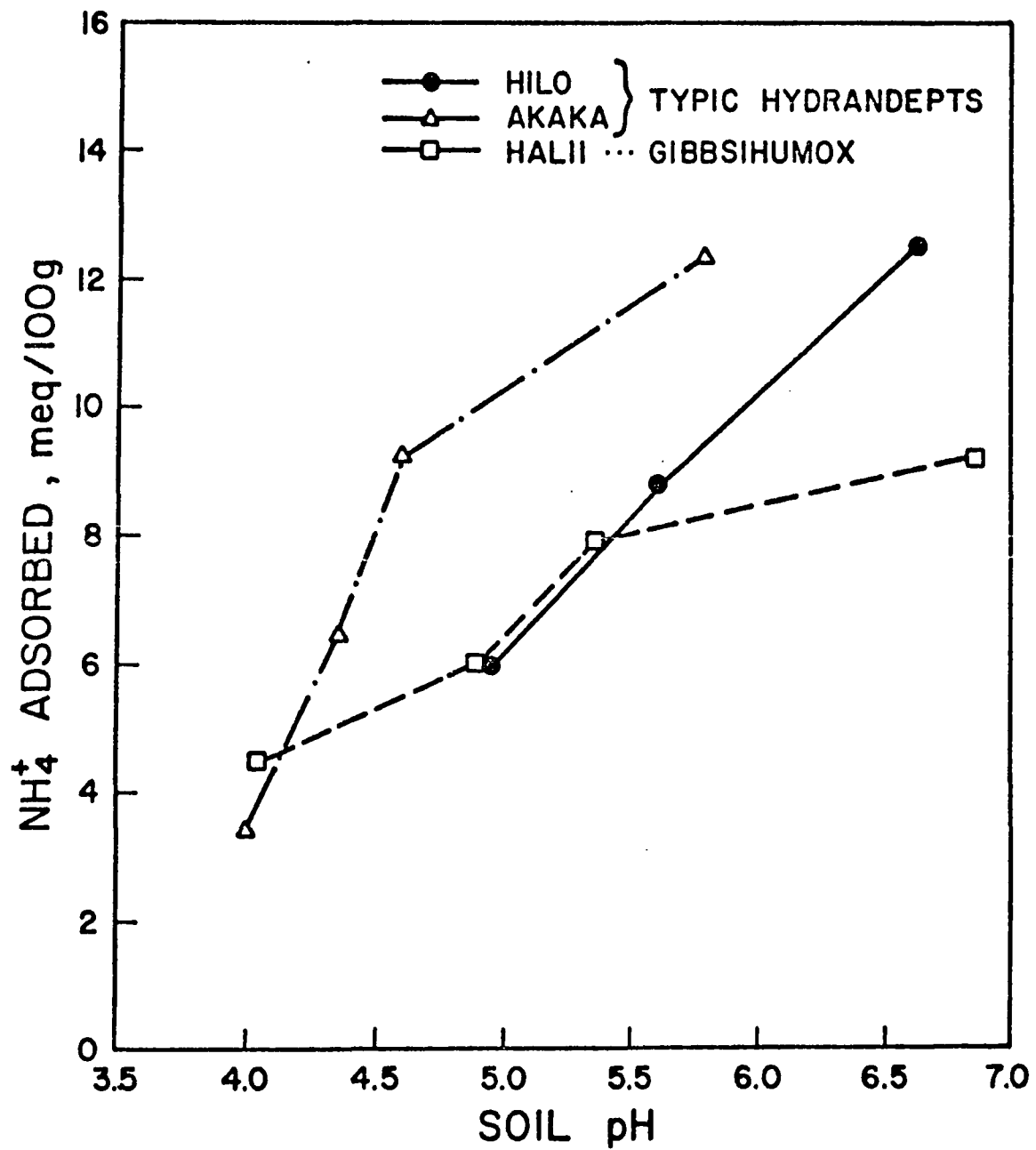
Figure 2-3. Soil pH vs. amount of nitrate adsorbed at 0.2 N equilibrium concentration.



conditions (Somasundaran and Agar, 1967) and to adsorb NO_3^- (Jurinak and Griffin, 1972), addition of CaCO_3 to soils as a liming material did not result in any increased NO_3^- adsorption. This is consistent with the latter authors who also pointed out that naturally occurring carbonates in calcareous soils did not increase NO_3^- retention in NO_3^- elution experiments with packed columns.

For the same pH in limed soils, the Hydrandepts showed a higher affinity for NH_4^+ than the Gibbsihumox (Fig. 2-4). This may be due to the higher surface area available for adsorption in the Hydrandepts. The rate of decrease of NO_3^- adsorption due to liming was almost the same in all the three soils examined (Fig. 2-3). Thus, liming of oxidic, acid soils results in decreased NO_3^- retention (or NO_3^- repulsion) and increased NH_4^+ adsorption.

Figure 2-4. Ammonium adsorption at 0.2 N equilibrium concentration vs. pH of limed soils.



SUMMARY AND CONCLUSIONS

The pH increased and the ZPC decreased due to liming of acid soils. The surface of the colloids in the limed soils became less positive or more negative, and this was reflected in the (increased) NH_4^+ and (decreased) NO_3^- adsorption by the limed soils. Raising of soil pH beyond 5.5 with liming produced NO_3^- repulsion in these soils. Although pure solid phase CaCO_3 has been shown by others to develop positive surface charge and to adsorb NO_3^- , CaCO_3 applied to these soils as a liming material did not increase NO_3^- adsorption.

CHAPTER THREE
DENITRIFICATION IN HAWAIIAN SOILS

ABSTRACT

Anaerobic denitrification was characterized in selected Hawaiian soils, using a specially designed incubation apparatus. N_2O gas was the major denitrification product in the Andepts and Vertisol. In the Oxisol and Ultisol and in near neutral soils with ample energy materials, N_2 gas was the prime denitrification product. The implication of this gas evolution pattern (in different soils) in evaluating natural denitrification in field profiles is discussed.

Denitrification loss did not appear to be important in the Molokai and unlimed Paaloa soils because of the lack of energy materials in the former and extremely acidic reaction in the latter. Denitrification capacity increased tremendously once the acidity was neutralized by liming in the Paaloa soil. The Andepts (Hilo, Akaka, and Waimea) and Vertisol (Lualualei) showed a significant tendency to denitrify applied nitrate under extreme conditions of low O_2 potential in soils.

If soil pH is not limiting, the denitrification potential of soils is more closely related to energy-rich, water-soluble organic C rather than total organic

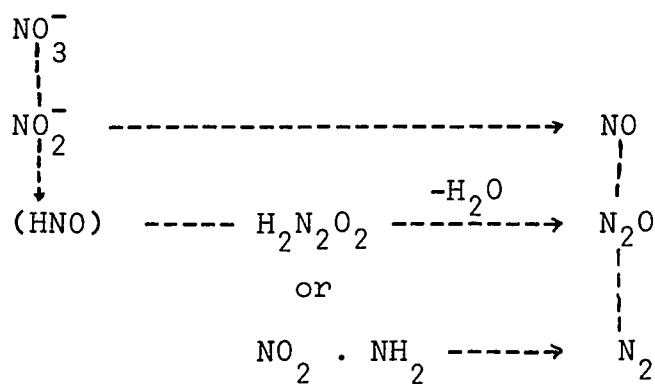
C content in soils. Addition of an easily available energy source, or treatment of soils with organic matter, resulted in increased denitrification in the Molokai surface soil and Hilo subsoil.

Initial nitrate level did not influence the denitrification capacity or pattern of these soils. Anaerobic reduction of NO_3^- to NH_4^+ was insignificant as compared to the denitrification loss.

DENITRIFICATION IN HAWAIIAN SOILS

INTRODUCTION

Use of ^{15}N tagged N fertilizers in research has yielded valuable gains to our knowledge of N losses from soils. Biological denitrification is considered to be one of the important processes accounting for gaseous N loss from soils (Wagner and Smith, 1958; Soulides and Clark, 1958). While reviewing the literature, Nason and Takahashi (1958) presented a diagrammatic biochemical pathway of denitrification as follows:



The mechanism of reduction of nitrite, the roles of N_2O and hyponitrite as intermediates, and the place of nitric oxide in the above denitrification scheme are as yet unresolved.

Using soils as a medium, Cady and Bartholomew (1960) and Cooper and Smith (1963) found experimental evidence for the pathway of denitrification in soils as:

$\text{NO}_3^- \text{ ----} \rightarrow \text{NO}_2^- \text{ ----} \rightarrow \text{N}_2\text{O} \text{ ----} \rightarrow \text{N}_2$. Other denitrification experiments in soils (Wijler and Delwiche, 1954; Nommik, 1956; and Cady, 1960) have tended to show that N_2O first accumulates, and that this can under certain conditions be further reduced to N_2 gas. The first two authors believed that above pH 7.0 N_2O could be readily reduced to N_2 but below pH 6.0 its reduction is strongly inhibited.

Major factors influencing denitrification in soils are water content, soil pH, soluble organic matter content, O_2 tension, aeration, temperature, and presence of denitrifying organisms (Nommik, 1956, Bremner and Shaw, 1958 a and b, McGarity, 1961, and Myers and McGarity, 1971). Cady (1960) observed that the higher the moisture level, the greater the rate of formation of N_2 gas. This could be due to the high solubility of N_2O gas in water which might be further reduced by denitrifying organisms. Cady and Bartholomew (1961) showed that only under conditions of high levels of carbonaceous materials, and available NO_3^- source, and O_2 level less than 7% by volume, would appreciable NO_3^- be reduced to gaseous forms. According to Nommik (1956) the optimum soil pH for denitrification is between 7 and 8, and denitrification is greatly reduced at pH 5.0

and below. Schwarzbeck et. al., (1961) pointed out that an alkaline pH retards oxidation of NO_2^- to NO_3^- , whereas an acid pH favors it. Initial level of NO_3^- does not affect denitrification rate or pattern (McGarity, 1961, Bremner and Shaw, 1958). The last two authors also found that between 25 and 60°C, the rate of denitrification was extremely rapid with little variation within this temperature range. Thus one can expect active denitrification in soils under tropical conditions if other factors of denitrification are favorable.

When anaerobic conditions favorable for denitrification exist in soils, there is also a possibility for the biological reduction of NO_3^- to NH_4^+ to take place. Woldendorp (1965) examined this phase of NO_3^- reduction using ^{15}N -labelled NO_3^- and found that less than 1% of $\text{NH}_4\text{-N}$ formed appeared to come from NO_3^- reduction, even though considerable amounts of $\text{NH}_4\text{-N}$ were formed from deamination of organic matter by denitrifying organisms.

High organic matter and water contents of Hydrandpeats coupled with a humid tropical climate in Hawaii leads to a speculation of high gaseous loss of N through denitrification in these soils. Working with ^{15}N -tagged fertilizers under field conditions, Takahashi (1968)

indicated that N loss by volatilization can be large and rapid when O_2 tension is low in soils which are wet for a long period. Any unaccounted for loss of N in N balance studies with lysimeters was attributed to volatilization of N in one form or another (Ayres and Hagihara, 1960). Thus, all previous studies on gaseous denitrification loss in Hawaiian soils are indirect and speculative. Hence the necessity to characterize denitrification in these soils.

This study aims to characterize denitrification in selected Hawaiian soils and to evaluate the relative importance of anaerobic NO_3^- reduction to NH_4^+ as compared to denitrification.

MATERIALS AND METHODS

Soils: Six soils differing widely in origin, chemical, biological, and mineralogical properties were selected for this investigation. The descriptions and pertinent properties of these soils are given in Table 3-1. The field moist surface and subsoils of Hilo and Akaka soils were passed through a 6 mm sieve and stored in double polyethylene bags at 2°C until they were used for the various experiments. All other soils were air-dried, ground to pass through a 2 mm sieve, and stored in double polyethylene bags at room temperature.

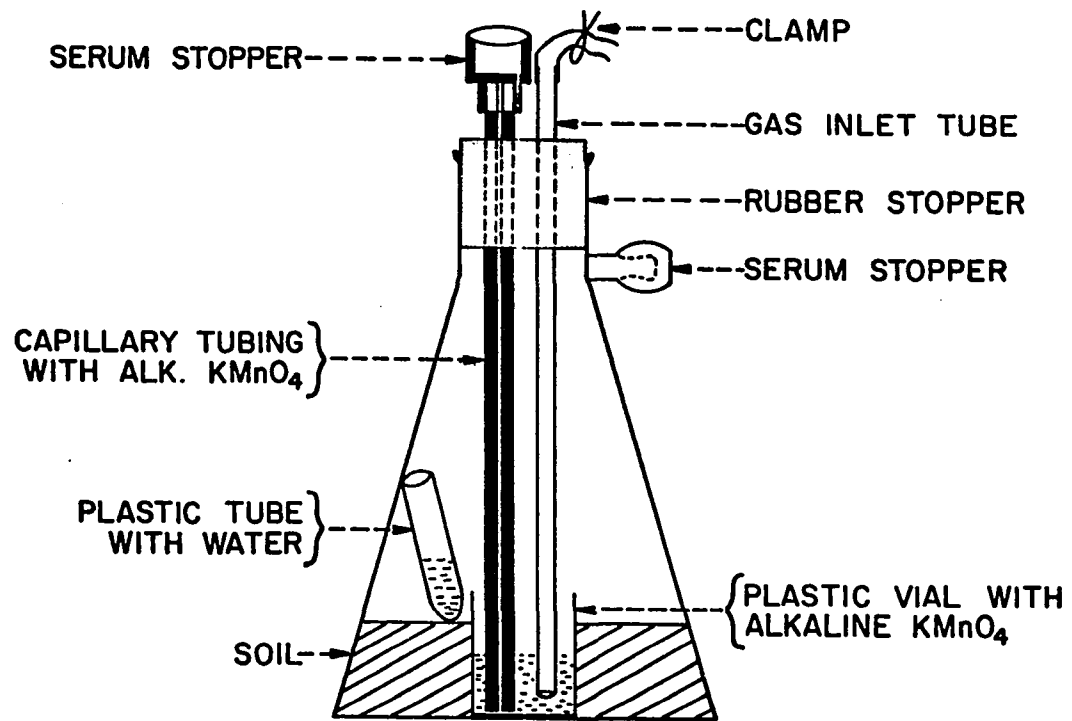
Description of Incubation Apparatus: All experiments in this investigation were conducted in a special incubation apparatus designed for this purpose. It essentially consists of a 1,000 ml suction flask fitted with a plastic vial (3 cm diameter and 5 cm height) glued to the center of the flask bottom (Fig. 3-1). This resembles a macroversion of a respiration flask. The flask is closed with a two-holed rubber stopper. A capillary glass tubing (1 mm I.D. and 40 cm long) is tightly inserted through one hole so that one end almost touches the bottom of the plastic vial inside the flask (This is the open end of the capillary). The other end of the capillary is closed with a 11 x 17 mm

Table 3-1
Some Properties of Soils Included in Denitrification Experiments

Soils	Great Group	Parent Material	Important* Secondary Minerals	Elevation m	Annual rainfall cm	Annual temperature °C	Permea- bility	Drain- age
Hilo	Typic Hydrandept	Volcanic ash (basaltic)	A, H.O	120	375	22	Rapid	Well
Akaka #1 (Akaka Falls)	"	"	"	820	560	15	"	Moderately well
Akaka #2 (Kaiwiki Forest)	"	"	"	350	435	21	"	Well
Waimea	Typic Eutrandept	"	A, K	1200	85	16	Moderately rapid	"
Molokai	Typic Torrox	Olivine basalt	K, Gi	220	50	23	Moderate	"
Paaloa	Tropohumult	"	Go, Gi, K, Mi,	400	200	21	"	"
Lualualei	Chromustert	Basaltic alluvium	Mo	20	60	24	Slow	"

*A = Amorphous aluminosilicates; H.O. = Hydrated oxides of Fe, Al, and Ti; K = Kaolinite, Gi = Gibbsite
Go = Goethite, M = Mica, Mo = Montmorillonite.

