



Influence of NH_3 from ammonium phosphate fertilizers on germination, seedling growth, and small plant yield of wheat (*Triticum aestivum* L.)
by Chaitat Pairintra

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Crop and Soil Science
Montana State University
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Abstract:

Influences of NH_3 from ammonium phosphate fertilizers on germination, seedling growth, and small plant yield of wheat (*Triticum aestivum* L.) were evaluated in laboratory, growth chamber, greenhouse, and field experiments. Measurements of NH_3 were made using techniques of diffusion from the soil-fertilizer system and distillation of NH_3 from the seed-plant system.

A "Diffusion Can" was designed for quantitative measurement of NH_3 production from the ammonium phosphates—mono (MAP, 11-48-0), di (DAP, 18-46-0), poly (APP, 15-62-0), and urea (UAP, 24-42-0)—upon reaction with 10 soils varying in moisture from 10 to 25% and in CaCO_3 contents from zero to 12%. Total amount of NH_3 produced from fertilizer reacting 6 days was in the order of magnitude: UAP \gg DAP \gg MAP $>$ APP, or the ratio of 18 : 4.5 : 1.5 : 1. This relationship was generally true for any soil, but the absolute values increased directly with % CaCO_3 in the soil and inversely with soil moisture. Averaging all soils, the total 6-day NH_3 production was in the soil moisture order of 10% $>$ 15% $>$ 20%.

Ammonia absorption by plants was measured directly from the seeds or seedlings by a "Distillation Technique", and indirectly by differences between "Soil-Fertilizer" mixed and "Soil-Fertilizer-Seed" systems. The patterns of NH_3 accumulation by seeds or seedlings were governed by the kinds and rates of fertilizer application, soil moisture, CaCO_3 content, and the stages of plant germination or growth.

Dry weight of wheat seedlings was less when germinating seeds, with radicles emerged, were exposed to NH_3 for one day than when seeds were treated with NH_3 one day after moistening.

Absorption of NH_3 by seedlings was directly related to NH_3 production from fertilizer-soil reactions. Maximum absorption occurred . in day 3 for 10% CaCO_3 soil and day 2 for 0% CaCO_3 , but the latter was a very low absorption except for UAP. Ammonia concentration in seeds or seedlings in the range 0.3 to 0.5 ppm- NH_3 inhibited seedling growth, and symptoms of NH_3 injury were evident. Radicles had a brown color as a "burnt off" appearance and coleoptiles were stunted. Germination of wheat seeds was completely prevented when the concentration of NH_3 in seeds reached about 0.8 ppm- NH_3 .

Plant yield results from growth chamber studies on 0% CaCO_3 soil indicated the same responses to fertilizers for roots as for tops with the fertilizers in the order: APP $>$ MAP $>$ DAP $>$ UAP. On the 10% CaCO_3 soil the order was APP $>$ MAP $>$ DAP $>$ UAP, and growth of roots for DAP and UAP increased relatively little from 6 to 12 days in contrast with APP and MAP. In all cases, plant growth was inversely related to concentration of NH_3 in plants. Ammonia measured by microdiffusion from soil samples taken from field experiments having fertilizer banded with wheat seed was directly related to reduction in numbers of crowns and stems and inversely related to dry weights of plants at the stem elongation stage of growth.

Using information developed in this research 4 ammonium phosphate fertilizers reacting with soils

varying in CaCO₃ content can be arranged according to NH₃ production. If greater than 0.5 µg NH₃/100g soil measured by the diffusion can technique is considered potentially hazardous for banding fertilizers with seeds, the fertilizers and allowable soil CaCO₃ percentages before serious seedling damage occurs are as follows: APP, 12% CaCO₃; MAP, 10.5% CaCO₃; DAP, 3.5% CaCO₃; and UAP exceeds the limit at 0% CaCO₃.

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ON GERMINATION, SEEDLING GROWTH, AND SMALL PLANT
YIELD OF WHEAT (*Triticum aestivum* L.)

by

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A thesis submitted to the Graduate Faculty in partial
fulfillment of the requirements for the degree

of

DOCTOR OF PHILOSOPHY

in

Crop and Soil Science

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June, 1973

ACKNOWLEDGMENTS

The author wishes to express his sincerely grateful appreciation to Dr. Charles M. Smith, his major advisor, for his enriching advice, constructive criticism, and patience in preparation of this thesis. Both "official capacity and personal concern" by Dr. Smith have been an inspiration, highly regarded by the author throughout this course of study.

