DOCTORAL DISSERTATION SERIES

TITLE A Study Of Cyanamide Decomposition In Soils

DATE 1941

AUTHOR Benjamin J. Birdsall

UNIVERSITY Mich. State College

DEGREE Ph. D.

PUBLICATION NO. 313

UNIVERSITY MICROFILMS
ANN ARBOR - MICHIGAN

A STUDY OF CYANAMIDE DECOMPOSITION IN SOILS

By

BENJAMIN JOSEPH BIRDSALL

A THESIS

Submitted to the Graduate School of Michigan
State College of Agriculture and Applied
Science in partial fulfilment of the
requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Soils

1941

ACKNOWLEDGMENT

I wish to express my appreciation and thanks to Dr. L. M. Turk, Dr. C. E. Millar and Dr. C. H. Spurway for guidance in the research reported in this paper and in the preparation of the manuscript, and to other members of the Soils Section of Michigan State College for cooperation and suggestions in the investigations; to Dr. H. G. Byers, of the Bureau of Plant Industry, U. S. D. A.; Dr. G. D. Scarseth, Purdue University; and Professor E. Truog, University of Wisconsin, for supplying certain soils, and to the American Cyanamid Company for supplying the cyanamid used in these studies.

CONTENTS

INTRODUCTION

The numerous investigations carried out by individuals interested in cyanamid[1] fall into the general classification of (1) chemistry of the decomposition of calcium cyanamide in solution and in the soil; (2) crop response to cyanamid as compared with other forms of nitrogenous fertilizers; (3) identification of the decomposition products of calcium cyanamide which are adsorbed by plants; (4) soil constituents and factors which are specifically responsible for the nature and rate of decomposition of calcium cyanamide.

The producers of commercial cyanamid recognize the peculiarities of the product and strongly suggest adherence to their recommendations in the use of the material in order to avoid unsatisfactory results.

The unsatisfactory results associated with improper use of the fertilizer are due to toxicity of hydrogen cyanamide and dicyanodiamide to plant growth. The avoidance of these difficulties usually involves the application of the fertilizer several days before the planting of the seed or other special precautions where plants are already established. The necessity of such practices produces a certain amount of discrimination against the product in competition with other nitrogenous fertilizers,

---

[1] Cyanamid is a commercial nitrogenous fertilizer consisting of 63 per cent calcium cyanamide as the nitrogen carrier, 17 per cent calcium hydroxide, 12 per cent free carbon and small amounts of calcium carbonate, calcium sulfide, silica, iron and alumina. The present commercial product has a total nitrogen content of from 21 to 22 per cent and has a total hydrated lime equivalent of 70 per cent. It can be secured in both the pulverized and granulated forms; the former is oiled to prevent undue dustiness and the latter is free of dust and consists of small pellets passing a twelve mesh screen.

Cyanamid or calcium cyanamid refers to the commercial product and cyanamide or calcium cyanamide refers to the pure salt.

in spite of its several advantages. Another undesirable inherent feature of the use of cyanamid is its delayed nitrification.

Previous investigations have provided much information which has been helpful in making judicial recommendations in the use of cyanamid in which its advantages over other nitrogenous forms can be utilized. Emphasis, in these investigations, has been placed on the segregation of soil constituents and factors which are responsible for rapid cyanamide conversion to non-toxic decomposition products and to catalytic agents which might be incorporated into the fertilizer to increase its rate of conversion or removal from the soil solution. Extremely sandy soils, soils low in organic matter, and alkaline soils are less responsive to rapid cyanamide decomposition. Incorporation of active catalytic agents in the fertilizer has not been found desirable due to the necessity of lowering the nitrogen content of the carrier. The failure, in some cases, of certain soils to readily decompose cyanamide has not been satisfactorily explained.

This investigation has been undertaken to provide additional information on the capacity of a number of soils to decompose cyanamide, the nature and quantity of the various decomposition products, soil constituents and factors involved in the cyanamide decomposition, and the effect of some catalysts on cyanamide decomposition.

LITERATURE REVIEW

The Hydrolysis of Calcium Cyanamide

Summarized accounts of the chemistry of calcium cyanamide decomposition, supplied by Pranke (16), McCool (12), Williams (20), and Buchanan and Barsky (2), as prepared by Smock (18), appear in the diagram, page 4. The major reactions involved in the decomposition of calcium cyanamide are represented.

Hydrogen cyanamide (also called "free cyanamide" and "acid cyanamide") is a nitrile of carbamic acid and has been assigned two possible structures, $NH=C=NH$ and $NH_2-C\equiv N$, by Conant (5). Both of these forms may be present in solution and they behave as a weak monobasic acid with a dissociation constant of 5.4×10^{-11} at 25° C, according to Crowther and Richardson (8). It precipitates as an insoluble salt from alkaline silver nitrate, the precipitate being insoluble in ammonium hydroxide.

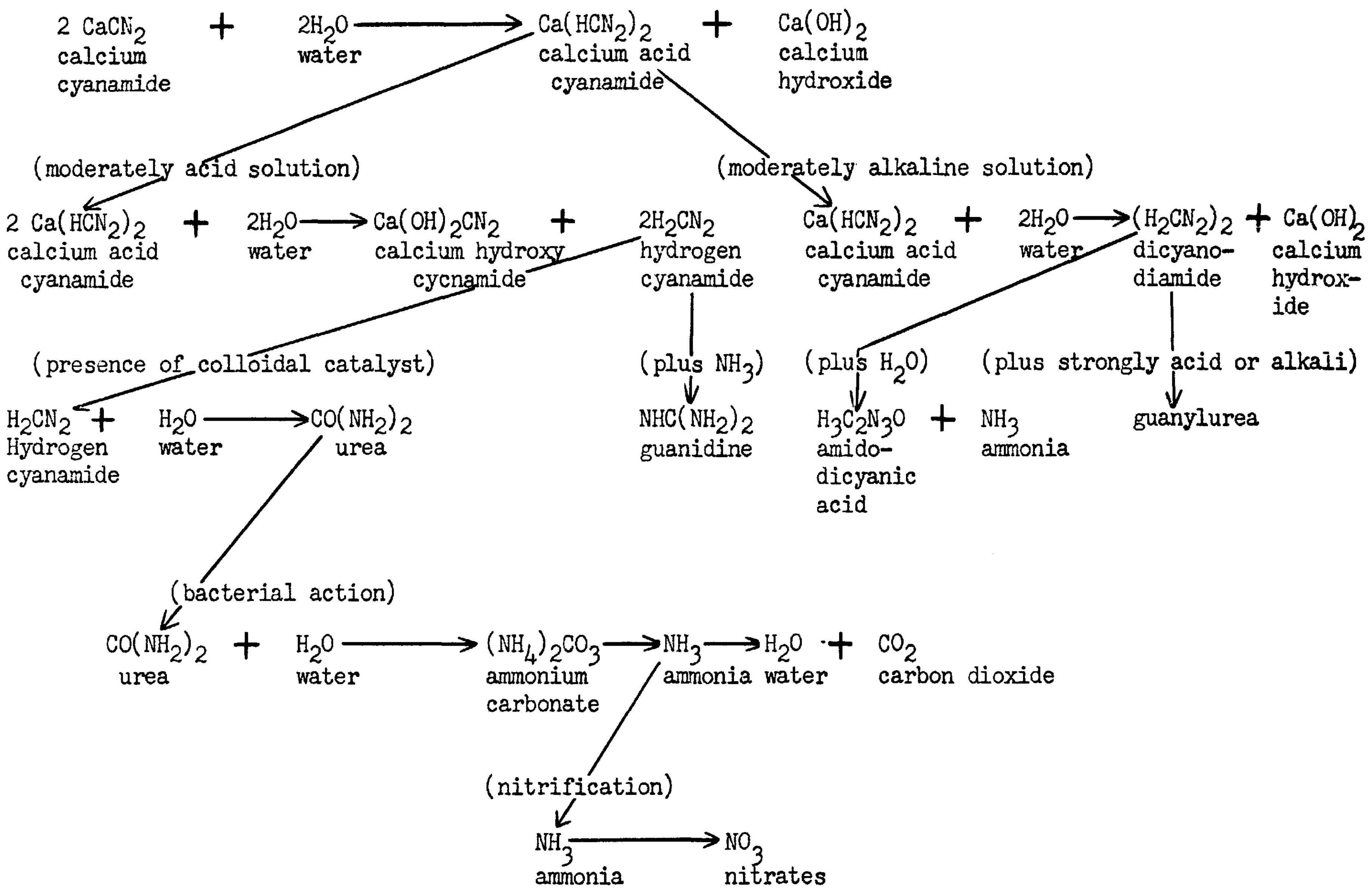
Calcium cyanamide is the calcium salt of hydrogen cyanamide and according to the diagram, may hydrolyze to form either hydrogen cyanamide or dicyanodiamide. The hydrogen cyanamide may further hydrolyze to yield urea in the presence of catalysts and a moderately acid medium, while in a moderately alkaline medium it may polymerize to form the relatively stable dicyanodiamide. The formation of dicyanodiamide proceeds very slowly between pH 7.0 and 8.0, increases with alkalinity and reaches its maximum between pH 9.0 and 10.0, then reduces rapidly in more alkaline solutions (pH greater than 10.0), while hydrolysis of urea begins and becomes almost quantitative at pH 12.0, according to Buchanan and Barsky (2).

The Decomposition of Cyanamide in the Soil

The decomposition of cyanamide in the soil under favorable conditions proceeds rapidly. Soils differ greatly, however, in their capacity to remove cyanamide from solution.

Sufficient moisture in the soil to permit hydrolysis of the cyanamide is necessary in the first stage of the decomposition reaction.

Decomposition of Calcium Cyanamide



Sufficient moisture to insure hydrolysis, yet a low enough content to insure contact with colloidal catalysts has been offered as an explanation for the more rapid disappearance of cyanamide from solution at lower moisture contents by Crowther and Richardson (8).

It has been amply demonstrated that urea is formed from cyanamide in soils. A physico-chemical reaction is involved in the production of urea from cyanamide, according to Pranke (16), Cowie (7), and the work of Kappen, Ulpiana and others reviewed by McCool (12). Crowther and Richardson (8) point out that normal agricultural soils are seldom devoid of the necessary catalysts that will produce urea from cyanamide. The absence of a direct biological effect in the formation of urea has been demonstrated by Cowie (7). A somewhat complete historical review of this phase of the problem has been presented by Jacob, Allison and Braham (11).

The accumulation of urea in normal agricultural soils, in most instances, does not reach great proportions after cyanamid treatment. The formation of ammonia from the urea and subsequent nitrification are accepted biological processes. The formation of the ammonia is a rapid process and its occurrence in solution and in the adsorbed form is generally accepted. The ammonia nitrogen may be immediately available for plant use or its adsorption by soil colloids insures against its loss from the soil by percolating water.

The nitrification of ammonia, formed from the decomposition of cyanamide in soils, is retarded, according to work reported by Crowther and Richardson (8), Mukerji (14), Allison (1), Jacob, Allison and Braham (11). The cause for the retardation of nitrification has been attributed to the toxic effect of cyanamide, as well as dicyanodiamide on the nitrifying organisms, according to Mukerji (14).

The formation of dicyanodiamide from cyanamid applications to soils may occur under certain soil conditions and improper methods of application. It is an undesirable decomposition product due to the fact that it is very stable, does not decompose and nitrify readily, and its toxicity is specific to nitrifying organisms (Cowie (7), Mukerji (14), Jacob, Allison and Braham (11)). The review of the literature on dicyanodiamide as presented by Jacob, Allison and Braham (11) and more recently by McCool (12) shows that under normal conditions and with reasonable care as to time and method of application of cyanamid, dicyanodiamide is not formed in the soil in sufficient amounts to be of any practical significance.

GENERAL PROCEDURE OF INVESTIGATIONS AND METHODS USED

In the studies dealing with soils, the general procedure was to mix thoroughly 0.1 gm. of granulated cyanamid, which was pulverized, equivalent to 21.21 mg. of nitrogen, with 200 gm. of dry soil. When the quantity of soil was limited, 0.05 gm. of cyanamid per 100 gm. of soil was used. The soils were brought up to optimum moisture content, well mixed and placed in jelly tumblers. The soils were maintained at optimum moisture content until examined. At definite intervals of time the soils were extracted.

The extraction process was accomplished by transferring the soil to 500 ml. Erlenmyer flasks and adding distilled water to bring the volume of water up to 150 or 160 ml., including that which the soil contained. The flasks were placed in a mechanical shaker and agitated for one-half hour, after which they were filtered, using large Buchner funnels. Since the first portion of the extracts was not clear in some instances, the first 100 ml. of the extracts were refiltered through the soil. After extraction was complete, the volume of the filtrate was measured in order to make the necessary corrections for soluble ammonia in the fixed ammonia nitrogen determinations. The extracted soil was dried at a low temperature and an aliquot portion, 50 or 100 gm., was extracted with 300 ml. of 4 per cent KCl solution. A 200 ml. aliquot was distilled in alkaline solution into 4 per cent boric acid solution which was titrated with 0.0357 N H_2SO_4. The results are reported as increases in fixed ammonia nitrogen, corrected for soluble ammonia nitrogen due to incomplete extraction and the normal fixed ammonia nitrogen in the non-treated soil.

Aliquots of 20 or 25 ml. of the soil extract were used for determinations of soluble nitrogen fractions by a micro-Kjeldahl procedure, as outlined by Niederl and Niederl (15). Cyanamide nitrogen was determined on aliquots of the extract by adding 6.0 ml. of 1-1 NH_4OH and precipitating the cyanamide with an excess of 0.1 M $AgNO_3$. After standing several hours the solutions were filtered and the precipitates collected on 7.0 cm., No. 42 Whatman filter paper. The precipitates were washed with distilled water until free of ammonia and transferred to 100 ml. micro-Kjeldahl flasks by dissolving with 8 ml. of warm 1-4 H_2SO_4 and washing with small portions of warm water until the filter papers were free of acid. A pinch of $CuSO_4$-K_2SO_4 salt mixture and two small glass beads were added and digestion completed. The use of the beads was found essential to prevent bumping and consequent loss by spattering. A micro-distillation unit of the Parnas and Wagner type was used and the ammonia distilled over into

0.01 N HCl and titrated with 0.01 N NaOH, using methyl red as an indicator.

Soluble ammonia nitrogen in the filtrate was determined by alkaline distillation, using the micro-distillation unit, and urea nitrogen was determined by the method of Fox and Geldard (10).

Nitrate nitrogen was determined by the phenol-disulphonic-acid method. No clarifying or flocculating agents were used since the extract of the Fox sandy loam on which nitrate determinations were made was free of colloidal material and no difficulty was experienced in securing accurate readings.

Total nitrogen, exclusive of nitrates, was determined by means of the micro-Kjeldahl method, using 3.0 ml. of concentrated H_2SO_4 and a pinch of K_2SO_4-$CuSO_4$ salt mixture for digestion.

The pH determinations were made on all soils, using the glass-electrode Beckman pH meter and on all extracts by colorimetric methods.

Dicyanodiamide nitrogen was determined by the difference method as used by Crowther and Richardson (8).

All results have been calculated and reported as mg. of nitrogen per 200 gm. of soil and as per cent of the total mg. of nitrogen added as cyanamid.

Silica sand was used for testing the effect of various materials on cyanamide decomposition. In these studies, 0.1 gm. of cyanamid was mixed with the material being studied and this mixture well distributed in the sand and maintained at optimum moisture content.

The extraction and determination of the nitrogenous fractions were carried out as outlined in the general procedure with soils. The results are reported in a similar manner.

In the solution culture work on cyanamide decomposition, cyanamid was added, along with materials used in the study, to a volume of distilled water, such that the cyanamid-water ratio was comparable to that which was used in the soil studies. The solutions were filtered and washed with sufficient water to provide a total volume of 125 or 150 ml. of filtrate. The nitrogen determinations were made on 20 to 25 ml. aliquots of the extract and reported as mg. of nitrogen per total volume and as per cent of the total nitrogen added as cyanamid.

All studies were carried out at laboratory temperatures unless indicated otherwise and plant growth was not permitted in any cultures except those involving seed germination tests.

RESULTS AND DISCUSSION

Cyanamide Decomposition and Transformation in Fox Sandy Loam

The Fox sandy loam was selected for detailed study because it is a strongly acid soil (pH 4.3) and one in which a rapid conversion of the cyanamide-nitrogen to other nitrogenous products was anticipated. Carter (3) found the nitrifying capacity of this soil to be low. An acid soil reaction favors rapid conversion of the cyanamide as reported by Fink (9) and others. Delayed nitrification of cyanamide-nitrogen, as reported by Jacob, Allison and Braham (11), Allison (1), and Mukerji (14), was an object of particular study in the Fox soil.

Many investigators have studied the disappearance of cyanamide from soil solution and its conversion to urea, ammonia and nitrates as separate phases of study. In this investigation, however, it was proposed to study the complete transformation of the added cyanamide-nitrogen to the soil through the urea-nitrogen, soluble ammonia-nitrogen, fixed ammonia-nitrogen and finally the nitrate-nitrogen stage. The disappearance of the cyanamide and the accumulation of urea, soluble ammonia, fixed ammonia and nitrate-nitrogen were studied at intervals over a period of fifteen weeks. Total nitrogen determinations on the soil extract were also made to ascertain the relation of its content to the nitrogen changes involved.

A sufficient number of tumblers were set up to provide triplicate extractions for the intervals selected during the period of fifteen weeks for both the treated and non-treated soils. To each 200 gm. of air dry soil, 0.1 gm. of fresh, pulverized cyanamid, equivalent to 21.21 mg. of nitrogen, was added to the dry soil and well mixed. The soils were all maintained at optimum moisture conditions.

The intervals of time for extraction, indicated in Table 1, were selected to permit adequate observation of the course of the nitrogen transformations. Extractions were made at short intervals of time during the early stages of the study. After the urea-nitrogen disappeared, extractions were made at intervals of one, two and three weeks. The methods used for the determination of the various nitrogenous forms and the usual method of extraction are given in that part of this paper devoted to methods.

The cyanamide remained in solution a relatively short period of time. After 12 hours over 53 per cent of the cyanamide-nitrogen had disappeared from solution; after 48 hours only a trace of cyanamide-nitrogen was found and after 72 hours it had disappeared entirely.

Apparently the cyanamide had been hydrolyzed, to a large extent, to urea, as indicated by the presence of 31.2 per cent of it in the urea

TABLE 1

Transformation of Added Cyanamid-Nitrogen to Fox Sandy Loam Soil[1]

Time	Cyanamide-N[2]		Urea-N		Soluble ammonia-N			Nitrate-N			Fixed ammonia-N			Total-N		
	Treatment		Treatment		Control	Treatment		Control	Treatment		Control	Treatment		Control	Treatment	
	mg.	%	mg.	%	mg.	mg.	%	mg.	mg.	%	mg.	mg.	%	mg.	mg.	%
12 hours	9.97	47.0	6.62	31.2	Tr.	1.50	7.1	0.43	0.34		7.89	8.24	1.7	Tr.	17.64	83.2
24 hours	4.65	21.9	7.81	36.8	Tr.	2.40	11.3	0.40	0.30		7.59	7.79	0.9	Tr.	15.86	74.8
72 hours	None		6.96	32.8	Tr.	3.21	15.1	0.41	0.16		6.82	13.03	29.3	Tr.	12.18	57.5
5 days			None		Tr.	3.55	16.8	0.50	0.18		4.08	11.90	36.9	Tr.	8.71	37.6
7 days					Tr.	3.94	18.6	0.84	0.27		2.87	12.67	46.2	Tr.	5.15	24.3
2 weeks					Tr.	3.57	16.8	1.50	0.42		2.81	13.28	49.3	Tr.	4.73	22.3
3 weeks					Tr.	4.05	19.1	1.55	0.81		1.89	12.57	50.4	Tr.	4.79	22.6
5 weeks					Tr.	4.85	22.9	2.41	2.04		2.28	10.72	39.8	Tr.	4.79	22.6
7 weeks					No	4.65	21.9	3.21	4.50	6.1	2.22	11.20	42.4	Tr.	4.67	22.0
9 weeks					No	3.89	18.4	3.54	8.50	23.4	3.89	12.02	38.4	Tr.	3.97	18.7
12 weeks					No	3.70	17.5	4.73	10.90	29.1	5.40	10.59	24.5	Tr.	3.75	17.7
15 weeks					No	3.00	14.2	4.17	10.90	31.7	4.75	9.86	24.1	Tr.	2.98	14.1
18 weeks								4.12	13.60	44.7						

---

[1] Figures represent averages of triplicate determinations. Cyanamide added at the rate of 21.21 mg. of nitrogen per 200 gm. of soil.

[2] All nitrogen fractions expressed as mg. of nitrogen per 200 gm. of soil and % of 21.21 mg. nitrogen added as cyanamid.

form at the end of 12 hours. That some of the cyanamide had already passed through the urea stage to ammonia was indicated by the occurrence after 12 hours of ammonia-nitrogen in solution to the extent of 1.50 mg. or 7.1 per cent of the cyanamide-nitrogen added. This process of transformation continued and after 72 hours the cyanamide-nitrogen had completely disappeared, urea-nitrogen was still high (6.96 mg. or 32.8 per cent of the total nitrogen added) and ammonia-nitrogen in the soluble and fixed forms increased to 3.21 mg. (15.1 per cent) and 6.21 mg. (29.3 per cent) respectively. Up to this point nitrate accumulation was depressed in contrast to the untreated soil.

