SOME PHYSICAL AND CHEMICAL ASPECTS OF AMMONIACAL NITROGEN IN SOILS

by

Tyng-Tsair Chao, B.S., M.S.

Thesis submitted to the Graduate Faculty of the
Virginia Polytechnic Institute
in candidacy for the degree of
DOCTOR OF PHILOSOPHY
in
AGRONOMY

January, 1961
Blacksburg, Virginia

ACKNOWLEDGEMENTS

The author wishes to express his deep appreciation to Dr. for his continuous encouragement and guidance throughout the course of this work and to the Smith-Douglass Company, Inc. of Norfolk, Virginia for their financial support and interest in these investigations.

He also appreciates the helpful suggestions and valuable discussions provided by members of the faculty and graduate students of the Agronomy Department. The author is particularly indebted to Dr. , Dr. , Dr. , Dr. and Dr. for making some important suggestions.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Transformation of inorganic nitrogen in soils can probably occur through three different processes, namely chemical, physical and biological. The biological processes in certain nitrogen transformations are considered to be by far the most important in soils. Chemo-autotrophic bacteria which play a key role in the biological process of inorganic nitrogen oxidation can only derive their energy from the oxidation of inorganic nitrogen compounds. Therefore, a knowledge and compilation of selected thermodynamic quantities involved in the transformation of inorganic nitrogen should be of considerable importance. On the basis of these values one should be able to predict to what extent certain reactions may occur and how much energy the micro-organisms can theoretically derive from these inorganic nitrogen transformations. In the first investigation calculated changes in free energy of oxidative inorganic nitrogen transformations in acid and basic solutions are related and used to interpret findings reported in the literature.

Much of the nitrogen in high analysis nitrogen fertilizer, as well as nitrogen contained in mixed fertilizer, often is in the ammonia and/or ammonium form(s). Ammonia is furthermore a product of microbiological activity in soils. With heavy nitrogen fertilization which has become an established practice for many crops, volatile ammonia losses are found to be of far greater importance than was previsously assumed. In order to learn more about the mechanisms involved in ammonia volatilization a series of experiments are conducted to study: (1) the effect of soil texture, soil moisture and speed of air flow over the soil surface on the relationship between water evaporation and ammonia volatilization, (2) the relationship between ammonia concentration and volatilization, (3) the kinetics of ammonia volatilization and (4) ammonia adsorption phenomena in acid and basic soils. The results and conclusions of these investigations are reported.

I OXIDATIVE INORGANIC NITROGEN TRANSFORMATION IN RELATION TO ASSOCIATED CHANGES IN FREE ENERGY

A. Introduction

Nitrogen, one of the most important elements in plant and animal nutrition, presents many complex and challenging problems to the investigator. One of the reasons for this complexity is that this element gives rise to so many compounds. The oxidation states of these compounds vary greatly, being (28) -3 for ammonia, NH_3; -2 for hydrazine N_2H_4; -1 for hydroxylamine, NH_2OH; +1 for nitrous oxide, N_2O and hyponitrous acid, $H_2N_2O_2$; +2 for nitric oxide, NO; +3 for nitrous acid, HNO_2; +4 for nitrogen dioxide, NO_2 and nitrogen tetroxide, N_2O_4; and +5 for nitric acid, HNO_3. It is not surprising that results from studies dealing with the existence and transformations of these and associated compounds in soils are often contradictory and/or inconclusive.

Oxidative nitrogen transformations may occur through chemical, physical , and biological processes. The latter are probably the most important since the activity of certain autotrophic bacteria is determined to a large extent by the energy released from the oxidation of inorganic nitrogen compounds. These reactions should therefore be thermodynamically spontaneous since no energy is available from nonspontaneous reactions. It should be realized, however, that chemical equilibria and thermodynamics involve only the initial and final states and that they do not describe the intermediate steps (15). Some nitrogen oxidation reactions may appear to be spontaneous, although, the reactants require the absorption of a definite amount of energy (activation energy) in order to put them into the activated forms for their complete oxidation. The function of bacteria in the nitrogen oxidation process is still largely unknown. It may well be that bacteria lower the activation energy of nitrogen oxidation reactions. The objectives of this investigation are: (1) to relate calculated changes in free energy of oxidative inorganic nitrogen transformations in acid and basic media, and (2) to use these theoretical values as an aid to interpret findings reported in the literature.

B. Materials and Methods

The free energy changes in nitrogen transformations can be calculated by three different equations, namely, $\Delta F^o = -nFE^o$, $\Delta F^o = \Delta H^o - T\Delta S^o$, and $\Delta F^o = \Sigma\Delta F^o{}_{f,\ \text{products}} - \Sigma\Delta F^o{}_{f,\ \text{reactants}}$, where ΔF^o is the free energy change in joules, n is the number of electrons transferred in the reaction, F is the Faraday (96,494 coulombs), E^o is the voltage or electromotive force of the cell, $\Sigma\Delta F'_f$ s is the summation of the changes in the free energies of formation, ΔH^o is the change in heat of reaction, T is the absolute temperature, ΔS^o is the change in entropy of the reaction.

For the calculations in this paper the author has used extensively the potential values and half-cell reactions summarized by Latimer (28) and free energy formation data compiled by Rossini et al. (48). The following wateroxygen couples were used in the calculations;

1. In acid solution, $2H_2O = O_2 + 4\,H^+ + 4e^-$ $E^o_{298} = -1.229$
2. In alkaline solution, $4OH^- = O_2 + 2H_2O + 4e^-$ $E^o_{298} = -0.401$
3. In pure water, $2H_2O = O_2 + 4H^+(10^{-7}M) + 4e^-$ $E^o_{298} = -0.815$

Examples for calculating the changes in free energy and the equilibrium constant, K, in the oxidation of nitrite to nitrate:

a. In acid solution,

$$\begin{array}{lll} HNO_2 + H_2O & = NO_3^- + 3H^+ + 2e^- & E^o_{298} = -0.940 \\ 2H_2O & = O_2 + 4H^+ + 4e^- & E^o_{298} = -1.229 \\ \hline HNO_2 + \frac{1}{2}\,O_2 & = NO_3^- + H^+ & E^o_{298} = 0.289 \end{array}$$

$$\Delta F^o = -nFE^o = \frac{-(2)(96494)(0.289)}{4.184 \times 1{,}000} = -13.33 \text{ kcal.}$$

Since "the free energy of a reaction is the sum of the free energies of formation of the products of the reaction less the sum of the free energies of formation of the reacting substances" (15), ΔF^o, therefore, might also be calculated. In symbols this is:

$$\Delta F^o = \Sigma \Delta F^o_{f,\text{ products}} - \Sigma \Delta F^o_{f,\text{ reactants}}$$

An example is;

$$\Delta F^o = F^o_{NO_3^-} - F^o_{HNO_2} = -26.41-(-12.82) = -13.59 \text{ kcal .}$$

Theoretically, the calculated values obtained by either method should agree very closely with each other as was found to be the case.

The equilibrium constant, K, becomes then;

$$\Delta F^o = -RT\ln K$$

where, ΔF^o is the free energy change, R is a constant (1.987), T is the absolute temperature.

$$\log K = \frac{-\ F^{o}}{2.303(1.987)(298.1)} = \frac{-13590}{1364.12} = 9.9624$$

$$K = 9.17 \times 10^{9}$$

b. In alkaline solution,

$$\begin{array}{ll} NO_2^- + 2OH^- = NO_3^- + H_2O + 2e^- & E^{o}_{298} = -0.010 \\ 2OH^- = \tfrac{1}{2}O_2 + 2H_2O + 2e^- & E^{o}_{298} = -0.401 \\ \hline NO_2^- + \tfrac{1}{2}O_2 = NO_3^- & E^{o}_{298} = 0.391 \end{array}$$

$$F^{o} = -nFE^{o} = \frac{-(2)(96494)(0.391)}{4.184 \times 1{,}000} = -18.04 \text{ kcal.}$$

$$\text{or } F^{o} = F^{o}_{NO_3^-} - F^{o}_{NO_2^-} = -26.41 - (-8.25) = -18.16 \text{ kcal.}$$

$$\log K = \frac{-18{,}160}{1364.12} = 13.3126 \qquad K = 2.05 \times 10^{13}$$

C Results and Discussion

The calculated values of the free energy changes of the oxidative inorganic nitrogen transformations are reported in tables 1 and 2. The interrelationships between the different reactions are presented in graphical form in figures 1 and 2. In either case a distinction is made between nitrogen oxidation reactions taking place in acid versus those taking place in basic solutions. That the acidity or basidity of the solutions are of great importance is not only demonstrated by the changes in the magnitude of free energy (compare reaction 1 in table 1 with reaction 1 in table 2) but sometimes the reaction may be reversed (compare reaction 10 in table 1 with reaction 9 in table 2). See also the illustrations in figures 1 and 2.

Table 1 - Some calculated thermodynamic quantities of oxidative inorganic nitrogen reactions in acid solution.

	Oxidation reactions			E^{o*}(volt)	F^{o**}(kcal.)	K
1.	$NH_4^+ + 3/2\ O_2$	=	$HNO_2 + H^+ + H_2O$	0.382	-50.51	1.07×10^{37}
2.	$3HNO_2$	=	$H^+ + NO_3^- + 2NO + H_2O$		-3.20	2.23×10^{2}
3.	$HNO_2 + 1/2\ O_2$	=	$NO_3^- + H^+$	0.289	-13.59	9.17×10^{9}
4.	$NH_3OH + 3/2\ O_2$	=	$NO_3^- + 2\ H^+ + H_2O$	0.499	-69.56	9.83×10^{50}
5.	$NH_4^+ + 1/2\ O_2$	=	NH_3OH^+	-0.121	5.46	9.94×10^{-5}
6.	$NH_3OH + 1/2\ O_2$	=	$1/2\ H_2N_2O_2 + H_2O + H^+$	0.789	-38.97	3.67×10^{28}
7.	$NH_4^+ + 2\ O_2$	=	$NO_3^- + 2\ H^- + H_2O$	0.359	-64.10	9.76×10^{46}
8.	$NH_4^+ + O_2$	=	$1/2\ H_2N_2O_2 + H^+ + H_2O$	0.334	-33.49	3.55×10^{24}
9.	$H_2N_2O_2 + O_2$	=	$2\ HNO_2$	0.429	-34.44	1.77×10^{25}
10.	HNO_2	=	$1/2\ N_2O + 1/2\ O_2 + 1/2\ H_2O$	0.061	-2.95	1.44×10^{2}
11.	$NO + 1/4\ O_2 + 1/2\ H_2O$	=	HNO_2	0.239	-5.39	9.00×10^{3}
12.	$NH_3OH^+ + 1/4\ O_2$	=	$1/2\ N_2 + H^+ + 3/2\ H_2O$	3.099	-71.50	2.58×10^{52}
13.	$H_2N_2O_2$	=	$N_2 + 1/2\ O_2 + H_2O$	1.521	-65.09	5.20×10^{47}
14.	$NO_3^- + H^+$	=	$1/2\ N_2 + 5/4\ O_2 + 1/2\ H_2O$	0.011	-1.94	26.2
15.	$NH_4^+ + 1/4\ O_2$	=	$1/2N_2H_5^+ + 1/2H^+ + 1/2\ H_2O$	-0.011	0.13	8.03×10^{-1}
16.	$N_2H_5 + O_2$	=	$N_2 + 2\ H_2O + H^+$	1.399	-132.33	1.02×10^{97}
17.	$H_2N_2O_2$	=	$N_2O + H_2O$	0.990	-40.33	3.67×10^{29}
18.	$NH_4^+ + 7/4\ O_2$	=	$1/2\ N_2O_4 + 3/2\ H_2O + H^+$	0.350	-54.29	6.29×10^{39}
19.	$NH_4^+ + 5/4\ O_2$	=	$NO + 3/2\ H_2O + H^+$	0.396	-45.31	1.66×10^{33}
20.	$NH_4^+ + O_2$	=	$1/2\ N_2O + H^+ + 3/2\ H_2O$	0.582	-53.65	2.15×10^{39}

* Calculated from data presented by Latimer (28).

** Calculated from free energy formation data compiled by Rossini et al. (48).

Table 2 - Some calculated thermodynamic quantities of oxidative inorganic nitrogen reactions in alkaline solution.

	Oxidation reactions			E^{o*}(volt)	F^{o**}(kcal.)	K
1.	$NH_3 + 3/2\ O_2 + OH^-$	=	$NO_2^- + 2\ H_2O$	0.531	-77.66	8.52×10^{56}
2.	$NO_2^- + 1/2\ O_2$	=	NO_3^-	0.391	-18.16	2.05×10^{13}
3.	$NH_2OH + 3/2\ O_2 + OH^-$	=	$NO_3^- + 2H_2O$	0.701	-96.40	4.62×10^{70}
4.	$NH_3 + 1/2\ O_2$	=	NH_2OH	-0.019	0.77	2.73×10^{-1}
5.	$NH_2OH + 1/2\ O_2 + OH^-$	=	$1/2\ N_2O_2^{-2} + 2\ H_2O$	1.131	-53.69	2.28×10^{39}
6.	$NH_3 + 2O_2 + OH^-$	=	$NO_3^- + 2\ H_2O$	0.501	-95.83	1.76×10^{70}
7.	$NH_3 + O_2 + OH^-$	=	$1/2\ N_2O_2^{-2} + 2\ H_2O$	0.556	-52.95	6.49×10^{38}
8.	$N_2O_2^{-2} + O_2$	=	$2\ NO_2^-$	0.581	-50.00	4.50×10^{36}
9.	$NO_2^- + 1/2\ H_2O$	=	$1/2\ N_2O + 1/2\ O_2 + OH^-$	-0.251	11.63	2.98×10^{-9}
10.	$NO + 1/4\ O_2 + OH^-$	=	$NO_2^- + 1/2\ H_2O$	0.861	-19.97	4.35×10^{14}
11.	$NH_2OH + 1/4\ O_2$	=	$1/2\ N_2 + 3/2\ H_2O$	3.440	-79.43	1.61×10^{58}
12.	$N_2O_2^{-2} + H_2O$	=	$N_2 + 1/2\ O_2 + 2\ OH^-$	1.199	-51.50	5.67×10^{37}
13.	$NO_3^- + 1/2\ H_2O$	=	$1/2\ N_2 + OH^- + 5/4\ O_2$	-0.161	17.16	2.63×10^{-13}
14.	$NH_3 + 1/4\ O_2$	=	$1/2\ N_2H_4 + 1/2\ H_2O$	0.301	-7.08	1.54×10^{5}
15.	$N_2\ H_4 + O_2$	=	$N_2 + 2\ H_2O$	1.551	-143.18	9.14×10^{104}
16.	$N_2O_2^{-2} + H_2O$	=	$N_2O + 2\ OH^-$	0.660	-26.74	4.00×10^{19}
17.	$NH_3 + 7/4\ O_2$	=	$1/2\ N_2O_4 + 3/2\ H_2O$	0.415	-66.92	1.14×10^{49}
18.	$NH_3 + 5/4\ O_2$	=	$NO + 3/2\ H_2O$	0.505	-57.95	3.01×10^{42}
19.	$NH_3 + O_2$	=	$1/2\ N_2O + 3/2\ H_2O$	0.721	-66.29	3.91×10^{48}

* Calculated from data presented by Latimer (28).
** Calculated from free energy formation data compiled by Rossini et al. (48).

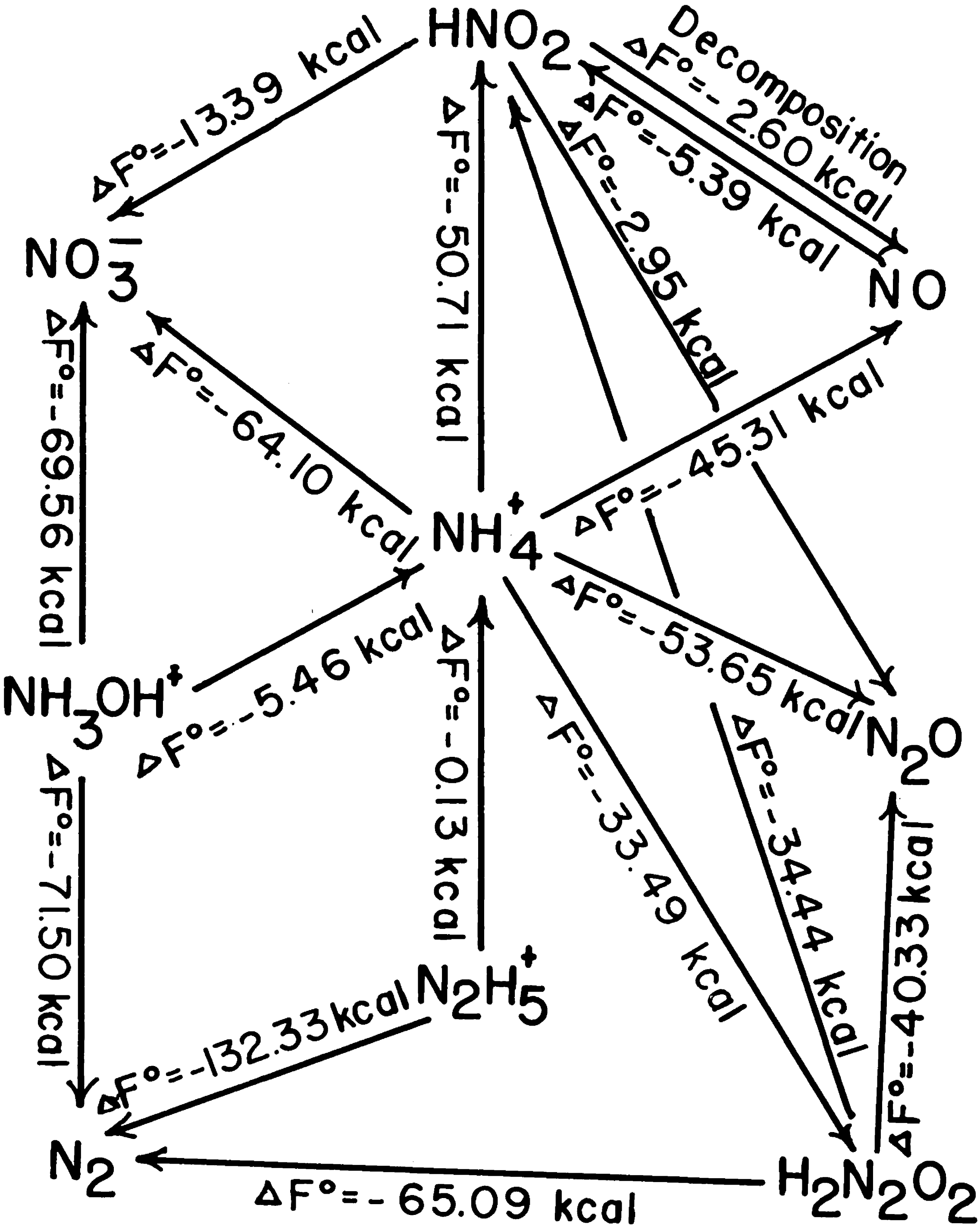


Figure 1-Nitrogen oxidation-reduction reactions in acid solution.

