EFFECT OF UREA AND UREA-AMMONIUM NITRATE SOLUTION (28-0-0) ON BARLEY EMERGENCE AND GROWTH

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ABSTRACT

Field studies in Manitoba have shown that urea in excess of 20 lb N/acre added with barley seed reduces seedling emergence and yield. The objective of this study was to obtain information on the effects of urea and 28-0-0 (urea and ammonium nitrate in solution) on barley emergence and early growth.

Greenhouse studies showed that on coarse-textured soils, 30 lb N/acre as urea and 60 lb N/acre as 28-0-0 reduced yield when applied closer than one-quarter inch from the seed. Sixty lb N/acre as urea or 28-0-0 placed one-half inch from the seed did not reduce yield. Yields were not influenced when 60 lb N/acre as urea and 120 lb N/acre as 28-0-0 were applied with the seed on heavy-textured soils. Urea, at rates of 40 or 60 lb N/acre, usually reduced emergence when placed closer than one-half inch from the seed. At equivalent rates of added N, emergence with urea was less than with 28-0-0. When equivalent amounts of urea nitrogen was added, emergence with 28-0-0 (120 lb N/acre) was less than with urea (60 lb N/acre). Thus, some damage was caused by the ammonium nitrate in the 28-0-0.

In a laboratory study it was found that a much greater amount of ammonia was lost from a coarse-textured soil than from a heavy-textured soil. High ammonia losses were associated with large reductions in emergence.

A study on the osmotic and toxic effects of various fertilizer solutions showed that ammonium carbonate or ammonium

hydroxide solutions reduced seed germination due to ammonia toxicity. Urea solutions reduced seed germination by a toxic effect. This toxicity appeared to be due to urea molecules moving into the seeds, followed by enzymatic hydrolysis of the urea and accumulations of toxic amounts of ammonia. Ammonium sulfate and ammonium nitrate solutions reduced germination by both a toxic and osmotic effect. The osmotic effect occurred only at high concentrations.

The studies revealed that reductions in barley emergence and yield appeared mainly due to accumulations of ammonia in the soil solution. To a lesser extent these reductions were attributed to: (1) accumulations of nitrite in the soils, (2) enzymatic hydrolysis of urea in the seed and subsequent accumulations of ammonia, and (3) high osmotic potentials in the soil solution caused by urea and its reaction products.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Figure		Page

I INTRODUCTION

Most non-fallow land in Manitoba does not contain sufficient quantities of available nitrogen to produce high yields of non-legumous crops. Nitrogenous fertilizers, ammonium nitrate, urea, and ammonium sulfate are widely used to correct these deficiencies. Nitrogen is also added in the form of mixed fertilizers such as 23-23-0. The nitrogenous fertilizers are applied broadcast or drilled in with the seed.

Studies have been conducted in Manitoba to determine the relative efficiency of ammonium nitrate and urea added with the seed and broadcast (93). These studies showed that urea broadcast did not increase yields as much as did the application of an equal rate of ammonium nitrate. Various reasons were given for the differences in efficiency: (1) a greater gaseous loss of ammonia from the urea nitrogen; (2) preferential immobilization of ammonium by soil microorganisms; (3) germination reduction and plant damage caused by urea and its hydrolysis products. Toews (93) also showed that urea in excess of 20 lb N/acre added with the seed reduced seedling emergence and yield. Court _et al._ (30, 31) suggested that the phytotoxicity from urea applied below the surface of the soil was caused by free ammonia and nitrite accumulation. He showed that the extent to which ammonia and nitrite accumulated in soils was influenced by soil factors, the rate and method of placement of the urea, and the materials applied with the urea.

The objectives of this study were as follows:

(1) To determine the effect of mode of placement of urea and 28-0-0 on the emergence and yield of barley using different watering techniques and soils.

(2) To study the relationship between ammonia volatilized from soils and reductions in seedling emergence.

(3) To determine the toxic effects of ammonia and urea on germination of barley.

II REVIEW OF LITERATURE

(A) Urea Hydrolysis

Urea hydrolyzes to ammonium carbamate, which hydrolyzes to ammonium carbonate in soils (13). Ammonium carbonate readily dissociates to form ammonium ions. The ammonium ions can be nitrified, used by crops and microorganisms, fixed by soil colloids, or lost from the soil through volatilization. Urea can be hydrolyzed both chemically and biologically in soils. Chin and Kroontje (19) found that chemical hydrolysis of urea is very slow and at low temperatures becomes insignificant. The enzyme that catalyzes biochemical urea hydrolysis is urease (23, 25). Urease is produced by many soil microorganisms and thus the hydrolysis of urea in soils is usually very rapid (13, 22).

(B) Factors Affecting Urea Hydrolysis

Chin and Kroontje (19) found the rate of urea hydrolysis to be related to the general microbial activity in the soil. Paulson (75) discovered that adsorbed urease and urease in solution had different activities. Urea hydrolysis increased with increases in the proportion of urease in solution.

Fisher and Parks (43) found that the optimum temperature for urea hydrolysis was 30^{o}C which coincides with the optimum temperature for growth of microorganisms. Broadbent _et al._ (13) found that 200 and 400 ppm nitrogen as urea was completely hydrolyzed in three of four California soils at 7.2^{o}C within seven days. Complete hydrolysis occurred in three days at 23.9°C. Working with Tennessee soils, Fisher and Parks (43) found that 80 percent of an application of 100 lb N/acre as urea was hydrolyzed at 10°C within a period of three weeks, while urea at 200 lb N/acre was completely hydrolyzed at 30°C within the same period of time.

The rate of urea application also affects the rate of urea hydrolysis. Some workers (43, 64) found that the rate of urea hydrolysis increased linearily with the rate of application up to 800 lb N/acre. Armstrong and Horton (3) found no influence of rate of application on rate of hydrolysis. Laidler and Hoare (57) found that the rate of urea hydrolysis increased linearily with rate of application, reached a maximum, and then declined at high concentrations of urea.

The moisture level in soils does not greatly affect the rate of urea hydrolysis (83, 38, 34). Hydrolysis was slightly faster at moderate soil moisture conditions than at field capacity. It was suggested that the oxygen content of the soil may not have been at optimum levels for microorganisms' activity at the high soil moisture contents.

Conrad (22) and Gibson (50) reported that soils high in organic matter hydrolyzed urea at a faster rate than comparable soils low in organic matter. Soils with higher organic matter contents probably have a higher number of soil microbes and a greater urease activity.

It has also been shown (24) that urea hydrolysis increases with the clay content of a soil. It was suggested that the urease enzyme could be stabilized by association with clays.

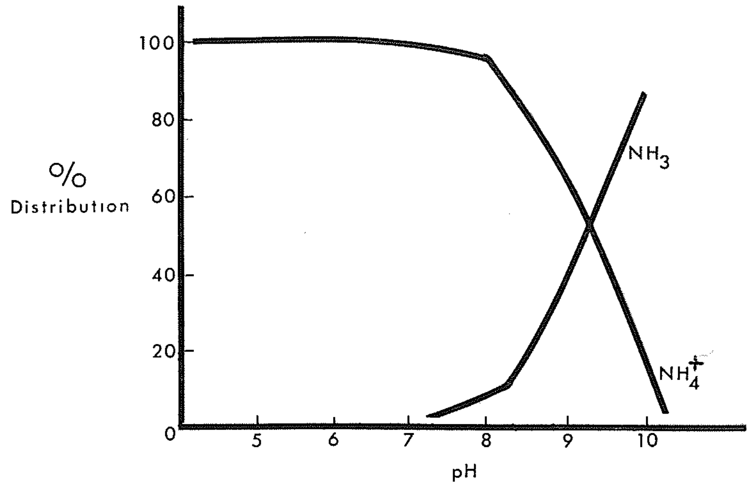
Simpson and Melsted (83) found that increasing the pH of an acid Illinois soil, increased the hydrolysis rate of urea. Gibson (50), however, showed that a highly acid (pH 3.1-3.3) peat sample was able to hydrolyze urea at a relatively high rate.

Adsorption and leaching of urea and the Van Slyke reaction could influence the rate of urea hydrolysis. This, however, seems unlikely as soils, in general, have a weak affinity for the urea molecule (18), and conditions favourable for the urea-nitrite Van Slyke reaction seldom occur in soils (82).

(C) Accumulation of Ammonia

The ammonium ions produced when urea hydrolyzes are removed from the soil solution by the numerous pathways mentioned previously. The amounts of ammonium in solution depends upon the relative rates of processes such as nitrification, immobilization, mineralization, leaching, fixation, and plant utilization.

The amount of ammonia in solution is directly related to the concentration of ammonium ions and the pH of the medium. In soil (13) adsorbed ammonium is in equilibrium with ammonium and ammonia in solution. Ammonium carbonate is found when urea hydrolyzes; thus, the pH increases and larger amounts of ammonia are formed. The following figure shows the percent distribution of ammonium and ammonia in aqueous equilibrium systems at 15°C (5).



The reactions of ammonia in the soil are varied and complex. Mortland (67) listed the following reactions for ammonia applied to soils:

(1) Ammonia can be chemically adsorbed by clay minerals and organic matter. Ammonia forms the ammonium ion in this complex. Mortland (67) found that chemical sorption is largest on clay minerals under acid conditions, and greatest by organic matter under alkaline conditions. Fixation of ammonia and ammonium ions declines with pH.

(2) Ammonia can react to form larger nitrogen compounds.

(3) Ammonia can be physically sorbed by soil colloids.

(4) Ammonia can be dissolved in soil moisture where it may react with hydrogen to form ammonium ions.

(5) Ammonia, not adsorbed, can diffuse through the soil and enter the atmosphere.

(D) Ammonia Volatilization

Ammonia volatilization is related to the amount of free ammonia present in the soil. There are many factors in the soil which affect the amount of free ammonia present. Considerable amounts of ammonia can be lost from the soil. Volk (97) applied urea to a series of light sandy soils and found up to 60 percent of the nitrogen applied was lost as ammonia. It has been pointed out by Martin and Chapman (61) that if the pH of a soil exceeds 7.0 either naturally or temporarily induced by the addition of fertilizer, some of the ammonia present will be lost by volatilization. Volk (97) reported that increasing soil pH decreased the ammonia-adsorption potential of Florida soils and increased ammonia volatilization from applied urea. Duplessi and Kroontje (40) also reported this trend. Ernst and Massey (42) showed that increasing pH resulted in a greater degree of calcium saturation of the soil exchange complex; therefore, there was less adsorption of ammonium. Liming a moderately acid silt loam soil increased losses of ammonia from applied urea; the losses increased with increasing soil pH (42). Mitsui et al. (63) also found that liming increased losses of ammonia from applied urea. More ammonia was lost from urea applied to recently limed turf than from unlimed grass (98).

Mixing of urea with an acid salt, such as superphosphate has been shown by Low and Piper (59) to reduce ammonia volatilization. The ammonium formed nonvolatile salts in the soil.

Soils having high clay contents and a corresponding high cation exchange capacity favour the sorption of ammonium and decrease ammonia volatilization. Gasser (47) concluded that if 100 lb N/acre of urea is broadcast on the soil surface, over 20 percent of the added nitrogen will be lost as ammonia if the cation exchange capacity is less than 10 me/100 g. Ammonia losses decrease to about 10 percent for soils with cation exchange capacities greater than 20 me/100 g. Wahhab and Ishaq (99) found that twice as much urea was lost from a sandy loam soil as compared to a sandy soil. The rate of urea hydrolysis was much greater in the sandy loam soil.

Incorporation of organic residues (67) with the soil reduces total ammonia loss, as it increases the cation exchange capacity. Ernst and Massey (42), Volk (97), and Doak (38) observed that increasing temperatures markedly increased ammonia volatilization. Soils under dry conditions have a higher rate of ammonia volatilization than under wet conditions, since ammonia concentrations are higher (19, 97, 99). Martin and Chapman (61) observed no volatilization of ammonia when moist air was passed over nitrogen fertilized soil, but volatilization occurred when dry air was used. Ammonia losses(97) were maximal at soil moisture contents at about halfway between air-dry and field capacity. Ernst and Massey (42) found that ammonia volatilization was greater when the soil was drying. However, if drying took place too rapidly, total ammonia loss was reduced due to a reduction in urea hydrolysis. Total ammonia loss was directly related to initial soil moisture contents since it was related to the duration of the drying process. The highest loss in the field would probably take place when initial moisture and temperature are sufficient to bring about rapid total conversion of the urea, followed by fast drying of the soil.

Kresge and Satchell (56) reported a marked decrease in ammonia losses from urea mixed with the soil compared to urea applied to the soil surface. Overrein and Moe (73) found that ammonia volatilization rates were inversely proportional to the depth of urea application and decreased more rapidly with depth in wet soil than in moist soil. Ernst and Massey (42) found little differences in ammonia volatilization between broadcast urea and urea mixed with shallow layers of soil.

Overrein and Moe (73) reported a higher percentage of volatile ammonia loss with increased rates of urea application.

Ammonium (67) is strongly adsorbed and will not move very readily through the soil, so leaching losses are very small. As conditions for ammonia volatilization become favourable, conditions for leaching become unfavourable.

Moe (64) reported that ammonia volatilization losses could probably be reduced significantly if a suitable specific inhibitor for urease could be found. He used p-chloromercuribenzoate, which decreased urea hydrolysis, but was even more effective in inhibiting nitrification; thus, ammonium contents remained high.

If nitrification is slow, ammonia is more likely to accumulate in the soil and persist for a longer period of time; thus, loss due to ammonia volatilization will be increased (64).

Ammonia loss varies considerably with soil type and type of fertilizer used (98). Little or no ammonia was lost when ammonium salts were applied to slightly acid soils, but losses were appreciable and comparable to those from urea, when applied to calcarious soils (61, 97). Volk (98) found that losses of ammonia, when ammonium sulfate was applied to recently limed turf, were similar to those from urea. Gässer (47) reported no differences in volatilization among pelleted urea, crystalline urea, and urea in solution. Volk (98) used pelleted urea, ammonium nitrate, and a solution of 16.5 percent urea and 15.5 percent ammonium nitrate and found that ammonia losses were 20.6, 0.3, and 11.5 percent, respectively. The loss of ammonia from the nitrogen solution of urea and ammonium nitrate was 22.3 percent of the applied urea, which is only slightly higher than the percent loss of the pelleted urea.

(E) Nitrite Accumulation in Soils

Nitrite is formed by bacterial oxidation of ammonium by _Nitrosomonas_. _Nitrobacter_, then, oxidizes nitrite to nitrate. Nitrite oxidation in soil is usually faster than nitrite formation and no accumulation of nitrite occurs (81). Clark _et al_. (20), however, found nitrite in 14 out of 41 soils supplied with 400 ppm urea -N and in seven of these soils the nitrite -N content exceeded 100 ppm. Jones and Hedlin (55) reported nitrite levels of up to 437 ppm in a soil incubated with 800 ppm urea for four weeks.

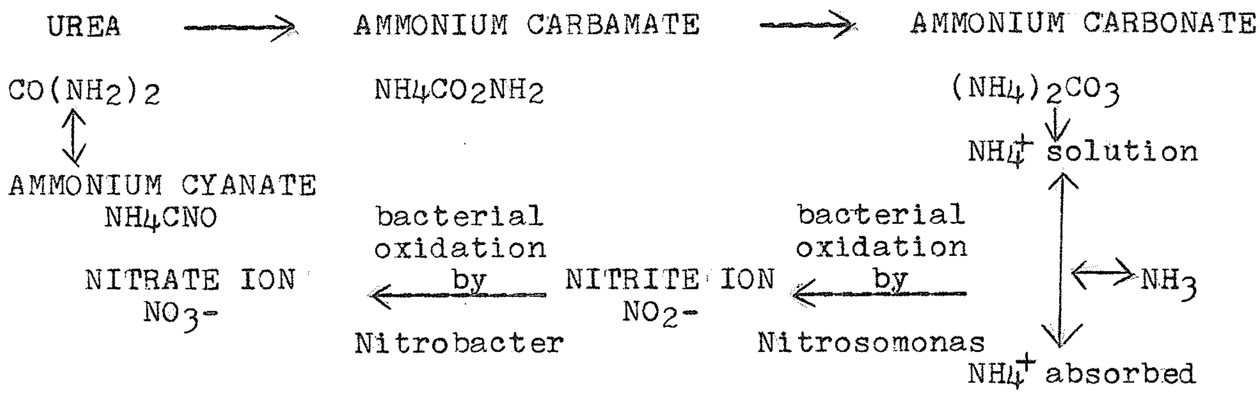
Nitrite accumulation would occur if nitrite oxidation by Nitrobacter was inhibited. Previous work has shown that urea applications can inhibit the action of these organisms. Martin and Chapman (61) reported little oxidation of nitrite to nitrate at soil pH values above 7.7. Volk (96) observed that nitrite accumulated when the pH exceeded 7.7. Optimum pH for ammonium oxidation by Nitrosomonas in pure culture is about 8.2 (53) with relatively high activities persisting even at pH values of 9.0. Nitrosomonas has a greater tolerance of alkalinity than has Nitrobacter. A high ammonium concentration inhibited the growth and metabolism of Nitrobacter and indirectly the oxidation of nitrite (58). Fry (44) found that the degree of inhibition increased with pH increases due to higher concentrations of ammonia. Stojanovic and Alexander (90) and Aleem and Alexander (1) found that ammonia inhibited Nitrobacter more severely than Nitrosomonas, and conditions therefore became more suitable for nitrite accumulation.

The growth of Nitrobacter is retarded by high concentrations of nitrite (1, 44, 58) and in soil the oxidation of applied nitrite is delayed as the concentration of nitrite is increased. Doak (38) observed that the oxidation of nitrite to nitrate was delayed by the presence of high concentrations of nitrite, despite the lowered ammonium concentration and pH resulting from ammonium oxidation.

It is thus obvious that soil conditions that favour ammonia accumulation in the soil, also favour the accumulation of nitrite.

(F) Toxicity of Urea and Its Transformation Products on Seed Germination and Early Seedling Growth

The following diagram shows the products formed during the manufacture of urea or during its transformation in soil or plants.