It is interesting to note that during the two initial intervals most of the soluble nitrogen was accounted for in the total nitrogen determinations, but for the longer incubation periods this was not the case; for example, at the 72 hour interval, 32.8 per cent of the added nitrogen appeared as urea-nitrogen and 15.1 per cent appeared as soluble ammonia-nitrogen, making a total of 48.0 per cent, yet 57.5 per cent of the nitrogen added as cyanamid appeared as total nitrogen. The possibility exists that some cyanamide had changed to the dicyanodiamide form and possibly other forms which were not determined. The quantity of nitrogen accounted for, expressed as a percentage of the amount added as cyanamid, is shown in Figure 1. When the soluble nitrogen of the extract is added to the fixed form in the treated soil, and corrected for that of the untreated soil, between 20 and 35 per cent is unaccounted for. This may be explained by the adsorption by the soil of cyanamide and urea during the earlier periods. Conrad (4) has reported that urea-nitrogen is temporarily adsorbed as such. Microbial assimilation may account for the

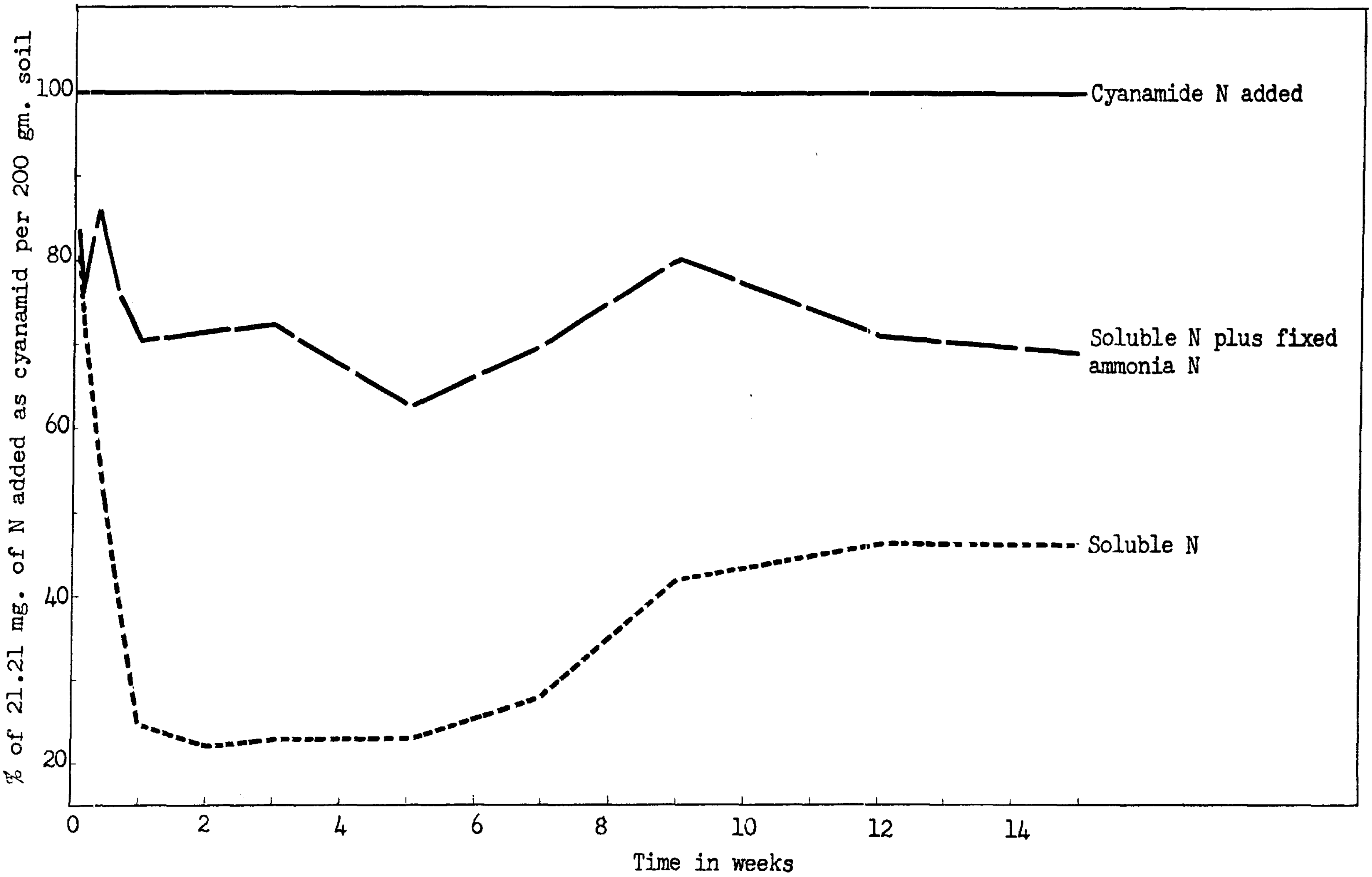


FIGURE 1. Nitrogen accounted for from an Application of 21.21 mg. of Nitrogen added as Cyanamid per 200 gm. of Fox Sandy Loam Soil.

disappearance of some of the soluble nitrogen during the earlier periods and possibly more as time went on. The relationship of the quantity of various nitrogenous decomposition products of cyanamide produced during the early stages of decomposition to the total quantity of nitrogen added as cyanamide is presented in Figure 2. Those fractions present only in minute quantities are not shown on the graph.

An analysis of the curves for the treated soil shows the following relationships between the various nitrogenous products. The quantity of cyanamide-nitrogen decreased very rapidly and had completely disappeared by the third day. In the meantime, an appreciable increase in the concentration of urea, soluble ammonia-nitrogen, and fixed ammonia-nitrogen was observed. This is an indication that the urea changed over to ammonia-nitrogen which was adsorbed by the soil. The concentration of total nitrogen in the extract decreased, coinciding with the disappearance of cyanamide-nitrogen and the change of urea-nitrogen to ammonia-nitrogen, which, in turn, was removed from the soil solution by adsorption.

After three days the soluble ammonia and fixed ammonia-nitrogen reached a temporary constant concentration and after seven days the total nitrogen reached a constant concentration. Urea-nitrogen disappeared from solution between the three and five day intervals.

The nitrate concentration of the treated soil suffered some depression during the first three days, followed by a slight increase by the end of fourteen days. The nitrate concentration of the non-treated soil increased slowly and was considerably higher than the cyanamid treated soil after fourteen days.

Only traces of ammonia-nitrogen or total nitrogen were found in

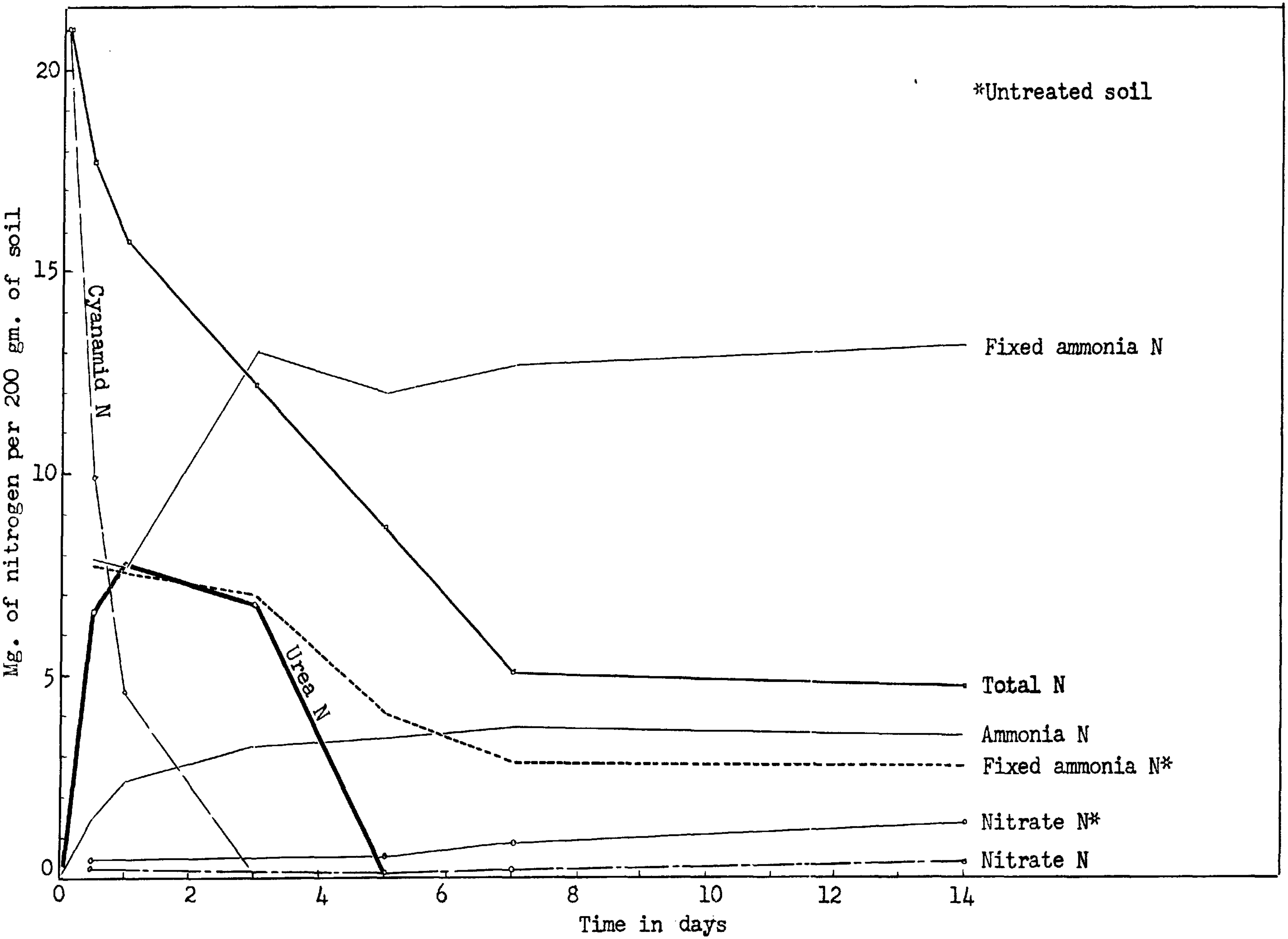


FIGURE 2. The Relationship of the Quantities of the Decomposition Products of Cyanamide in Fox Sandy Loam Soil over a Period of Two Weeks. (21.21 mg. of Nitrogen added as Cyanamid per 200 gm. of Soil)

the extract of the non-treated soil and, of course, no cyanamide-nitrogen or urea-nitrogen. The fixed ammonia-nitrogen of the untreated soil decreased from 7.80 mg. to 2.87 mg. within seven days, at which level it was apparently maintained for the next seven days. This decrease in fixed ammonia-nitrogen was not accompanied, however, by a corresponding increase in nitrate, as might be anticipated; microbiological assimilation of nitrates may be the explanation.

A further analysis of these nitrogen fractions, for the more extended periods of study, can be continued with Figure 3.

The soluble ammonia-nitrogen concentration of the cyanamid treated soil reached its maximum by the fifth week and then slowly decreased to the fifteenth week. It is of interest to point out that after the fifth week the concentration of ammonia-nitrogen followed the same level as the total nitrogen concentration of the soil extract.

The nitrate content of the untreated soil increased slowly from the initial periods to a maximum of 4.73 mg. at the twelfth week. The nitrate content of the treated soil increased more rapidly after the second week but did not reach the concentration found in the untreated soil until shortly after the fifth week, from which point it increased rapidly to a total concentration of 13.60 mg. for the eighteenth week. This represents 44.7 per cent of added nitrogen (Table 1). Here again the retardation of nitrification of cyanamide-nitrogen, which has been reported in the literature, has been established.

The level of the fixed ammonia-nitrogen in the untreated soil began a slow upward trend after the seventh week. This was accompanied by a decrease in the nitrate level. The concentration of the soluble

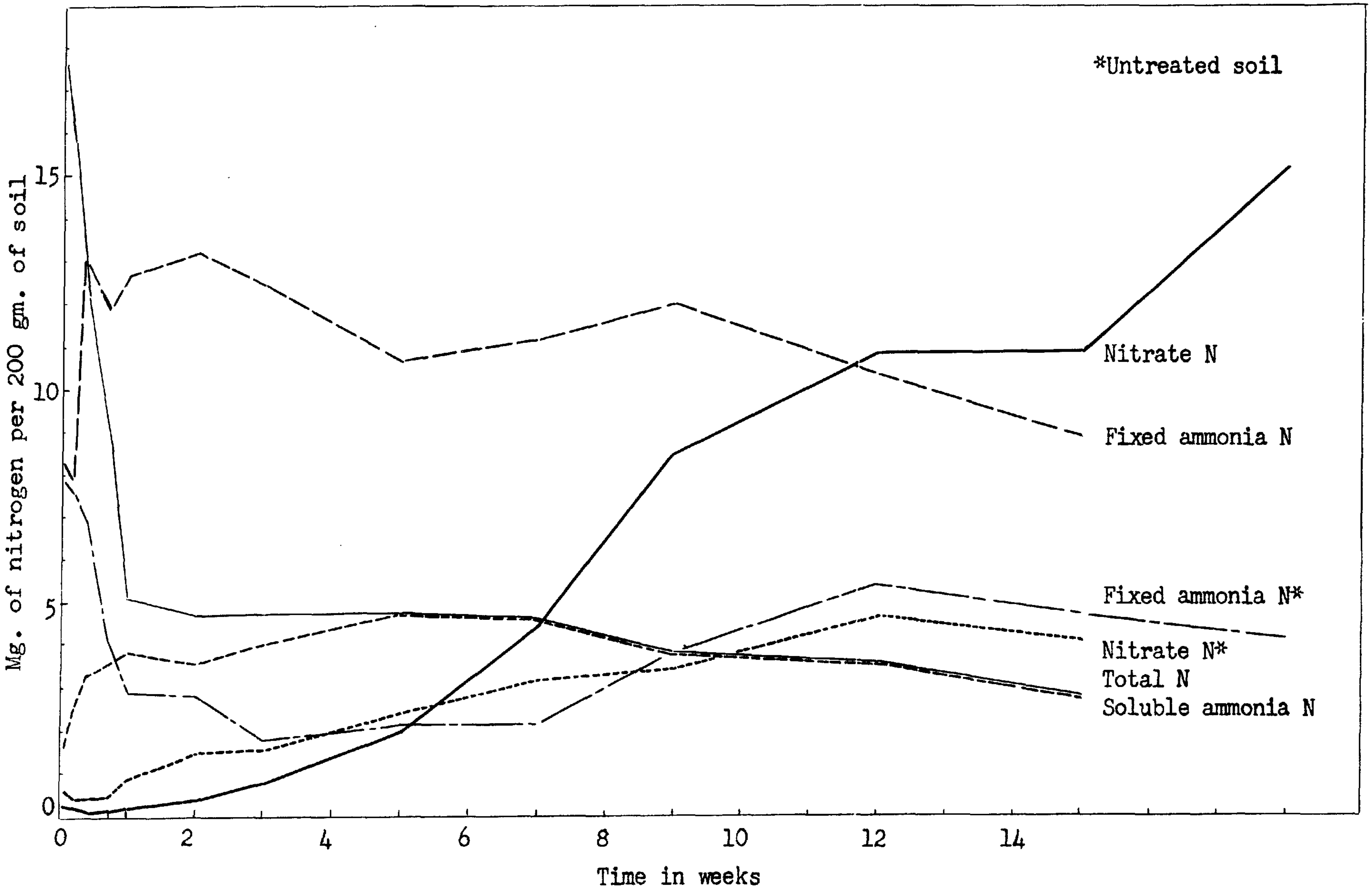


FIGURE 3. The Relationship of the Quantities of the Decomposition Products of Cyanamide in Fox Sandy Loam over a Period of 15 Weeks. (21.21 mg. of Nitrogen added as Cyanamid per 200 gm. of Soil)

and fixed ammonia-nitrogen in the treated soil decreased and this was accompanied by an increase in nitrate concentration.

Influence of Varying Moisture Contents

Since soil moisture has been designated as an important factor affecting the hydrolysis of cyanamide, a study of this phase of the problem was undertaken.

Fox sandy loam soil, employing two moisture levels - 5.0 and 7.5 per cent respectively - was used for this study. The moisture percentages were both lower than the optimum moisture content (10 per cent) used in the preceding experiments; otherwise the plan of the experiments was similar in all respects to those reported above. It was found that unless a uniform distribution of moisture throughout the soil was secured, no consistent results between replications could be secured during the initial intervals of examination. This applied particularly to cyanamide-nitrogen, urea-nitrogen and soluble ammonia-nitrogen.

The results of the investigations dealing with the influence of moisture on the transformation of cyanamid are summarized in Table 2 and in Figures 4 and 5.

The lower moisture levels (7.5 and 5.0 per cent) did not increase the concentration of cyanamide-nitrogen during the first 24 hours. After 12 hours the concentration (cyanamide-nitrogen) was definitely less for the lower moisture levels than for the optimum moisture content; however, the cyanamide-nitrogen, at low concentrations, persisted approximately 24 hours longer at the lower moisture levels. It is believed that greater toxicity due to cyanamide in solution would not be exhibited by the lower moisture concentrations.

TABLE 2

The Effect of Three Moisture Levels on the Decomposition of Cyanamide in Fox Sandy Loam Soil*

Nitrogen Fraction mg. - per 200 gm. of soil	Cyanamide-N			Urea-N			Ammonia-N			Nitrate-N			Fixed ammonia-N		
Moisture Content-%	10.0	7.5	5.0	10.0	7.5	5.0	10.0	7.5	5.0	10.0	7.5	5.0	10.0	7.5	5.0
Time interval															
12 hours	10.0	8.6	7.3	6.6	7.6	7.0	1.5	0.7	0.7	0.3	0.3	0.4	8.2	5.3	5.1
24 hours	4.7	6.5	5.0	7.8	7.3	8.2	2.4	1.0	1.0	0.3	0.3	0.3	7.8	6.0	5.9
48 hours	Tr.	2.3	1.2		7.2	9.0		1.3	1.3		0.2	0.2		8.5	7.6
72 hours	None	Tr.	Tr.	7.0	7.8	7.8	3.2	2.0	1.9	0.2	0.2	0.2	13.0	8.6	8.1
96 hours		None	None	None	4.2	4.8		2.2	2.3						
120 hours					3.4	3.9	3.6	2.6	2.8	0.2	0.2	0.2	11.9	14.2	14.1
1 week					None	None	3.9	3.1	3.4	0.3	0.3	0.3	12.7	14.6	13.8
2 weeks							3.6	3.5	3.4	0.4	0.5	0.5	13.3	14.8	14.3
3 weeks							4.1	3.6	3.4	0.8	0.9	0.9	12.6	14.4	13.7
5 weeks							4.9	3.9	3.5	2.0	2.0	1.8	10.7	16.0	15.7
7 weeks							4.7	4.3	4.1	4.5	3.0	3.3	11.2	12.3	12.9
9 weeks							3.9	4.5	4.1	8.5	6.0	6.0	12.0	12.9	12.9
12 weeks							3.7	4.0	3.6	10.9	10.0	8.3	10.6	9.4	9.3
15 weeks							3.0	2.8	3.2	10.9	10.7	10.7	9.9	5.8	7.2

* Cyanamide (21.21 mg. N) added to 200 gm. air dry soil.

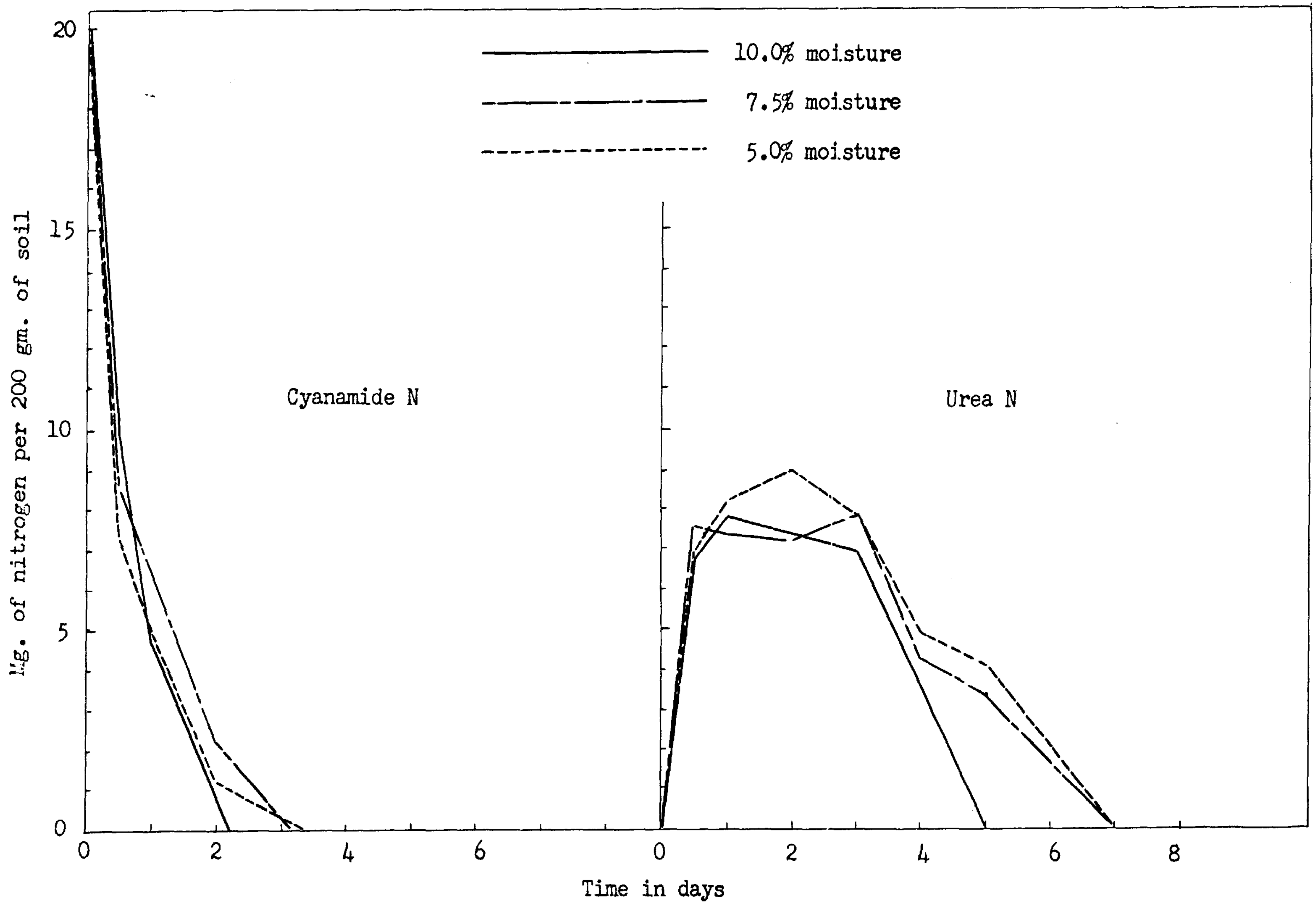


FIGURE 4. The Effect of Moisture Content on the Disappearance of Cyanamide and Accumulation of Urea in Fox Sandy Loam from an Application of 21.21 mg. of Nitrogen added as Cyanamid.