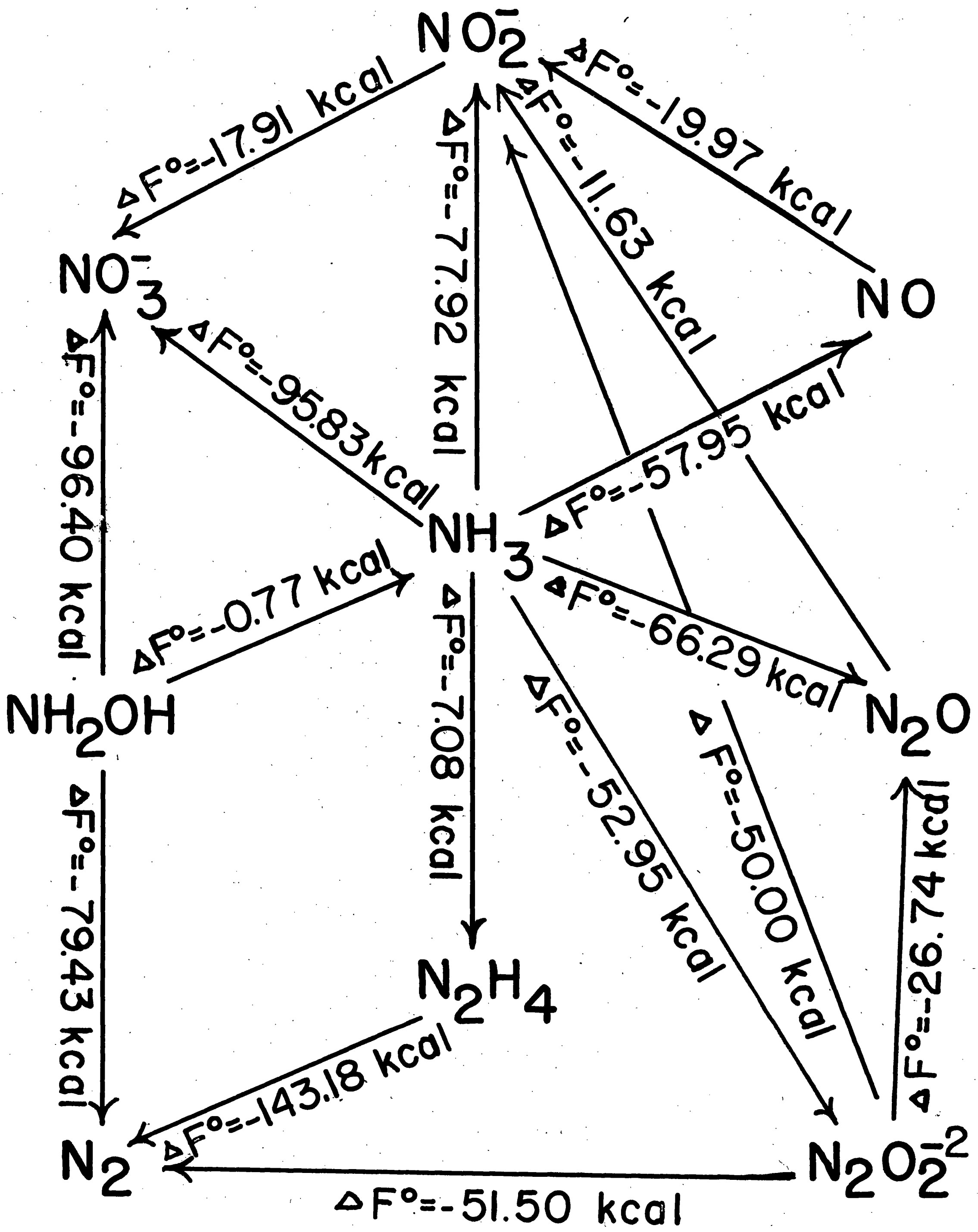


Figure 2-Nitrogen oxidation-reduction reactions in alkaline solution.

Reactions involving nitrification:

The data obtained were not always found to be in complete agreement with those reported in the literature. Some of the deviations are discussed and their significance explained.

Allen (2) described the nitrification process by means of the following reactions:

(a) $2NH_3 + 3O_2 \longrightarrow 2HNO_2 + 2H_2O + 79$ cal. of energy

(b) $HNO_2 + \frac{1}{2}O_2 \longrightarrow HNO_3 + 21.6$ cal. of energy

Baas-Becking et al. (6) found that nitrification reactions with their subsequent free-energy changes were as follows;

(c) $NH_4^+ + 3/2\ O_2 \longrightarrow NO_2^- + H_2O + 2H^+$ $\Delta F = -66.5$ kcal.

(d) $NO_2^- + 1/2\ O_2 \longrightarrow NO_3^-$ $\Delta F = -17.5$ kcal.

In comparing the nitrification reactions of Allen (2) with those given by Baas-Becking et al. (6) it becomes apparent that these reactions differ with respect to their reactants as well as their products and changes in energy. Apparently no consideration was given to the conditions under which the given reactions occurred. The first reaction (a) as given by Allen (2) is somewhat similar to equation 1 in table 2, while the second reaction (b) is similar to equation 3 in table 1. It should be pointed that equation 1 occurs in basic solutions while equation 3 occurs in an acid solution. Similar observations can be made with respect to the nitrification reactions given by Baas-Becking et al. (6) in that reaction (c) will most likely occur in an acid solution (see equation 1, table 1). From the thermodynamic point of view it is of great importance to know the initial form of nitrogen which participates in the reaction, this in turn is often determined by the acidity or basidity of the medium. For example, the free energy of formation of HNO_2 is -13.02 kcal. while that for NO_2^- is -8.50 kcal.

The free-energy change in the oxidation of nitrite to nitrate as given by Baas-Becking et al. (6) agrees very closely with equation 2 in table 2. The difference in free energy change between the oxidation of NH_4^+ to HNO_2 as given by Baas-Becking et al. (6) and reaction 1 in table 1, is probably caused by the use of incorrect thermodynamic quantities. It appears that they used the potential data of the oxidation of NH_4^+ to NO_3^- rather than to NO_2^- for calculating the free energy change of reaction (c). According to Latimer's potential data (equation 7, table 1) the value of free-energy change for the oxidation of NH_4^+ to NO_3^- is -66.24 kcal. This value resembles the ΔF^o associated with the oxidation of NH_4^+ to NO_2^- as given by Baas-Becking et al. (6). Therefore, the free-energy change in equation (c) might be the free energy of oxidation of NH_4^+ to NO_3^- rather than to NO_2^- .

Intermediates in soil nitrification: Although the nitrification reactions are often reported in rather simple equations, it is recognized that they are in essence rather complex and may involve the formation of many intermediates. Some of the possible intermediate products are discussed with respect to the changes in free energy.

A. Hyponitrous acid. Early in 1914, Mumford (43) obtained evidence that hyponitrous acid is an intermediate product between ammonia nitrogen and nitrite. Other investigators (31, 13) also concluded that the formation of hyponitrous acid is an intermediate compound in the biological or photochemical oxidation of ammonia to nitrous acid. The data presented in figures 1 and 2 show that the oxidation of ammonium ion and ammonia to hyponitrous acid are thermodynamically spontaneous reactions. The changes in free energy of the reactions are -33.49 kcal. in acid and -52.95 kcal. in alkaline solutions, respectively. This would indicate that hyponitrous acid, therefore, thermodynamically may be one of the intermediate products in soil nitrification.

B. Nitrous oxide. Nitrous oxide (N_2O) may be one of the intermediate products in soil nitrification only under alkaline conditions. Under such conditions the reactions will proceed as follows; $NH_3 \rightarrow N_2O \rightarrow NO_2^-$ (figure 2). It should, however, be pointed out that N_2O is a gas and may therefore be lost through volatilization.

In acid conditions N_2O may not exist as an intermediate product of soil nitrification since the reaction of $N_2O \rightarrow HNO_2$ is thermodynamically nonspontaneous (figure 1).

C. Nitrous trioxide. This compound is not presented in the tables and graphs since no data on the free energy of formation of N_2O_3 were found in the literature. Waksman (60) suggested that the following reaction is most likely to occur in the oxidation of ammonia, $2NH_3 + 3\ O_2 \rightarrow N_2O_3 + 3\ H_2O$. This reaction may occur spontaneously since the free energy of formation of 3 molecules of water (170.07 kcal.) is of far greater magnitude than the free energy of formation of 2 molecules of

NH_3(12.72 kcal.). Furthermore, from the magnitude of the free energy of formation of other nitrogen compounds it seems rather unlikely that the free energy of formation of N_2O_3 would exceed 157.35 kcal. a quantity required to make the reaction nonspontaneous.

Nitrogen trioxide can be obtained as a blue unstable liquid by cooling a mixture of nitric oxide and nitrogen dioxide to 0°C. The reaction $NO + NO_2 = N_2O_3$ reverses when the system is warmed (29). Reacting with water, it forms nitrous and nitric acids and nitric oxide according to the equation, $2N_2O_3 + H_2O = HNO_3 + 2NO$.

D. Hydroxylamine. Mumford (43) reported that hydroxylamine is an intermediate product between ammonia and nitrite. Other workers (5, 38) came to similar conclusions. Lees (31), however, was unsuccessful in proving that hydroxylamine was an intermediate in the first stage of soil nitrification.

On the bases of the data presented in figures 1 and 2 one might conclude that hydroxylamine may not exist as an intermediate between ammonia and/or ammonium ion and nitrite since the oxidation of NH_4^+ to NH_3OH^+ in acid and NH_3 to NH_2OH in basic solutions are thermodynamically nonspontaneous. The associated changes in free energy being 5.46 kcal. and 0.77 kcal., respectively. On the other hand, if hydroxylamine is present in the soil or produced by other reactions it may, because of its instability, decompose into ammonium ion or ammonia and nitrous oxide. According to Latimer (28), the reaction can be presented as follows:

In acid solutions, $4\ NH_3OH^+ = N_2O + 2NH_4^+ + 3H_2O + 2H^+ \triangle F^o = -129.15$ kcal
In alkaline solution[1]; $4NH_2OH = N_2O + 2NH_3 + 3H_2O \angle F^o = -135.63$ kcal.
That such reactions may indeed occur in the soil is substantiated by Arnold (5), who found very large evolutions of nitrous oxide when hydroxylamine was added to a wet soil.

The formation of hydroxylamine may occur through the reduction of nitrous acid. Latimer (28) states that "On the reduction of nitrous acid, ferrous ion, a weak reducing agent, and titanous ion, a powerful reducing agent, both reduce nitrous acid to nitric oxide; while staneous ion, which is intermediate in potential, reduced nitrous acid to hydroxylamine when the solution is cold, and nitrous oxide when the solution is hot". If some other reducing agent, intermediate in potential, besides staneous ion is present in soils, hydroxylamine may be formed by reduction of nitrous acid.

Reactions involved in oxidation of nitrite to nitrate:

Broadbent et al. (10) reported that after 7 days the added 50 ppm of NO_2-N in Sacramento clay, initial pH 5.54, disappeared, but there was only an 8 ppm increase in NO_3-N. However, the added 50 ppm of NO_2-N in Salinas clay, initial pH 8.11, seemed completely oxidized to NO_3-N after 7 days of incubation. They concluded that "when nitrite is added to soils it disappears rapidly, but in acid soils it is not quantitatively converted to nitrate, some of it being lost from the system. This loss is not due to a biological process, since it also occurs in sterilized acid soils." As shown in figure 1, in acid solutions, nitrite would thermodynamically undergo three different

---

[1] This reaction is based upon calculations by the author.

reactions, namely, nitrite decomposition to NO with a free-energy change of -2.60 kcal., nitrite oxidation to nitrate with a free-energy change of -13.39 kcal., and nitrite reduction to nitrous oxide with a free-energy change of -2.95 kcal. In alkaline soils as shown in figure 2, nitrate seems to be the only product. It is, therefore, reasonable to assume that part of the NO_2-N in acid soils might be either reduced to N_2O or decomposed to NO gas which may be lost in the air.

Nitrogen losses:

Nitrogen losses from soil can in general be classified into three categories; (1) loss or reduction resulting from nutrient uptake by plants, (2) losses caused by leaching, (3) losses in gaseous forms. It is the latter that is recently receiving increased attention and seems to be of a far greater magnitude than was previously assumed.

a. Loss of ammonia.

The loss of nitrogen in ammonia form might be either due to improper application of liquid NH_3-N to soil or to the reaction of ammonium salts with soil bases to form NH_3. Ammonium salts, like free bases, are largely ionized. In the presence of OH^- in the soil solution, an equilibrium will be established resulting in a conversion of NH_4 to NH_3 according to the reaction,

$$NH_4^+ + OH^- = NH_3 + H_2O$$

with a $\Delta F^o = -6.46$ kcal. Increasing concentrations of OH^- in the soil solution will shift the equilibrium to the right and the NH_3 may under certain conditions, be subject to volatilization. Such losses of NH_3 from ammonium salts have been reported (24, 56, 55).

b. Other gaseous nitrogen losses.

Wagner and Smith (55) found that 65% of the gaseous nitrogen loss from a urea treated Weldon silt loam was in the form of nitrous oxide. However, no nitrous oxide losses were obtained from a similarly treated Sharkey clay. Broadbent (9) pointed out that denitrification in soils may give rise to nitrous oxide as well as free nitrogen, and that this reaction can occur under aerobic conditions. Arnold (5) found that soils which are approaching saturation, may rapidly release large amounts of their available nitrogen as nitrous oxide, which in turn indicates that oxygen deficiency enhances nitrous oxide production.

Data presented in figures 1 and 2 may elucidate this reaction further. Considering hyponitrous acid an intermediate in nitrification (13, 31, 43), it is evident that N_2O as well as N_2 can easily be obtained from this compound under anaerobic conditions since the reduction of hyponitrous acid to N_2O as well as N_2 are thermodynamically spontaneous. On the other hand, N_2O can also be formed under aerobic conditions since the oxidation reactions of NH_3 or NH_4^+ to N_2O are spontaneous reactions with $\Delta F^{o\prime}$s of -66.29 and -53.65 kcal., respectively. The data also show that NO may result from the oxidation of NH_3 and NH_4^+. It is well recognized that these intermediates also arise by reduction of NO_3^- and NO_2^- as the result of heterotrophic microbial activity.

c. Losses resulting from nitrogen compound interactions:

1. The interaction of ammonium ion with nitrite ion. Dahr (16) concluded that the loss of nitrogen from soil was due to an oxidation process followed by photochemical and catalytic decomposition. When a a solution of NH_4NO_2 was exposed to light it decomposed into nitrogen and water. This decomposition was facilitated by acids and different solid surface. Wahhab and Uddin (57) also concluded from their work that light had a profound influence on the loss of nitrogen due to a reaction between the NH_4^+ and NO_2^- ions. According to Treadwell and Hall (54) small quantities of ammonium salts in solution can be removed by boiling with a little sodium nitrite and acetic acid. The reaction seems similar to the photochemical reaction suggested by Dahr (16);

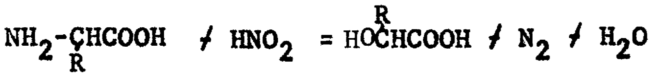
$$NH_4 + NO_2^- = N_2 + 2H_2O \qquad \Delta F^o = -85.88 \text{ kcal.}$$

Elemental nitrogen might be released in soil this way since it is a spontaneous reaction.

2. <u>The reaction between nitrite and urea</u>. The presence of nitrite and urea in soil solution may result in the evolution of elemental nitrogen according to the equation:

$$2HNO_2 + CO(NH_2)_2 = CO_2 + 3H_2O + 2N_2 \quad \Delta F^o = -109.67 \text{ kcal.}$$

3. <u>Van Slyke reaction</u>. Ammino acids might be produced in soil through the decomposition of soil organic matter. The "Van Slyke reaction", therefore, might be carried out in soil solution causing evolution of elemental nitrogen.



$$NH_2\text{-}\underset{R}{C}HCOOH + HNO_2 = HO\overset{R}{C}HCOOH + N_2 + H_2O$$

The reaction is favored by acid solution and characterized with aliphatic primary amines. Allison (3) obtained evidence that nitrous acid can react with alanine to evolve nitrogen gas at pH values of 4.5 or lower.

D. Summary

Free energy changes of oxidative inorganic nitrogen transformations in acid and basic media were calculated, interrelated and used to interpret research data reported in the literature. The results obtained may be summarized as follows:

1. With respect to reactions involving nitrification, the data obtained were not always found to be in agreement with those reported in the literature. The primary reason for these deviations was that the pH of the medium had often not been considered in formulating these reactions.

2. Hyponitrous acid might well be one of the intermediate products in soil nitrification since the oxidation of either the ammonium ion or ammonia are thermodynamically spontaneous reactions.

3. Under alkaline conditions nitrous oxide (N_2O) may be one of the intermediate products in soil nitrification.

4. Hydroxylamine can not exist as an intermediate between ammonia and/or ammonium ion and nitrite because the oxidation of NH_3 to NH_2OH in basic and of NH_4^+ to NH_3OH^+ in acid solutions are nonspontaneous.

5. In acid solutions nitrite will thermodynamically undergo three reactions; it may decompose to NO, oxidize to NO_3^- or be reduced to N_2O. In alkaline solutions NO_3^- seems to be the only product.

6. Elemental nitrogen may evolve from reactions between NH_4^+ and NO_2^-, NO_2^- and $CO(NH_2)_2$, and NO_2^- and $NH_2\underset{R}{C}HCOOH$.

II RELATIONSHIPS BETWEEN AMMONIA VOLATILIZATION, AMMONIA CONCENTRATION AND WATER EVAPORATION

A. Introduction

It has become recognized that such factors as soil pH, texture, moisture and temperature as well as sources, depth of placement and rate of nitrogen application are of great importance in the evaluation of volatile nitrogen losses in general. Consideration of these losses has become especially important since heavy nitrogen fertilization has become an established practice for many crops.

Ammonia is among the many compounds which contribute to volatile nitrogen losses. The mechanisms by which ammonia leaves the soil require further investigation. Of particular interest is the relationship between ammonia volatilization and water evaporation. The popular concept has been that these two phenomena occur simultaneously and in definite relationship to each other. Wahhab et al. (56) found that NH_3 was not entirely independent of the original soil moisture content and that there was a constancy of ratio between NH_4-N and moisture losses when $(NH_4)_2SO_4$ was applied to alkaline soils. Jewitt (24) concluded from his work that moisture content did not appear to have an important effect upon NH_3-N volatilization but that loss of ammonia from some alkaline soils upon application of $(NH_4)_2SO_4$ was closely related to moisture loss. Martin and Chapman (37) stated that increasing the amount of ammonium nitrogen to an alkaline soil increased the total quantity of nitrogen lost but did not appreciably effect the percentage lost and that the moisture content of the soil had little effect except that evaporation of water was necessary for appreciable volatilization of ammonium from the soil to occur. It was shown by Jackson and Chang (22) that moisture content, air-dry soil as compared to field-moist, exerted only a slight effect on the sorption capacity for gaseous ammonia.