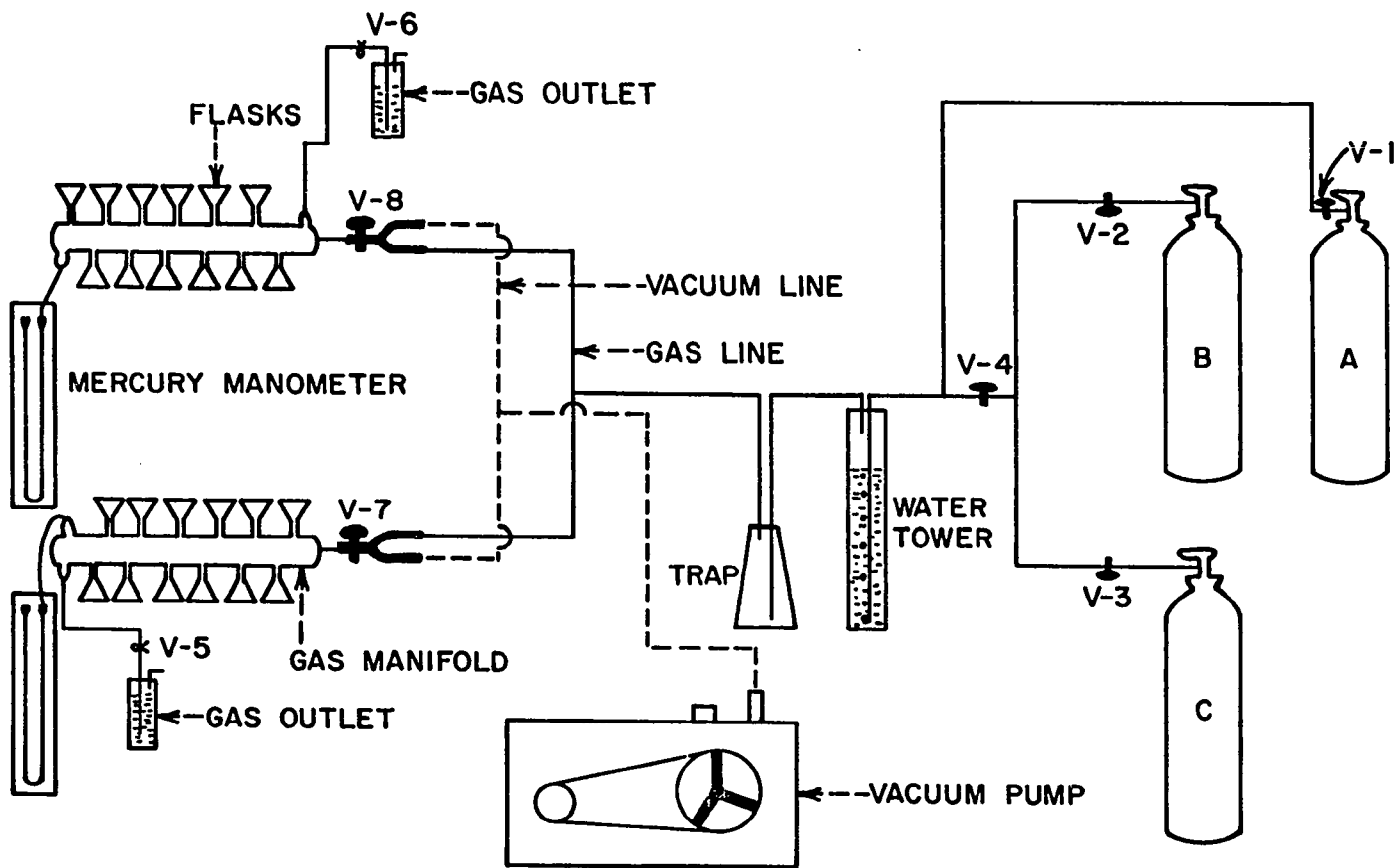
Figure 3-1. Incubation apparatus used in soil denitrification study.



serum rubber stopper by tightly fitting the capillary end into the smaller depression of the serum stopper. Through the other hole passes a glass tube (5 mm inner diameter and 30 cm long), the lower end of which lies about 0.5 cm above the bottom of the plastic vial. To the top end of the glass tube is attached a rubber tubing. The side arm of the suction flask is closed with a serum rubber stopper. Twelve such flasks are connected to a glass manifold by means of rubber tubings as shown in Fig. 3-2. The manifold in turn is connected to a gas exchange system consisting of a vacuum pump, manometer, compressed gas tank, and a water tower to saturate the incoming gas with moisture (Fig. 3-2). The flask can be detached at will from the manifold by removing the rubber stopper.

General Incubation Procedure: When this apparatus was used for soil denitrification study, the procedure was as follows: A weighed sample of soil was mixed with required amounts of water, nitrogen solution, amendments, etc., and transferred to the flask, taking care not to spill any soil into the central plastic vial (This can be done by closing the plastic vial with a rubber stopper attached to a long rod while pouring the soil inside the flask). A 50 ml centrifuge (plastic)

Figure 3-2. Schematic diagram of the experimental set up used in soil denitrification study.



- A = CYLINDER 100% HELIUM
- B = CYLINDER 80% HELIUM + 20% OXYGEN
- C = CYLINDER 100% OXYGEN
- V-1 TO V-6 = TWO WAY VALVES
- V-7 & V-8 = THREE WAY VALVES

tube containing 10 ml of water was placed over the soil to keep the inside atmosphere always saturated with moisture. The flask was then closed air tight with the rubber stopper and connected to the gas manifold system. The air inside the flask was replaced by He (anaerobic incubation) or He-O₂ mixture (aerobic incubation), by alternately evacuating the flasks and filling them with the required gas. This cycle of evacuation and filling a known gas was repeated until N₂ concentration in the system was less than 2,000 ppm by a check on the gas chromatograph. The final pressure inside the flask was adjusted to and maintained throughout the experimental period at a pressure of 2.5 cm Hg above ambient pressure. This was done by periodically opening screw clamps between manifold and each flask to replace the gas removed for gas chromatographic analysis. (In the case of aerobic incubation, periodical opening of clamps allows the O₂ used by chemical or microbiological processes to be replaced, thus maintaining the pressure and O₂ concentration inside the flask). The positive pressure prevents possible contamination of atmospheric N₂ during gas sampling. By means of a syringe fitted with a 20-gauge needle, 5 ml of alkaline KMnO₄ (0.2 N KMnO₄ in 2 N KOH) solution were injected through the capillary tubing

into the central plastic vial to absorb any evolved NO, NO₂, and CO₂ gases. The capillary tubing was then always kept filled with KMnO₄ solution; positive pressure inside the flask helped to maintain a certain height of permanganate solution column inside the capillary. The other glass tube through which the gas comes in also dipped into the KMnO₄ solution in the central vial. This acts as a one-way valve in that it lets in gas only when the positive pressure inside the flask falls below 2.5 cm Hg. The temperature of incubation was maintained at 26 ± 1°C.

Analytical Methods

Gas Analysis: Periodically a 1 ml sample of gas was removed from the flask by means of a gas-tight syringe fitted with a 27-gauge needle and subjected to gas chromatograph (G.C.) analysis. The basic instrument employed for gas analysis was the Beckman G.C.2A gas chromatograph fitted with two chromatographic columns arranged in parallel and connected to a Honeywell 6½" strip chart recorder. A 240-cm stainless steel column (0.32 cm O.D.) packed with 60/80 mesh molecular sieve 5a was used to separate N₂ from other gases, and a 360-cm column packed with 50/80 mesh Porapak Q was used to separate N₂O, H₂, CH₄, and CO₂ gases. Before each set

of analysis, the molecular sieve column was activated by heating at 220°C for 24 hours. Helium was used as a carrier gas under the following operating conditions:

Carrier gas pressure	35 psi
Detector bridge current	250 ma
Column temperature	Ambient (26 ± 1°C)
Carrier gas flow	33 ml/min.

The calibration curves used to calculate the amounts of N₂, N₂O, CH₄, H₂, etc., gases were constructed from the recorder responses obtained when known amounts of these gases were injected into the gas chromatograph. With each gas, peak height was a linear function of the amount of gas injected. Standard gas was injected between every six analyses of unknown gas samples to check the performance of the column and instrument. To calculate the volume of gas inside the incubation flasks sampled, the total volume of the flasks was determined and corrections were applied for the volume occupied by soil, various amendments, alkaline KMnO₄ solution and water. A soil particle density (specific gravity) of 2.65 g/cm³ was assumed in calculation of the volume occupied by soil.

Nitrogen in the forms of gaseous NO and NO₂ was determined by absorption of these gases in alkaline

KMnO_4 solution. Periodically, a certain portion of the alkaline absorbent was removed for analysis and an equivalent volume of fresh alkaline KMnO_4 was injected into the central vial. Great care was exercised to avoid pushing air bubbles inside the flask while removing used-up KMnO_4 from or injecting fresh KMnO_4 into the vial.

The procedure of Nelson and Bremner (1970) was slightly modified as follows to determine $(\text{NO} + \text{NO}_2)\text{-N}$ absorbed in alkaline KMnO_4 : Five ml of the KMnO_4 - KOH solution was placed into a 100-ml distillation flask. Six ml of acidified FeSO_4 solution ($1\text{N } \text{FeSO}_4$; $2\text{N } \text{H}_2\text{SO}_4$) was added and swirled gently until the color due to permanganate and effervescence due to CO_2 evolution disappeared. The flask was heated over a boiling water bath for 10 minutes to remove the last traces of CO_2 from the solution and cooled. Then 2 ml of $10\text{ M } \text{NaOH}$ and 0.2 g of Devarda's alloy were added and steam distilled. The distillate was collected in a 125 ml conical flask containing 10 ml of boric acid-indicator (bromcresol green, methyl red mixed indicator) solution. When the volume of distillate reached the 35 ml mark on the receiving flask, distillation was stopped and the $\text{NH}_4\text{-N}$ in the distillate was titrated

against 0.005 N H_2SO_4 from a microburet (1 ml of 0.005 N H_2SO_4 = 70 mg of $\text{NH}_4\text{-N}$ = 70 mg of $(\text{NO}+\text{NO}_2)\text{-N}$).

NH_4^+ , NO_3^- , and NO_2^- in Soil: Exchangeable NH_4^+ , NO_3^- , and NO_2^- in the soil were extracted with 1 N KCl solution. The soil to solution ratio was 1:5 and the shaking time was one hour. Microbial activity during extraction and subsequent determination of various N forms was arrested by adding a few drops of toluene to the soil suspension in KCl solution. Nitrate in the extract was determined by the modified Griess-Ilosvay colorimetric method and NH_4^+ and NO_3^- by the steam distillation method (Bremner, 1965).

Total Soil N: This was determined by the modified Olsen method (1929) which is directly applicable to moist or water-logged soils and which permits quantitative recovery of both NO_3^- and NO_2^- . Here the sample was treated before Kjeldahl digestion with KMnO_4 and concentrated H_2SO_4 to oxidize NO_2^- to NO_3^- , and then with reduced iron to reduce NO_3^- to NH_4^+ , the reduction being effected by the nascent H_2 formed by reaction of iron with H_2SO_4 .

Total Organic Carbon: This was determined by the wet digestion method.

Water-Soluble Organic Carbon: The colorimetric procedure of Perrier and Kellog (1960) was used to determine the water-soluble organic carbon in soils. Twenty grams O.D. weight equivalent of a soil were mixed with 100 ml boiling water for 10 min. in waring blender, transferred to a 500 ml Erlenmeyer flask, placed over a boiling water bath, stirred intermittently for 4 hours, and filtered through Whatman No. 5 filter paper. The filtrate was concentrated to about 10 ml at 50°C under partial vacuum. Then 5 ml of 1 N $K_2Cr_2O_7$ solution was added and mixed, followed by the addition of 5 ml of concentrated H_2SO_4 . The mixture was heated over a water bath for 5 minutes, cooled, and diluted to 1 liter with water. One ml of this solution was pipetted out into a 100 ml volumetric flask; 2 ml of 10 N H_2SO_4 and 1 ml of saturated S-diphenyl carbazide solution in 95% ethanol were added and the solution brought to the mark with distilled water. This solution was mixed well and the optical density of the pink color was determined at 540 mu within 10 minutes after the addition of the S-diphenyl carbazide reagent. A blank was run with each series of experiments.

Different volumes (0.0, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0, ml) of 1% Sucrose solution were used to construct the standard graph (Klett reading vs. water-soluble organic carbon content): unknown readings were referred to this standard graph to calculate the amount of water-soluble organic carbon.

Gravimetric Water Content of Soil (θ): This was determined by drying the soil at 110°C for 36 to 48 hours.

Soil pH: Soil pH was determined in saturated soil paste.

Anaerobic Denitrification Experiments

Soil Denitrification Capacity and Pattern of Gas Production: This experiment was designed to find out the natural denitrification capacity of selected Hawaiian soils under a He atmosphere and also to examine the production pattern of gaseous denitrification products in those soils. One hundred grams O.D. weight equivalent of each soil were mixed with 3 ml of KNO_3 solution containing 30 mg of $\text{NO}_3\text{-N}$. Except for the naturally moist Hilo, Akaka No. 1, and Waimea soils, water was added to other soils to raise the moisture to 1/3 bar water content or 60% saturation capacity. The incubation procedure was the same as that described in the general

incubation procedure. Gas samples and alkaline absorbents were analyzed for 25 days at 5 day intervals.