The author's respect is extended to Dr. E. R. Hehn, the former Department Head, for his continual concern regarding the author's research and academic potential. Special appreciation is due Dr. Earl O. Skogley, his co-advisor, for his expanded opinion, willing support and "availability" since the initiation of this research.

Thanks are extended to: Dr. R. A. Olsen for the valuable advice for high research caliber; Dr. R. E. Lund for his unselfish and generous assistance with statistical analysis; Dr. G. A. Nielsen for his strong support, thoroughness in the research work; Dr. K. C. Feltner for his helpful suggestions; and all those who have shared the wisdom of their experience to make this thesis possible.

Special gratitude is expressed to Mrs. Martha S. Smith for her kind assistance of a "fast, competent and energetic" typing of the manuscript. Mrs. Smith's unselfish service as well as technical assistance during preparation of the manuscript at "the author's second home far away from home" were deeply appreciated by the author.

The author wishes to express his special thanks to his family in Thailand--to his parents with love and gratitude, to his brother and late sister-in-law for their concern and unfailing support throughout years of this research--to his wife and children with love for their faithful strengths, sustaining companionship, and a love which enriches the author's arduous task. Their many years of patience, understanding and encouragement during the author's advance training abroad have brought much sunshine and joy to the author's life.

Also, the author acknowledges with thanks to: Some of the work study students for their help in research work, Mr. C. Skunvichayathada for his help in research and Miss P. Sirirugsa for her help in drawing, Mrs. J. Julian for her competent, energetic and long-hour work typing this thesis, Mr. and Mrs. J. F. Reagan for their kind cooperation, instruction and providing a wonderful home for preparing this manuscript.

Finally, the author extends his special thanks to: The Tennessee Valley Authority (TVA) for the Grant-in-Aid which fully financed the research work, the Montana Cooperative Extension Service and Montana State University Experimental Station for their partially supporting the work, and Canadian International Development Agency for providing transportation, and the Thai Government for its courtesy of the advance study grant which made this study possible.

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ABSTRACT

Influences of NH_3 from ammonium phosphate fertilizers on germination, seedling growth, and small plant yield of wheat (*Triticum aestivum* L.) were evaluated in laboratory, growth chamber, greenhouse, and field experiments. Measurements of NH_3 were made using techniques of diffusion from the soil-fertilizer system and distillation of NH_3 from the seed-plant system.

A "Diffusion Can" was designed for quantitative measurement of NH_3 production from the ammonium phosphates--mono (MAP, 11-48-0), di (DAP, 18-46-0), poly (APP, 15-62-0), and urea (UAP, 24-42-0)--upon reaction with 10 soils varying in moisture from 10 to 25% and in CaCO_3 contents from zero to 12%. Total amount of NH_3 produced from fertilizer reacting 6 days was in the order of magnitude: UAP >>>> DAP >>> MAP > APP, or the ratio of 18 : 4.5 : 1.5 : 1. This relationship was generally true for any soil, but the absolute values increased directly with % CaCO_3 in the soil and inversely with soil moisture. Averaging all soils, the total 6-day NH_3 production was in the soil moisture order of 10% > 15% > 20%.

Ammonia absorption by plants was measured directly from the seeds or seedlings by a "Distillation Technique", and indirectly by differences between "Soil-Fertilizer" mixed and "Soil-Fertilizer-Seed" systems. The patterns of NH_3 accumulation by seeds or seedlings were governed by the kinds and rates of fertilizer application, soil moisture, CaCO_3 content, and the stages of plant germination or growth. Dry weight of wheat seedlings was less when germinating seeds, with radicles emerged, were exposed to NH_3 for one day than when seeds were treated with NH_3 one day after moistening.

Absorption of NH_3 by seedlings was directly related to NH_3 production from fertilizer-soil reactions. Maximum absorption occurred in day 3 for 10% CaCO_3 soil and day 2 for 0% CaCO_3 , but the latter was a very low absorption except for UAP. Ammonia concentration in seeds or seedlings in the range 0.3 to 0.5 ppm- NH_3 inhibited seedling growth, and symptoms of NH_3 injury were evident. Radicles had a brown color as a "burnt off" appearance and coleoptiles were stunted. Germination of wheat seeds was completely prevented when the concentration of NH_3 in seeds reached about 0.8 ppm- NH_3 .

Plant yield results from growth chamber studies on 0% CaCO_3 soil indicated the same responses to fertilizers for roots as for tops

with the fertilizers in the order: $APP \geq MAP > DAP > UAP$. On the 10% $CaCO_3$ soil the order was $APP > MAP > DAP > UAP$, and growth of roots for DAP and UAP increased relatively little from 6 to 12 days in contrast with APP and MAP. In all cases, plant growth was inversely related to concentration of NH_3 in plants. Ammonia measured by microdiffusion from soil samples taken from field experiments having fertilizer banded with wheat seed was directly related to reduction in numbers of crowns and stems and inversely related to dry weights of plants at the stem elongation stage of growth.

