that in the neutral sulfates, cannot be removed by the action of silver sulfate. The protection of the halogen by the sulfuric acid is explained on the ground that in the acid sulfates the sulfuric acid is combined directly with the para-halogen of the quinoid nucleus. The explanation is supported by data resulting from observation both of the inhibitive effect of sulfuric acid upon the reaction between para-halogenated carbinol chlorides and silver sulfate, and of the nature of the reaction between sulfuric acid and carbinol chlorides alone.

7. No evidence of the formation to the slightest degree of the orthoquinoid nuclei could be obtained by experiments with ortho-brominated derivatives, either with the neutral sulfates by means of silver sulfate, or with the carbinol chlorides in sulfur dioxide solution on treatment with silver chloride, or in the triphenylmethyl analogs on treatment with molecular silver. Apparently only para-quinoid rings are formed.

ANN ARBOR, MICH.

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[FROM THE DEPARTMENT OF AGRICULTURAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN.]

# THE SULFUR REQUIREMENTS OF FARM CROPS IN RELATION TO THE SOIL AND AIR SUPPLY.[1]

BY E. B. HART AND W. H. PETERSON.

Received January 2, 1911.

Preliminary to a special investigation on the relation of the form and supply of sulfur in feeds to wool production, it was necessary to determin the total sulfur in a number of our common crop materials. The results secured led to a further consideration of the question of the adequacy of the natural sources of supply of this element for continuous crop production and the data relating to that problem are presented in this paper.

It is generally recognized to-day by agricultural chemists that the amount of sulfur in plant materials, as determined in the ash, is in most cases entirely too low; that in the process of ashing, sulfur is lost and the residual amount found in the ash may represent but a fraction of that originally present in the plant tissue. Such losses of sulfur by ignition have been the subject for study by a number of investigators. Contributions to this phase of the question have been made by Berthelot,[2] Barlow,[3] Fraps,[4] Goss,[5] Beistle,[6] Sherman,[7] and others. The work of

[1] Published with permission of the Director of the Wisconsin Experiment Station, University of Wisconsin.

[2] *Compt. rend.*, 128, 17.

[3] THIS JOURNAL, 26, 341 (1904).

[4] Reports of N. C. Experiment Station, 1901–1903.

[5] New Mexico Experiment Station, *Bull.*, 44.

[6] THIS JOURNAL, 24, 1903.

[7] *Ibid.*, 24, 1100.

these several investigators has served to emphasize the inaccuracy of determining the total sulfur of plant tissue by an estimation of that element in the ash.

For the purpose of our work a large number of total sulfur determinations have been made on our common farm products by the peroxide method, as outlined by Osborne.[1]

### Amounts of Sulfur Trioxide in Feeding Materials.

The results secured by the Osborne method are reported in Table I. All determinations were made on the air-dried materials. For convenience of reference the results are reported both as elemental sulfur and as sulfur trioxide, although in our discussion of the subject the latter formula for expressing the amount of sulfur will be used. In addition to the total amounts of sulfur trioxide reported there are given in a number of cases the amounts contained in the ash as secured by Wolff.

TABLE I.—SULFUR IN FEEDING STUFFS—AIR-DRY.

| Material. | Sulfur. Per cent. | Sulfur trioxide. Per cent. | Sulfur trioxide in ash.[2] Per cent. |
|---|---|---|---|
| Alfalfa hay | 0.287 | 0.717 | 0.425 |
| Alfalfa seed | 0.292 | 0.730 | ... |
| Barley | 0.153 | 0.382 | 0.060 |
| Barley straw | 0.147 | 0.367 | 0.207 |
| Beans (white garden) | 0.232 | 0.580 | 0.130 |
| Buckwheat | 0.136 | 0.341 | ... |
| Cabbage | 0.819 | 2.047 | 1.317 |
| Clover, red | 0.164 | 0.410 | 0.222 |
| Cornmeal, white | 0.170 | 0.425 | 0.010 |
| Cornmeal, yellow sample 1 | 0.139 | 0.347 | ... |
| Cornmeal, yellow sample 2 | 0.139 | 0.347 | ... |
| Corn stover, sample 1 | 0.126 | 0.315 | 0.282 |
| Corn stover, sample 2 | 0.116 | 0.290 | ... |
| Corn stover, sample 3 | 0.115 | 0.287 | ... |
| Corn stover, sample 4 | 0.128 | 0.320 | ... |
| Corn silage | 0.122 | 0.305 | ... |
| Cottonseed meal | 0.487 | 1.217 | 0.092 |
| Flour, wheat | 0.180 | 0.450 | ... |
| Flour, graham | 0.183 | 0.457 | ... |
| Gluten feed, sample 1 | 0.560 | 1.399 | ... |
| Gluten feed, sample 2 | 0.500 | 1.249 | ... |
| Hay, mixed | 0.160 | 0.400 | 0.354 |
| Linseed meal, sample 1 | 0.404 | 1.010 | 0.190 |
| Linseed meal, sample 2 | 0.375 | 0.937 | ... |
| Oats, sample 1 | 0.189 | 0.472 | 0.055 |
| Oats, sample 2 | 0.180 | 0.450 | ... |
| Oatmeal, sample 1 | 0.223 | 0.557 | ... |
| Oatmeal, sample 2 | 0.228 | 0.570 | ... |
| Oat straw, sample 1 | 0.195 | 0.487 | 0.230 |

[1] THIS JOURNAL, 24, 142.

