HYDROGEN ION STUDIES OF WATER, PEAT, AND SOIL, IN RELATION TO ECOLOGICAL PROBLEMS AT BACON'S SWAMP, MARION COUNTY, INDIANA.

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In connection with vegetational studies of Bacon's Swamp[1] it was found advisable to examine the hydrogen ion concentration of various zones to corroborate certain opinions as to the past vegetational history and the conditions under which the present vegetation is existing. Certain other information contained herein was obtained incidental to the real purpose of the studies and is included for what value it may have.

The swamp proper consists of a wet meadow surrounded by a more or less definite number of concentric vegetational zones. The normal sequence here runs from the center towards the periphery in the following stages: (a) *Calamagrostis canadensis,* (Mx.) Beauv. meadow with a peripheral zone of *Carex impressa,* (Wright) Mack; (b) *Cephalanthus occidentalis,* L. and *Salix nigra,* Marsh. occupying the moat, a region of deeper water; and (c) the forest region, first of the swamp forest type and last the upland forest climax.

The peripheral zones are distinctly of the half-drained type of vegetation but in the central meadow there are indications that the former vegetation has pertained more to the undrained or bog type. Conspicuous in this connection are sphagnum and "islands" of *Decadon verticellatus,* (L.) Ell., a notorious bog-mat shrub, here found in isolated patches in the fen-like meadow and fringing the outer natural open patch of water in what is perhaps the deepest portion of the swamp basin.

A study of the hydrogen ion concentration of surface water from various points over the swamp reveals a higher acid condition in the center of the southwest lobe. If the zones are considered from the outside inward, and, in the main, they are concentric and are to be found on almost any radius, it will be seen that the acidity increases towards the center where the vegetation is more of the acid type. (Table I.)

Perhaps the most interesting observation to be made is that of the diurnal variation in the pH at any one station. This phenomenon, first

[1] Cain, S. A. Airplane Photography and Ecological Mapping. Proc. Ind. Acad. Soc., 36, 1926. 1927.

[2] Philip, C. Diurnal Fluctuation in the Hydrogen Ion Activity of a Minnesota Lake. Ecology 8:74-89, 1927.

"Proc. Ind. Acad. Sci., vol. 37, 1927 (1928)."

TABLE I. Range in pH Values of Hydrophytic Associations.

The Association Station No.	Sample Number	Time of Reading	pH Value	pH Range	Amount of Range
1. Salix Nigra Algae	83a 83b 83c 83d	5:15 a. m. 10:25 a. m. 12:30 p. m. 3:30 p. m.	7.2 7.4 7.5 7.8	7.2–7.8	0.6
2. Cephalanthus Little Algae	88a 88b 88c 88d	5:05 a. m. 10:12 a. m. 12:50 p. m. 2:45 p. m.	6.9 6.9 7.1 7.2	6.9–7.2	0.3
3. Typha-Lemna Much Algae	86a 86b 86c 86d	5:01 a. m. 10:10 a. m. 12:45 p. m. 2:42 p. m.	6.8 7.5 7.8 7.6	6.8–7.8	1.0
4. Nymphaea Little Algae	71a 71b 71c 71d	4:52 a. m. 10:05 a. m. 12:40 p. m. 2:40 p. m.	6.9 6.8 7.0 7.1	6.9–7.1	0.2
5. Sedge Meadow Much Algea	62 69 43 65 72	11:05 a. m. 11:10 a. m. 11:20 a. m. 11:25 a. m. 4:00 p. m.	6.9 6.5 6.0 6.2 5.8	5.8–6.9	1.1
6. Grass Meadow	63 73 70 47	11:00 a. m. 11:15 a. m. 11:30 a. m. 3:30 p. m.	6.9 6.4 6.6 5.9	5.9–6.9	1.0
7. Water Holes in Meadow Due to Burning Algae	61 60	11:30 a. m. 3:45 p. m.	5.5 5.8	5.5–5.8	0.3
8. Decodon Island No Algae S. W. Lobe	67 42 72 48 40 82	11:35 a. m. 11:40 a. m. 11:45 a. m. 11:50 a. m. 3:45 p. m. 4:05 p. m.	5.1 5.5 5.3 5.1 5.9 6.0	5.1–6.0	0.9

noted by Philip,[2] is related to the photosynthetic-respiratory ratio, consequently the hydrogen ion concentration at any hydrophytic station will vary with the factors affecting the quantitative CO_2 and O_2 production and utilization.