The objectives of the investigations to be reported here were (1) to measure the effect of soil texture, soil water and speed of air flow over the soil surface on the relationship between water evaporation and ammonia volatilization, (2) to study the relationship between ammonia concentration and ammonia volatilization and (3) to express obtained differences or similarities in mathematical terms.

B. Materials and Methods

An acid Davidson clay (pH5.4), a slightly acid Norfolk fine sandy loam (pH 6.7) and two basic soils, Yolo loam[1] (pH 7.4) and Salinas clay[1] (pH 7.8) were used in these investigations.

After many preliminary trials the following method was used; fifty gram portions of air-dry soil were placed in 500-ml. suction flasks. A calculated amount of NH_4OH was diluted in a certain volume of water and applied to the soil surface in order to bring the soils to the desired water and nitrogen levels. After the soil had become thoroughly penetrated with the solution, aeration was begun and continued until the soil was air dry. Ammonia free air was drawn over the soil surface and was passed through a standard H_2SO_4 solution. This solution was back titrated with NaOH using methyl orange as an indicator to determine the amount of ammonia volatilized. The water loss was measured by weighing the bottles at given time intervals. In some cases the air was saturated with water by bubbling it through water prior to being led over the soil surface. The experiments were conducted at room temperature and repeated. The rate of air flow was measured by a "Precision" Wet Test Meter[2].

C. Results and Discussion

A series of experiments were conducted to study the relationship between ammonia volatilization and water evaporation under varying conditions. The soils used in these investigations were a fine textured soil, Davidson clay, and a coarse textured soil, Norfolk fine sandy loam.

a. Ammonia Volatilization in a Water Unsaturated Atmosphere

Ammonia free air was passed over a moist soil surface by suction force. The subsequent losses of ammonia and water from a Norfolk fine

---

[1] Obtained from Dr. F. E. Broadbent, College of Agriculture, Davis, Cal.

[2] "Precision" Wet Test Meter, Precision Scientific Co., Chicago, Ill.

sandy loam and Davidson clay are presented in tables 3 and 4. The results show that the rate of ammonia volatilization decreased with increasing time (figure 3) and followed in general the equation;

$$\frac{N}{t} = at^b \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 1$$

where N is the ammonia loss in ppm, t is time in hours, a and b are constants. By plotting the logarithm of ammonia volatilization per hour against log t, straight lines were obtained (figure 4). The equations became;

(a) for Norfolk fine sandy loam $N/t = 190.7\ t^{-0.7886}$ 2

(b) for Davidson clay $N/t = 48.43\ t^{-0.6819}$......... 3

By using these equations, the average calculated experimental errors for the ammonia volatilization from the Norfolk fine sandy loam and Davidson clay were found to be 3.5% and 1.6% respectively, indicating that these equations described very well the ammonia volatilization from these soils. The rate of water evaporation for either soil stayed constant with increasing time (figures 5,6) and followed the general equation;

$$M = kt \text{ or } M/t = k \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 4$$

where M/t is the percent water loss per hour, and k is a constant. The magnitude of the latter depends upon such factors as speed and relative humidity of the air flown over the soil surface, temperature, soil texture, etc. The equations describing water loss from the soils studied became;

<u>Table 3.</u> Ammonia volatilization and water loss from a Norfolk fine sandy loam in a water unsaturated atmosphere.

Time Intervals	Water Content	Water Loss	NH_3-N Content	NH_3-N Loss	NH_3-N/water Loss
Hrs.	%	%	ppm	%	
0	41.0	0	600.0	0	0
3	37.7	3.3	325.2	45.8	13.9
6	33.2	7.8	317.4	47.1	6.0
8	32.6	8.4	302.4	49.6	5.9
14.5	25.2	15.8	273.6	54.4	3.4
17.0	21.8	19.2	259.8	56.7	3.0
19.5	20.2	20.9	249.0	58.5	2.8
22.5	16.3	24.7	233.4	61.1	2.5
30.5	8.3	32.7	200.4	66.6	2.0
40.5	0.5	40.5	164.4	72.6	1.8
46.0	0.0	41.0	152.4	74.6	1.8

Table 4. Ammonia volatilization and water loss from Davidson clay in a water unsaturated atmosphere.

Time Intervals	Water Content	Water Loss	NH_3-N Content	NH_3-N Loss	NH_3-N/water Loss
Hrs.	%	%	ppm	%	
0	41.0	-	552.0	-	-
3	36.7	4.3	483.0	12.5	2.9
6	31.9	9.1	469.0	15.0	1.7
9	26.4	14.6	455.0	17.5	1.2
12	21.6	19.4	443.6	19.6	1.0
22.5	6.9	34.1	419.6	24.0	0.7
25.5	3.3	37.7	414.4	24.9	0.7
29.5	1.8	39.2	407.7	26.1	0.7
33.5	1.2	39.8	402.7	27.0	0.7
47.0	1.2	39.8	393.2	28.6	0.7

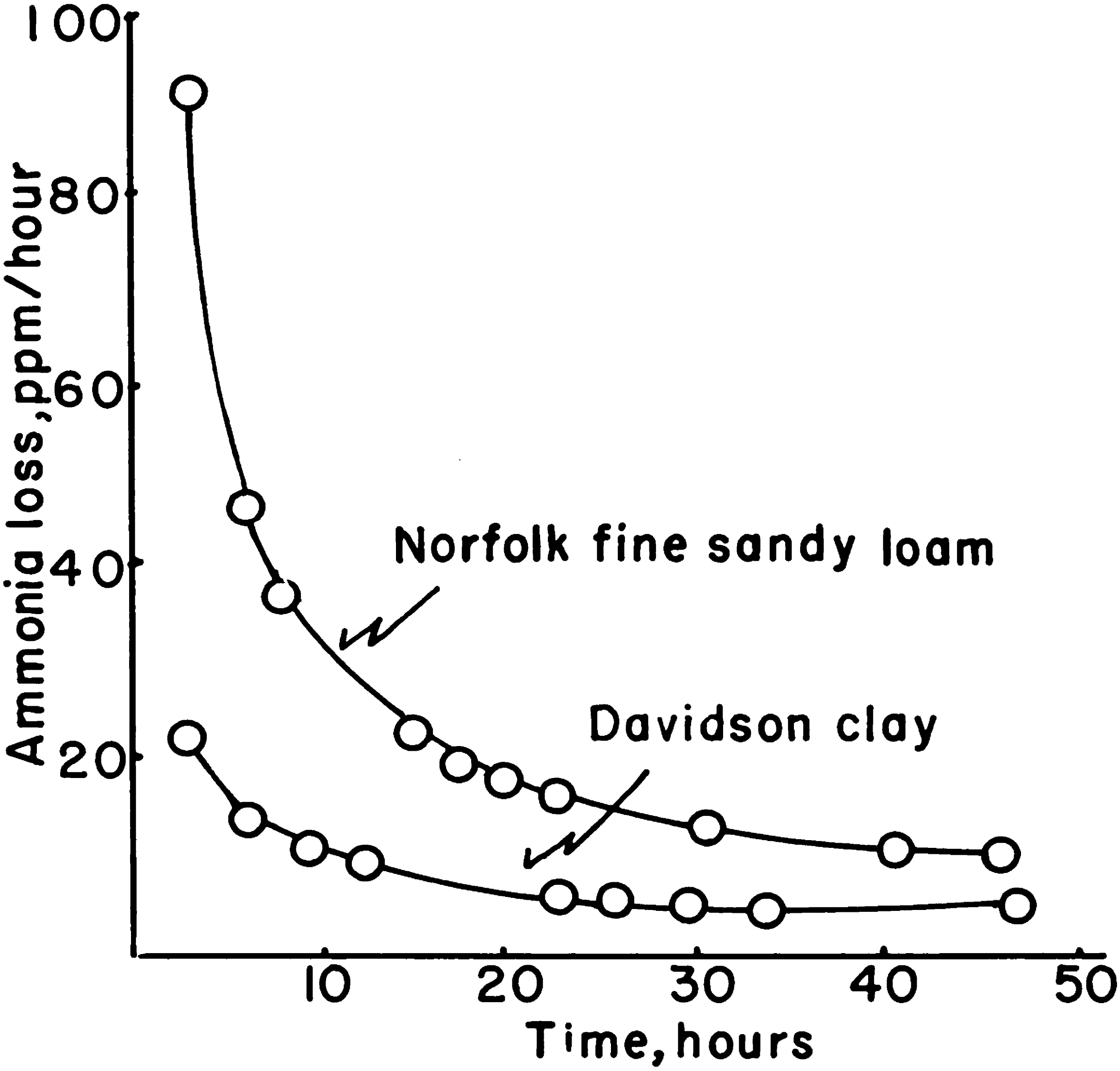


Figure 3-Rate of ammonia volatilization from two soils in a water unsaturated atmosphere.

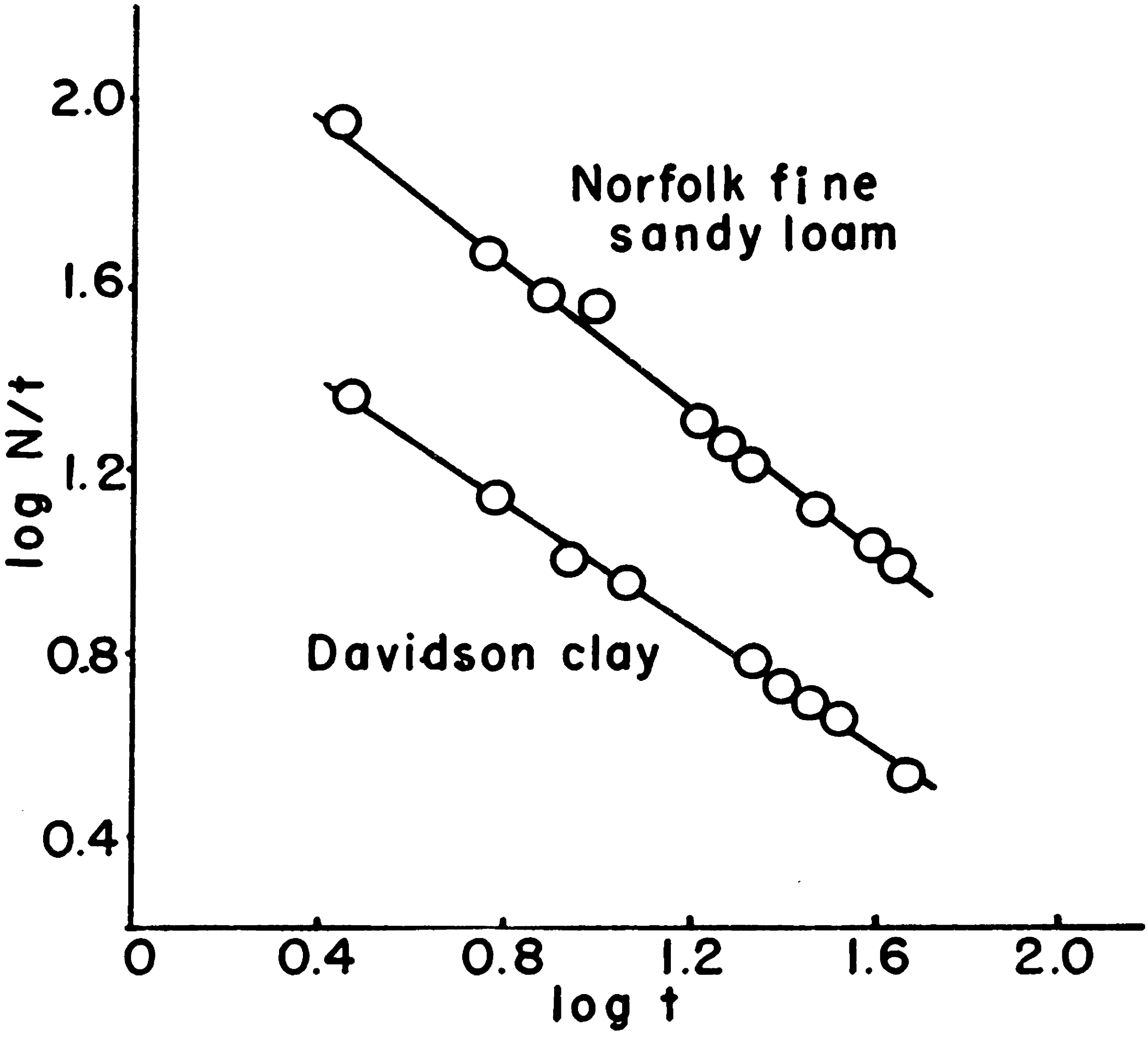


Figure 4-Ammonia volatilization in a water unsaturated atmosphere plotted according to the proposed equation $N/t = at^b$.

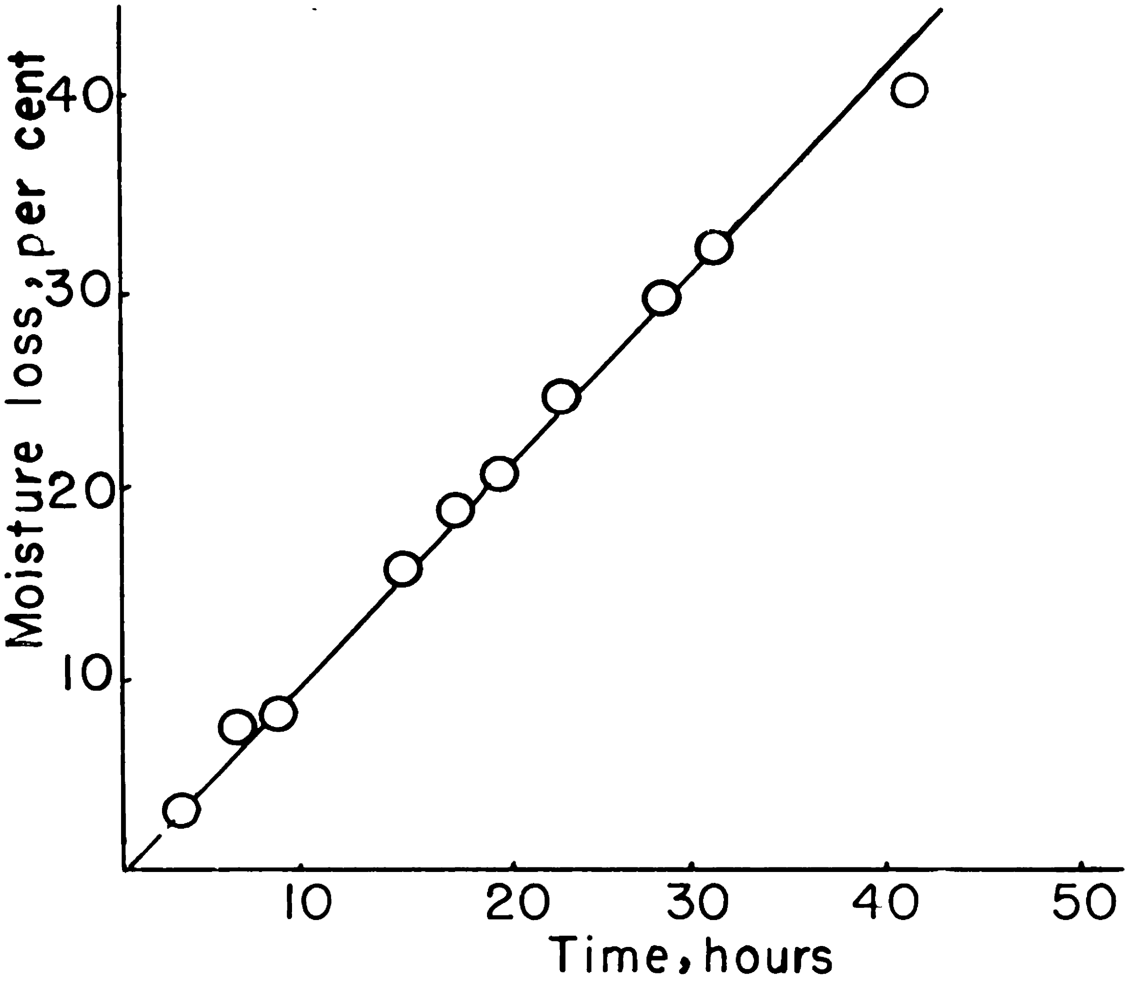


Figure 5-Water evaporation from Norfolk fine sandy loam.

(a) for Norfolk fine sandy loam $M = 1.071\ t$ or $M/t = 1.071$ 5

(b) for Davidson clay $M = 1.480\ t$ or $M/t = 1.480$ 6

The average calculated error for water loss by using above equations was 8.6% and 4.1% respectively.

The results obtained in this experiment show then that the rate of ammonia volatilization decreases with time, while the rate of water evaporation stays constant. This conclusion does not agree with the results obtained by Wahhab et al. (56) who found a constancy of ratio between ammonia loss and moisture loss.

b. Ammonia Loss in a Water Saturated Atmosphere

In this experiment ammonia-free water saturated air was led over a Norfolk fine sandy loam and Davidson clay. The water content stayed constant indicating that an equilibrium was maintained between the water and its vapor.

The results (table 5 and 6) showed that ammonia volatilization in a water saturated atmosphere followed the same function obtained in a water unsaturated atmosphere (compare figure 7 with figure 3). By plotting the logarithm of ammonia loss per hour against the logarithm of the units of time straight lines were obtained (figure 8). It appears that after a 20-hour period the ammonia volatilization on a Norfolk fine sandy loam in a water saturated atmosphere (figure 7) is roughly of the same magnitude as that in a water unsaturated atmosphere. The equation for Norfolk fine sandy loam became;

$$n/t = 161.5\ t^{-0.7390} \quad \text{..................} \quad 7$$

and for Davidson clay

$$n/t = 10.43\ t^{-0.3714} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 8$$

By using equations 7 and 8 the average calculated experimental error for ammonia volatilization into a water saturated atmosphere was 2.3 and 1.5 percent, respectively. These results indicate that there is no relationship between ammonia volatilization and water evaporation since ammonia volatilization took place in absence of water evaporation from the soil.

c. Ammonia volatilization with varying speeds of air-flow

The objective of this experiment was to study the effect of varying speeds of air-flow on water evaporation and ammonia volatilization from a Davidson clay. Two speeds of air-flow were used, 201.6 and 15.0 liters per hour per 78.5 cm^2 of soil surface respectively. The data are presented in table 7.

When the rate of ammonia loss obtained with the high speed of air flow, was plotted against that obtained with the low speed of air flow, using the same time intervals (figure 9), a linear function was obtained, indicating that ammonia volatilization followed the same function irrespective of variation in speeds of air-flow. The equation read,

$$A_n = 1.9750B_n - 1.0609 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 9$$

where A_n is the ammonia loss in ppm per hour with an air flow of 201.6 $l/hr/78.5\ cm^2$, and B_n is the ammonia loss in ppm per hour with an air flow of 15.0 $l/hr/78.5\ cm^2$.