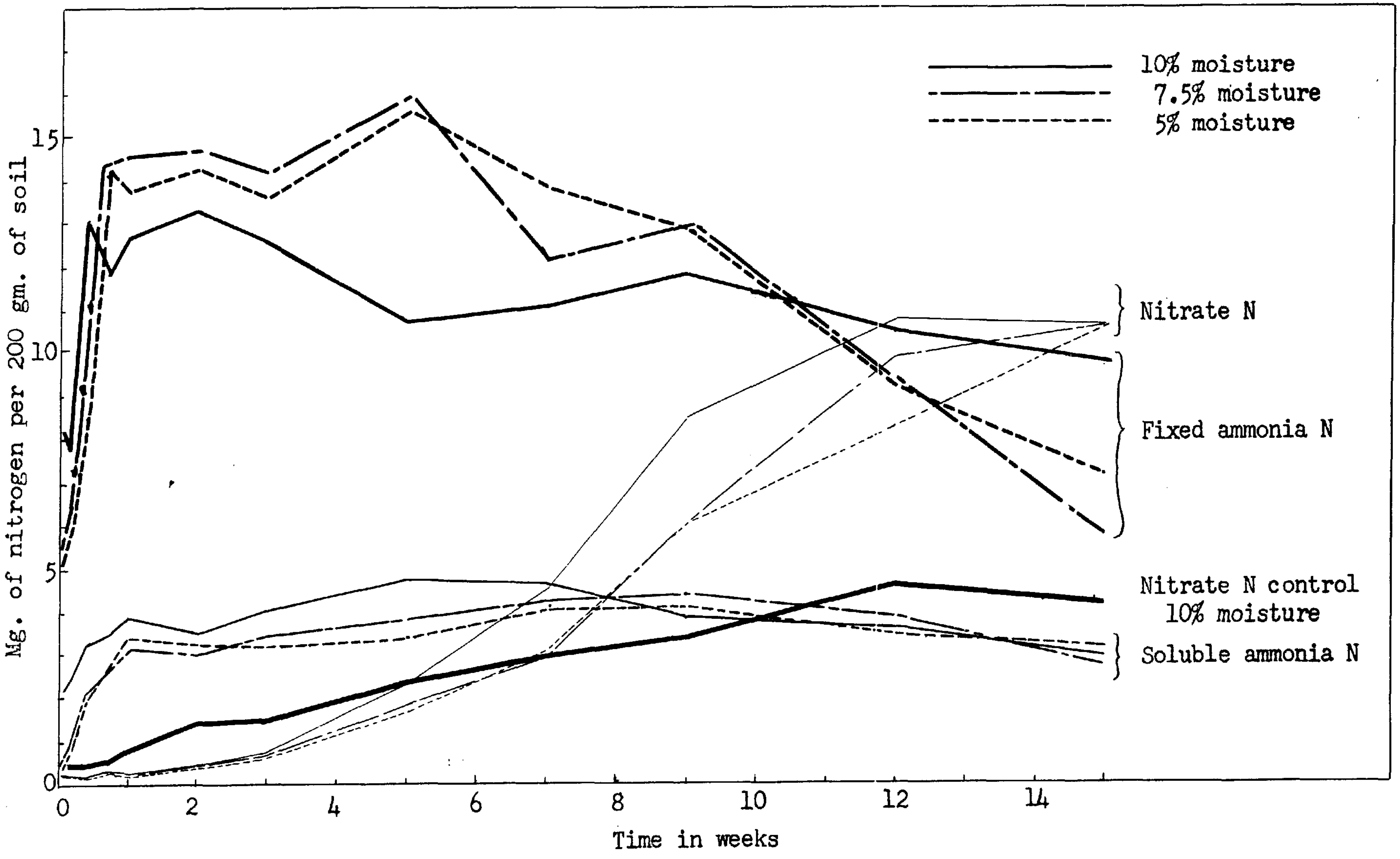


FIGURE 5. The Effect of Moisture Content on the Formation of Nitrate, Soluble Ammonia and Fixed Ammonia Nitrogen in Fox Sandy Loam from an Application of 21.21 mg. of Nitrogen added as Cyanamid.

The urea concentrations with the lower moisture levels were higher and remained in solution approximately two days longer than in the soil maintained at optimum moisture (Table 2 and Figure 4). The evidence indicates that the reduced moisture conditions did reduce either microbiological or enzyme activity and that the rate of ammonification of the urea is retarded; however, since urea-nitrogen in normal quantities is neither toxic to plants nor to microorganisms and since there is little danger of loss by percolating water, this condition would result in no practical danger.

The concentrations of soluble ammonia-nitrogen at the three moisture levels were of about the same order of magnitude, although up to the seventh week the concentrations were somewhat greater for the higher moisture levels (Table 2 and Figure 5).

The nitrate concentrations in the soils at the different moisture levels were almost identical up to the fifth week, at which time the concentration in the soil containing 10 per cent moisture increased more rapidly than in the other soils. During the ninth week the nitrate concentration in the soil at 7.5 per cent moisture began to increase more rapidly than in the soil with a moisture content of 5.0 per cent (see Figure 5). Not until the seventh week were the cyanamid treated soils of 7.5 and 5.0 per cent moisture levels able to reach the nitrate concentration of the control. These data definitely indicate a retarding effect of a low moisture content on the rate of nitrification in this soil; furthermore, it shows that cyanamide had a very pronounced effect in retarding nitrification in this soil.

The fixed ammonia-nitrogen concentrations at the three moisture levels followed the same general trend but with the greater concentrations at the lower moisture levels.

The results of this phase of the investigation have verified the results of the initial study. The transformations of the cyanamide through the urea, soluble ammonia, fixed ammonia and ultimately nitrate forms were of similar rates and quantities in both studies. The lower moisture levels had little effect in delaying the disappearance of cyanamide from solution. Retardation of nitrification by cyanamid was verified.

The Fox sandy loam used in these studies is a very acid soil (pH of 4.3). It is known to have a low nitrifying capacity, due, perhaps, to the intense acidity and low calcium supply (Carter (3)). This soil was very active in converting the added cyanamide to urea and to ammonia, but nitrification was retarded. This retardation of nitrification has been attributed to the sensitivity of the nitrifying organisms to cyanamide, according to Mukerji (14).

The application of cyanamid to this acid soil supplied active calcium and resulted in a less acid condition of the soil. The pH value of the extracted soil was raised from 4.3 to 5.8 and then gradually reduced to about pH 5.0 near the end of the 15 week period. This, however, failed to eliminate the retardation of nitrification.

The Nitrifying Rates of Different Nitrogenous Fertilizers

In the previous studies it was found that a high soluble ammonia-nitrogen concentration persisted in the cyanamid treated soil for several days and it was believed that the effect of ammonia concentration on nitrification should be studied; furthermore, since this soil has been characterized as one of low nitrifying capacity and it has been shown to exhibit a slow nitrification of cyanamide-nitrogen, it was believed worthwhile to study its nitrifying capacity of other nitrogenous fertilizer materials for domparative purposes.

Urea was selected as one of the materials in order that its action in this soil might clear up the question of the effect of soluble ammonia-nitrogen concentration on nitrification. Urea is one of the intermediate products in the transformation of cyanamide-nitrogen to nitrate and it permitted a study of the nitrifying capacity of this soil in the absence of the added calcium ion, the absence of the cyanamide ion, and in a less favorable reaction.

Ammonium sulphate was also selected for this study in order to determine its rate of nitrification in this soil in comparison to that of cyanamide and urea-nitrogen.

A sufficient number of 200 gm. samples of soil were placed in tumblers to provide triplicate determinations at the intervals indicated in Table 3. Nitrogen,in the form of urea, ammonium sulphate and cyanamid, was added in solution in amounts equivalent to 21.21 mg. per 200 gm. of soil. The soils were brought up to optimum moisture content, thoroughly mixed and maintained at optimum moisture content at room temperature.

At the specified intervals, three tumblers of each treatment were extracted in a manner previously described. The total amount of extract was measured and the extracted soils were allowed to dry at an oven temperature of 65° C. Urea, soluble ammonia and nitrate-nitrogen determinations were made on the soil extract and fixed ammonia-nitrogen was determined on the dried extracted soils.

The data from these determinations appear in Table 3 and in Figures 6 and 7 along with data obtained previously for the control and the cyanamid treatment. The fixed ammonia-nitrogen concentrations are corrected for soluble ammonia-nitrogen remaining in these soils. This was done by calculating the amount of ammonia in the water still in the soil after extraction, assuming it had the same concentration of ammonia-nitrogen as the extract.

It was found that when nitrogen was added as urea it remained in the soil solution a longer period of time than when formed from the decomposition of cyanamide. At the five day interval no urea was present where cyanamid was added, but 2.42 mg. were present where urea was added.

The soluble ammonia-nitrogen concentrations (Figure 6) for the cyanamid and urea treatments were essentially the same throughout, although they were somewhat higher for the latter treatment. If the soluble ammonia concentrations were inhibiting nitrification, it might be expected that both treatments would have similar nitrate concentrations. This, however, was not the case, as is shown in Figure 6.

Not until approximately the sixth week was the nitrate-nitrogen concentration of the cyanamid treatment as great as that of the control, after which time nitrification of the cyanamide-nitrogen proceeded rapidly (Figure 6). The urea treatment suffered no retardation of nitrification; nitrification of the added nitrogen proceeded rapidly. A maximum concentration of nitrates was found at the seventh week for the urea treatment, but the maximum for the cyanamid treatment was not reached until the twelfth week.

Nitrification of the ammonium sulphate was practically nil.

TABLE 3

Transformation of Nitrogen Added in the Form of Cyanamide, Urea, and Ammonium Sulphate to Fox Sandy Loam

	mg.*	mg. Urea-N		mg. Soluble ammonia-N				mg. Nitrate-N				mg. Fixed ammonia-N			
treatment	Cyanamid	Cyanamid	Urea	Control	Cyanamid	Urea	Ammonium sulphate	Control	Cyanamid	Urea	Ammonium sulphate	Control	Cyanamid	Urea	Ammonium sulphate
24 hrs.	4.65	7.81	17.64	Tr.	2.40	3.79	12.40	0.40	0.30	0.34	0.30	7.59	7.79	6.86	10.41
48 hrs.	Tr.		13.44	Tr.		3.90	11.85			0.38	0.38				
72 hrs.	None	6.96	10.67	Tr.	3.21	3.86	12.00	0.41	0.16	0.30	0.26	6.82	13.03	11.69	9.62
120 hrs.		None	2.42	Tr.	3.55	3.66	11.58	0.50	0.18	0.56	0.33	4.08	11.90	16.32	11.07
1 wk.			None	Tr.	3.94	3.30	11.25	0.84	0.27	1.00	0.37	2.87	12.65	16.17	10.66
2 wks.				Tr.	3.57	4.37	12.01	1.50	0.42	3.00	0.60	2.81	13.28	15.36	10.20
3 wks.				Tr.	4.05	5.88	11.34	1.55	0.81	7.08	0.75	1.89	12.57	13.96	12.79
5 wks.				Tr.	4.85	6.27	10.86	2.41	2.04	10.00	0.94	2.28	10.72	10.94	12.96
7 wks.				None	4.65	5.96	10.58	3.21	4.50	11.66	1.75	2.22	11.20	10.52	12.74
9 wks.					3.89	5.54	10.81	3.54	8.50	10.90	1.81	3.89	12.02	8.77	12.81
12 wks.					3.70	4.54	10.64	4.73	10.90	10.00	1.92	5.40	10.59	9.23	13.13
15 wks.					3.00	4.48	10.40	4.17	10.90	10.90	2.50	4.75	8.96	7.40	11.85

* Milligrams of nitrogen, of the form indicated, per 200 gm. of soil. Treatments consisted of 21.21 mg. of nitrogen as cyanamid, urea and ammonium sulphate per 200 gm. of soil.

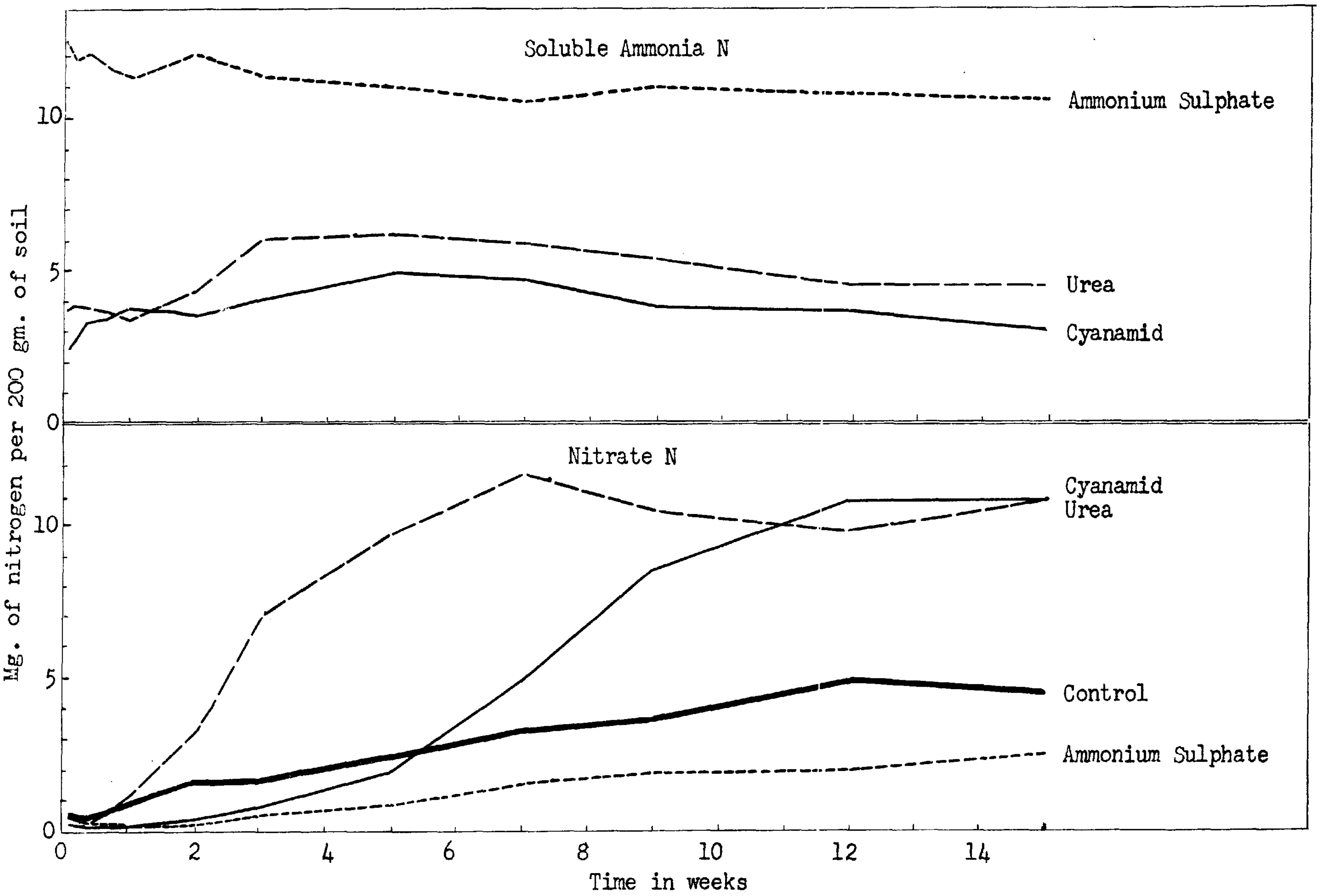


FIGURE 6. Soluble Ammonia and Nitrate Concentrations in Fox Sandy Loam with Applications of 21.21 mg. of Nitrogen added as Cyanamid, Urea and Ammonium Sulphate.

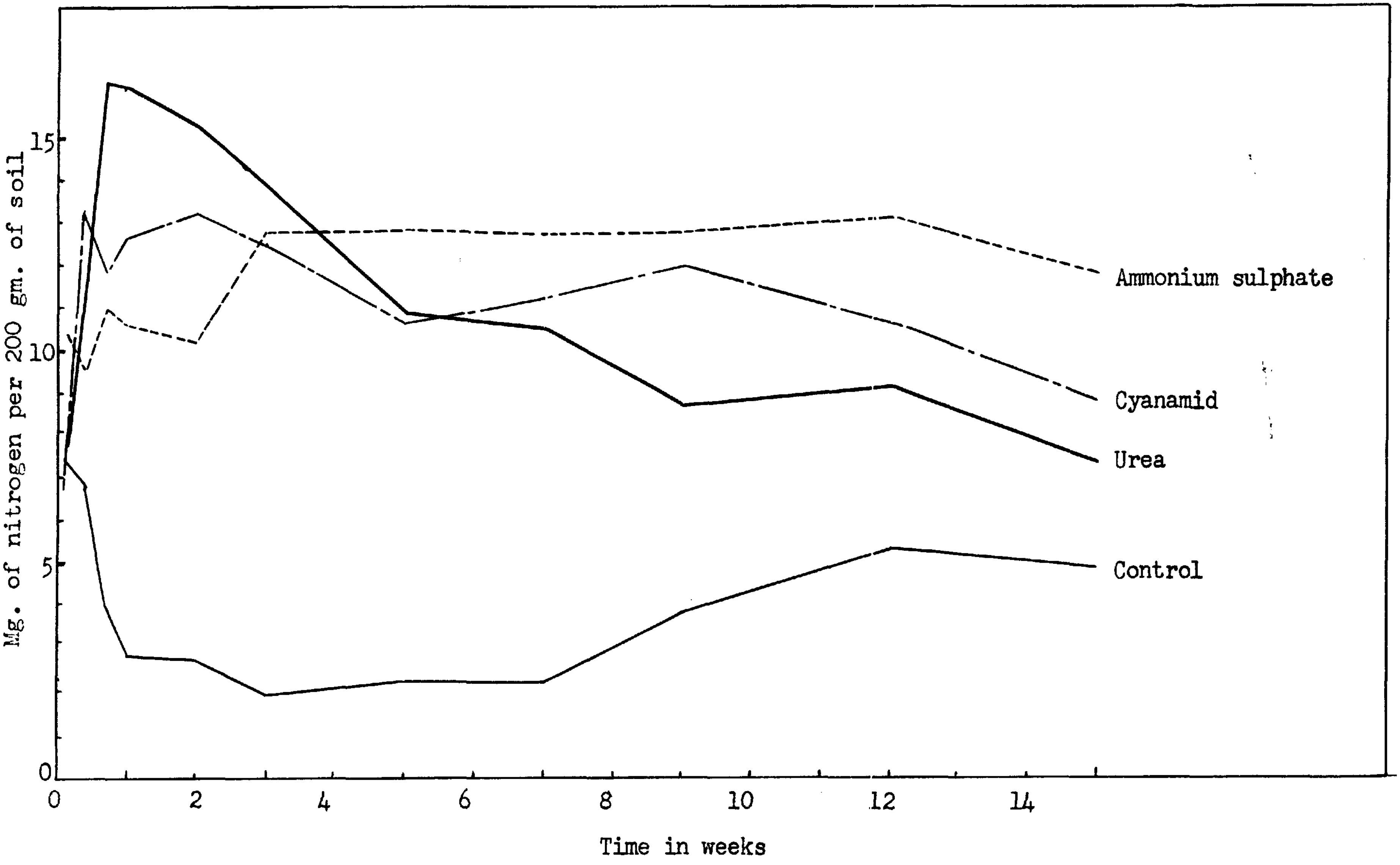


FIGURE 7. Fixed Ammonia Nitrogen Concentrations in Fox Sandy Loam with Applications of 21.21 mg. of Nitrogen added as Cyanamid, Urea and Ammonium Sulphate.

That nitrification was suppressed is supported by the fact that the nitrate concentrations were consistently below those of the control. This conclusion is further substantiated by the consistently high soluble ammonia and fixed ammonia-nitrogen concentrations throughout the fifteen weeks.

The reduction of fixed ammonia concentration tends to follow nitrate accumulations in the urea and cyanamide treatments. The ammonium sulphate treatment exhibits a somewhat lower initial fixed ammonia-nitrogen concentration than the urea and cyanamid treatments. The maximum concentration was not reached until along about the third week and showed little further variation throughout the fifteen weeks. These constant levels of soluble and fixed ammonia-nitrogen concentrations might be expected, since nitrification remained at a low level.

This phase of the study has shown that the soluble ammonia concentrations were not a deterrent to nitrification of cyanamide-nitrogen; ammonia concentrations of the urea treatments were even higher than those of the cyanamid treatment, yet nitrification proceeded normally. Nitrogen added as urea, one of the transformation products of cyanamide in the soil, nitrified readily. It remained in the soil as urea somewhat longer than urea produced from cyanamide. Nitrogen added as ammonium sulphate was not readily nitrified; even less nitrate accumulated with this treatment than with the control. It would appear that added cyanamid-nitrogen, though somewhat delayed in nitrification, should occupy a somewhat more favorable position than ammonium sulphate as a nitrogenous fertilizer for this soil, particularly if the plants grown demand nitrogen in the nitrate form. It is possible that this may apply to most very acid soils.

Decomposition of Cyanamide in Lateritic Soils

Five lateritic soils were studied in order to determine their capacity to remove cyanamide from solution and also to determine the nature of the decomposition products. These soils all had a high iron content with silica-sesquioxide ratios near 1.0. Samples of subsoil Columbiana clay from Costa Rica, two subsoil clays from Hawaii, and a surface soil sample of Nacogdoches sandy loam were furnished by H. B. Byers of the Division of Soil Chemistry and Physics of the Bureau of Plant Industry. A Cuban laterite clay was obtained from Professor Truog of the University of Wisconsin.

