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Some effects of ammonium sulfate on soils

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Some Effects of Ammonium Sulfate on Soils

R. W. Ruprecht, B. Sc.

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by

R. W. Ruprecht, B. Sc.

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SOME EFFECTS OF AMMONIUM SULFATE

ON SOILS.

SOME EFFECTS OF AMMONIUM SULFATE ON SOILS.

By R. W. Ruprecht, B. Sc.

For some years the crops of two of the plots on one of the fields of the experiment station farm had been very poor. These two plots had been receiving ammonium sulfate as a source of nitrogen for a long period of years and it seemed evident that the poor yield might be due to the continued use of this salt. In order to determine whether or not this was the case, the following investigations were undertaken.

Considering the general use of ammonium sulfate as a fertilizer and the reputation it has acquired of causing so-called acid soils, it is strange that so little work of a chemical nature has been done to determine to what the bad effects are due. Most of the work has consisted in finding methods for determining the acidity of these soils and in conducting field experiments. One of the earliest investigators who worked with ammonium sulfate on soils was Way[1]. He found that the ammonia was

1. Jour. Roy. Agr. Soc., Vols. 11 and 13.

retained by the soil and that the sulfate ions united with the calcium in the soil and were subsequently removed in

the drainage waters as calcium sulfate. In a second paper he attributes the absorption to the presence in the soil of double silicates of aluminum and lime, and aluminum and potash. Voelcker[1] who continued the investigations

1. Jour. Roy. Agr. Soc., Vols. 21, 60, 62.

started by Way states as one of the conclusions that the acid radicals are not absorbed by the soil and that soils will absorb more ammonia from strong solutions than from weak ones. Lawes and Gilbert[2] in their studies of drainage

2. Roth. Mem., Vol. V., p. 97.

waters at Rothamstead found that the annual loss of calcium and magnesium by drainage from a continuously unmanured wheat plot was about 223 pounds, while where ammonium salts had been applied the loss was 389 pounds. In conclusion they say, "When ammonium salts are applied to the land the quantity of matter removed is much increased. The solid matter removed by the agency of ammonium salts consists chiefly of sulfate, chloride and nitrate of calcium. Probably the whole of the sulfates contained in ammonium salts unites with calcium and magnesium".

Wheeler[3] found that the continued use of ammonium

3. R. I. Expt. Sta., Ann. Rpt., 1893.

sulfate brought the soils into an acid condition and that liming corrected this acidity. In a later publication[4]

4. R. I. Expt. Sta., Bul. 62.

he describes various methods of determining the acidity or lime requirements of the soil.

Hall and Gimingham[1] found that continuous application of ammonium salts brought soils into acid condition, but that this was not the case where an abundance of lime was present. They further found that the acid radical was not fixed by the soil and that the absorption of ammonia from its salts by light grey clay produced no free acid and no change in the reaction of the salt solution. They concluded that the action was one of double decomposition between calcium humate and ammonium salts with the ammonia replacing the calcium, magnesium and potassium.

1. Jour. Chem. Soc., Vol. 91 (1907), p. 677.

None of the investigators separated or determined what this acid was which gave the so-called acid reaction to the soil.

The field from which the samples were taken is on the experiment station farm and known as Field A, or the nitrogen field. It was first laid out in its present form in 1883 and has been under the present fertilizer scheme since 1889.

The field is divided into eleven plots of one-tenth acre area each with a four foot row between the plots. Each plot is, in addition, divided into two sections, one of which is limed and the other unlimed. The soil is a fine sandy loam with a clay subsoil. Each of the plots has

a two-inch tile drain running through the center of the plot at an average depth of two feet. The drains open into a larger drain running the whole length of the field. This main drain is laid at a depth of four feet and consists of six-inch round tiles.

The following fertilizers have been applied[1] during each of the past twenty-five years.

