

OCCURRENCE OF SULFIDES IN MINNESOTA PEAT SOILS¹

CLAYTON O. ROST

Minnesota Agricultural Experiment Station

INTRODUCTION

The common occurrence of iron sulfide in peat has long been recognized. As early as 1810, Rennie in classifying peats (4, p. 160), described "pyritous, or vitriolic peat" (4, p. 640) and mentioned several even earlier writers, including Brougmart (4, p. 640) and Bomare (4, p. 642), who had not only recognized pyrite in peat soils but had also observed its behavior upon coming into contact with the air and the resulting toxicity to crop plants. He quotes Bomare (4, p. 643) to the effect that "the ashes furnish an excellent manure, though the moss itself when applied as a top dressing, is *utterly destructive to vegetation*." Wollny in 1897 (7, p. 231) mentions the occurrence of iron sulfide in peat as marcasite as well as pyrite.

Pyrite and marcasite are formed where water carrying some iron compound comes into contact with a solution of calcium sulfate, under conditions which favor the reducing action of plant residues (7, p. 231, 3, p. 100). The sulfides themselves, being insoluble in water, are not toxic, but upon contact with oxygen and water vapor are converted into ferrous sulfate and sulfuric acid, both of which strongly affect plants and, when present in large quantities, destroy all vegetation.

As the sulfides are the source of the toxic substances, the amount of these, their distribution in the soil profile, and relation to soil layers rich in lime are of chief interest in the present discussion. The quantities of ferrous sulfate and sulfuric acid found at any time will depend upon the amount of sulfides present and their distribution as well as upon the aeration and the rainage conditions. Ditching and tiling, while facilitating the removal of these harmful substances, at the same time increase the aeration and hasten the oxidation of the remaining sulfides. So under the influence of drainage alone the toxic compounds will not disappear until the whole of the sulfide has been oxidized and there has been sufficient movement of water through the soil to leach out the oxidation products (1, p. 63).

Both ferrous sulfate and sulfuric acid are rendered harmless when any form of agricultural lime, either the carbonate, oxide, or hydroxide, is mixed with

¹ Published with the approval of the Director as Paper No. 299, Journal Series of the Minnesota Agricultural Experiment Station.

the toxic layer. It is not uncommon, however, to find these substances at the bottom of bogs in which the peat at the surface and for some distance downward is well supplied with lime, and in the mineral substratum of which, only a few inches below, there is an abundance of carbonate. In some cases, also, the same layer contains both carbonate and pyrites, but under this circumstance the toxic oxidation products will be neutralized almost as rapidly as formed.

In the reclamation of a bog the presence of a toxic layer becomes of importance since, if the peat is shallow, it may prevent the penetration of plant roots into the underlying mineral soil which otherwise might provide for any deficiencies of the peat in potash and phosphoric acid. Further, when material from such a toxic layer is thrown up in the course of ditching, and spread over adjacent land with the intention of improving it, it may prove injurious.

EXPERIMENTAL

In the autumn of 1918 several series of samples were collected from the Golden Valley Peat Experimental Fields in northern Minnesota. The chemical composition of the peat, the underlying muck and the mineral substratum is shown in table 1. In case of series A, B and C taken from the bank of a large drainage ditch adjacent to one of the experimental fields, it was found that the upper portion of the muck substratum and the section of peat immediately above it had a more strongly acid reaction, Truog method (6), than the layers above and below (table 2). From the surface down to this acid zone the peat was well supplied with lime, while the lowest part of the muck layer and the light-colored mineral substratum carried an abundance of calcium carbonate as shown by effervescence with dilute acid (table 2). Series D, taken from an excavation made in one of the experimental fields nearly a half mile back from the drainage ditch, did not show such marked differences in reaction.

The relative amounts of sulfide (table 2) were compared by using lead acetate paper. The procedure was briefly as follows:

A 10 gm. sample was placed in an Erlenmeyer flask of appropriate size, 100 cc. of distilled water and a few cubic centimeters of concentrated sulfuric acid added, a strip of filter paper moistened with lead acetate solution placed across the mouth of the flask and the contents of the flask brought to a boil and the boiling continued just 2 minutes. The degree of blackening of the lead acetate paper, or *sulfide coloration*, indicated the relative amounts of sulfide present which were designated by the same terms as are used on Truog's standard color chart (6, p. 8) to express the degrees of acidity.