Fink (9) found that a Cuban laterite soil, used in some of his investigations,was very active in removing cyanamide from solution, although the nature and quantity of the various decomposition products were not reported.

The method used for measuring the activity of these soils was similar to that used for the Fox soil, with the exception that 0.05 gm. of cyanamid (10.45 mg. of nitrogen) was used with 100 gm. of soil instead of 0.1 gm. per 200 gm. of soil, due to the limited quantity of lateritic soils available. The cyanamid was well mixed with the soil and sufficient water added for a favorable moisture content. The soils were placed in tumblers and allowed to stand at room temperature until extraction. The treatments were in duplicate for each extraction period.

The soils were extracted with 150 ml. of water, including that which was in the soils, and cyanamide, urea, ammonia and total nitrogen were determined on 20 or 25 ml. aliquots of the extract. Fixed ammonia-nitrogen was determined on the extracted soil and the results reported as increases in fixed ammonia-nitrogen rather than the total quantity.

The results of this study appear in Table 4 and are reported as mg. of nitrogen per 100 gm. of dry soil. These data can be compared directly with those obtained for the other soils in which treatments were 0.1 mg. of cyanamid to 200 gm. of soil, since the latter are reported as mg. of nitrogen per 200 gm. of soil.

These five lateritic soils were very active in decomposing cyanamide, particularly the Nacogdoches sandy loam, Columbiana clay and Hawaiian clay, C-944. The surface soils, Cuban laterite clay and Nacogdoches sandy loam, converted the urea-nitrogen readily to ammonia-nitrogen. In the case of Nacogdoches sandy loam, this was indicated by a high fixed ammonia-nitrogen concentration and a rapid reduction in the total nitrogen concentration of the extracts. The strong activity of this soil in converting cyanamide was indicated by the 8.51 mg. of nitrogen as soluble and fixed ammonia of the 10.45 mg. of cyanamid-nitrogen added within a 24 hour period. The total quantity of nitrogen accounted for as urea and ammonia-nitrogen at the 120 hour period was 10.20 mg. of the 10.45 mg. of nitrogen added.

The Cuban laterite clay soil had apparently been exposed to ammonia while in storage and had adsorbed considerable quantities. The lack of sufficient soil to secure correction factors for soluble and fixed ammonia-nitrogen made it more difficult to follow the nitrogen transformation of the decomposing cyanamide. In this soil, however, cyanamide disappeared from solution more slowly and did not accumulate as urea. The quantity of soluble ammonia increased temporarily at first, followed by a decrease with a corresponding increase in the concentration

TABLE 4

Cyanamide Decomposition in Lateritic Soils

Treatment	Time interval hours	mg. of nitrogen per 100 gm. of soil				
0.05 gm. cyanamid per 100 gm. of soil		Cyanamide	Urea	Soluble ammonia	Fixed* ammonia	Total
Cuban Laterite clay	24	1.79	Tr.	11.45	38.71	16.21
Cuba	48	0.56	None	10.95	41.86	14.22
Surface soil-pH 6.4	72	None	"	6.83	49.49	9.45
Nacogdoches sandy loam	24	Tr.	0.29	1.34	7.17	3.32
Tyler, Texas	48	None	0.34	1.34	7.02	2.92
0"-10", pH 5.3	120	"	0.21	1.26	8.75	2.02
Columbiana clay	24	"	5.88	0.25	2.23	7.73
Costa Rica	48	"	5.94	0.34	2.47	7.12
25"-40", pH 5.0	120	"	6.05	0.34	3.07	6.68
Hawaiian clay C-944	24	Tr.	5.88	0.17	1.02	7.06
Hawaii	48	None	5.80	0.76	3.00	7.06
19"-31", pH 4.9	120	"	3.19	0.42	5.77	4.24
Hawaiian clay C-948	24	2.48	1.89	1.09	5.82	6.80
Hawaii	48	1.34	2.14	0.25	6.67	5.54
13"-25", pH 4.9	120	None	1.68	0.50	9.90	3.49

* For Cuban Laterite only: The fixed ammonia concentrations are not corrected for fixed ammonia nitrogen in the untreated soil. They represent the composite of that already in the soil plus that which has been adsorbed from the decomposition of cyanamide.

of fixed ammonia. The quantity of total nitrogen, made up mostly of soluble ammonia, decreased as the quantity of fixed ammonia-nitrogen increased. Conclusive evidence that complete conversion to ammonia occurred was found in the increase in fixed ammonia-nitrogen from 38.71 to 49.49 mg., a 10.78 mg. increase from a 10.45 mg. nitrogen treatment.

The Columbiana clay possessed a high capacity to convert cyanamide to urea but lacked the capacity to completely change urea to ammonia. This might be expected since this was a subsoil sample and perhaps low in biological activity. Most of the cyanamide-nitrogen added appeared as urea and fixed ammonia with small amounts of soluble ammonia. Approximately 9.5 mg. of the 10.45 mg. of nitrogen added as cyanamid was accounted for at the 120 hour interval of extraction.

The Hawaiian clay, C-944, also exhibits a high capacity to decompose cyanamide. At the 24 hour interval of extraction only a trace of cyanamide-nitrogen existed in solution. This soil had a low capacity to convert urea to ammonia, as indicated by the persistently high concentration of urea. This may be explained by the fact that the sample was also of subsoil. The soluble ammonia concentration remained at a low level with an increase in fixed ammonia-nitrogen, indicating the soil's capacity to adsorb the ammonia as it is produced. The increase in fixed ammonia accompanied the reduction of urea as well as total nitrogen in the extract. The sum of the quantities of urea, soluble ammonia and fixed nitrogen accounts for 9.39 of the 10.45 mg. of nitrogen added as cyanamid.

The Hawaiian clay, C-948, though relatively an active soil in cyanamide conversion, was less active than the other four lateritic soils studied. Some cyanamide remained in solution at 48 hours. This was also a subsoil sample but seemed to have a greater capacity to convert the urea to ammonia than the other subsoil samples. Soluble ammonia-nitrogen remained at a low level, while the fixed ammonia reached a high concentration at the initial period and increased through the 120 hour interval of extraction. The total nitrogen found as urea, soluble ammonia and fixed ammonia amounts to 11.06 mg. at the 120 hour interval, although 10.45 mg. of cyanamid-nitrogen was originally added. A discrepancy in this same direction was observed for the determinations at the other time intervals. An error in the correction factor for fixed ammonia-nitrogen is suspected, in that the correction figure is low, resulting in high net increases in this nitrogen fraction as reported in Table 4.

These five lateritic soils may be classified as active soils in so far as their capacity to change cyanamide to urea and ammonia-nitrogen is concerned. They are all high in iron, low in organic matter and slightly to medium acid. Since these soils are low in organic matter, it is logical to expect their activity in the conversion of cyanamide to be associated with the inorganic rather than the organic constituents. The fact that the conversion capacity is high in the subsoil samples, where the biological activity is so low that urea is not readily ammonified, is added evidence that inorganic constituents may play the primary role as catalysts in the reaction.

The use of nitrogenous fertilizers supplying readily available calcium warrants some consideration in the fertilizer practices of many crops on tropical soils. The use of cyanamid as a nitrogenous fertilizer in tropical agriculture might have several advantages when moisture conditions are favorable. The general readiness with which these lateritic soils convert cyanamide to the more desirable decomposition products eliminates the dangers involved from toxicity to plants from the cyanamide form. The formation of ammonia and its subsequent adsorption permits smaller losses due to leaching where rainfall is considerable; furthermore, the supply of readily available calcium on these low calcium, medium acid soils is an important factor in plant growth. The use of cyanamid may provide an economic means of supplying not only nitrogen, but calcium as well in a fertilizer program in tropical agriculture.

The Disappearance of Cyanamide from Solution in a Number of Soils

The data on the rate of cyanamide disappearance from the soil solution for a number of soils, other than the lateritic soils already reported, are summarized in Table 5. The data on three of these soils are presented elsewhere in this report in connection with other specific objectives in the investigation.

From this group of soils, the Berrien sand, Hillsdale sandy loam, sandy soil, and Wisner loam were selected as soils with a low capacity to remove cyanamide from solution and were used in other phases of the investigation. The Napanee silt loam and the Miami clay loam were also found to be inactive with respect to the removal of cyanamide from solution.

Four out of the six inactive soils were either neutral or alkaline. The Berrien is a light, sandy soil, low in organic matter and slightly acid and the Hillsdale sandy loam is also low in organic matter content, as well as in colloids and is slightly acid. The Thomas sandy soil and Parnell silt loam are alkaline soils and both were quite active in removing cyanamide from solution, although the former was less active

TABLE 5

The Disappearance of Cyanamide from Solution in Several Different Soils

Treatment 0.1 gm. of cyanamid per 200 gm. of soil 21.21 mg. of nitrogen	Organic matter content	pH of soil	mg. of cyanamide-nitrogen per 200 gm. of soil 1 day	2 days	3 days	4 days	5 days
Fox sandy loam	low	4.4	7.14	2.90	0.21	None	None
Berrien sandy soil	low	5.9	11.80	9.24		6.16	present
Hillsdale sandy loam	low	6.1	8.36	5.33	3.19		1.18
Traverse sandy soil[1]	low	6.9	7.18	2.73	Tr.	None	None
Cecil sandy clay loam	low	5.3	4.75	Tr.	None	"	"
Brookston silt loam	med.	6.5	7.30	3.27	"	"	"
Parnell silt loam[2]	high	7.8	3.10	2.26	"	"	"
Warsaw silt loam	high	4.8	8.43	3.40	"	"	"
Sandy soil[3]	low	7.0	8.90	6.90	4.62	3.10	present
Wisner loam	med.	7.4	10.12	7.73	5.96	4.39	2.65
Napanee silt loam	med.	7.5			4.20		
Miami clay loam	med.	7.2			3.11		
Thomas sandy loam	high	8.0			1.05		
Macomb clay loam	med.	6.0			None		
Muck A 10% plus silica sand	very high	6.7	8.69	5.04	2.71	1.05	Tr.
Muck B 10% plus silica sand	very high	4.3	5.71	2.23	0.81	None	None

[1] Soil secured from Old Mission Peninsula, Grand Traverse County, Michigan, where cyanamid has been used successfully for several years as a source of nitrogen for cherry trees. This is probably the Emmet series.

[2] 10.45 mg. of cyanamid nitrogen per 100 gm. of soil.

[3] The series identity of this soil is not known.

than the latter. The alkaline effect may have been compensated by the high organic content (15 to 20 per cent) in these two soils. The more acid muck-sand mixture was more active in removing cyanamide from solution than the less acid muck-sand mixture.

The general conclusion that the use of cyanamid as a source of nitrogenous fertilizer offers fewer hazards on acid soils, soils high in colloidal content and high in organic matter is borne out by these studies performed in the laboratory. The use of this product, in accordance with the producer's recommendations in method of application, on alkaline soils and extremely sandy soils low in organic matter, is worthy of due consideration.

The Effect of Soil Reaction on Cyanamide Decomposition

The reaction of the soil has been attributed by several investigators as an important factor affecting the rate of decomposition of calcium cyanamide. In moderately alkaline solutions, up to pH 9.6, free cyanamide polymerizes slowly to dicyanodiamide, but in more alkaline solutions, above pH 10.0, it hydrolyzes to urea, according to Buchanan and Barsky (2). The alkaline reaction resulting from the hydrolysis of calcium cyanamide in aqueous solution is buffered by soils, the extent depending upon the reaction of the soil and its buffering capacity.

In acid solutions free cyanamide is hydrolyzed to urea and theoretically acid soils with sufficiently high buffering capacities should favor the formation of urea rather than the dicyanodiamide.

Fink (9) studied the effect of soil reaction on cyanamide disappearance from cyanamid treated soils. Four acid soils, which had been limed to three different pH levels, exhibited a lower capacity for removing cyanamide from solution as the reaction approached pH 7.0.

Fox sandy loam soil was treated with $Ca(OH)_2$ in two different amounts which resulted in a pH level of 6.1 in one case and 6.9 in the other. The $Ca(OH)_2$ was well mixed with the soil and the mixture brought up to and maintained at slightly above the optimum moisture conditions for a period of six weeks, after which the soil was dried and used for this study. The untreated soil (pH 4.3) and the two treated soils (pH 6.1 and 6.9) were used in an attempt to study the effect of soil reaction on cyanamide decomposition. The object was to study the disappearance of cyanamide as well as accumulation of urea, soluble ammonia and fixed ammonia-nitrogen.

Wisner loam, a calcareous soil with a pH of 7.4, was found to be an inactive soil in cyanamide decomposition. The pH of this soil was lowered to 6.7 by the addition of sulphur. After mixing sulphur with the soil it was brought up to and maintained at the optimum moisture content for six weeks and then dried. The untreated soil and the treated soil were used to study the effect of soil reaction on cyanamide decomposition.

Two organic soils were used in this study. Muck A, secured from the college muck plots at East Lansing, was a well decomposed organic soil with a pH value of 6.7. It had been burned over at one time. Muck B, secured only a few yards from the source of Muck A, was not well decomposed and had a pH of 4.3. The decomposition of the cyanamide in these two soils was studied by mixing 10 per cent muck with 90 per cent silica sand.

The treatment for all the soils consisted of 0.1 gm. of cyanamid (21.21 mg. of nitrogen) per 200 gm. of soil in duplicate. Extractions were made at 24, 48, 72, 96, 120 and 168 hour intervals.

The data for this study are reported in Table 6 as mg. of nitrogen per 200 gm. of soil. The fixed ammonia-nitrogen figures represent net increases, since they are corrected for the fixed ammonia-nitrogen in the untreated soil.

The liming and subsequent decrease in acidity had a pronounced effect on the Fox sandy loam soil in reducing its capacity to remove cyanamide from solution. The magnitude of this effect increased with the larger lime applications. Over 3.0 mg. of cyanamide nitrogen remained in solution after 168 hours with the heaviest lime application. The urea concentrations were reduced slightly in the soil at pH 6.1 and were considerably reduced in soil having a pH of 6.9. There was little difference in the amounts of ammonia, either soluble or fixed, in the untreated soil and the lime treated soil of pH 6.1 throughout the study. The urea concentration remained at an extremely low level in the soil of pH 6.9 in comparison with the soil at pH 4.3 and also at pH 6.1. The low urea concentration may have been due to the lower rate at which it is formed from cyanamide or to the greater capacity of this soil of pH 6.9 to convert the urea to ammonia. The presence of considerable quantities of soluble and fixed ammonia, however, indicates that the urea was changed to ammonia. The fixed ammonia was significantly lower in the soil of pH 6.9, probably due to the lower rate of decomposition of the cyanamide.

Increasing the acidity of the Wisner loam by sulphur treatment had a slight, but significant, effect on the rate of cyanamide disappearance from solution. Not only was the rate of removal of cyanamide from

TABLE 6

The Effect of Soil Reaction on Cyanamide Decomposition

Treatment	pH	Time interval	Mg. of N per 200 gm. of soil			
0.1 gm. cyanamid per 200 gm. of soil		Hours	Cyanamide	Urea	Soluble NH_3	Fixed NH_3
Soil						
Fox sandy loam	4.3	24	7.14	6.38	0.80	4.13
		48	2.90	6.89	1.68	4.57
		72	0.21	3.99	2.60	8.34
		96	None	1.68	3.15	10.06
		120	"	None	3.40	10.64
Fox sandy loam	6.1	24	8.88	4.45	1.74	5.22
plus		48	6.58	3.95	2.60	6.38
$Ca(OH)_2$		72	2.60	2.27	3.50	5.78
		120	1.99	1.10	3.89	9.39
		168	None	Trace	4.09	10.96
Fox sandy loam	6.9	24	12.39	0.84	0.92	3.08
plus		48	9.37	0.84	1.64	3.45
$Ca(OH)_2$		72	7.90	0.25	2.31	3.92
		120	3.99	0.12	3.15	4.79
		168	3.19	0.08	3.65	5.19
Wisner loam	7.4	24	11.25	0.42	0.50	1.70
		48	9.74	0.25	0.63	1.98
		72	8.44	0.21	0.84	2.31
		120	7.39	None	1.39	2.79
		168	4.33	"	1.34	3.74
Wisner loam	6.7	24	10.12	0.21	1.30	2.70
plus		48	7.73	0.29	1.85	2.98
Sulphur		72	5.96	None	2.77	3.07
		120	4.39	"	3.19	3.34
		168	2.65	"	3.40	3.54
Muck A, 10%	6.7	24	8.69	0.13	0.34	2.92
Silica sand, 90%		48	5.04	0.21	1.85	2.79
		72	2.71	None	2.19	3.07
Well decomposed		120	1.05	"	2.43	3.55
		168	0.25	"	2.60	3.39
Muck B, 10%	4.3	24	5.71	4.16	1.97	2.53
Silica sand, 90%		48	2.23	5.80	3.15	2.91
		72	0.81	4.28	4.71	3.33
Not well decomposed		120	None	2.06	5.96	4.71
		168	"	0.34	7.22	4.94

solution increased, but this was reflected in the rate of accumulation of soluble ammonia and fixed ammonia-nitrogen.

Another fact that can be secured from a study of the data on the Wisner soil is that the formation of dicyanodiamide, or decomposition products other than urea and ammonia, is a slow process. Considering the 168 hour interval of extraction, Table 6, 4.33 mg. of nitrogen remained as cyanamide and 5.08 appeared as ammonia-nitrogen. This represents approximately 44 per cent of nitrogen added as cyanamide. A total nitrogen determination on the extract yielded 9.45 mg., whereas only 5.67 mg. of nitrogen were accounted for in the soluble fractions. The difference, 3.78 mg. or 17.82 per cent, represents soluble nitrogen which existed as dicyanodiamide or other forms of nitrogen not determined.

The less acid, well decomposed Muck A was considerably less effective in removing cyanamide from solution than the more acid Muck B. Urea concentrations failed to develop in the less acid Muck A, although considerable quantities were produced in the more acid Muck B. Larger soluble ammonia concentrations, as well as fixed ammonia, developed in the more acid muck.

The role of reaction in cyanamide decomposition in the soil is still somewhat obscured. In solution culture studies reported elsewhere in this paper, in which the calcium of the cyanamid was precipitated and a pH value of 4.0 was induced by acid additions, cyanamide failed to decompose to a great extent with subsequent urea production at room temperatures of 23° C, yet in the soil, reaction seems to play an important role. As far as these studies are concerned, the more acid reactions favored more rapid decomposition of the cyanamide. It is believed that the hydrogen ion itself does not play the major role but its indirect effect on other soil constituents increases their catalytic activity to decompose cyanamide into urea.

The Effect of Organic Matter on the Disappearance of Cyanamide from Soil Solution and its Decomposition Products

In the search for soil constituents which are responsible for the decomposition or conversion of cyanamide to more desirable nitrogenous products from the standpoint of the plant, several investigators have attributed a part of the soil's conversion power to the organic matter. Fink (9) in a recent study found a close correlation between peat-sand mixtures containing 7.4 per cent peat and the organic matter content of several soils used in his study in their capacity to remove cyanamide from solution. He asserts that this correlation indicates that organic matter is chiefly responsible for the removal of cyanamide from solution. He found that the state of saturation of this peat with respect to calcium or hydrogen was not the controlling factor; however, in the study of the two different peats in sand cultures, the one with the greater base exchange capacity was more active in removing cyanamide from solution. There is considerable disagreement in the literature on this subject, yet heretofore no concentrated effort has been devoted to a study of this phase of the problem.

The object of this phase of the work was to make a detailed study of the role of organic matter of soils and added organic materials on cyanamide decomposition or conversion.

The Effect of Soil Ignition on the Extent and Nature of Cyanamide Decomposition: An attempt was made to segregate the effects of organic and inorganic constituents of the soil on cyanamide decomposition by igniting the soils at 325° C for ten hours, after which they were used for study in comparison with the non-ignited soils. Ignition at this temperature, according to Mitchell (13), does not affect the exchange capacity of the inorganic soil constituents; however, some change in the state of oxidation of compounds, as well as a rise in the pH values, takes place on ignition. These factors must be taken into consideration in studying any effects that are produced by the treatment. It was believed that this procedure might reveal some light on the subject under investigation.

The ignited and normal soils were treated in duplicate with 0.1 gm. of cyanamid for the extraction intervals of 24, 48, 72, 96 and 120 hours. The results are reported in Table 7 as mg. of nitrogen per 200 gm. of soil.

In all five soils studied, ignition definitely reduced the soil's capacity to convert cyanamide to decomposition products through the five day interval in which they were studied. It was found that the cyanamide concentration of the ignited soils did not change greatly throughout the five day period and that all the soils had about the same concentration. In contrast, the non-ignited soils had a lower total concentration of cyanamide at the initial period which completely disappeared from solution within the 72 hour interval of examination.

The quantities of soluble ammonia of the ignited soil were insignificant. The non-ignited soils, on the other hand, had an increasing amount with time.