Anaerobic Nitrate Reduction to Ammonium: This experiment was conducted to study the inorganic nitrogen changes which occur during anaerobic incubation of soils with and without added NO_3^- . Specifically, it was desired to compare the NH_4^+ production of NO_3^- treated soil with that of control. If NO_3^- respiration resulting in NH_4^+ formation occurs to any appreciable extent in the tested soils, the NH_4^+ contents for the nitrate series would be expected to be higher than those for the corresponding control treatments. KNO_3 at the rate of 30 mg $\text{NO}_3\text{-N}/100\text{g}$ of O.D soil was applied to the nitrate series while the control series did not receive any NO_3^- application. Twenty grams O.D. weight equivalent of soil were incubated in a He atmosphere for 25 days. Sufficient number of flasks were incubated to provide for periodic soil sampling for inorganic-N analysis. The interval of sampling was 5 days. At each sampling two NO_3^- treated and two control samples were used for analysis.

Factors Affecting Anaerobic Denitrification

Surface vs. Subsoil: This experiment was planned to find out the extent of denitrification in surface and subsoils of Hilo soil. Thirty mg of $\text{NO}_3\text{-N}$ in the

form of KNO_3 were mixed with 100g O.D. weight equivalent of soil and incubated as described in the general incubation procedure. Gas samples and alkaline absorbents were analyzed at periodic intervals (0, 2, 5, 10, 15, 20, and 25 days).

Effect of Initial Nitrate Content: Two levels of NO_3^- (10 and 30 mg $\text{NO}_3^-/\text{N}/100\text{g}$) were established by adding the calculated amounts of KNO_3 to the Hilo, Waimea, and Lualualei soils and incubated for 25 days as in other experiments.

Effect of Soil Moisture Level: Two soils, Molokai and Akaka, were used in this experiment. In the Molokai soil, two levels of moisture ($\theta_g = 33.4$ and 42.1%) corresponding to 60 and 80% saturation capacity were established by adding calculated amounts of water to the same soil. In the Akaka, field moist soils of the same Akaka series were collected from two different locations constituting two moisture levels (112.3 and 172.3%). The rate of NO_3^- addition was 30 mg NO_3^-/N per 100g of O.D. soil.

Effect of Liming on Denitrification: Calcium carbonate was used as a liming material at the rate of 40 meq $\text{Ca}^{++}/100\text{g}$ of O.D. soil. Added lime was allowed to react with the soil for two months at field moisture

for the Akaka and Hilo soils, and at 60% saturation capacity for the Paaloa soil before denitrification study was carried out.

Effect of Available Energy Materials on Denitrification: This experiment was designed to test the effect of added energy materials on denitrification. Sugarcane trash was applied to the Molokai soil at the rate of 112 metric tons/hectare and incubated for one year at 60% saturation capacity. The incubated soil was then air-dried, ground to pass a 2 mm sieve, and stored in a polyethylene bag. In the case of sucrose treatment, the Molokai and Hilo soils were treated with 1 and 2% (O.D. soil basis) sucrose, respectively.

RESULTS AND DISCUSSION

Denitrification Capacity and Pattern of Gas

Production: In Fig. 3-3 is depicted the production pattern of various gaseous denitrification products, viz, N_2 , N_2O and $(NO+NO_2)$ and total gaseous N loss with time. The gaseous denitrification loss was the largest in the Waimea soil which lost a little more than 70% of the initial nitrate in the form of various N gases in 25 days. The Hilo, Akaka No. 1, and Lualualei soils followed suit, each losing in the gaseous form about 40 to 50% of the available nitrate. Only 10% of the initial nitrate was reduced to gaseous N products in the Molokai and Paaloa soils. Except for these two soils, the rest of the soils seemed to have N_2O as the major denitrification product. In the Molokai soil N_2 gas seemed to be the principal denitrification product, while in the Paaloa $(NO+NO_2)$ gases were the most important.

The near neutral pH and high content of water-soluble organic carbon appeared to be the main factors responsible for the high denitrification potential in the Waimea soil (Table 3-2). In spite of the high total organic carbon content in the Hilo and Akaka No. 1 soils, the amount of water soluble-organic carbon was low in

Figure 3-3. Denitrification pattern and capacity in selected soils.

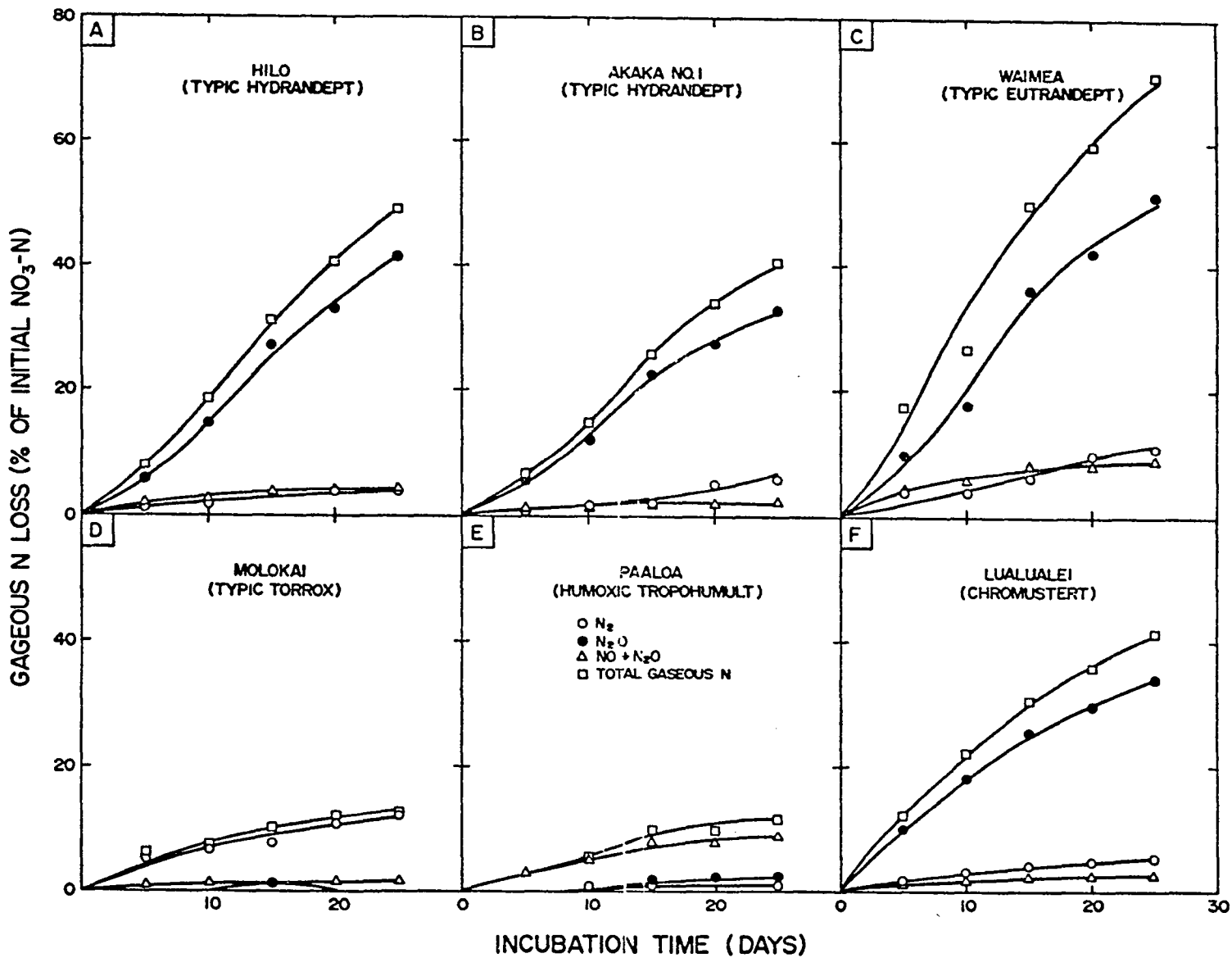


Table 3-2
 Characteristics of Soils Included in the Experiment on Denitrification Capacity
 and Pattern of Gas Production

Soil series	Depth cm	Incubation* moisture (O.D. Wt. % basis)	pH Saturated paste	Organic C (%)		Total-N %	C/N	Total gaseous N loss in 25 days, mg N/100g
				Water- Soluble	Total			
Hilo	0-13	70.6	4.42	0.028	8.01	0.553	14.5	16.78
Akaka #1	0-13	112.3	5.01	0.029	9.44	0.608	15.5	13.98
Waimea	0-15	53.7	6.54	0.063	6.63	0.586	11.3	27.61
Molokai	0-30	33.4	6.76	0.012	1.66	0.146	11.4	3.95
Paaloa	0-5	32.5	3.80	0.065	4.82	0.337	14.3	4.53
Lualualei	0-10	34.2	6.82	0.018	0.55	0.077	7.1	13.17

*The first three soils were incubated at field moisture without adding any additional water; the latter three were incubated at 1/3 bar moisture content or at 60% saturation capacity.

these two soils as compared to the Waimea soil. Thus, it can be concluded that the organic matter in the two Hydrandepts is relatively stabilized and is a poor source of available energy for microbial activity. The low denitrification capacity of the Paaloa soil, inspite of its high organic carbon content (total and water-soluble), may be attributed to its extremely acidic pH. Lack of energy-yielding material in the Molokai soil is the main reason for its low denitrification potential. Inspite of the very low total and water soluble organic carbon contents, the Lualualei soil showed a moderately high denitrification capacity. This could be due to the high availability of nutrients plus the favorable pH responsible for high denitrification in this soil.

The magnitude of NO_3^- disappearance was closely related to the total gaseous N loss (Table 3-3), but the decrease in total soil N does not indicate the gaseous N loss during anaerobic denitrification. Thus the change in the content of soil $\text{NO}_3\text{-N}$ will be a better indicator of the extent of denitrification in soils than that of total soil N.

The concentration of N_2O gas in soil air in undisturbed profiles should indicate the extent of denitrification under field conditions in Andepts and

Table 3-3

Nitrate Disappearance, Rate of Gaseous Nitrogen
Loss, and Decrease in Total Nitrogen Content
of Soils During Anaerobic Incubation

Soil	NO ₃ -N disappear- ance	Total gaseous N loss	Decrease in total soil N
	----- mg/100g -----		
Hilo	14.23	16.78	9.0
Akaka #1	12.64	13.98	11.0
Waimea	23.80	27.61	38.0
Molokai	5.87	3.95	3.0
Paaloa	9.96	4.53	22.0
Lualualei	11.18	13.17	8.0

Vertisols. In soils where N_2 gas is the prime denitrification product, measurement of denitrification potential in field soils necessitates the use of ^{15}N tagged fertilizers which will help to identify the source of N_2 gas.

Anaerobic Nitrate Reduction to Ammonium: Ammonium content of anaerobically incubated soils showed some increase with time in both control and NO_3^- treated soils (Table 3-4). The magnitude of ammonium production was about the same in soils with and without added nitrate. Therefore, it can be concluded that the anaerobic reduction of NO_3^- to ammonium was negligible as compared to the loss due to gaseous denitrification. With the use of ^{15}N labeled nitrate, Wijler and Delwiche (1954) and Woldendorp (1965) also found that reduction of added nitrate to ammonia was negligibly small during anaerobic incubation of soils. The high amounts of ammonium produced in the Paalooa and Waimea soils presumably were from deamination of soil organic matter by denitrifying organisms.

Denitrification Capacity of Surface vs. Subsoil:

The surface soil possessed a higher denitrification capacity than the corresponding subsoil in the Hilo soil, even though the moisture content of the subsoil

Table 3-4

Change in $\text{NH}_4\text{-N}$ Content With Time During Anaerobic Incubation
of Soils With and Without Added Nitrate

Soil	Treatment	Soil $\text{NH}_4\text{-N}$					
		Days					
		0	5	10	15	20	25
		mg N/100g					
Hilo	Control	0.20	0.35	0.70	1.60	2.14	2.12
	NO_3^- treated	0.45	1.16	1.45	1.30	2.08	3.36
Akaka #1	Control	0.49	0.91	1.20	1.10	1.63	2.09
	NO_3^- treated	0.63	0.76	1.47	1.60	1.68	2.67
Waimea	Control	0.74	1.65	3.10	--	5.01	5.13
	NO_3^- treated	1.01	2.03	2.42	3.17	5.01	5.28
Molokai	Control	1.00	1.09	1.07	1.12	1.91	2.05
	NO_3^- treated	1.10	1.27	1.39	1.39	1.91	2.05
Paaloa	Control	1.35	1.49	9.53	9.89	10.28	10.18
	NO_3^- treated	1.55	1.74	9.87	10.10	10.28	10.32
Lualualei	Control	0.89	1.73	1.81	2.05	2.31	3.05
	NO_3^- treated	1.38	1.69	1.75	1.40	2.30	2.67

(213%) was about three times that of the surface soil (70.3%) as shown in Fig. 3-4. This is likely due to the higher organic carbon content of the surface soil (8.01%) as compared to that of the subsoil (3.17%). Focht and Joseph (1973) reported that the number of denitrifying bacteria in two different soil profiles decreased logarithmically with depth. Thus, a paucity of denitrifying organisms in the Hilo subsoil could lead one to believe that it is another factor responsible for its very low denitrification capacity. However, this concept does not hold true in the Sucrose-amended Hilo subsoil which showed a very high denitrification capacity (See the later section on "Effect of Available Energy Materials on Denitrification"). This clearly brings out the fact that subsoils in Hydrandepts lack adequate energy sources to support vigorous growth and activity of denitrifying organisms.

Effect of Initial Nitrate Content: The level of initial nitrate did not seem to influence either the rate and capacity or pattern of denitrification products (Fig. 3-5). As long as there was an adequate NO_3^- supply in the soil, N_2O gas formed the principal denitrification product in both high and low NO_3^-

Figure 3-4. Denitrification capacity of surface soil compared with that of subsoil in the Hilo silty clay loam.