Using information developed in this research 4 ammonium phosphate fertilizers reacting with soils varying in $CaCO_3$ content can be arranged according to NH_3 production. If greater than $0.5 \mu g NH_3/100g$ soil measured by the diffusion can technique is considered potentially hazardous for banding fertilizers with seeds, the fertilizers and allowable soil $CaCO_3$ percentages before serious seedling damage occurs are as follows: APP, 12% $CaCO_3$; MAP, 10.5% $CaCO_3$; DAP, 3.5% $CaCO_3$; and UAP exceeds the limit at 0% $CaCO_3$.

INTRODUCTION

Fertilizing has long been proved to be an effective method to increase crop production. In spite of the advantages of fertilizer application, increased emphasis is now being placed on the problem of plant damage resulting from improper fertilizer use. Nitrogenous fertilizers, one of the greatest consumptive use, when applied to soils under certain conditions, can release free NH_3 . This ammonia may injure small plants. Detrimental effects as a consequence of NH_3 toxicity would be expected to be associated with the concentration of NH_3 produced and the various susceptible stages of plant development (Smith et al., 1970).¹ Therefore, the questions of how NH_3 is released, how it produces toxic effects on germination and seedling growth and/or how it influences yield components of plants, become matters of practical as well as theoretical interest.

It is hypothesized that, upon the hydrolysis of ammonium phosphate fertilizers in the soil, NH_3 is released and it is the major factor in producing toxic symptoms to germination and seedlings, and it may influence yield components of wheat. Therefore, to achieve a systematic interrelation of facts, the investigations of this hypothesis were conducted intensively in field, greenhouse, and laboratory experiments. Specific objectives and experimental procedures pertinent to

¹Smith, C. M., E. O. Skogley, and C. Pairintra. 1970. Farm test demonstrations. Ann. Report to TVA (Unpublished).

the different types of experiments are illustrated under each later section.

LITERATURE REVIEW

Tisdale and Nelson (1966) wrote that progress in agriculture depends on research of a high caliber. For every problem solved by the scientist today, many more are raised. Agricultural scientists must delve into questions of a fundamental nature, questions that deal more with the WHY of things than with the WHAT.

It is, therefore, the purpose of this review to bring together some of the pertinent findings so that causes and effects can be evaluated and some possible corrective addition may be established.

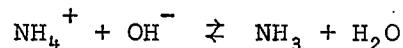
Because ammonia volatilization and toxicity vary depending upon chemical composition of fertilizer and properties of soils, this presentation is, therefore, divided into three distinct parts: (I) Theory, (II) Ammonia Volatilization, and (III) Ammonia Toxicity. All of these aspects are discussed in relation to fertilizer and soil properties.

I. Theory

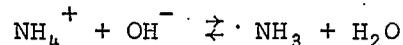
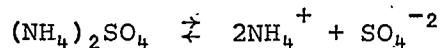
Bennett and Adams (1970) stated recently that ammoniacal-N loss from soil and toxicity to seedlings are parallel manifestations of the same phenomenon. Both depended upon the $\text{NH}_3(\text{aq})$ concentration in the soil solution and are thus governed by the same chemical equilibria. Failure to adequately consider all equilibria have prevented previous investigators from establishing general applicable

quantitative parameters for ammonia losses or toxicity (Blanchar, 1967; Du Plessis and Kroontje, 1964; Ernst and Massey, 1960; Larsen and Gunary, 1962; Megie et al., 1967; Wahhab et al., 1957).

Mechanisms of NH_3 volatilization from soil by chemical reaction have been postulated and almost all systems are pH-dependent. Du Plessis and Kroontje (1964) investigated the relationship between pH and ammonia equilibria in soil and suggested that NH_3 volatilized from acid soils was due to the equilibrium.



Also, there has been a proposal (Wahhab et al., 1957) that NH_3 losses occurred from slightly acid soils to which $(\text{NH}_4)_2\text{SO}_4$ was added, and could be due to the equilibrium of the following nature:



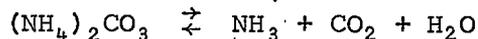
That the effective hydroxyl concentration in such a case would depend on the pH of the system. This postulation was given some support by Ernst and Massey (1960) who stated that liming would cause an increase in soil pH and thus favor the increase in the activity of OH^- . This would encourage the shift in the reaction to the right and increase the volatilization of NH_3 .