The concentration of urea in the ignited soils varied somewhat among different soils and reached slightly greater proportions in some instances. It was observed that the urea concentration of the ignited

TABLE 7

The Effect of Ignition of Soils on Cyanamide Decomposition*

Soil	pH of soil		Time	mg. of nitrogen per 200 gm. of soil									
				Total-N		Soluble ammonia-N		Urea-N		Cyanamide-N		Fixed ammonia-N	
	Normal	Ignited	hrs.	normal	ignited	normal	ignited	normal	ignited	normal	ignited	normal	ignited
Warsaw loam	4.8	6.7	24	12.94	18.14	1.18	0.12	1.60	1.18	8.48	14.78	7.23	2.82
			48	7.01	18.23	1.76	0.17	0.34	1.76	3.40	13.99	11.44	2.66
			72	4.79	18.06	2.35	0.17	0.17	2.27	None	13.31	12.05	1.61
			96	4.45	17.85	2.56	0.25	0.08	2.65	"	12.47	13.05	0.54
			120	3.95	18.19	2.81	0.21	0.00	2.94	"	12.81	13.60	
Fox sandy loam	4.3	6.1	24	16.30	18.00	0.80	None	6.38	1.30	7.14	14.95	4.13	1.80
			48	13.23	18.44	1.68	"	6.89	1.81	2.90	14.78	4.57	1.72
			72	10.88	18.27	2.60	Tr.	3.99	2.52	0.21	13.86	8.34	1.72
			96	7.70	17.89	3.15	"	1.68	2.69	None	13.48	10.06	1.80
			120	5.38	18.10	3.40	"	None	2.90	"	13.44	10.64	2.12
Brookston silt loam	6.5	7.6	24	12.28	17.79	1.40	None	"	None	7.30	14.87	9.40	2.20
			48	9.99	18.59	1.84	"	"	"	3.27	15.10		2.10
			72	7.75	17.88	2.63	"	"	1.08	None	14.96		2.70
			96	6.63	17.25	2.58	"	"	1.21	"	14.60	16.80	3.10
			120	5.82	17.79	2.58	"	"	1.25	"	14.69	16.10	3.00
Traverse sandy soil	6.9	8.3	24	10.79	18.69	3.75	"	Tr.	0.50	7.18	15.04	3.80	0.45
			48	8.74	18.56	3.53	"	None	1.01	2.73	14.87	4.59	0.45
			72	8.11	18.27	4.58	"	"	1.09	None	14.49	3.57	0.52
			96		18.44		"		1.51		14.45		0.45
			120	6.93	18.35	4.07	"	None	1.47	None	14.45	4.32	0.52
Cecil sandy clay loam	5.3	7.5	24	11.05	18.35	3.75	"	Tr.	1.00	4.75	15.25	6.61	1.05
			48	8.44	17.72	4.28	"	None	1.05	Tr.	14.41	8.33	1.05
			72	7.22	18.02	4.66	"	"	1.47	None	14.45	9.30	0.97
			96		18.35		"		1.85		14.53		0.97
			120	6.04	18.40	3.78	"	None	1.85	None	13.94	8.59	1.20

* Normal and ignited soils treated with 21.21 mg. of cyanamid nitrogen per 200 gm. of soil.

soils increased with time, while that of the non-ignited soils decreased. The increase in urea concentration, without ammonia accumulation, may be explained by the fact that ignition inactivated the enzymes and microorganisms which are responsible for the rapid conversion of urea to ammonia. It may also be stated that ignition did not entirely destroy the catalytic power of the soils to change cyanamide to urea.

Further evidence that ammonia did not accumulate in the ignited soils is the fact that the quantity of fixed ammonia was low and did not increase during the time of the study. The fixed ammonia of the non-ignited soils increased with time, except in the Traverse soil.

Another contrasting feature of these data is the fact that the total nitrogen concentration in the extract of the ignited soils remained fairly constant throughout the period of study, while that of the non-ignited soil was consistently reduced. This is usually associated with an increase in fixed ammonia.

The ignition treatment definitely raised the pH values of the soils. The Warsaw and the Fox, originally the most acid soils, were still below pH 7.0. There may be some significance in the fact that in these two ignited soils the urea concentrations increased with time and the cyanamide concentrations decreased in greater proportions than in the other three ignited soils.

This study definitely establishes the fact that ignition of all these soils for ten hours at 325° C reduced their capacity to change cyanamide to other decomposition products in 120 hours. Just how much of this inactivation was due to destruction of biological agents cannot be stated; however, it appears that the inorganic constituents of the soil play the lesser role unless the temperature used had also inactivated the inorganic colloidal constituents by dehydration, oxidation, or by changing the reaction. This latter possibility cannot be enlarged upon, since a detailed study of that particular feature of the problem was not undertaken. That the inorganic constituents may have been partially inactivated is suggested in view of the extreme conversion capacity of the lateritic subsoil, very low in organic matter, reported previously in this paper. Ignition of the Cuban laterite decreased the rate of cyanamide conversion as compared to the non-ignited soil.

The Effect of Extracted Humus on Cyanamide Conversion: In an effort to determine the catalytic or active agents in the soil on cyanamide conversion, the humus was removed from the soils and its effects were studied apart from the soil.

Four soils were selected from which the humus was removed for the purpose of securing humus of possible different properties: very acid soils - Fox (pH 4.3) and Warsaw (pH 4.8); less acid soils - Berrien (pH 5.9) and Brookston (pH 6.5). The soils were also selected on the basis of organic matter content in order to secure a difference in concentrations of the extracted humus; the Warsaw and Brookston were medium in content of organic matter, whereas the Fox and Berrien were low. The choice of these soils, it was believed, would bring out the effect of quantity, as well as the nature of the humus, on its capacity to remove cyanamide from solution.

The humus was removed by the method suggested by Wakesman (19). One hundred gm. of soil was treated with 200 ml. of 2.5 per cent NaOH and allowed to stand in the cold for 48 hours with periodic shaking. It was then filtered on a Buchner funnel with suction and washed with 100 ml.

more of 2.5 per cent NaOH. The humus was precipitated from the alkaline extract by adding 1-1 HCl until flocculation began and allowed to stand for 12 hours. The flocculated humus was filtered and the acid extract (suspension A) was saved for study. The humus was then washed free of chlorides with water. The washed precipitated humus from each soil was dispersed in 500 ml. of distilled water by prolonged periods of agitation in a Bouyoucos dispersing machine. A stable suspension (suspension B) was secured and the concentration of the suspension varied, as indicated in Table 8.

The acid extracts (suspension A) from which the humus had been precipitated were titrated to pH 5.6 with NaOH using the Beckman pH meter. This represented the acid soluble humus and some inorganic colloids. The color intensity of the solutions varied in the order of the organic matter content indicated in Table 8.

To duplicate 25 ml. portions of the above solutions 0.05 mg. of cyanamid, equivalent to 10.45 mg. of nitrogen, was added and allowed to stand 24 hours. Precipitation of the acid soluble humus colloids occurred upon addition of the cyanamid. Periodic agitation was carried out during the 24 hour period, after which they were filtered and washed with water until the total volume reached 100 ml. Twenty-five ml. aliquots were used for cyanamide determinations. The results of this study (Part 1) and those which follow (Parts 2, 3 and 4) are reported in Table 8 as mg. of cyanamide nitrogen still in solution after 24 hours and also as per cent of the 10.45 mg. of nitrogen added. There was no difference in the four acid soil humus extracts in their ability to remove cyanamide from solution and none of the extracts were able to

TABLE 8

The Effect of Extracted Humus on Removal of Cyanamide from Solution

Soil	Organic matter content	pH of soils	Color intensity suspension A.	Humus concentration suspension B.	Part 1 Cyanamide-N		Part 2 Cyanamide-N		Part 3 Cyanamide-N		Part 4 Cyanamide-N	
					mg.	%*	mg.	%*	mg.	%*	mg.	%*
Fox sandy loam	Low	4.3	Very light	Low	7.56	72.3	7.25	69.4	7.90	75.6	7.78	74.5
Warsaw loam	Medium	4.8	Dark	High	7.50	71.8	7.36	70.4	7.84	75.0	7.62	73.0
Brookston silt loam	Medium	6.5	Very dark	Very high	7.48	71.6	7.36	70.4	7.73	74.0	6.94	66.4
Berrien sandy soil	Low	5.9	Light	Very low	7.36	70.4	7.75	69.4	7.50	71.8	7.25	69.4
Blank					7.50	71.8	7.50	71.8	7.56	72.3	7.56	72.3
Time interval					24 hours		24 hours		72 hours		72 hours	

* 10.45 mg. of nitrogen added as cyanamid.

change the cyanamide concentration beyond that which occurred in ordinary water solutions.

To duplicate 25 ml. aliquots of suspension B, 0.05 gm. of cyanamid was added and allowed to stand for 24 hours with intermittent agitation. They were then filtered, washed to a total volume of 100 ml. of extract and cyanamide nitrogen determined on 25 ml. aliquots. Very little difference in cyanamide content was found in the humus suspensions of the four different soils (Table 8, Part 2). The effect of the nature of the humus from the different soils was apparently not an important factor in cyanamide conversion as far as this study was concerned.

In order to determine the effect of more concentrated suspensions of humus on cyanamide conversion, the volume of suspension B was reduced by slow evaporation to one-half that used in Part 2. Fifty ml. of this was treated with 0.05 gm. of cyanamid, in duplicate, giving a concentration of humus four times that used previously in Part 2. These were allowed to stand for a period of 72 hours with intermittent agitation. It will be noted from Table 8, Part 3, that no great differences occurred in the effect of the humus from four different soils; furthermore, the greater concentration and longer interval of time did not decrease the cyanamide concentration in solution.

The effect of humus of the four soils at higher concentrations and in sand cultures, rather than solution cultures, was studied. Fifty ml. portions of the humus concentrations used in Part 3 were evaporated down to 20 ml. and added to 100 gm. of silica sand treated with 0.05 gm. of cyanamid. These cultures were allowed to stand 72 hours, filtered and washed to a volume of 100 ml. of extract. Cyanamide was determined on 25 ml. aliquots and the results appear in Table 8, Part 4. In sand cultures the difference in nature of humus from four different soils and the effect of increased concentration of the humus produced no significant reduction in the cyanamide concentration.

These studies, on the role of extracted humus on cyanamide removal from solution, failed to demonstrate the conversion or adsorptive powers of humus under the conditions in which this study was carried out. The differences in the nature of the humus from four essentially different soils and at various concentrations were studied. It is to be borne in mind, however, that in the extraction process the form of the humus was undoubtedly changed and its activity modified; furthermore, its actual concentration and surface exposure to the cyanamide, as it exists in the soil, was not duplicated in this study.

<u>The Effect of Added Organic Matter to the Soil on Cyanamide Conversion</u>: In another attempt to ascertain the effect of the nature of organic matter on cyanamide decomposition, a Hillsdale sandy loam soil which had received previous additions of organic materials was used for study. This soil (untreated) was known to be inactive in removing cyanamide from solution. The soil had been treated at the rate of 20 tons of crop residue materials per acre and in two instances lime had been added. The moisture content had been maintained at an optimum level and they were allowed to stand for a period of two years, at which time they were dried, mixed well and stored.

The treatments consisted of duplicate 0.1 gm. portions of cyanamid per 200 gm. of soil and extractions at 24, 48 and 72 hour intervals. The cyanamide nitrogen concentrations, reported as mg. of nitrogen per 200 gm. of soil and as per cent cyanamide nitrogen of the 21.21 mg. added as cyanamid, are reported in Table 9.

A study of these data shows that the organic matter content, expressed as combustible loss, was increased by the plant residue additions from 2.3 per cent in the control to 2.8 per cent in the case of the alfalfa roots. The other materials raised the organic matter content to a less extent.

The difference between 56.1 per cent of the cyanamide in solution at the end of 24 hours for the control and 51.5 per cent for the lowest concentration of any treatment is considered of no practical significance. The difference of 34.3 per cent for the control and 26.4 per cent for the lowest concentration at 72 hours is also considered insignificant. The lime treatment along with the crop residues, which raised the pH value above the neutral point, did not affect the rate of disappearance of cyanamide from solution; therefore, the addition of organic matter to this soil, which has been allowed to decompose and which increased the organic matter content of the soil, did not seem to be a factor in increasing the rate of cyanamide removal from the soil solution; furthermore, the nature of the humus formed from different types of vegetative material had no apparent effect. This experiment failed to show any increase in the cyanamide conversion capacity of an inactive soil through the addition and subsequent decomposition of the crop residue. The effect of freshly added materials remained open for investigation.

Another inactive soil as far as cyanamide conversion is concerned is the Berrien sand. Samples of this soil were treated as follows:

TABLE 9

Effect of Organic Matter added to Hillsdale Sandy Loam on the removal of Cyanamide from the Soil solution

Treatment 0.1 gm. Cyanamid per 200 gm. of soil	% Organic matter content	pH of soil	Time interval Hours	Cyanamide-N mg.	Cyanamide-N % *
None	2.34	5.30	24	11.89	56.1
			48	8.86	41.8
			72	7.27	34.3
Straw 20 tons per acre	2.64	5.45	24	11.05	52.1
			48	7.90	37.8
			72	5.88	27.7
Alfalfa roots 20 tons per acre	2.82	5.43	24	10.92	51.5
			48	8.19	38.6
			72	5.59	26.4
Sweet clover 20 tons per acre	2.73	5.41	24	11.59	54.6
			48	9.28	43.8
			72	7.43	35.0
Alfalfa roots 20 tons per acre plus lime	2.76	7.58	24	11.09	52.3
			48	9.11	43.0
			72	6.38	30.1
Sweet clover 20 tons per acre plus lime	2.67	7.72	24	11.80	55.6
			48	9.83	46.4
			72	7.70	30.5

* 21.21 mg. nitrogen added as cyanamid.

2.0 gm. of alfalfa per 198 gm. of soil, 2.0 gm. of straw per 198 gm. of soil, 1.0 gm. of alfalfa and 1.0 gm. of straw per 198 gm. of soil, and a control (200 gm. of soil with no crop residue). The crop residues were ground finely and well mixed with the soil, brought to and maintained at an optimum moisture content for six days at room temperature. They were then air dried. The pre-treated soils were treated in duplicate with 0.1 gm. of cyanamid per 200 gm. of soil and extracted at 24, 48 and 96 hour intervals.

The results of this experiment appear in Table 10. They reveal that this is definitely an inactive soil in cyanamide conversion, since over one-fourth of the cyanamide was still in solution after four days in the control. The action of the alfalfa and the alfalfa plus straw pre-treatments were very effective in reducing the cyanamide nitrogen concentrations to 24.1 and 36.8 per cent respectively at the 24 hour interval of examination and none appeared at 48 hours. The straw pre-treatment was not quite as effective, since 5.9 per cent of cyanamide nitrogen was present at the 48 hour interval but none was found at the 96 hour interval of extraction.

Another soil, a sandy loam soil, also found to be inactive, was used to study the effect of alfalfa pre-treatment on cyanamide removal. The results of this study also appear in Table 10. The pre-treatment with alfalfa increased the capacity of this very inactive soil to reduce the concentration of cyanamide from solution. No cyanamide was found in the extract of the pre-treated soil after 24 hours, while in the soil which was not pre-treated 42.0 per cent of the cyanamide nitrogen was present at 24 hours and 14.6 per cent remained after 96 hours.

TABLE 10

The Effect of Pre-treatment with Fresh Organic Material on the Removal of Cyanamide from the Soil Solution

Treatment	Time interval Hours	Cyanamide-N per 200 gm. of soil mg.	% *
198 gm. Berrien sandy soil 0.1 gm. cyanamid	24	11.80	55.6
	48	9.24	43.6
	96	6.18	29.0
198 gm. berrien sandy soil 20 gm. alfalfa 01 gm. cyanamid	24	5.12	24.1
	48	None	-
	96	"	-
198 gm. berrien sandy soil 2.0 gm. straw 0.1 gm. cyanamid	24	8.07	38.0
	48	1.26	5.9
	96	None	-
198 gm. berrien sandy soil 1.0 gm. alfalfa 1.0 gm. straw 0.1 gm. cyanamid	24	7.81	36.8
	48	None	-
	96	"	-
200 gm. sandy loam soil 0.1 gm. cyanamid	24	8.90	42.0
	48	6.80	32.1
	72	4.62	21.8
	96	3.10	14.6
200 gm. sandy loam soil 2.0 gm. alfalfa 0.1 gm. cyanamid	24	None	-
	48	"	-
	72	"	-
	96	"	-

* 21.21 mg. of nitrogen added as cyanamid.

A further study of this soil was undertaken for the purpose of determining the effect of alfalfa added immediately, along with the cyanamid. The results of the immediate alfalfa treatment, the alfalfa pre-treatment and the control for the 24 hour interval are reported in Table 11, Treatments 4 through 6, for comparative purposes. These show that the immediate addition of the alfalfa was less effective than the pre-treatment, yet it is significant.

The immediate treatment of silica sand with alfalfa (Treatments 1 and 2) gave a beneficial effect of the alfalfa treatment on cyanamide conversion, though considerably less than that which occurred in the soil.

A study was made of the influence of low temperatures (5 - 10° C) on the effectiveness of the immediate alfalfa treatment of silica sand, the immediate alfalfa treatment of the sandy loam soil, the alfalfa pre-treatment of the sandy loam soil and the no alfalfa treatment of the soil at the 24 hour interval, in removing cyanamide from solution. The results of these experiments appear in Table 11, Treatments 3, 7, 8 and 9.

The reduced temperature decreased the rate of cyanamide removal from soil solution in all instances, but the effect was less for the alfalfa treatments.

The Hillsdale sandy loam soil previously used, which failed to show any effect on cyanamide removal after the added organic matter had decomposed, was used to determine the effect of the alfalfa pre-treatment. The pre-treatment consisted of 2.0 gm. of ground alfalfa per 200 gm. of soil at optimum moisture content and room temperature for seven days. The cyanamid treatment was comparable to that in the previous studies of this nature. The effect of the lower temperature (5 - 10° C) was also

TABLE 11

Effect of Organic Matter Treatments and Temperature on Removal of Cyanamide from Solution

No.	Treatment 0.1 gm. cyanamid to 200 gm. soil or sand	Temp.* C.	Time interval hours	Cyanamide-N mg.	Cyanamide-N %[1]
1	Immediate alfalfa treatment Silica sand	Room	24	11.59	54.6
2	No alfalfa treatment Silica sand	Room	24	14.99	70.7
3	Immediate alfalfa treatment Silica sand	5-10	24	11.26	53.1
4	Immediate alfalfa treatment Sandy loam soil	Room	24	5.84	27.5
5	Alfalfa pre-treatment Sandy loam soil	Room	24	None	None
6	No alfalfa treatment Sandy loam soil	Room	24	8.90	42.0
7	Immediate alfalfa treatment Sandy loam soil	5-10	24	11.93	56.3
8	Alfalfa pre-treatment Sandy loam soil	5-10	24	11.63	54.8
9	No alfalfa treatment Sandy loam soil	5-10	24	12.96	61.2

* Room temperature about 24°C.

[1] 21.21 mg. of nitrogen added as cyanamid.

studied. The results are reported in Table 12.

The study of alfalfa pre-treatment and low temperature on cyanamide disappearance from solution in the Hillsdale sandy loam gave results similar to those of the other soils studied, Berrien sandy soil and the sandy loam soil. The alfalfa pre-treatment was not as efficient as it was in the other soils. A low cyanamide nitrogen concentration (24.4 per cent) remained at 24 hours and only a trace at 48 hours. This is low in comparison with the non-alfalfa treated soil, with 49.3 per cent cyanamide nitrogen at 24 hours and 5.9 per cent still in solution after 120 hours. The effect of low temperature was similar to that observed in the sandy loam soil previously studied. The conversion properties of the non-alfalfa and pre-treated alfalfa soils were considerably reduced, but the latter was less affected, since the concentration of cyanamide nitrogen in solution of the pre-treated alfalfa soil was from 7 to 11 per cent less than that in the non-alfalfa treated soil.

The results of this study indicate that the addition of crop residues to the soil, particularly alfalfa and straw, increased the capacity of the soil to remove cyanamide from solution. The pre-treatment was much more effective than the immediate treatment.

The effect of low temperature on the disappearance of cyanamide from the soil has been reported by Crowther and Richardson (8). Low temperatures were found to slow up the rate of disappearance of cyanamide, with a subsequent reduction in germination. These data confirm the work of the aforementioned investigators in that low temperatures reduced the rate at which cyanamide was removed from solution.

The pre-treatment of Hillsdale and the sandy loam soil with

TABLE 12

Effect of Alfalfa Pre-treatment of Hillsdale Sandy Loam on Removal of Cyanamide from the Soil Solution

Treatment 0.1 gm. cyanamid to 200 gm. of Hillsdale sandy loam	Temperature*	Time interval hours	Cyanamide-N mg.	 %[1]
Alfalfa pre-treatment	Room	24	5.17	24.4
		48	0.59	2.8
		72	None	None
		120	"	"
No alfalfa pre-treatment	Room	24	8.36	49.3
		48	5.33	25.1
		72	3.19	15.0
		120	1.18	5.9
Alfalfa pre-treatment	5-10°C.	24	11.84	55.8
		48	10.33	48.7
		96	7.73	36.5
No alfalfa pre-treatment	5-10°C.	24	13.61	64.2
		48	11.84	55.8
		96	10.08	47.5

* Room temperature about 24°C.

[1] 21.21 mg. of nitrogen added as cyanamid.

alfalfa increased their capacity to remove cyanamide from solution. In this study, not only the cyanamide was determined, but also the urea and soluble ammonia on the soil extract and the fixed ammonia on the extracted soil at the 24, 48, 72 and 120 hour interval of extraction. The data are summarized in Table 13.

These data are reported to show that the cause of the cyanamide disappearance due to alfalfa pre-treatments is due, at least partially, to its decomposition into urea and subsequent ammonia formation and not to the adsorption of the cyanamide ion. This offers evidence of the presence of an activating, possibly catalytic agent, which is responsible for the decomposition. It was noted from the data that the concentrations of soluble and fixed ammonia were considerably greater for the treated soils, especially during the initial periods and that this effect was evident through all the periods in the case of the Hillsdale sandy loam.

An explanation was sought for the activity of the added crop residues, particularly alfalfa, in the soil in increasing the removal of cyanamide from solution. Since decomposition seemed to be involved, rather than adsorption of the cyanamide ion, two series of experiments were run in an attempt to identify the active agent.

The indirect microbial effect of enzyme production due to a large supply of energy material and its subsequent effect on cyanamide decomposition was studied. This study was not considered complete enough to justify submission of the results in this report, but the problem seemed worthy of a more complete investigation. The effect of water extracts of the various crop residue materials was studied and the preliminary studies indicate that these extracts are effective to a

TABLE 13

The Nature of Cyanamide Decomposition Products Resulting from Fresh Organic Matter Pre-treatment of Soil

Soil and treatment	Time interval hours	Non pre-treatment				Pre-treatment			
		mg. of nitrogen per 200 gm. of soil							
		Cyanamide	Urea	Soluble ammonia	Fixed* ammonia	Cyanamide	Urea	Soluble ammonia	Fixed* ammonia
Hillsdale sandy loam,	24	8.36	1.89	1.09	4.62	5.17	0.34	4.03	8.42
Alfalfa pre-treatment,	48	5.33	1.43	2.98	6.54	0.59	0.21	5.80	9.67
2.0 gm. per 200 gm. of soil,	72	3.19	0.63	3.36	8.07	None	0.13	6.05	10.71
0.1 gm. of cyanamid per 200 gm. of soil.	120	1.18	0.38	3.57	8.23	"	0.11	6.01	10.88
Sandy loam soil,	24	8.90	0.25	2.86	2.23	Tr.	0.13	5.38	3.66
Alfalfa pre-treatment,	48	6.80	0.46	4.87	3.30	None	0.42	7.43	3.61
2.0 gm. per 200 gm. of soil,	72	4.62	0.34	6.34	4.24	"	0.25	7.60	3.81
0.1 gm. of cyanamid per 200 gm. of soil.	96	3.10	0.08	6.26	4.24	"	0.34	7.60	4.33

* Corrected for fixed ammonia nitrogen in the non-cyanamid treated soil.

certain extent in removing cyanamide from solution.