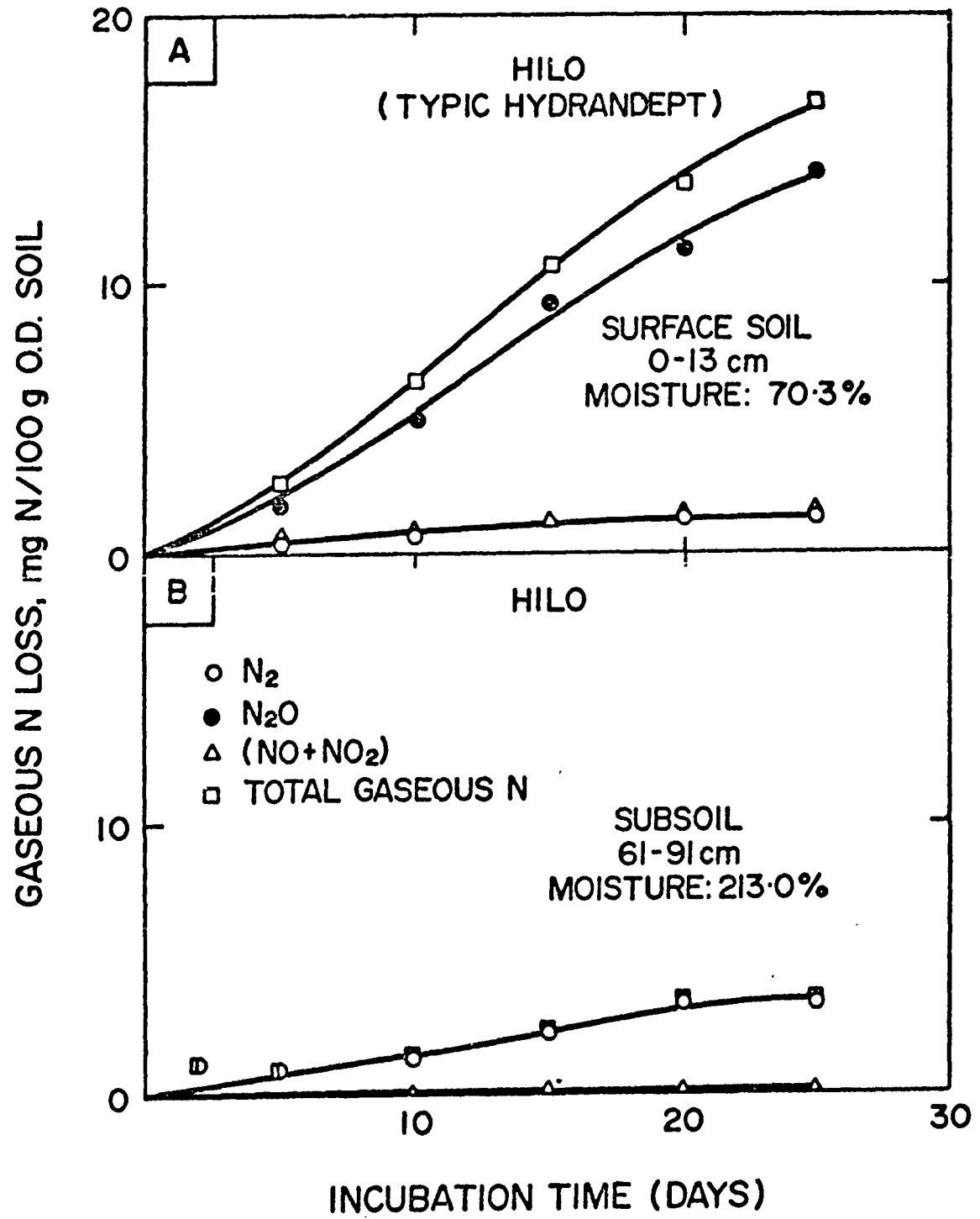
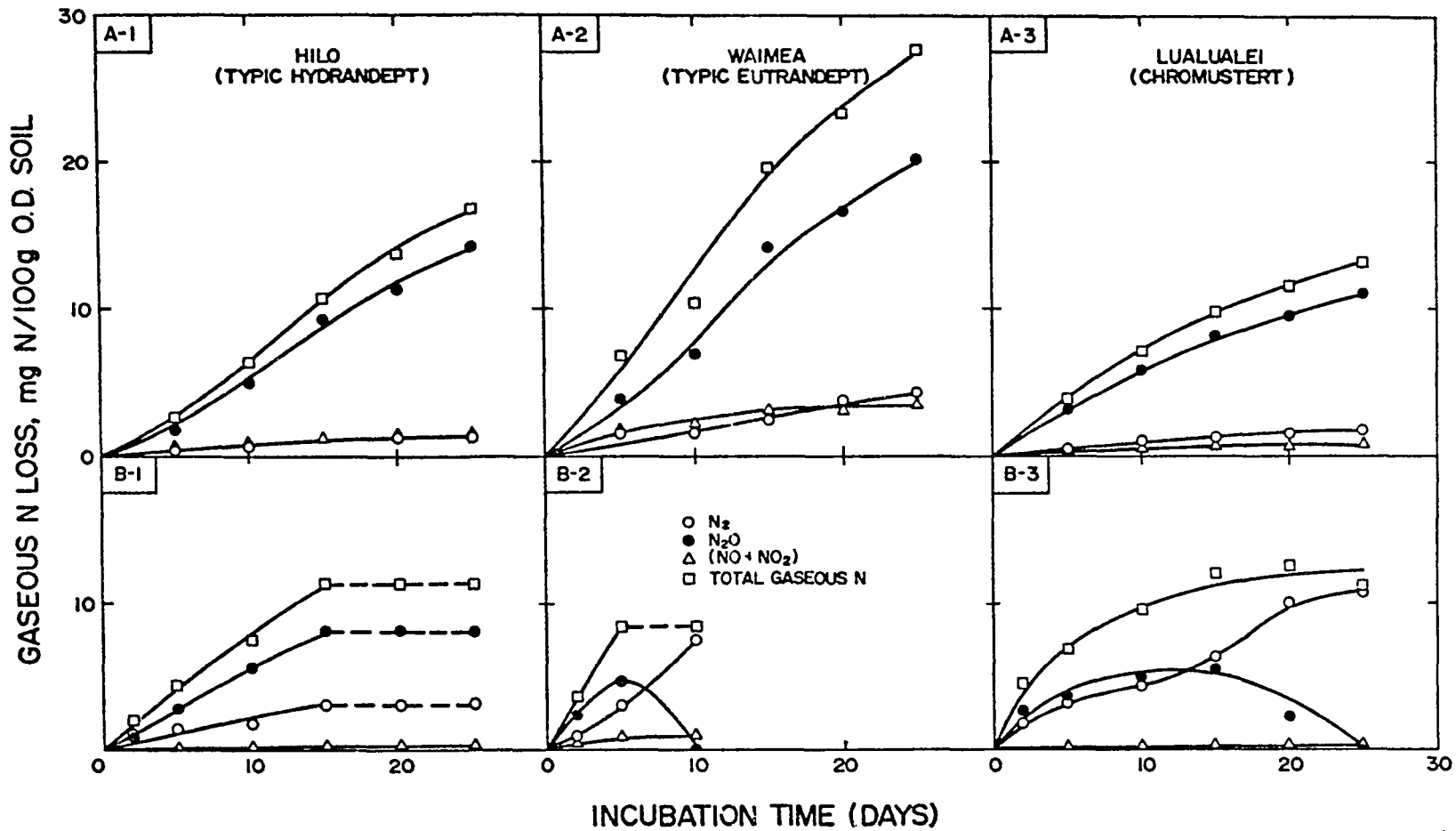


Figure 3-5. Effect of initial NO_3^- level on denitrification in selected soils. A-1 to A-3 represent 30 mg of initial NO_3^- -N per 100g of oven-dry soil, while B-1 to B-3 refer to 10 mg of initial NO_3^- -N per 100g of O.D. soil.



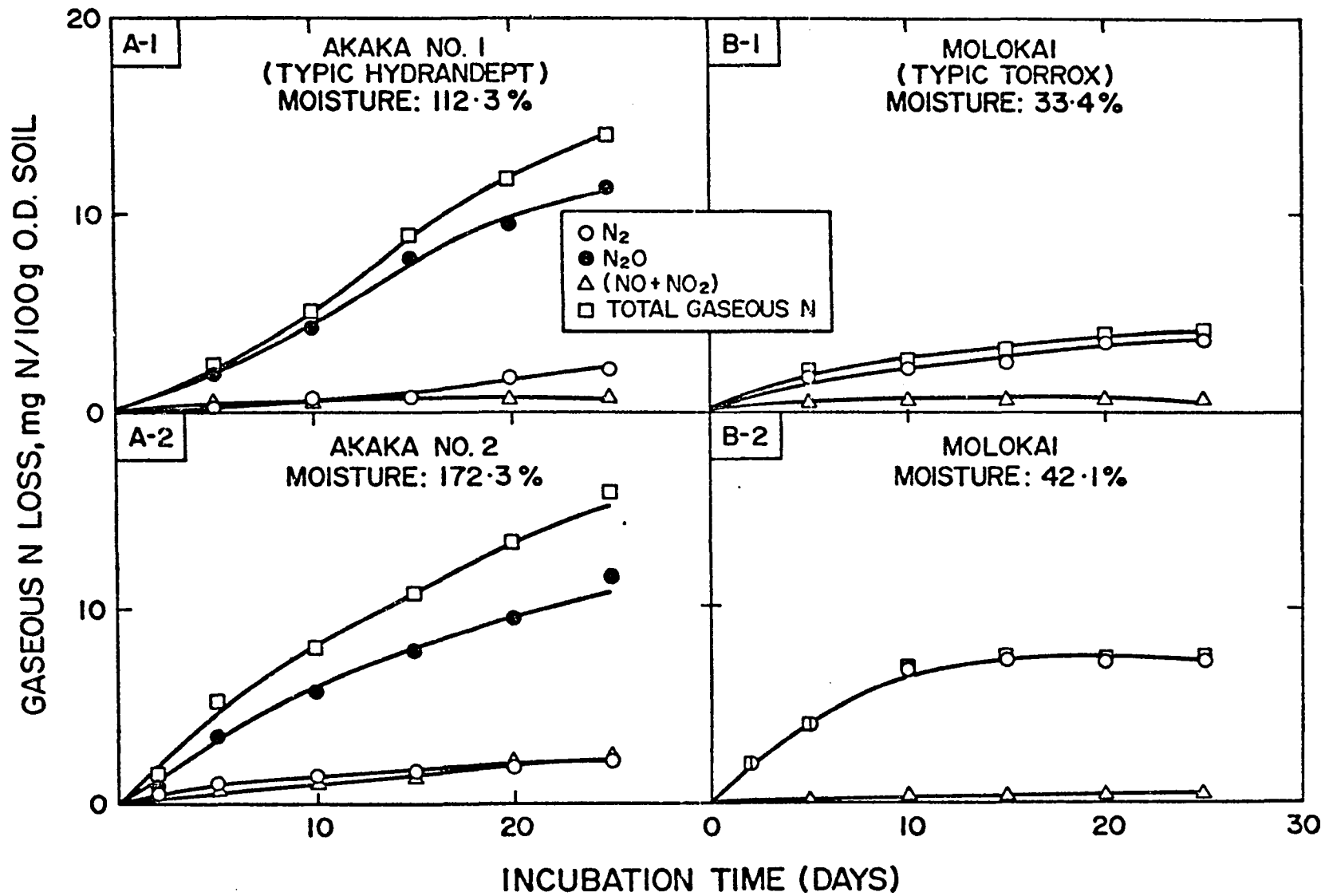
treatments. The total gaseous N loss was approximately equal in both treatments at comparable times when soil NO_3^- was not exhausted. These results are consistent with the observations of McGarity (1961), Bremner and Shaw (1958), and Wijler and Delwiche (1954).

When the initial NO_3^- was exhausted in the low NO_3^- treatment (B-Series in Fig. 3-5), N_2O gas was further reduced to N_2 in the Waimea and Lualualei soils with near neutral pH; in soils having pH five or lower, N_2O gas was stable and was not easily reduced to N_2 , as exemplified by the low NO_3^- treatment of the Hilo soil. Wijler and Delwiche (1954) obtained similar results on the effect of pH on N_2O gas stability.

Even in the Waimea and Lualualei soils with near neutral pH, N_2O gas was not attacked as long as there was available NO_3^- in the soil (A-2 and A-3 of Fig. 3-5). Thus, NO_3^- has a great influence on the reduction of N_2O gas to N_2 during denitrification.

Effect of Soil Moisture Level: Anaerobic denitrification was not affected very much by increasing the soil moisture from 112.3 to 172.3% in the Akaka soil, but an increase of soil moisture from 33.4 to 42.0% in the Molokai soil slightly increased its denitrification capacity (Fig. 3-6). This beneficial effect of higher

Figure 3-6. Effect of moisture on denitrification
in Hydrandepts and Oxisols.

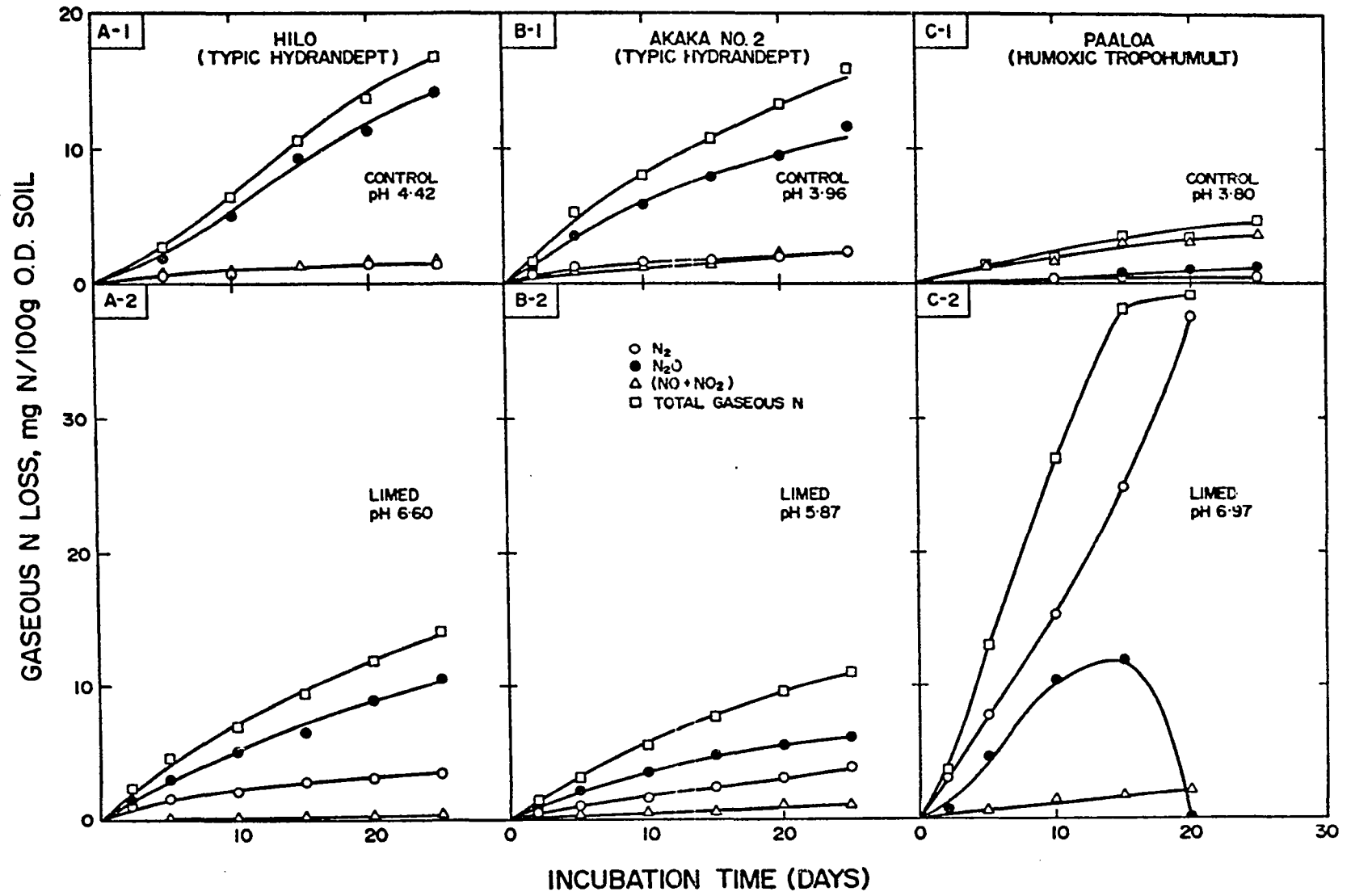


moisture content in an ordinarily low moisture soil could be due to the high mobility and better distribution of nutrients and denitrifying organisms. High moisture effect is more pronounced in aerobic denitrification than in anaerobic denitrification. Wijler and Delwiche (1954) indicated that only those moisture contents below the permanent wilting point depressed anaerobic denitrification directly and that the indirect effect of high moisture content of soils was very much pronounced only in aerobic denitrification.

