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SULFOFICATION IN SOILS.

P. E. BROWN AND E. H. KELLOGG.

Sulfur has long been known to be one of the essential plant food constituents. It has always been believed, however, that there was sufficient present in all soils for optimum crop production. This assumption has been very largely based on Wolff's analyses of the ash of various crops which showed the presence of very small amounts of sulfur. Several investigators have found a considerable loss of sulfur upon ignition of plants for ash determinations, and recently Hart and Peterson, of Wisconsin, pointed out definitely the inaccuracy of determining the total sulfur of plant tissues by examinations of the ash. They analyzed numerous feeding stuffs for total sulfur, using the Osborn method, and compared their results with the earlier analyses of Wolff. This comparison showed quite conclusively that a large proportion of the sulfur in crops is lost upon ignition. It is evident, therefore, that considerably larger amounts of sulfur are removed from soils by common farm crops than has been supposed.

Analyses of various soils have shown the presence of only a limited amount of sulfur, the subsoil containing no more than the surface soil. The renewal of the sulfur supply in the surface soil from the lower soil layers is possible, therefore, for only a limited period.

The suggestion of Hart and Peterson that soils may be deficient in sulfur and crops may suffer for a lack of this element seems worthy of considerable attention.

Several other interesting suggestions are contained in the work of these men. For instance, it is pointed out that acid phosphate may produce increased yields, not entirely because of the phosphorus added to the soil, but because of the sulfur which is present in the form of calcium sulfate. Ammonium sulfate and potassium sulfate, when applied to soils, may bring about greater crop production, because of their sulfur content as well as their nitrogen or potassium content. Gypsum, which has ordinarily been considered an indirect fertilizer, because of its power to free other constituents, such as potassium, from an insoluble form, may exert a beneficial effect on some soils because of the sulfur contained in it. The fact that soils to which farm manure has been applied contain more sulfur than untreated soils is also clearly shown.

The possibility immediately suggests itself that the benefits from the use

of manure may be due in part to the sulfur present, even although it does occur in complex form.

It is evident from this work that the problem of the sulfur fertilization of soils is one which may be of considerable importance, and is at least worthy of careful study.

Sulfur, as is well known, occurs in crops and in manures in complex organic form in the proteins and must be transformed into sulfates before it can be of use to plants. The rate of production of sulfates in soils must, therefore, be of considerable importance in keeping plants supplied with the amounts necessary for optimum growth. This transformation of sulfur from the protein form into sulfates, like the production of nitrates from proteins, takes place in several stages. First, there is the production of hydrogen sulfide from the proteins. Large numbers of organisms, apparently, are able to decompose proteins with the liberation of this gas. All the decay bacteria are able to bring about this reaction, and, in fact, wherever protein destruction is occurring there is a production of hydrogen sulfide.

Further oxidation of this material immediately occurs through the activities of the sulfofying bacteria, or sulfur-oxidizing bacteria. There are two groups of these, the red, Rhodobacteriaceae, or Pupur-bakterien, and the Thiobacteriaceae, or colorless group. These organisms, as far as we now know, bring about the oxidation of sulfur in two stages. The first is the change from hydrogen sulfide to free sulfur, which is then deposited in granules in the cells of the bacteria. The second stage in the process is the oxidation of this free sulfur to sulfates, in which form the sulfur is available to plants. Winogradsky has isolated nine different organisms which have the power of oxidizing hydrogen sulfide with the production first of sulfur and then of sulfates, and he has shown also the rather extensive distribution of these organisms in nature. It is evident, therefore, that bacteria play an important part in the preparation of sulfates for plant nourishment and the cycle through which sulfur passes in nature would be incomplete without bacterial action.

The rate of production of sulfates in a soil, therefore, must be of considerable significance in the problem of the sulfur feeding of crops. If the sulfur present in organic form is very slowly oxidized to sulfates, crops will not be properly supplied with the element. In other words, if soils do not have a vigorous sulfofying power, there may be an abundance of total sulfur present and still there be an insufficient production of sulfates for optimum crop growth.