In the levels nearest to the dividing line between the peat and the muck, the samples from the ditch bank showed a greater degree of acidity than corresponding samples taken from the excavation. There was, however, no difference in sulfide coloration. Along the bank of the ditch, which had been dug seven years before, some of the sulfide had been oxidized with consequent formation of sulfuric acid. This accounts for the more acid reaction of the sections carrying the larger amounts of sulfide. In general the most sulfide

TABLE 1
Chemical composition of Golden Valley peat

DEPTH OF SECTION	WEIGHT PER CUBIC FOOT	LOSS ON IGNITION	ASH	NITROGEN	LIME (CaO)	PHOSPHORIC ACID	REACTION BY TRUOG METHOD
<i>in.</i>	<i>lbs.</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	
0-6	7.9	87.0	13.0	2.43	2.05	0.18	} Very slight
7-12	9.9	80.0	20.0	2.46	3.29	0.20	
13-18	9.9	89.2	10.8	2.56	2.35	0.14	
19-24	12.6	88.2	11.8	2.57	2.39	0.15	} Slight
25-30	13.9	87.4	12.6	2.96	2.21	0.15	} Strong
31-33		32.8	67.2	1.23	2.12	0.14	} Very strong
34-36		6.8	93.2	0.238	3.05		
37-39				0.163	8.99		
40-42				0.120	12.15		

TABLE 2
Reaction and relative amounts of sulfide in successive levels
Samples of 1918*

DEPTH	SAMPLES FROM DITCH BANK						SAMPLES FROM EXCAVATION	
	Series A		Series B		Series C		Series D	
	Acidity	Sulfide coloration	Acidity	Sulfide coloration	Acidity	Sulfide coloration	Acidity	Sulfide coloration
<i>in.</i>								
0-6	} v. sl†	} sl	} v. sl	} sl	} v. sl	v. sl	v. sl	sl
7-12						v. sl	v. sl	sl
13-18						med	sl	med
19-24	sl	med	v. sl	med	sl	sl	v. sl	med
25-27	} str	} str	} v. sl	} med	sl	med	v. sl	sl
28-30					v. sl	v. sl	neut	sl (e)
31-33	v. str	med	sl	med	neut	sl (e)	neut	sl (e)
34-36	} neut	} sl (e)	sl	med	neut	v. sl (e)	neut	v. sl (e)
37-39			v. sl	sl	neut	v. sl (e)	neut	v. sl (e)
40-42			sl	sl	neut	v. sl (e)	neut	v. sl (e)
43-45	neut	sl	sl	neut	none
46-48	neut	neut	sl
49-51	neut	sl (e)
52-54	neut	v. sl (e)
55-57	neut

* Determinations were made 2 months after the samples were collected. The heavy cross lines indicate the approximate boundary between the peat layer and the underlying mineral soil.

† neut = neutral, v. sl = very slight, sl = slight, med = medium, str = strong, v. str = very strong, e = effervesces with dilute acid.

was found in the layer of peat immediately above the muck and not in the muck layer itself, just the opposite of Ramann's conclusion as to European peats. Ramann considered the sulfide more common in the muck layer underlying the peat than in the peat itself (3, p. 100).

In the samples dealt with, the sulfide occurred in such a finely divided state that it was not visible to the naked eye, and could be identified only by chemical tests. Typical samples showed the presence of iron while the two that were most strongly acid, those from the 28-30 and 31-33 inch sections of Series A, showed the presence of ferrous iron.

Two areas in the northwestern and one area in the northeastern part of the state were examined for sulfides and acidity during the season of 1919. Samples were collected only from the six-inch layer of peat immediately above the muck and from the upper portion of the muck layer. One of the northwestern areas extended from Golden Valley eastward some 6 miles and included the Golden Valley Peat Experimental Fields, of which a thorough examination was made, while the other, some 25 miles southeast of the first, embraced an area of shallow peat to the east of Thief River Falls. The one in the northeastern part of the state, was in the vicinity of Meadowlands, in St. Louis County, embracing an area 15 by 5 miles. In order to avoid any oxidation of the sulfide between the time of taking the samples and their laboratory examination, a field outfit was carried and the samples tested within a few hours after being taken. When shipped and later stored at the laboratory for some time before testing, samples had been found to show a more strongly acid reaction and less sulfide coloration.

Of the 20 series of samples taken from the Experimental Fields at Golden Valley in the second season, only one showed a strongly acid reaction in the peat layer, while all responded to the test for sulfides (table 3). Also the muck showed less acidity and less sulfide than the peat and in the case of three of the muck series, both acidity and sulfide were absent. This difference from the results of the first season is to be attributed to a flood (2, p. 51) following a torrential rain in the early part of July. Erosion of the walls of the large drainage ditch from which samples had been taken the year before widened it some 12 or 15 feet and exposed fresh sections on both sides. Samples taken from freshly exposed portions showed the same general condition as found farther back. There was no markedly acid peat or muck layer (table 3), and the sulfide coloration was about the same as the year before.