A series of pH readings is necessary for any adequate information as to the acid conditions under which any group of plants exists. No longer can random observations be give any importance.

From Table I it can be seen that there is a diurnal fluctuation exhibited on this particular day (May 13, 1927, cloudy) ranging from 0.2 variation in one instance to 1.1 variation in another and from the most acid to the least acid situation we have the extremes from Decadon with pH 5.1-6.0 to Salix with pH 7.2-7.8.

The diurnal range on a bright, warm day would no doubt be more than twice that shown here for a rather dull day.

A study of the pH of the submersed peat in which the various wet-meadow plants are rooted shows higher acidity in the southwest bog-like region (Table II), when the acidity may be 100 times that in the north lobe. It will also be noted that the peat runs more acid than the water which covers it.

TABLE II. H-ion of Peat Samples.

Sample No.	Location of Station	Depth	pH Colorimetric
55	Calamagrostis	Surface	6.0
56	Calamagrostis	36″ deep	6.4
57	North lobe swamp	Surface	6.4
58	Calamagrostis	16″ deep	6.6
85	Edge of open water S.w. lobe	Surface	4.8
42	S.w. lobe	18″ deep	5.3
80	Is. of Decadon S.w. lobe	Surface	5.0
23	S.w. lobe	18″ deep	4.4

TABLE III. pH Values of Soil Samples.

Depth of Sample in Inches		Lowland Forest		Upland Forest	
		Number	pH	Number	pH
A	0	27	6.7	10	7.3
	5	41	6.8	30	7.1
	10	21	6.9	6	7.3
	15	37	6.7	29	7.4
	20	3	7.0	11	7.4
B	0	39	5.9	34	6.4
	5	4	6.3	35	6.4
	10	33	6.1	19	6.5
	15	17	6.5	46	6.3
C	0	32	6.7	24	7.0
	5	25	6.7	20	6.5
	10	12	7.1	8	6.3
	15	14	7.2	15	6.6
	20	22	7.4	28	6.6
D	0	16	7.0		
	10	31	7.2		
	20	26	7.1		

TABLE IV. Total Ranges of pH at Different Levels of Soil.

Depth of Sample	Swamp Forest	Upland Forest
0″	5.9–7.0	6.4–7.3
5″	6.3–6.8	6.4–7.1
10″	6.3–7.2	6.3–7.3
15″	6.5–7.2	6.3–7.4
20″	7.0–7.4	6.6–7.4

A brief study was made of the soil stratification and the pH relations of the upland and lowland forests. Four pairs of stations were selected typical of the two types of forest. The results of the readings are given in Tables III and IV. For colorimetric readings see the description of the La Motte apparatus.[3] The electrometric readings were made on a Kelley electrical titration apparatus. It will be seen from the preceding data that there is no particular contrast between the soil

[3] Taylor, W. A. The A. B. C. of Hydrogen Ion Control. The La Motte Chemical Co. Baltimore, Md. 1926.

reaction of the two types of forest which differ so much floristically. Some other factor is evidently the limiting one. (It seems that the upper level of inundation at periods of high water coincide with the limits of the rather narrow swamp forest.)

In the case of the swamp forest there seems to be a definite gradient in pH, alkalinity increasing with increasing depth. The greatest range is from pH 5.9 at the surface to pH 7.4 at a depth of 20 inches. This is the same sort of situation Salisbury[4] found. It is, of course, not assumed that so few readings are sufficient to establish conclusive evidence as to stratification in the soil. It is maintained, however, that these four sets of samples are sufficient, in this case at least, to show that pH is not the significant factor in determining the limits of the swamp and upland forests.

These soil samples were obtained by use of a spring-steel excavater instead of the customary soil-auger. This tool is a coiled spring with a flat outer surface and a convex inner face with a maximum width of

TABLE V. Colorimetric and Electrometric Check of pH.