The results of one experiment on the effect of extracts of five different materials on cyanamide removal from solution are submitted in Table 14. The extracts were prepared by adding the materials in two different amounts to 200 ml. of water and allowing them to stand for 18 hours, after which they were filtered. Duplicate portions of the extracts were treated with 0.05 gm. of cyanamid and allowed to stand for a period of 48 hours with frequent stirring. They were then filtered and washed to a total volume of 100 ml. and cyanamide determined on 25 ml. aliquots.

Studies of the effects of reducing sugars found in another part of this paper revealed that they could reduce cyanamide concentration in solution culture studies. Germination studies showed that a higher germination of wheat seeds could be secured when increasing concentrations of these sugars were added. The same studies also showed that this effect could not be produced when the solution was acid. Accordingly, a similar set-up was prepared for the study of the extracts, except that 10.5 ml. of 0.102 N HCl was added to the 25 ml. portions of the extract before the cyanamid was added. This addition of acid produced a final pH value of the cyanamid treated extracts of 3.5 to 4.5, depending upon the organic material used.

It cannot be concluded from these data that the extracts from the organic materials had no influence on the disappearance of cyanamide from solution. It does appear that in the larger amounts in the alkaline medium, the alfalfa, sugar beet and, to a less extent, the straw extracts had some effect. The acid medium prevented the cyanamide conversion, except in the case of the sugar beet extract. If the reducing sugars are

TABLE 14

The Effect of Extracts from Organic Materials on Removal of Cyanamide from Solution

Treatment 0.05 gm. of cyanamid to 25 ml. of extract	Time interval hours	No HCl Cyanamide-N mg.	 %*	10.5 ml. 0.102N HCl Cyanamide-N mg.	 %*
1.0 gm. alfalfa to 200 ml. of water for 18 hours	48	7.36	70.4	7.56	72.3
5.0 Ditto	48	5.01	47.9	7.45	71.3
1.0 gm. straw to 200 ml. of water for 18 hours	48	7.08	67.8	7.84	75.0
5.0 Ditto	48	6.44	61.6	7.36	70.4
1.0 gm. wood shavings to 200 ml. of water for 18 hours	48	7.45	71.3	7.84	75.0
5.0 Ditto	48	6.97	66.7	7.84	75.0
1.0 gm. compost to 200 ml. of water for 18 hours	48	7.39	70.3	8.01	76.7
5.0 Ditto	48	7.64	73.1	7.84	75.0
1.0 gm. sugar beet roots to 200 ml. of water for 18 hours	48	6.83	65.4	7.11	68.0
5.0 Ditto	48	5.18	49.6	5.25	50.3
Control - 0.05 gm. cyanamid to 25 ml. of water	48	7.58	72.5	7.94	76.0

* 10.45 mg. of nitrogen added as cyanamid.

the active agents in these materials, then the acid medium must have destroyed the reducing properties and inhibited their effect on cyanamide conversion.

Catalysts

Many citations occur in the literature of the catalytic effect of acids, strong alkalies, inorganic salts, particularly the oxides of iron and manganese on cyanamide decomposition. The work of C. Ulpiana and H. Kappen, as reported by Pranke (16), is frequently cited in regard to the subject of catalysis and cyanamide conversion. Kappen determined the relative decomposing ability of what were called well known constituents of ordinary soils. The greatest activity was exhibited by a manganese ore, principally manganese hydroxide, followed by an iron ore, principally iron hydroxide containing some manganese hydroxide, and third, an iron ore, chiefly iron hydroxide free of manganese. The manganese oxide was quite effective and of the other compounds studied, their decreasing activity was associated with a decreasing iron content. Aluminum ores free of iron were ineffective.

The study of the catalytic effects of zeolites by Ulpiani was reported by Pranke (16). Cowie (7), Crowther and Richardson (8) and Smock (18) have also reported successful results with certain zeolites, but particularly prehnite, a zeolitic mineral with the formula $(H_2Ca_2Al_2(SiO_4)_3)$.

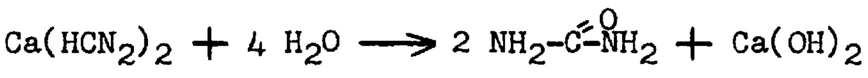
Ulpiani's use of animal charcoal, as a material helpful in the decomposition of cyanamide, was reported by Pranke (16). This effect was also reported by Rhodin (17), Fink (9), Smock (18) and Yoneda (21). Other materials have also been used; such as, kaolin, various types of bentonite clay, filter paper, silica gel and humic acid. In some instances these have exhibited catalytic activity in cyanamide decomposition.

Crowther and Richardson (8) state that two soil minerals, prehnite and apophylite, designated as zeolites or related substances, were active in producing urea from calcium cyanamide. They are of the opinion that these zeolites which contain hydrogen other than water are able to take up the excess lime in the calcium cyanamid and make the solution less alkaline. Whether this condition enhances the catalytic activity of these zeolites or the less alkaline condition favors urea formation is not definitely stated; however, another inference, that not only the presence of a catalyst but removal of the excess lime seems to be a necessary step for urea formation. This associates the base adsorbing complex of the soil, more definitely its degree of hydrogen saturation, with cyanamide decomposition to urea.

Fink (9) concluded from his studies that the total base exchange capacity was not a factor of major importance, nor was the degree of hydrogen saturation important.

The effect of the removal of the excess calcium, as well as the calcium produced in the hydrolysis of calcium cyanamide, seems to be two-fold. The hydrolysis of calcium cyanamide may occur as follows:

$$2\ CaCN_2 + 2\ H_2O \longrightarrow Ca(HCN_2)_2 + Ca(OH)_2$$



$$Ca(HCN_2)_2 + 4\ H_2O \longrightarrow 2\ NH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH_2 + Ca(OH)_2$$

First, the removal of the calcium hydroxide end product would induce the reaction strongly toward the right, and second, the alkalinity of the medium would be reduced. The presence of an excess of hydrogen ions in solution might be expected to produce high urea concentrations if they are active catalysts.

The Effect of Calcium Precipitation and Acidity on Cyanamide Decomposition: It was believed that the effect of the calcium removal and increased hydrogen ion concentration might be studied by the use of oxalic acid. The presence of oxalic acid in the solution would accomplish two purposes; it would affect (1) the removal of calcium by complete or partial precipitation and (2) produce an increase in acidity.

The period over which this study was made, 108 hours, was sufficient for cyanamide to completely disappear from solution for most of the soils studied. The cyanamid-water ratio used was slightly less concentrated with respect to cyanamid than in any of the soils used at optimum moisture content.

Two and one-half gm. of cyanamid were placed in 500 ml. of water and allowed to stand with intermittent shaking for 1.5 hours. The solution was filtered and washed to a total volume of 1000 ml. Twenty ml. of this solution was found to contain 10.21 mg. of total nitrogen on analysis.

Two and one-half hours after the cyanamid was placed in solution, as already described, thirty-six 20 ml. aliquots were placed in 150 ml. beakers for duplicate determinations for nine different intervals of examination, with and without oxalic treatment. In the oxalic acid treatments, 1.65 ml. of 0.693 N oxalic acid was added to 20 ml. aliquots of the cyanamide solution. It was found that 1.65 ml. of 0.693 N oxalic acid, when added to a 20 ml. aliquot of cyanamid solution, was sufficient to completely precipitate the calcium and produce a pH of about 4.0. The solutions were allowed to stand at room temperature and at the indicated interval of time (measured from the time the oxalic acid was added in each instance) the cyanamide was precipitated and determined. The results of this work appear in Table 15. Since the volume of calcium oxalate precipitate was considerable and since it was filtered out with the silver cyanamide precipitate, it offered some difficulty in the digestion of the cyanamide to ammonia due to the high salt content. Consequently, a similar series of oxalic acid treatments was set up in which the calcium oxalate was filtered out before the cyanamide was precipitated. These results are also shown in Table 15.

The oxalic acid treatment failed to significantly change the cyanamide concentration over a period of 108 hours of study; the oxalic acid treatment reduced the cyanamide concentration from 81 to 78.1 per cent in contrast to a reduction of 81.2 to 77.5 per cent for the non-oxalic acid control treatment. The series prepared, in which the calcium oxalate was filtered out before the cyanamide was precipitated, also failed to show any significant difference from the non-oxalic or control treatment.

The formation of dicyanodiamide in an alkaline solution (the control) is apparently a relatively slow process, since 77.5 per cent of the added nitrogen was still in the cyanamide form at the end of 108 hours.

Another experiment was set up in which five different amounts of oxalic acid were used and the cyanamide concentration determined at intervals over a period of 72 hours. To 20 ml. aliquots of the cyanamid solution prepared for the previous experiment, containing 10.21 mg. of cyanamide nitrogen per aliquot, 0.693 N oxalic acid was added in increasing quantities, as indicated in Table 16. The various oxalic acid treat-

TABLE 15

The Effect of Removal of Calcium and Reaction on the Disappearance of Cyanamide from Solution

Time interval hours	No oxalic acid		Oxalic acid[1]		Oxalic acid[1] calcium oxalate removed	
	Cyanamide-Nitrogen					
	mg.	%*	mg.	%*	mg.	%*
1	8.29	81.2	8.27	81.0	8.39	82.2
12	8.18	80.1	8.33	81.6	8.39	82.2
24	8.34	81.7	8.11	79.4	8.32	81.5
36	7.84	76.8	8.39	82.2	8.05	78.8
48	7.90	77.4	8.08	79.1	7.99	78.3
72	8.11	79.4	8.05	78.8	8.02	78.6
84	7.84	76.8	8.12	79.5	7.90	77.4
96	7.74	75.8	8.19	80.2	7.88	77.2
108	7.91	77.5	7.97	78.1	7.90	77.4

* 10.21 mg. of nitrogen added as cyanamid.

[1] 1.65 ml. 0.693N oxalic acid.

TABLE 16

The Effect of Varying Oxalic Acid Concentrations on the Disappearance of Cyanamide from Solution

Ml. 0.693N oxalic acid	1 hour		24 hours		36 hours		48 hours		72 hours	
	Cyanamide-Nitrogen									
	mg.	%*	mg.	%*	mg.	%*	mg.	%*	mg.	%*
0.0	8.18	80.1	8.18	80.1	7.88	77.2	8.05	78.8	8.18	80.1
0.5	8.20	80.3	8.05	78.8	8.13	79.6	8.09	79.2	8.32	81.5
1.0	8.36	81.9	8.37	81.9	8.29	81.2	8.18	80.1	8.25	80.8
1.2	8.33	81.6	8.25	80.8	8.04	78.7	7.95	77.9	8.32	81.5
2.0	8.25	80.8	8.15	79.8	8.06	78.9	7.98	78.2	7.88	77.2

* 10.21 mg. of nitrogen added as cyanamid

ments produced various calcium levels from a high concentration for the control to near complete precipitation for the 2.0 ml. treatment. The reaction of the solutions varied from pH 8.0 for the non-treatment to approximately pH 3.5 for the 2.0 ml. oxalic acid treatment. It is obvious that the removal of calcium and the increased hydrogen concentration had little influence on the disappearance of cyanamide from solution.

From these studies one might conclude that an increase in the rate of hydrolysis of calcium cyanamide (equations, page 43) by removing the calcium and inducing an acid medium by a slight excess of oxalic acid, failed to develop any obvious catalytic effect by the hydrogen ion in increasing the rate of disappearance of cyanamide from solution.

The application of this principle can be made to the soil. With the removal of the calcium an increased rate of hydrolysis might occur where the exchange capacity of the soil is high and where the degree of base saturation is low. The hydrogen ions of the acid soils, where cyanamide decomposes most readily, may not serve as the active catalysts but it is their indirect effect on the state of colloids and other soil constituents which may play the principal role in cyanamide disappearance from the soil solution and its decomposition into urea and ammonia.

The Effects of Sugars on Cyanamide Conversion: In a biological test on cyanamide conversion, in which dextrose was used as a source of energy, it was discovered that cyanamide disappeared from solution more rapidly than normally. It was believed that the effect of fresh organic matter in increasing the rate of cyanamide disappearance from the soil solution might be in some way related to the effect of sugars and related compounds. The first indication of the effect of dextrose was the result of an experiment in which the effect of microorganisms on cyanamide decomposition was studied. To 200 gm. of silica sand, 0.1 gm. of cyanamid was added and well mixed; 35 ml. of solution (made up of 5.4 ml. of oxalic acid to precipitate the calcium, a suitable nutrient solution containing no nitrogen and water) was added to the sand-cyanamid mixtures to bring them to a favorable moisture condition for incubation. The energy material of the nutrient solution was supplied as dextrose in solution and added separately from the remainder of the nutrient solution. The cultures were inoculated with 1.0 gm. of the Fox soil and allowed to stand for 72 hours at room temperature before extraction and examination for cyanamide.

The results of duplicate treatments of this experiment appear in Table 17, Treatment 4. The cyanamide concentration was reduced to 15.5 per cent of the total of 21.21 mg. of nitrogen added as cyanamid. In view of the lack of a biological effect in cyanamide conversion and since the concentration of cyanamid used in this unbuffered medium was great enough to partially sterilize the culture, some other constituent must have been responsible for the reduction of the cyanamide concentration.

Results of subsequent treatments, 5 through 7, at three different oxalic acid levels with no soil inoculation, disclosed that when sufficient acid was added (more than 6.0 ml.) to produce an acid reaction (pH 3.0), the cyanamide was not reduced to very low levels, 47.9 per cent remaining in solution after 72 hours. The non-oxalic acid and 6.0 ml. treatments yielded 3.3 and 7.5 per cent of the cyanamide in solution, respectively. This indicated that the conversion capacity of the agent was at least

TABLE 17

Effect of Dextrose on Cyanamide-Nitrogen Conversion

No.	Treatment 0.1 gm. cyanamide per 200 gm. Silica sand	0.345N oxalic acid ml.	Cyanamide-N		pH of extract
			mg.	%*	
Not sterilized					
1	Control	None	14.95	70.5	8.0
2	"	6.0	15.30	72.1	5.5
3	"	10.0	12.85	60.6	3.0
4	Nutrient solution, 1 gm. Fox soil 0.5 gm. dextrose	5.4	3.29	15.5	7.7
5	Nutrient solution, 0.5 gm. dextrose	None	0.70	3.3	8.0
6	Ditto	6.0	1.58	7.5	8.0
7	"	10.0	10.15	47.9	3.0
8	Nutrient solution, 1 gm. Fox soil 0.5 gm. dextrose	None	0.70	3.3	8.0
9	Ditto	6.0	0.88	4.2	8.0
10	"	10.0	0.56	2.6	5.5
11	Nutrient solution, 1 gm. Traverse soil, 0.5 gm. dextrose	None	0.84	4.0	8.0
12	Ditto	6.0	0.81	3.0	8.0
13	"	10.0	0.56	2.6	5.5
Sterilized					
14	Control	None	15.33	72.3	8.0
15	"	6.0	16.52	71.3	5.5
16	"	10.0	13.69	64.6	3.0
17	0.5 gm. dextrose	None	0.46	2.2	8.0
18	Ditto	6.0	15.12	71.3	5.5
19	"	10.0	13.37	63.0	3.0
20	Nutrient solution, 0.5 gm. dextrose	None	0.32	1.5	8.0
21	Ditto	6.0	14.11	66.5	7.0
22	"	10.0	14.42	68.0	5.5
23	Nutrient solution, 1 gm. Fox soil 0.5 gm. dextrose	None	0.56	2.6	8.0
24	Ditto	6.0	15.47	72.9	7.0
25	"	10.0	15.68	73.9	5.5

* 21.21 mg. of nitrogen added as cyanamid.

partially inhibited by the strongly acid condition.

The control treatments, 1 through 3, (cyanamide added to silica sand) showed no great reduction in cyanamide concentration, even at the most acid condition. This conforms with the previous studies with oxalic acid in which it was found ineffective in removing cyanamide from solution. The introduction of the nutrient solution, without the dextrose, produced results similar to the control. This eliminated the possibility of any constituent in the nutrient solution except the dextrose as the agent responsible for the disappearance of the cyanamide.

Treatments 8 through 13 (with nutrient solution, including the dextrose and soil inoculation) at three oxalic acid levels resulted in very low cyanamide concentrations. These results confirm those of Treatment 4.

As a further check on the biological effect, experiments were run in which all materials, except the cyanamid, were sterilized with steam at 15 pounds pressure for 10 hours. These experiments are represented by Treatments 14 to 25 inclusive, Table 17. The various materials used were sterilized simultaneously in separate Erlenmyer flasks. The 0.1 gm. cyanamid portions were carefully transferred to the Erlenmyer flasks to avoid contamination and mixed with the silica sand. The necessary amounts of sterilized nutrient solution, dextrose, soil and additional water in a constant volume of 35 ml. were added together and carefully transferred to the cyanamid-sand mixtures. These were allowed to stand at room temperature for 72 hours, at which time sufficient sterilized water was added to bring the total volume of solution to 125 ml. The flasks were shaken periodically for an hour and the extractions were made in the usual manner. Duplicate cyanamide determinations were made on 25 ml. aliquots.

The results on the sterilized series show that the effect of the dextrose is present even when the cultures are sterilized. The addition of acid completely inhibited its effect in most instances and to a greater extent than occurred under the non-sterilized treatments.

A summary of these studies reveals the following: (1) The disappearance of cyanamide from solution was not due to the oxalic acid treatments, except possibly to a certain extent at the higher concentrations for both the sterilized and non-sterilized treatments, represented by Treatments 1 through 3 and 14 through 16 in Table 17; (2) Treatments 5 to 13 inclusive, in which dextrose was used with or without soil inoculation, resulted in active conversion of cyanamide except for Treatment 7. It is apparent that the highly acid condition produced by this treatment inhibited the action of the converting agent. The one gram of soil used for inoculation produced sufficient buffering effect in the case of Treatments 10 and 13 to maintain the pH value near 5.5 and extremely low cyanamide concentrations were found at the end of 72 hours; (3) Sterilization failed to change the effect of the oxalic acid on cyanamide conversion, Treatments 14 through 16; (4) With the sterilized treatments (17, 20 and 23) in which dextrose was used with no oxalic acid, conversion was almost complete. This indicates the absence of a biological effect; (5) The constituents of the nutrient solution or the soil inoculation were apparently not the active agents (Treatments 17, 20 and 23); (6) The higher oxalic acid concentrations, 6.0 and 10 ml., produced different results under sterilized conditions than under non-sterilized conditions. The conversion resulting from these treatments (18, 19, 21, 22, 24 and 25) was not great, although dextrose was added in all cases.

These results show that the active agent involved in cyanamide conversion is dextrose and that it is not a biological effect. The dextrose seems to possess its greatest conversion capacity at the higher pH levels.

To further substantiate the effect of dextrose on cyanamide conversion, another series of experiments was carried out. The objectives were: (1) to again segregate the dextrose effect from those of the nutrient solution and soil inoculation, (2) to determine the effect of various acid concentrations on the activity of the dextrose, (3) to determine the effect of varying dextrose concentrations, and (4) to determine to what extent urea is a decomposition product of cyanamide decomposition.

The cyanamid was mixed with 200 gm. of silica sand. The other components of the treatments were added in solution, in constant volume of 35 ml., to provide favorable uniform moisture conditions in the silica sand. After a 24 hour incubation period, at room temperature, extractions were carried out, as previously described, and determinations of cyanamide and urea made on duplicate 25 ml. aliquots of each treatment. The data for this series of experiments appear in Table 18.

Treatments 1, 2 and 3 gave little difference in cyanamide concentration, although there was slightly more conversion of cyanamide with the greatest oxalic acid treatment. The results of Treatments 4, 5 and 6 show that the addition of the nutrient solution without the dextrose failed to change the cyanamide concentration. Treatments 7, 8 and 9, in which 0.5 gm. of dextrose was used without nutrient solution, gave almost complete

TABLE 18

Effect of Dextrose on Disappearance of Cyanamide from Solution

Treatment 0.1 gm. cyanamid per 200 gm. silica sand-24 hr. interval					Urea-N		Cyanamide-N		
No.	Soil inoculations	Nutrient solution	ml. 0.345N oxalic acid	Dextrose gm.	mg.	%*	mg.	%*	pH of extract
1	No	No	None	None	1.14	5.4	15.27	72.0	8.0
2	"	"	6.0	"	0.63	3.0	15.33	72.3	5.5
3	"	"	10.0	"	1.68	7.9	13.93	65.7	3.0
4	"	Yes	None	"	1.33	6.3	15.30	72.1	8.0
5	"	"	6.0	"	0.98	4.6	15.09	71.2	5.5
6	"	"	10.0	"	0.70	3.3	15.51	73.1	3.0
7	"	No	None	0.5	2.17	10.2	0.67	3.2	8.0
8	"	"	6.0	0.5	1.47	6.9	10.22	48.2	5.5
9	"	"	10.0	0.5	1.61	7.6	14.11	66.5	3.0
10	Yes	Yes	None	0.5	2.87	13.5	0.67	3.2	8.0
11	"	"	6.0	0.5	1.54	7.3	12.39	58.4	7.5
12	"	"	10.0	0.5	1.19	5.6	16.10	75.9	5.5
13	"	"	15.0	0.5	1.09	5.1	15.47	72.8	3.0
14	"	"	None	0.1	2.38	11.2	8.19	38.6	8.0
15	"	"	6.0	0.1	0.59	2.8	15.72	74.1	7.5
16	"	"	10.0	0.1	0.46	2.2	16.12	76.0	5.5
17	"	"	15.0	0.1	0.63	3.0	16.10	76.0	3.0

* 21.21 mg. of nitrogen added as cyanamid.

removal of cyanamide at the higher pH level with less removal at lower pH levels. Treatments 10 through 13, in which both nutrient solution and dextrose were used and inoculated with one gm. of Fox sandy loam soil, gave results similar to Treatments 7, 8 and 9. The soil used for inoculation had a buffering effect and the pH level was not reduced to the same extent as in Treatments 7 through 9.