Plot	Source of Nitrogen	Source of Potash	Source of Phosphoric Acid.
0	Barnyard manure[2]	--	--
1	Nitrate of soda	Muriate of potash	Dissolved bone-black
2	Nitrate of soda	Sulfate of potash-magnesia	Dissolved bone-black
3	Dried blood	Muriate of potash	Dissolved bone-black
4	Nothing	Sulfate of potash-magnesia	Dissolved bone-black
5	Sulfate of ammonia	Sulfate of potash-magnesia	Dissolved bone-black
6	Sulfate of ammonia	Muriate of potash	Dissolved bone-black
7	Nothing	Muriate of potash	Dissolved bone-black
8	Sulfate of ammonia	Muriate of potash	Dissolved bone-black
9	Nothing	Muriate of potash	Dissolved bone-black
10	Dried blood	Sulfate of potash-magnesia	Dissolved bone-black

1. The materials are used at the following rates per acre:

	Pounds.
Nitrate of soda, ...	290
Sulfate of ammonia, ...	225
Dried blood, ...	525
Muriate of potash, ...	250
Sulfate of potash, ...	485
Dissolved bone-black, ...	500
Manure, ...	8,000

2. In addition, nitrate of soda, dissolved bone-black and sulfate of potash-magnesia have been applied to equalize the nitrogen, phosphoric acid and potash on plots 1-10.

One-half of each plot received an application of lime in 1909 and 1913 and the whole field was limed in 1898 and 1905. The lime was applied at the rate of one ton per acre in 1898 and 1905 and at the rate of two tons in 1909 and 1913.

During the twenty-four years of the experiment the crops grown have been: 1890, oats; 1891, rye, 1892, soy beans; 1893, oats; 1894, soy beans; 1895, oats; 1896, soy beans; 1897, oats; 1898, oats; 1899, clover; 1900, potatoes; 1901, soy beans; 1902, potatoes; 1903, soy beans; 1904, potatoes; 1905, oats and peas; 1906, corn; 1907, clover; 1908, clover; 1909, clover; 1910, clover; 1911, corn followed by clover; 1912, corn followed by clover; and 1913, millet.

Of the crops which have come under the observation of the author, the clover has made the poorest growth. The clover was planted in the corn in the early fall and made a fair catch. As soon as the corn was cut the clover began to go back and before the first frost the unlimed ends of the plots had pretty well died down. The following spring showed that most of the clover which had not died in the fall had been winterkilled or else badly heaved. This was soon choked out by the growth of weeds, which were largely chickweed. The worst plots in the field were the unlimed ends of plots 5 and 6 which had very little vegetation of any kind. Plot 0 had a fair stand of clover with quite a few weeds. As it was evident that nothing would come of the clover, it was plowed

up and the field sown to corn.

The corn crop showed the greatest differences early in the season; plots 6 and 8, both ends, not having as good a stand as the other plots; plot 0 to all appearances had the best stand, being taller than any of the others. As the season advanced, the early differences disappeared to a large extent, only the unlimed ends still showing the differences. The leaves on the plants on plots 6 and 8 had a reddish striped appearance similar to those mentioned by Wheeler as occurring under similar conditions in Rhode Island.

On harvesting the crop the following yields were obtained:

Average Yields per Acre, 1912.

Plot.	Hard Corn, Ears (Bushels).	Soft Corn, Ears (Bushels).	Stover. (Pounds)
No nitrogen (4, 7, 9),	67.86	1.61	5,116.70
Nitrate of soda (1, 2),	93.00	1.79	5,700.00
Dried blood (3, 10),	89.57	1.31	5,450.00
Sulfate of ammonia (5,6, 8),	78.26	1.62	5,133.30
Manure (0),	80,00	1.29	5,000,00

Clover was again sown between the corn and, as in the previous year, made a fair stand so long as the corn remained uncut, after which it began to die down. In the spring the clover, being largely winterkilled, was plowed

under and Japanese millet sown.