In recent years there have been several reports showing that urea provides less nitrogen to plants than does other nitrogen fertilizers (27, 59, 91, 102, 103). Also, urea fertilizer drilled in with the seed has been shown to cause severe seed and seedling damage (35, 72, 93, 102, 103). Urea applied broadcast or as a sideband application caused little or no damage. Devine and Holmes (36) applied different fertilizers on spring barley and found that 35 to 105 lb N/acre as ammonium sulfate and ammonium nitrate drilled with the seed sometimes retarded early plant growth. Higher rates of these fertilizers, however, still gave as good or higher yields than those obtained with 35 to 105 lb N/acre. Urea at 45 lb N/acre had no large effect on early plant growth; but at 70 to

90 lb N/acre, it seriously delayed and reduced plant population. Higher applications of urea reduced yields. Yields were similar for all nitrogen sources when applied broadcast. Stephen and Waid (86, 88) obtained similar results and also found that there was little effect of urea on seedling emergence when the fertilizer was mixed with the soil. Brage et al. (9) found that in field experiments with winter wheat, placing urea or ammonium nitrate with the seed in a clay soil reduced stands by 25 and 60 percent with 40 and 80 lb N/acre as urea, respectively, and by 10 percent with ammonium nitrate at 80 lb N/acre. Court et al. (31) and Stephen and Waid (86) also observed a phase of toxicity associated with the death of established plants following urea applications with the seed. Toews (93) concluded that the application of 20 lb N/acre with the seed as urea did not cause appreciable damage on soils of medium to fine texture and if moist at time of seeding. The reduction in yield and plant damage that results from high levels of urea fertilizer application with the seed may be caused by the urea itself, or by substances formed during its manufacture or during its transformation in soil or plants (31). Some workers attributed the damage to ammonia and nitrite accumulation (36, 86, 87). Stephen and Waid (86) reported the death of established plants due to nitrite toxicity even when the urea had little effect on seedling emergence.

Urea may reduce seed germination and seedling growth especially when urea hydrolysis is extremely slow, and high concentrations of urea occur near seeds for a considerable period of time (31). The effects of urea are as follows (31):

(1) osmotic effects (water stress in the seed),

(2) toxic effect of the urea molecules *per se*.

Court *et al*. (31) postulated that urea absorbed by seedlings could cause damage indirectly since the enzymatic hydrolysis of urea within plant cells could lead to toxic amounts of free ammonia in many plant species. Solutions of three percent urea inhibit cell activities of bacteria and may also affect plant cells (94). It has been shown (37) that the C in C^{14} labelled urea and C^{14} labelled sodium carbonate have similar patterns of incorporation into amino acids. This suggests that hydrolysis takes place before entry into the plant. The carbon must have been incorporated in the form of the carbonate ion in both cases.

Biuret is formed during urea manufacture (31). However, biuret does not cause toxicities when present in fertilizers in amounts of less than one percent (26, 59, 85, 102). Biuret at levels greater than one percent has been shown to be toxic to plants (9, 84).

Ammonium cyanate is the product of urea isomerization and could be toxic (80). Low and Piper (59) showed that cyanate concentrations likely to occur in urea solutions (0.01 percent) had a negligible effect on the growth of Italian ryegrass.

Brage *et al*. (9) suggested that ammonium carbamate, the first product of urea hydrolysis, could be toxic when urea is applied in large amounts, or close to seeds or roots.

Many authors have attributed damage caused by fertilizer applications to the toxicity of ammonia on the seeds or seedlings (4, 27, 46, 59, 96). Brage et al. (9) established that the enzymatic hydrolysis of urea produced enough gaseous ammonia to be toxic to germinating seeds under conditions where the seeds were placed near a mixture of urea and urease in a closed system. Stephen and Waid (88) reported that the time of application of urea was important. Maximum damage occurred when urea was added two days before seeding in an acid sand. Urea hydrolyzed more slowly in the acid sand and toxic amounts of ammonia took longer to accumulate. It has been found that ammonia toxicity can also result from the addition of ammonium phosphates to the soil (2, 6, 54, 89). Bennett and Adams (6) reported calcium deficiencies after the addition of diammonium phosphate as a result of precipitation. Ensminger et al. (41) reported that diammonium phosphate may cause inactivation of magnesium in seeds. It is difficult to determine the amount of damage caused by ammonia *per se* to plants as other factors also have to be considered. Colliver and Welch (21) found that applications of anhydrous ammonia caused serious plant damage. He discovered that P deficiency symptoms were associated with plants that had been damaged by ammonia. Seedlings could not absorb sufficient phosphorus for normal growth due to damaged roots. The incipient toxic level of ammonia in soil solution was 0.15 to 0.20 mM (7). Blanchar (8) found that germination of corn seeds was reduced when the partial pressure of ammonia was 0.156 mm. Colliver and Welch (21) found that germination and early growth was retarded when the soil ammonium and ammonia concentration reached 944 ppm (pH 8.1) and essentially, completely inhibited germination when the ammonium plus ammonia concentration reached 1,628 ppm (pH 9.0). Roots grew through 3 cm layers of soil containing 1,172 ppm nitrogen (pH 8.4) but did not grow into layers containing 1,485 ppm nitrogen (pH 8.7).

Court _et al_. (31) found several ammonia toxicity symptoms. Roots had more branching and root tips were scorched. Shoots were delayed and usually were deformed; leaves remained furled and dark, and frequently became pale and later necrotic.

The mechanism of ammonia toxicity to seeds and seedling growth remains obscure. Warren (101) reported that living organisms may tolerate ammonia administered at a slow rate because of their highly efficient detoxifying mechanisms in which urea, glutamine, or asparagine is formed. Cell membranes are relatively impermeable to ammonium while ammonia passes tissue barriers with ease. Vines and Wedding (95) found that ammonia caused inhibition of respiration in plants. He suggested that the site of toxicity to plants is located on DPNH-DPN reaction in the electron transport system. He found that high levels of ammonia also increased the permeability of red beet root discs to water. Gamborg (45), using soybean cells, found that ammonium inhibited the conversion of isocitrate to α-ketoglutarate and thus limited glutamate formation. Using ammonium as the source of nitrogen for plants can lead to plant damage resulting in soluble nitrogen increases in the plant, chlorosis, restricted growth, and in some cases, death.

Nitrite is known to be toxic to plants and the degree of toxicity varies with pH; less nitrite is tolerated under acid conditions than at higher pH values (33). Damage to plants which have received applications of urea has been attributed to nitrite (21, 29, 31, 51, 96). Chapman and Liebig (17) reported nitrite accumulation from urea applied to alkaline or neutral soils in citrus orchards, but there were no adverse effects, possibly because of a high natural soil pH. Colliver and Welch (21) found that two to four weeks after anhydrous ammonia had been applied to a soil, nitrite in excess of 40 to 50 ppm developed, and this was toxic to seedling root growth. Nitrite toxicity was associated with the death of established plants.

Symptoms of nitrite toxicity (70) are a sparse lignified root system and small chlorotic plants that are prone to wilting.

Phipps (77) found that increasing the concentration of nitrite -N decreased dry matter yields, total acidity, the concentration of nitrogen, phosphorus, and potassium in tomato plants, and increased the chlorois of leaves and lignification of roots. It was postulated that nitrite could block one stage in the carboxylic acid cycle as the sap becomes more acidic.

(G) The Effect of Solutions of Varying Osmotic Strengths on Seed Germination

The moisture stress exerted on germinating seeds in the soil by the total potential of soil water is made up of three components (49):

(1) osmotic potential-produced by soluble salts in the soil;

(2) capillary potential-produced by capillarity and surface adsorption of water in soil;

(3) gravitational potential-produced by the vertical position of the water. Gravitational potential is equal to zero for germinating seeds in soil solution. George and Sands (49) reported that matric and osmotic potentials affected seed germination differently even though their free energy measurements were identical. He found that in some cases, 100 cm (H_2O) of matric potential was as effective as 10,000 cm (H_2O) of osmotic potential in retarding seed germination rates. Calculated values of osmotic potential for fertilizers in solution are only valid if the seed coat acts as a semipermeable membrane which prevents solute from entering into the seed. Manohar (65) reported that the degree of restriction imposed by the seed coat was roughly proportional to the size of the molecules of the chemicals used. He also found that the seed coat was virtually impermeable to solutions containing large molecules such as polyethylene glycols of molecular weight of 6000. McWilliam _et al_. (62) showed that the effect of carbowax solutions on germination

was due solely to osmotic activity, since a close relationship was found between the average moisture content of seeds and the potential of the solution in which they were imbibed. There seemed to be no other toxic effect, since viability of seeds imbibed in various concentrations of polyethylene glycol was unaffected when subsequently germinated in water. Molecules such as sodium chloride (65) have very little osmotic effect as they easily enter into the seed and the influence of such chemicals on germination is due to their toxic effect within the seed. Toxicity, in cases like this, depends on the nature of the solute present within the seed. Other molecules, such as mannitol (65, 74), have a certain transient osmotic effect as it enters the seed with some degree of difficulty. Parmar and More (74) reported that when the osmotic potential was increased from 0 to 10 atm, the weight of water imbibed by seedlings in 48 hours was restricted 10, 6, and 10 percent with mannitol, sodium chloride, and carbowax 6000, respectively. He found that adverse effects on corn germination was greatest with carbowax 6000, intermediate with mannitol, and smallest with sodium chloride as osmotic substrates. Manohar (65) reported that solutions of sodium chloride, glycerol, and to some extent, mannitol may enter pea seeds with little restriction through the micropyle. He found that sodium chloride reduced germination the most, glycerol the least, and mannitol intermediate. It appears that sodium chloride had a toxic effect and no osmotic effect; glycerol had no toxic effect and no osmotic effect; mannitol had no toxic effect but had a transient osmotic effect as it delayed germination. Therefore, a chemical can affect germination in either of two ways or possibly both. There is an osmotic effect which must involve a differentially permeable membrane and a toxic effect within the seed.

It has been shown in the field that high applications of fertilizer reduced plant germination (2, 9, 15, 32, 66, 68, 69). Chapin and Smith (15) and Read and Beaton (78) found that lowering soil moisture contents increased the damage to plants by fertilizer applications. Read and Beaton (78) found that lowering temperatures slightly reduced germination. Cummins and Parks (32) reported that the damage to maize and wheat by various salts decreased in the order: anhydrous ammonia, urea, sodium nitrate, ammonium nitrate, ammonium sulfate, and potassium sulfate. Dubetz *et al*. (39) reported that with increasing osmotic pressures at iso-osmotic concentrations, germination was lower in ammonium nitrate than in mannitol solutions. He suggested that the nitrate or ammonium ions were toxic. Gasser (48) suggested that urea decreases the germination of kale, barley, and wheat because of its osmotic effects. Some urea may have been hydrolyzed in the seed but urea itself did not seem to be toxic. He also found that ammonium-salts were more damaging than potassium-salts, and that sulfate was less damaging than nitrate or chloride. He suggested that the differences between sulfate and nitrate or chloride could have been due to an osmotic effect. It is also possible that the nitrate and chloride ions were toxic.

Thimann (92) reported that an osmotic recovery phenomena by potato discs in mannitol solutions could not be explained by mannitol uptake for it was negligible. He suggested that it must have been due to a temporary release of osmotic material within the cells, such as hydrolysis of a stored polymer.

III METHODS AND MATERIALS

(A) Soils

During the summer of 1969 surface soil samples (0-6 inches) were obtained from the various fields, air dried, and sieved through a one-quarter inch screen. These soils (Table I) were obtained from the approximate locations of field experiments conducted by Toews (93) in 1968 and 1969 in order that the greenhouse and laboratory experiments reported in this manuscript could be compared with the data obtained by Toews (93) in field experiments. The soils, selected by Toews (93) varied in texture, cation exchange capacity, pH, and organic matter contents (Tables I and II). All of these soil properties have been reported (47, 97) to have an effect on the degree of toxicity of urea to field crops.

(B) Fertilizer Materials

The following modes of fertilizer placements and fertilizer materials were used in this study:

<u>Fertilizer Placements:</u>

(1) Randomly spread with seed—Pelleted fertilizer was spread randomly in a one-half inch band with the seed.

(2) Contact with seed—Pelleted fertilizer was placed closely around each seed.

(3) One-quarter inch from seed—Pelleted fertilizer was placed one-quarter inch from the seeds, along each side of the seed row.

(4) One-half inch from seed—Pelleted fertilizer

Table I. Characteristics of soils studied

Soil	pH	Cation exchange capacity (me/100g)	Organic matter (%)	Conductivity (mmhos/cm)	NO_3-N content (ppm)	$NaHCO_3$ ext. P (ppm)	Exch. K (ppm)	Carbonate content (% CO_3)	Moisture content at field capacity (%)
Altona	6.6	26.2	6.50	0.5	35	34	890	0.15	28
Almasippi	6.8	19.9	1.92	0.4	10	9	190	3.24	24
Stockton	6.5	17.0	4.41	0.2	4	8	300	0.26	25
Red River	7.3	51.3	5.81	1.0	45	13	790	0.90	56
Lakeland	8.0	29.4	6.90	0.6	2	19	451	15.60	33

Table II. Subgroup designation, legal location, and texture of soils studied

Soil	Subgroup	Legal location	Texture
Altona	Orthic Black	S.E.5-4-4	VFSCL
Almasippi	Orthic Black	S.E.22-6-6	LVFS
Stockton	Orthic Black	N.E.16-13-15	FSL
Red River	Rego Black	S.W.1-5-3	C
Lakeland	Calcareous Rego Black	N.E.19-16-3	CL

was placed one-half inch from the seeds, along each side of the seed row.

Fertilizer Materials:

(1) Nitrogen solution (28-0-0)—Consisted of 39.5 percent ammonium nitrate, 30.5 percent urea, and 30.0 percent water.

(2) Urea solution—50 g of urea in 100 ml of solution.

(3) Pelleted urea—Commercial grade 46-0-0.

(4) Urea powder—Finely ground commercial grade 46-0-0.

(5) Pelleted ammonium nitrate—Commercial grade 34-0-0.

(C) Analytical Procedures

Soil Organic Matter:

Soil organic matter was determined according to the method of Walkley and Black (100). Excess potassium dichromate was used to oxidize the organic matter, and the unreacted dichromate back-titrated with ferrous sulfate using barium diphenylamine sulphonate as indicator.

Soil Carbonate Content:

The carbonate content of the soils was determined gravimetrically using a method outlined by Ridley (79). A one-gram soil sample was digested in ten percent hydrogen chloride for ten minutes. The carbon dioxide evolved was sucked through a drying and adsorption train and absorbed on ascarite in a Nesbitt tube. The weight of carbon dioxide absorbed on the ascarite was determined and the carbonate content of the soil calculated.

Sodium Bicarbonate Extractable Phosphorus (Available Phosphorus):

Five g of soil was shaken with 100 ml of 0.5M sodium bicarbonate (pH 8.5) and the phosphorus extracted determined colorimetrically (71).

Soil Exchangeable Potassium:

Exchangeable potassium was extracted by shaking a 2.5 g sample of soil with 25 ml of neutral, 1N ammonium acetate for 30 minutes (90). The amounts of potassium in the extracts was determined by the use of a Baird Atomic Flame Photometer, Model KY2.

Soil Nitrate Nitrogen:

Nitrate -N was extracted by shaking 10 g soil with 2N potassium chloride for two hours. The amounts of nitrate in the extracts were determined using the colorimetric nitrophenol disulfonic acid method as modified by Harper (52).

Soil pH:

Soil pH was determined electrometrically on a soil-water suspension as described by Peech (76). A 50-gram soil sample in 50 ml of distilled water was shaken for 30 minutes on a vertical shaker and the pH of the suspension measured with a Fisher Combination Electrode on a Coleman Metrion III pH meter.

Conductivity:

The electrical conductivity of the soil-water suspension used for pH measurements was measured by the use of a direct Reading Radiometer Conductivity Bridge.

Extraction and Determination of Ammonium and Nitrate -N:

The method of equilibrium extraction of exchangeable ammonium and nitrate described by Bremner and Keeney (12) was adopted. A 10-gram sample of soil was shaken with 100 ml of 2N potassium chloride for one hour at room temperature in a 250 Erlenmyer flask. Blank determinations were conducted with each set of extractions. The method of Bremner and Keeney (12) was used for determining the nitrate -N and ammonium -N content of the potassium chloride extracts. The extract was steam distilled in the presence of magnesium oxide, and the volatilized ammonium collected in a mixed indicator/ boric acid solution, and estimated by titration with standard sulfuric acid. The apparatus employed was similar to that described by Bremner (10, 11).

Devarda's alloy was then added to the extracts to reduce the nitrate -N to ammonium -N and distillation continued. The nitrate -N content of the extracts was estimated by titration of the distillate with the standard sulfuric acid.

Standard solutions, containing known amounts of nitrogen, were used to check the operation of the apparatus prior to each set of determinations.

Volatilization of Ammonia:

The amounts of ammonia volatilized from soils were determined as described by Toews (93). However, in this study, small plastic containers ($5\frac{1}{2}$ in l, $5\frac{1}{2}$ in w, $5\frac{1}{2}$ in h) were used. The containers were sealed with vaseline and tape, and inlet and outlet holes bored in opposite sides of each container. The air inlets of each pan were connected to an air pump using rubber and plastic tubes. The apparatus used was similar to that illustrated by Toews (93). Tubing, placed into the outlets in the containers, was connected to flasks containing 25 ml of 0.005N sulfuric acid. Air was continuously circulated through the apparatus using air pressure. The ammonia volatilized was determined by backtitrating the 0.005N sulfuric acid with 0.005 sodium hydroxide. Blank determinations, (no soil), were conducted for each experiment.

Soil Field Capacity Moisture Content:

Soil, sieved through a 0.25-inch screen, was placed in a 400 ml beaker and sufficient water added to wet the top one-half of the soil. The beaker was sealed with plastic and allowed to equilibrate for 48 hours. Soil samples were then taken above the wetting front, weighed and placed in preweighed 100 ml beakers. The samples were placed in an oven at 100°C for 24 hours, removed, cooled, and reweighed. The percent moisture, expressed on an oven dry basis, was then calculated.

Soil Texture:

Soil texture was approximated by using the hand texturing method.