[2] Wolff's Aschen Analysen.

TABLE I (*Continued.*)

| Material. | Sulfur. Per cent. | Sulfur trioxide. Per cent. | Sulfur trioxide in ash.[1] Per cent. |
|---|---|---|---|
| Oat straw, sample 2 | 0.218 | 0.545 | ... |
| Onions | 0.568 | 1.419 | 0.300 |
| Potatoes | 0.137 | 0.343 | ... |
| Rape tops | 0.988 | 2.470 | 1.132 |
| Rapeseed meal | 0.456 | 1.140 | 0.381 |
| Rice | 0.126 | 0.315 | 0.003 |
| Rice bran | 0.181 | 0.452 | 0.022 |
| Rutabagas, sample 1 | 0.817 | 2.041 | ... |
| Rutabagas, sample 2 | 0.632 | 1.579 | ... |
| Rye | 0.123 | 0.309 | ... |
| Rye straw | 0.049 | 0.123 | ... |
| Soy bean | 0.341 | 0.852 | 0.085 |
| Sugar beet, late field sample | 0.128 | 0.320 | 0.160 |
| Sugar beet, stored roots | 0.089 | 0.222 | ... |
| Sugar beet, early field sample | 0.069 | 0.172 | ... |
| Sugar beet tops | 0.433 | 1.082 | 0.790 |
| Timothy | 0.190 | 0.475 | 0.195 |
| Turnips | 0.740 | 1.849 | 0.897 |
| Turnip tops | 0.900 | 2.249 | 1.095 |
| Wheat sample 1 | 0.170 | 0.425 | 0.007 |
| Wheat sample 2 | 0.164 | 0.410 | ... |
| Wheat sample 3 | 0.176 | 0.440 | ... |
| Wheat bran, sample 1 | 0.200 | 0.499 | 0.005 |
| Wheat bran, sample 2 | 0.224 | 0.559 | ... |
| Wheat gluten | 0.860 | 2.149 | 0.011 |
| Wheat straw, sample 1 | 0.119 | 0.297 | 0.132 |
| Wheat straw, sample 2 | 0.160 | 0.399 | ... |

Table I discloses some very interesting facts. The results are in harmony with those of other investigators in showing a much higher content of total sulfur trioxide in plant materials than is found in the ash. This is particularly true in the seeds where the sulfur exists largely in organic form in the protein molecule. There the loss by ignition is very large.

There is one hundred times as much sulfur trioxide in rice grain as in the ash of that grain and forty times as much in the corn grain as in its ash. In wheat the same condition is true, while in the oat, cottonseed and soy bean the total sulfur trioxide recovered in the grain by the fusion method is about ten times that found in the ash. In onions, cabbage and turnips the amounts found in the green tissue were from two to four times that recovered in the ash. These materials contain volatil sulfur oils which are in part responsible for the sulfur lost on ignition.

In the case of the hays and straws the losses of sulfur by ignition have not been so large as in the seeds and in those plants rich in sulfur oils. Presumably a considerable part of the sulfur exists in plant stems as sulfates and consequently is permanent on ignition. In mixed hay, for

[1] Wolff's Aschen Analysen.

example, the amount of sulfur trioxide recovered in the ash is nearly as large as that found in the original material, but in alfalfa and clover hay the recovery amounts to about 50 per cent. Of course the probable variation in the total sulfur content of different samples of material must be taken into consideration. This would apply especially to such parts of the plant as the stem and leaf, but not in the same degree to the seed.

## Amounts of Sulfur Trioxide Removed by Crops.

The very important fact which the above data furnishes is that farm crops remove much more sulfur from the soil than has been supposed. Based on Wolff's ash analysis a 100-bushel corn crop per acre (grain only) would remove about one-half pound of sulfur trioxide, while the actual total sulfur trioxide removed, according to our analysis, would be over 20 pounds. For the purpose of clearly showing what amounts of sulfur trioxide are removed by average farm crops Table II has been constructed. The average figures used for these crops are quoted, in part, from a table constructed by Warington.[1]

TABLE II.—POUNDS OF SULFUR TRIOXIDE AND PHOSPHORUS PENTOXIDE REMOVED PER ACRE BY AVERAGE CROPS.