The results of Treatments 14 through 17 demonstrated that the conversion of cyanamide increased with an increase in the quantity of dextrose added under comparable conditions. In this series, the first increment of the oxalic acid nullified the effect of the lower dextrose addition on cyanamide conversion.

A study of the urea concentration of those treatments in which the cyanamide concentration was reduced by the action of the dextrose shows that, though they were slightly higher, they did not account for the cyanamide that was removed from solution.

This study further confirms the effect of dextrose on cyanamide removal from solution and that the activity of the dextrose was inhibited to a large extent by acid conditions. Smaller additions of dextrose failed to have the same effect in removing cyanamide from solution as that of the larger concentrations. The accumulation of urea following the disappearance of the cyanamide failed to account for the cyanamide reduction. This indicates that urea is not the primary product of cyanamide decomposition resulting from the effect of the dextrose.

A more elaborate study of the concentration of dextrose on cyanamide removal from solution was undertaken. This was carried out in solution cultures rather than in sand cultures. It was found in preliminary work that the removal of cyanamide by dextrose could be accomplished in water solution cultures as well as the sand cultures. It was also found that 21.0 ml. of 0.102 N HCl, which reduced the pH value of a 0.1 gm. cyanamide treatment to 3.5, would inhibit the capacity of the dextrose to remove cyanamide from solution.

The dextrose was placed in solution and the quantities indicated in Table 19 were added to 0.1 gm. of cyanamide along with enough water to bring the total volume of solution to 35 ml., the same quantity of solution used in the silica sand cultures in the preceding experiments. In those treatments, in which 21.0 ml. of acid was used, the total volume of the culture solution was also 35.0 ml. The cultures were allowed to stand for 24 hours at room temperature with frequent stirring, after which they were filtered and washed to a total volume of 135 ml. The treatments were set up singly and duplicate urea and cyanamide determinations were made on 25 ml. aliquots of extract. The data from this study appear in Table 19.

It is obvious that with an increase in concentration of dextrose, there was an increase in the capacity of cyanamide removal from solution. The additions of 0.3, 0.4 and 0.5 gm. of dextrose resulted in complete removal of cyanamide from solution in 24 hours. Concentrations of less than 0.3 gm. of dextrose resulted in increasing amounts of cyanamide in solution. The addition of 21.0 ml. of 0.102 N HCl, inducing a pH of 3.5, inhibited the activity of the dextrose in removing cyanamide from solution at each of the concentrations used. Urea concentrations failed to develop with the reduction of the cyanamide in solution.

From the evidence secured on the effect of acid conditions on

TABLE 19

Effect of Various Concentrations of Dextrose on Cyanamide Conversion

No.	Treatment 0.1 gm. cyanamid per 35 ml. of solution - 24 hr. time interval ml. 0.102N HCl	Dextrose gm.	Urea-N mg.	Urea-N %*	Cyanamide-N mg.	Cyanamide-N %*	pH of extract
1	None	None	1.74	8.2	16.25	76.6	8.0
2	"	0.01	2.19	10.3	14.67	69.2	8.0
3	"	0.02	2.33	11.5	14.48	68.3	8.0
4	"	0.05	2.38	11.2	11.49	54.2	8.0
5	"	0.10	2.38	11.2	7.75	36.5	8.0
6	"	0.20	2.65	12.5	1.25	5.9	8.0
7	"	0.30	2.80	13.2	None	-	8.0
8	"	0.40	2.72	12.8	"	-	8.0
9	"	0.50	2.84	13.4	"	-	8.0
10	21.0	0.10	0.87	4.1	16.25	76.6	3.5
11	21.0	0.20	0.87	4.1	16.22	76.5	3.5
12	21.0	0.40	0.95	4.5	16.33	77.0	3.5
13	21.0	None	0.76	3.9	16.52	77.9	3.5

* 21.21 mg. of nitrogen added as cyanamid.

the conversion capacity of dextrose, it was believed that the acid concentrations produced a change in the aldehyde form of the sugar, perhaps inducing a ring structure with a consequent reduction in the catalytic activity. To test this hypothesis, several additional reducing sugars, as well as a non-reducing sugar, were tested in alkaline and acid medium. Dextrose, mannose and galactose of the reducing aldo-hexose sugars; levulose, a keto-hexose reducing sugar; arabinose, a reducing aldo-pentose; rhamnose, a reducing methyl aldo-pentose; lactose, a reducing disaccharide; and sucrose, a non-reducing disaccharide were chosen for study.

The manner in which these experiments were carried out was comparable to that of the preceding series described. The treatments were set up singly and duplicate determinations were made on 25 ml. aliquots of extract. The 0.3 gm. sugar treatment was used in view of the fact that a like amount of dextrose was found sufficient to remove cyanamide from solution in the previous studies in 24 hours. The data are reported in Table 20.

All the reducing sugars yielded but a trace or no cyanamide in solution after 24 hours. The acid treatments, inducing a pH of 3.5, inhibited the activity of the sugars. The sucrose, a non-reducing sugar, failed to reduce the cyanamide concentration a great extent; it was only about 10 per cent below that of the control in contrast to complete removal for the other sugars. Urea concentration failed to increase with corresponding decrease in cyanamide concentration.

<u>The Nature of the Decomposition Products of Cyanamide due to the Effect of Reducing Sugars:</u> A review of the data reported in Tables 18 and 19 reveals that the decrease in concentration or complete removal

TABLE 20

Effect of Sugars on Cyanamide Decomposition

	Treatment 0.1 gm. cyanamid per 35 ml. of solution - 24 hr. time interval		Urea-N		Cyanamide-N		
No.	ml. 0.102N HCl	Sugar 0.3 gm.	mg.	%*	mg.	%*	pH of extract
1	None	None	1.44	6.8	15.80	74.5	8.0
2	"	Dextrose	2.38	11.2	None	-	8.0
3	"	Levulose	2.27	10.7	"	-	8.0
4	"	Mannose	1.74	8.2	"	-	8.0
5	"	Galactose	1.74	8.2	"	-	8.0
6	"	Lactose	1.66	7.8	0.15	0.7	8.0
7	"	Arabinose	2.12	10.0	None	-	8.0
8	"	Rhamnose	2.00	9.4	"	-	8.0
9	"	Sucrose	1.74	8.2	13.72	64.7	8.0
10	21.0	Mannose	1.09	5.1	15.57	73.4	3.5
11	21.0	Galactose	1.09	5.1	15.54	73.3	3.5
12	21.0	Arabinose	0.91	4.3	15.20	71.7	3.5
13	21.0	Rhamnose	0.83	3.9	15.84	74.7	3.5

* 21.21 mg. of nitrogen added as cyanamid.

of cyanamide from solution by reducing sugar was not followed by a corresponding increase in urea concentrations. Qualitative as well as quantitative tests for ammonia indicated its complete absence in many cases and presence in only insignificant amounts in others. These circumstances led to the belief that the product of cyanamide decomposition by the reducing sugars might be dicyanodiamide.

One experiment was carried out in which it was sought to determine the identity of the decomposition products. The procedure in this experiment was identical with that of the preceding one, except that the period between setting up the experiment and time of extraction was 96 hours instead of 24 hours and they were set up in duplicate instead of singly. The results appear in Table 21.

An analysis of this data shows that (1) urea concentrations reached a higher level with the dextrose treatment than with the sucrose or no sugar treatments; (2) the dextrose treatment completely removed the cyanamide from solution in 96 hours, while sucrose reduced the concentration to 58.8 per cent or about 10 per cent below that of the control; (3) the dicyanodiamide concentration, as determined by difference, reached a high level of 42.7 per cent in the dextrose treatment, 31.3 per cent in the sucrose treatment and only 3.7 per cent in the control; (4) the total nitrogen recovered was lowest (63.1 per cent) for the dextrose treatment, 80.1 per cent for the control and almost complete recovery for the sucrose treatment. These facts indicate that dextrose, a reducing sugar, induces dicyanodiamide formation to a large extent as well as the formation of other compounds not determined, as evidenced by the incomplete recovery of the soluble nitrogen added.

TABLE 21

The Decomposition Products of Cyanamide When Treated with Sugars

Treatment 0.1 gm. cyanamid per 35 ml. of solution - 96 hr. time interval	Total-N mg.	Total-N %*	Ammonia-N mg.	Ammonia-N %*	Urea-N mg.	Urea-N %*	Cyanamide-N mg.	Cyanamide-N %*	Dicyanodiamide mg.	Dicyanodiamide %*	% of total-N recovered
Control - no sugar added	19.54	100.0	None	-	1.51	7.7	13.42	68.7	0.72	3.7	80.1
0.3 gm. dextrose	19.13	100.0	Trace	-	4.01	21.0	None	-	8.17	42.7	63.1
0.3 gm. sucrose	19.43	100.0	None	-	1.80	9.3	11.42	58.8	6.08	31.3	99.3

* Total nitrogen in extract.

The Effect of Sugars on Cyanamide Toxicity to Germination of Wheat Seeds: Fink (9) and others have used germination tests to determine the effectiveness of catalysts in removing the toxic effect of cyanamide treatments. In this study the germination tests were carried out as follows: One-tenth of a gm. of cyanamid was well mixed with 200 gm. of silica sand and placed in small granite pans. Wheat seeds, 50 in number, were distributed in the cyanamid-sand mixture. The sugars were added in solution and the sand brought to and maintained at a satisfactory moisture content during the germination period. The counts were made after seven days. The results of duplicate trials are reported in Table 22.

The results of the germination tests show that 0.1 gm. of cyanamid in 200 gm. of silica sand reduced germination to 26 per cent. The presence of 0.4 gm. of sucrose raised the germination from 26 to 57 per cent. A similar application of dextrose raised the germination to 96.5 per cent, the normal germination for this lot of seeds. With applications of less than 0.3 gm. of dextrose with 0.1 gm. of cyanamid, germination was lowered significantly (38 and 36 per cent). Cyanamide was found in the solution, when the germination counts were made after seven days, in the no sugar treatment and to a less extent in the sucrose treatment.

The data, already reported, indicated that at least 0.3 gm. of dextrose was necessary to remove from solution in 24 hours cyanamide of a 0.1 gm. application. This is confirmed by the germination tests, in that the removal of the cyanamide at an early period, even though in contact with the seed, permitted germination. Dicyanodiamide and other decomposition products of cyanamide, the identity of which are not

TABLE 22

Effect of Sugars on Cyanamide Toxicity to Germination of Wheat Seeds

Treatment 200 gm. Silica sand		Number seeds	Per cent Germination	Cyanamide present after 7 days
Sugar gm.	Cyanamid gm.			
None	None	50	96.0	None
None	0.1	50	26.0	xx*
Sucrose 0.4	0.1	50	57.0	x*
Dextrose 0.4	0.1	50	96.5	None
Dextrose 0.3	0.1	50	93.0	"
Dextrose 0.2	0.1	50	38.0	"
Dextrose 0.1	0.1	50	36.0	"

* Indicates relative concentration of cyanamide.

definitely known, were not toxic, at least to the extent of preventing germination. It was observed, however, that the rate of germination, as well as the vigor of the seedlings, was lower for all treatments in which any form of sugar was used. Whether the retarded rate of germination, as well as lower vigor of the seedlings, can be attributed to the temporary effect of the cyanamide, the decomposition products of the cyanamide or to the direct or indirect effect of the sugars cannot be stated.

The application of this particular principle, the increased rate of removal of cyanamide from solution by reducing sugars or related compounds, seems to be limited. In view of the fact that dicyanodiamide, rather than urea, is the primary decomposition product, the use of reducing sugars as catalysts would not be reasonably recommended; furthermore, the amount of reducing sugars necessary to reduce the concentration of cyanamide rapidly, as reported for the solution and sand culture studies, would be three parts of sugar to one part of cyanamid, which does not appear to be feasible in the use of cyanamid as a fertilizer. The effect of reducing sugars on cyanamide decomposition as it may be produced in the soil was not studied. From the work reported here, however, an acid reaction inhibits the effect; from the standpoint of soils, many of which are acid, the conversion of cyanamide by the reducing sugars may be of little consequence. In alkaline or neutral soils with a low buffering capacity, the effect of reducing sugars may be of some importance.

A detailed study of sugars was carried out in an attempt to explain the effect of fresh organic matter additions to the soil in cyanamide decomposition. To what extent reducing sugars and related compounds are responsible for decomposition of cyanamide by the addition of fresh organic matter to the soil cannot be definitely stated. Since the reducing sugars yield primarily dicyanodiamide as a decomposition product, which is very stable, and the organic matter additions to the cyanamide treated soil produced high ammonia concentration, it might be concluded that the sugars do not play the primary role in the latter case.

The Effect of Manganese Compounds on Cyanamide Conversion: The effect of several manganese compounds (manganese dioxide, potassium permanganate, manganous acetate, manganous carbonate and manganous sulphate) on cyanamide conversion was studied. These compounds, in quantities of 0.3 to 0.5 of a gm., were mixed with 0.1 of a gm. of cyanamid and this mixture well distributed in 200 gm. of silica sand. A favorable moisture content was secured by adding 35 ml. of water and the culture was allowed to stand for 72 hours at room temperature. Extractions were carried out in the usual manner to a total volume of 135 ml. and duplicate cyanamide and urea determinations were made on 25 ml. aliquots from single culture set-ups. The reactions of the extracts were also determined.

A comparable treatment for each of the materials used, except that 10.0 ml. of 0.345 N oxalic acid made up part of the 35 ml. volume of solution added for favorable moisture conditions, was set up. The oxalic acid was used to precipitate the calcium and acidify the solution.

The results of these experiments are found in Table 23, Treatments 1 through 11. The 0.5 gm. of manganese dioxide treatment, though somewhat effective without the oxalic acid treatment, proved much more so with the acid treatment. A high urea concentration resulted, as well as some ammonia which was detected by qualitative tests. The unusual

TABLE 23

Effect of Manganese Compounds on Cyanamide Conversion

No.	Time hrs.	Treatment 0.1 gm. cyanamid	Compound gm. added		Acid[1] ml. added		Urea-N		Cyanamide-N		pH of extract
							mg.	%*	mg.	%*	
1	72	200 gm. Silica sand	None		None		**2.66**	**12.5**	14.95	70.5	8.0
2	72		"		$H_2C_2O_4$	10	**3.89**	18.3	12.85	60.6	3.0
3	72		MnO_2	0.5	None		0.63	3.0	9.73	45.9	8.0
4	72		Ditto	0.5	$H_2C_2O_4$	10	14.84	70.0	0.42	2.0	8.0
5	72		K_2MnO_4	0.3	None				2.52	11.9	
6	72		$Mn(C_2H_3O_2)_2$	0.3	"		Trace	-	9.14	43.1	8.0
7	72		Ditto	0.3	$H_2C_2O_4$	10	"	-	14.21	67.0	5.5
8	72		$MnCO_3$	0.3	None		2.10	9.9	14.14	66.7	8.0
9	72		Ditto	0.3	$H_2C_2O_4$	10	1.05	5.0	14.88	70.2	8.0
10	72		$MnSO_4$	0.3	None		1.09	5.1	9.94	46.9	8.0
11	72		Ditto	0.3	$H_2C_2O_4$	10			11.10	52.3	3.0
12	24		None		None		1.14	5.4	15.27	72.0	8.0
13	24		MnO_2	0.3	"		1.40	6.6	16.07	75.8	8.0
14	24		Ditto	0.3	$H_2C_2O_4$	6	9.10	42.9	7.74	36.5	8.0
15	24		"	0.3	Ditto	10	9.45	44.5	7.39	34.8	8.0
16	24		"	0.3	"	15	8.30	39.1	8.33	39.3	8.0
17	24	35 ml. solution	None		None		1.47	6.9	15.80	74.5	8.0
18	24		MnO_2	0.3	"		1.40	6.6	14.36	67.7	8.0
19	24		Ditto	0.3	$H_2C_2O_4$	10	10.21	48.1	6.01	28.3	7.5
20	24		"	0.3	HCl	21	14.52	68.5	None	-	6.5
21	24		"	0.1	$H_2C_2O_4$	10	2.19	10.3	15.65	73.8	7.5
22	24		"	0.1	HCl	21	14.36	67.7	1.21	5.7	6.5
23	24	200 gm. Berrien soil	MnO_2	0.3	None		4.70	22.2	1.76	8.3	7.5
24	24		None		"		0.08	0.4	12.47	58.8	7.5

* 21.21 mg. of nitrogen added as cyanamid.

[1] $H_2C_2O_4$- 0.345N; HCl - 0.102N

feature of the results of this acid treatment on the manganese dioxide is that it effected almost complete conversion of the cyanamide to urea; about 2.0 per cent of the 21.21 mg. of cyanamide nitrogen added as cyanamide still remained in solution at the end of 72 hours, about 70 per cent existed as urea and some in the form of ammonia.

Potassium permanganate (0.3 gm.) was effective in reducing cyanamide concentration to a very low level, although no decomposition product was determined.

The manganous salts (0.3 gm.) were not very active in removing cyanamide from solution. The manganous acetate was somewhat active in the alkaline medium but not in the slightly acid medium. Manganous carbonate failed to lower significantly the cyanamide concentration, with or without the acid treatment. The pH, however, was not reduced by the quantity of oxalic acid added. Although manganous sulphate lowered the cyanamide concentration to some extent, a corresponding increase in urea concentration was not found.

Another series of experiments was carried out using a lower concentration of manganese dioxide (0.3 gm.) and three levels of acid treatment. These were carried out in a manner similar to the previous series except that the period between setting up the cultures and extraction was 24 hours instead of 72. The results are reported in Table 23, Treatments 12 through 16. Treatment 12 represents a control. The acid treatments produced a large, yet uniform reduction in cyanamide concentration, whereas the no acid treatment failed to reduce the concentration below that of the control. High urea concentrations, resulting from the decomposition of the cyanamide, were again significant and ammonia in small concentrations was detected qualitatively. The lower manganese dioxide treatment (0.3 gm.) was not as effective as the larger treatment (0.5 gm.) of the previous series.

The results of another series of experiments are reported in Table 23, Treatments 17 through 22, in which the effect of oxalic acid and hydrochloric acid on manganese dioxide and cyanamide decomposition was studied. These studies were made in solution cultures rather than in sand cultures. Again the manganese dioxide treatment without the acid was relatively ineffective in reducing the cyanamide concentration or increasing the urea concentration beyond that of the control. The oxalic acid treatment reduced the cyanamide concentration to 28.3 per cent and increased the urea concentration to 48.1 per cent (Treatment 19). The manganese dioxide, along with the hydrochloric acid treatment, resulted in an even greater reduction or complete removal of the cyanamide from solution. A corresponding increase in urea concentration, 68.5 per cent, resulted. A more acid reaction resulted from the hydrochloric acid treatment than that of the oxalic acid treatment.

The oxalic acid treatment with the lower manganese dioxide concentration (0.1 gm.) failed to effect a reduction in the cyanamide concentration or an increase in urea concentration (Treatment 21). The hydrochloric acid treatment was effective, however, but the complete removal of the cyanamide was not effected (Treatment 22) as occurred at the higher manganese dioxide treatment (Treatment 20).

The Effect of Manganese Dioxide on Cyanamide Conversion in Berrien Soil: The effect of manganese dioxide on the conversion of cyanamide in an inactive Berrien sandy soil (pH 5.9) is indicated in the results of Treatments 23 and 24 of Table 23. In these treatments, set up in duplicate, 0.3 gm. of manganese dioxide was mixed with 0.1 gm. of cyanamide and distributed in 200 gm. of soil. The soils were brought to a favorable moisture content and incubated at room temperature for 24 hours. The extractions were made as previously described for soils, and cyanamide and urea were determined on 25 ml. aliquots of the total 125 ml. of extract.

The manganese dioxide treatment was very effective in reducing the concentration of cyanamide in the soil extract (8.2 in contrast to 58.8 per cent for the control). Higher urea concentrations were found as well as higher ammonia concentrations, although the latter were not determined quantitatively.

The Effect of Manganese Dioxide on Cyanamide Toxicity in Germination Tests: In the germination tests, the procedure described in the part of this report devoted to sugar studies, additions of 0.1 and 0.2 gm. of manganese dioxide failed to improve the germination of wheat with 0.1 gm. of cyanamid used per 200 gm. of silica sand. The 0.3 gm. of manganese dioxide treatment raised the germination percentage from 26 for the control to 47 per cent. The 10 ml. of 0.102 N hydrochloric acid treatment, along with 0.3 gm. of manganese dioxide, raised the germination of the wheat seeds to 79 per cent in the cyanamide treated silica sand.

The manganese studies indicate that manganous salts were not very effective in converting cyanamide to urea at the concentrations used. Manganese dioxide was very effective in acid media in decomposing cyanamide to urea. Potassium permanganate was also very effective in removing cyanamide from solution, although the nature of the decomposition product was not determined.

The mechanism of manganese catalysis on cyanamide conversion is not known as far as the writer is aware. The conversion of cyanamide to urea, in the literature which was reviewed, has been designated as a hydrolysis reaction with oxidation not mentioned in the chemistry of cyanamide conversion. The possibility of oxidation is suggested by the fact that the manganous salts failed to induce conversion to any great extent, yet the manganese dioxide along with the acid treatment, in which a reduction in valence occurs, effected almost complete conversion of cyanamide to urea in some instances.

