

ORGANIC PHOSPHORUS CONTENT OF OHIO SOILS

C. J. SCHOLLENBERGER

Ohio Agricultural Experiment Station

Received for publication June 22, 1920

INTRODUCTORY

Considering the nature of the changes which are brought about in soil constituents through biochemical agencies, it has been the opinion of various soil investigators that an appreciable part of the soil's total supply of phosphorus is in organic combinations.

The methods used in the earlier work on this subject gave indications of a qualitative nature only, and did not approach with any degree of exactness to an accurate measure of the organic phosphorus of the soil. In fact, until recently the evidence that a significant part of the soil's supply of phosphorus is organically combined was largely circumstantial. It was assumed that the presence of an excess of phosphorus in the surface soil accompanied by an excess of organic carbon and nitrogen, while potassium and other inorganic constituents were about the same as in the subsurface, was conclusive evidence of the presence of organic phosphorus. Other methods of estimation, such as increased solubility of phosphorus in dilute acids after ignition or treatment with oxidizing agents, have been proposed, but the indications of some of these have been called into question, while others have perhaps never received the extended study their possibilities would warrant.

Previous to the work of Potter and Benton (4), who developed what is apparently a reliable procedure for the determination of the organic phosphorus in ammonia extracts of soil, there has been no method for the estimation of any part of the organically combined phosphorus in soil which could be considered in any degree satisfactory. In a former paper (7) from this laboratory, attention has been directed to defective features in some of these earlier methods and data published which were obtained in an extended study of the method described by the authors named. The procedure necessary for securing the maximum possible extraction of organic phosphorus from the soil studied was described in the paper cited. The data there reported led to the conclusion that the organic phosphorus obtained in ammoniacal extracts of the acid-extracted soil is a very close approximation to the soil's entire content of phosphorus so combined.

As a part of a comprehensive plan for the study of the phosphorus combinations in soils, and for the purpose of obtaining further information on the

general subject of organic phosphorus in soils, it has been considered desirable to compare virgin and cultivated surface and subsurface samples from a number of representative types of Ohio soils, with respect to organic phosphorus content and such other data as may appear to be related thereto. The work done in pursuance of this plan forms the subject matter of the present paper.

SOILS STUDIED

The samples considered here are from two depths, 0-7 inches and 7-15 inches, designated "a" and "b" respectively, in the laboratory numbers. They have been selected from a number of samples taken from important soil types of the state. The points considered in their selection have included similarity in total potassium content, as indicating similarity in mineralogical composition, between the virgin and cultivated samples and the surface and subsurface. In addition, samples showing any abnormal departure from the average of the type or inconsistencies in total phosphorus or nitrogen content have not been included. Another point to which much importance was attached is similarity in reaction to litmus paper, although several exceptions to this have been admitted if otherwise suitable. The reaction of these soils, as well as the calcium, magnesium and carbonate content have been discussed at length in a former publication (1). The names applied to the soil types represented by these samples are those of the Ohio soil survey.

The history of none of the cultivated samples is known with exactitude. Sample 36 was stated by the owner to have been cultivated not less than 70 years. Numbers 19 (from a dairy farm) and 34 had been cropped for 50 years, 21 and 38 "a long time," and 32 for 30 years. It is believed that none of the cultivated soils has been under the plow for less than a generation, and so far as could be learned none had ever been limed or had received any commercial fertilizer. The virgin samples were all taken from land, usually woodland with large trees, which was known with reasonable certainty never to have been cropped. In selecting locations for samples, care was taken to secure the virgin samples in as close proximity as possible to the place where the cultivated samples were obtained and from land of similar topography, in each case typical of the soil area being sampled.

ANALYTICAL METHODS

The methods of analysis employed were essentially those described in a former paper (7). The extractions with acid and dilute ammonia were conducted as follows. Three hundred grams of ground soil were weighed into a liter Florence flask and the flask filled with approximately 1 per cent hydrochloric acid (25 cc. concentrated acid per liter), stoppered and shaken frequently for 1 hour. The contents of the flask were then shaken up and poured upon a 15-cm. Büchner funnel with two filter paper circles upon the plate.