| Crop. | Dry weight. Pounds. | From Wolff's ash analyses, sulfur trioxide. Pounds. | Actual sulfur trioxide. Pounds. | Phosphorus pentoxide. Pounds. |
|---|---|---|---|---|
| Wheat grain, 30 bushels | 1530 | 0.15 | 6.4 | 14.2 |
| Wheat straw | 2653 | 3.40 | 9.3 | 6.9 |
| Total crop | 4183 | 3.55 | 15.7 | 21.1 |
| Barley grain, 40 bushels | 1747 | 1.0 | 6.6 | 16.0 |
| Barley straw | 2080 | 4.1 | 7.7 | 4.7 |
| Total crop | 3827 | 5.1 | 14.3 | 20.7 |
| Oat grain, 45 bushels | 1625 | 0.8 | 7.5 | 13.0 |
| Oat straw | 2353 | 5.4 | 12.2 | 6.4 |
| Total crop | 3978 | 6.2 | 19.7 | 19.4 |
| Corn grain, 30 bushels | 1500 | 0.15 | 6.4 | 10.0 |
| Corn stalk | 1877 | 5.20 | 5.6 | 8.0 |
| Total crop | 3377 | 5.35 | 12.0 | 18.0 |
| Meadow hay | 2822 | 9.8 | 11.3 | 12.3 |
| Red clover hay | 3763 | 8.2 | 15.4 | 24.9 |
| Alfalfa hay | 9000 | 37.8 | 64.8 | 39.9 |
| Bean grain, 30 bushels | 1613 | ... | 9.4 | 22.8 |
| Bean straw | 1848 | ... | 4.9 | 6.3 |
| Total crop | 3461 | ... | 14.3 | 29.1 |

[1] "Chemistry of the Farm, 9th Edition", p. 64.

TABLE II (*Continued*).

| Crop. | Dry weight. Pounds. | From Wolff's ash analyses, sulfur trioxide. Pounds. | Actual sulfur trioxide. Pounds. | Phosphorus pentoxide. Pounds. |
|---|---|---|---|---|
| Turnip root | 3126 | 27.8 | 57.8 | 22.4 |
| Turnip leaf | 1531 | 16.6 | 34.4 | 10.7 |
| Total crop | 4657 | 44.4 | 92.2 | 33.1 |
| Sugar beet root | 4320 | 6.9 | 9.5 | 20.2 |
| Sugar beet leaf | 1848 | 14.5 | 20.0 | 13.1 |
| Total crop | 6168 | 21.4 | 29.5 | 33.3 |
| Potatoes | 3360 | ... | 11.5 | 21.5 |
| Tobacco leaf | 1800 | ... | 16.0 | 8.0 |
| Tobacco stalk | 3200 | ... | 5.0 | 8.0 |
| Total crop | 5000 | ... | 21.0 | 16.0 |
| Cabbage | 4800 | 62.8 | 98.0 | 61.0 |

For purposes of comparison, the amounts removed as calculated from Wolff's ash analyses are given in a number of cases. In addition to the above figures there are also included the amounts of phosphorus pentoxide removed by average crops. This is done for the purpose of comparing the amounts of these two very essential constituents removed by plant growth. It will also serve as a basis for the proper treatment of the question of sulfur fertilization.

A study of Table II reveals the fact that the average crop of seed from the cereal plants removes from the soil about half as much sulfur trioxide as phosphorus pentoxide and that the straws remove a somewhat larger quantity. The hays are not widely different in the proportion of these important ingredients removed, although alfalfa removes annually about twice as much sulfur trioxide as phosphorus pentoxide. The Cruciferae are heavy sulfur-using plants and the total sulfur trioxide removed by these is large. An average acre crop of turnips or cabbage appropriates nearly 100 pounds of this compound.

## Amounts of Sulfur Trioxide in Soils.

No one questions the absolute necessity of sulfur for plant growth. It is necessary for the production of plant proteins and all the plant proteins that have been investigated contain sulfur. Only one class of proteins is known to be free from sulfur and that is the class of protamines of animal origin which, however, have not as yet been isolated from plant tissue.

The imperative necessity of maintaining an ample supply of this element for plant production is as important as maintaining a supply of phosphorus, nitrogen or any of the other elements essential for plant development. The apparent reason why so little attention has been given to this element in the schemes of fertilization for permanent plant production has been due to the fact that it was believed that crops removed but little from the soil and consequently the supply was ample for continuous production.

Bogdanov[1] in 1899 called attention to the practical importance of sulfur in agriculture and believed that it should be applied occasionally as a sulfate for the express purpose of maintaining in the soil an adequate supply of this element. Dymond, Hughes and Dupe[2] have also touched upon this subject and concluded that there was not sufficient sulfur in the soil for the greatest yield of crops rich in protein, but that for *cereal crops* and permanent pasture the soil and rain would provide a sufficient quantity. So far as we can find in the literature no further treatment of the subject has been made.

Investigation of the forms of sulfur in soils has been made by Berthelot and Andre.[3] According to these investigators sulfur exists in soil as (1) sulfates and sulfides; (2) ethereal sulfur; (3) in organic compounds. Very probably the chief forms in all normal soils will be those existing as sulfates and those in the organic matter of the soil. Sulfides would rarely exist except in water-logged soils where reducing processes are prominent. Ethereal sulfates would probably be found only after fertilization with the urin of animals, and then only in small amounts.