The Effect of Iron Compounds on Cyanamide Conversion: A series of experiments was carried out to determine the effect of various iron salts on cyanamide conversion. Two oxides, Fe_2O_3 and Fe_3O_4, were used in this series along with ferric and ferrous carbonate, sulphate, oxalate and chloride. The 0.1 gm. of cyanamid and 0.3 gm. of the iron compounds were well mixed and this mixture distributed in 200 gm. of silica sand. Thirty ml. of solution, containing 5.4 ml. of 0.345 N oxalic acid to precipitate the calcium, was added to each culture to provide a favorable moisture content. These stood 72 hours at room temperature, after which they were extracted in the usual manner to a total volume of 125 ml. of extract. The treatments were set up singly and cyanamide and urea determinations were made on duplicate 25 ml. aliquots of the extract. The results of these experiments appear in Table 24.

For the concentration of iron compounds used, only the ferric carbonate significantly lowered the cyanamide concentration in 72 hours with a corresponding increase in urea concentration. Except for the

TABLE 24

Effect of Iron Compounds on Cyanamide Conversion

Treatment	ml. 0.345N oxalic acid	Urea-N		Cyanamide-N	
0.1 gm. cyanamid per 200 gm. of Silica sand - 72 hr. time interval		mg.	%*	mg.	%*
Control	5.4	0.56	2.6	15.30	72.1
0.3 gm. Fe_3O_4	5.4	0.67	3.2	15.02	70.8
0.3 gm. Fe_2O_3	5.4	0.77	3.6	15.05	71.0
0.3 gm. $FeCO_3$	5.4	1.79	8.4	14.63	68.5
0.3 gm. $Fe_2(CO_3)_3$	5.4	4.41	20.8	11.66	55.0
0.3 gm. $FeSO_4$	5.4	0.95	4.5	13.86	65.4
0.3 gm. $Fe_2(SO_4)_3$	5.4	2.21	10.4	14.07	66.3
0.3 gm. FeC_2O_4	5.4	0.81	3.8	13.86	65.4
0.3 gm. $Fe_2(C_2O_4)_3$	5.4	1.16	5.5	14.39	67.8
0.3 gm. $FeCl_2$	5.4	0.91	4.3	14.46	68.2
0.3 gm. $FeCl_3$	5.4	2.24	10.6	14.04	66.2

* 21.21 mg. of nitrogen added as cyanamid.

carbonate, no great differences existed in the results between the ferrous and the ferric salts.

The effect of the oxide of iron, Fe_2O_3, was further studied over a longer period of time in silica sand cultures. The powdered oxide adheres to the sand particles and 1.0 gm. of Fe_2O_3 to 200 gm. of sand provides a large surface exposure of the oxide. A 0.1 gm. sample of cyanamid was mixed with the oxide-sand preparation, brought to a favorable moisture condition and allowed to stand at room temperature. Extractions from duplicate treatments were made at 12, 24, 48 and 72 hour intervals and cyanamide and urea determinations were made on 25 ml. aliquots of the 150 ml. volume of extract.

Coincident with the tests using Fe_2O_3, activated carbon was tested in a similar experiment, using 1.0 gm. of carbon and 0.1 gm. of cyanamid to 200 gm. of sand. The carbon did not adhere to the surface of the sand particles. The results of these experiments are found in Table 25.

The oxide of iron, Fe_2O_3, showed no positive capacity to convert cyanamide in 72 hours. The activated carbon, however, was active in removing cyanamide from solution in 72 hours, but was primarily an adsorption of either cyanamide or one of its decomposition products. This is indicated by the reduction in the total nitrogen, as well as the cyanamide, in the extract. Urea concentrations did not increase materially.

<u>The Effect of Quinone, Quinhydrone, Hydroquinone and Aluminum Compounds on Cyanamid Conversion</u>: The results of a series of experiments using aluminum compounds and hydroquinone in silica sand cultures are reported in Table 26, Treatments 1 through 13. The 0.1 gm. of cyanamid and 0.3 gm. of the respective compounds were well mixed, distributed in

TABLE 25

Effect of Fe_2O_3 and Activated Carbon on Cyanamide Conversion

Treatment 0.1 gm. cyanamid per 200 gm. of Silica sand	Time hours	Total-N mg.	Total-N %*	Urea-N mg.	Urea-N %*	Cyanamide-N mg.	Cyanamide-N %*
Control	12	19.48	91.8	0.40	1.9	16.00	75.4
	24	19.57	92.3	1.68	8.8	15.25	71.9
	48	19.11	90.1	1.68	8.8	14.70	69.3
	72	19.23	90.7	2.10	9.9	14.03	66.2
1.0 gm. Fe_2O_3	12	19.82	93.5	0.80	3.8	16.17	76.2
	24	19.61	92.5	1.26	5.9	14.99	70.7
	48	19.11	90.1	1.26	5.9	14.78	69.7
	72	18.68	88.1	1.26	5.9	14.41	67.9
1.0 gm. activated carbon	12	10.92	51.5	0.80	3.8	10.25	48.3
	24	10.67	50.3	0.84	3.9	8.48	40.0
	48	8.99	42.4	0.84	3.9	6.72	31.7
	72	7.26	34.2	1.26	5.9	5.21	24.6

* 21.21 mg. of nitrogen added as cyanamid.

TABLE 26

Effect of Quinone, Quinhydrone, Hydroquinone and Aluminum Compounds on Cyanamide Conversion

No.	Treatment	Time hrs.	Acid ml.	Urea-N		Cyanamide-N		pH of extract
				mg.	%*	mg.	%*	
	0.1 gm. cyanamid per 200 mg. Silica sand		0.345N oxalic					
1	Control	72	None	2.66	12.5	14.95	70.5	8.0
2	0.3 gm. aluminum dust	72	"	2.35	11.1	12.50	58.9	8.0
3	Ditto	72	10	2.14	10.1	9.24	43.6	5.5
4	0.3 gm. aluminum hydroxide	72	None	2.31	10.9	14.84	70.0	8.0
5	Ditto	72	10	2.49	11.7	14.14	66.7	3.0
6	0.3 gm. aluminum carbonate	72	None	2.59	12.2	14.60	68.8	8.0
7	Ditto	72	10	1.02	4.8	16.45	77.6	5.5
8	0.3 gm. aluminum oxide	72	None	2.07	9.8	14.04	66.2	8.0
9	Ditto	72	10	1.54	7.5	14.77	69.6	5.5
10	0.3 gm. aluminum sulphate	72	None	0.98	4.6	15.82	74.6	5.5
11	Ditto	72	10	2.98	14.1	14.35	67.7	3.0
12	0.3 gm. hydroquinone	72	None	0.91	4.3	2.03	9.6	
13	Ditto	72	10	1.65	7.8	0.56	2.6	
	0.1 gm. cyanamid per 35 ml. of solution		0.102N HCl					
14	Control	24	None			16.07	75.8	8.0
15	Control	24	21			16.33	77.0	3.0
16	.05 gm. hydroquinone	24	None	2.34	11.0	4.20	19.8	8.0
17	Ditto	24	21	1.06	5.0	12.25	57.8	3.0
18	.05 gm. quinhydrone	24	None	0.38	1.8	2.38	11.2	8.0
19	Ditto	24	21	0.23	1.1	7.56	35.6	3.0
20	.05 gm. quinone	24	None	0.34	1.6	5.41	25.5	8.0
21	Ditto	24	21	0.42	2.0	8.32	39.2	3.0

* 21.21 mg. of nitrogen added as cyanamid.

200 gm. of silica sand, brought to a favorable moisture content and allowed to stand for 72 hours. An acid treatment of each one of the compounds consisted of sufficient oxalic acid to induce an acid reaction and precipitate the calcium of the cyanamid. The treatments were set up singly and cyanamide and urea determinations were made on duplicate 25 ml. aliquots of 125 ml. total volume of extract. Determinations of pH were also made.

None of the aluminum compounds were particularly effective in reducing the cyanamide concentrations or increasing the urea concentrations during the 72 hour period. Aluminum dust had some effect which was increased by the acid treatment.

Hydroquinone was definitely effective in reducing cyanamide concentration and the acid treatment increased its effectiveness. Urea concentrations were not accordingly increased so the nature of the decomposition product was not determined. That hydroquinone may have served in the capacity of an oxidation-reduction system suggested further study of this and related compounds. Since hydroquinone, quinone and quinhydrone are not stable in solution and serve as oxidation-reduction systems, all three were used in solution culture studies.

Quantities of 0.05 gm. of each compound were added to 35 ml. of water containing 0.1 gm. of cyanamid. An acid treatment of 21 ml. of 0.102 N HCl as part of the 35 ml. of water was also used. These were allowed to stand 24 hours before extracting and washing to an extract volume of 135 ml. Cyanamide and urea were determined on duplicate 25 ml. aliquots of each treatment. Since hydroquinone is more stable in alkaline solution and would partially change to quinone in an acid solution, and since quinone is more stable in acid solution and would change to hydroquinone in an alkaline solution, it was believed possible that this experiment might reveal whether a reducing or an oxidizing system was responsible for the catalysis. The results of this experiment are reported in Table 26, Treatments 14 through 21.

With all three compounds - hydroquinone, quinone and quinhydrone - reductions in cyanamide concentration resulted in the non-acid treatment which are considered extremely significant for the concentrations of the compounds used. The acid treatment, which induced an acid reaction of the extract, inhibited cyanamide conversion to some extent with all three compounds but to a greater extent for the hydroquinone. A lack of urea accumulation indicates that it is not the primary product of cyanamide conversion. These data show that these compounds are effective in removing cyanamide from solution and that they are more effective in alkaline than in acid solutions. It cannot be stated, however, from these results, whether or not an oxidation-reduction reaction is involved in the catalysis of these compounds.

DISCUSSION AND SUMMARY

This investigation was undertaken for the purpose of securing a better understanding of soil conditions and constituents which are responsible for the rapid decomposition of cyanamide and ascertaining, if possible, by laboratory studies, under what conditions this nitrogenous fertilizer can be used with confidence that detrimental results will not be incurred.

The investigations included the following: (1) A detailed study of the decomposition of cyanamide and nitrogen transformation in an acid

Fox sandy loam soil; (2) The nitrification of added urea and ammonium sulphate nitrogen in the same soil; (3) The rate of disappearance of cyanamide from the soil solution of a number of soils, including five lateritic soils; (4) The effect of soil reaction on the rate of cyanamide disappearance from the soil solution and the nature of the decomposition of the cyanamide; (5) The effect of soil organic matter and crop residues added to the soil on cyanamide decomposition; (6) The catalytic effect of the hydrogen ion concentration, manganese compounds, iron compounds, aluminum compounds, activated carbon, quinone, hydroquinone, and quinhydrone on the decomposition of cyanamide.

Studies were made by treating soils with quantities of commercial cyanamid maintaining at favorable moisture conditions in tumblers for given intervals and then extracting the soils. Cyanamide and its decomposition and transformation products were determined in the soil extracts and on the extracted soils. The effect of organic matter content and of added organic materials was studied by removing the organic matter from the soil by ignition and by the addition of crop residues to the soil. These soils were treated with cyanamid and the quantities of cyanamide and its decomposition products were determined at given intervals of time. The humus was also extracted from the soil and its effects were studied in cyanamide treated solution cultures. The effect of the various catalysts were studied in solution or silica sand cultures and when added to the soil.

It was found that cyanamide decomposes actively in Fox sandy loam, passing readily through the urea and ammonia stages. High concentrations of ammonia persisted and nitrification of the cyanamide nitrogen was retarded until the fifth week, from which time it nitrified rapidly. An attempt to account for the added nitrogen revealed that 20 to 35 per cent remained unaccounted for in the soluble forms of nitrogen and fixed ammonia throughout the fifteen weeks of study.

Two moisture levels below the optimum moisture content effected no great change in the rate of cyanamide disappearance in the Fox sandy loam soil. Urea concentrations were maintained at slightly higher levels and over a longer interval of time at the lower moisture levels and nitrification was somewhat slower. Retardation of nitrification of cyanamide nitrogen was again exhibited, though active calcium was supplied to this acid soil by the cyanamid and a more favorable reaction for nitrification resulted from the cyanamid treatment. It appears that low moisture contents do not seriously interfere with the rate of disappearance of cyanamide from solution if it is well mixed in the soil and there is sufficient moisture present to effect hydrolysis of the cyanamide. The moisture content at which hydrolysis will proceed under such conditions seems to be considerably below the optimum moisture content of this soil.

Since urea was found to be the primary decomposition product of cyanamide in the Fox soil, nitrogen was added as urea to study the nitrification capacity of this soil in the absence of the cyanamide ion, the added calcium and more favorable reaction of the cyanamid treatment. Urea was found to nitrify very rapidly in the presence of ammonia concentrations which were greater than those which existed in the cyanamid treatment. From this it was concluded that the ammonia concentrations were not the cause of the retardation of nitrification of the cyanamide nitrogen in this soil. Nitrogen added as ammonium sulphate to the Fox soil failed to nitrify to any great extent throughout the period of study, indicating that cyanamid may occupy a more favorable position as far as the nitrification of the nitrogen is concerned in some acid soils.

Cyanamide was found to decompose rapidly to urea and ammonia in the five lateritic soils studied. The rate of ammonification of the urea varied between soils, probably due to the low biological activity in some samples which were subsoils. The high conversion capacity of laterite subsoil samples, low in organic matter and biological activity, identifies the inorganic colloids as the major catalysts in cyanamid conversion to urea in these soils. In view of the high conversion capacity of the lateritic soils, it is believed that the use of cyanamid may provide an economic means of not only supplying nitrogen but also active calcium in a nitrogenous fertilizer program in tropical agriculture.

In a comparative study of the rate of cyanamide disappearance from a number of non-lateritic soils, it was found that four out of the six alkaline or neutral soils were inactive. The high organic matter content (15 to 20 per cent) of the two active alkaline soils probably offset, to a certain extent, the retarding influence of the alkalinity and gave these soils a relatively high activity in removing cyanamide from solution. Two acid soils, one quite sandy and the other a sandy loam, both low in organic matter and colloidal content, were found inactive. All other acid soils were found to be quite active. A very acid muck proved to be much more active than one of pH 6.7 taken from an adjacent area which had been burned over.

Further studies on the effect of soil reaction on cyanamide decomposition showed that liming a Fox soil to two pH levels reduced the rate at which cyanamide disappeared from solution, especially at the higher level of pH 6.9. Increasing the acidity of an inactive alkaline Wisner soil by sulphur treatments, induced a slight but significant increase in the rate of removal of cyanamide from solution. The results of these studies conform with those of other investigators in that cyanamide decomposes very slowly in alkaline soils, unless they are very high in organic matter content, and in acid soils which are very low in organic matter and inorganic colloidal content.

Studies of the effect of soil organic matter on cyanamide decomposition, carried out by removing the organic matter by ignition at 325° C. for 10 hours, showed that this treatment greatly reduced the capacity of the soils to remove cyanamide from solution or to decompose it to any great extent over a period of five days. These studies also revealed that this treatment reduced the five soils used in the study to about the same level in their capacity to remove cyanamide from solution. The assignment of the conversion capacity to the organic constituents of the soil is not made on the basis of these results, since the pH values were raised and oxidation and dehydration of the inorganic colloids undoubtedly occurred, which destroyed their catalytic activity.

The studies on the role of extracted humus on cyanamide conversion and removal from solution failed to ascribe any conversion or adsorptive properties to this soil constituent. The nature of the humus from four different soils and variation in concentration of humus extract showed no effect on rate of cyanamide decomposition under the conditions in which the experiment was carried out. It is recognized, however, that in the extraction process, the form and activity of the humus was modified; furthermore, its actual concentration and surface exposed to the cyanamide as it exists in the soil was not duplicated.

The effect of the addition of various crop residues, which were permitted to decompose for two years, to an inactive Hillsdale sandy loam soil failed to increase the rate of disappearance of cyanamide from the soil solution. The nature of the humus formed from the decomposition of the various materials added was not reflected significantly in the results. This same soil pre-treated for a few days with alfalfa induced rapid rate of cyanamide removal from solution in 48 hours.

Similar pre-treatments with alfalfa or straw on two other inactive soils induced rapid disappearance of the cyanamide from solution within 24 hours. The nature of the decomposition products produced in the reduction of cyanamide concentration showed that decomposition to urea and ammonia was the probable major effect, rather than mere adsorption of the cyanamide ion.

Low temperatures of 5 to 10° C. slowed up the rate of cyanamide disappearance in the sand, regular soil and pre-treated soils to a great extent.

Water extracts of the crop residues and organic materials used exhibited some effect on cyanamide removal from solution at the higher concentrations used in an alkaline medium. These effects were not as great under these conditions as they were when equivalent quantities were added to the soil.

The studies of the effect of pre-treatment with fresh crop residues suggested the possibility of enzyme catalysis studies on cyanamide conversion which yielded some positive results in preliminary studies.

Increased hydrogen ion concentration failed to show any catalytic activity in cyanamide conversion in which oxalic acid was used to influence the equilibrium reaction of cyanamide hydrolysis by precipitating the calcium and inducing an acid medium of various hydrogen ion concentrations. From these studies and a review of those reported by other investigators, it is believed that the hydrogen ion plays an indirect role, in that acid conditions affect the physico-chemical state of the organic and inorganic colloids and other catalytic agents in the soil, in which state they more effectively function as catalysts and play the dominant role in decomposing cyanamide to urea and ammonia.

Studies with sugars revealed that reducing sugars are effective in removing cyanamide from solution and permitting normal germination of wheat seeds at certain concentrations. The nature of the effect was found to be primarily the formation of dicyanodiamide and decomposition products other than urea and ammonia. The effect of reducing sugars was found to be inhibited by an acid medium. In view of the nature of the decomposition product and other evidence available, it was concluded that reducing sugars are not the active catalysts in the effect of fresh crop residue pre-treatments on cyanamide conversion in the inactive soils studied. The use of reducing sugars in soils or as an ingredient of the fertilizer is limited by the nature of the decomposition product and the concentration of sugar necessary to promote rapid conversion.

The catalytic activity of manganese compounds on cyanamide conversion revealed that manganese dioxide was an active catalyst in changing cyanamide to urea in an acid medium. This effect was only slightly in evidence in an alkaline medium. Germination tests demonstrated reduced cyanamide toxicity where manganese dioxide was added in an acid medium. Potassium permanganate also proved effective in removing cyanamide from solution. Several manganous salts failed to produce any evidence of catalytic activity. Oxidation was suggested as the mechanism of manganese catalysis, since only where a reduction in valence was involved was there evidence of activity.

Oxides of iron failed to demonstrate any effect on cyanamide conversion. Of several ferrous and ferric salts studied, only ferric carbonate showed a significant effect on the conversion of cyanamide at the concentrations used.

Activated carbon demonstrated a high capacity to remove cyanamide from solution and the nature of the removal was established as adsorption of cyanamide or its decomposition products and not to the conversion to urea or other soluble forms of nitrogen over the period studied.

The various aluminum compounds used in the studies exhibited no significantly strong catalytic power in cyanamide conversion at the concentrations used.

Quinone, hydroquinone and quinhydrone all proved active in removing cyanamide from solution at the concentration used; however, urea was not the decomposition product as far as could be ascertained. An attempt to determine if oxidation or reduction might be involved in the mechanism of catalysis in these studies failed to provide any positive evidence.

LITERATURE CITED

1. ALLISON, F. E. The effect of application of cyanamid on nitrate content of field soils. Jour. Agr. Res., 34:657-662. 1927.

2. BUCHANAN, G. H., and BARSKY, GEORGE. The hydrolysis and polymerization of cyanamide in alkaline solutions. Jour. Amer. Chem. Soc., 51:195-205. 1930.

3. CARTER, L. S. Some chemical and biological changes produced in a Fox sandy loam by certain soil management practices. Soil Sci., 40:223-236. 1935.

4. CONRAD, JOHN P. Hydrolysis of urea in soils by thermolabile catalysts. Soil Sci., 49:253-265. 1940.

5. CONANT, J. B. Chemistry of organic compounds. McMillan Co., New York. 1933.

6. COWIE, G. A. Decomposition of cyanamide and dicyanodiamide in the soil. Jour. Agr. Sci., 9:113-133. 1919.

7. __________. Mechanism of the decomposition of cyanamide in the soil. Jour. Agr. Sci., 10:163-176. 1920.

8. CROWTHER, E. M., and RICHARDSON, H. L. The decomposition of calcium cyanamide in the soil and its effects on germination, nitrification and soil reaction. Jour. Agr. Sci., 22:300-334. 1932.

9. FINK, D. S. Soil factors which prevent toxicity of calcium cyanamide. Jour. Amer. Soc. Agron., 26:929-939. 1934.

10. FOX, E. J., and GELDARD, W. J. The determination of urea alone and in the presence of cyanamide. Ind. Eng. Chem., 15:743. 1923.

11. JACOB, K. D., ALLISON, F. E., and BRAHAM, J. N. Chemical and biological studies with cyanamid and some of its transformation products. Jour. Agr. Res., 28:37-70. 1932.

12. MCCOOL, M. M. Properties and uses of calcium cyanamide. Boyce Thompson Institute Professional Paper, 1 (24). 1933.

13. MITCHELL, J. The origin, nature and importance of soil organic constituents having base exchange properties. Jour. Amer. Soc. Agron., 24:256-275. 1932.

14. MUKERJI, K. B. Microbiological aspects of nitrification in soils under varied environmental conditions. Jour. Agr. Sci., 22:335-347, Part 2. 1933.

15. NIEDERL, J. B., and NIEDERL, V. Organic quantitative micro-analysis. John Wiley and Sons, New York. 1938.

16. PRANKE, E. J. Cyanamid, its manufacture, chemistry and uses. Chem. Pub. Co., Easton, Pa. 1913.

17. RHODIN, S. Continuation of field trials with newer nitrogenous fertilizers. Kg. Land. Akad. Hand. Tid., 57:443. Chem. Abst., 13: 986. 1918.

18. SMOCK, R. M. Some physiological studies with calcium cyanamide and certain of its decomposition products. Ohio Agr. Exp. Sta. Bul. 555. 1935.

19. WAKSMAN, S. A. Humus. The Williams and Wilkins Co., Baltimore. 1936.

20. WILLIAMS, H. The chemistry of the cyanogen compounds. P. Blakeston's Son & Co., Philadelphia, Pa. 1915.

21. YONEDA, SHIGO. The catalytic action of colloidal constituents on conversion of cyanamide. Jour. Sci. Soil Manure. Japan. 11:447-454. 1937. Chem. Abst., 32:701. 1937.