Soil Cation Exchange Capacity:

Soil cation exchange capacity was determined by the ammonium saturation method outlined by Chapman (16). Exchange sites of a 10.0 gram soil sample were saturated with ammonium by shaking for one hour in 100 ml of 1N NH_4OAc solution containing 250 ppm lithium and adjusted to a pH 7.0 using hydrogen chloride. The suspension was filtered under suction and washed with NH_4OAc solution until 250 ml was collected. The soil was washed with 250 ml of 95 percent ethanol. The adsorbed ammonium was displaced by leaching the soil with 250 ml of acidified 1N sodium chloride. The filtrate was collected and transferred to an 800 ml Kjeldahl flask. Twenty-five ml of 10N sodium hydroxide was added and the ammonia distilled into 50 ml 2 percent boric acid solution using a Kjeldahl distillation apparatus. The absorbed ammonium was titrated with standardized 0.1N sulfuric acid and the cation exchange capacity of soils calculated.

IV PRESENTATION OF EXPERIMENTAL RESULTS AND DISCUSSION

(A) Greenhouse Experiments

Toews (93) noted reductions in emergence and seedling damage when urea at rates greater than 20 lb N/acre was added with the seed of barley grown in field experiments. In order to obtain more information on the effects of urea on emergence an experiment was designed to study:

(1) Effect of mode of placement and rate of urea on the emergence and yield of barley using three watering practices.

(2) Effect of rate, mode of placement, and form of nitrogen carrier on the emergence and yield of barley.

(3) Effect of soil moisture level on the emergence and yield of barley treated with 60 lb N/acre as urea.

(4) Effect of soil type on the emergence and yield of barley treated with various rates of urea and 28-0-0.

Effect of Mode of Placement and Rate of Urea on the Emergence and Yield of Barley Using Three Watering Practices.

Due to limited greenhouse space, this experiment was done in three sections. Each section was grown at different times in the greenhouse. One-half gallon pots were used in the first part. The Stockton soil was used, as Toews (93) had reported considerable reduction of seedling emergence, due to urea applications with the seed in field experiments located on this soil. Two thousand g of soil was placed into each pot. The surface one inch of soil was then removed and the soil remaining in the pot watered to field capacity moisture content. Barley seeds and the various fertilizers were then added and the one-inch layer of soil replaced and watered to field capacity. Conquest barley (hordeum vulgare; 'L. Conquest') was used as a test crop and was sown at the rate of two bu/acre. The amounts of barley seed and fertilizer added per foot of seed were the same as used by Toews (93) in his field experiments and were equivalent to those in a seed row sown by a drill with seven-inch spacings between the discs. In each pot, six seeds were sown in a single four-inch row. Plastic containers ($14\frac{1}{2}$ in l, $12\frac{1}{2}$ in w, $5\frac{1}{2}$ in h) were used in the following sections. The procedures as outlined above were followed with the following exceptions: (1) 8000 g of soil was placed into each container and, (2) 32 barley seeds were sown in two one-foot rows placed seven inches apart.

A randomized block design with 18 treatments and four replicates was used. Three rates, 0, 40, and 60 lb N/acre, and four methods of placement were studied. The methods of placement were randomly spread with the seed, one-quarter inch from the seed, one-half inch from the seed, and in contact with the seed. Three watering techniques were used. In the first section, the soil was watered on the fourth and sixth day after seeding with 100 ml of water, and then maintained at field capacity. This would represent a field condition in which the soils were at field capacty at time of seeding and then received light rains four to five days after seeding. In the second section, the soil in the containers, initially at field capacity, was allowed to stand without watering for eighteen days and then watered and maintained at field capacity moisture content until harvest. This watering technique would simulate a situation in which rain would not occur for a considerable time after seeding. In the final section, the soil was maintained at field capacity for the duration of the experiment. Plastic covers were placed over the containers for two weeks to prevent evaporation. The above watering technique was used to reduce movement of urea and its transformation products from the site of fertilizer application. The watering technique used simulated a situation in which only very slight amounts of rainfall would be received after seeding, but with the soils remaining at field capacity moisture content. All rates of fertilizer and methods of placement, listed previously, were studied using only the first watering technique. Only a few of the fertilizer rates and methods of placement were studied in the second and third sections. Each treatment was replicated four times. Emergence counts were taken every day. The plants in sections one and three were harvested 23 days after seeding, and the plants in section two were harvested 26 days after seeding. The plant material was oven dried for 48 hours at 80°C and weighed. The percent emergence for each container was calculated as follows:

$$\text{Percent emergence} = \frac{\text{Number of plants emerged with fertilizer added}}{\text{Number of plants emerged with no fertilizer added}} \times 100$$

The yields of barley varied with rate of urea added, method of fertilizer placement, and watering practice used

(Table III). The highest yields on the soils watered four days after seeding were obtained when no fertilizer or when 40 or 60 lb N/acre, as urea, was placed one-half inch from the seed. Yields were significantly reduced when 40 lb N/acre as urea was randomly spread with the seed and when 60 lb N/acre was randomly spread with the seed or placed closer than one-half inch from the seed. The lowest yield, at both the 40 and 60 lb N/acre rates, occurred when the fertilizers were randomly spread with the seed.

The number of plants which emerged on the soils watered four days after seeding was not significantly influenced by treatment. However, delays in emergence (Figures 1 and 2) were noted for all fertilizer treatments. The delays in emergence were much shorter for treatments receiving 40 lb N/acre as urea than for the corresponding placement treatment at 60 lb N/acre. The delays in emergence appeared to be closely related to yields. The delay in emergence, when 40 lb N/acre was added, was greatest when the urea was randomly spread with the seed (Figure 2). It would be expected that the urea placed in contact with the seed would result in the greatest emergence delay and the lowest final emergence. However, it is possible that when the urea was randomly spread with the seed it hydrolyzed at a greater rate, as the pellets would be exposed to more soil and moisture than when placed in contact with the seed. This would lead to higher accumulations of reaction products. Delays in emergence, when 60 lb N/acre was added, were similar for the

Table III. Effect of placement, rate of urea-N added, and watering practice on emergence and yield of barley.

Placement with seed	Rate (lb N/acre)	Yield (g)	Final emergence (%)	Weight per plant (g)
		Watered 4 days after seeding		
No fertilizer	0	0.850 ab[1]	100 a	0.141 a
½" from seed	40	0.900 a	100 a	0.150 a
¼" from seed	40	0.762 abcd	100 a	0.127 ab
Randomly spread	40	0.635 cde	92 a	0.121 ab
In contact	40	0.765 abcd	96 a	0.133 ab
½" from seed	60	0.807 abc	92a	0.148 a
¼" from seed	60	0.572 de	96 a	0.100 b
Randomly spread	60	0.544 e	92 a	0.098 b
In contact	60	0.570 de	96a	0.099 b
		Watered 18 days after seeding		
No fertilizer	0	2.65 a	100 a	0.086 a
½" from seed	40	2.93 a	90 b	0.105 a
Randomly spread	40	2.52 a	80 c	0.102 a
½" from seed	60	2.65 a	86 bc	0.100 a
Randomly spread	60	0.50 b	18 d	0.085 a
		Maintained at field capacity moisture content		
No fertilizer	0	2.87 a	100 a	0.096 a
¼" from seed	60	1.44 b	96 a	0.050 b
Randomly spread	60	1.07 c	65 b	0.055 b
In contact	60	0.68 d	43 c	0.066 b

1 Duncan's Multiple Range Test - Treatments followed by the same letter, within each watering practice, are not significantly different (P = 0.05).

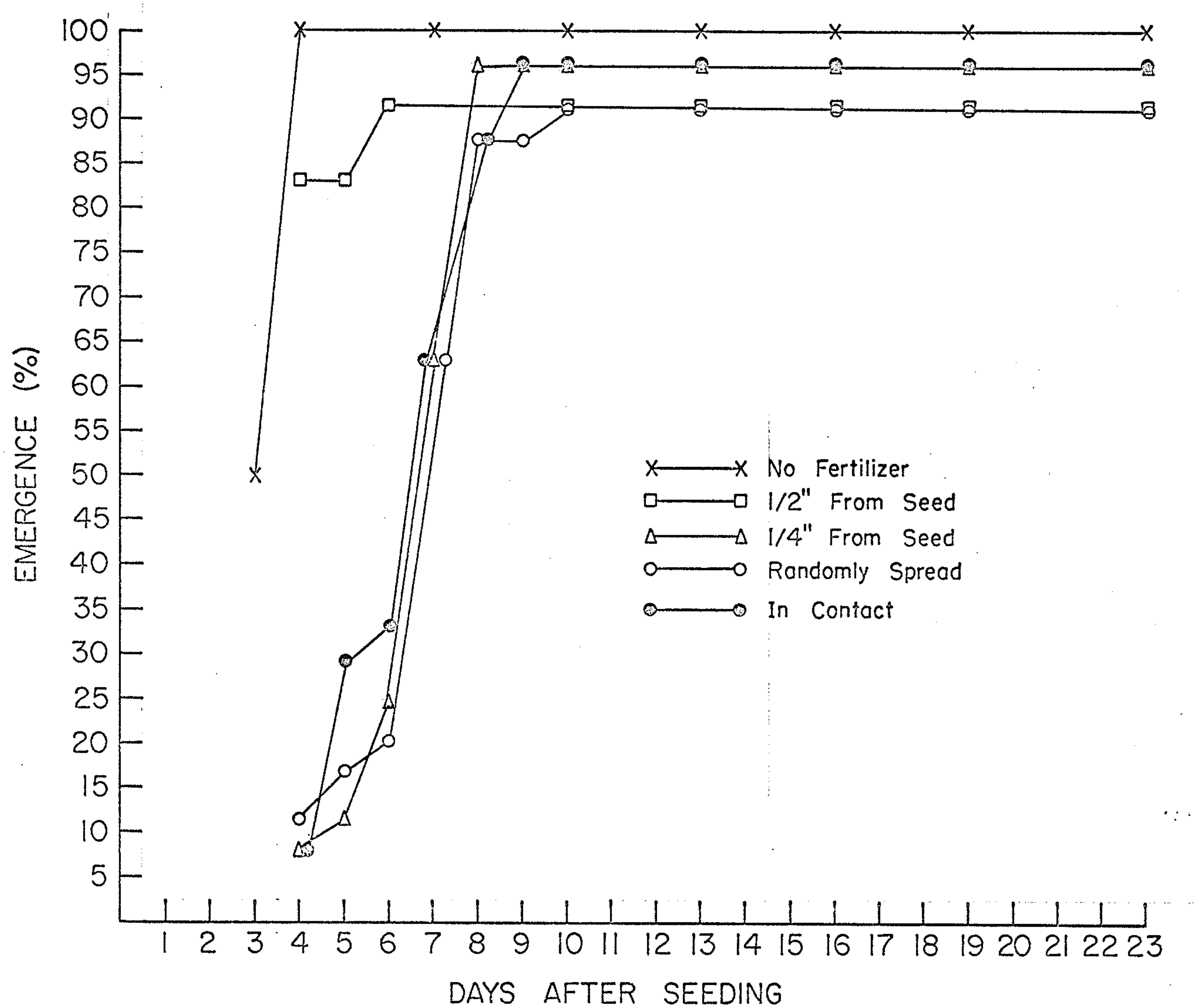


Figure 1. Influence of 60 lb N/acre as urea on emergence of barley at various times after seeding - soils watered four days after seeding.

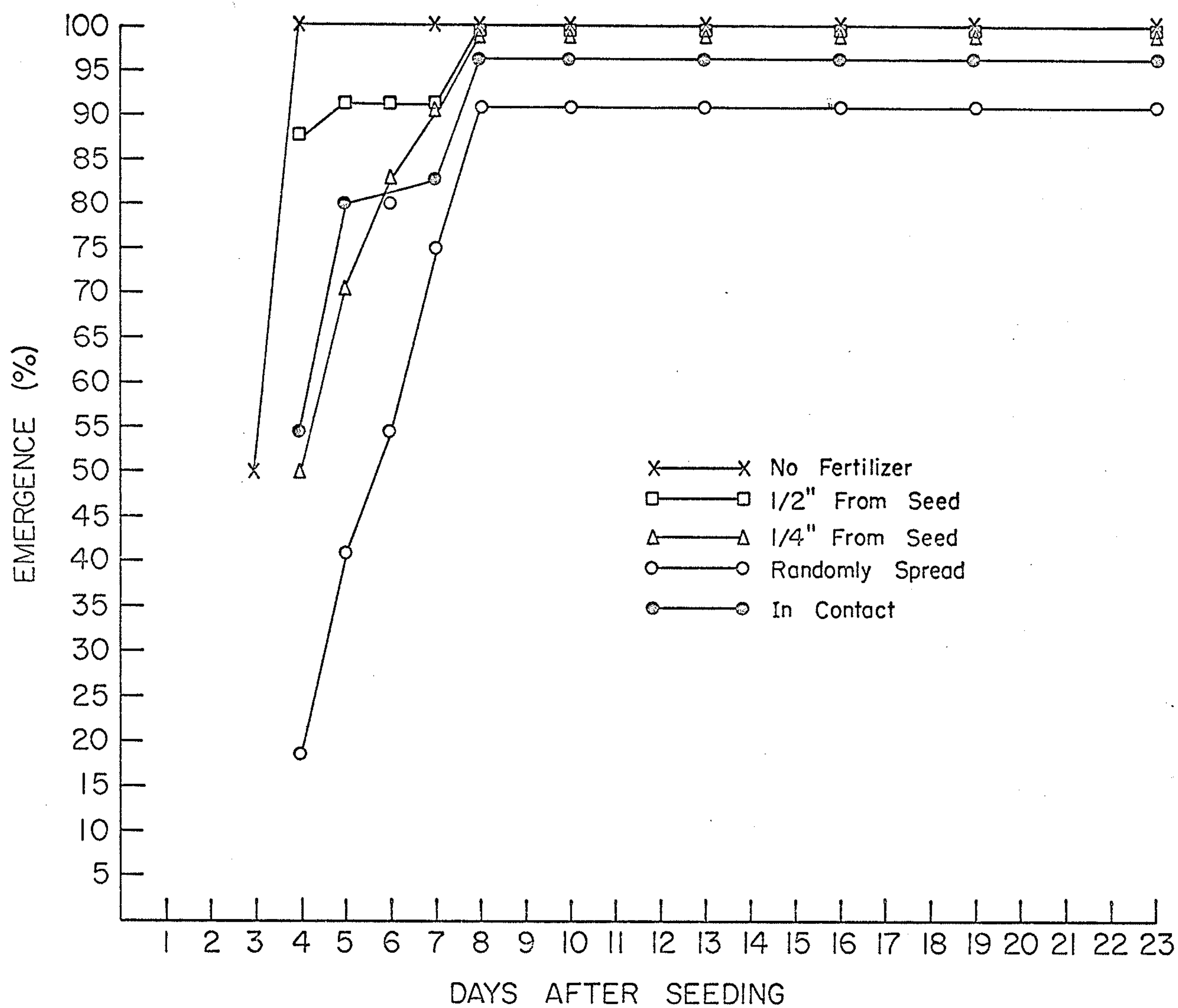


Figure 2. Influence of 40 lb N/acre as urea on emergence of barley at various times after seeding - soils watered four days after seeding.

following treatments: randomly spread, one-quarter inch from seed, and in contact with the seed.

Final emergence counts were not reduced significantly in any of the treatments probably because of the watering method used. If the urea hydrolyzed rapidly with little water movement or even a subsequent loss of moisture due to evaporation, then a high concentration of urea reaction products would accumulate and be very harmful to the seeds. In this experiment urea hydrolysis was probably retarded, as no additional water was added until the fourth day after seeding. The addition of water may have leached some of the urea away from the seeds and reduced the ammonia concentration near the seeds. Thus, emergence of seeds may have been temporarily delayed due to a combination of toxic and osmotic effects. After watering, more favourable conditions may have been created and the plants emerged.

The weights of individual plants are important in that they reflect the influences of the fertilizer added in two ways. They reflect the toxicity of urea and its reaction products on the growing seedling, and also the beneficial effects of the fertilizer when it is used as a nutrient. Addition of 40 lb N/acre one-half inch from the seed, to the soils watered four days after seeding, gave the highest plant weights. Placing urea one-half inch from the seed would minimize the toxic effects of urea and yet provide the growing seedling with available nitrogen. Placement of 60 lb N/acre as urea one-half inch from the seed also produced high plant weights. The weights of individual plants were low when the urea was in contact, randomly spread, or placed one-quarter inch from the seed at 60 lb N/acre. These three placements at 40 lb N/acre produced slightly higher (not significant) plant weights than at 60 lb N/acre.

The yields of barley obtained when the second watering method was used (watered 18 days after seeding) were similar except when 60 lb N/acre was randomly spread with the seed (Table III). The yield of barley was significantly reduced when 60 lb N/acre was randomly spread with the seed.