There are some difficulties in the estimation of the total sulfur of soils. Fusion of the soil with an alkali is somewhat tedious, although probably the most accurate procedure. The large amount of silicates and their incomplete removal before final precipitation with barium chloride may endanger the absolute accuracy of the method. Extraction in the wet way with strong oxidizing agents, while probably not absolute, will, nevertheless, give the amount of sulfur that can reasonably be expected to become available to the crop in future years. Van Bemmelen[4] compared several methods for the estimation of sulfur in soils, obtaining the highest results by extraction with aqua regia. Trials by the method of ignition with sodium carbonate and potassium nitrate and the method of ignition in a stream of oxygen as used by Berthelot gave him slightly lower results than with aqua regia. It is safe to assume that digestion and extraction with a strong oxidizing agent will remove all sulfates, oxidize sulfides to sulfates, and split up any ethereal sulfates present to form sulfuric acid, and at least partly oxidize the sulfur existing in organic forms. It probably will not give the total sulfur present in the organic material of the soil.

[1] Abstract, *Expt. Sta. Record*, 11, 723.
[2] *J. Agr. Sci.*, Vol. 1 (1905).
[3] *Ann. chim. phys.*, **25**, 305 (1892).
[4] *Landw. Versuch. Sta.*, **37**, 284 (1890).

Most of the determinations of sulfur in soils carried out heretofore have been made by extraction with strong hydrochloric acid. This has been done either by the long-time extraction method as recommended by Hilgard or by the method adopted by the Association of Official Agricultural Chemists. These methods will presumably give all sulfates and ethereal sulfur, but not that existing as sulfides, or the sulfur in combination with the organic matter of the soil. Hilgard found from his analyses of many types of soil that the average amount of sulfur trioxide in sandy soils was 0.055 per cent. while in the clay soils examined it amounted to 0.075 per cent. This, on the basis of an acre foot of three million pounds, would amount in the first instance to 1650 pounds, and in the latter case to 2250 pounds. The average amount of phosphorus pentoxide as given by Hilgard for the same sandy soils was 0.087 per cent. and 0.141 per cent. for the clay soils. On the same basis of calculation an acre foot would contain in the first case 2610 pounds and in the second 4230 pounds of phosphorus pentoxide. Whitson and Stoddart[1] also have shown that the average phosphorus pentoxide content of the surface eight inches of many Wisconsin soils is about 2940 pounds.

These figures are introduced for the purpose of showing that the amount of sulfur in all normal soils is comparatively low.

**Effect of Continuous Cropping on the Sulfur Content of the Soil.**

To determin definitly the effect of continuous cropping on the sulfur content of soils, a number of analyses of both cropped, virgin and manured soils have been made. Two methods were used for the determination of sulfur trioxide.

The first was a slight modification of the Van Bemmelen method. That investigator used aqua regia for the extraction, while in our method nitric acid and bromine were used.

The second method consisted of fusion with sodium peroxide, and as it gave more accurate results will be described in detail. Ten grams of soil were placed in a 100 cc. nickel crucible, moistened with water, about 10 grams of a weighed 20-gram portion of sodium peroxide added, and the mixture thoroughly stirred with a platinum rod. The crucible was placed over an alcohol flame and heated moderately until the mass was dry. The remainder of the sodium peroxide was then added, the cover placed on the crucible, strong heat applied until the mass melted, and kept in this condition for 10 minutes. It was then allowed to stand over a lower flame for 1 hour. The crucible was removed, cooled, placed in a 600 cc. casserole, hot water added and the fused mass removed. It was neutralized with hydrochloric acid and then further acidified with 10 cc. of hydrochloric acid. The volume was made up to about 450 cc. and boiled for 15 minutes, or until no undecomposed portion of the fused

[1] *Research Bulletin*, 2, 1909, Wisconsin Expt. Station.

mass remained on the bottom. The covered casserole was allowed to stand on the steam bath over night, filtered through a "nutsche" and the residue thoroughly washed with successive small portions of hot water. The filtrate and washings, if over 500 cc., were evaporated below that volume, refiltered and the volume made up to 500 cc. Aliquot portions of 250 cc. each were heated to boiling, barium chloride added, boiled for 5 minutes and set aside on a steam bath for 24 hours. The volume was not allowed to decrease, as silicic acid may be precipitated out if much evaporation takes place. After standing for this length of time the barium sulfate was filtered off, washed, ignited and weighed. In the determinations made by this method the precipitate was free from silica as demonstrated by the hydrofluoric acid test.

Both these methods were compared with the method of the Official Agricultural Chemists with the following results: The soil used was from the surface 8 inches of one of the experimental plots at the University Hill Farm.

| | Per cent. of $SO_3$. |
|---|---|
| Official method | 0.019 |
| Fusion method | 0.043 |
| Nitric acid bromine method | 0.037 |

Since the official method gave lower results than either the fusion or wet extraction method it was not used for our work. Instead, for the purpose of greater completeness, all the soils investigated were subjected to both the fusion and nitric acid bromine methods. There was close agreement between the results secured by the two methods, but with a uniform tendency for the fusion method to give slightly higher results. This is to be expected as that method should include the total sulfur of the soil, while by the wet method some of the organic sulfur may escape complete oxidation. In the analyses reported only those results secured by the fusion method are recorded.