The millet came up quite evenly on all the plots and made a good growth during the first part of the season. Plots 6 and 8, limed ends, had the best stand on the field. The unlimed ends also had a fair stand and about equal to any of the other unlimed ends. Owing to a continued dry spell the millet stopped growing about the third week in August, and the leaves began to turn yellow. It was cut September second and gave the following yields:

Average Yield per Acre.

Plot.	Pounds.
No nitrogen (4, 7, 9),	6,900
Nitrate of soda (1, 2),	10,125
Dried blood (3, 10),	11,200
Sulfate of ammonia (5, 6, 8),	6,900
Manure (0),	9,000

Chemical Work on Field A.

The plots chosen for further chemical study were plots 0, 1, 6, 7 and 8. All of these plots, 0 excepted, received their potash and phosphoric acid in the same form, the nitrogen only varying. The fertilizers applied were as follows:

Plot 0, manure,
" 1, nitrate of soda,
" 6, sulfate of ammonia,
" 7, no nitrogen,
" 8, sulfate of ammonia.

In addition to the above, all plots, except 0, received a like application of muriate of potash and dissolved boneblack. One-half of each plot received an application of lime in 1913. Plot 0 had the manure supplemented by an application of sulfate of potash-magnesia and dissolved boneblack.

Samples were taken in the spring of 1912 and 1913. In 1912 the samples were taken just before the fertilizers were applied and after the land had been plowed. In 1913 the samples were taken immediately after the lime had been applied and harrowed in. The samples were taken from both the limed and unlimed ends of the plots by means of a post-hole digger. A bushel sample was taken in every case, immediately mixed and air-dried. In subsampling, the soil was passed through a sieve having seven holes to the linear inch. As it was desired to have the soil in as near actual field conditions as possible, no finer sieve was used.

The largest part of the work was carried on with different strengths of ammonium sulfate solutions. Four different strengths were employed, i.e., N/10, N[1], 2 1/2 N, 5N.

1. N, in each case, meaning Normal.

Unless otherwise stated, the soil was treated as follows: One hundred and fifty grams of the air-dried soil were treated with 750 c.c. of the ammonium sulfate solution. The mixture was allowed to stand with frequent shakings for two hours and then filtered through an unwashed filter paper. In every case the filtrate was perfectly clear but colored yellow, the intensity varying with the strength of the sulfate solution used. The solutions were neutral to litmus and phenolphthalein.

The solutions were analyzed for the amount of ammonia absorbed, and for the iron and alumina, calcium, potassium, sodium and sulfates removed.

The Absorption of Ammonia.

The ammonia was determined by the magnesium oxide method[1]. From 1 to 10 c.c. of the solution was used for a determination according to the concentration of the solution. Table I gives the amounts, in grams, of ammonia absorbed by 100 grams of air-dried soil.

1. Bulletin 107, Bureau of Chemistry, p. 9, 1910 edition.

Table I.

Plot.	N/10 $(NH_4)_2SO_4$	N $(NH_4)_2SO_4$	2 1/2N $(NH_4)_2SO_4$
0 L*	.071	.213	---
0 UL	.060	.178	.170
1 L	.071	.175	.245
1 UL	.060	.200	.244
6 L	.076	.178	.175
6 UL	.041	.063	.115
7 L	.061	.200	.115
7 UL	.056	.125	.220
8 L	.064	.150	.155
8 UL	.041	.078	.195

* 0 L = Plot 0, limed end; 0 UL = Plot 0, unlimed end, etc.

The results obtained are similar to those reported by the early workers, namely, that with an increase in concentration of the ammonium sulfate solution an increase in the amount of ammonia absorbed is observed.

A comparison of the ammonia absorbed by the different plots shows that with two exceptions all the plots absorb the same amounts. The two exceptions--the unlimed ends of plots 6 and 8 show consistently a smaller absorption than any of the others. This is the first indication of some change due to the continued use of ammonium sulfate. The slight

variations in amount absorbed on the remaining plots is entirely within the limit of possible error[1].