Delay of emergence (Figure 3) and final emergence reductions were much greater in some of these treatments than was found for the soils watered four days after seeding (Table III and Figure 1). The reductions in emergence when urea was randomly spread at 40 or 60 lb N/acre with the seed were significantly greater than when placed one-half inch from the seed. All fertilizer additions significantly reduced emergence when compared with the treatment with no fertilizer added. The delays in emergence were closely related to the final emergence. The results show that the emergence of barley when urea was applied was lower when the soils were not watered for 18 days than when watered four days after seeding. Under the drying conditions used in this experiment, hydrolysis of urea was probably retarded; but the loss of soil moisture probably increased the concentration of urea and its reaction products. Gasser (47) suggested, that under conditions such as these, urea molecules might be an important factor in

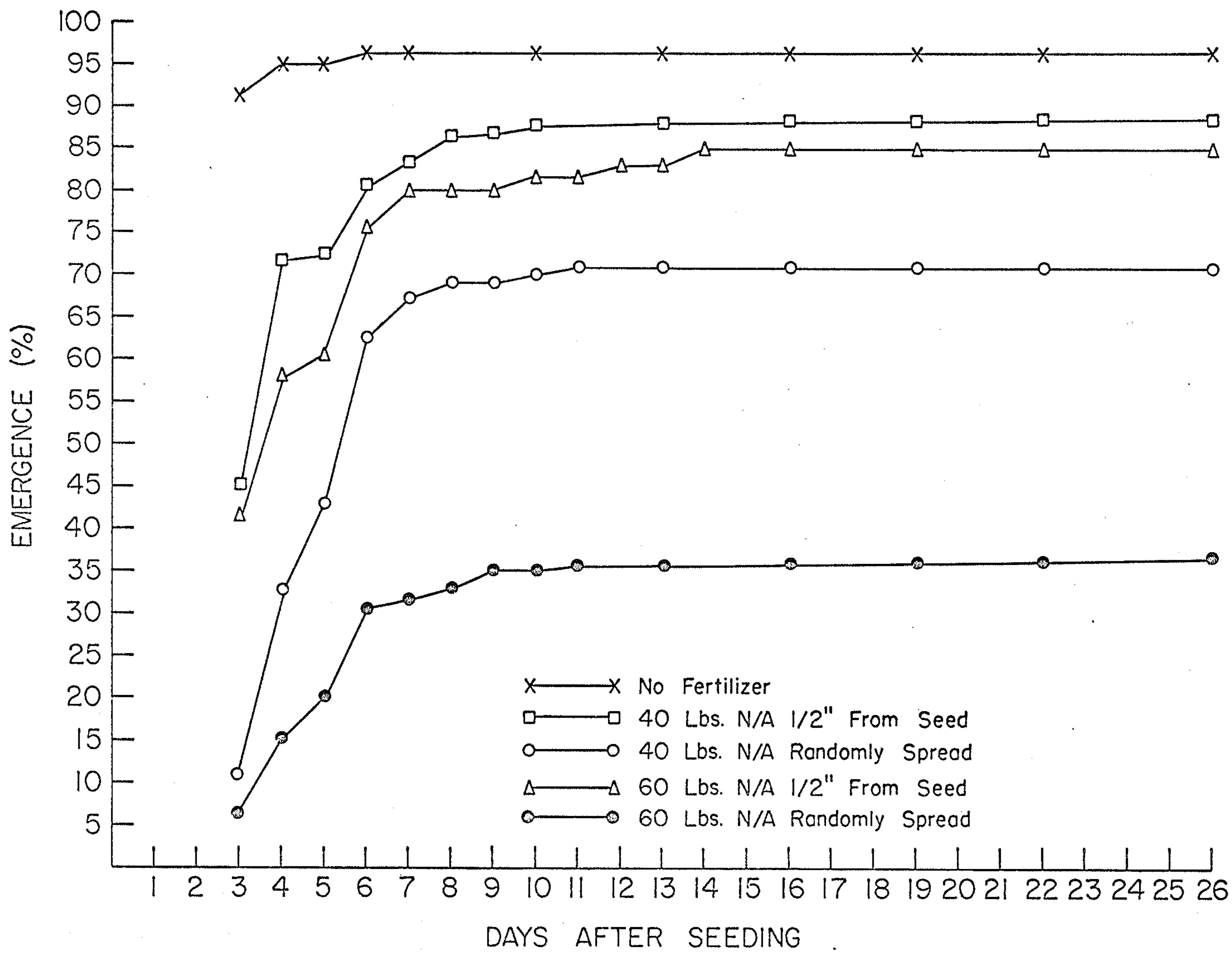


Figure 3. Influence of 40 and 60 lb N/acre as urea on emergence of barley at various times after seeding - soils watered eighteen days after seeding.

reducing seedling emergence due to an osmotic effect.

The plant weights for the treatments which received the second watering technique did not differ significantly. An inadequate supply of moisture in the soil may have limited plant growth in this experiment.

The yields of barley for the treatments receiving the third watering technique (maintained at field capacity moisture content) all varied significantly (Table III). In this experiment water movement was reduced in the soil by reducing evaporation. The yields for the fertilizer treatments were directly related to the distance of fertilizer placement from the seed. The lowest yield was obtained when the fertilizer was placed in contact with the seed. The delays in emergence (Figure 4) were related to the final emergence counts. The emergence counts for the fertilizer treatments were also directly related to the distance the fertilizer was placed from the seed. Only 43.3 percent of the barley emerged when 60 lb N/acre was placed in contact with the seed. The emergence of barley was not significantly reduced when the urea was placed one-quarter inch from the seed. The emergence of barley for the randomly spread treatment was greater when the soils were maintained at field capacity than when not watered for 18 days after seeding. It is most likely that with the soils maintained at field capacity, the urea hydrolyzed quite readily, but was not as toxic as with the previous watering practice, as there was very little moisture loss and the concentrations of urea and its reaction products in the soil

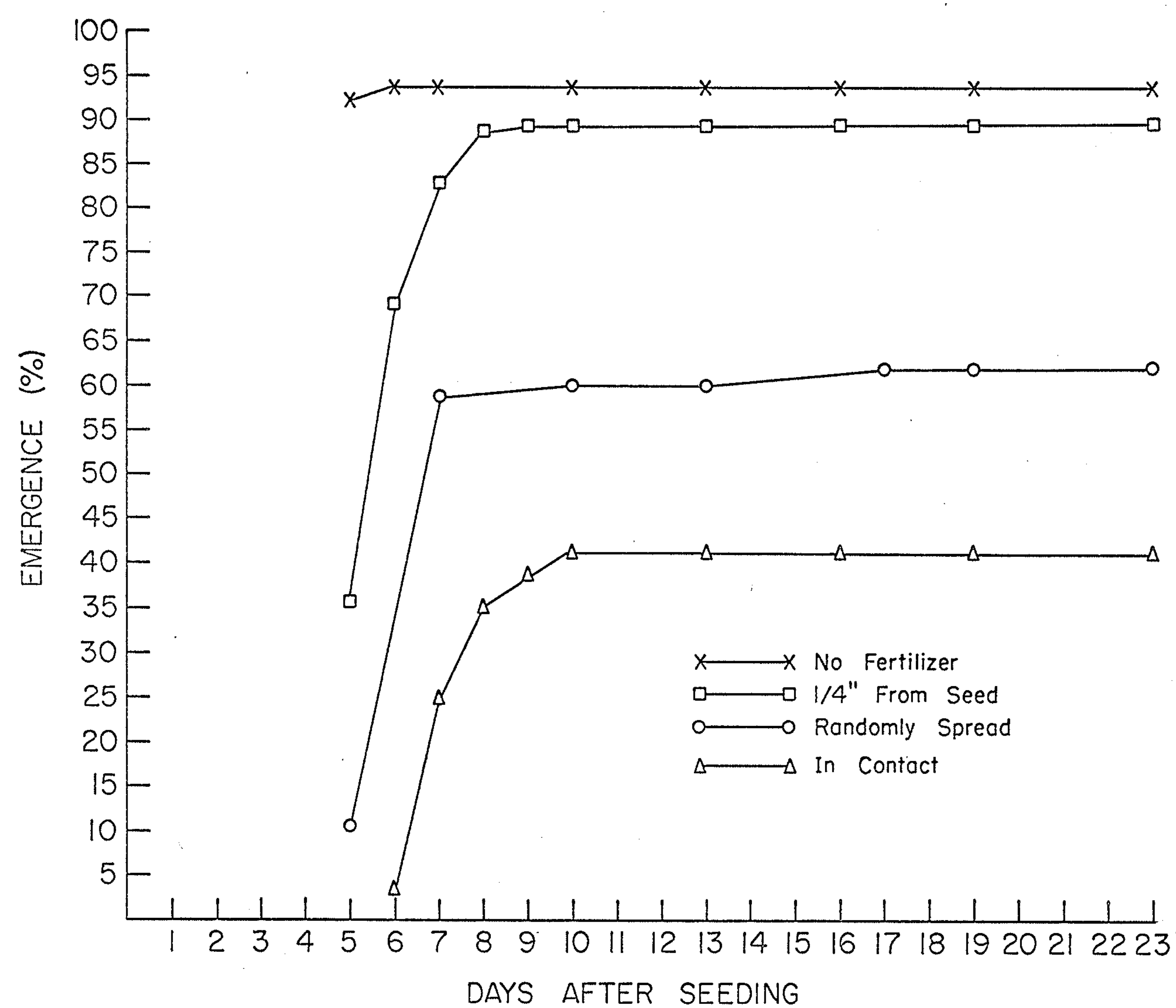


Figure 4. Influence of 60 lb N/acre as urea on emergence of barley at various times after seeding - soils maintained at field capacity.

solution were probably lower.

Individual plant weights were not significantly influenced by placement of urea, but all plant weights were significantly lower than with no fertilizer added. Thus, although emergence of the plants was influenced by mode of placement, the growth of the plants after emergence was not influenced. During the first few days after application, the fertilizer would not have sufficient time to move very far from the original placement position; thus, the highest concentrations of urea and its reaction products would occur when the urea was placed in direct contact with the seed. After the seed germinated and started growing, however, the concentration of urea and its reaction products would probably be quite similar in all urea treatments, as the urea and its reaction products would probably have moved from the placement site. This would result in a similar growth medium for all modes of placement; thus, the growth of all plants treated with urea would be similar.

The three watering techniques used in this experiment produced very different results, as water movement in the soil could leach urea and its reaction products away from the seed and reduce the damage to the germinating seeds and growing seedlings. The best method of placement of urea fertilizer was one-half inch from the seed at a rate of 40 lb N/acre. Addition of 60 lb N/acre as urea, one-half inch from the seed was found to reduce the emergence of barley.

Effect of Rate, Method of Placement, and Form of Nitrogen Carrier on the Emergence and Yield of Barley.

An experiment was designed to compare different forms of added urea and 28-0-0. The procedures employed were identical to the previous experiment. This experiment was divided into two sections which were grown at separate times in the greenhouse. A randomized block design with fifteen treatments and four replicates was used. The methods of placement were randomly spread with the seed and one-half inch from the seed. Four nitrogen forms, urea pellets, urea solution, urea powder, and 28-0-0 solution at rates equivalent to 0, 30, 60, and 120 lb N/acre were used. The Stockton soil was selected for study. In the second section covers were kept on the containers for two weeks. These covers were not used in the first section. The soil was maintained at field capacity moisture content until harvest time. Not all treatments listed above were studied in each section. Emergence counts were taken every day. The crops were harvested 26 days after seeding in the first section and 23 days after seeding in the second section. The plant matter was oven dried at 80°C for 48 hours and weighed. The percent emergence was calculated as previously described.

The yield of barley, grown on soil not covered to prevent evaporation, was affected by rate, method of placement, and form of nitrogen carrier (Table IV). Yields obtained with 60 lb N/acre of urea or 28-0-0 placed one-half inch from the soil were significantly higher than when randomly spread with

Table IV. Effect of rate, method of placement, and form of nitrogen carrier on the emergence and yield of barley

Source of nitrogen	Rate (lb N/acre)	Yield (g)	Final emergence (%)	Weight per plant (g)
		Soil not covered		
	0	3.28 ab[1]	100 a	0.104 ab
Urea[2]	60	3.35 ab	99 ab	0.108 ab
28-0-0[2]	60	3.54 a	97 ab	0.117 a
Urea	60	1.69 d	77 c	0.070 d
28-0-0	60	2.37 c	92 ab	0.083 cd
NH_4NO_3	60	2.99 b	92 ab	0.105 ab
28-0-0	120	0.94 e	61 d	0.050 e
28-0-0[2]	120	2.59 c	89 b	0.093 bc
		Soil covered to prevent evaporation		
	0	2.96 a	100 a	0.093 a
Urea pellets	30	2.05 b	79 b	0.081 a
Urea solution	30	1.89 bc	76 b	0.078 ab
28-0-0	60	1.65 c	80 b	0.065 bc
Urea pellets	60	0.66 d	42 c	0.048 cd
Urea solution	60	0.66 d	47 c	0.043 d
Urea powder	60	0.42 d	24 e	0.055 d

1 Duncan's Multiple Range Test - Treatments followed by the same letter, within each section (covered and not covered), are not significantly different ($P = 0.05$).

2 Fertilizer was placed one-half inch from seed.

the seed. This indicates that 60 lb N/acre as urea or 28-0-0 caused serious damage to barley emergence and growth when applied close to the seeds. The yields obtained when 120 lb N/acre as 28-0-0 (approximately one-half of nitrogen in 28-0-0 is present as urea) was placed one-half inch from the seed or randomly spread was significantly lower than placements of 60 lb N/acre as urea. These results show that damage from the 28-0-0 was due to both the urea and ammonium nitrate present in the solution. The yields of barley when ammonium nitrate was randomly spread with the seed were significantly higher than when the other fertilizers were randomly spread with the seed. Although ammonium nitrate randomly spread with seed did not reduce yields as greatly as did the other nitrogen fertilizers, the yields when ammonium nitrate was added were significantly lower than when 28-0-0 at 60 lb N/acre was placed one-half inch from the seed.

The number of plants which emerged when grown on the uncovered soil with normal evaporation was affected by the rate, method of placement, and form of nitrogen carrier added. The emergence of barley with 60 lb N/acre as urea randomly spread with the seed was significantly lower than when no fertilizer was added. Both placements of 120 lb N/acre as 28-0-0 significantly reduced emergence; the 28-0-0 randomly spread with the seed had a much more severe effect on emergence than did the 28-0-0 placed one-half inch from the seed. Addition of 28-0-0 at 120 lb N/acre, randomly spread with the seed, reduced emergence more than urea added at 60 lb N/acre.

The results indicate that reductions in emergence were associated with corresponding decreases in yield. However, decreases in yield were not always associated with emergence reductions but with the occurrence of smaller stunted plants. This inhibition of growth of seedlings was probably caused by the accumulation of ammonia and/or nitrite. There is also a possibility that the osmotic effect of urea and its reaction products retarded growth. This inhibition of plant growth is reflected by the individual plant weights. Plant weights were greater when the fertilizer was placed one-half inch from the seed than when the fertilizer was randomly spread with seed. Plant weights when ammonium nitrate was applied at 60 lb N/acre were greater than when the other fertilizers were added. These data indicate that urea and 28-0-0 applied with the seed cannot only reduce emergence, but can also retard the growth of the seedlings.

The rates of emergence of barley for the various treatments are shown in Figure 5. The delays in emergence were longer for the treatments which caused large reductions in final emergence. The longest delays occurred in the treatments in which urea was randomly spread with the seed.

The yields of barley grown on soil with reduced evaporation were affected by the rate and form of nitrogen carrier added. All the yields with nitrogen added were significantly lower than with no fertilizer. The yields of barley when 30 lb N/acre as urea pellets or urea solution was added were greater than with 60 lb N/acre as 28-0-0 or urea.

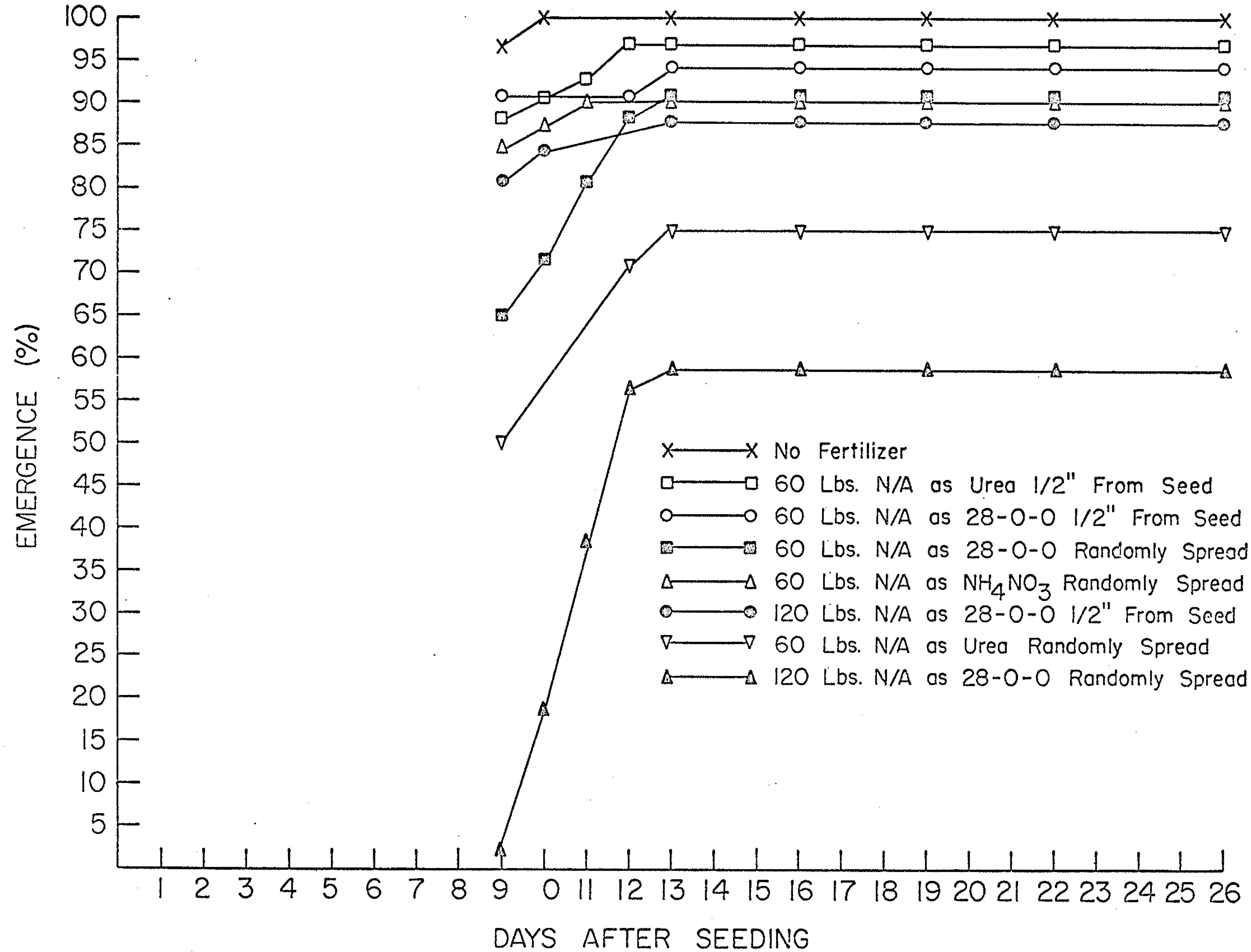


Figure 5. Influence of rate, method of placement, and form of nitrogen carrier on emergence of barley at various times after seeding - soil not covered.

The number of plants which emerged followed trends similar to those noted for the yields. However, the emergence with 28-0-0 at 60 lb N/acre was similar to that of urea pellets applied at 30 lb N/acre. Emergence of barley treated with urea powder was significantly lower than when treated with urea pellets or urea solution. The urea powder was probably more toxic to seedling emergence than the other forms of urea, as it probably would hydrolyze faster than the urea pellets and may not have moved from the placement site as much as did the urea solution.