## Sulfur Trioxide in Soil Samples.

Ten different soils from several parts of this state were first investigated. They were both virgin and (the same soils) cropped but generally unmanured. The determinations of sulfur trioxide were made on pairs of samples, one from the cropped field and the other from the adjacent virgin soil. In each case the surface 8 inches were taken and every precaution to secure virgin soils of drainage and topography similar to that of the cropped soil was observed. Analyses are also given in the later part of this article of virgin soils and the same soils heavily manured, but in two instances continuously cropped to such heavy sulfur-using plants as the cabbage.

The following is a brief history of the *unmanured* samples:

No. 1 (cropped). "Janesville. Cropped 63 years. During the first

34 years wheat was grown almost continuously. Since 1878 it has been rotated to corn, barley, oats and rye. It has never been seeded down or manured and is in a badly exhausted condition."

No. 2 (cropped). "Edgerton. Cropped about 60 years, largely to wheat at first, but during the last 40 years it has been farmed in a rotation, consisting of two crops of corn, one of oats and two of clover and timothy of which the first was cut and the second pastured. The field has not produced good crops during the last 10 years. It has been manured but once."

No. 3 (cropped). "Milton Jct. Cropped 52 years, chiefly to wheat during the first 15 years, since then it has been rotated to oats and barley with a few years of timothy. It has been manured 10 times with an average of 10 loads per acre each time. The field does not now produce good crops."

No. 4 (cropped). "Milton Jct. Cropped 50 years. Rotated to corn and oats for about 40 years, then grew one crop of barley, one of corn, one of beets and now in alfalfa. Alfalfa doing poorly. Soil acid. Manured once."

No. 5 (cropped). "Evansville. Cropped 60 years, early years chiefly wheat. History for last 28 years—10 years timothy and clover; 12 crops of corn; 6 crops of oats. Manured three times. Manure usually sold."

Table III gives the results of the analyses of the virgin and cropped soils; the loss of sulfur trioxide by cropping as determined from the analyses; the estimated amount of sulfur trioxide removed by the crops; the amount added in the manure; and the amount removed by the crop in excess of that added in the manure. It is estimated that the average amount of sulfur trioxide removed every year by corn, the small grains, clover and timothy was 12 pounds. This amount is somewhat below the figure given in Table II for average crops, but the smaller amount is taken because of the falling off of crop yields in the later years of the field's history. The average amount of sulfur trioxide added in the manure was estimated on the basis of several analyses, at two pounds per ton of manure with an application of 10 tons yearly.

Table III indicates that on the average about 40 per cent. of the sulfur trioxide has been lost from the cropped soils. In every case there is a lower percentage of sulfur trioxide in the cropped soil than in the virgin soil. The estimated amount removed by the crops, minus that supplied in the manure, is in two cases in excess of that indicated to have been lost by the analysis. Such discrepancies are due, possibly, to variations in the soil itself, inaccurate estimates of the amounts of crop removed, and the influence of the influx of sulfates with the upward movement of soil water. On the other hand the estimated average amounts of sulfur trioxide removed by the crops and that indicated by the analyses, are almost identical. This estimate on the soil is based on the surface 8 inches and the weight of two million pounds per acre. Little importance, however, should be attached to these estimated amounts removed, as there must still be losses of sulfur trioxide due to drainage, which the figures do not include. The important thing that the table teaches is that continuous cropping without adequate fertilization shows a large decrease in the sulfur trioxide content of the soils examined.

TABLE III.—INFLUENCE OF EXHAUSTIVE CROPPING ON THE SULFUR TRIOXIDE CONTENT OF SOILS.

| Soil sample. No. | $SO_3$ in virgin soil. Per cent. | $SO_3$ in cropped soil. Per cent. | Amount per acre (estimated). Loss by cropping according to analyses. Pounds. | Removed by crops. Pounds. | Added in manure. Pounds. | Removed by crop in excess of that added in manure. Pounds. |
|---|---|---|---|---|---|---|
| 1 | 0.107 | 0.066 | 820 | 756 | ... | 756 |
| 2 | 0.101 | 0.058 | 860 | 720 | 20 | 700 |
| 3 | 0.033 | 0.019 | 280 | 624 | 200 | 424 |
| 4 | 0.127 | 0.088 | 780 | 600 | 20 | 580 |
| 5 | 0.055 | 0.032 | 460 | 720 | 60 | 660 |
| Average, | 0.084 | 0.052 | 640 | 684 | 60 | 624 |

### Effect of Liberal Manuring on the Sulfur Trioxide Content of Soils.

In order to determin what would be the effect of liberal manuring with farm manure on the sulfur trioxide content of soils, several samples of known history were subjected to an examination. The corresponding virgin soils were also examined. The history of the cropped samples is as follows:

No. 6 Evansville. Cropped 60 years. Wheat up to 1860. Since 1860 general rotation of two years in corn, one to two years in meadow, and one year in pasture. Manured every year while in corn at the rate of 10 loads to the acre. Crop yields good.