When the rate of water loss (M_1) obtained with the low speed of

Table 5 - **Ammonia volatilization from Norfolk fine sandy loam in a water saturated atmosphere**

Time Intervals	Water content	Water Loss	NH_3-N Content	NH_3-N Loss
Hrs.	%	%	ppm	%
0.0	28.6	0.0	600.0	0.0
3.0	28.5	0.1	378.0	37.0
6.0	28.6	0.0	336.0	44.0
8.0	28.5	0.1	321.0	46.5
14.5	28.1	0.5	294.0	51.0
17.0	28.1	0.5	273.0	54.5
19.5	28.7	-0.1	250.2	58.3
22.5	28.6	0.0	232.8	61.2
30.5	28.1	0.5	205.8	65.7
40.5	27.1	1.5	163.8	72.7

Table 6 - Ammonia volatilization from Davidson clay in a water saturated atmosphere

Time Intervals	Water Content	Water Loss	NH_3-N Content	NH_3-N Loss
Hrs.	%	%	ppm	%
0	41.0	0	600	0
3	41.8	0.8	585.6	2.4
6	41.7	0.7	567.0	5.3
9	41.7	0.7	559.8	6.7
12	41.8	0.8	550.8	8.2
14.5	41.8	0.8	543.0	9.5
22.5	41.5	0.5	532.2	11.3
33.5	40.4	-0.6	507.0	15.5
45.5	41.4	0.4	483.0	19.5
69.5	40.5	-0.5	463.2	27.3

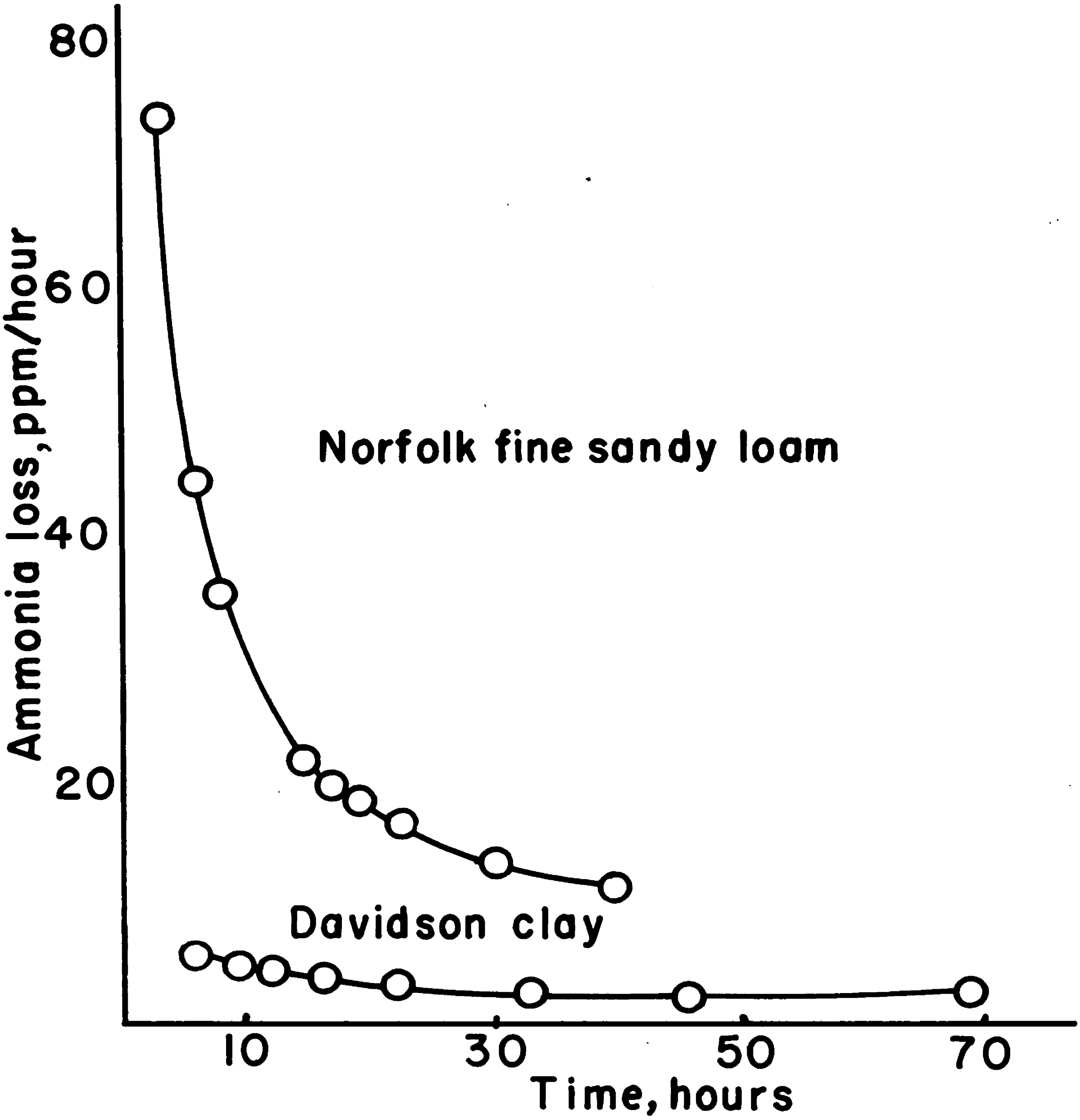


Figure 7-Rate of ammonia volatilization from two soils in a water saturated atmosphere.

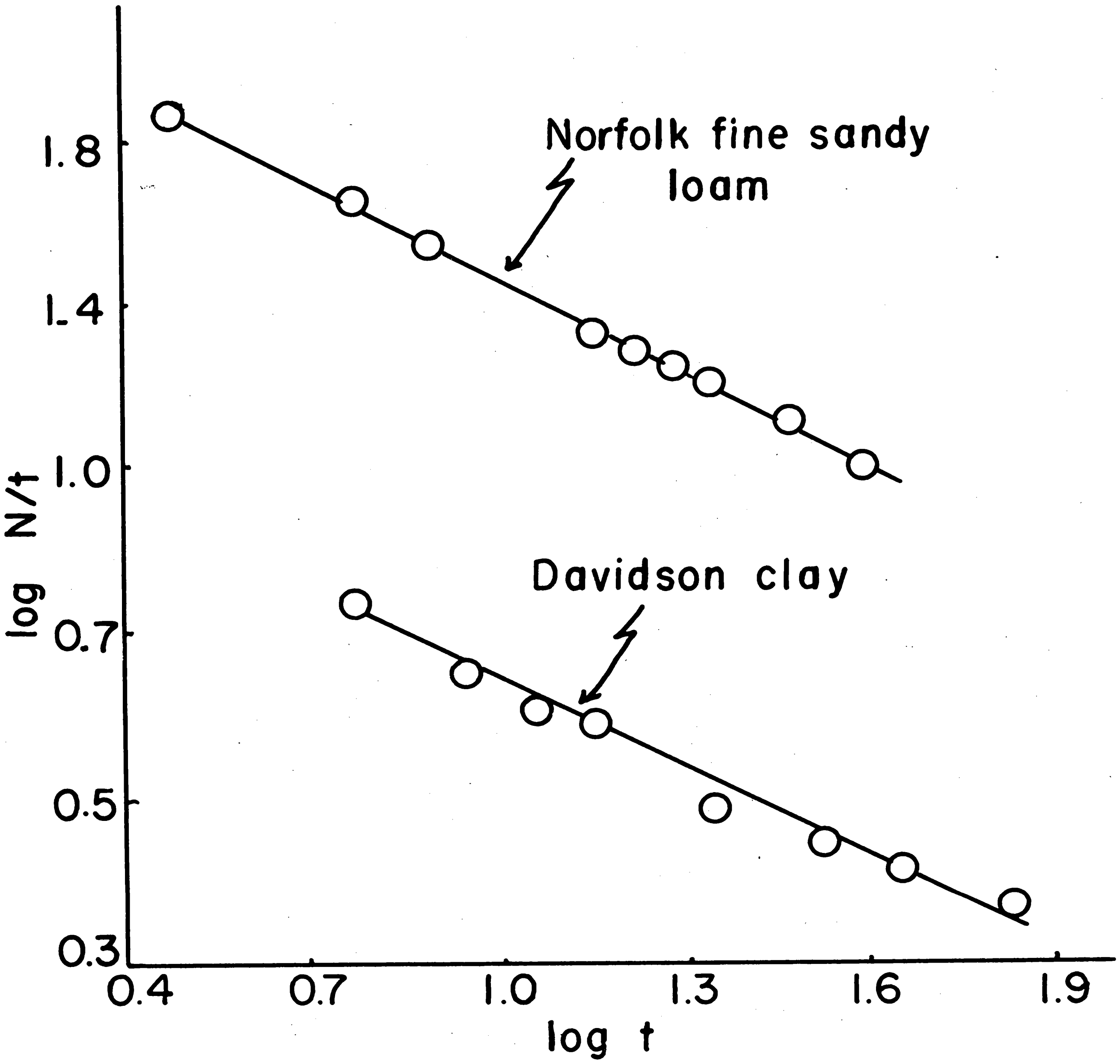


Figure 8-Ammonia volatilization in a water saturated atmosphere plotted according to the proposed equation $N/t = at^b$.

Table 7 - Ammonia volatilization and water evaporation from Davidson clay at different speeds of air-flow.

Time Intervals	201.6 liter per hour per 78.5 cm^2				15.0 liter per hour per 78.5 cm^2			
	Water Content	Water Loss	NH_3-N Content	NH_3-N Loss	Water Content	Water Loss	NH_3-N Content	NH_3-N Loss
Hrs	%	%	ppm	%	%	%	ppm	%
0	41.0	----	552	----	41.0	----	552	----
3	36.7	4.3	483	12.5	40.3	0.7	516	6.5
6	31.9	9.1	469	15.0	39.6	1.4	504.5	8.6
9	26.4	14.6	455	17.5	39.0	2.0	497.8	9.8
12	21.6	19.4	443.6	19.6	38.5	2.5	491.8	10.8
22.5	6.9	34.1	419.6	24.0	36.3	4.7	474.9	14.0
25.5	3.3	37.7	414.4	24.9	35.1	5.9	470.0	14.9
29.5	1.8	39.2	407.7	26.1	34.8	6.2	465.1	15.7
33.5	1.2	39.8	402.7	27.0	33.6	7.4	457.8	16.9
47	1.2	39.8	393.2	28.6	30.2	10.8	442.0	20.0
59					27.5	13.5	429.0	22.2
71					25.2	15.8	420.0	24.0
83					22.0	19.0	413.0	25.4
95					20.5	20.5	407.5	26.2
107					18.5	22.5	403.2	27.0
119					15.8	25.2	399.6	27.6
143					11.4	29.6	397.5	28.0
158.5					6.8	34.2	394.6	28.5
174.0					4.1	36.9	393.6	28.6
187.5					1.6	39.4	391.7	29.1

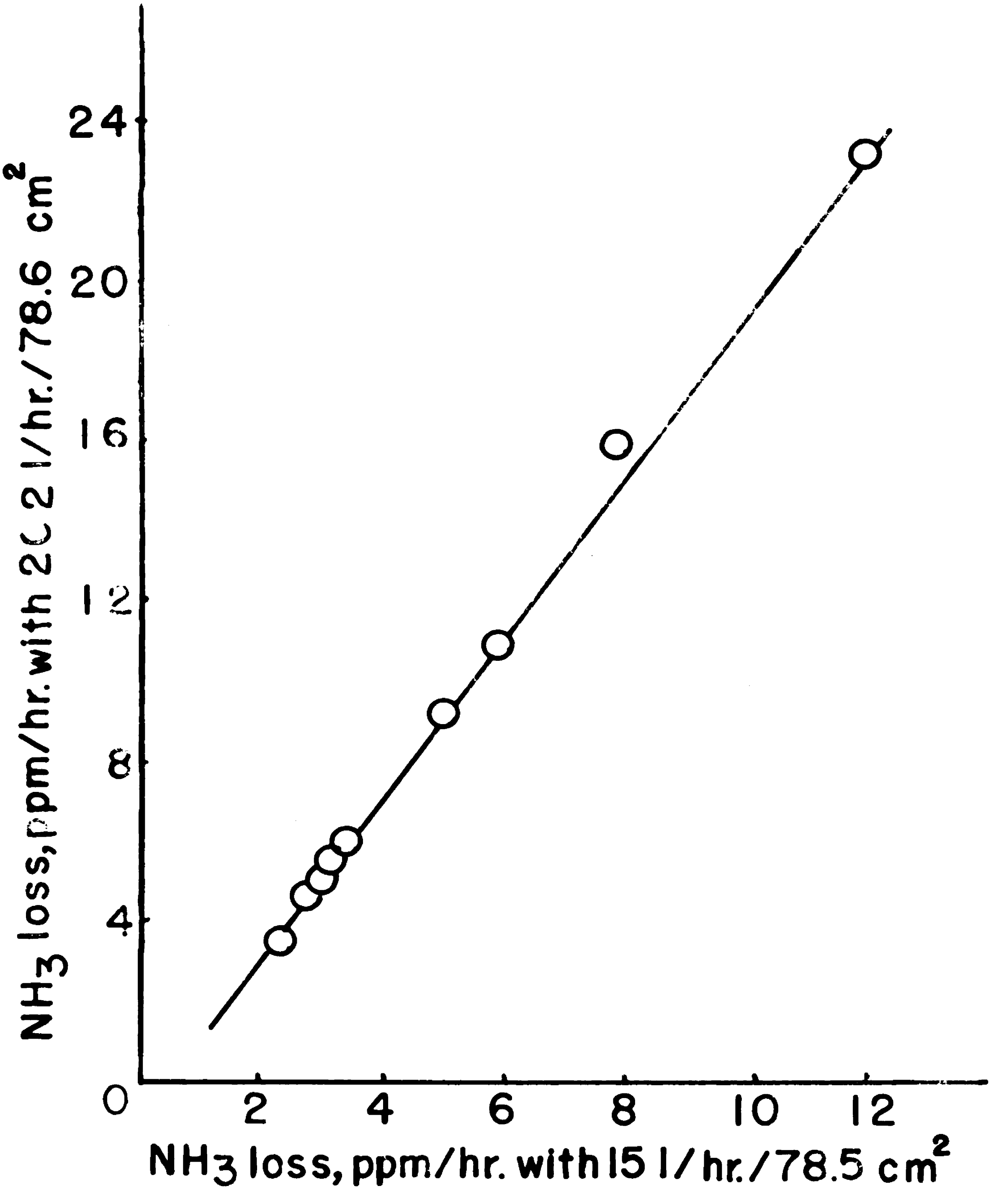


Figure 9-Ammonia volatilization from Davidson clay with different speeds of air flow.

air-flow was plotted against the water loss (M_2) obtained with a high speed of air-flow, using the same time intervals, a linear function was obtained (figure 10), which is expressed by the equation:

$$M_2 = 6.73\ M_1 \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ 10$$

In comparing equation 9 with equation 10 it is evident that with an increase in speed of air-flow the rate of water evaporation proceeds much more rapidly than the rate of ammonia volatilization. The data show that ammonia volatilization and water evaporation follow different functions under this condition, hence, no constancy of ratio between volatilization and water evaporation is observed.

d. Ammonia volatilization related to its concentration in soils

The loss of ammonia was determined after the soils had become completely air-dry (table 8). A graphical presentation of the data (figure 11) shows that when ammonia loss is plotted against the amount of ammonia applied a linear function is obtained. This function can be expressed by the general equation:

$$Y = bX + C \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ 11$$

where Y is the amount of ammonia volatilized in ppm, X the amount of ammonia applied to the soil, b and C are constants. For the soils investigated the following equations were obtained:

Norfolk fine sandy loam	$Y = 0.6977\ X - 2.11$
Davidson clay	$Y = 0.2665\ X - 34.94$
Yolo loam	$Y = 0.3097\ X - 22.66$
Salinas clay	$Y = 0.4194\ X - 14.85$

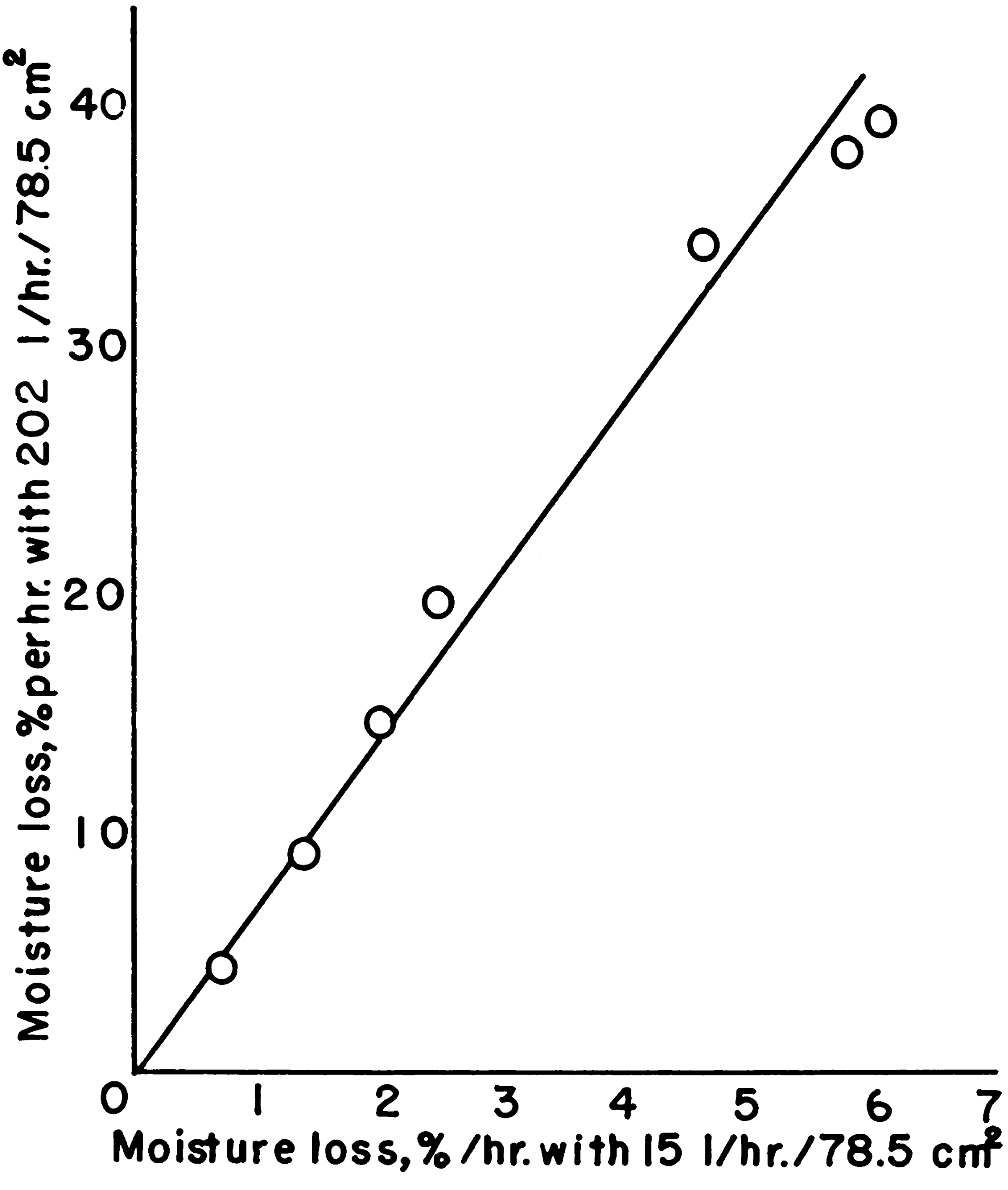


Figure 10–Water evaporation from Davidson clay with different speeds of air flow.