Larsen and Gunary (1962) considered that losses of NH_3 from fertilizers applied on alkaline or calcareous soils depend on the

equilibrium:

$$P_{\text{NH}_3} = K[\text{NH}_4^+]/([\text{Ca}^{2+}]P_{\text{CO}_2})^{1/2}$$

where K is a constant equal to $K_{\text{NH}_4}/K_{\text{CaCO}_3}$ and P_{CO_2} is partial pressure of CO_2 . The mechanism affecting the right side is to reduce $[\text{NH}_4^+]$, thus increasing NH_3 volatilization loss. They suggested NH_4^+ can be removed from the system by precipitation of insoluble calcium ammonium phosphates. Terman and Hunt (1964) reported that the $(\text{NH}_4)_2\text{CO}_3$ which is formed from chemical reactions of fertilizers and CaCO_3 in the soil is unstable and decomposes easily due to the equilibrium:



II. Ammonia Volatilization

It has been established that NH_3 may be volatilized readily from soils under a number of conditions and that many factors are involved. Several investigators studied factors affecting NH_3 volatilization losses from nitrogen fertilizer carriers. Mortland (1958) in reviewing work on the reaction of NH_3 in soils listed soil moisture, texture, pH, organic matter, placement, and soil tilth as the factors affecting sorption and loss of NH_3 in soils.

Recently, Pesek et al. (1971) stated that the likelihood of ammonia losses from surface applications is dependent primarily on the chemical nature of the fertilizer material and the pH and other

properties of the soil. They concluded that the modifying influences include soil water content, temperature, surface roughness and residue, air movement, presence of carbonates, granule size of fertilizer and time elapsed between application and the next rainfall, irrigation or before incorporation by tillage.

Stanley and Smith (1955) and Tseng and Wang (1967) observed in the laboratory that losses of ammonia from sandy soil were greater than from finer textures such as silt loam and clay. However, Jenny et al. (1945) reported that ammonia retention was a function of soil texture.

Martin and Chapman (1951) conducted a laboratory experiment on volatilization of ammonia from surface-fertilized soils. The experimental results indicated that percentages of $\text{NH}_3\text{-N}$ lost were in the order of magnitude: $\text{NH}_4\text{OH} > (\text{NH}_4)_2\text{SO}_4 > \text{Urea} > \text{NH}_4\text{NO}_3 > \text{NaNO}_3 = \text{check}$. They reasoned that NH_4OH application raised the pH of the surface of acid soils to the alkaline range and thus permitted greater $\text{NH}_3\text{-N}$ volatilization losses. Increasing rates of application also increased the rates of $\text{NH}_3\text{-N}$ volatilization losses in acid soils but not for alkaline soils.

In laboratory studies, Kresge and Satchell (1960) compared the amount of NH_3 lost by volatilization from several fertilizers. Experimental results showed that the NH_3 volatilization was in the order of magnitude: $\text{Urea} > \text{Ca}(\text{CN})_2 > (\text{NH}_4)_2\text{SO}_4 > \text{NH}_4\text{NO}_3$. The rates of NH_3 losses

were significantly different among fertilizers and were increased as the rates of application increased. In a series of field, greenhouse, and laboratory experiments, Meyer et al. (1961) obtained the same trend of NH_3 volatilization losses.

Regardless of pH and soil type, the magnitudes of NH_3 volatilization presented by Larsen and Gunary (1962) were in the order:

$(\text{NH}_4)_2\text{SO}_4 > (\text{NH}_4)_2\text{HPO}_4 = \text{NH}_4\text{H}_2\text{PO}_4 = \text{NH}_4\text{NO}_3$, whereas Terman and Hunt (1964) reported that NH_3 volatilization losses were in the order: Urea > Urea ammonium phosphate > $(\text{NH}_4)_2\text{HPO}_4 > (\text{NH}_4)_2\text{SO}_4 >$ Ammonium polyphosphate = $\text{NH}_4\text{NO}_3 > \text{NH}_4\text{H}_2\text{PO}_4$.

Jewitt (1942) reported that when $(\text{NH}_4)_2\text{SO}_4$ was applied to soils, considerable amounts of NH_3 were lost through volatilization and these losses were influenced by the rate of fertilizer application. A recent study (Mills et al., 1970) reported similar experimental findings.

Mitsui (1954) and Terman and Hunt (1964) reported a marked decrease in NH_3 losses from urea mixed with the soil compared to surface application. Overrein and Moe (1967) added that NH_3 volatilization rates were inversely proportional to the depth of urea application. Steenbjerg (1944) noted that in 4 weeks the losses from NH_3 from surface application of urea ranged from 5-60%, but if the placement of fertilizer was at 6 cm depth, there was no loss of NH_3 .