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1. A difference of 1/100 cubic centimeter in taking the aliquot for a determination causing a ± error in ammonia absorbed from .01 gram in the case of the N/10 to .47 gram with the 5N.

This difference in the absorption capacity of the different plots is even more strikingly shown by a study of the dye absorption. The dyes used were aniline blue, aniline green and eosine. The eosine passed through the soil without any measurable absorption having taken place. One hundred cubic centimeters of the aniline blue and of the aniline green in concentrations below 50 parts per million were entirely decolorized by 10 grams of soil. The higher concentrations used were 50 and 100 parts per million.

Table II. Dye Absorption.*

Plot.	Aniline Blue 50 Parts per Million.	Aniline Blue 100 Parts per Million.	Aniline Green 100 Parts per Million.
0 L	.312	1.55	3.00
0 UL	.285	1.50	5.00
1 L	--	.88	3.33
1 UL	.233	1.06	4.03
6 L	.270	1.42	4.70
6 UL	.666	6.46	12.50
7 L	.250	1.60	4.00
7 UL	.303	1.76	5.25
8 L	.270	1.39	5.50
8 UL	--	2.24	8.00

* The figures give, in parts per million, the dye left in solution after shaking up 10 grams of soil with 100 c.c. of dye.

The dye seems to have a deflocculating effect on the clay in the soils, as they settle very much slower than with a corresponding water treatment. This is particularly noticeable on plot 1, the solution from the limed end of which even at the end of twenty-four hours, was still too turbid to be used in a colorimeter.

From a comparison of the dye absorption and the ammonia absorption, it would appear that the ammonia might be held by physical means rather than chemical. The proof at

present is insufficient, however, to warrant a definite statement to that effect.

The Removal of Calcium Oxide.

That ammonium sulfate has a solvent action on the calcium in the soil has been known for a number of years, many investigators[1] having shown this to be true. The

1. Way, Jour. Roy. Agr. Soc., Vols. 11 and 13.
Lawes and Gilbert, Roth. Mem., Vol. V., p. 97.
Armsby, Amer. Hour. Sci., 14 (1877), p. 25.
Van Bemmelen, Landw. Vers. Stat., Vol. 21.
Hall and Gimingham, Jour. Chem. Soc., Vol. 91 (1907),p. 677.

present experiments confirm these earlier results as will be seen by a study of Table III.

Table III. Calcium Oxide removed in Parts per 100,000.

Plot.	H_2O Extract	N/10 $(NH_4)_2SO_4$	N $(NH_4)_2SO_4$	2 1/2N $(NH_4)_2SO_4$	5N $(NH_4)_2SO_4$*
0 L	2.37	20.75	43.64	51.48	--
0 UL	1.41	12.39	21.69	23.31	--
1 L	2.19	19.13	41.09	48.57	34.20
1 UL	1.38	12.26	23.33	24.12	26.92
6 L	2.24	16.44	31.34	36.98	21.10
6 UL	1.56	3.64	5.42	5.05	10.78
7 L	2.09	19.81	41.04	48.77	35.10
7 UL	1.36	8.62	14.05	14.28	15.50
8 L	1.98	18.59	39.81	44.73	21.30
8 UL	1.64	7.41	12.02	12.13	13.17

* These figures are from 1912 soil samples.

A marked increase in the calcium removed by the agency of ammonium sulfate over that removed by water is noticed. Furthermore, with the increase in concentration of ammonium sulfate up to and including the normal solution, there is an increase in the amount of calcium removed. While the table shows an increase on the limed ends with the 2 1/2 Normal, this was due to the large amount of calcium hydrate applied just previous to sampling. The 1912 samples do not show this increase but behave similar to the unlimed ends in the present table.