The individual plant weights followed approximately the same trends as was noted for total plant yields. Small plant weights were associated with the use of high rates of applied urea.

Delays in emergence (Figure 6) were greater for the treatments with severe reductions in final emergence. In some treatments, after reaching a maximum, emergence decreased slightly with increases in time after seeding. This was due to the death of some seedlings. The death of seedlings was probably due to accumulations of nitrite in the soil.

Effect of Moisture Level on the Emergence and Yield of Barley Treated with 60 lb N/acre as Urea.

An experiment was designed to determine if the initial soil moisture level influenced the degree of seed and seedling damage caused by urea placed with the seed. The procedures employed were similar to those previously described. The Red River and Almasippi soils were used. A randomized

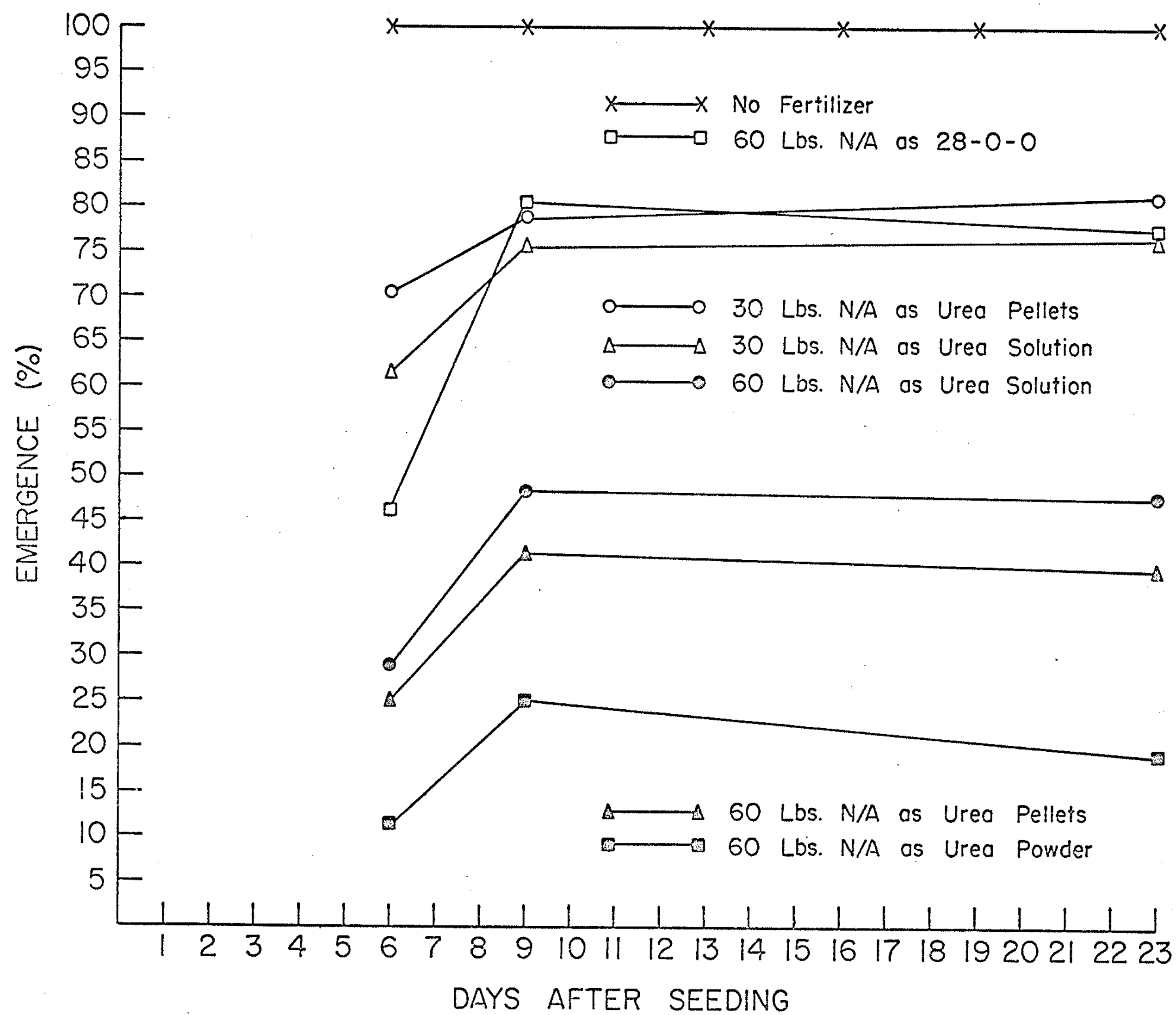


Figure 6. Influence of rate and form of nitrogen carrier, randomly spread with the seed, on emergence of barley at various times after seeding - soil covered to prevent evaporation.

block design was used with eleven treatments and four replicates. The fertilizer, pelleted urea, was spread randomly with the seed at rates of 0 and 60 lb N/acre. Covers were kept on the soil for two weeks. Three moisture levels, field capacity, three-quarters of field capacity, and one-half field capacity were used. Water was added daily to the surface of the soil to maintain the total soil moisture content at the desired level. The distribution of moisture was not uniform throughout the soil volume at seeding time. Watering the surface of the soil to the desired moisture contents did limit moisture near the seed for a few days following seeding, especially at the lowest moisture content. As water was added to the soil maintained at one-half field capacity, the surface layer of soil would approach field capacity moisture content while the lower layers of soil would contain a much lower level of moisture. Emergence counts were taken every day. The crop was harvested 23 days after seeding. The plants were oven dried at 80°C for 48 hours and weighed. The percent emergence was calculated as previously described.

The yields decreased with decreasing moisture contents on the Red River soil (Table V). The yields, with and without fertilizer, were similar for any one particular moisture level except at a moisture level of one-half of field capacity, where the addition of fertilizer decreased the yield. These results show that soil moisture levels on heavy-textured soils have to be quite low before 60 lb N/acre as urea randomly

Table V. Effect of moisture level on the emergence and yield of barley treated with 60 lb.N/acre as urea.

Soil	Rate[1] (lb N/acre)	Moisture level	Yield (g)	Final germination (%)	Weight per plant (g)
Red River	0	F.C.[2]	5.65 abc[3]	100 a	0.197 ab
Red River	0	¾ F.C.	5.39 c	100 a	0.182 b
Red River	0	½ F.C.	3.01 d	73 b	0.151 b
Red River	60	F.C.	6.92 a	100 a	0.241 a
Red River	60	¾ F.C.	5.40 bc	98 a	0.193 b
Red River	60	½ F.C.	1.15 e	23 c	0.187 b
Almasippi	0	F.C.	3.41 a	100 a	0.115 a
Almasippi	0	½ F.C.	2.53 b	100 a	0.082 b
Almasippi	60	F.C.	0.72 c	47 b	0.053 c
Almasippi	60	¾ F.C.	0.44 cd	36 b	0.042 cd
Almasippi	60	½ F.C.	0.10 d	16 c	0.026 d

1 Fertilizer was randomly spread with the seed.

2 Field capacity.

3 Duncan's Multiple Range Test - Treatments followed by the same letter are not significantly different (P = 0.05).

spread with the seed causes serious damage to barley growth.

The yields on the Almasippi soil were significantly decreased by decreases in moisture levels and by the addition of fertilizers. The data show that 60 lb N/acre as urea randomly spread with the seed caused serious damage at all three soil moisture levels. Toews (93) found that the extent of damage to barley growth decreased with increasing cation exchange capacity. These data also support the above observation. The Red River and Almasippi soils had cation exchange capacities of 51.3 and 19.9 me/100 g of soil, respectively. The high ammonium absorption capacity of the Red River soil probably prevented accumulations of ammonium and ammonia in the soil solution thereby reducing the toxicity of the added fertilizer.

Addition of fertilizer significantly reduced emergence on the Red River soil maintained at one-half field capacity moisture content. The urea fertilizer, added to the Almasippi soil significantly reduced emergence at all moisture levels. The reductions in emergence were much greater on the Almasippi soil than on the Red River soil.

The urea applied with the seed delayed the emergence of barley (on both soils) when maintained at one-half or three-quarters field capacity moisture content (Figures 7 and 8).

The individual plant weights on the Almasippi soil followed the same trends as noted for total yields. On the Red River soil, however, the plant weights were similar except when 60 lb N/acre was added to the soil at field capacity moisture

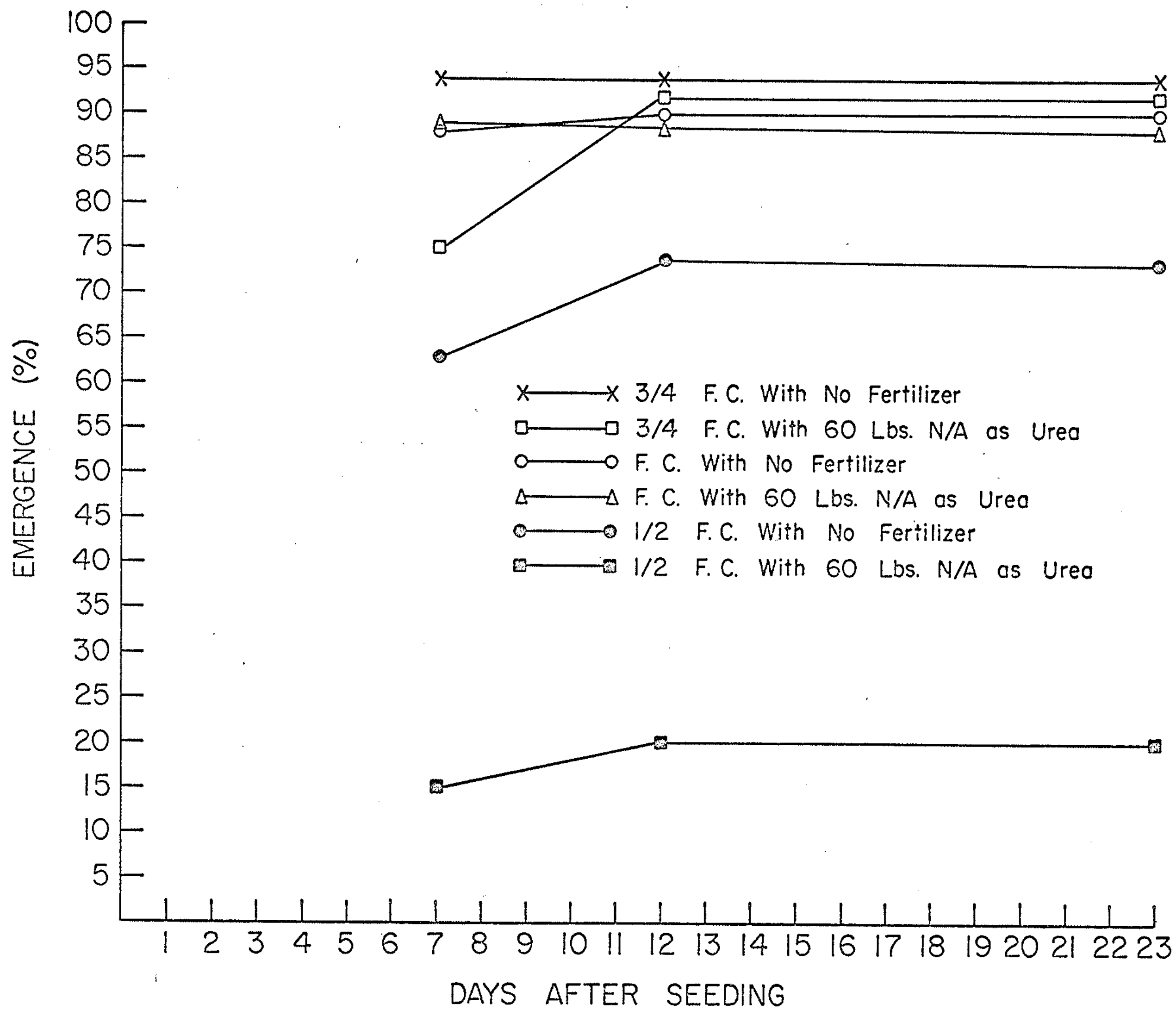


Figure 7. Influence of moisture level on the emergence of barley on the Red River soil treated with 60 lb N/acre as urea.

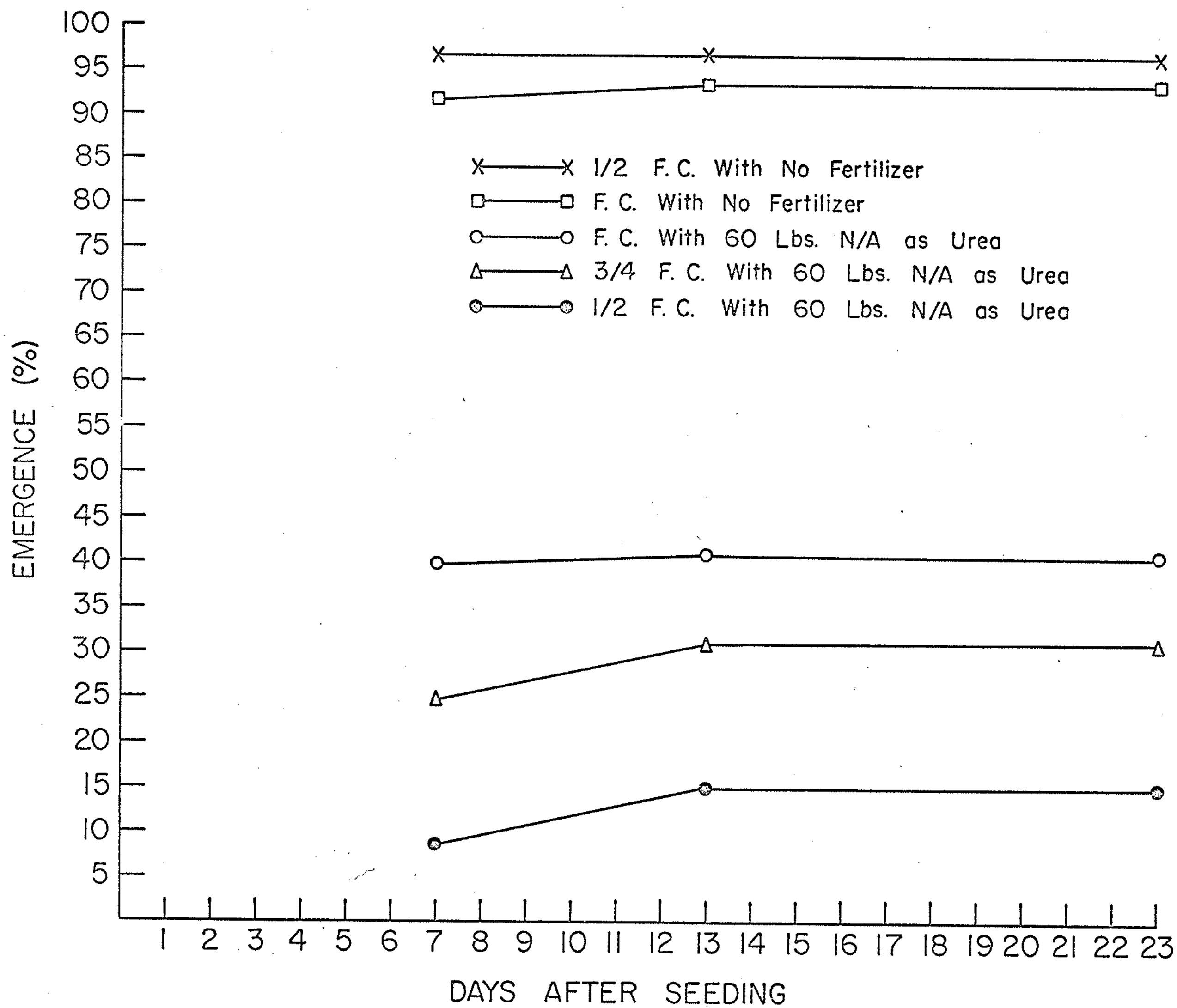


Figure 8. Influence of moisture level on the emergence of barley on the Almasippi soil treated with 60 lb N/acre as urea.

content. An increase in weight of plants was noted in the above instance. data indicate that in the Red River soil, the toxic effects of urea and its reaction products had very little effect on the growing seedlings. This was evident even when the emergence was greatly reduced.

Effect of Soil Type on the Emergence and Yield of Barley Treated with Various Rates of Urea and 28-0-0.

Since little is known about the effects of liquid 28-0-0 on seed germination and since 28-0-0 contains 30.5 percent urea, experiments were conducted to compare the effects of urea and 28-0-0 on seed germination and early plant growth on various soil types. The procedures employed were similar to those used for the previous experiments. The containers, however, were not covered with plastic. The Red River, Lakeland, and Almasippi soils were selected for study. A randomized block design with twelve treatments and four replicates was used. Urea at 0 and 60 lb N/acre and 28-0-0 at 0, 60, and 120 lb N/acre were used. The fertilizer was spread randomly with the seed. The soil was maintained at field capacity moisture content until harvest. Emergence counts were taken every day. The crop was harvested 23 days after seeding. The plants were oven dried at 80°C for 48 hours and weighed. The percent emergence was calculated as shown previously.

The yields of barley were significantly reduced by fertilizer applications to the Almasippi soil (Table VI). Yields of barley grown on the Red River and Lakeland soil were not influenced by fertilizer additions. The yields on

Table VI. Effect of soil type on the emergence and yield of barley treated with various rates of urea and 28-0-0.

Soil	Source of nitrogen	Rate[1] (lb N/acre)	Yield (g)	Final emergence (%)	Weight per plant (g)
Almasippi		0	3.29 a[2]	100 a	0.111 a
Almasippi	Urea	60	1.67 c	86 a	0.065 c
Almasippi	28-0-0	60	2.62 b	93 a	0.095 b
Almasippi	28-0-0	120	0.60 d	31 b	0.064 c
Red River		0	4.03 a	100 a	0.141 a
Red River	Urea	60	4.29 a	99 a	0.151 a
Red River	28-0-0	60	4.13 a	100 a	0.138 a
Red River	28-0-0	120	4.24 a	88 a	0.171 a
Lakeland		0	3.55 a	-[3]	-
Lakeland	Urea	60	3.15 a	-	-
Lakeland	28-0-0	60	3.67 a	-	-
Lakeland	28-0-0	120	3.43 a	-	-

1 Fertilizer randomly spread with the seed.

2 Duncan's Multiple Range Test - Treatments followed by the same letter, for treatments within each soil, are not significantly different (P = 0.05).