Ernst and Massey (1960) stated that NH_3 volatilization from soil was essentially the same when urea was topdressed or mixed with the top 1/4 inch of soil. However, the data of cumulative losses of NH_3 from urea and $(\text{NH}_4)_2\text{SO}_4$ reported by Gasser (1964) indicated that NH_3 volatilization losses were influenced by placement and varied depending on the kind of fertilizers.

Martin and Chapman (1951) reported that CEC (cation exchange capacity) of the soil was important in determining losses of ammonia. Gasser (1964) stated that effects of soils on ammonia losses depend largely on base exchange capacity. He said that property was the most likely one to be related to the ability of the soil to retain ammonium nitrogen and ammonia. The results indicated that ammonia loss decreased as the base exchange capacity increased. Volk (1959) illustrated the effect of CEC as it influenced loss of ammonia by volatilization from surface application of urea and $(\text{NH}_4)_2\text{SO}_4$. During the first week, there was a significant decrease in loss from the application of urea but not for $(\text{NH}_4)_2\text{SO}_4$, and the losses were directly related to the increases in CEC of the 11 acid soils.

Pertaining to reaction of ammonia with clay minerals such as bentonite, Mortland (1958) concluded that the effect of exchangeable cations on ammonia desorption was found to follow the order $\text{H}^+ > \text{Ca}^{+2} > \text{Na}^+ > \text{K}^+$. He stated that the fixation of K^+ by bentonite particularly reduced the sorption of ammonia. This is in agreement with the

work by Martin and Chapman (1951) who found more NH_3 volatilization losses when the exchangeable cation was Na^+ or K^+ than when it was Ca^{+2} or Mg^{+2} . They attributed the effect to the high pH of the Na- and K-saturated soils. Also, other investigators have shown CEC to have a very marked effect on the amount of NH_3 volatilization loss (Brown and Bartholomew, 1962; Ernst and Massey, 1960).

A recent investigation by Rolston et al. (1972) on desorption of ammonia from soil during ion displacement studies indicated that a moist soil has a greater capacity for ammonia desorption than a dry one. In Russia, Lyakh (1972) reported that addition of NPK fertilizers with decreasing soil moisture increased NH_3 losses.

In reviewing literature on ammonia reaction, Mortland (1958) concluded that sorption of ammonia in the soil was influenced by soil moisture. He stated that since ammonia will dissolve in water, the concentration would depend on the partial pressure of NH_3 . Any ammonia that does dissolve in the soil water is in transitory condition; it either will react chemically with organic matter or will volatilize into the air if the partial pressure of NH_3 is exceeded. Stanley and Smith (1955) explained that losses of ammonia from the wet soils were the result of upward movement and subsequent evaporation of water containing dissolved ammonia, whereas from dry soils the losses of ammonia resulted from gas flow out of the soil as a part of gas vapor pressure.

Wetting and drying caused greater losses of NH_3 than maintaining the soil at constant moisture content (Jones, 1932). Ernst and Massey (1960) reported that some NH_3 volatilization occurred without a concurrent drying process in the soil, but greater volatilization occurred when moisture was lost from the soil. When the soil became dry after 4 to 5 days of aeration, NH_3 volatilization was markedly decreased, presumably because hydrolysis of urea was retarded due to the lack of moisture. Therefore, they concluded that NH_3 volatilization was directly related to initial soil moisture content. In contrast, Jewitt (1942) found the loss of ammonia from $(\text{NH}_4)_2\text{SO}_4$ fertilized soils to be dependent on a drying process in the soil but not on the initial soil moisture content.

Martin and Chapman (1951) observed no volatilization of ammonia when moist air was passed over N-fertilized soil (NH_4^+ forms), but loss of ammonia did occur when the samples were aerated with dry air and thus were losing moisture. Meyer et al. (1961) concluded that in favorably moist soils, volatilization of NH_3 took place rapidly in the first few days after application, then tapered off to an insignificant rate in the second week.

Several investigators (Broadbent et al., 1958; Doak, 1952; Fisher and Parks, 1958) reported that urea is readily soluble in water, and the dissolved urea is hydrolyzed to ammonium carbonate by soil bacteria and enzymes. The rate of hydrolysis apparently varies a great

deal among soils, but is temperature-dependent in a particular soil. Overrein and Moe (1967) observed that the rate of urea hydrolysis was shown to be directly proportional to the rate of urea application when soils were incubated at 28°C.