No. 7 Berryville. Continuously in cabbage until the crop failed some 10 years ago. Manured heavily with stable manure until three years ago. The last three years fertilized annually with 1400 pounds per acre of Homestead fertilizer. Surface two inches rejected in taking samples.

No. 8 Kenosha. Past 15 years in cabbage, alternating every year with corn or potatoes. Chicago stable manure freely applied with yearly applications of about 10 loads. None used in 1909.

The results are given in Table IV.

The results show that the sulfur content of these soils was maintained and even slightly increased by the liberal application of farm manure.

TABLE IV.—INFLUENCE OF LIBERAL MANURING WITH FARM MANURE ON THE SULFUR TRIOXIDE CONTENT OF SOILS.

| Soil sample. No. | $SO_3$ in virgin soil. Per cent. | $SO_3$ in cropped and manured soil. Per cent. |
|---|---|---|
| 6 | 0.061 | 0.075 |
| 7 | 0.108 | 0.115 |
| 8 | 0.119 | 0.140 |
| Average | 0.096 | 0.110 |

**Other Factors in the Gain and Loss of Sulfur Trioxide from Soils.**

In addition to the sulfur added to the soil with applications of farm manure or certain commercial fertilizers there is also a small amount brought to the land by rain water. This sulfur in the atmosphere has its origin almost wholly in the burning of fuel, especially soft coal. The amount of sulfur trioxide brought to an acre surface yearly has been determined at Rothamsted, England. Warington[1] gives the amount as about 17 pounds and adds further that sulfates in rains "will, to a considerable extent, meet the demands of most cultivated crops."

Later determinations made at Rothamsted and furnished us by Director Hall show an average annual precipitation per acre of about $18^1/_2$ pounds of sulfur trioxide.

In England large amounts of soft coal are burned and it was believed not improbable that the amount brought to a surface acre annually by the rain in the open country of our northern states, especially where soft coal is used to but a limited extent, would not be as large as the amount found in England. For the purpose of collecting data on this point a rain gage with a collecting surface equal to one square foot was set up at the University Hill Farm located three miles west of the city of Madison, Wisconsin. It was placed in an open field and at least a mile from any chimney using considerable quantities of coal. The rain water was collected in a copper bottle, containing a trace of sodium bicarbonate in order to fix any sulfurous acid. A fine wire screen was placed above the funnel of the gage for the purpose of excluding any material accidentally blown or falling into the gage.

The samples of water collected were analyzed for total sulfur at the end of each month. The results are given in Table V and reported as pounds per acre of sulfur trioxide; the monthly rainfall at the time the analyses were made is also recorded.

Not enough data are at hand to warrant establishing an average annual figure, but until such data are accumulated the tentative statement can be made that the amount of sulfur trioxide brought yearly by rain to an acre surface of land at this location will probably not be less than that

[1] "Chemistry of the Farm," p. 19, 9th edition.

found at Rothamsted, England, which is 17–18 pounds. The total amount brought down in the five months recorded was 10.70 pounds with a rainfall of 11.14 inches.

TABLE V.—AMOUNTS IN POUNDS OF SULFUR TRIOXIDE BROUGHT TO THE SURFACE ACRE MONTHLY.

| Month. | $SO_3$ Pounds. | Rainfall. Inches. |
|---|---|---|
| June, 1910 | 2.36 | 1.31 |
| July, 1910 | 0.60 | 0.81 |
| August, 1910 | 4.47 | 6.56 |
| September, 1910 | 2.66 | 1.83 |
| October, 1910 | 0.61 | 0.63 |
| Total | 10.70 | 11.14 |

## Losses of Sulfur Trioxide from Soils by Drainage.

While the atmosphere can serve as a considerable source of sulfur trioxide to the soil, nevertheless as a compensating factor, it is probably more than offset by the losses that soils sustain by drainage. It is well known that most river and lake waters, which in part represent the drainage waters from our soils, contain considerable quantities of sulfates. These have been dissolved out of the soil. The Rothamsted Experiment Station gives some definit data on the losses of sulfur trioxide in the drainage water from soils. The drainage waters from the wheat plots of Broadbalk field have been collected from time to time and completely analyzed by Voelcher and Frankland. From the unmanured plots they report the quantity of sulfur trioxide in the drainage water at 24.7 parts per million, while the quantity varied from 41.0–106.1 parts per million in the waters from the plots receiving various fertilizer treatments.