Table 8 - Ammonia volatilization in relation to amount of ammonia applied.

Soil type	Ammonia applied (ppm)	Ammonia lost (ppm)	Ammonia lost (%)	pH initial	pH final
Davidson clay	150	7.5	5.0	5.4	6.0
	400	71.6	17.9	5.4	6.6
	500	92.8	18.6	5.4	6.9
	600	122.0	20.3	5.4	7.0
	690	155.0	22.5	5.4	7.3
Norfolk fine sandy loam	50	35.3	70.6	6.7	7.5
	100	67.2	67.2	6.7	7.6
	200	132.8	66.4	6.7	7.8
	400	278.0	69.5	6.7	8.0
	546	402.0	73.7	6.7	8.1
Yolo loam	263	59.0	22.4	7.4	7.7
	439	113.0	25.8	7.4	8.0
	615	168.0	27.4	7.4	8.1
Salinas clay	91	26	28.6	7.8	8.9
	272	94	34.6	7.8	9.0
	454	178	38.8	7.8	9.0
	636	252	36.5	7.8	9.0

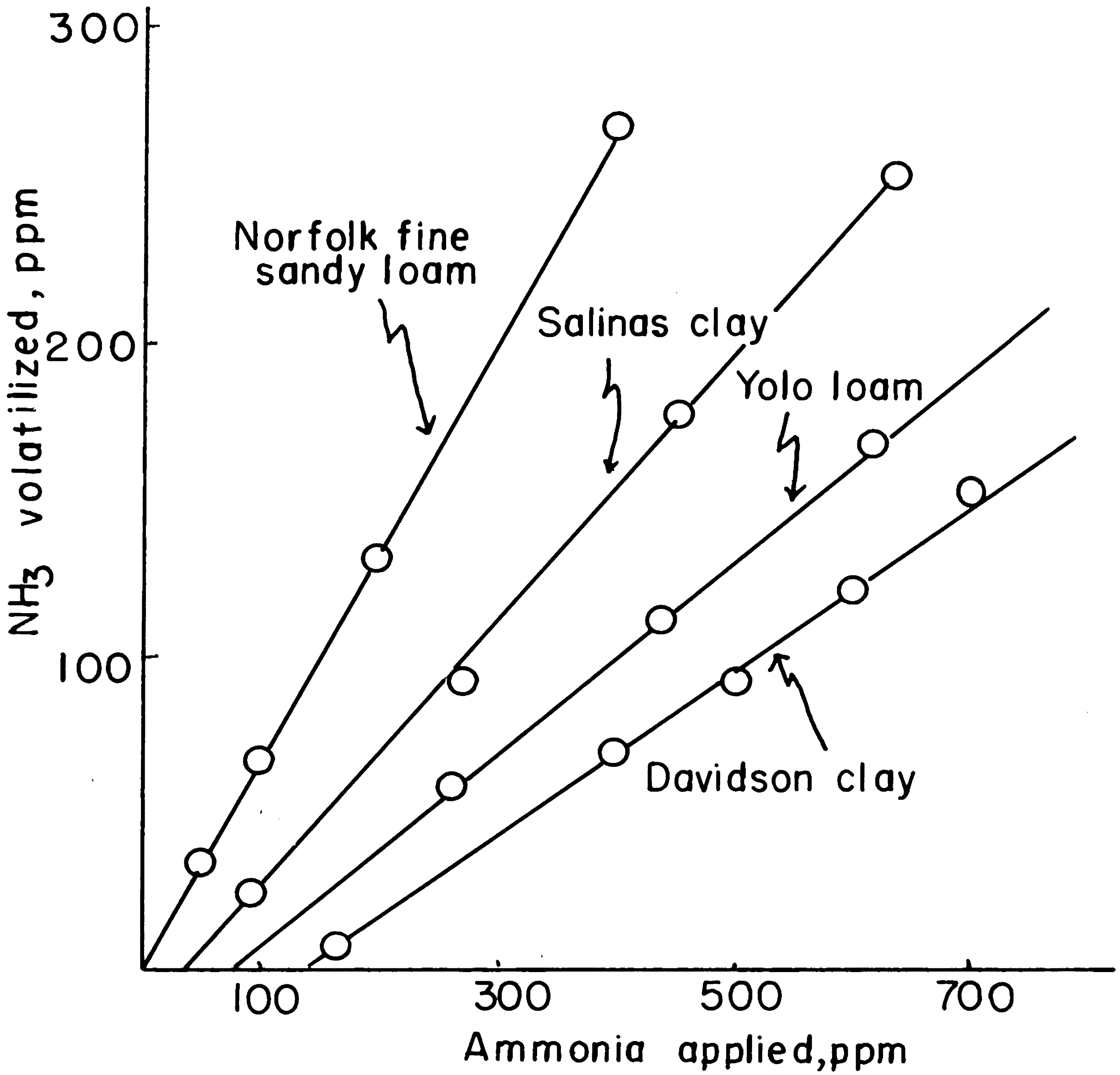


Figure 11-Ammonia volatilization in relation to amount of ammonia applied.

The slopes for these different soils (figure 11) indicate that when equal amounts of ammonia are applied to these soils, the loss of ammonia stands in the order of: Norfolk fine sandy loam > Salinas clay > Yolo loam > Davidson clay. It was found that the ammonia losses from the three finer textured soils were proportional to their original soil pH's. This phenomenon indicates a relationship between the OH^- concentration and the ammonia loss; the OH^- ions reacting with the NH_4 in the soil solution which in turn results in the subsequent release of NH_3.

The large ammonia losses from the Norfolk fine sandy loam may be a reflection of its coarser texture.

By extrapolating the straight lines in figure 11 beyond the region of experimental measurements until they interact the X axis ($Y = 0$), one finds the corresponding X values for the soils to be;

Norfolk fine sandy loam	3.02
Salinas clay	35.41
Yolo loam	73.17
Davidson clay	131.11

These theoretical values suggest the rate of ammonia application at which a minimum amount of ammonia volatilization can be expected. In areas where large amounts of anhydrous ammonia are used as a fertilizer such values may become of practical importance.

D. Summary

Ammonia volatilization and water evaporation from soils followed different functions. These functions were not affected by differences in soil texture, soil water, speed and relative humidity of air flowing over the soil surface.

A linear relationship was observed between the rate of ammonia applied (up to 600 ppm) and ammonia volatilized. The ammonia losses from finer textured soils were proportional to their original soil pH's. The large ammonia losses from the coarse textured soil indicate that soil texture is a keen factor in ammonia volatilization.

III KINETICS OF AMMONIA VOLATILIZATION IN SOILS

A. Introduction

The application of any kind of fertilizer to soil results in the initiation of many chemical and physical reactions. The extent to which these reactions are completed at equilibrium depends upon the nature of, as well as the relationship between, the different soil components, solid, liquid and gas, and hence will vary between, as well as within soil types. Other factors such as soil temperature, rates of fertilizer application and microbial activity will further influence these reactions.

It can then be visualized that at a given temperature and pressure different equilibria will be established when ammonia or ammonium sources are applied to soil, namely:

$$\begin{array}{lcl} NH_3 \text{ (soil air)} & & \\ \downarrow\uparrow & & \\ \left.\begin{array}{l} NH_3 \text{ (soil solution)} \\ \downarrow\uparrow \\ NH_4^+ \text{ (soil solution)} \end{array}\right\} & \rightleftharpoons & \left\{\begin{array}{l} NH_3 \\ NH_4^+ \end{array}\right. \text{(soil solids)} \end{array}$$

Any change in the ammonia and/or ammonium concentrations in the soil air and soil solution may shift the equilibria.

The primary objective of this study is to investigate the kinetics of ammonia volatilization from different soils after applications of varying rates of ammonium hydroxide.

B. Materials and Methods

An acid soil, Davidson clay, a neutral Norfolk fine sandy loam, and two basic soils, Yolo loam and Salinas clay, were used in this investigation. After air drying and sieving, 50 grams of soil was introduced into 500 ml. suction flasks. After the addition of ammonium hydroxide solutions, the soils were shaken intermittently for two hours in order to hasten equilibrium. Air suction was then applied until the soils were air-dry. The ammoniacal air was passed through sulfuric acid and the amount of volatilized ammonia determined by back titration with sodium hydroxide using methyl orange as an indicator.

C. Results and Discussion

It is found that when varying rates of NH_4OH (actually NH_3 / H_2O) are applied to different soils the rate of ammonia volatilization followed in each instance a first order reaction. A first order reaction describes the relationship between rate of reaction and the concentration of the reacting substance by means of the following mathematical equation (15);

$$-\frac{dc}{dt} = kc \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

where c is the concentration of the reactant, t is the time, k the velocity constant and $-\frac{dc}{dt}$ the rate at which the concentration decreases. Upon integration, equation 1 becomes;

$$\log c = \frac{-k}{2.303}\, t - \text{constant} \;\ldots\ldots\ldots\ldots 2$$

A characteristic of a first order reaction is that when log c is plotted against t, a straight line is obtained. That the concept of a first order reaction is applicable to the reported experimental results is shown in figures 12-15. In each case straight lines are obtained when the logarithms of ammonia concentrations are plotted against time irrespective of the variations between soils. The equations associated with

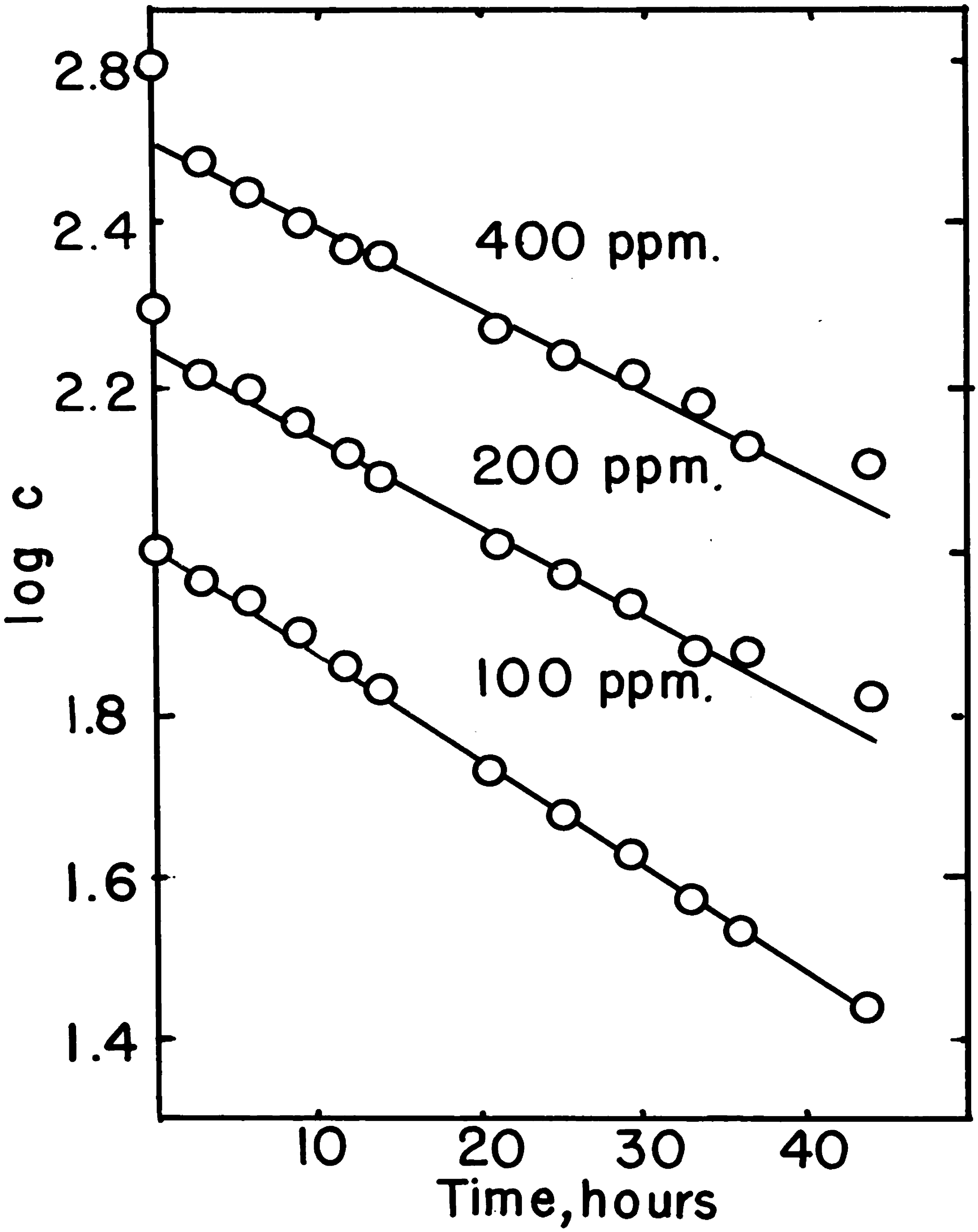


Figure 12-First order kinetics of ammonia volatilization from Norfolk fine sandy loam.

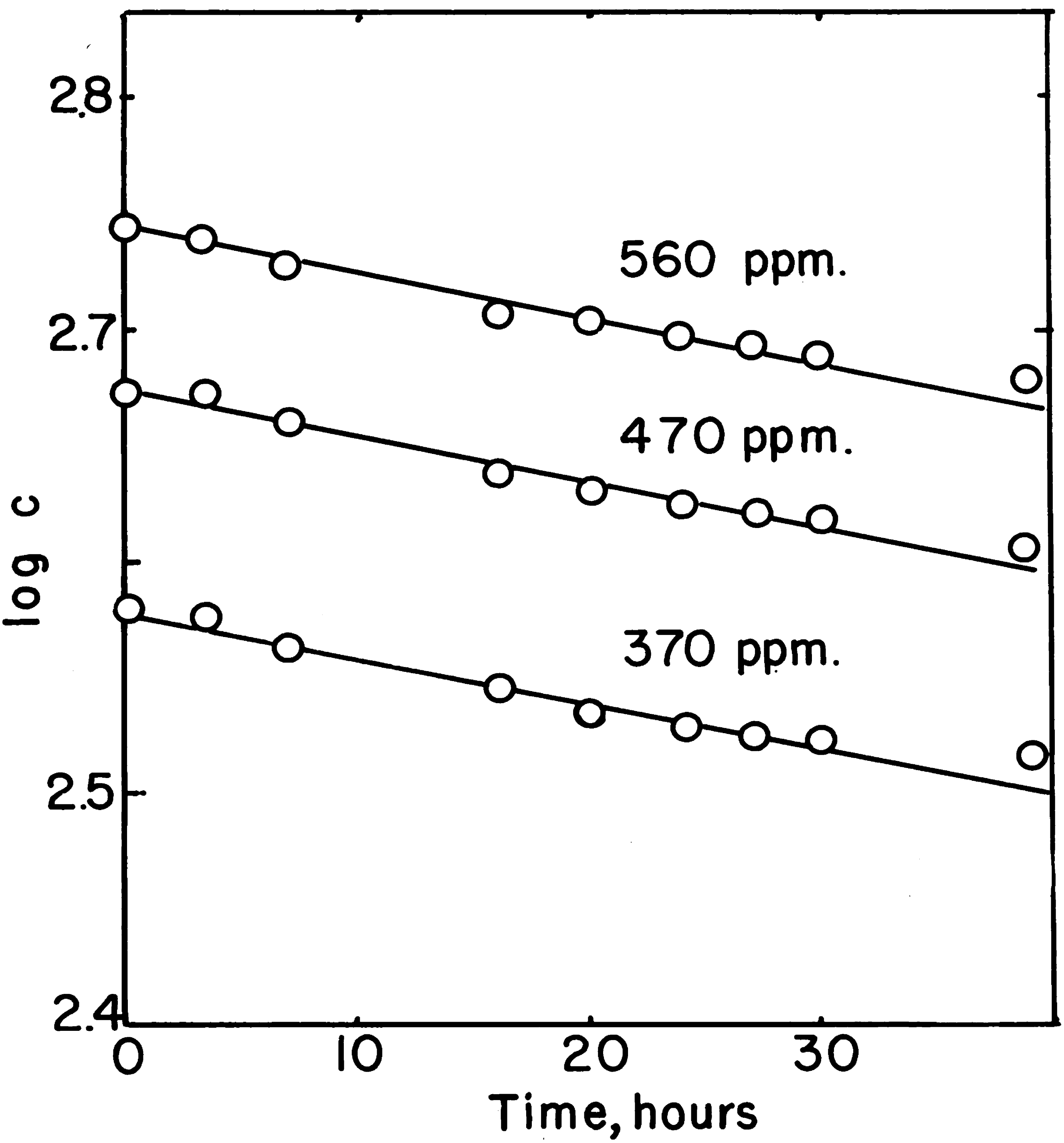


Figure 13-First order kinetics of ammonia volatilization from Davidson clay.