The samples taken at one-mile intervals east of Golden Valley and those taken east of Thief River Falls very closely resembled those taken on the Experimental Fields, in both reaction and sulfide content. Thus in general the results were very similar to those secured in 1918 with samples taken from the excavation on the experimental tract.

In only one place in the Meadowlands area was sulfide found. This was in a small "pocket" in which there was an unusual depth of muck—about two feet. In this instance the sulfide was more abundant in the uppermost por-

tion of the muck layer than in the peat. A summary of the samples tested and the number of these showing a sulfide coloration is given in table 4.

During the field work of the second season a set of 19 samples was collected for chemical analysis. These consisted of nine pairs of samples made up of the upper 6-inch layer of muck substratum and the 6-inch layer of peat immediately above this, taken at different places on the Experimental Fields at Golden

TABLE 3
Reaction and relative amounts of sulfide in peat soil from northwestern Minnesota
Samples of 1919

SERIES	PEAT		MUCK		SERIES	PEAT		MUCK	
	Acidity	Sulfide coloration	Acidity	Sulfide coloration		Acidity	Sulfide coloration	Acidity	Sulfide coloration
<i>Golden Valley Peat Experiment Field</i>					<i>Ditch Bank at Golden Valley</i>				
1	v. sl	sl	neut	v. sl	21	v. sl	v. sl		v. sl
2	v. sl	v. sl		sl	22	v. sl	v. sl	sl	v. sl
3	str	sl	sl	sl	23	v. sl	v. sl		none
4	sl	v. sl		none	24	v. sl	v. sl		v. sl
5	sl	sl		v. sl	25	v. sl	v. sl		sl
6	sl	v. sl		none	<i>East of Golden Valley</i>				
7	v. sl	sl	v. sl	none	26	v. sl	sl		sl
8	v. sl	sl		v. sl	27	v. sl	sl		v. sl
9	v. sl	sl		v. sl	28	neut	sl		v. sl
10	v. sl	sl		v. sl	29	neut	sl		v. sl
11	v. sl	sl		v. sl	30	v. sl	sl		sl
12	v. sl	sl	neut	v. sl	31	neut	v. sl		none
13	neut	sl		sl	<i>Near Thief River Falls</i>				
14	neut	sl		sl	32	sl	sl	neut	v. sl
15	v. sl	sl		v. sl	33	sl	sl	neut	v. sl
16	v. sl	sl		v. sl	34	sl	sl	neut	v. sl
17	v. sl	sl		v. sl	35	neut	sl	neut	v. sl
18	neut	sl	neut	v. sl					
19	neut	med	v. sl	sl					
20	v. sl	sl		sl					

TABLE 4
Number of samples showing the presence of sulfides
Samples of 1919

AREA	PEAT		MUCK	
	Number of samples collected	Number showing sulfide	Number of samples collected	Number showing sulfide
Golden Valley.....	50	50	51	46
Thief River Falls.....	4	4	4	4
Meadowlands.....	18	1	18	1

Valley, and of one sample of peat taken 4 miles southeast of Thief River Falls. To insure the exclusion of any air and the consequent oxidation of the sulfide present, the samples were packed firmly into 2-quart tin cans, tightly covered and sealed with paraffin. When the samples were opened in the laboratory the seals on all were found to be in good condition. The acidity and the sulfide coloration, as well as the amount of sulfide, expressed as H_2S , are reported in table 5. The iodine method (5, p. 398) used in determining the last is briefly as follows:

Twenty-five grams of moist peat or 50 gm. of muck is weighed into a 500-cc. Erlenmeyer flask, 100 cc. of distilled water and 10 cc. of stannous chloride added. The flask is then attached to a condenser in turn connected with another flask containing an ammoniacal solution of cadmium sulfate. Twenty cc. of hydrochloric acid is added to the contents of the flask through a separatory funnel and the whole brought to boiling and then gently boiled for 20 minutes. The contents of the flask containing cadmium sulfide are then nearly neutralized with hydrochloric acid and titrated with thirtieth normal iodine in the usual manner.

TABLE 5
Sulfide, reaction, and sulfide coloration of 19 samples of peat and muck

SAMPLE	PEAT			MUCK		
	Reaction	Sulfide coloration	Sulfide*	Reaction	Sulfide coloration	Sulfide
			<i>per cent</i>			<i>per cent</i>
4	sl	med	0.060	str	sl	0.006
1	str	med	0.058	neut	v. sl	0.002
5	v. sl	med	0.047	med	sl	0.014
3	sl	sl	0.037	neut	v. sl	0.005
9	sl	sl	0.036	str	v. sl	0.004
8	sl	sl	0.032	sl	v. sl	0.002
2	sl	sl	0.028	neut	v. sl	0.003
6	str	sl	0.025	neut	v. sl	0.003
7	v. sl	sl	0.016	v. sl	v. sl	0.002
10	sl	sl	0.016			

* Expressed as H_2S .