Martin and Chapman (1951) stated that if the soil solution is alkaline in nature, then parts of ammonia will be present as hydrated ammonia, ammonium hydroxide, ammonium bicarbonate or carbonate, or both, depending on the alkalinity, concentration, and other factors. They found that in aqueous solution of these compounds, the NH_3 and water have their own partial vapor pressures and evaporate together in varying proportions depending on the concentration and character of the NH_3 containing solutions. Therefore, they concluded that increasing the amounts of ammonium nitrogen applied to alkaline soil tended to increase the total quantity of ammonia loss but did not appreciably affect the total percent loss.

Terman and Hunt (1964) stated that the differences in ammonia losses among nitrogenous fertilizers can be explained largely in terms of reaction of certain acid radicals of ammonium salts with calcium compounds in the soils. They illustrated the overall reactions which presumably occurred in limed acid or naturally calcareous soils and concluded that ammonium carbonate which is formed by hydrolysis processes is unstable and decomposes easily into NH_3 , CO_2 and H_2O . Bates and Pinching (1950) demonstrated that when ammonium carbonate is

formed, and if the pH of the system is above 7, the concentration of NH_3 increases while NH_4^+ decreases.

III. Ammonia Toxicity

The detrimental effects of ammoniacal-N from fertilizers on germination and seedling growth of plants have received attention in recent years (Bennett and Adams, 1970; Colliver and Welch, 1970; Guttay, 1957; Warren, 1962). Although ammonia is known to be toxic to most forms of plant and animal life, some of the specific toxicity mechanism and physiological effects of plant have not been adequately explained.

Vines and Wedding (1960) studied the mechanism of ammonia toxicity to intact plants and postulated that the site of ammonia toxicity to plants is located in the electron transport system, especially the $\text{DPNH} \rightarrow \text{DPN}$ reaction. Warren (1962) pointed out that the cell membranes were relatively impermeable to NH_4^+ , whereas NH_3 passed tissue barriers with ease. Therefore, he concluded that toxicity depended largely upon the NH_3 which entered the organism and cell. Along the same principle, Stuart and Haddock (1968) reported that $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)_2\text{CO}_3$ or gaseous NH_3 inhibited water uptake in sugarbeet roots whenever the pH was sufficiently high. They suggested that the site of inhibition lies within the root epidermis.

Strogonov (1964) stated that the toxic effect of gaseous NH_3 is expressed by a change in the pH of the cell sap, by deformation of chloroplast, and by a destruction of the cell protein. Several investigators reported that NH_3 inhibits both photosynthetic (Kramer, 1955) and oxidative (Racker, 1961) formations. Murata (1969) concluded that heavy application of nitrogen very likely deteriorate the photosynthesis-respiration balance of the crop stand. He added that this is because if nitrogen supply is too abundant in comparison with the rate of carbohydrate production, the plants will sooner or later be depleted of carbohydrate reserve. Therefore, such plants face the danger of NH_3 toxicity.

Although there is recognition of ammonia release that is toxic to plants, there is no general agreement among researchers defining applicable quantitative parameters and concentrations for ammonia toxicity. Furthermore, it has been a subject of controversy.

Blanchar (1967) proposed a method to determine partial pressure of NH_3 in soil air. The partial pressure of NH_3 (P_{NH_3}) in a closed soil system was measured by expelling it from a collapsible plastic bottle into dilute HCl. The P_{NH_3} in the soil air was calculated from the ideal gas law. Since concentration of $\text{NH}_3\text{-N}$ was governed by different pH levels, Megie et al. (1967) concluded that the toxicity was pH-dependent and the toxicity was attributed to ammonia.

Sample (1963)¹ presented a comprehensive literature review on the effect of fertilizer materials on the germination of seeds. He concluded that free NH_3 gas is the main toxic substance.

Many workers have reported injury or delay in germination and emergence of various crops as a result of fertilizers, especially $(\text{NH}_4)_2\text{HPO}_4$. Hood and Ensminger (1964) reported that the detrimental effect of $(\text{NH}_4)_2\text{HPO}_4$ was not caused by osmotic effect, or by release of free ammonia alone, or by ammonium or phosphate ions per se. They suggested that $(\text{NH}_4)_2\text{HPO}_4$ might adversely affect Mg availability in the seed resulting in reduced enzymatic activity. In studying the mechanism of ammonium phosphate injury to seeds, Ensminger et al. (1965) concluded that germination injury from $(\text{NH}_4)_2\text{HPO}_4$ appeared to be largely due to the inactivation of Mg in seeds.