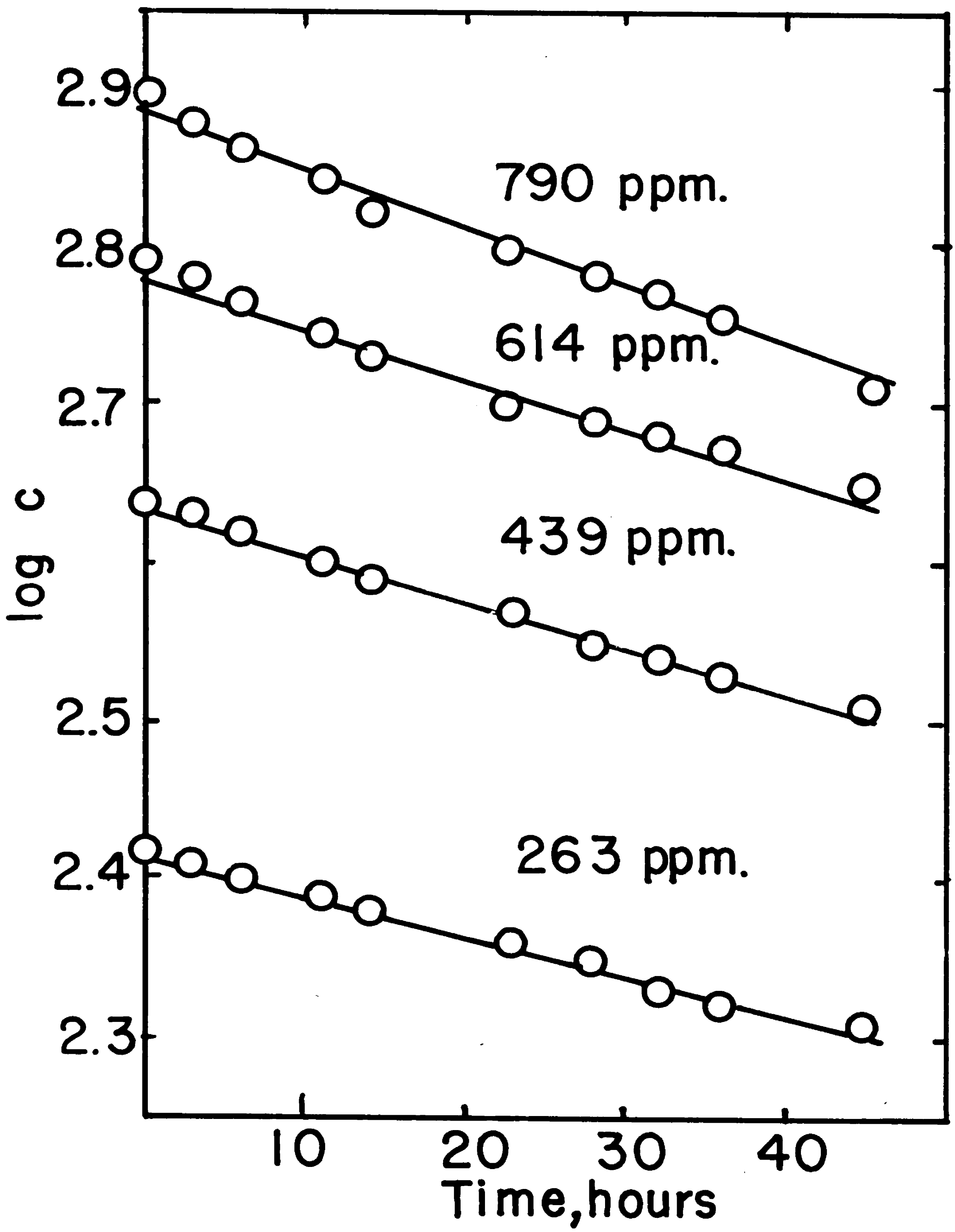


Figure 14-First order kinetics of ammonia volatilization from Yolo loam.

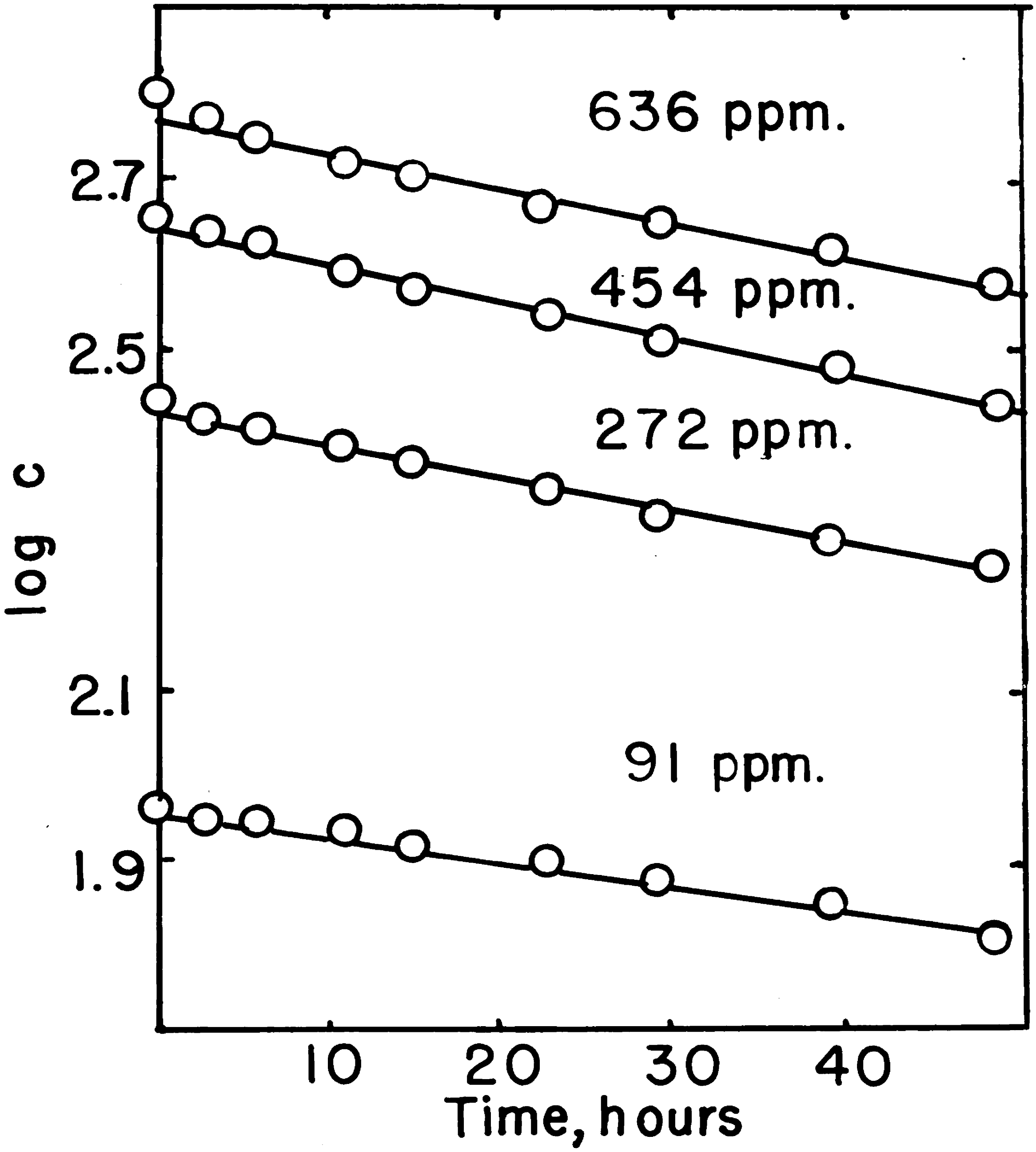


Figure 15-First order kinetics of ammonia volatilization from Salinas clay.

the straight lines presented in figures 12-15 are as follows;

for Norfolk fine sandy loam,

for 50 ppm ammonia applied $\log c = 1.7335 - 0.0125t$

for 100 ppm ammonia applied $\log c = 2.0087 - 0.0130t$

for 200 ppm ammonia applied $\log c = 2.2423 - 0.0101t$

for 400 ppm ammonia applied $\log c = 2.4941 - 0.0094t$

for 600 ppm ammonia applied $\log c = 2.5909 - 0.0094t$

for Davidson clay,

for 370 ppm ammonia applied $\log c = 2.5740 - 0.0017t$

for 470 ppm ammonia applied $\log c = 2.6721 - 0.0018t$

for 560 ppm ammonia applied $\log c = 2.7399 - 0.0017t$

for Yolo loam,

for 263 ppm ammonia applied $\log c = 2.4198 - 0.0027t$

for 439 ppm ammonia applied $\log c = 2.6401 - 0.0031t$

for 615 ppm ammonia applied $\log c = 2.7845 - 0.0033t$

for 790 ppm ammonia applied $\log c = 2.8850 - 0.0037t$

for Salinas clay,

for 91 ppm ammonia applied $\log c = 1.9662 - 0.0030t$

for 272 ppm ammonia applied $\log c = 2.4324 - 0.0039t$

for 454 ppm ammonia applied $\log c = 2.6485 - 0.0044t$

for 636 ppm ammonia applied $\log c = 2.7810 - 0.0043t$

A further examination of the graphs shows that by extrapolating the straight lines to $t = 0$, the values on the y-axis in almost all instances coincide with those obtained by taking the logarithm of the particular applied ammonia concentration. A very notable exception is encountered with Norfolk fine sandy loam, the extrapolated values greatly deviate from the calculated values (figure 12). The extrapolated values at t = 0 for the 200 ppm is 175 ppm, for 400 ppm is 312 ppm and for 600 ppm is 390 ppm; the differences increase when increasing concentrations of ammonia are applied. However, when 100 ppm of ammonia are applied, no difference between the extrapolation and calculated value are observed. These deviations, so very noticeable in the case of Norfolk fine sandy loam, also occur, but to a far lesser extent, with Yolo loam at the 790 ppm rate (figure 14) and Salinas clay at 636 ppm (figure 15). In the instances cited, part of the concentration of the ammonia applied is apparently still readily volatile after equilibrium has been established. Only after the initial rapid volatilization of the excess ammonia has taken place does the release of ammonia follow a first order phenomenon.

The specific ammonia-volatilization rate constants, k, which are obtained by multiplying the slopes by 2.303, are presented in table 13. These data indicate that the k-values in acid soils, Davidson clay and Norfolk fine sandy loam, stay fairly constant with applications of increasing ammonia concentrations, while in the basic soils, Yolo loam and Salinas clay, a modest increase in k-values is observed. In comparing the k-values of acid and basic soils, it becomes evident that, with exception of Norfolk fine sandy loam, the higher the original soil pH, the larger will be the specific ammonia volatilization-rate constant. This relationship is of course due to an increase in

Table 9 - Ammonia volatilization with time from Norfolk fine sandy loam.

Time (hours)	Changes in NH_3 concentration (ppm)			
0.0	50.0	100.0	200	400
3.0	48.8	91.5	164	302
6.0	47.6	86.3	158	277
9.0	43.1	79.1	144	253
12.0	38.9	72.4	133	235
14.0	35.7	67.4	124	234
21.5	30.7	54.0	103	188
25.5	26.5	47.3	94	173
29.5	23.0	42.2	86	164
33.5	20.5	37.1	76	151
36.5	18.7	33.8	75	135
44.0	14.7	27.3	67	128

Table 10 - Ammonia volatilization with time from Davidson clay.

Time (hours)	Changes in NH_3 concentration (ppm)		
0.0	377	470	560
3.5	377	470	551
7.0	367	458	535
16.0	351	434	510
20.0	341	427	508
24.0	337	421	500
27.0	334	419	594
30.0	332	416	490
39.0	328	407	478

Table 11 - Ammonia volatilization with time from Yolo loam.

Time (hours)	Changes in NH_3 concentration (ppm)			
0.0	263	439	615	790
3.0	259	428	598	753
6.0	252	418	581	727
11.0	246	402	556	690
14.0	239	391	542	669
23.0	230	371	511	626
28.0	223	358	493	604
32.0	216	347	481	585
36.0	210	337	467	569
45.1	204	326	447	514

Table 12 - Ammonia volatilization with time from Salinas clay.

Time (hours)	Changes in NH_3 concentration (ppm)			
0.0	91	272	454	636
3.0	89	266	436	591
6.0	89	257	422	564
11.0	87	245	391	527
15.0	84	235	375	505
23.0	80	218	347	471
29.0	76	206	328	445
39.0	70	191	303	413
48.0	65	178	276	384

Table 13 - Specific volatilization-rate constant of different soils.

Soil type	C(ppm)	K
Norfolk fine sandy loam	50	0.0288
	100	0.0299
	200	0.0233
	400	0.0217
Davidson clay	377	0.0040
	470	0.0041
	560	0.0040
Salinas clay	91	0.0069
	272	0.0090
	454	0.0101
	636	0.0099
Yolo loam	263	0.0060
	439	0.0072
	614	0.0075
	790	0.0085

hydroxyl ions in the soil solution which will readily react with ammonium ions to form ammonia and water $(NH_3 + H_2O \longleftrightarrow NH_4^+ + OH$ $\Delta F^o = 6.5$ kcal.). The large k-values obtained with Norfolk fine sandy loam seem to indicate that on Norfolk fine sandy loam soil texture may have greater influence than soil pH on rate of ammonia volatilization.

D. Summary

The rate of ammonia volatilization from soils was investigated. It was found that when varying rates of ammonium hydroxide were applied to different soils the rate of ammonia volatilization followed a first order reaction. Deviations from the first order reaction were observed on Norfolk fine sandy loam when 200 to 400 ppm of ammonia was applied.

On the finer textures soils the specific ammonia-volatilization rate constant were found to be related to the original pH. On Norfolk fine sandy loam, soil texture seems to have a greater influence than soil pH on the rate of ammonia volatilization.

IV AMMONIA ADSORPTION PHENOMENA IN SOILS

A. Introduction

Studies dealing with ammonia adsorption by soils are becoming of increasing importance since much of the nitrogen in high analysis nitrogen fertilizers, as well as the nitrogen contained in mixed fertilizers often is in the ammonia and/or ammonium form(s). Ammonia also is a product of microbiological activity in soils, arising from deaminization, and reduction of several nitrogen compounds.

The complex nature of ammonia adsorption by soils has been demonstrated by many investigators. Cornet (14) found that a dry hydrogen bentonite would retain ammonia to the extent of its cation exchange capacity. Jenny et al. (23), however, found that nitrogen taken up from NH_4OH by K-saturated clays greatly exceeded the amount of K replaced. This phenomenon did not occur when $(NH_4)_2SO_4$ was used. Brown and Bartholomew (11) showed that chemisorption of ammonia exceeded that predicted from conventionally determined cation-exchange capacities.

Ammonia can be sorbed chemically as well as physically, each process proceeding according to different physico-chemical principles (42). Rijnders and Schuit (47) found ammonia sorption by different alumina preparations to be a monomolecular layer type and chemisorption to be the responsible mechanism. Mortland (41) studying the characteristics of ammonia sorption by Wyoming bentonite, kaolinite, and muck, found that an initial small amount of ammonia was adsorbed irreversibly through chemisorption but that major reversible adsorption was due to strong van der Waal's type bonding. Tamele (53) stated that chemisorption, physical adsorption and capillary condensation of ammonia may occur simultaneously. Brown and Bartholomew (11) concluded that chemisorption of NH_3 was not due to weakly acidic groups on the edges of the clay; neither did it react with the hydroxyl groups of the clay lattice to form $-ONH_4$ groups.

The primary objective of this investigation was to study the characteristics of ammonia adsorption isotherms of natural soils in light of some established adsorption theorems (15, 27).

B. Materials and Methods

Two acid soils, Davidson clay and Tatum silt loam, a neutral Norfolk fine sandy loam and two basic soils, Yolo loam and Salinas clay, were used in this investigation. Some of the chemical and physical characteristics of the surface 0-6 inches of these soils, determined by conventional methods (45) are given below;

				Exchangeable Cations					Available
Soil type	pH	O.M.	CEC	Ca	Mg	K	Na	H	P
		%		---------me. per 100 grams---					ppm
Tatum silt loam	4.1	1.90	11.2	0.02	0.48	0.28	0.075	10.32	2
Davidson clay	5.4	3.71	18.0	3.58	1.20	0.74	0.019	12.43	11
Norfolk fine sandy loam	6.7	1.02	4.7	2.04	0.57	0.15	0.000	1.89	5
Yolo loam*	7.4	1.63	24.0	8.80	11.75	0.91	0.290	2.21	159
Salinas clay*	7.8	3.43	38.8	29.20	6.95	1.18	0.490	0.99	249

* Obtained from Dr. F. E. Broadbent, College of Agriculture, Davis, Cal.

After air drying and sieving, 20 grams of soil was introduced into 500 ml. suction flasks. Dilute ammonia water was added, and after moisture equilibrium had been attained at approximately saturation percentage, air suction was applied until the soils were air-dry to compare ammonia retention of soils at a naturally occurring condition. It was found that ammonia loss ceased when the samples became dry. The ammoniacal air was passed through standard sulfuric acid and amount of volatilized ammonia determined by back titration with standard sodium hydroxide using methyl orange as an indicator. The amount of adsorbed ammonia was taken as the difference between the amount applied less that volatilized. Any ammonia which was in the soil sample initially was not accounted for in this method. A buffer medium used to simulate soil conditions was prepared by adding 1 cc of buffer solution to 20 grams of quartz sand. The buffer solution was made up by diluting 50 cc of 0.1 M KH_2PO_4 and 29.63 cc of 0.1 N NaOH to 100 cc. (54).

C. Results and Discussion

At equilibrium when the rate of adsorption equals the rate of desorption, the Langmuir equation is expressed as $\alpha\mu(1-\theta) = V\theta$ ... 1 where V is the rate of evaporation when the whole surface is covered, θ the fraction of the surface covered by ions, α the fraction of ions adhering to the surface, μ the number of ions striking the surface and $1-\theta$ the fraction of the surface not covered by ions. Expressing equation 1 in θ, it becomes;

$$\theta = \frac{\frac{\alpha}{V}\mu}{1 + \frac{\alpha}{V}\mu} \qquad \text{........................} \; 2$$

Since μ is proportional to either concentration or pressure, one obtains by substituting kc for μ, where k is a constant, and c the equilibrium concentration;

$$\theta = \frac{\frac{\partial}{V} kc}{1 + \frac{\partial}{V} kc} \text{ .... } 3$$

Since $\frac{\partial}{V}$ k is a constant = a, then $\theta = \frac{ac}{1 + ac}$ 4

Since θ can also be expressed by x/m x 1/b, where x/m is the amount (ppm) of ammonia absorbed and 1/b a constant, equation 4 can be written as;

$$\frac{c}{x/m} = \frac{1}{ab} + \frac{c}{b} \text{ .... } 5$$

where c is the equilibrium concentration or the amount of ammonia volatilized, x/m the amount (ppm) of ammonia adsorbed, a and b being constants.