3 Emergence counts not obtained due to volunteer growth.

the Almasippi soil with 28-0-0 at 60 lb N/acre were significantly greater than that with urea at 60 lb N/acre or with 28-0-0 at 120 lb N/acre (60 lb urea-N/acre). These results indicate that 60 lb N/acre as urea or 120 lb N/acre as 28-0-0 can be applied with the seed without serious seed or seedling damage on heavy-textured soils such as the Lakeland and the Red River, providing there is adequate soil moisture. However, on coarse-textured soils, such as the Almasippi soil, serious seed and seedling damage can occur when 60 lb N/acre as urea or 60 lb N/acre as 28-0-0 is applied with the seed.

Emergence counts were not taken on the Lakeland soil due to volunteer barley growth. The number of plants which emerged did not vary significantly on the Red River soil. Emergence on the Almasippi soil with 120 lb N/acre as 28-0-0 was significantly less than that for the other treatments.

Delays in emergence (Figure 9) were much greater for the Almasippi soil than for the Red River soil. Since some of the plants died after emergence, it is possible that nitrite may have been present in some of the soils.

The individual plant weights were not affected by fertilizer added to the Red River soil. Weight of plants, on the Almasippi soil, was reduced by the additions of fertilizer. The plant weights for 28-0-0 at 120 lb N/acre and urea at 60 lb N/acre were similar and significantly lower than that obtained for 28-0-0 at 60 lb N/acre.

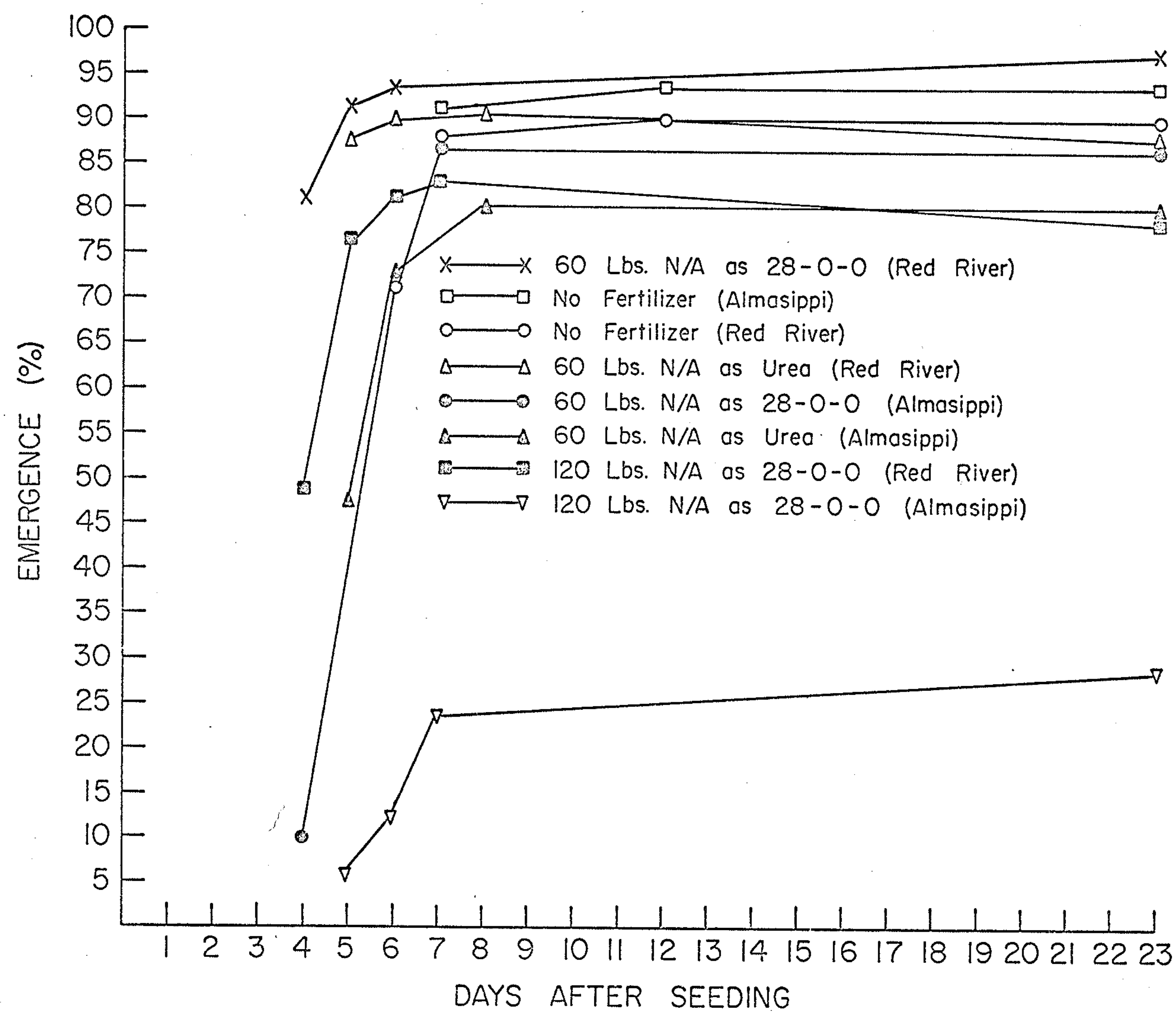


Figure 9. Influence of soil type on the emergence of barley treated with various rates of urea and 28-0-0.

(B) Ammonia Volatilization as Related to Seedling Emergence

The previous studies, conducted in the greenhouse, showed that urea not only reduced emergence but also inhibited the growth of seedlings. The latter was evident from the variations in weight of the individual plants. Some workers have attributed the plant damage to ammonia accumulation (4, 9, 28, 46, 59, 96). The purpose of this study was to relate ammonia volatilization from the soils to the extent of emergence reduction. Since ammonia volatilization is directly related to the amount of ammonia in soil solution, a measure of ammonia volatilization reflects concentrations of ammonia in the soil solution. This study was conducted using a fine (Red River) and a coarse-textured soil (Altona).

The procedure employed was similar to that described for the greenhouse studies. Small containers ($5\frac{1}{2}$ in l, $5\frac{1}{2}$ in w, $5\frac{1}{2}$ in h) were used. The containers were filled with 1125 g of soil and watered to field capacity moisture content. Conquest barley was used as a test crop and sown at the rate of two bu/acre. Sixteen seeds were sown in three four-inch rows spaced two inches apart in each pan. After seeding and fertilization, 75 g of soil was added and watered to field capacity moisture content. A randomized block design with six treatments and three replicates was used. Four nitrogen carriers, 28-0-0, urea, ammonium nitrate, and ammonium carbonate, and three rates, 0, 60, and 120 lb N/acre were used. The fertilizer was randomly spread with the seed. The ammonia volatilized from the soil was measured as described in the methods and materials section. The soils were maintained at field capacity moisture content by saturating the air with water prior to passing through the containers. Volatilization of ammonia was measured for a period of eleven days in each experiment. After eleven days the containers were opened and soil samples obtained for analysis. A round cylinder, three inches in diameter, was pushed into the center of each pan to a depth of 1½ inches. The soil core was removed, well mixed, and stored at 4°C (14) prior to ammonium and nitrate analysis. The percent emergence was calculated as described in previous experiments.

Ammonia volatilization varied considerably with the rate and form of applied nitrogen in the Altona soil (Table VII). The highest losses of ammonia occurred from the 28-0-0 applied at 120 lb N/acre and urea applied at 60 lb N/acre. Since relatively large amounts of urea nitrogen were added in these treatments, large amounts of ammonium carbonate would form and would increase the soil pH. The high concentration of ammonium ions plus the high soil pH would favour conditions for ammonia volatilization. Also, the low cation exchange capacity of this soil (26.2 me/100 g) would favour ammonia volatilization, as very little ammonium from the soil solution would be adsorbed by the soil. The 28-0-0 applied at 60 lb N/acre lost approximately one-half as much ammonia as did the 28-0-0 applied at 120 lb N/acre. This indicates that very little of fertilizer's reaction products were adsorbed by the soil, as ammonia volatilization appeared to be directly related to the

Table VII. Effect of rate and nitrogen source on the concentrations of ammonium and nitrate in the fertilizer band, total ammonia volatilized and emergence of barley in the Altona soil.

Source of nitrogen	Rate[1] (lb N/acre)	Ammonium (ppm)	Nitrate (ppm)	Total Nitrogen (ppm)	Ammonia Loss (me)	Emergence (%)
	0	0.6 c[2]	27.8 d	28.4 e	0	100 a
28-0-0	120	322.0 a	363.0 b	685.0 b	0.441	45 b
28-0-0	60	31.8 c	347.0 b	378.8 cd	0.219	95 a
Urea	60	151.0 b	248.0 c	399.0 c	0.434	43 b
NH_4NO_3	120	182.0 b	595.0 a	777.0 a	0.008	102 a
$(NH_4)_2CO_3$	60	6.0 c	314.0 b	320.0 d	0.228	32 b

1 Fertilizer randomly spread with the seed.

2 Duncan's Multiple Range Test - Treatments followed by the same letter are not significantly different (P = 0.05).

amount of fertilizer added. There was very little ammonia lost from the ammonium nitrate applied at 120 lb N/acre. This is probably due to a lower pH being maintained in the fertilizer band as compared to the urea sources. The ammonia volatilized when ammonium carbonate was added was much lower than expected. Theoretically, as much ammonia should have been volatilized from the ammonium carbonate as was from urea applied at 60 lb N/acre. However, considerable losses of ammonia from ammonium carbonate occurred when it was being added to the soils and prior to sealing of the pans. Since about eight hours was required to assemble the apparatus, a large part of the ammonia from ammonium carbonate could have been lost during this time. As a result ammonia lost from ammonium carbonate was about the same as from the 28-0-0 at 60 lb N/acre.

Very little of the nitrogen applied to the soil was lost by ammonia volatilization. The highest amount of ammonia loss accounted for about only two percent of the nitrogen added to the soil. Much higher losses would probably have occurred if the fertilizer applications had been broadcast or if the soil had been maintained at a moisture level lower than field capacity (93).

Reductions in emergence were associated with high rates of ammonia volatilization except when ammonium carbonate was added. Ammonium nitrate added at 120 lb N/acre and 28-0-0 added at 60 lb N/acre did not significantly reduce emergence. However, 120 lb N/acre as 28-0-0 and 60 lb N/acre as urea or ammonium carbonate greatly reduced emergence.

Most of the ammonia volatilized was lost in the first four to five days after application of the fertilizer (Figure 10). The results from the graph show that the maximum rates of ammonia loss for the 60 lb N/acre as urea or ammonium carbonate and 120 lb N/acre as 28-0-0 occurred in the first few days. This means that ammonia accumulation occurred during the first few days when the barley seeds were in their initial stages of germination. It is quite possible that barley is more sensitive to accumulations of ammonia during its early stages of germination when it is taking up water quite quickly. At early stages of germination, damage is probably due mainly to urea or accumulations of ammonia, since nitrite would not have had time to accumulate.

Conditions for urea hydrolysis would probably be favourable in this soil, as moisture was adequate and the temperature was optimum for microbial activity. This soil also contained a fairly high amount of organic matter and was probably able to support a high population of microorganisms. As a result, urea hydrolysis occurred very quickly in this soil, which has a relatively low cation exchange capacity (26.2 me/100 g), and very high amounts of ammonia accumulated.

The concentrations of ammonium and nitrate in the Altona soil, eleven days after seeding, varied considerably (Table VII). Considerable nitrification occurred and more than one-half of the urea applied was nitrified to nitrate. The amount of ammonia volatilized was not related to the amount or form of nitrogen in the soil after eleven days.

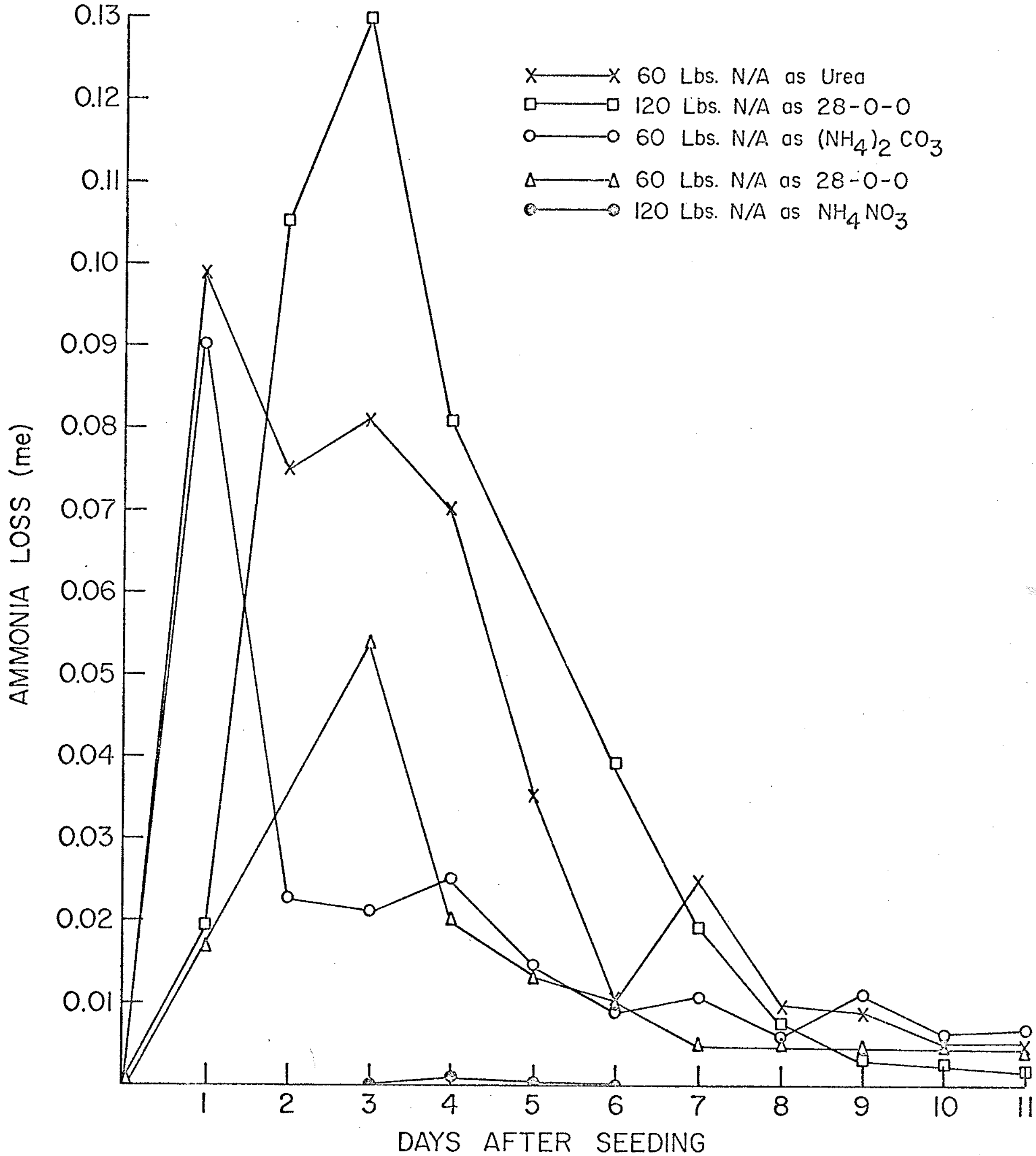


Figure 10. Daily loss of ammonia from the Altona soil as affected by rate and nitrogen source added.

Very little ammonium was left in the soil treated with ammonium carbonate. This was probably due to loss of ammonia and a rapid rate of nitrification. The amounts of nitrogen recovered from the soils were similar in treatments which received equivalent rates of nitrogen except for the soil treated with ammonium carbonate. Considerably less nitrogen was recovered from the soil treated with ammonium carbonate than from the soils treated with equivalent rates of the other fertilizers. This is probably due to loss of ammonia from the ammonium carbonate during application to the soil.

Ammonia volatilization varied considerably with the rate and source of applied nitrogen in the Red River soil (Table VIII). The losses from the Red River soil were very small in comparison to the ammonia losses from the Altona soil. The high cation exchange capacity of the soil (51.3 me/100 g) was probably responsible for minimizing ammonia loss as considerable amounts of ammonium would be adsorbed. Ammonia loss from urea applied at 60 lb N/acre was less than from 28-0-0 applied at 120 lb N/acre. Very little ammonia was volatilized when ammonium nitrate and 28-0-0 was applied at 60 lb N/acre. Loss of ammonia from ammonium carbonate was intermediate. Loss of ammonia from 28-0-0 applied to the Red River soil at 120 lb N/acre was proportionately much greater than the loss from 60 lb N/acre as urea and very much greater than the loss from 60 lb N/acre as 28-0-0. Thus, in the Red River soil, ammonia loss was not proportional to the amounts of urea added. In contrast loss of ammonia from the Altona soil was proportional to the amount of urea added.

These differences are most likely due to the differences in ammonium adsorption capacities of the two soils.

There were no significant reductions in seedling emergence except for the ammonium carbonate treatment. This reduction was not nearly as great as was observed when ammonium carbonate was added to the Altona soil. The data also show that unhydrolyzed urea was probably not responsible for reduction in seedling emergence, as it did not reduce emergence on this fine-textured clay soil.

Most of the ammonia was lost in the first few days (Figure 11). A reduction in air flow developed in the apparatus on the third day; thus, erratic results were obtained for the third to sixth days. Due to the reduction in air flow less ammonia than expected was volatilized on the third and fourth days, and much more ammonia than expected was volatilized on the fifth and sixth days. However, this fluctuation would have no large effect on the total amounts of ammonia volatilized.