The questions, therefore, immediately arise: Can we determine the sulfonating power of soils? How? Is there any relation between the sulfonating power of soils and the proper sulfur feeding of plants? Can methods be devised to increase the sulfonating power of soils, or, in other words, the efficiency of the sulfonating bacteria?

This work was begun mainly to answer the first question: "Is it possible to determine the sulfonating power of soils? If so, how?" Further work is being carried on looking toward the solution of the other questions and considerable data are being accumulated which will be published in the near future. Most of this material is not in shape for presentation at this time and we will merely outline the work which has been carried on and the results, which have shown us that soils do have a sulfonating power and that this power is exceedingly variable in different soils and in soils under different treatment.

Most of the difficulties which have confronted us in this work have been of a chemical nature and we will mention some of them, with the methods which we have devised for their elimination. In the first place, one of the main troubles we have had has been in the extraction of the sulfates from the soil. The methods given in text-books and in all the references available suggested the extraction with dilute hydrochloric acid. A great many tests were run with this acid in varying strengths and comparisons were made with the results obtained by extraction with water. The latter method was found in every case to extract more sulfates than the hydrochloric acid. Magnesium sulfate and calcium sulfate were added to soils in known quantities, and, while practically the entire amounts were obtained according to the extraction with water, only very small proportions were secured when hydrochloric acid was used as a solvent. The calcium sulfate is more insoluble than the magnesium sulfate and its formation is probably more common in soils, hence the complete extraction of this material is regarded as of special significance in showing the value of the method. The stronger the acid employed the smaller was the proportion of the sulfates recovered from the soil. The interference of iron and organic matter undoubtedly explains the low results obtained with the acid. Tests were then made to ascertain how long it was necessary to shake the soil with water in order to extract the sulfates and it was found that six hours in the shaking machine was ample for complete extraction. At first the sulfates were determined by precipitating with barium chloride in the usual way and weighing the barium sulfate produced. This was found to be a very slow method of procedure and the sulfur photometer was obtained and has proved invaluable in giving quicker and quite as

accurate results. Comparisons made of the gravimetric and photometric methods show absolute agreement.

Then came the question of deciding on some method of determining the power of the soil to produce sulfates, or its sulfofying power. Taking advantage of the results which have been secured in the study of the ammonifying and nitrifying power of soils, it was decided to use fresh soil as a medium. It was then necessary to employ some material containing sulfur to permit of an accumulation of sulfates to a measurable extent, or, in other words, to accentuate the sulfofying power of the soil just as dried blood or casein have been used in ammonification and ammonium sulfate in nitrification. Various sulfides were first employed, namely, calcium sulfide, barium sulfide, potassium sulfide, and sodium sulfide, and, with the exception of the barium sulfide, there was found to be very rapid transformation of these materials into sulfates, large amounts being produced in three or four days' incubation. There was probably a transformation of the barium sulfide also, but it was impossible to extract the sulfate formed from the soil. So rapid an oxidation occurred that our suspicion was aroused that the action was not entirely bacterial. Careful tests were made and it was found that on shaking any of the sulfides with soil for seven hours without incubation there was a large percentage of oxidation to sulfates. This showed that in the shaking process there was a purely chemical oxidation of the sulfides. This oxidation was much greater for the calcium and potassium sulfides than for the sodium sulfide. The change did not occur in sand and the oxidation varied considerably in extent in different soils.

It is evident, therefore, that it is necessary to ascertain how much chemical oxidation a sulfide will undergo in any particular soil by shaking it with water seven hours before that sulfide can be used as a measure of the sulfofying power of the soil. The percentage transformation of the sulfur into sulfate by chemical means is then subtracted from the total sulfate production after incubation and the difference gives the bacterial oxidizing power of the soil for sulfur.

In order to secure some material in the use of which this chemical oxidation would be avoided pure sulfur and iron sulfide have recently been employed. The former shows practically no oxidation upon shaking with soils and the latter none whatever.

Tests upon these materials are not sufficient yet, however, for any conclusions to be reached, as they have not been carried out with a sufficient number and variety of soils. The results which appear on the tables show the oxidation of sodium sulfide and of sulfur by chemical means and by bacterial action in several different types of soil. The

SULFOFICATION IN SOILS.