On plotting $\frac{c}{x/m}$ against c the linear relationship obtained is considered evidence of the applicability of Langmuir's equation to ammonia adsorption in the soils studied (tables, 14, 16, figures 16 and 19). However, it becomes apparent from these curves that different mechanisms, responsible for NH_3 adsorption, are characterized by a change in slope. The first part of the curve possibly reflects reactions involving "hydrogen" while the second part of the curve may represent adsorption of ammonia by exchange sites. If we assume that $\theta = q/q^o$, where q equals the amount of ammonia adsorbed and q^o maximum exchange sites available for ammonia adsorption, then equation 4 may be expressed as;

$$\frac{q_o}{q^o} = \frac{ac}{1 + ac} \text{ .... } 6$$

The ammonia adsorption due to "hydrogen" (q_1^o) and CEC (q_2^o) can then be obtained by calculating the slopes of different sections of

Table 14 - **Ammonia adsorption of two acid soils.**

Tatum silt loam (pH 4.1)			Davidson clay (pH 5.4)		
Ammonia (ppm)			Ammonia (ppm)		
Volatilized (c)	Adsorbed (x/m)	Final pH	Volatilized (c)	Adsorbed (x/m)	Final pH
9	691	5.4	72	328	6.6
15	785	5.4	93	407	6.9
33	967	5.8	122	478	7.0
100	1280	7.0	155	535	7.3
239	1411	7.3	489	891	7.9
991	1769	7.9	1466	1294	8.1
2127	2013	7.9	2674	1466	8.1
3421	2099	7.9	5175	1725	8.2

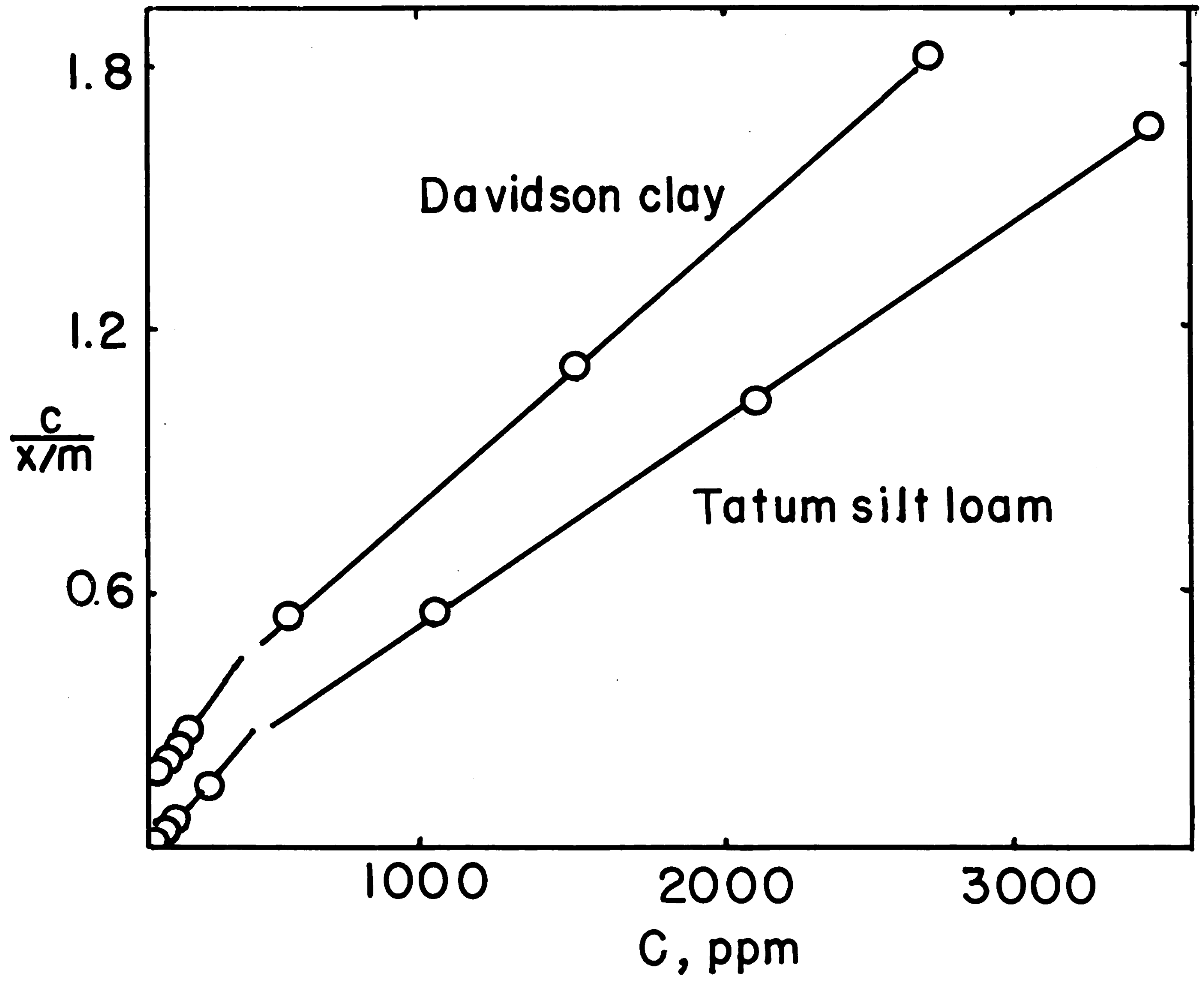


Figure 16-Ammonia adsorption isotherms of two acid soils.

each curve (table 15). For Davidson clay, Tatum silt loam and Norfolk fine sandy loam the calculated values for q_1^o involving reactions with "hydrogen" agree closely with the values obtained by titration of these soils with 0.1 N sodium hydroxide to pH 9 (figure 17). The selection of this pH was based on the theoretical consideration proposed by Jackson and Chang (22). They pointed out that in acid soils ammonia will combine with the hydrogen colloid (X) to form ammonium colloid, while in neutral soils ammonia combines with the soil colloid which is partially saturated with calcium but contains many weakly ionized hydrogen ions to form calcium colloid. The pH goes up to 8-9. The reaction can be presented as;

$$\underset{pH_7}{NH_3 + CaHX} \longrightarrow \underset{pH\ 8\text{-}9}{CaNH_4X}$$

For all soils studied, with the exception of Salinas clay, the calculated values (q_2^o) involving reactions due to exchange sites, showed a close agreement with the CEC determined by summation of the cations using titratable hydrogen (figure 18). The deviation encountered with Salinas clay may be ascribed to the presence of free calcium carbonate, since it is partially dissolved by the NH_4Ac used to remove exchangeable Ca.

When increasing concentrations of ammonia were applied to Yolo loam and Salinas clay a continuous change in slope was observed (figure 19). The S-shaped curve resembles one type of van der Waal's or physical adsorption isotherms (64). According to Weiser (64) the upper part of the curve could represent physical adsorption involving the formation

Table 15 - Relationships between ammonia adsorption, acidity and cation exchange capacity of soils.

Soil Type	q_1^o	H [*]	q_2^o	CEC [**]
Tatum silt loam	8.6	9.0	10.9	9.9
Davidson clay	7.4	8.0	9.9	13.5
Norfolk fine sandy loam	0.9	1.0	4.9	3.8
Yolo loam	5.3	1.5	20.2	23.3
Salinas clay	-	1.0	11.8	38.8

[*] Titratable hydrogen

[**] The CEC includes titratable hydrogen

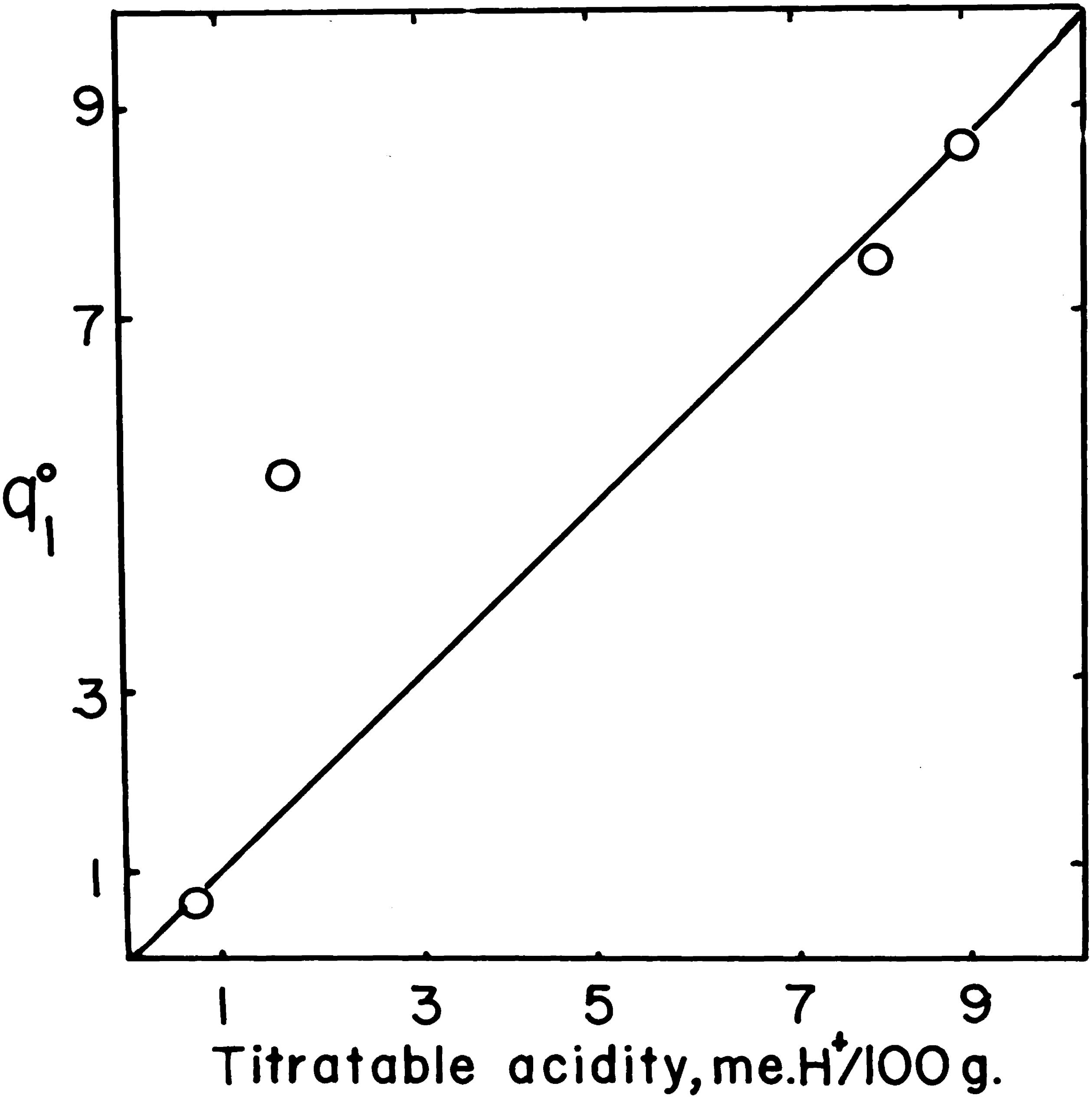


Figure 17-Ammonia adsorption due to soil acidity.

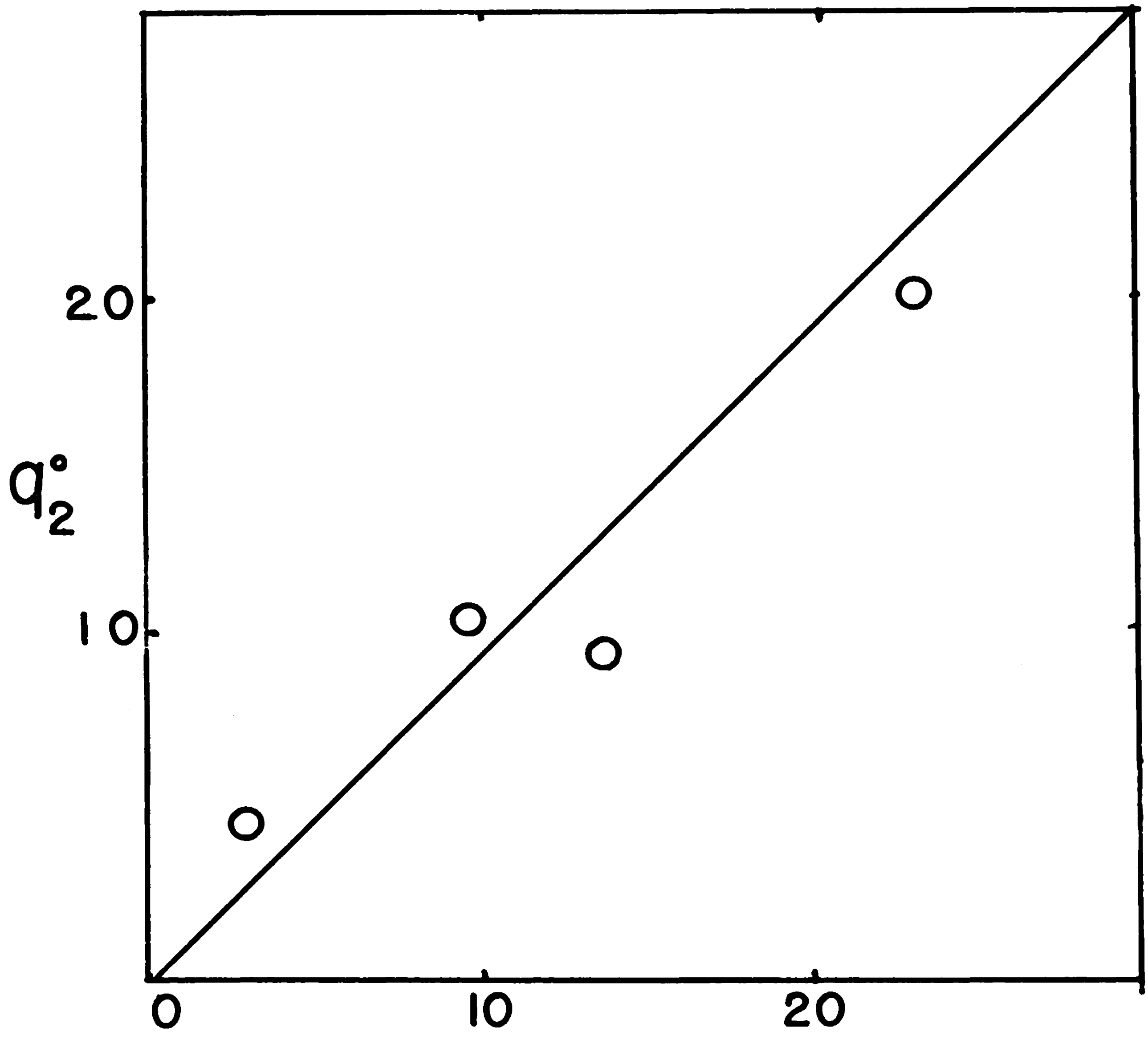


Figure 18-Ammonia adsorption due to cation exchange capacity.

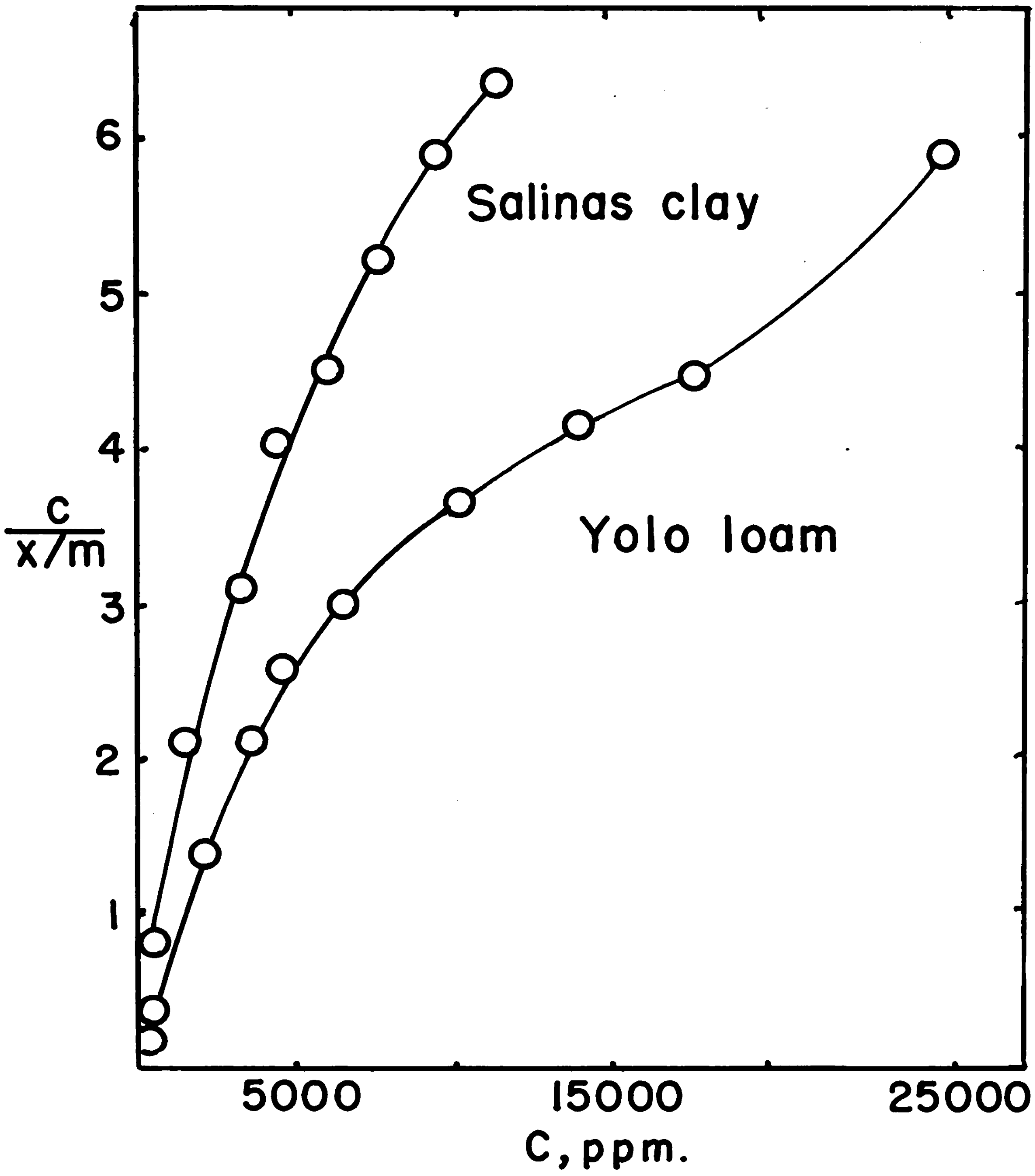


Figure 19-Ammonia adsorption isotherms of two basic soils.

of polymolecular layers. At low concentration of NH_3 the curve not only followed Langmuir's equation but approximated the form of the Freundlich isotherm. Therefore, an attempt was made to plot the data according to the Freundlich equation, since the latter is frequently used to study adsorption phenomena. The Freundlich equation may be expressed as $x/m = kc^n$, where x/m is the amount of ammonia adsorbed, c the amount of ammonia applied, k and n being constants. It is known that this equation is a purely interpolation formula without theoretical foundation. In contrast to the acid soils, the adsorption data of the neutral and basic soils followed the Freundlich equation very closely (figure 20). The pH of the Yolo loam remained practically constant at 8.6 over a range of NH_3 adsorption varying from 1663-4437 ppm while for the Salinas clay no further increase in pH was obtained over a range between 442-1666 ppm of NH_3 adsorbed (table 16). These soils also contained higher amounts of available phosphorus and exchangeable sodium. The mechanism of ammonia adsorption in these soils showed a close similarity to buffer solutions. To test this possibility a buffer medium was prepared and treated exactly like the soils. The close agreement obtained (figure 20) seems to confirm the postulation that the characteristic of the ammonia adsorption isotherms on the basic soils resemble buffer reactions.