Effect of Liming and pH: Liming did not influence the denitrification capacity or the pattern of gas production in the Hydrandepts (Hilo and Akaka soils) as shown in Fig. 3-7. This implies that pH was not the major factor limiting denitrification in these soils. Even at pH 6.60 in the limed Hilo soil, N_2O gas was the principal denitrification product, which suggest that N_2O is spared from further reduction to N_2 in the presence of nitrate in the soil.

The picture is completely different in the limed Paaloa soil which showed a significant increase in denitrification capacity when it was limed from pH 3.80 to 6.97 (Fig. 3-7). All the applied and native nitrate in this soil was lost as gases in 15 days;

Figure 3-7. Effect of liming on denitrification
in selected soils.



N_2O was readily reduced to N_2 which was the major denitrification product in this limed Paaloa soil. Water-soluble organic carbon was high in the control and limed Paaloa soils as shown below:

<u>Condition of the soil</u>	<u>Water-Soluble organic C (%)</u>
unlimed	0.065
limed	0.146

This increase in water-soluble energy material could have complemented the pH effect in enhancing the denitrification potential in the limed Paaloa soil. The dominance of $(NO+NO_2)$ gas production in the acidic Paaloa soil (pH 3.80) could be due to the self-decomposition of nitrite, an intermediate product in denitrification. Nelson and Bremner (1970) showed that the self-decomposition of nitrite in acid soils proceeded according to the equation: $2HNO_2 = NO+NO_2+H_2O$.

Effect of Available Energy Materials: When Sucrose was added to the Hilo subsoil and Molokai surface soil at the concentrations of 2 and 1% respectively, there was a tremendous increase in denitrification capacity of both soils (Fig. 3-8 and 3-9). A similar effect was observed in the Molokai soil pretreated with sugarcane trash at the rate of 112 met. tons/hect. (Fig. 3-9).

Figure 3-8. Effect of added sucrose on denitrification in the Hilo subsoil.

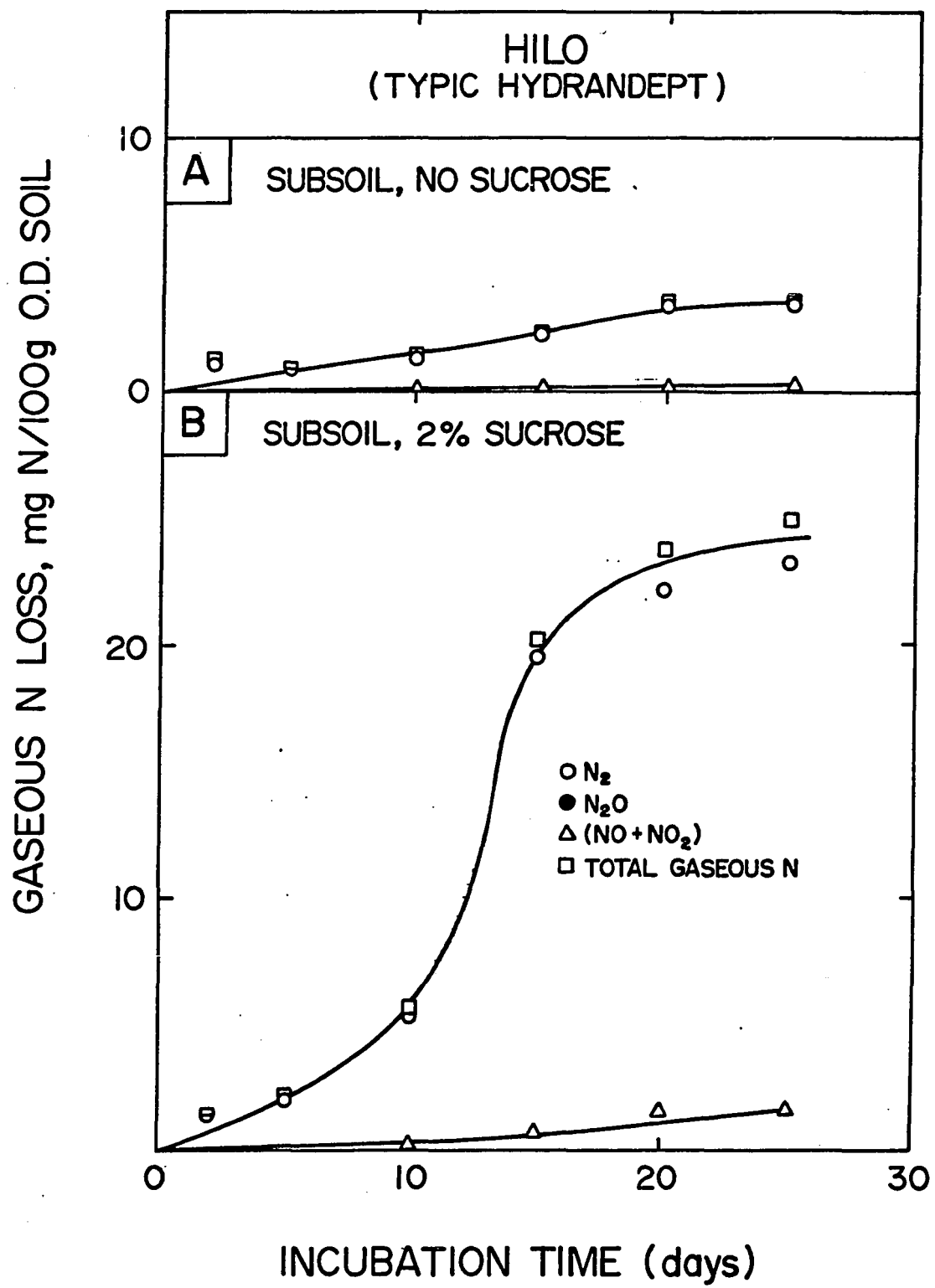
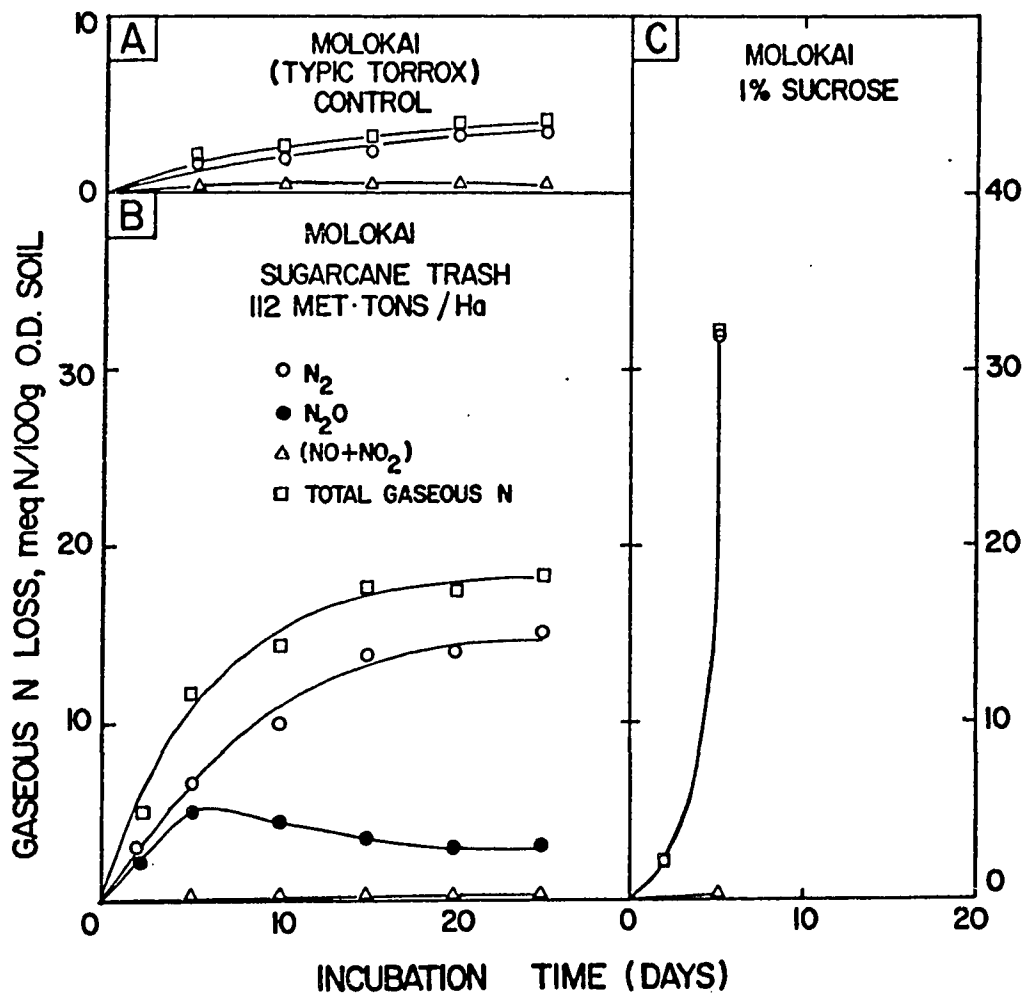


Figure 3-9. Denitrification as affected by the addition of energy materials in the Molokai soil.



This clearly points out the prime importance of available energy source in controlling the activity of denitrifying organisms. This has also been exemplified by other works (Myers and McGarity, 1971; Nelson and Bremner, 1970; Cady and Bartholomew, 1961; and Bremner and Shaw, 1958). The absence of N_2O gas in the sucrose-amended soils suggest that either N_2O gas was not produced at all or it was reduced to N_2 as soon as it was formed. Thus, in the presence of excess energy-rich materials, N_2 gas forms the major denitrification product. The data in Table 3-2 also reveal that at near neutral pH, denitrification capacity of soils is more closely related to energy-rich, water-soluble organic carbon rather than to the total organic carbon contents in soils.

SUMMARY AND CONCLUSIONS

Denitrification loss did not appear to be important in the Molokai and unlimed Paaloa soils because of the lack of energy materials in the former and extremely acidic reaction in the latter. Denitrification capacity increased tremendously once the acidity was neutralized by liming in the Paaloa soil. The Andepts (Hilo, Akaka, and Waimea) and Vertisol (Lualualei) showed a significant tendency to denitrify applied nitrate under extreme conditions of very low oxygen in soil air.

N_2O gas was the principal denitrification product in the Andepts and Vertisol; hence, in these soils, the N_2O concentration of soil air should give a good estimate of natural denitrification under field conditions. In the Oxisol and Ultisol, and in near neutral soils with ample energy materials, N_2 gas was the leading denitrification product, and hence an ^{15}N tagged fertilizer should be used to measure the extent of denitrification in field soils. Since anaerobic reduction of nitrate to ammonia was shown to be insignificant, NO_3^- disappearance can form an indirect estimate of denitrification in the absence of other sources of N loss.

The organic matter in Hydrandepts (Hilo and Akaka) is highly stable and is not easily leachable by percolating water; even though the total organic carbon is high in these soils, the energy-rich, water-soluble portion of the organic matter is very low. Thus the absence of easily available energy materials in the subsoils of the Hilo and Akaka makes them ineffective in denitrifying whatever nitrate leached down from the surface soil. Initial nitrate level did not have any influence in the denitrification pattern or capacity of these soils.

When a soil was extremely acidic, liming increased the denitrification potential as shown with the Paaloa soil. Liming of other acidic soils like the Hilo and Akaka did not have any influence on denitrification. This was likely due to the fact that denitrification was already high in these two soils.

Addition of an easily available energy source, or treatment of soil with organic matter, resulted in an increased denitrification in the Molokai surface soil and Hilo subsoil. If soil pH is not limiting, the denitrification potential of soils is more closely related to energy-rich, water-soluble organic carbon rather than to total organic carbon content in soils.

There was a strong indication that NO_3^- , NO_2^- , and N_2O are sequentially reduced during denitrification. In the presence of NO_3^- , N_2O is not attacked by the denitrifying organisms and thus nitrate has a sparing effect on N_2O gas, even in soils with near neutral pH.

CHAPTER FOUR
MOVEMENT OF APPLIED AMMONIUM AND NITRATE
DURING INFILTRATION IN A HIGHLY
AGGREGATED OXISOL

ABSTRACT

The movement of applied NH_4^+ and NO_3^- during infiltration in an aggregated Oxisol (Molokai silty clay) was studied in laboratory columns. Column - segmentation procedure was used to monitor the solute and solvent profiles immediately after infiltration. The practically irreversible adsorption of NH_4^+ was responsible for its retention in the Molokai soil. The differential effect of K^+ and Ca^{2+} on NH_4^+ movement was explained by their adsorption characteristics and by the (accompanying) anion effect. The relative depths of the NO_3^- peak with reference to the wetting front were the same for different infiltration depths in soils with the same initial water content. The use of this relative depth of NO_3^- peak as a retardation factor in predicting NO_3^- movement in soils is discussed. This retardation factor changed with the initial water content prior to solute displacement. The lower the rate of water application, the deeper were the positions of NO_3^- peak and wetting front, thereby maintaining the relatively constant ratio of NO_3^- peak depth to wetting front. An explanation is given on how to take advantage of the lag of NO_3^- peak

with respect to the wetting front in the initially moist soil to control solute transport during infiltration.