The amounts removed from the limed ends of all the plots are practically the same with the exception of plot 6. The unlimed ends do not show this similarity, plots 6 and 8 having much less removed than any of the others. This indicates that the continued use of ammonium sulfate on these two plots has decreased their supply of calcium to a marked degree. This is further borne out by the determination of the total calcium in these soils which shows the unlimed end of plot 6 to be poorer in calcium than the others.

The question now arises, in what combination is the calcium removed from the soil. The earlier writers[1] are

1. Way, Jour. Roy. Agr. Soc., Vols. 11 and 13.
Lawes and Gilbert, Roth. Mem., Vol. V., p. 97.
Hall and Gimingham, Jour. Chem. Soc., Vol. 91 (1907),p. 677.

unanimous in the statement that the calcium unites with the acid radical and is removed as sulfate. Whether this is so in the present instance cannot be determined by a comparison

of the sulfates and calcium removed in the soil extracts owing to the unsatisfactory sulfate figures. A study of the composition of the drainage water from this field (Tables IV. and V.), however, would seem to indicate that the calcium is removed as sulfate. The ratio between the calcium and sulfates is a fairly constant one for each of the plots.

Table IV. Average Composition of Drainage Waters.

Parts per 100,000.

1912.

Plot	Total Solids.		Loss on Ignition		CaO		SO_3		Cl	
	Spring	Fall	Spring	Fall	Spring	Fall	Spring	Fall	Spring	Fall
0	16.86	17.95	5.0	6.6*	2.06	4.25	5.36	6.07	1.42	1.66
1	24.6	27.6	7.2	7.9	2.43	4.30	8.16	7.87	3.05	4.27
6	27.6	35.5	5.7	8.9	4.39	11.85	11.61	13.29	2.81	3.99
7	21.3	23.4	7.0	6.9	2.49	7.20	8.72	8.17	2.15	3.58
8	30.3	32.9	7.5	7.8	4.82	10.45	12.95	12.79	2.55	3.15

* One sample.

1913.

Plot	Total Solids		Loss on Ignition		CaO		NaCl & KCl	SO_3		Cl	
	Spring	Fall	Spring	Fall	Spring	Fall	Spring	Spring	Fall	Spring	Fal
0	17.9	22.6	3.78	6.4	4.05	4.51	5.0	6.92	7.67	1.26	1.45
1	22.7	27.5	3.50	5.0	3.82	3.99	10.2	6.86	7.61	3.19	4.97
6	24.0	33.1	5.46	6.3	6.71	8.30	4.6	8.88	11.13	2.79	4.83
7	20.2	26.9	4.72	6.0	5.24	6.73	4.9	6.49	6.65	2.72	5.62
8	26.4	36.8	5.28	6.5	8.03	9.67	5.2	9.79	11.70	2.88	5.35

Table V. Ratio of CaO to SO_3 in Drainage Waters.

1913.

Plot	Mar.9	Mar.14	Mar.21	Mar.28	Apr. 5	May 29	Dec. 6
0	1.60	1.82	1.65	1.82	1.59	1.90	1.70
1	2.03	1.67	1.65	1.92	1.87	--	1.90
6	1.29	1.39	1.32	1.40	1.33	1.44	1.34
7	1.10	1.34	1.29	1.11	1.17	1.22	--
8	1.51	1.10	1.19	1.24	1.17	1.35	1.20

A study of Table IV shows that there is more calcium being removed from the two sulfate plots 6 and 8 than from any of the others. Otherwise the drainage waters run very uniform. As the waters from the limed and unlimed ends of the plots cannot be kept separate, they do not show the differences due to liming one might expect.

The early writers further state that the ammonia absorbed replaces the calcium and have even in some cases[1] found the

1. Way, Jour. Roy. Agr. Soc., Vols. 11 and 13.

calcium removed to be exactly equal to the ammonia absorbed. This would not seem to be true with the soils here dealt with for three reasons: (1) while the amount of ammonia absorbed is alike on all the plots except 6 and 8 unlimed, the calcium removed varies between the limed and unlimed; (2) while the calcium removed reached a limit with the normal solution, the ammonia absorptions

increase with each concentration; (3) with but few exceptions the amount of ammonia absorbed is greater than the equivalent bases removed.