Less nitrification took place in the Red River soil than in the Altona soil, as much higher levels of ammonium were recovered from the Red River soil (Table VIII). The amounts and rate of ammonia loss was not related to the amount or form of nitrogen in the soil. Nitrate concentrations were similar in all fertilizer treatments and were generally lower than those obtained for the Altona soil. Even on the treatment where maximum amounts of ammonia was lost, only about 0.5 percent of the added fertilizer nitrogen was lost as ammonia. The low loss is probably due to the high ammonium adsorption

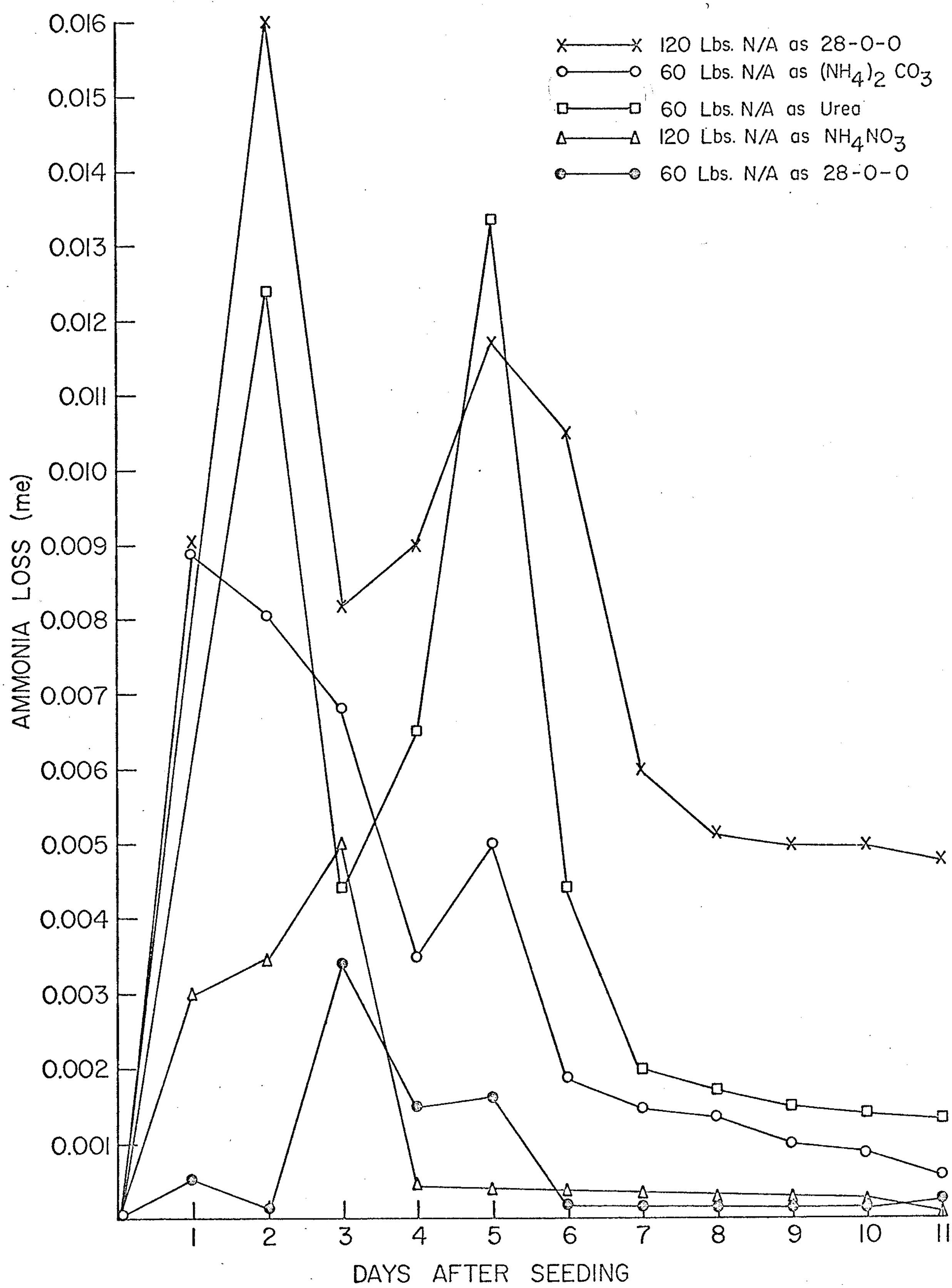


Figure 11. Daily loss of ammonia from the Red River soil as affected by rate and nitrogen source added.

Table VIII. Effect of rate and nitrogen source on the concentration of ammonium and nitrate in the fertilizer band, total ammonia volatilization and emergence of barley in the Red River soil.

Source of nitrogen	(lb N/acre)	Ammonium (ppm)	Nitrate (ppm)	Total Nitrogen (ppm)	Ammonia Loss (me)	Emergence (%)
	0	28.8 d[2]	44.4 b	73.2 e	0	100 a
28-0-0	120	750.0 a	195.0 a	945.0 a	0.088	95 a
28-0-0	60	295.0 c	211.0 a	506.0 cd	0.009	108 a
Urea	60	385.0 bc	174.0 a	559.0 bc	0.051	105 a
NH_4NO_3	120	420.0 ab	202.0 a	622.0 ab	0.017	103 a
$(NH_4)_2CO_3$	60	20.2 d	253.0 a	273.0 d	0.037	73 b

1 Fertilizer randomly spread with the seed.

2 Duncan's Multiple Range Test - Treatments followed by the same letter are not significantly different at ($P = 0.05$).

capacity of the Red River soil.

The data obtained for the two soils indicates that ammonia volatilization losses are very small when nitrogen fertilizers are placed with the seed providing the moisture supply is adequate. The degree of emergence reduction increased with increases in the amounts of ammonia volatilized from the soils. Liquid nitrogen fertilizer (28-0-0) was not as toxic to barley seeds as was an equivalent amount of urea nitrogen. The data showed that 60 lb N/acre as urea reduced emergence to about the same degree as 120 lb N/acre as 28-0-0. Since 60 lb N/acre as urea applied to heavy textured soils, such as the Red River in the greenhouse experiments, did not cause reductions in emergence, it appears that the damage was caused by high concentrations of ammonia. The Red River soil can adsorb large amounts of ammonium from the soil solution and thus prevents the accumulation of high amounts of ammonia in the soil solution. The urea concentration would be similar in both soils, as it is only very weakly adsorbed. Thus, the difference in barley emergence between the two soils would not be due to urea itself. The osmotic or toxic effect of ammonium ions could be responsible for some damage, but since ammonium nitrate at 60 lbN/acre had no effect on final emergence, this mechanism of damage does not seem plausible.

(C) Osmotic Stress and Toxic Effects of Fertilizer Solutions on the Germination of Barley

The results of the previous experiment showed that percent germination decreased rapidly with increases in the amounts of ammonia in solution. It was, however, impossible to differentiate between ammonia toxicity and toxicity from the urea molecule per se. Court et al. (31) suggested that some of the early damage to the seed and seedlings was due to urea molecules. Urea molecules could produce an osmotic effect which would cause moisture stress in the seed. Urea molecules could also pass through the seed membrane into the seed and be hydrolyzed by enzymes to produce toxic amounts of free ammonia. The objective of this experiment was to measure the reduction in barley seed germination as a result of the osmotic effect of urea molecules and the uptake of urea molecules by the seed. Carbowax 6000 and ammonium hydroxide were used as standards. Carbowax 6000 is a polyethylene glycol with a nominal molecular weight of 6000. Carbowax solutions are not toxic to seeds; thus, germination reduction would be due to an osmotic effect. Ammonium hydroxide is very toxic to seeds at concentrations where it would have a negligible osmotic effect. The effect of seed water content, at time of placement, on germination was also determined.

(1) Five seeds were placed into a nine cm petri dish containing three seven-cm filter papers. Three ml of solution was placed into each petri dish, sealed with vaseline, and stored at 22.2^{o}C. The treatments were replicated six times. Solutions of carbowax 6000, urea, ammonium hydroxide, ammonium carbonate, ammonium sulfate, ammonium nitrate, and ethanol were used. The osmotic

strengths of these solutions ranged from 0 to 28 atm. Germination counts were made every day for a period of six days. On the sixth day the number of coleoptiles was counted and their lengths measured.

(2) The water uptake pattern of barley seeds was determined by soaking barley seeds in distilled water for varying periods of time. Sixteen seeds were weighed and placed into small 50 ml Erlenmyer flasks containing 30 ml of distilled water. At the appropriate times, the seeds were taken out of the flasks and quickly weighed. The seeds were then dried in the oven for 48 hours at 110°C and weighed. The moisture content of the seeds was then calculated and expressed on a dry weight basis. Treatments were replicated six times.

In addition to this experiment another experiment was designed to determine the water uptake by barley seeds from various osmotic solutions. Solutions of carbowax 6000, urea, ammonium sulfate, ammonium nitrate, and ethanol were used. The osmotic strengths ranged from 0 to 28 atm. The procedures employed were the same as described previously. The seeds were removed from the petri dishes after three days and the moisture content determined as described above.

(3) Imbibed seeds (seeds placed in water for 48 hours) were placed in solutions of carbowax 6000, urea, and ammonium hydroxide with osmotic strengths ranging from 0 to 14 atm. The seeds were germinated in petri dishes as described previously. Germination counts were taken every day for six days. On the sixth day the coleoptiles were counted.

The amounts of urea hydrolyzed during the experiments were determined by titration of the urea solutions with 0.005 N sulfuric acid. Titrations were conducted prior to initiation and at the termination of each experiment using the solution which contained the highest level of added urea.

The osmotic pressures of the various solutions were calculated using van't Hoff's formula (60).

$$\pi = icRT$$

where i = van't Hoff factor

c = molarity

R = gas constant = .0827 l-atm $degree^{-1}$ $mole^{-1}$

T = temperature in ^{o}K

The carbowax 6000 solutions lowered the water potential more than would be predicted by this formula and the discrepancy increased both with increasing concentrations and particularly with increasing molecular weight. The relationship between soil water potential and concentration of carbowax 6000, determined by calibration with a thermocouple psychrometer[1], is shown in Table IX. The osmotic pressures for the carbowax solutions were obtained from this data. The relationship between soil-air ammonia and soil solution ammonia at 25°C is given by (21):

$$NH_{3(g)} = 12.9\ NH_{3(aq)}$$

$NH_{3(g)}$ = partial pressure of NH_3 in mm of Hg

$NH_{3(aq)}$ = molarity of unionized NH_3 in solution

[1]Shaykewich, C.F. and J. Williams. 1969. Unpublished data, University, of Manitoba, Winnipeg, Manitoba.

Table IX. Relationship between soil water potential and concentration of carbowax 6000

Osmotic pressure (atm)	Weight of carbowax in 500 g solution (g)
0	0
0.5	27
0.8	30
1	36
2	41
4	52
6	88
10	110
14	127

Soil-solution NH_4^+, H^+, and $NH_{3(aq)}$ are related by the equilibrium:

$$\frac{K_b}{K_w} = \frac{(NH_4^+)}{(NH_3)_{aq}(H^+)}$$

K_b = equilibrium constant for $NH_{3(aq)} \rightleftharpoons NH_4^+ + OH^-$

K_w = equilibrium constant for water

The concentration of ammonia in the ammonium hydroxide solutions was calculated from the above equations. Since some of the ammonia escaped from the solutions into the air within the petri dish, corrections were made for the resulting slight change in concentration. The solution uptake by the five seeds in each petri dish was negligible in relation to the total solution added; thus, no corrections for uptake were necessary.

The rate of water uptake by barley seeds (Table X) placed in water was rapid during the first few hours but gradually decreased with time. The seeds began to germinate after being placed into the water. The maximum water content of the barley seeds was 90.2 percent and coincided with the visible signs of germination.

Water uptake after 72 hours, expressed as a percent of dry weight, varied with type of solution and osmotic strength of solution used (Table XI). Final germination counts, obtained six days after being placed into the solutions, also varied with the type of solution and osmotic strength of the solution. Seeds germinating in distilled water contained 77.6 percent water. Solutions of urea and ethanol had only a small osmotic effect, as the water content of seeds decreased only slightly

Table X. Water uptake by germinating barley seeds in water.

Time in solution (hr)	Water content (%)
0	12.5
¼	14.3
½	28.6
1	30.8
2	37.0
3	36.1
4½	43.8
5	44.9
12	55.7
16	56.4
20	62.9
28	64.0
40	69.8
48	87.2
68	90.2

Table XI. Effect of osmotic pressure of different solutions on water uptake by barley seeds and final germination

Solution	Osmotic pressure (atm)	Water content (%)	Final germination (%)
Water	0	77.6	97
Carbowax	4	62.4	93
	10	50.3	0
	14	42.0	0
Urea	4	76.9	70
	10	71.3	43
	14	69.4	17
$(NH_4)_2SO_4$	6	68.4	83
	15	63.1	63
	21	57.7	10
NH_4NO_3	28	62.1	0
Ethanol	14	68.0	87

with increasing osmotic potentials. Carbowax solutions had a large osmotic effect, as the water content of seeds decreased sharply with increasing osmotic potentials. The carbowax solution with an osmotic strength of 14 atm greatly reduced the water content of the seeds. The germination of barley in the carbowax solution with an osmotic strength of four atm was close to 100 percent after six days. However, the seeds did not germinate in the carbowax solution with an osmotic strength of 10 atm. The water contents of the seeds in the four and ten atm carbowax solutions were 62.4 and 50.3 percent respectively. Thus, from these results it was assumed that if the water content of seeds in any solution was lower than approximately 62 percent, then large germination reductions could result from an osmotic effect. The effect of carbowax solutions on seed germination was assumed to be due entirely to its osmotic effect. With the concentrations used, urea and ethanol did not have a large enough osmotic effect to greatly reduce the water content of seeds. Ammonium sulfate and ammonium nitrate solutions, at high concentrations, reduced seed water content to levels at which reductions in germination would occur due to an osmotic effect. The higher osmotic effects produced by the ammonium sulfate and ammonium nitrate solutions as compared to those of the ethanol and urea solution could be due to the charges on the ammonium, sulfate, and nitrate ions. The charges may have restricted the movement of the ions through the seed membrane. Urea and ethanol molecules, although larger in size than ammonium or nitrate ions have no charge, and can perhaps move through the seed membrane with little difficulty and thus not create a large osmotic potential. Carbowax molecules are very large and cannot penetrate the seed membrane, thus creating a large osmotic potential.

Germination of seeds after six days, varied with the type of solution and osmotic potential of the solution used (Figure 12). Ammonium hydroxide and ammonium carbonate solutions were very toxic to the seed. Since the osmotic potentials of the above two solutions were very low, the reductions in germination were mainly due to the toxic effects of the ammonium hydroxide and ammonium carbonate. The toxicity was probably due to ammonia which is present in high concentrations in ammonium solutions of high pH (Table XII). Since carbowax has been shown to be non-toxic to seeds (92), carbowax solutions had only an osmotic effect on seed germination. There was a sharp decrease in germination as the osmotic potential of the solutions increased from four to six atm. This reduction in germination was due mainly to the reduction in water uptake by by the seed. The ethanol solutions had no osmotic effect, as they did not limit water uptake in seeds. Apparently, ethanol solutions have no toxic effects either, because germination was not reduced. The urea solutions did not prevent water uptake by the seed and thus, the germination reductions were probably due to a toxic effect. Toxicity of urea could manifest itself in two ways. Firstly, small amounts of ammonia in the solution resulting from urea hydrolysis could be toxic.

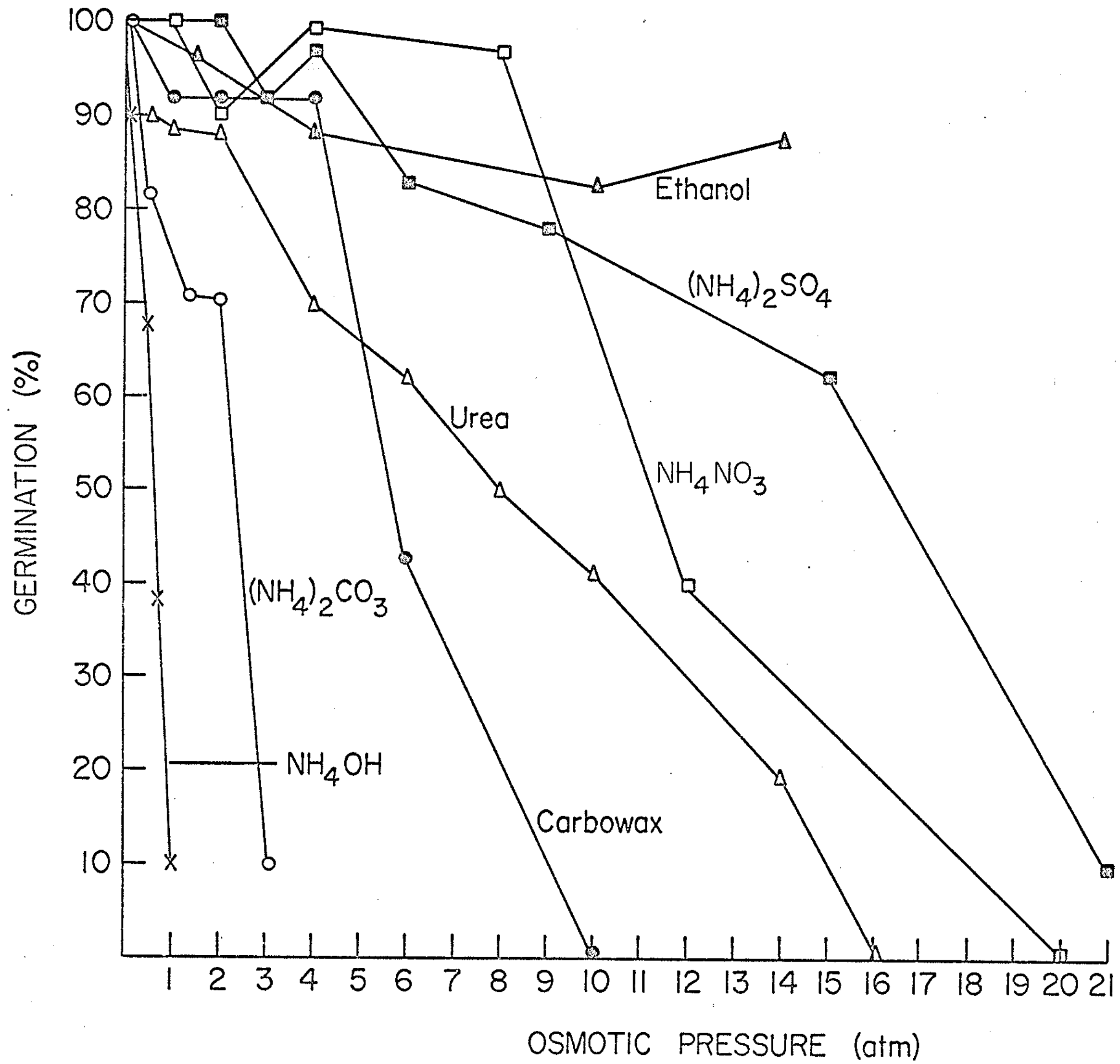


Figure 12. Effect of osmotic pressure and type of solution on barley germination.