MOVEMENT OF APPLIED AMMONIUM AND NITRATE
DURING INFILTRATION IN A HIGHLY
AGGREGATED OXISOL

INTRODUCTION

Water soluble materials (such as some fertilizers and pesticides) applied to the soil surface are carried underground by the percolating water. Many processes control the movement of solutes through soils down to the ground water table. Adsorption on the soil surface, chemical or microbial conversion of soluble ions into insoluble or less soluble forms, mass flow and diffusion of solutes into the slowly moving micropore water, and presence of soil layers restricting water movement are some of the processes which retard the downward transport of solutes. At the other end, processes such as ion repulsion from the surface, high velocity of macropore water, etc., tend to enhance ion movement in soils. Understanding of these processes will be helpful in developing optimum management practices which will maximize crop utilization of applied nutrients and minimize environmental pollution.

The problem of solute transport under saturated and steady state water flow has been very well

investigated (Biggar and Nielson, 1967). The equal importance of solute movement under unsaturated flow conditions has been recognized recently by soil scientists. Nonsteady convection, ionic diffusion, mechanical dispersion, and anion exclusion have been identified as important processes involved in solute transport with unsaturated water flow (Bresler, 1973 a, b; Kirda et. al., 1971; Bresler and Hanks, 1969; Evans and Levin, 1969).

The transport of surface-applied N fertilizer is of considerable interest because of the importance of N in crop production, as well as the possible pollution of underground water by nitrate. Because NO_3^- is negatively charged, its participation in adsorption reactions will be predominant in soils with a net positive charge. In soils with a high negative surface charge, anion exclusion may enhance the movement of NO_3^- (Thomas, 1970; Bresler, 1973b).

Recent trends in irrigation practice in Hawaii show that the less efficient furrow irrigation is increasingly being replaced by the more efficient drip and sprinkler irrigation methods. Unsaturated flow is the predominant form of water movement under the drip and sprinkler irrigation systems. Therefore, it is desirable to characterize the solute transport under

transient unsaturated water flow conditions in the aggregated soils. The purpose of this study is to investigate the transport of NH_4^+ and NO_3^- with infiltration of water into an unsaturated soil.

MATERIALS AND METHODS

Soil: The Molokai silty clay (Typic Torrox) subsoil (50-70 cm depth) was used in this experiment. The soil sample was passed through a 2 mm sieve before being packed into the columns. The general description and properties of this soil are given elsewhere. (Balasubramanian et. al., 1973).

Columns: Sectionable columns were constructed from 1-, 2-, and 5- cm segments of acrylic tube, 4.4 cm internal diameter. Shorter 1- cm segments were used near the wetting front. These segments were taped together to get desired lengths. An acrylic end plate provided stable support at one end of the column.

Packing procedure: The length of the main column was increased by attaching a 15 cm long extension tube (of the same internal diameter as the main column) on each end of the column. The extension tubes served as buffer zones to the main column. One end of this column was covered with an acrylic end plate.

A glass tubing (1.7 cm internal diameter) with a wide funnel attached to one end was used to pour soil into the main column. This glass tubing was filled with the soil and the funnel was covered with a wax paper. The soil-filled glass tubing was inverted over the table

(the top end was open) and it was inserted into the main column and held in such a way that the open end of the soil-filled glass tubing touched the bottom of the main column. Both the column and the glass tubing were brought back to an upright position and the wax paper covering of the funnel was removed. The outer column was attached to a rotating disc. The inner tubing was slowly raised while the outer column was being rotated at a constant speed (about 100 rpm). When the soil was falling through the glass tubing, the thoroughly mixed soil was continuously being poured into the funnel until the main column was filled up to the desired height. A 2-lb weight was then placed over the soil column and a vibrator was used to vibrate the column on four sides until the soil column reached a precalculated height (to get a particular bulk density). The 15 cm extension tubes were severed off at this time and one end of the column was closed with an acrylic end plate, which had a hole in the center for air to escape. This procedure yielded columns of uniform bulk densities with minimum segregation of different sized aggregates for air-dry soil.

A different procedure was followed to prepare the moist soil columns. The air-dry soil was spread on a wax

paper, the calculated amount of water was added slowly, drop by drop, and the soil was thoroughly mixed. The moistened soil was equilibrated for 2 days in a double polyethylene bag so as to achieve a better distribution of the added moisture. This soil was then packed into the acrylic column by tamping small constant increments with a constant weight plunger. Between the increments of soil, the packed surface was stirred so as to avoid any layering effect suspected to occur by this manner of packing.

Solute Addition and Infiltration: In both air-dry and moist soil columns, the top 5 cm was packed with NH_4NO_3 -treated soil. The initial solute content (S_0) of this treated soil was 5 meq of NH_4NO_3 per 100g of soil. The solute content (S) of each representative section (layer) of the column was divided by the initial solute content (S_0) to get the relative solute content (S/S_0) and this was plotted against depth in all the figures.

The water was applied from a constant head reservoir to the column through an extra coarse fritted-glass plate, whose hydraulic resistance was much lower than that of the soil. A head of -5 cm was maintained during water application in these experiments. The cumulative

inflow and the advance of the wetting front were frequently recorded. In one experiment, the water was sprayed at a lower rate through an atomizer. At the end of the infiltration period, the column was sectioned as quickly as possible. The contents of the segments were put in preweighed moisture cans and dried at 110°C to determine water content.

Analysis of Ammonium and Nitrate: The oven-dried samples were extracted with 1 N KCl (1:5 soil to solution ratio). A steam distillation procedure (Bremner, 1965) was employed to determine NH_4^+ and NO_3^- in the extract.

There was some loss of mineral nitrogen (particularly NH_4^+) during oven-drying. Therefore a small separate experiment was conducted to determine the difference in NH_4^+ and NO_3^- contents in moist and oven-dried samples. Moist soil was treated with NH_4NO_3 to get a series of concentrations. Two samples from each concentration were extracted with KCl solution under moist conditions, while two other samples were oven-dried before extraction. The NH_4^+ and NO_3^- contents in the moist and oven-dried samples were correlated to get a factor which was then used to convert the N contents from oven-dried soil to moist soil. The conversion factor for NO_3^- was independent of concentration whereas that of NH_4^+ was

dependent on concentration. The conversion factors were verified to be repeatable.

The initial moisture contents (θ_0) of the two air dry soil samples, hereafter called air dry No. 1 and air dry No. 2, were 0.183 and 0.098 $\text{cm}^3\text{cm}^{-3}$, respectively. The initial moisture content (θ_0) of the moist soil was 0.309 $\text{cm}^3\text{cm}^{-3}$ which was roughly equivalent to 50% of saturation. The essential features of various treatments included in the column study are listed in Table 4-1.

Table 4-1

Essential Features of Various Treatments Included in the Column Study

Treatment* number	Initial water content θ_o	Water content at surface θ_s	Wet front depth	Depth of NO_3^- peak	Retardation [†] factor	Amount of water applied	Movement of NO_3^- peak per cm of added water	Soil sample used
	-----cm ³ cm ⁻³ -----		----- cm -----			----- cm -----		
1a	0.183	0.535	20.6	13.0	0.63	6.6	2.0	Air dry #1
1b	0.183	0.535	40.3	25.4	0.63	13.4	1.9	"
1c	0.183	0.535	60.6	36.5	0.60	20.8	1.8	"
2	0.098	0.535	20.2	16.5	0.82	8.4	2.0	Air dry #2
3	0.309	0.520	21.5	8.5	0.40	3.7	2.3	Moist
4	0.183	0.500	22.5	15.0	0.67	6.6	2.3	Air dry #1

*In treatment No. 4, the water was sprayed with an atomizer at a low rate of 1.4 cm/hour on the soil surface.

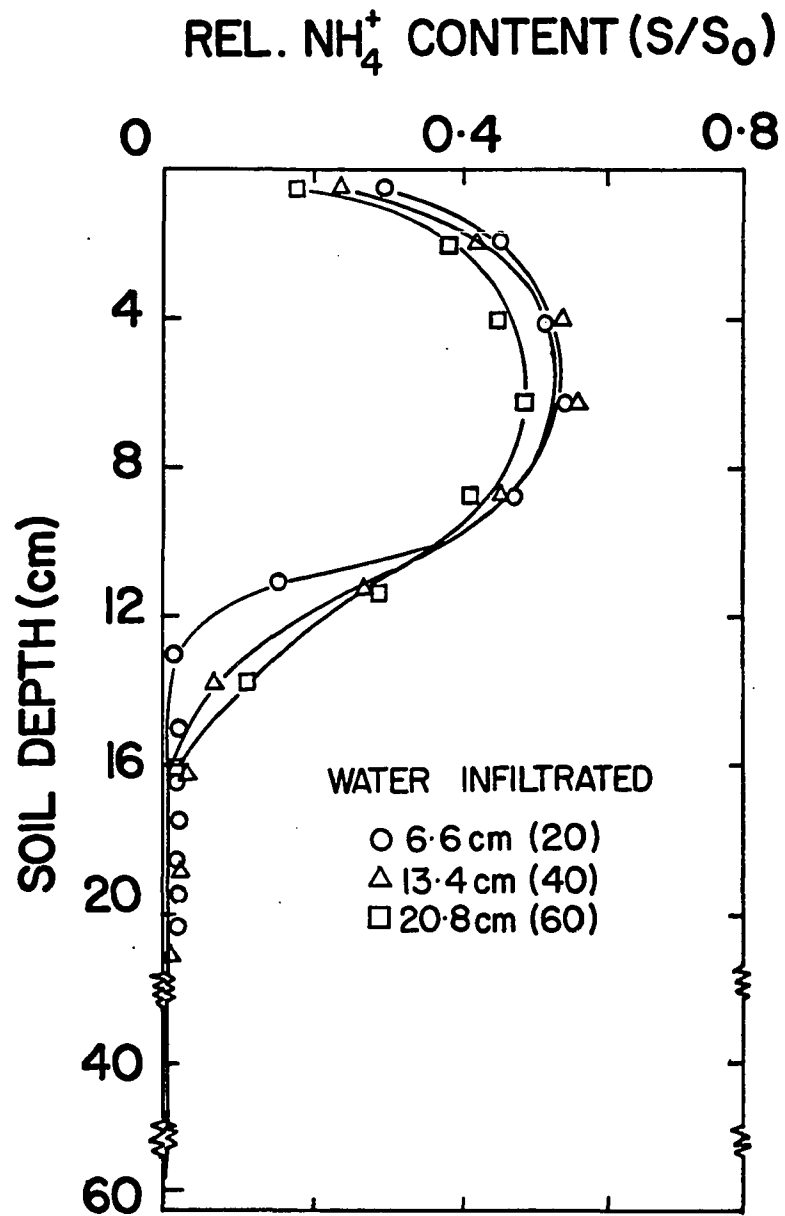
[†]Retardation factor is taken as the depth of NO_3^- peak divided by the depth of wetting front.

RESULTS AND DISCUSSION

Ammonium Movement: The distribution of NH_4^+ in the soil after infiltration of water to different depths (20, 40, and 60 cm) is depicted in Fig. 4-1. The NH_4^+ profile formed a smooth curve (without any prominent peak) up to the 15 cm depth from the surface. Very little NH_4^+ was found in the soil beyond 15 cm. This indicates that added NH_4^+ was effectively adsorbed on the soil surface even under transient flow conditions. Equilibrium adsorption measurements showed that this soil adsorbed 4 meq of NH_4^+ per 100g of soil at 0.2 N solution concentration. It was also found that 95% of the maximum NH_4^+ adsorption was completed within 5 minutes after the addition of NH_4NO_3 solution to the soil. This fast adsorption of NH_4^+ was considered responsible for the retention of NH_4^+ in the upper sections of the column during infiltration.

The NH_4^+ distribution for 20, 40, and 60 cm wet front positions were not significantly different from each other (Fig. 4-1). This suggests that the NH_4^+ adsorption in this soil is irreversible. The adsorbed NH_4^+ was not easily desorbed when the amount of water infiltrated increased from 6.6 cm to 20.8 cm, even though there was a tendency for very slow desorption. Since the

Figure 4-1. Ammonium distribution in the profile after different quantities of infiltrated water into an air-dry ($\theta = 0.183 \text{ cm}^3\text{cm}^{-3}$) Molokai soil. The numbers in the parentheses indicate the wetting front depth.



Molokai soil is negatively charged (CEC is about 14 meq/100g), the irreversible retention of added NH_4^+ is not surprising.

In the simultaneous presence of competing cations, the desorption movement of NH_4^+ was increased as shown in Fig. 4-2. While the presence of Ca^{2+} affected the NH_4^+ distribution only slightly, the simultaneous addition of K^+ , either as Cl^- or SO_4^{2-} , shifted the NH_4^+ profile deep into the soil. Both NH_4^+ and K^+ are non-specifically adsorbed and as such they compete for similar adsorption sites on the soil surface. On the other hand Ca^{2+} and NH_4^+ are believed to be adsorbed on different sorption sites with specific and non-specific binding mechanisms, respectively. Moreover, the adsorption of phosphate anion accompanying the Ca^{2+} would have created more negative charges (Mekaru and Uehara, 1972) which might have increased the adsorption of both Ca^{2+} and NH_4^+ .

Nitrate Movement: The nitrate profiles for 6.6, 13.4, and 20.8 cm of water infiltration are given in Fig. 4-3. Movement of nitrate from a zone of high concentration formed curves which resembled normal curve. The larger the amount of water infiltrated, the deeper was the position of maximum NO_3^- concentration. The peak height

Figure 4-2. Effect of the simultaneous presence of Ca^{2+} and K^+ on NH_4^+ movement during infiltration into an air-dry ($\theta = 0.183 \text{ cm}^3\text{cm}^{-3}$) Molokai sil. θ is the volumetric water content in the profile.