Sodium and Potassium Removed.

Owing to the large mass of ammonium sulfate and the small amounts of sodium and potassium in solution, it is difficult to make an exact determination of these elements. Several methods were tried, but the old Fresenius method of weighing the sodium and potassium as the combined chlorides and then determining the potassium as the chloroplatinate was finally adopted. The amounts of sodium and potassium are, as might be expected, very much smaller than the calcium. Like the calcium the amounts increase with the concentration of the solutions. Unlike calcium, however, the amounts removed from the limed and unlimed plots are of the same magnitude. The continued use of ammonium sulfate evidently does not affect the solubility of the sodium and potassium salts in the soil. The single high result on plot 6 UL with the normal solution was undoubtedly due to an error in the determination. Another point worthy of mention is that the amounts of sodium and potassium removed are practically alike. This is not so apparent from a comparison of the oxides, but the weights of the chlorides show that 21 out of the 27 determinations made agree closely.

Table VI.

Sodium Oxide removed in Parts per 100,000.

Plot	N/10 $(NH_4)_2SO_4$	N$(NH_4)_2SO_4$	2 1/2N $(NH_4)_2SO_4$
0 L	2.65	6.52	---
0 UL	2.28	4.08	5.09
1 L	2.81	---	4.61
1 UL	2.70	4.08	4.51
6 L	1.59	3.55	4.24
6 UL	1.96	7.05	3.77
7 L	1.91	3.98	4.40
7 UL	2.02	3.66	4.88
8 L	1.75	3.98	4.40
8 UL	1.64	---	3.77

Potassium Oxide removed in Parts per 100,000.

0 L	2.40	2.72	---
0 UL	2.15	5.43	4.17
1 L	3.09	---	5.43
1 UL	2.15	4.74	4.61
6 L	2.00	4.30	4.99
6 UL	2.53	8.65	4.30
7 L	3.54	6.25	5.75
7 UL	2.78	5.37	5.81
8 L	2.91	5.24	5.05
8 UL	2.34	---	4.55

Hydrochloric Acid Removed.

The large amount of ammonium sulfate made it impossible to determine the chlorides by titration. No precipitate formed with silver nitrate in 100 c.c. of thes soil extract, showing the chlorides were present in concentrations of less than .1 part per 100,000.

Nitric Acid Removed.

Here again we have the interference of the ammonium sulfate in making the determinations. However, some results were obtained which show that the amount removed from the different plots and with the different strengths of ammonium sulfate are practically identical. The average amount removed is 1.45 parts per 100,000.

Sulfuric Acid Removed.

In the sulfate determinations as well as in the chlorides and nitrates, the presence of the large mass of ammonium sulfate interfered with the exact determination of the sulfates though not in the same way. The small amount taken for analysis caused an error of .0001 gram in weighing the barium sulfate precipitate to make a difference of 3 parts sulfuric acid per 100,000 solution. The one statement that can be made with certainty is that more sulfuric acid is removed from the soil than was applied by the ammonium sulfate. The amount varies from 27 to 650 parts per 100,000.

Iron and Aluminum Oxides Removed.

The amount of iron removed through the agency of ammonium sulfate is nil in most cases, only with the 5 Normal sulfate solution was a trace found in the extract. The determinations were made colorimetrically.

In the water extracts and those from the solutions of N/10 and Normal strength, no precipitate of any kind formed on the addition of ammonium hydrate, showing the absence of aluminum oxide as well as iron. With the 2 1/2 Normal solution a precipitate formed with ammonium hydrate on the unlimed ends of plots 6, 7 and 8, and with the 5 Normal a precipitate appeared on all of the plots. The precipitate was flocculent and light in color and to all appearances was aluminum oxide. The weights of the precipitate after ignition show that plot 6, unlimed end, had the largest amount removed with the unlimed end of plot 8 nearly equal to it.