Ammonia adsorption with soil pH and texture The calculated data obtained by using the Langmuir and Freundlich equations are presented in table 18. The results show that ammonia adsorption in the four finer textures soils, Tatum silt loam, Davidson clay, Yolo loam and Salinas clay, was initially inversely related to the original soil pH. However, with

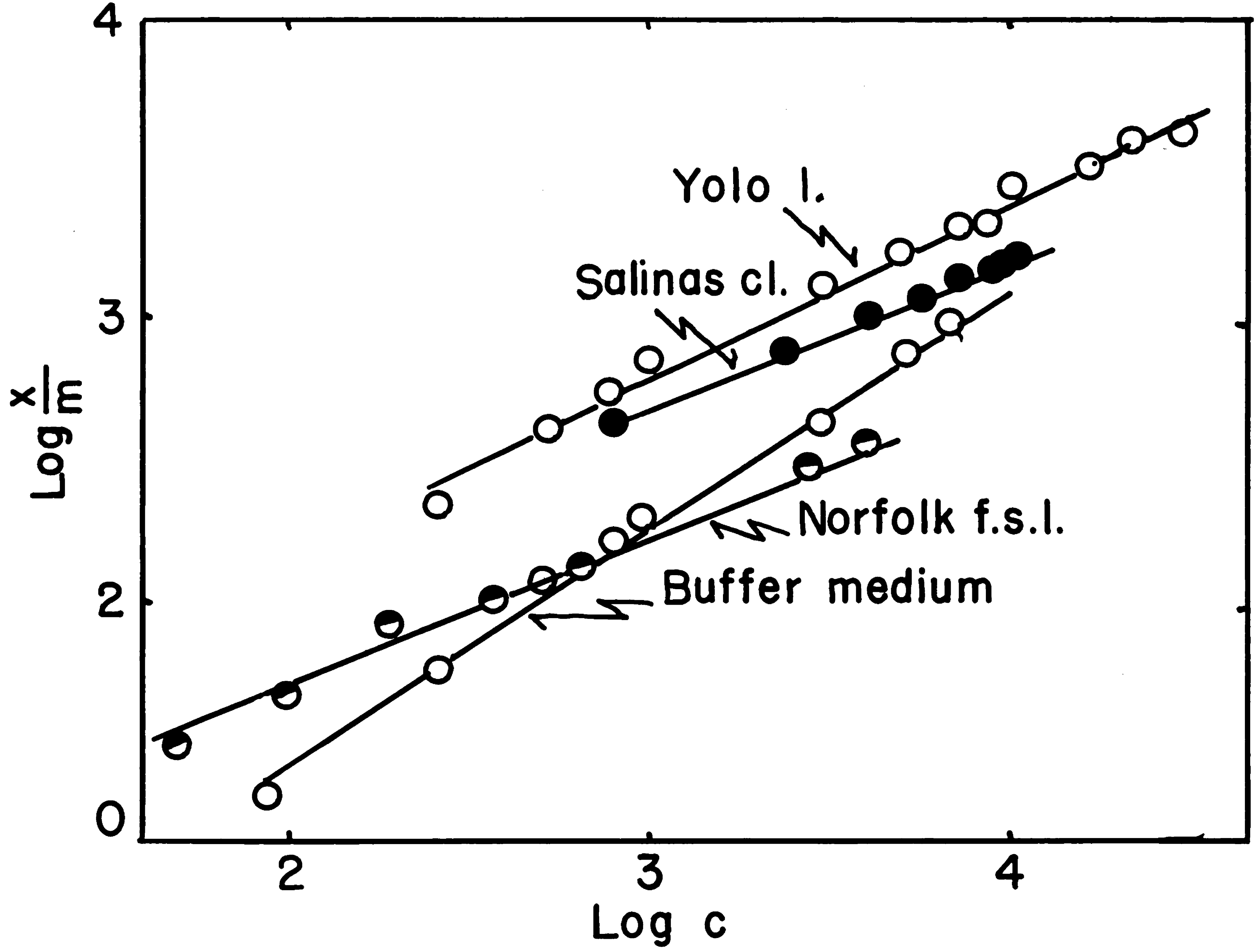


Figure 20-Ammonia adsorption isotherms according to Freundlich equation.

Table 16 - Ammonia adsorption of two basic soils.

Salinas clay (pH 7.8)			Yolo loam (pH 7.4)		
Ammonia (ppm)			Ammonia (ppm)		
Volatilized (c)	Adsorbed (x/m)	Final pH	Volatilized (c)	Adsorbed (x/m)	Final pH
387	442	8.7	111	416	8.1
1694	792	8.8	233	557	8.3
3140	1003	8.8	1778	1295	8.4
4659	1142	8.8	3518	1663	8.5
6104	1353	8.9	5223	1977	8.6
7632	1482	8.7	10352	2819	8.6
9206	1565	8.7	14142	3420	8.6
10762	1666	8.7	17931	4021	8.6

Table 17 - Ammonia adsorption of a neutral soil and a buffer medium.

Norfolk fine sand loam (pH 6.7)			Buffer medium		
Ammonia (ppm)			Ammonia (ppm)		
Volatilized (c)	Adsorbed (x/m)	Final pH	Volatilized (c)	Adsorbed (x/m)	Final pH
16	34	7.2	66	22	7.1
52	48	7.4	202	61	7.1
111	89	7.6	405	122	7.1
293	107	7.9	620	170	7.1
546	144	--	852	202	7.1
2473	288	8.1	2626	447	7.1
3766	374	8.2	4418	763	7.1
			6169	1031	7.1

Table 18 - Ammonia adsorption of different soils in the range of 2000 to 4000 ppm of NH_3 applied.

Soil type	Initial pH	Ammonia adsorption		
		2000 ppm	4000 ppm	Difference
Tatum silt loam	4.1	1547	1963	416
Davidson clay	5.4	1047	1463	391
Norfolk fine sandy loam	6.7	254	366	112
Buffer medium	7.1	325	583	258
Yolo loam	7.4	921	1400	479
Salinas clay	7.8	694	975	281

increasing amounts of NH_3 added, the subsequent increase in ammonia adsorption was no longer inversely related to the original soil pH. Furthermore, it is evident that the Norfolk fine sandy loam adsorbed less ammonia than the Yolo loam or Salinas clay which shows that soil texture can take precedent over soil pH.

The difference in adsorption capacity for ammonia between Yolo loam and Davidson clay (table 16) and between Norfolk fine sandy loam and the buffer medium (table 17) seems to indicate that the kind and amount of salt and/or weak acid in the soil may have a greater effect on ammonia adsorption than pH and soil texture. However, when the average adsorption of the coarse samples (Norfolk fine sandy loam, pH 6.7 and Buffered sand, pH 7) are compared with the average adsorption for the finer soils (Yolo loam, pH 7.4 and Davidson clay, pH 5.7) it is evident that the largest difference in adsorption was obtained. It appears unlikely that this was due to pH because Yolo is higher than either Norfolk fine sandy loam or Buffered sand. Therefore, major texture differences appear to exert the most influence.

D. Summary

At low concentrations, ammonia adsorption on all soils studied followed Langmuir's monomolecular adsorption theory. The differential slopes obtained for different sections of the curves were explained as likely related to reactions involving "hydrogen", exchange sites and physical adsorption. The S-shaped curve obtained for high concentrations suggests the formation of polymolecular layers.

The ammonia adsorption on neutral and basic soils, however, also gave typical Freundlich's adsorption isotherm and furthermore closely simulated the behavior of a buffer medium.

In fine textured soils the amount of ammonia retained was inversely related to the original soil pH. The subsequent difference in adsorption capacity for ammonia between Yolo loam and Davidson clay, and between the buffer medium and Norfolk fine sandy loam seems to indicate that kind and amount of salt and/or weak acid may have a greater effect on ammonia adsorption than pH. Between texture groups, texture appears to exert the major influence upon ammonia adsorption capacity.

BIBLIOGRAPHY

1. Aldrich, D. G., and Buclanen, J. R. Laboratory studies of reactions between injected liquid nitrogen dioxide and various soils, with special reference to its possible use as a fertilizer. Soil Sci. Soc. Amer. Proc. 19:42-47. 1955.

2. Allen, O. N. Experiments in Soil Bacteriology. Burgess Publishing Co., Minneapolis 15, Minnesota. p. 14. 1957.

3. Allison, F. E., and Doetsch, J. H. Nitrogen gas production by reaction of nitrite and amino acids in slightly acidic medium. Soil Sci. Soc. Amer. Proc. 15:163-166. 1950.

4. Andrews, W. B., Edwards, F. E., and Hammons, J. G. Ammonia as a source of nitrogen. Mississippi Agr. Expt. Sta. Bul. 451. 1948.

5. Arnold, P. W. Losses of nitrous oxide from soil. J. Soil Sci. 5:116-126. 1954.

6. Baas-Becking, L. G. G., and Parks, G. S. Physiol. Rev. 7:85. 1927.

7. Bancroft, W. E. Action of metals on nitric acid. J. Phys. Chem. 28:475-493. 1924.

8. Broadbent, F. E. Denitrification in some California soils. Soil Sci. 72:129-137. 1951.

9. Broadbent, F. E., and Stojanovic, B. F. The effect of partial pressure of oxygen on some soil nitrogen transformations. Soil Sci. Soc. Amer. Proc. 16:359-263. 1952.

10. Broadbent, F. E., Tyler, K. B. and Hill, G. N. Nitrification of ammonia compounds. Proceedings of the Thirty-Third Annual Meeting of the National Joint Committee on Fertilizer Application. pp. 50-77. 1957.

11. Brown, J. M., and Bartholomew, W. V. Sorption of anhydrous ammonia by various dry clay systems. Agron. Abstracts p. 15. 1959.

12. Chapman, H. D., Liebig, G. F., and Payer, D. S. A lysimeter investigation of nitrogen gains and losses under various systems of cover-cropping and fertilization, and a discussion of error sources. Hilgardia 19:57-128. 1950.

13. Corbet, A. S. Formation of hyponitrous acid as an intermediate compound in the biological or photochemical oxidation of ammonia to nitrous acid. I. Chemical reactions. Biochem. Jour. 28: 1575-1582. 1934.

14. Cornet, I. Sorption of NH_3 on montmorillonitic clay. J. of Chem. Physics, 11:217-226. 1943.

15. Daniels, F., and Alberty, R. A. Physical Chemistry. John Wiley and Sons, Inc., New York. p. 522. 1956.

16. Dhar, N. R. Denitrification in sunlight. Nature 134:572-573. 1934.

17. Duisberg, P. C. and Buehrer, T. F. Effect of ammonia and its oxidation products on rate of nitrification and plant growth. Soil Sci. 78:37-49. 1954.

18. Eno, C. F., and Blue, W. G. The effect of anhydrous ammonia on nitrification and the microbiological population in sandy soil. Soil Sci. Soc. Amer. Proc. 18:178-181. 1954.

19. Forde, H. I., and Proebsting, E. L. Utilization of ammonia supplied to peaches and prunes at different seasons. Hilgardia 16:411-425. 1945.

20. Hogness, T. R., and Johnson, W. C. Qualitative Analysis and Chemical Equilibrium. Henry Holt and Company, New York. pp. 217-219. 1947.

21. Jackson, M. L. Soil Chemical Analysis. Prentice-Hall, Inc., Englewood Cliffs, N. J. pp. 191-192. 1958.

22. Jackson, M. L., and Chang, S. C. Anhydrous ammonia retention by soils as influenced by depth of application, soil texture, moisture content, pH value and tilth. J. Amer. Soc. Agron. 39:623-633. 1947.

23. Jenny, G., Ayers, A. D., and Hosking, J. S. Comparative behavior of ammonia and ammonium salts in soils. Hilgardia 16:429-475. 1945.

24. Jewitt, T. N. Loss of ammonia from ammonium sulphate applied to alkaline soils. Soil Sci. 54:401-409. 1942.

25. Juza, G., and Powell, R. E. Kinetics of gas adsorption as a method of area determination. J. Chem. Phys. 19:251-252. 1951.

26. Krantz, B. A., Ohlrogge, A. J., and Scarseth, G. C. Movement of nitrogen in soils. Soil Sci. Soc. Amer. Proc. 8:189-195. 1943.

27. Langmuir, I. The adsorption of gases on planes of surfaces of glass, mica and platinum. J. Am. Chem. Soc. 40:1361-1403. 1918.

28. Latimer, W. M. The Oxidation States of the Elements and their Potentials in Aqueous Solutions. Prentice Hall, Inc., New York, pp. 82-97. 1938.

29. Laubengayer, A. W. General Chemistry, Rinehart Co., Inc., New York. pp. 280-298. 1949.

30. Lees, H., and Quastel, J. H. Kinetics of, and the effects of poisons on, soil nitrification, as studied by a soil perfusion technique. Biochem.J.40:803-815. 1946.

31. Lees, H. Intermediates in soil nitrification. Nature 162:702. 1948.

32. Lewis, G. N. The free energy of chemical substances. J. Am. Chem. Soc. 35:1-30. 1913.

33. Loewenstein, H., Engelbert, L. W., Attoe, O. J., and Allen, O. N. Nitrogen loss in gaseous form from soils as influenced by fertilizers and management. Soil Sci. Soc. Amer. Proc. 21:397-400. 1957.

34. Lyon, T. L., Buckman, H. O., and Brady, N. C. The nature and properties of soil. The Macmillan Co., New York. p. 452. 1952.

35. MacIntire, W. H., Winterberg, S. H., Dunham, H. W., and Clements, L. B. Response of Sudan grass to ammonium hydroxide in pot cultures. Soil Sci. Soc. Amer. Proc. 8:205-210. 1944.

36. Mann, H. H., and Barnes, T. W. The behavior of nitrogeneous manures in the soil I. The loss of manurial nitrogen. J. Agr. Sci. 41: 309-314. 1951.

37. Martin, J. P., and Chapman, H. D. Volatilization of ammonia surface-fertilized soils. Soil Sci. 71:25-34. 1951.

38. Martin, W. P., Buehrer, T. F., and Caster, A. B. Threshold pH values for the nitrification of ammonia in desert soils. Soil Sci. Soc. Amer. Proc. 7:223-228. 1942.

39. McDowell, L. L., and Smith, G. E. The retention and reaction of anhydrous ammonia on different soil types. Soil Sci. Soc. Amer. Proc. 22:38-42. 1958.

40. Meyerhof, O. Pflüz. Arch. Ges. Physiol. 166-262. 1957.

41. Mortland, M. M. Adsorption of ammonia by clays and muck. Soil Sci. 80:11-18. 1955.

42. ____________, Reactions of ammonia in soils. Advances in Agronomy, Vol. X, 325-348. 1958.

43. Mumford, E. M. The mechanism of nitrification. Chem. Soc. Proc. (London) p. 30:36. 1914.

44. Nagata, T., Okabe, T., and Uesono, S. Volatilization of ammoniacal nitrogen. J. Agr. Chem. Soc. Japan. 20:480-486, pp. 535-538. 1944.

45. Peech, M., Alexander, L. T., Dean, L. A., and Reed, J. F. Methods of soil analysis for soil fertility investigations. USDA Cir. 757. 1947.

46. Quastel, J. H., and Scholfield, P. G. Organic nitrogen compounds on nitrification. Nature. 164:1068-1072. 1949.

47. Rijnders, G. W. A., and Schuit, G. C. A. Adsorption of ammonia on surfaces of oxides. Rec. Trav. Chim. 69:668-670. 1950.

48. Rossini, Wagman, Enaus, Levire, and Jaffe. Selected values of chemical Thermodynamic Properties. Circular of the National Bureau of Standards 500. U. S. Government Printing Office, Washington D. C. 1952.

49. Schlosing, T. H. and Muntz, A. Reacherches Sur La Nitrification. In Compt. Rend Acd. Sci (Paris) 89:1074-1077. 1879.

50. Screenivasan, A., and Subrahmanyan, V. Biochemistry of waterlogged soils. IV. J. Agr. Sci. 25:6-21. 1935.

51. Sen, A. Fixation of nitrogen from ammonium sulphate by Indian soils. Indian J. Agr. Sci. 24:111-126. 1951.

52. Steenbjerg, F. Ammonia loss from nitrogen containing commercial fertilizers when applied to top soil. Tidsskr. Planteavl 48:516-543. 1944.

53. Tamele, M. W. Chemistry of the surface and the activity of alumina-silica cracking catalyst. Farady Soc. Disc. 8:270-279. 1950

54. Treadwell, F. P., and Hall, W. T. Analytical Chemistry II. Henry Holt & Co., New York, p. 493. 1942.

55. Wagner, G. H., and Smith, G. E. Nitrogen losses from soils fertilized with different nitrogen carriers. Soil Sci. 85:125-129. 1958.

56. Wahhab, A., Randhawa, M. S., and Alam, S. Q. Loss of ammonia from ammonium sulfate under different conditions when applied to soils. Soil Sci. 84:249-255. 1957.

57. Wahhab, A. and Uddin, F. Influence of light on nitrification of ammonium and nitrite ions. Soil Sci. 80:121-125. 1955.

58. ________________ Loss of nitrogen through reaction of ammonia and nitrite ions. Soil Sci. 78:119-126. 1954.

59. Waksman, S. A. and Nahdok, M. R. Influence of light and heat upon the formation of nitrate in soil. Soil Sci. 44:361-375. 1937.

60. Waksman, S. A. Soil microbiology. John Wiley & Sons, Inc. p . 181. 1952.

61. ________________ Principles of soil microbiology. The Williams & Wilkins Co. , Baltimore, p. 384. 1927.

62. Warington, R. On nitrification: Part 3, J. Chem. Soc. 45:637-671. 1884.

63. Waynick, D. D. Anhydrous ammonia as fertilizer. Calif. Citrograph. 19, No. 11. 1934.

64. Weiser, H. B. Colloid Chemistry. John Wiley & Sons, Inc., New York, 2nd ed. pp.49-67. 1950.

ABSTRACT

Free energy changes of oxidative inorganic nitrogen transformations in acid and basic media were calculated and interrelated. The free energy values of reactions involving nitrification were not always found to be in agreement with those reported in the literature. The primary reason for the deviations was that the pH of the medium had often not been considered in formulating these reactions. It was also found that thermodynamically, hyponitrous acid and nitrous oxide might well be intermediates in the process of nitrification. The existence of hydroxylamine as an intermediate between ammonia and/or ammonium ion and nitrite was not supported by the data obtained. It was shown that in acid solutions nitrite may thermodynamically undergo three reactions; it may decompose to nitric oxide, oxidize to nitrate or be reduced to nitrous oxide. In alkaline solutions nitrate seems to be the only product.

Ammonia volatilization and water evaporation from the soils investigated followed different functions and may be independent of each other. The functions were not affected by differences in soil texture, soil water, speed and relative humidity of air flowing over the soil surfaces. Ammonia losses from finer textured soils were proportional to their original soil pH's. Norfolk fine sandy loam, pH 6.7, lost most ammonia indicating that soil texture is also an important factor in ammonia volatilization. A linear relationship was observed between rate of ammonia applied (up to 600 ppm) and ammonia volatilized. The rate of ammonia volatilization followed a first order reaction. Deviations from a first order reaction were observed when higher levels of ammonia were applied.

In regard to mechanisms of ammonia adsorption by soils it was found that at low concentrations, ammonia adsorption followed Langmuir's monomolecular adsorption theory. The differential slopes obtained for different sections of the curves were related to reactions involving "hydrogen", exchange sites and physical adsorption. The S-shaped curve obtained for high concentrations suggests the formation of polymolecular layers. Ammonia adsorption by neutral and basic soils also gave a typical Freundlich adsorption isotherm and furthermore closely simulated the behavior of a buffer medium. In fine textured soils the amount of ammonia retained was inversely related to the original soil pH. The subsequent difference in adsorption capacity for ammonia between Yolo loam and Davidson clay, and between the buffer medium and Norfolk fine sandy loam seems to indicate that kind and amount of salt and/or weak acid may have a greater effect on ammonia adsorption than pH. Between texture groups, texture appears to exert a major influence on ammonia adsorption capacity.