A recent investigation (Weir et al., 1972) illustrated that ammoniacal-N exists in more than one form in the soil solution; NH_4^+ -N and NH_3 -N. Their experimental results indicated that plants responded similarly to NH_3 and NH_4^+ . Growth was reduced as the NH_3 concentration increased to an optimum level of 17 ppm of NH_4^+ -N for radish and 36 ppm for lettuce. Vines and Wedding (1960) reported, however, that the nonionized ammonia (NH_4^+) and gaseous ammonia (NH_3) inhibited

¹Sample, E. C. 1963. The effect of fertilizer materials on the germination of seeds: A literature review. TVA Report, 1963 (Unpublished).

respiration in concentrations of these two forms of NH_3 ranging from $1 \times 10^{-3} \text{ M}$ to $3 \times 10^{-3} \text{ M}$.

Warren (1962) stated that in most biological fluids ammonia exists in two forms, ionized (NH_4^+) and nonionized (NH_3), the relative proportions of which are determined primarily by the pH of the solution. He pointed out that the toxicity depended upon the NH_3 which entered the organism and cell.

Megie et al. (1967) used an aeration method for determining NH_3 . They stated that toxicity of nonionized ammonia (NH_3) was the primary reason for inhibited germination and reduced growth of cotton seedling. Plant growth decreased sharply with increasing NH_3 and levels above 10 ppm were lethal.

Blanchar (1967) developed a direct method to determine partial vapor pressure of NH_3 (P_{NH_3}) in soil air and found that germination of corn seed was inhibited when the initial P_{NH_3} value was 0.156 mm Hg and final values were between 0.077 and 0.104 mm Hg. Allred and Ohlogge (1964) postulated that free NH_3 associated with DAP fertilizer was toxic to germinating corn. They concluded that NH_3 at a partial vapor pressure as low as 0.125 mm Hg was toxic to corn when it was exposed to this environment for 2 days during the initial stage of germination.

Hunter and Rosenau (1966) measured gaseous NH_3 by a diffusion method. They found germination of corn seeds and growth of seedlings

were greatly inhibited or completely prevented in flasks containing 1 mg or more of gaseous NH_3 . In laboratory experiments, Brage et al. (1960) placed wheat seeds in a petri dish, but not in contact with a mixture of urea and urease. They found that urea to the extent of 20 mg or more produced enough NH_3 gas to prevent any germination of wheat.

Bennett and Adams (1970) considered $\text{NH}_3(\text{aq})$ in the soil solution was the agent of toxicity to plants. They found that symptoms of NH_3 toxicity were evident at $\text{NH}_3(\text{aq})$ concentrations in soil solution in situ above 0.17 mM for sudangrass foliage, and above 0.24 mM for cotton roots. They stated that the critical concentration for incipient NH_3 toxicity was concluded to be 0.15 to 0.20 mM $\text{NH}_3(\text{aq})$.

Colliver and Welch (1970) used a steam distillation method for determining ammonium $(\text{NH}_3 + \text{NH}_4^+)$ -N from anhydrous ammonia. They reported concentrations in excess of approximately 1000 ppm of $(\text{NH}_3 + \text{NH}_4^+)$ -N resulted in significant corn stand reduction. Germination and early growth of corn was retarded when the concentration reached 994 ppm and essentially inhibited when it reached 1628 ppm. By using a similar technique of ammonia determination, Openshaw and Frederick (1970) found that germination of corn and cotton seeds was greater than 87% when anhydrous ammonia added was less than 7 meg/100g soil.

Low and Piper (1961) concluded that NH_3 formed during ammonification caused phytotoxic effects to germinating wheat seeds from as little as 1.3 pounds of biuret per acre applied to urea. Under laboratory studies, Khan and Mandal (1968) observed no emergence of jute seedlings when urea was applied at the rate of 180 and 360 lb-N per acre.

Inorganic sources of N such as anhydrous ammonia or ammonium salts have been reported injurious to plants due to improper placement of fertilizers (Brage et al., 1960; Olson and Drier, 1956). Parr and Papendick (1966) reported that when anhydrous ammonia was injected into soil according to different application schedules, corn yield was considerably reduced at the higher N-levels when compared to equivalent applications of urea and NH_4NO_3 . Yield reduction in this case, they stated, was attributed in part to root damage due to NH_3 toxicity. Colliver and Welch (1970) concluded that such injury generally increased as the rate of anhydrous ammonia application increased.

Brage et al. (1960) stated that enzymatic hydrolysis of urea produced enough gaseous NH_3 to be toxic to germinating seeds, where the seeds were placed near to the mixture of urea or urease in a closed system. Guttay (1957) conducted a series of greenhouse experiments in which he showed that complete fertilizer, applied at the rate of 100 pounds of N (NH_4^+), P_2O_5 , and K_2O per acre in contact with wheat seeds, seriously delayed and curtailed germination and emergence.