Soil Solutions						Peat Solutions		
Lowland			Upland					
No.	Colorimetric	Electrometric	No.	Colorimetric	Electrometric	No.	Colorimetric	Electrometric
27	6.7	6.70	10	7.3	7.32	9	6.4	6.50
41	6.8	6.85	30	7.1	7.08	45	6.4	6.38
21	6.9	6.92	6	7.3	7.32	7	6.1	6.15
37	6.7	6.65	29	7.4	7.42	13	6.2	6.18
3	7.0	6.90	11	7.4	7 32	36	6.6	6.60
39	5.9	6.07	34	6.4	6.53	51	6.5	6.38
4	6.3	6.23	35	6.4	6.30	52	6.2	6.02
33	6.1	6.03	19	6.5	6.38	53	6.4	6.37
17	6.5	6.54	46	6.3	6.25	54	6.3	6.32
32	6.7	6.72	24	7.0	7.10	55	6.0	6.04
27	6.7	6.68	20	6.5	6.50	56	6.4	6.33
12	7.1	6.88	8	6.3	6.25	57	6.4	6.37
14	7.2	7.04	15	6.6	6.58	58	6.6	6.58
22	7.4	7.33	28	6.6	6.43			
16	7.0	6.88						
31	7.2	7.43						
26	7.1	7.12						

about one-fourth inch. The spring is about 15 inches long and two inches in outer diameter. It is tapered onto a short length of one and one-fourth inch pipe and fitted on in convenient lengths as greater depth of samples is desired. The advantages of this hollow spring excavator are two: first, it is easy to use and, second, it secures a core of fair size diameter the inner parts of which are not contaminated by soil water from above if the operation is performed quickly. The outer moister parts of the core which have been subjected to friction and contamination can be quickly removed and a "pure" sample obtained from the interior.

In order to determine the reliability of the colorimetric method a

[4] Salisbury. Stratification of Hydrogen-ion Concentration of the Soil in Relation to Teaching and Plant Succession. Jour. Ecol. 9. 1922.

TABLE VI. Changes in pH of Collected Samples.

WATER SAMPLES—

Association	Sample No.	pH May 13th	pH May 16th	H-ion Increase	Decrease
Salix	83a	7.2	7.3		0.1
Cephalanthus	88a	6.9	7.9		1.0
Typha	86a	6 8	7.2		0.4
Nymphaea	71a	6.9	7.3		0.4
S. W. Meadows	47	5.9	5.6	0.3	
S. W. Meadows	72	5.8	5.6	0.2	
S. W. Meadows	60	5.8	5.7	0 1	

PEAT SOLUTIONS—

Sample Depth	Sample No.	pH May 10th	pH May 18th	H-ion Increase	Decrease
Surface Peat	9	6.4	5.9	0.5	
Surface Peat	51	6.5	6.5	0	
Surface Peat	55	6.0	6.0	0	
Peat 1″ deep	45	6.4	6.4	0	
Peat 2″ deep	7	6.1	6.2		0.1
Peat 3″ deep	13	6.2	6.2	0	
Peat 15″ deep	54	6.3	6.0	0.3	
Peat 66″ deep	56	6.4	6.4	0	
Peat 66″ deep	58	6.6	6.4	0.2	

SOIL SOLUTIONS (LOWLAND SAMPLES)—

Sample Depth	Sample No.	pH May 9th	pH May 17th	pH May 18th	Increase	Decrease
Surface	27	6.7	6.7	....	0	
Surface	39	5.9	6.0	....		0.1
Surface	32	6.7	....	6.3	0.4	
Surface	16	7.0	....	6.6	0.4	
Depth, 5 inches	41	6.8	6.4	....	0.4	
Depth, 5 inches	4	6.3	6.3	....	0	
Depth, 5 inches	25	6.7	....	6.5	0.2	
Depth, 10 inches	21	6.9	....	6.6	0.3	
Depth, 10 inches	31	7.2	6.8	....	0.4	
Depth, 15 inches	37	6.7	6.6	....	0.1	
Depth, 15 inches	14	7.2	7.1	....	0.1	
Depth, 20 inches	22	7.4	7.0	....	0.4	
Depth, 20 inches	26	7.1	6.7	....	0.4	

SOIL SOLUTIONS (UPLAND SAMPLES)—

Sample Depth	Sample No.	pH May 9th	pH May 17th	pH May 18th	Increase	Decrease
Depth, surface	10	7.3	....	7.0	0.3	
Depth, surface	34	6.4	....	6.1	0.3	
Depth, surface	24	7.0	....	6.6	0.4	
Depth, 5 inches	30	7.1	6.9	....	0.2	
Depth, 5 inches	35	6.4	6.2	....	0.2	
Depth, 5 inches	20	6.5	....	6.2	0.3	
Depth, 10 inches	19	6.5	....	6.1	0.4	
Depth, 15 inches	29	7.4	....	6.9	0.5	
Depth, 15 inches	46	6.3	....	6.3	0	
Depth, 20 inches	11	7.4	6.8	....	0.6	
Depth, 20 inches	28	6.6	....	6.4	0.2	

number of soil solutions were read by the electrometric method as well as by the La Motte system. The readings were made at the same time by different individuals. The results were checked on completion. (Table V.)