Assuming, as Hall does[1] in his discussion of losses by drainage from these plots, a mean annual drainage equal to 10 inches of water, the unmanured plots would lose approximately 50 pounds of sulfur trioxide annually per acre, while those receiving fertilizers containing varying amounts of sulfates would lose from 85–220 pounds annually per acre. It will be seen from the above data that the loss of sulfur trioxide by drainage is considerable and in the case of the unmanured plots it is nearly treble the amount brought by rain to an acre surface from the atmosphere. While these figures may not be applicable to all climates and all soils, nevertheless it would be conservative to state that the loss by drainage at least equals and probably exceeds the amount brought to the soil from the atmosphere in the humid regions of America.

## General Discussion.

The general question raised by the data presented above is one of great importance. The fact that common crops remove from the soil con-

[1] "The Soil," p. 200.

siderable quantities of the element sulfur, while the compensating factor of supply from the atmosphere is very probably offset by the losses which the land sustains by drainage, makes it apparent that for the maintenance of a permanent supply of sulfur in the soil, this element must be added systematically either as a constituent of commercial fertilizers, or with the farm manure.

The supply of sulfur in soils is low, the surface eight inches of a normal soil containing sulfur trioxide sufficient for about 100 crops of barley, and this would suppose that the crop could produce normal yields with a steadily decreasing supply of sulfur. The upward movement of water within the soil occasioned by surface evaporation would possibly aid in bringing sulfates from the lower soil areas, but this could not continue indefinitly. The sulfur trioxide content of subsoils according to the analyses made by Hilgard is no greater than that of the surface soil.

Many factors are operative in the maximum production of crops; ample supplies of essential elements, proper biological agents, absence of toxic substances, and proper physical environment are all important soil factors. So many factors are operative that an optimum condition is probably seldom obtained. For this reason the disturbance of the equilibrium in the soil by the addition of a single agent is often followed by better crop production. Whether it affects the biological agents, improves the sanitary conditions, alters the physical status of the soil, or acts by furnishing an ample supply of the elements essential for plant growth is always difficult to answer, but that there must be maintained an ample supply of the essential elements, is one of the first principles of plant production.

Most normal soils contain an abundance of the essential elements, potassium, iron, magnesium and calcium. Nitrogen, phosphorus and sulfur alone are of a low percentage. The former two are to-day recognized as valuable essentials of commercial fertilizers, and field experiments in many instances have shown the utility of the application of potash salts in available form. When calcium is added it is usually as a carbonate and more for the purpose of maintaining a neutral or slightly alkaline reaction in the soil solution than as a source of calcium for plant growth.

The use of sulfates in fertilizers has been unconsciously practiced for many years. The acid phosphate of the fertilizer industry is a product containing a large proportion of calcium sulfate. Whether the beneficial results accruing from its application are to be attributed alone to the phosphorus it supplies or whether they are twofold and due to both the phosphorus and sulfur contained in this material are questions raised by this investigation. It is not impossible that the superior results sometimes obtained in field practice with acid phosphates over other phosphates, such as Thomas slag, or ground rock phosphate, are not due entirely to differences in solubilities, but to the additional sulfur supplied by the former material. The superior results so often noted from the use of potash salts when furnished as sulfates rather than chlorides may rest in part upon the sulfur content of the material added.

It was once common practice to use gypsum as a fertilizer. The beneficial effects often resulting from the use of this material have been explained on the basis of its action as a stimulant. Boussingault showed that its application increased the amount of potassium taken up by the plant. This was accomplished through a double decomposition of potassium silicates with liberation of potassium sulfate. Consequently its action was said to be indirect and it was classed as a stimulant for the reason that while it often produced increased plant growth, it furnished no necessary plant elements. While the above reaction may be entirely true, the explanation appears to be only partial. If the idea here presented, that sulfur may become a limiting element in crop production, is true, then the beneficial result accruing from the use of gypsum may result in part from its sulfur content.

In the 25 years of carefully recorded plot fertilization experiments by the Pennsylvania Experiment Station,[1] the evidence for the necessity of occasional sulfur applications is negative. While these experiments were not planned to answer the question of sulfur requirements, nevertheless they are the only experiments available so far as the authors are aware, which shed any light at all on the question involved. In plots 9 and 17 the treatment consisted of dried blood, muriate of potash and dissolved boneblack, which contained calcium sulfate sufficient to furnish probably from 30–40 pounds of sulfur trioxide per acre. On plots 12 and 35 the treatment was dried blood, muriate of potash and ground bone. Identical quantities of phosphorus pentoxide and potassium oxide were added in the two treatments, with 24 pounds of nitrogen in the first mixture and 30 pounds in the latter.

Unless the muriate of potash and dried blood used contained sulfates sufficient[2] for all crop needs, then the only difference in the kinds of essential elements added was in the greater amount of sulfur contained in the first mixture; yet the total annual yield in crops over a period of 25 years was slightly in favor of the second treatment. Nevertheless, while an annual removal of 15 pounds of sulfur trioxide per acre by the crops grown in the above experiment may not as a single factor be sufficient to reduce the productivity of the soil receiving sufficient nitrogen, phosphorus and potassium in 25 years, it appears probable that this could

[1] "Report of Penn. State College," 1907–1908, p. 80.