In trying to determine the purity of the precipitate by dissolving in concentrated hydrochloric acid and reprecipitating with ammonium hydrate, part of the precipitate was found to be insoluble in hot concentrated hydrochloric acid. This was the first indication that the substance was other than aluminum oxide. On further investigation the precipitate was found to contain silicic acid and aluminum oxide.

Further attempts to obtain this substance in water extracts from the soil were finally successful on using a smaller ratio of water to soil. An inverted bell jar with the opening plugged with glass wool and a linen cloth filter was filled with 2 1/2 Kilos of soil. Enough water was added to just saturate the soil and allowed to remain in contact for two hours. Suction was then applied and all the water possible so removed. A second treatment similar to the first followed. The two filtrates were then combined. In this filtrate a precipitate similar to the one obtained by ammonium sulfate treatment was obtained.

That the ammonium sulfate and even water when in contact with the soil long enough, has a solvent action on the iron in the soil would seem to be proved by the following experiment.

Tin cans lined with paraffine were filled with 500 grams of air-dried soil from plots 6 L and 6 UL. Some were saturated with N/10 ammonium sulfate and others with distilled water. One set was saturated with the ammonium sulfate and washed out immediately while a second set was placed outdoors and another indoors. It was during the winter months so that the soils outdoors were frozen solid most of the time. They were kept in this condition for three months when they were all washed with distilled

water. The extracts from the soils which had been kept indoors were very highly colored by iron oxide, while those outdoors were only slightly colored. It was thought that perhaps the iron might have come from the tin cans even though they showed very little signs of having rusted. In order to determine whether this was the case or not, the experiment was repeated in pint glass jars. After three months the soils were treated as above described and these, too, gave a highly colored solution. Fifty cubic centimeters of the N/10 ammonium sulfate extract from the outdoor sample of 6 L gave a weight of .0313 gram of iron oxide. Thus it is seen that if the ground remained saturated or even very wet for a long time, a large amount of iron would go into solution.

In testing the soil for acidity according to Hopkins' method[1] by treating with potassium nitrate and a modified Vietch's method[2] using calcium hydrate, quite large quantities of iron were brought into solution from plot 6 UL.

1. Bureau of Chemistry, Bul. 107 (Revised), 1912 Reprint, p.20.

2. Veitch, Jour. Amer. Chem. Soc., Vol. 24, p. 1120.

By shaking up the soils with calcium hydrate solution very little difference was found in the absorption properties of the different soils. Practically all of the calcium was absorbed from 500 c.c. of a saturated solution of calcium hydrate by 100 grams of soil, the largest

variations in titration amounting to but .10 c.c. N/2 acid.

By using Hopkins' method for soil acidity quite a difference was found in the absorption. Plots 6 UL and 8 UL required more N/10 sodium hydrate than any of the others. The average titration of the plots exclusive of 6 UL and 8 UL was .20 c.c. N/10 sodium hydrate while plot 6 UL required 2.30 c.c. and 8 UL .70 c.c. As was stated above, a heavy precipitate of iron formed on the addition of the sodium hydrate, showing that the potassium had evidently replaced iron.

In order to determine whether the infertility of the plots extended to their water solutions, culture work was started. Soil extracts were made by treating one part soil with two parts water and these were then used as culture media for barley and red clover plants. The plants were grown for a period of three weeks. At the end of two weeks changes became noticeable in the barley plants, the plants on the unlimed ends of the plots showing signs of wilting. The roots of all were alike except the cultures in the extract from 6 UL which had a stunted and thickened appearance. At the end of the third week the barley in the extract from plot 6 UL was badly wilted. At the discontinuance of the experiment the roots and tops were weighed green. The tops of all from the unlimed ends weighed less than those from the limed ends. The roots of both limed and unlimed varied

greatly in weight, the most noticeable being 6 UL. Here, while the roots appeared much stunted and were not so numerous as on the others, yet the weight was among the heaviest. This can be explained in that the roots were thicker than on any of the others.