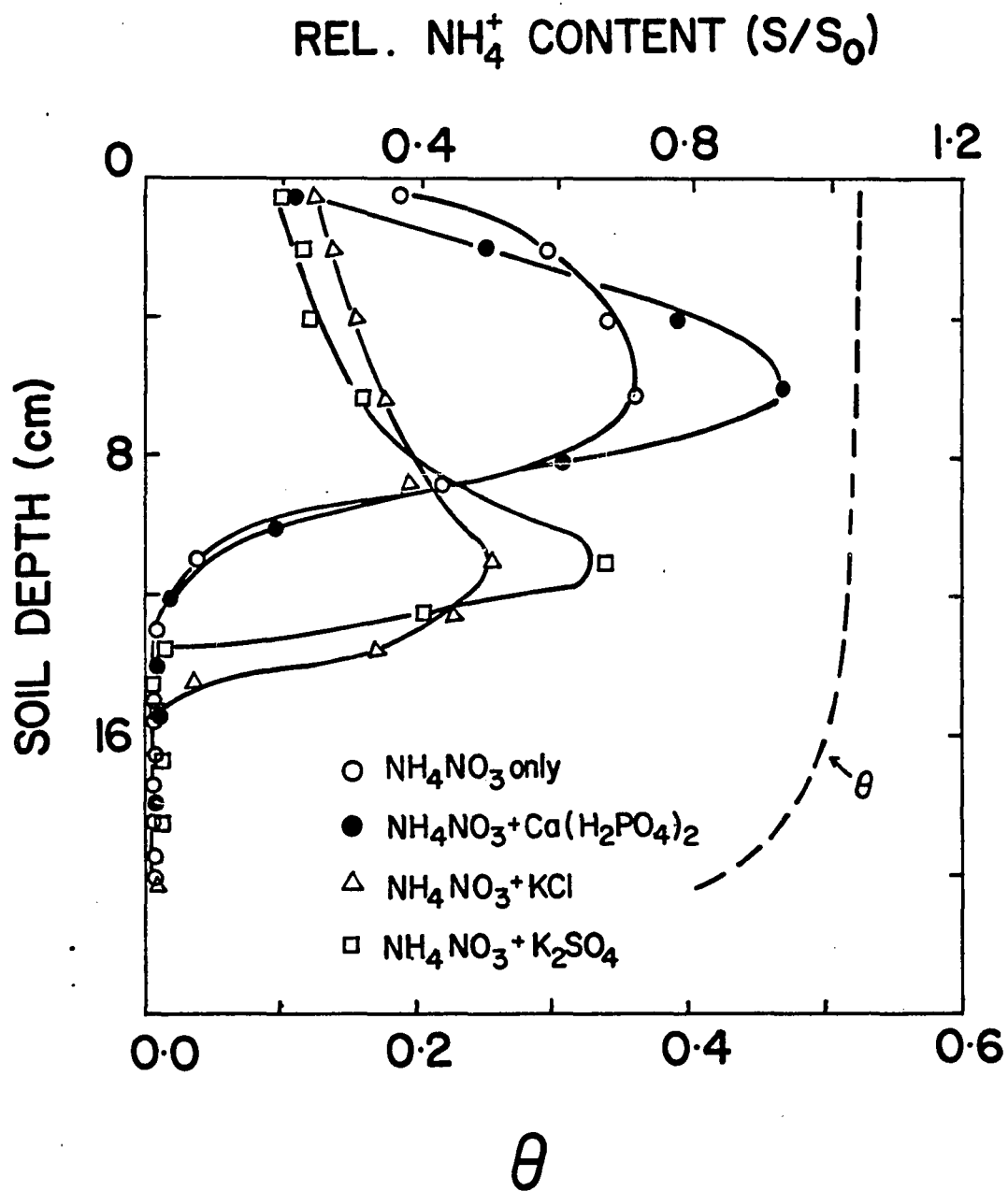
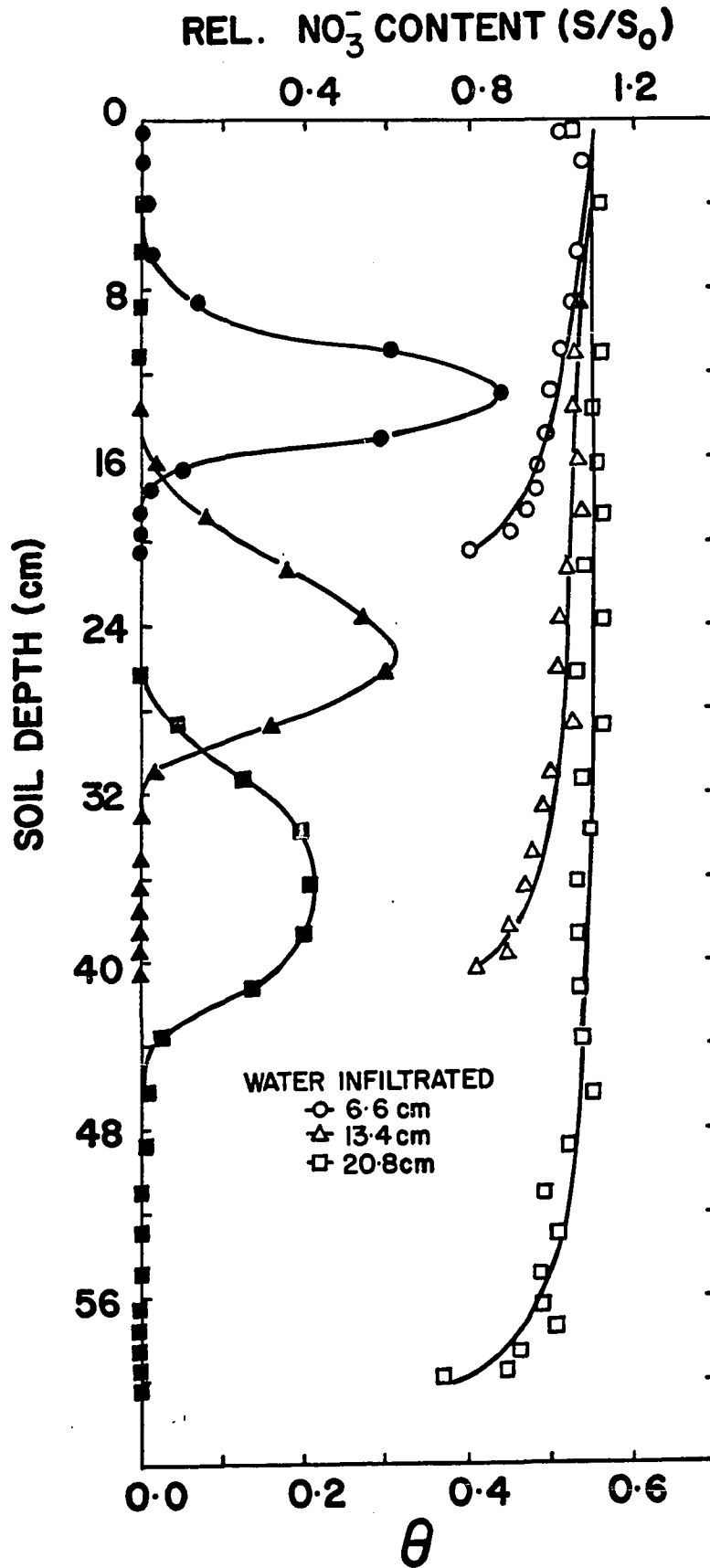


Figure 4-3. Distribution of NO_3^- and water during infiltration of different amounts of water into an air-dry ($\theta = 0.183 \text{ cm}^3\text{cm}^{-3}$) Molokai soil.



decreased and the spreading of the profile increased as the NO_3^- moved down in the soil. Mass flow, dispersion, and diffusion were considered as main factors responsible for the downward movement and spread of applied NO_3^- in the profile.

The lag of NO_3^- peak with respect to the wetting front (Fig. 4-3) indicates that there was a retentive mechanism withholding the NO_3^- against the downward movement of water. This soil was shown to repel NO_3^- ions (Balasubramanian *et. al.*, 1973) and hence adsorption could not be the factor responsible for this retention. Velocity of water in the intra-aggregate pores is far less than that of the interaggregate pores in this aggregated soil (Green *et. al.*, 1972). The NO_3^- ions which went into the micropore water might be expected to move slower than the NO_3^- in the macropore water. This could have caused the retarded movement of NO_3^- with respect to water. A similar mechanism was considered responsible for the retention of NO_3^- (Balasubramanian *et. al.*, 1973) and picloram herbicide (Rao *et. al.*, 1974) in field profile studies.

When the profile depth was normalized by dividing the depth (X) by the wetting front (X_0) and when NO_3^-

distribution was plotted against this reduced or relative depth as shown in Fig. 4-4, it was observed that the NO_3^- peaks for the different amounts of water infiltrated were one above the other at a particular relative depth. This fractional depth will give the retardation factor for NO_3^- movement under the conditions encountered in this experiment. A retardation factor of 0.615 ± 0.015 was obtained which suggests that for every cm of water movement under filtration, the NO_3^- peak moved only 0.615 cm. The depth of maximum NO_3^- concentration can be obtained by multiplying the depth of wet front by the retardation factor. Thus, if we can accurately determine the wet front position in the field profile, we would be able to predict the depth of maximum NO_3^- concentration under field conditions.

When the initial soil water content changed from 0.098 to 0.309 $\text{cm}^3\text{cm}^{-3}$, the NO_3^- peak shifted downward from 8.5 cm to 16.5 cm for the same depth of infiltration (Fig. 4-5). When the amounts of water infiltrated in different columns were compared with the depths of NO_3^- peaks it was found that the peak depth was in direct correlation with the quantity of water infiltrated (Compare the values for NO_3^- movement per cm of added water in Table 4-1). Thus the movement of NO_3^- peak was

Figure 4-4. Nitrate profiles for different amounts of infiltrated water plotted against relative depth (actual depth, X , divided by the depth of wetting front, X_w). The numbers in the parentheses indicate the actual depths of wetting front.

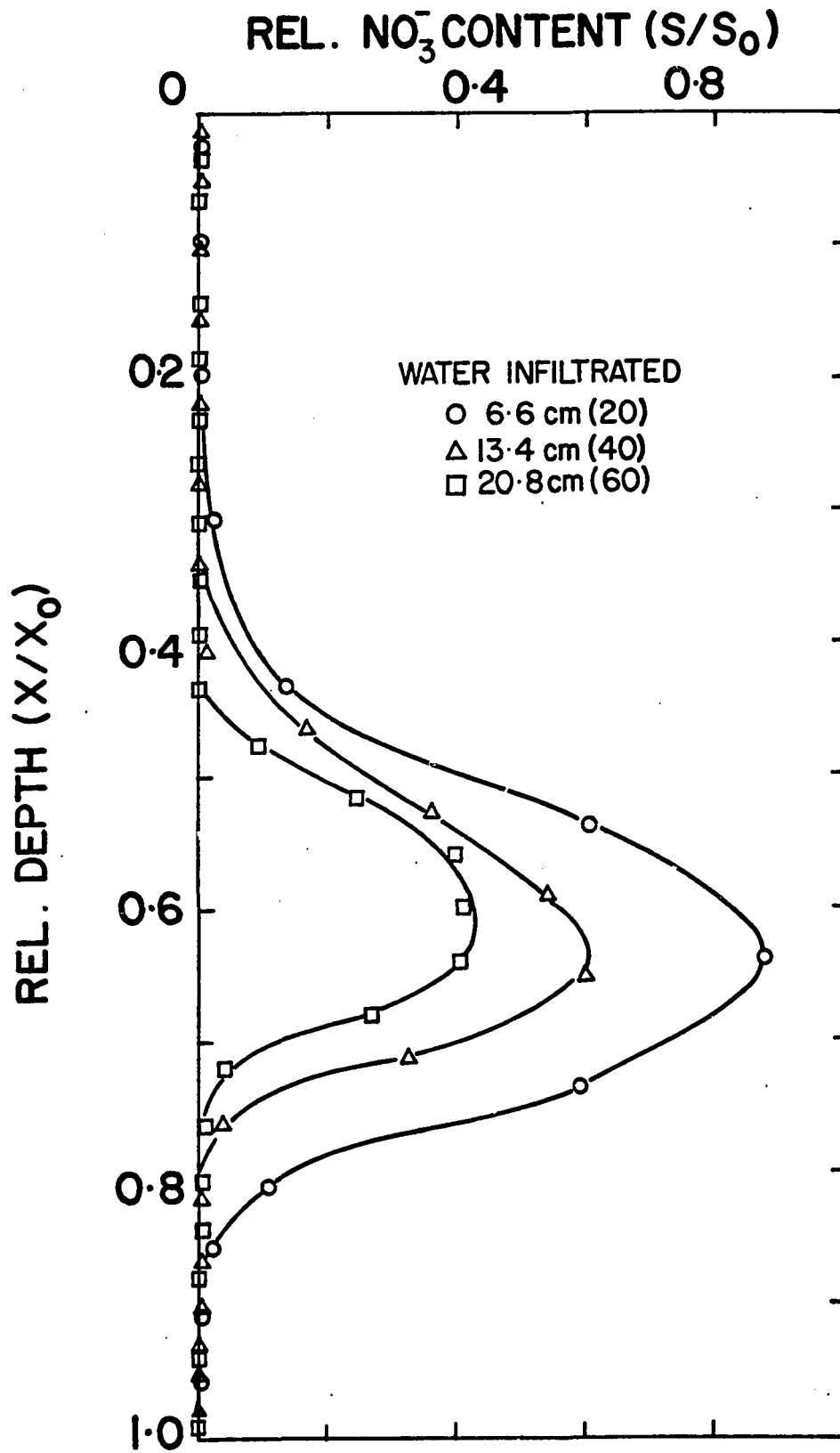
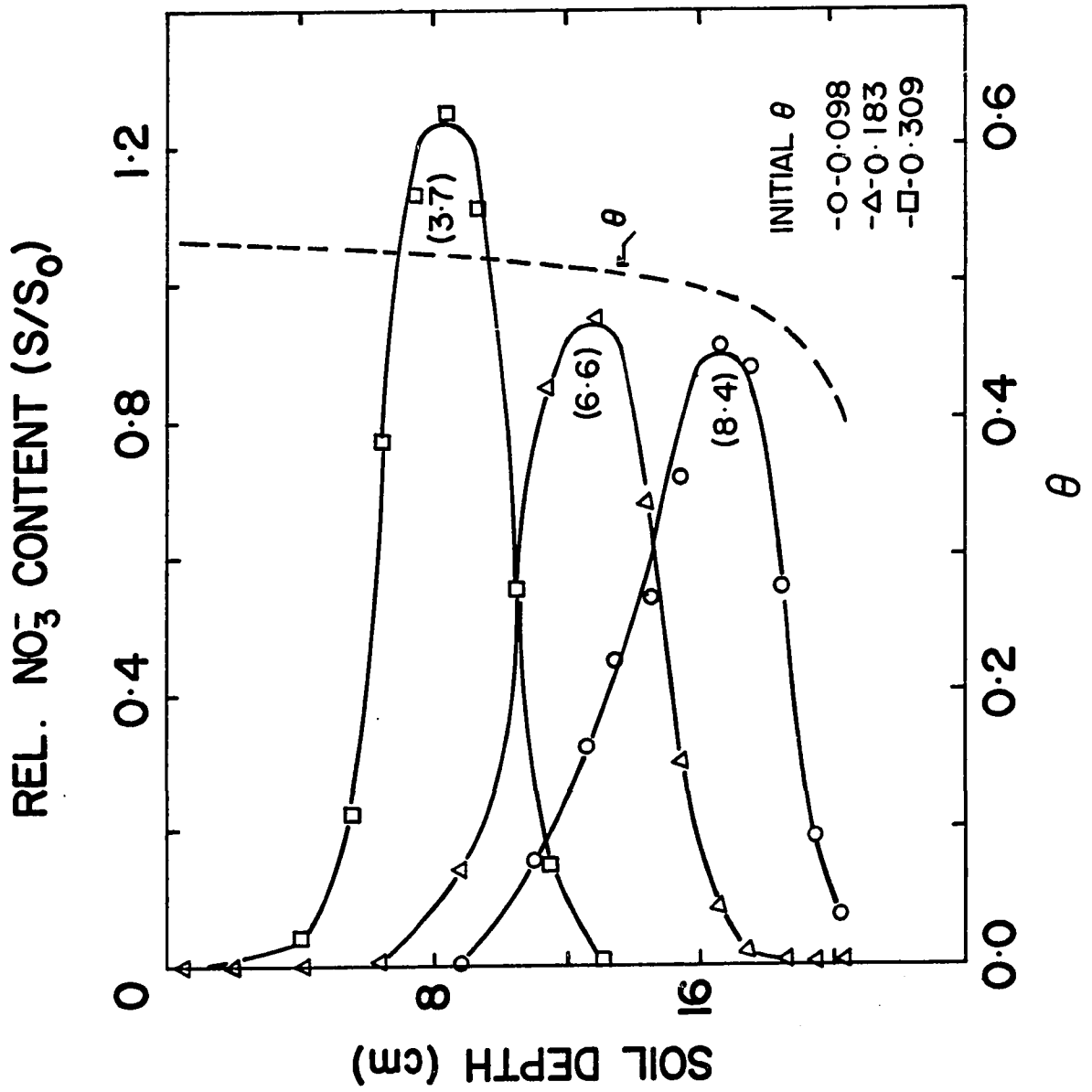


Figure 4-5. Effect of initial soil water content, θ_0 , on NO_3^- movement in columns wetted up to nearly 20 cm. The numbers in the parentheses indicate the amounts of water infiltrated to get the nearly same wetting depth(20 cm).



strictly a function of the amount of water infiltrated regardless of the initial soil water content (Table 4-1). Kirda et. al., (1973) showed that initial soil water content prior to displacement did not appreciably change the resulting Cl^- distribution for a given quantity of displacing solution. These authors suggested that the wetting front in initially moist columns was not formed by the invading water but by the original solute free water. They also concluded that the displacing solution does not necessarily bypass the smaller pores but rather displaces both small and large pore sequences. Using the miscible displacement technique with tritiated water as a tracer, Green et. al., (1972) showed that there was no apparent exclusion of water-filled pores from the flow process in the Molokai soil.