Table XII. Calculated ammonia concentrations and molarities of osmotic solutions.

Carbowax-Osmotic pressure(atm)	0.5	0.8	1.0	4.0	6.0	10.0	14.0		
Concentration($Mx10^3$)	9	10	12	17	29	37	42		
Urea - Osmotic pressure(atm)	0.5	0.8	1.0	2.0	4.0	6.0	8.0	10.0	14.0
Concentration ($Mx10^2$)	2.06	3.30	4.12	8.24	16.50	24.80	33.00	41.20	58.00
Ethanol-Osmotic pressure(atm)	0.5	1.0	4.0	10.0	14.0				
Concentration ($Mx10^2$)	2.06	4.12	16.50	41.20	58.00				
$(NH_4)_2SO_4^-$Osmotic pressure(atm)	.75	1.20	1.50	3.00	6.00	9.00	15.00	21.00	
Concentration ($Mx10^2$)	1.04	1.67	2.07	4.16	8.32	12.50	20.80	29.00	
$[NH_3]$ ($Mx10^6$)	4.80	6.08	6.74	9.60	13.60	16.70	21.60	25.40	
NH_4NO_3 - Osmotic pressure(atm)	1.0	1.6	2.0	4.0	8.0	12.0	20.0	28.0	
Concentration ($Mx10^2$)	2.06	3.00	4.12	8.24	16.50	24.80	41.20	58.00	
$[NH_3]$ ($Mx10^6$)	3.37	4.27	4.68	6.76	9.50	11.70	15.10	18.00	
NH_4OH - Osmotic pressure(atm)	0.02	0.05	0.10	0.20	0.50	0.80	1.00	2.00	
Concentration ($Mx10^3$)	0.83	2.07	4.13	8.26	20.60	33.10	41.30	82.60	
$[NH_3]$ ($Mx10^3$)	0.80	1.89	3.89	8.10	19.80	33.00	41.20	82.30	
$(NH_4)_2CO_3$-Osmotic pressure(atm)	0.03	0.08	0.15	0.75	1.20	1.50	3.00		
Concentration($Mx10^3$)	0.42	1.04	2.07	10.40	16.70	20.80	41.60		
$[NH_3]$ ($Mx10^3$)	0.83	2.08	4.13	20.80	33.40	41.60	83.20		

However, the amount of urea hydrolyzed in the urea solution with the highest concentration was about 0.8 percent of the original concentration. This is equivalent to an ammonium concentration of about 0.009 N which would not reduce germination as large reductions in germination did not occur until the ammonium concentrations were about 0.033 N in the ammonium hydroxide solutions. Secondly, actual movement of urea molecules through the seed membrane into the seed and enzymatic hydrolysis of urea could produce toxic accumulations of ammonia within the seed. It appears that this latter mechanism of toxicity accounted for most of the seed germination reduction, as very little ammonia was found in solution. If all the urea had hydrolyzed, the toxic effect would have been similar to an equivalent concentration of ammonium carbonate. The ammonium sulfate and ammonium nitrate solutions also had a toxic effect on seed germination. At high concentrations of ammonium nitrate and ammonium sulfate both a toxic and osmotic effect would reduce germination, as osmotic potentials at high concentrations did markedly limit water uptake by the seeds. There would be negligible amounts of ammonia present in these solutions as the pH of these solutions was acidic. Therefore, the toxic effects of these solutions must be due to the ions themselves.

Final germination was plotted versus molarity (Figure 13) for each solution. The seed water contents and germination for each molar solution were shown in Table XI. When adding equivalent amounts of nitrogen to a soil, approximately the

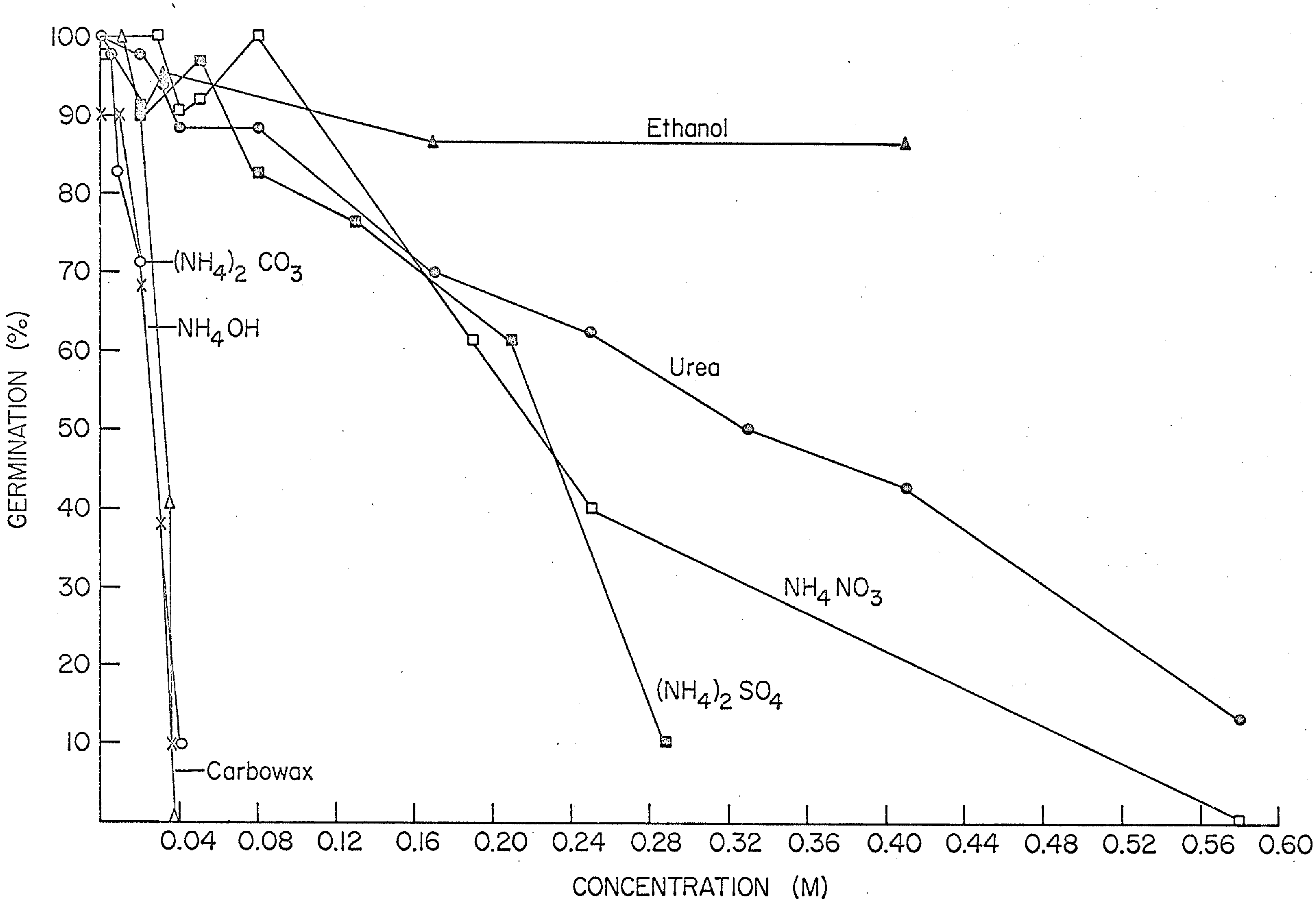


Figure 13. Effect of molarity and type of solution on barley germination.

same number of moles of each fertilizer must be added. Therefore, 60 lb N/acre as urea, ammonium nitrate, and ammonium sulfate would initially have similar molarities in the soil solution but different osmotic potentials. The osmotic effect of ammonium sulfate was relatively larger than of ammonium nitrate and urea when compared at equivalent molarities. The ammonium sulfate molecule dissociates into three ions, the ammonium nitrate molecule dissociates into two ions, and the urea molecule does not dissociate at all. Therefore, the theoretical osmotic potential of a one molar solution of ammonium sulfate is approximately three times the osmotic potential of a one molar solution of urea (Table XII).

The data indicate that urea did not reduce germination or water uptake as much as did an equal molar concentration of ammonium nitrate or ammonium sulfate (Figure 13). The sharp decrease in germination in the ammonium sulfate solutions between 0.21 to 0.29 molar corresponds to the sharp decrease in germination at an osmotic potential of 4 atm in the carbowax solutions. The ammonium sulfate solutions of concentrations greater than 0.21 molar, therefore, limited water uptake by the seed which sharply decreased germination. The seeds did not germinate in the 0.58 molar ammonium nitrate solution. Since the seed water content was below the critical level of approximately 62 percent in the 0.58 molar ammonium nitrate solution, the reduction in germination was in part due to an osmotic potential. The effects of ammonium carbonate and ammonium hydroxide on seed germination were similar.

The number of coleoptiles (Table XIII) decreased more rapidly with increasing osmotic potential than did the number of germinating seeds. Coleoptile growth appeared to be much more sensitive to osmotic effects, as very little growth occurred in the carbowax solutions even at low concentrations. The length of the coleoptiles (Table XIV) also decreased with increasing osmotic potential. Ammonium sulfate solutions inhibited growth more than urea or ethanol solutions. Ammonium carbonate solutions reduced coleoptile growth at low concentrations.

Imbibed seeds were affected by the fertilizer solutions in a different manner than were dry seeds (Table XV). The results show that germination in the carbowax solution was about the same as for dry seeds. However, germination increased in the urea and ammonium hydroxide solutions. This occurred because carbowax affects germination by an osmotic effect while urea and ammonium hydroxide affect germination by a toxic effect. It was shown in another experiment, not reported here, that a carbowax solution with an osmotic potential of 10 atm decreased the water content of imbibed seeds by 22 percent in 72 hours. This water loss immediately stopped germination. Urea and ammonium hydroxide solutions probably diffused into the imbibed seeds at a much slower rate than into the dry seeds in the previous experiment where the solutions would move into the seed by convective flow. As a result, germination would occur before toxic concentrations of

Table XIII. Effect of osmotic pressure and type of solution on the number of coleoptiles

Solution	Osmotic pressure (atm)																	
	0	0.5	0.8	1.0	1.2	1.5	1.6	2.0	3.0	4.0	6.0	8.0	9.0	10.0	12.0	14.0	15.0	21.0	28.0
Carbowax	25	6	8	12						0	0			0		0			
Urea	23	19	25	17				12		16	9	9		3		0			
$(NH_4)_2SO_4$	24		26		26	25			18		4		1				0	0	0
NH_4NO_3	27			30			24	17		21		14			0			0	0
Ethanol	29	28		26						9				0		0			
	Osmotic pressure (atm)																		
	0	0.02	0.03	0.05	0.08	0.10	0.15	0.20	0.50	0.75	0.80	1.00	1.20	1.50	2.00	3.00			
$(NH_4)_2CO_3$	30		30		29		27			23			8	6		0			
NH_4OH	25	27		25		21		27	18		5	0			0				

Table XIV. Effect of osmotic strength and type of solution on the length of coleoptiles (cm).

Solution	Osmotic pressure (atm)																
	0	0.5	0.8	1.0	1.2	1.5	2.0	3.0	4.0	6.0	8.0	9.0	10.0	14.0	15.0	21.0	28.0
Urea	3.5	3.8	4.1	3.9			4.1		3.3	2.4	2.0		0.9	0			
$(NH_4)_2SO_4$	2.4		1.8		1.8	1.8		0.9		0.2		0			0	0	0
Ethanol	3.6	2.8		2.3					1.9				1.5	1.5			

	Osmotic pressure (atm)							
	0	0.03	0.08	0.15	0.75	1.20	1.50	3.00
$(NH_4)_2CO_3$	3.5	3.5	2.8	2.8	1.6	0.2	0.3	0

Table XV. Effect of osmotic strength and type of solution on barley germination using imbibed seeds (%).

	Osmotic pressure (atm)									
Solution	0	0.1	0.2	0.5	0.8	1.0	2.0	4.0	10.0	14.0
Carbowax	100				80			83	0	0
Urea	83				70			70	60	68
NH_4OH	83	80	87	63	70	40	17			

ammonia developed in the seed. This is a very important aspect when placing fertilizer near seeds in the soil. More seeds would germinate if they took up enough water to germinate before the fertilizer came in contact with them. The number of coleoptiles was reduced by the increasing osmotic strength of the solutions (Table XVI). Urea, at equivalent osmotic potentials, did not decrease the number of coleoptiles as greatly as did carbowax or ammonium hydroxide.

Table XVI. Effect of osmotic strength and type of solution on the number of coleoptiles using imbibed seeds.

	Osmotic pressure (atm)									
Solution	0	0.1	0.2	0.5	0.8	1.0	2.0	4.0	10.0	14.0
Carbowax	12				9			1	0	0
Urea	11				8			11	4	0
NH_4OH	11	15	4	6	10	3	0	0		

V SUMMARY AND CONCLUSIONS

The objective of this study was to obtain information on the effects of urea and 28-0-0 (urea and ammonium nitrate in solution) on barley emergence and early growth. Various soils, methods of application, rates of application, and watering practices were studied. Attempts were made to determine the mechanisms by which urea or 28-0-0 reduced barley emergence and growth.

Greenhouse experiments were conducted to determine the effect of placement of urea and 28-0-0 on the emergence and yield of barley using different watering techniques and soils. The results from these studies showed that, on coarse-textured soils, 30 lb N/acre as urea and 60 lb N/acre as 28-0-0 reduced yield when applied closer than one-quarter inch from the seed. However, 60 lb N/acre as urea or 28-0-0 placed one-half inch from the seed did not reduce yields. Yields were not influenced when 60 lb N/acre as urea and 120 lb N/acre as 28-0-0 were applied with the seed on two heavy-textured soils providing soil moisture levels were maintained near field capacity. Yields on a Red River soil, maintained at a low soil moisture level, were reduced when 60 lb N/acre as urea was added with the seed.

The greatest reductions in barley emergence occurred when soil moisture levels were low at seeding time or for an extended period of time after seeding. Reduction in seedling emergence was lowest when maximal watering was needed to maintain the soil at field capacity and conditions were favourable for leaching urea and its reaction products. Urea, at rates of 40 or 60 lb N/acre, usually reduced emergence when placed closer than one-half inch from the seed. Sixty lb N/acre as urea reduced emergence to a greater degree than did 40 lb N/acre when placed with the seed. Seedling emergence with urea in powdered form was lower than with urea in pelleted or solution form placed with the seed. At equivalent rates of added nitrogen, emergence with urea was less than with 28-0-0. However, when equivalent amounts of urea nitrogen were added, emergence with 28-0-0 (120 lb N/acre) was less than with urea (60 lb N/acre). Thus, some damage was caused by the ammonium nitrate in the 28-0-0. Ammonium nitrate, applied at a rate of 60 lb N/acre with the seed, reduced emergence only slightly (not significantly) but did not increase yields as greatly as did 28-0-0 applied one-half inch from the seed.

The data, from the above greenhouse experiments, indicated that decreases in emergence and plant yields were mainly due to accumulations of ammonia and/or nitrite in the soil. It is also possible that these reductions were, in part, due to the high osmotic potentials in soil solution caused by urea and its reaction products.

A laboratory study, using a Red River and Altona soil, was conducted and the amounts of ammonia volatilized from the soil related to the extent of emergence reduction. The results were as follows:

Amounts of ammonia volatilized increased with increases in the amounts of urea added to the soil. At equivalent rates of added nitrogen, ammonia losses decreased in the order: urea, 28-0-0, ammonium nitrate. Ammonia loss from the ammonium nitrate was very small. Ammonia loss from the Altona soil treated with 120 lb N/acre as 28-0-0 or 60 lb N/acre as urea were similar, but losses from the 28-0-0 treatment were greater than from the urea treatment on the Red River soil. A much greater amount of ammonia was lost from the Altona soil than from the Red River soil. The low loss of ammonia from the Red River soil was attributed to its high cation exchange capacity. However, only a very small percent of the fertilizer added to either soil was lost by ammonia volatilization and was lost during the first few days after application.

Large reductions in emergence occurred in the Altona soil; emergence on the Red River soil was not significantly affected except when ammonium carbonate was added. High ammonia losses were associated with large reductions in emergence.

The osmotic and toxic effects of various fertilizer solutions on seed germination was investigated. Ammonium carbonate and ammonium hydroxide solutions reduced germination due to ammonia toxicity. Osmotic effects of these solutions on seed germination appeared to be negligible. Urea solutions reduced barley germination by a toxic effect. The water uptake by the seeds was not severely limited; thus, the urea solutions had only a small osmotic effect. The toxicity of urea appeared to be due to urea molecules moving into the seed, followed by enzymatic hydrolysis of the urea and accumulations of toxic amounts of ammonia.

The ammonium sulfate and ammonium nitrate solutions reduced germination by both a toxic and osmotic effect. The osmotic effects occurred only at high concentrations. The toxic and osmotic effects of these solutions were due to the ions themselves.

Urea and ammonium hydroxide solutions were found to be less toxic to imbibed seeds (seeds soaked in water for 48 hours) than to dry seeds.

The studies reported indicate that nitrogen fertilizers containing urea can reduce emergence and early plant growth on coarse-textured soils when added with the seed at rates of 30 lb N/acre or greater. The reductions in barley emergence and yield appeared to be mainly due to accumulations of ammonia in the soil solution. To a lesser extent, these reductions were attributed to: (1) accumulations of nitrite in the soils; (2) enzymatic hydrolysis of urea in the seed and subsequent accumulations of ammonia; (3) high osmotic potentials in soil solution caused by urea and its reaction products. The adverse effects of urea on barley emergence and growth can be avoided by placement of the urea at distances greater than one-half inch from the seed.

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