21

examination of the last column, which shows in each case the percentage transformation of the sodium sulfide, or the sulfur into sulfates by bacterial means, will give some interesting comparisons.

TABLE I.—THE SULFOFICATION OF SODIUM SULFIDE.

Soil No.	Soil Source	Percent water in soils	Mgs. S. as sulfide	Av. mgs. S. as sulfate	Mgs. S. as sulfate in soils	Mgs. S. as sulfate oxidized by shaking	Mgs. S. as sulfate oxidized in soils	Per cent sulfur added oxidized in soils
1	Sandy loam, graveyard-----	16	9.21					
1	Same -----	16	10.95	10.08	trace	2.61	7.47	56.03
2	Sandy loam, low, poorly drained area -----	21	16.91					
2	Same -----	21	17.29	17.10	5.56	3.61	7.93	59.48
3	Heavy, black woodland soil-----	26	18.17					
3	Same -----	26	18.98	18.57	-----	13.13*	5.44	40.81
4	Typical sand, river bank-----	11	4.41					
4	Same -----	11	4.02	4.21	trace	trace	4.21	31.58
5	Wisconsin drift soil, untreated -----	18	15.55					
5	Same -----	18	15.37	15.46	3.19	2.33	9.94	74.56
6	Wisconsin drift soil, manured at rate of 25 tons per acre--	15	12.15					
6	Same -----	15	13.92	13.03	1.52	1.18	10.33	77.49

TABLE II.—THE SULFOFICATION OF FREE SULFUR.

1	Sandy loam, graveyard-----	16	6.15					
1	Same -----	16	6.01	6.08	trace	1.48	4.60	4.69
2	Sandy loam, low, poorly drained area -----	21	12.43					
2	Same -----	21	11.98	12.20	5.56	1.76	4.88	4.88
3	Heavy, black woodland soil-----	26	11.57					
3	Same -----	26	lost	11.57	-----	9.87*	1.70	1.70
4	Typical sand, river bank-----	11	3.61					
4	Same -----	11	3.51	3.56	trace	trace	3.56	3.56
5	Wisconsin drift soil, untreated -----	18	10.05					
5	Same -----	18	10.34	10.19	3.19	1.37	6.63	6.63
6	Wisconsin drift soil, manured at rate of 25 tons per acre--	15	12.48					
6	Same -----	15	13.11	12.79	1.52	0.48	10.79	10.79

*Includes sulfate from soil and that due to oxidation by shaking.

The method, as we are employing it, may be given as follows: Fresh soil is obtained, with the usual precautions that it shall be representative and that it shall not be contaminated in the sampling. 100 gm. quantities are weighed out in tumblers and thoroughly mixed. The sulfide is then added, 0.1 gm. of the sodium sulfide or the sulfur. The moisture conditions are then brought up to the optimum by additions of sterile

water. The soils are then incubated for five to ten days at room temperature, at the end of which time the sulfates are leached out with water by shaking for seven hours in the shaking machine. The sulfates present are estimated by the use of the sulfur photometer.

The sulfates present in untreated soils are also determined and the purely chemical oxidation of the sulfide in the particular soil is ascertained. The difference between the sum of these two determinations and the total sulfur as sulfates at the end of the incubation period gives the sulfur oxidation or sulfification by bacteria.

The results so far secured by the use of this method show that soils may vary considerably in their sulfur oxidizing power and that this variation in sulfofying power may be of considerable importance from the fertility standpoint. The possibilities of the future development of this subject are so clearly evident that it is unnecessary to mention them here. Suffice it to say that the question of sulfur fertilization is one which is commanding more and more attention, and if deficiencies in sulfur are to be avoided means must be employed which will return to the soil some of the element removed by crops, just as is the case with other elements. Farm manure and green manure are the logical farm materials which can be employed for this purpose and when the sulfur is applied in this form it must be transformed into sulfate and the rate at which this change occurs will determine the efficiency of the means of applying sulfur. The efficiency of the bacteria which oxidize sulfur to sulfates in the soil, or the sulfofying power of soils, will determine, therefore, the material which should be employed to prevent the depletion of the soil in the element sulfur.

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