It was interesting to compare the retardation of NO_3^- peak with the fractional water depth attributable to the added water. If all the initial water (θ_o) were completely ahead of the applied water, approximately θ_o/θ_s fraction of the water depth could be assigned to the initial water, where θ_s is the water content at the surface. This means that the applied water will form

$1 - (\theta_o/\theta_s)$ fraction of the water depth. An examination of the Table 4-2 will reveal that the fractional water depth due only to the added water compares closely with the corresponding NO_3^- retardation factor for soils with different initial moisture contents. This assumption of complete displacement of initial soil water by the added water is not entirely true, since there will be mixing at the interface between the added and initial water and some NO_3^- will move ahead of the peak due to dispersion and diffusion. However, the foregoing analysis supports the hypothesis that the added water did not form the observed wetting front in the initially moist soil. This analysis also brings out the importance of taking into account the initial soil water content in solute transport studies.

The lagging of the NO_3^- peak with respect to the wetting front in the initially moist soil has a practical advantage in the field. If one fertilizes the soil under moist condition and irrigates to wet up to a particular depth, the depth of displacement of NO_3^- will be less (see the retardation factor for treatment No. 3 in Table 4-1). On the contrary, if the fertilizer is added to a dry soil and it is wetted to the same depth with irrigation, the NO_3^- will be displaced to deeper zones.

Table 4-2
 Comparison of Fractional Water Depth
 Formed by the Added Water With
 the Nitrate Retardation
 Factor*

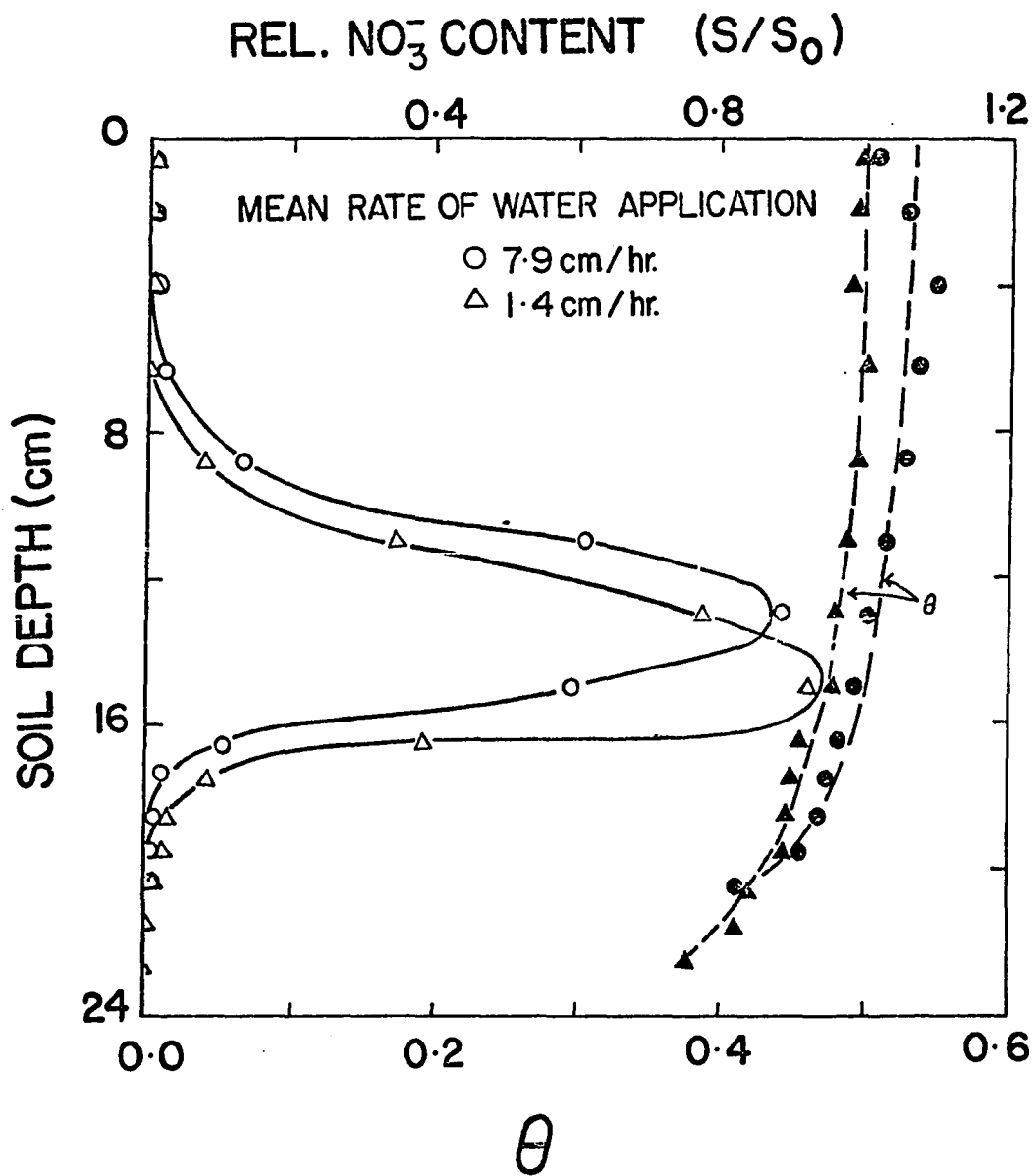
Soil sample	Initial water content θ_o	Water content at surface θ_s	Fractional water depth due to added water $1-(\theta_o/\theta_s)$	Nitrate* retardation factor
	----- cm ³ cm ⁻³ -----			
Air-dry #1	0.098	0.530	0.815	0.820
Air-dry #2	0.183	"	0.655	0.630
Moist	0.309	"	0.417	0.400

*Nitrate retardation factor is taken as the depth of NO₃ peak divided by the depth of wetting front.

By selecting the proper initial moisture content before solute addition, one can effectively control the depth of solute displacement with respect to the wetting front.

The rate of water application to the soil surface was found to markedly alter the depth of NO_3^- movement (Fig. 4-6). When the water application rate was reduced from 7.9 cm/hour to 1.4 cm/hour, the water content in the surface was decreased from $0.535 \text{ cm}^3 \text{ cm}^{-3}$ to $0.500 \text{ cm}^3 \text{ cm}^{-3}$. For the same amount of water infiltrated (6.6 cm), the NO_3^- peak and the wetting front were shifted to lower depths with the low rate of water application (Fig. 4-6). Thus the lower the rate of water application, the deeper is the movement of NO_3^- and water in the profile. Kirda *et. al.*, (1973) obtained similar results for chloride movement in Hanford sandy loam. This implies that any irrigation system which applies the water at a very low rate will move the solutes to deeper zones for any given quantity of water applied.

Figure 4-6. Effect of the rate of water application on NO_3^- transport during infiltration into air-dry ($\theta_o = 0.183 \text{ cm}^3\text{cm}^{-3}$) Molokai soil.



SUMMARY AND CONCLUSIONS

The practically irreversible adsorption of NH_4^+ was responsible for its retention in the Molokai soil. The simultaneous presence of K^+ either as Cl^- or SO_4^{2-} , shifted the NH_4^+ profile to deeper zones, whereas the effect of Ca^{2+} on NH_4^+ movement was not very significant. This was explained by the adsorption specificity of Ca^{2+} vs. NH_4^+ and K^+ , and by the (accompanying) anion effect.

The higher the amount of water infiltrated, the deeper was the position of NO_3^- peak. The relative depths of the NO_3^- peak with reference to the wetting front were the same for different infiltration depths when the initial water content was the same. The use of this relative depth of NO_3^- peak as a retardation factor in predicting NO_3^- movement in soils is discussed. This retardation factor changed with the initial water content prior to solute displacement. By selecting the proper initial moisture content, one can effectively control the depth of solute displacement with respect to the wetting front. The lower the rate of water application, the deeper was the movement of NO_3^- and

water. For soils with the same initial moisture content, the depth of NO_3^- peak is in direct proportion to its wetting front. Thus, by controlling the wetting front, one can control the depth of maximum solute concentration irrespective of the irrigation system.

GENERAL SUMMARY AND CONCLUSIONS

Precise control of N fertilizer use depends on a thorough understanding of the behavior of applied N in soils through research; this will result in maximum crop utilization of added N with a minimum opportunity for the potential pollution of ground water by nitrate. With this primary objective in view, the factors influencing the adsorption, denitrification, and movement of applied NH_4^+ and NO_3^- in tropical Hawaiian soils were studied.

Soil colloids in general are negatively charged in the pH ranges encountered in cultivated fields and, therefore, sorption of NH_4^+ will retain this cation against the leaching action of percolating water. Studies on NH_4^+ movement indicate that NH_4^+ in the form of phosphate will be retained more strongly than NH_4^+ in any other form (Kanehiro et. al., 1960). This shows that N leaching in the cationic form is negligible. However, in tropical soils, high temperature and moisture conditions favor the conversion of applied NH_4^+ to NO_3^- within a relatively short period of time. Thus, the application of NH_4^+ fertilizers to soils gives only a temporary protection against N leaching. The rate and kinetics of nitrification of applied NH_4^+ can be controlled by the addition of chemical inhibitors like N-serve,

potassium azide, etc. Most of the crops prefer $\text{NO}_3\text{-N}$ to $\text{NH}_4\text{-N}$, because NO_3^- moves readily in the soil to absorbing root sites. Thus, the timing of fertilizer application should be adjusted in such a way that the added NH_4^+ is nitrified at the exact time when crops will utilize most of the converted NO_3^- .

Nitrate, either applied as fertilizers or mineralized from the soil, is highly susceptible to leaching (Ayres, 1955). Some oxidic tropical soils such as the Hydrandepts and Gibbsihumox in Hawaii were found to adsorb NO_3^- significantly in pH ranges below 6. Non-specific anion adsorption is believed to be the major mechanism by which NO_3^- was adsorbed. The zero point of charge (ZPC), which has a close relation with non-specific anion adsorption, is defined as the pH where the net sum of charges is zero. Non-specific anion adsorption is common only at pH values below the ZPC. Any change in the ZPC will bring about a change in non-specific anion adsorption. The significant decrease of NO_3^- adsorption due to dehydration of the Hydrandepts has been discussed in relation to the change in the ZPC, pH, crystallinity, and surface area on drying. Since this dehydration process was shown to be irreversible in previous studies (Kanehiro and Sherman, 1956), it was

concluded that these soils should not be allowed to dry excessively by exposure to direct sun and wind so as to preserve their high exchange capacities, both for anions and cations. The surface of these soils became less positive or more negative on liming, and this was reflected in the (increased) NH_4^+ and (decreased) NO_3^- adsorption by the limed soils. Raising of soil pH beyond 5.5 with liming produced NO_3^- repulsion in these soils.

In an infiltration study with an aggregated Oxisol (Molokai silty clay), it was found that the relative depths of NO_3^- peak with reference to the wetting front were the same for different amounts of water infiltrated into soils with the same initial moisture content. The use of this relative depth of NO_3^- peak as a retardation factor in predicting NO_3^- movement during infiltration in soils is discussed. Also an explanation is given on how to take advantage of the lag of NO_3^- peak with respect to the wetting front in the initially moist soil to control solute transport during transient water flow. It was also found that the lower the rate of water application, the deeper were the positions of NO_3^- peak and wetting front, thereby maintaining the ratio of NO_3^- peak depth

to wetting front. This suggests that any irrigation system, which applies the water at a very low rate, will move the weakly adsorbed solutes to deeper zones in the profile for any given quantity of water applied.

Denitrification loss seemed to be important only in soils with large amounts of water-soluble organic matter and nutrients (eg. Inceptisols and Vertisols). Available energy source appeared to play a dominant role in denitrification. N_2O gas was the prime denitrification product in the majority of the soils studied. However, in near neutral soils with ample energy materials, N_2 was the most important. The implication of this gas evolution pattern in evaluating natural denitrification in field profiles is discussed. Anaerobic reduction of NO_3^- to NH_4^+ was found to be insignificant in these soils as compared to the denitrification loss.

Denitrification potential was very low in the Molokai soil because of the lack of energy materials. Therefore, any NO_3^- leached beyond the root zone will not undergo any denitrification loss in the substratum of this soil and will be carried down to the ground water, thereby increasing the possible contamination of water by NO_3^- . However, the well-aggregated nature

of this soil offers a solution for this problem; the diverse distribution of water-flow velocities in the micro- and macro-pores can be exploited to retard the downward transport of NO_3^- (Balasubramanian et. al., 1973).

In short, modified management practices based on the knowledge of N transformation and movement in soils as well as N uptake by crops will ensure maximum crop utilization of added and mineralized N with minimum loss through leaching and volatilization including denitrification. Concurrently with the efficient use of N fertilizers, the chances of ground water pollution by NO_3^- will also be reduced.

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