With both the peat and the muck there is a general agreement between the coloration of the lead acetate paper and the amount of sulfide found, i.e., the darker the sulfide coloration the larger is the amount of sulfide found. However, when a peat and a muck which show the same degree of sulfide coloration, are compared, no direct relation is shown between the degree of coloration and the amount of sulfide. The peat layer contains the larger amounts of the latter, varying between 0.016 and 0.060 per cent as compared with 0.002 to 0.014 per cent in the muck, and, for any given degree of sulfide coloration, shows a higher actual content of sulfide.

No concordance was found between the degree of acidity and either the sulfide coloration or the amount of sulfide the acidity being governed largely by conditions favoring oxidation and by the presence of carbonate.

Crops on the untreated plots on the Golden Valley field were comparative failures, with the exception of flax (2, p. 33), but when given a dressing of acid phosphate they yielded as well as on the surrounding mineral soil. On properly fertilized plots near the places where samples 1, 2, 5 and 6 were taken, the living plant roots were found to penetrate both the lowermost layer of peat and the muck, and even to extend down into the mineral subsoil. Thus either the amount of sulfide oxidized must be regarded as too small to harm the growing plants or the carbonate present neutralized most of the acid as rapidly as formed.

In a vegetation experiment with a pyrite-carrying muck from a shallow bog near Goodridge, 15 miles southeast of Golden Valley, clover plants on the untreated muck watered with distilled water made almost no growth, although at the end of a year were still alive. On the same muck treated with the ash obtained by burning a portion of the overlying peat and watered with tap water carrying large amounts of lime the growth of clover was excellent, the calcium carbonate in the ash and water being sufficient to render the two toxic compounds harmless. In the same Goodridge field complete reclamation was effected by the application of acid phosphate (1, p. 63).

In a similar vegetation experiment carried out in the plant house a year later with untreated muck from the Golden Valley Experimental Fields sweet clover did well when watered freely with the tap water.

On the surface of the peat in northwestern Minnesota, gypsum often occurs as a white incrustation sometimes so heavy that it crackles under the foot. It is also always to be found on the faces of ditches. A sample of the material intermixed with more or less peat from Golden Valley was subjected to repeated extractions with warm water until the leachings failed to give a test for sulfates, the extract evaporated on the water bath, and analyzed with the following results:

Fe ₂ O ₃	0.0 per cent
Al ₂ O ₃	0.0 per cent
CaO.....	28.5 per cent
MgO.....	4.1 per cent
So ₃	55.5 per cent
Total Solids.....	0.1015 gram

SUMMARY

In samples of peat and muck from the Golden Valley Peat Experimental Fields in northwestern Minnesota in 1918, sulfides were generally found at all levels in the peat, in the muck substratum and in the upper portion of the mineral subsoil below. The greatest amount was found in the lowest portion of the peat layer and not in the muck.

The reaction of the peat and muck was found to be but little related to the relative amount of sulfides present, but to conditions permitting the oxidation of the sulfide to sulfuric acid and ferrous sulfate.

The layers in an exposed ditch face strongly impregnated with sulfide gave in 1918 a more acid reaction than did those at some distance from the ditch. But a year later, just after an unusual flood had widened the ditch and exposed fresh material, the peat of the ditch face was found to be similar in reaction to the corresponding layers farther back.

Expressing the sulfide content as hydrogen sulfide, nineteen samples of peat and muck showed a maximum of 0.060 and a minimum of 0.016 per cent for the lowermost layer of peat and 0.013 and 0.002 per cent for the muck substratum immediately below.

Sulfides appear to be much more commonly associated with peat in northwestern than in northeastern Minnesota, where in an area of approximately 75 square miles, sulfides were found at only one place.

REFERENCES

- (1) ALWAY, F. J. 1920 Agricultural value and reclamation of Minnesota peat soils. Minn. Agr. Exp. Sta. Bul. 188.
- (2) ALWAY, F. J. 1920 Report of Golden Valley Peat Experimental Fields, 1918 and 1919. Minn. Agr. Exp. Sta. Bul. 194.
- (3) RAMANN, E. 1911 Bodenkunde, 3d ed., Julius Springer, Berlin.
- (4) RENNIE, REV. R. 1810 Essays on the Natural History and Origin of Peat Moss. Edinburgh.
- (5) SCOTT, W. W. 1917 Standard Methods of Chemical Analysis. D. van Nostrand Co., New York.
- (6) TRUOG, E. 1915 A new test for soil acidity. Wis. Agr. Exp. Sta. Bul. 249.
- (7) WOLLNY, 1897 Die Zersetzung der organischen Stoffe und die Humusbildungen. Carl Winter, Heidelberg.