Lawton and Davis (1960) reported that contact placement of wheat seeds with 5-20-20 fertilizer ($\text{NH}_4\text{-N}$) at 500 pounds of material per acre delayed and reduced emergence of seedlings and subsequent growth. Applying this mixed fertilizer in a band below, or 1 1/2 inches to the side and 1 1/2 inches below, the seed was not desirable from the standpoint of emergence and growth. Cook et al. (1958) found that the application of 12-12-12 fertilizer per acre with the seeds influenced the emergence of wheat seeds, and at the end of 9 weeks, they observed a 20% reduction in stand. The yields were reduced where the greatest emergence injury occurred. Tillering and other yield components were influenced.

Andrews et al. (1956) observed seedling injury when anhydrous ammonia was applied in contact with germinating seeds. In studying the injurious effects of preplant anhydrous ammonia to germination and early growth of corn, Colliver and Welch (1970) reported severe damage when anhydrous ammonia was applied at 10 cm deep immediately before planting at 5 cm deep. Lorenz et al. (1955) concluded that aqua ammonia placed in the bed under the potato row resulted in low yields and caused severe plant toxicity. They suggested that the toxicity could be lessened by placing the fertilizer farther away from the plant, using split application or delaying application until the crop was well established.

Comparing different methods of fertilizer placements, Stephen and Waid (1963a) reported greater adverse effects of urea when placed near the seeds than when mixed throughout the soil.

Guttay (1957) reported that fertilizer placement in contact with wheat seeds had greater effects on delaying and reducing emergence under dry than moist conditions. Dubetz et al. (1959) proposed that moisture levels alone had no significant effect on the germination of any crop. However, moisture levels in combination with nitrogen fertilizers, they explained, reduced germination, and the reduction became progressively pronounced with decreasing moisture.

MATERIALS AND METHODS

Influence of NH_3 from ammonium phosphate fertilizers on germination, seedling growth, and production of wheat (*Triticum aestivum* L.) were investigated in (I) laboratory, (II) growth chamber, (III) greenhouse, and (IV) field experiments. Specific objectives and experimental procedures are illustrated under each section. The statistical plan is also included for some experiments. The series of experiments are as follows:

I. Laboratory Experiment

Objectives. Although general concepts of volatilization losses and toxicity of ammoniacal-N fertilizers have been recognized and well documented by previous investigators, physio-chemical processes and quantitative determination pertaining to fertilizer-soil-plant systems have not been considered simultaneously and adequately explained. In order to draw a basic sound inference, this laboratory experiment was comprised of 2 investigative studies. The first study is referred to as the " NH_3 Production Study". The investigations involved mainly, i) the patterns of NH_3 release, and ii) the amounts of NH_3 produced from monoammonium phosphate (MAP:11-48-0), diammonium phosphate (DAP:18-46-0) ammonium polyphosphate (APP:15-62-0), and urea ammonium phosphate (UAP:24-42-0) upon reaction with soils varying in moisture and % CaCO_3 contents. The second study is called the " NH_3 Absorption Study". The purposes of this study were: i) develop a procedure of measuring free

NH_3 concentration in soils and define a concentration of NH_3 required to be toxic to spring wheat (*Triticum aestivum* L., 'Fortuna'); ii) evaluate the most susceptible stage of wheat plant development to NH_3 toxicity.

Experimental Procedures

NH_3 Production Study. A "Diffusion Can" with soil and fertilizer mixed, as illustrated in Fig. 1, was designed for this study. The can is a Buckeye, style No. 201, Seamless Tin, outside dimension-- diameter, 7 cm, - depth 5 cm, and total capacity 110 cm^3 . The units consist of two portions, the inner and the outer chambers. The inner cell is a replaceable plastic vial of boric acid solution and located at the center of the diffusion can. The outer is a chamber of soil and fertilizer mixed. The can is kept closed with a lid to allow diffusion to proceed within a closed system and at room temperature. Therefore, the "Diffusion Can" resembles the microdiffusion unit (Bremner and Shaw, 1955) with some modifications.

To evaluate NH_3 production from ammonium phosphate fertilizers on different soils, diffusion cans were set up as a series of laboratory experiments. Six soils at a total of 10 different contents of CaCO_3 were used in "Diffusion Can" experiments. The soil series, pH, and % CaCO_3 equivalent data are in Table 1. There are four ammonium phosphate fertilizers: MAP, DAP, APP, UAP; and three moisture levels: 10%,