The 44 checks of the colorimetric method show an average deviation from the electrometric of 0.061 pH. It is probably realized that this is sufficiently close to warrant the field use of the colorimetric method, as the divergence from the true soil reaction is less than the difference in pH that can be interpreted to have any effect on the distribution of plants.

The soils here tested ranged from heavy blue clay to rich vegetable loam and peat. Olsen,[5] working on Danish soils, has found a satisfactory check in the two methods for a variety of soils.

An observation was made on the charge in pH of collected samples with a view to determining the safety with which readings could be delayed. The soil and peat samples had to be taken into the laboratory before they could be read colorimetrically. This necessitated a lapse of a few hours, which was found to make no great difference in the pH of the samples. After soil extracts were derived by centrifuging, a lapse of 12 hours in four instances tested made no difference. In order to see if longer lapses of time would change the solutions, although corked, some were read after a lapse of three days, and others were read after eight and nine days.

It will be noted from table VI that there is considerable variation in some cases and hardly any appreciable change in others. The water samples from the hydrophytic associations behave in two ways. The samples from the meadow show an increase in acidity. The samples from the deeper zones, 83, 88, etc., show a decrease in acidity. The differences here are probably related to the ratio of respiration to photosynthesis. This idea is substantiated by the apparent quantities of plants in the latter regions, and of animals in the former.

The peat samples gave extracts (with three times as much water as peat) which were apparently well buffered and contained few organisms, as five out of nine of the extracts were unchanged after a lapse of eight days.

The soil extracts showed what may be considered slight changes. They were, with one exception, changes towards increased acidity. This is explainable by respiration of micro-organisms which remained in the centrifuged extracts. Photosynthetic micro-organisms were not present in any quantity sufficient to use up much CO_2 and so give increased alkalinity. The average change in soil extracts over a period eight to nine days was 0.278 of a pH in increased acidity.

From this evidence it can be concluded that soils may be kept for quite a length of time after collecting without there being any considerable change in pH; but after the extract is made the readings should be made within a few hours.

[5] Olsen, Carsten. Studies on the H-ion Concentration of the Soil and its Significance to the Vegetation, Especially the Natural Distribution of Plants. Comptes-Rendus, Laboratoire Carlsberg. **15**, No. 1. 1923.

SUMMARY AND CONCLUSIONS.

In the lowland forest particularly there seems to be a definite downward gradient in pH, alkalinity increasing with increasing depth.

The peat samples were all acid, although those taken from the northern end of the swamp were only slightly acid. The samples from the southwest end of the swamp were more acid, reaching pH 4.4.

Soils can best be tested in the laboratory because of the necessity in most instances of filtering or centrifuging the soil extracts to clear them for colorimetric readings. Centrifuging is most satisfactory.

A series of 44 checks of the colorimetric method with the electrometric method, on different types of soils and peat, gave an average deviation of 0.061 pH. From this it may be concluded that the standard colorimetric methods are sufficiently accurate, i. e., closer to the actual effective acidity, than can be interpreted in the field in relation to vegetation.

In the hydrophytic associations there is a diurnal trend in pH. The habitats are most acid in the morning, at the close of a period of darkness and are less acid after the photosynthetic period. This trend is evidently directly correlated with the respiratory-photosynthetic ratio.

Water samples should be tested for pH in the field, as they will rapidly change in pH, due to the respiratory-photosynthetic relations of the micro-organisms present in the water.

Peat samples, even when extracted, show very little change in pH, although allowed to stand for a number of days. This is evidently correlated with the relative absence of micro-organisms. Divers soils vary in this respect.

In both soil and aquatic habitats there seems to be certain pH ranges within which the various associations are found. In most instances in this particular study the ranges of different associations overlapped or are so broad that little emphasis can be placed on acidity as a limiting factor in the present vegetation. (The greater acidity of the peat in the southwest end of the swamp can be considered as significant, as already indicated.)

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