The clover results were inconclusive as the weather was so cold that they made little growth.

While it is hardly fair to draw definite conclusions from this single culture experiment, yet the results would seem to indicate that the water extracts from the unlimed ends of the plots were inferior to the limed. Owing to ack of facilities it was impossible to repeat this experiment.

Summary and Conclusion.

The treatment of the soils with the different concentrations of ammonium sulfate shows that

(a) The absorption of the ammonia varies but slightly between the different plots.

(b) The absorption increases with the concentration but not in the same proportion.

(c) The unlimed ends of the ammonium sulfate plots absorb the least ammonia.

(d) The ammonium sulfate has a solvent action on the calcium in the soil and its long-continued use has

caused a deficiency of this constituent in the ammonium sulfate plots.

(e) The continued use of the ammonium sulfate does not affect the solubility of the sodium and potassium compounds.

(f) Up to the present the injurious effect of ammonium sulfate has been ascribed to the presence of free acid in the soil. While this has been the generally accepted belief, no one has as yet been able to isolate any acid from these acid soils. Wheeler in Rhode Island obtained an acid solution when ammonium sulfate soils were extracted with water, but he did not determine to what this acidity was due. Other investigators[1] have, from time to time, separated the so-called humic acids from soils but it is yet a disputed question whether these are true acids or not. These "acids" were in every case found in peat soils and not in soils which had been continuously treated with ammonium sulfate. That the infertility of our plots is not due to the accumulation of free acid is shown since the sulfuric acid removed in the soil extracts is in every case in excess of that added as ammonium sulfate; furthermore, a comparative study of the drainage waters from these plots (Table IV.) shows that the sulfates removed from the two sulfate plots are greater than from any of the

1. Sprengel (1826), Berzilius, Mulder (1840), Detmer (1871), Eggertz (1888), Berthelot and Andre (1892) and Tacke.

others. That no free acid exists in the soil is shown by the treatment of the soils with calcium hydrate and with potassium nitrate in the Hopkins' method for soil acidity. If free acid had been present in the soil it would have reacted with the calcium hydrate solution and left simply a water solution as extract, but instead of simply a water extract we find large amounts of iron showing that instead of neutralizing free acid there has been an exchange of bases with the calcium replacing theiron. The same is true with the potassium nitrate solution; as Hopkins states, a du double decomposition takes place but this does not necessarily mean that a free acid or even an acid salt was present in the soil. The resulting soil extract gives an acid reaction but this may be due to the presence of ferric nitrate and not a free acid. Here again we have the iron replaced by another base. Lastly, the continuous recurrence of neutral extracts with water and ammonium sulfate solutions, no matter what the concentrations, shows that in our soils at least no free acid exists.

(g) With the two hour treatments of the soil with ammonium sulfate, no iron was dissolved, but onllonger standing it was shown that even water and dilute ammonium sulfate solutious dissolve considerable quantities.

(h) The long-continued fertilization with ammonium sulfate, caused a compound containing aluminum and silica to become soluble. From culture experiments at present being

conducted at this station with clover plants in nutrient solutions with the addition of aluminum salts, it is quite evident that aluminum has a toxic action on plants causing a stunted root development. Connors[1] in a recent bulletin also showed that aluminum salts have a very toxic action on seedlings, he having used corn seedlings instead of clover.

1. Connors, Purdue University Agr. Exp. Sta., Bul. 170.

As the infertility of our plots is not due to any accumulation of harmful fertilizer residues, all the results indicate that it is due to the absence of a necessary soil constituent as, for instance, calcium. In the absence of calcium the ammonium sulfate reacts on the iron and aluminum salts in the soil, causing them to become soluble and exert a toxic action on the plants.