[2] From some of our own analyses of dried blood and muriate of potash the amounts of these materials used in the Pennsylvania experiments could have furnished about 14 pounds of sulfur trioxide per acre.

not continue indefinitly. Our own data on the partial depletion of sulfur in soils unmanured but cropped for 50–60 years is evidence in support of this view.

Unfortunately none of the experimental plots at Rothamsted, England, have been deliberately planned with respect to the effect on long-continued cropping, of fertilizers with and without applications of sulfur.

Careful experimentation and practical agriculture must decide in what form sulfur, when needed, should be added to the soil. Economy and safety are the factors involved. The principal sulfates normal to the soil are those of calcium, magnesium, and potassium. No harm can result from a judicious use of any of these. Sulfur can be added to the soil either as land plaster; with acid phosphate, in which it exists as calcium sulfate; or as a sulfate of potassium or ammonium. All these materials are now offered by the trade.

## Conclusions.

1. The sulfur content of a number of our common farm products has been determined and in agreement with other investigations the quantity is much larger than found by Wolff in the ash from such products.

2. The amount of sulfur trioxide removed by crops is considerable, being equal in the case of average crops of cereal grains and straws to about two-thirds of the phosphorus pentoxide removed by these crops; the grasses of mixed meadow hay remove quite as much sulfur as phosphorus, while the legume hays may approach, and in the case of alfalfa, even exceed in this respect. Members of the Cruciferae, as the cabbage and turnip, are heavy sulfur-using crops and may remove two to three times as much sulfur trioxide as phosphorus pentoxide. An average acre crop of cabbage will remove about 100 pounds of sulfur trioxide.

3. Normal soils are relatively poor in total sulfur trioxide, a limited number of analyses showed a percentage content of from 0.033–0.140; most of them contained less than 0.10. An acre foot will contain from 1000–3000 pounds of total sulfur trioxide. About the same quantity of phosphorus pentoxide will be found in an acre foot of normal soil. These results for sulfur trioxide are based on analyses made by the method of fusion with sodium peroxide. Determinations by extracting with hydrochloric acid or with nitric acid and bromine will not give the total sulfur content of soils.

4. Soils cropped for 50–60 years and either unmanured or receiving but slight applications during that period have lost on the average 40 per cent. of the sulfur trioxide originally present as determined by comparison with virgin soils.

5. Where farm manure has been applied in regular and fairly liberal quantities the sulfur content of the soil has been maintained and even increased.

6. The total sulfur trioxide precipitated at Madison, Wis., with the rain amounted in the five months of June to October, 1910, inclusive, to 11.7 pounds per acre. The annual amount may tentatively be placed at 15–20 pounds.

7. The losses of sulfur trioxide by drainage, based on the analysis of the drainage waters at Rothamsted, England, and on a yearly drainage of 10 inches, would amount to about 50 pounds per acre yearly.

8. Even with much less loss by drainage it does not appear that the atmosphere can serve as a complete compensating factor for losses of sulfur trioxide which soils sustain through both cropping and drainage. The partial depletion of the sulfur of the soil by continued cropping without fertilization is evidence in support of this view.

9. From the data here presented it appears that for permanent and increased production of farm crops such systems of fertilization must be inaugurated as will supply to the soil from time to time, in addition to the elements now recognized as necessary, a sufficient quantity of sulfur to meet the losses sustained by cropping and drainage.

10. Such sources of sulfur are farm manures; the trade fertilizers, such as superphosphate, ammonium sulfate and sulfate of potassium; and the so-called soil stimulant, gypsum or calcium sulfate.

No attention, so far as we are aware, has been directed to this problem in America. It is hoped that the thesis here presented may be made the subject for further research by chemists and agronomists and the relative importance and necessity for sulfur in systems of fertilization finally established.

UNIVERSITY OF WISCONSIN, MADISON, WIS.

## TWO COMPOUNDS ISOLATED FROM PEAT SOILS.

BY CHAS. S. ROBINSON.

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Although the organic nitrogenous compounds in peat have been under investigation for over a hundred years the actual isolation of such compounds in the crystallin form had been attained only very recently. Suzuki,[1] by means of Fischer's esterification method, succeeded in isolating several of the mono- and di-aminoacids from a natural humic acid. Previous to this, Shorey[2] had isolated picolinecarboxylic acid from a soil containing 12.47 per cent. humus and Schreiner and Shorey[3] have since isolated this compound from several other soils. They have also isolated several diamino acids, purine bases and pyrimidine derivatives.[4] In all cases they extracted the soil with dilute alkali.

[1] *Bull. Coll. Agric. Tokyo*, 7, 513; abst. in *Chem. Zentr.*, 1907, II, 1.

[2] *Rept. Agr. Exp. Sta. Hawaii*, 1906, 37.

[3] U. S. Dept. of Agr., Bur. of Soils, *Bull.* 53.

[4] *Ibid.*, *Bull.* 74.