As soon as filtered, the soil was washed with 2 liters of the 1 per cent hydrochloric acid and finally with 1 liter of saturated carbon dioxide solution, which was found sufficient to remove the hydrochloric acid in every case. Suction was employed in the filtration but care was taken not to allow the wash liquids to be drawn through too rapidly in case a very permeable sample was being filtered. The filtrates were made to 4 liters, by weight, mixed and 300-cc. aliquots taken for the determination of phosphorus removed from the soil by washing with 1 per cent hydrochloric acid. The cake of soil was transferred to a Winchester bottle, the rinsings from the funnel, etc. added, and the requisite amount of strong ammonia to make the finished solution 2.5 per cent NH_3 (150 cc.). The bottle was finally made to such weight with water that the volume of the 2.5 per cent ammonia in contact with 300 gm. of soil was 1500 cc. The two filters partially compensate for the loss in weight from acid extraction, and as none of these soils contained an undue amount of acid-soluble material, this and the slight evaporation during filtration were considered sufficient compensation. After shaking for 6 hours in a mechanical shaker 3 gm. of powdered ammonium carbonate were added and the mixtures shaken and allowed to stand some time. The contents of the bottles were finally shaken and poured into 25-cm. Büchners with two paper circles, connected by large rubber stoppers to 4-liter wide-mouth bottles. The funnels were covered with well fitting glass plates and after several hundred cubic centimeters had run through and the filtrates were free from clay, the apparatus was disconnected, the filtrates poured back and the apparatus again connected. The bottles were partially exhausted (a 25-cm. mercury vacuum was found safe) sealed and allowed to stand until the extract had passed the filter, renewing the vacuum from time to time if necessary. A very small amount of glycerine was found indispensable as a lubricant for the rubber stoppers.

The method for inorganic phosphorus in ammonia extracts has been very satisfactory with all these samples with the exception of those representing the Brookston silty clay loam (36 and 37). In these cases all the precipitates were abnormal in appearance and behavior, and only by redissolving the ignited magnesium pyrophosphate and reprecipitating with official molybdate solution and magnesia mixture could the results of two determinations be made to agree. As the extracts of these samples gave no unusual difficulty in the total phosphorus determination, it is probable that the contaminant was partly organic. In the determination of total phosphorus in ammonia extracts by the wet combustion method, it was found that the final precipitates of magnesium ammonium phosphate from some of these samples were contaminated with iron, therefore it was necessary to resort to reprecipitation by molybdate and magnesia mixture. Although not absolutely necessary in all cases, this was always done in the work here reported.

The phosphorus in the soil was determined by the magnesium nitrate-volumetric method (2). Total nitrogen was determined by the official method (2). Ammonia-soluble organic matter (humus) and humus ash were deter-

mined by evaporating 50 cc. of the ammonia extract to dryness in a weighed platinum dish on the steam bath, drying 4 hours at 100°C. in vacuo over P_2O_5 , weighing, igniting, and again weighing. No correction for combined water in the ash was applied.

Comparative color of the ammonia extracts was determined by diluting 2 cc. to 100 cc. and comparing in a Schreiner colorimeter with an extract similarly treated and arbitrarily given the value 100. It should be noted that the numbers serving as the index for comparative intensity of color vary directly with the intensity of color. Thus, an extract with the number 50 has one-half the color intensity of the standard.

SIGNIFICANCE OF ANALYTICAL DATA CONSIDERED

In table 1, the analytical data for these soils, of interest in the present connection, are presented. These include total phosphorus in the soil, inorganic and organic phosphorus in ammonia extracts and phosphorus removed from the soil by washing with 1 per cent hydrochloric acid and saturated carbon dioxide solution in preparing the samples for extraction with ammonia solution.

While the direct connection between the acid-soluble and the organic phosphorus content of the soil may not be apparent, the amount of phosphorus removed from the soil by leaching with dilute hydrochloric acid is considered to be of some significance in a soil study of this nature, for the reason that it may serve to indicate variations in the state of combination of soil phosphorus or serve as an index to the more readily soluble or presumably more available part of the total phosphorus, as other procedures of extraction with dilute acids have been supposed to do. It should be understood that the hydrochloric-acid leaching removes much more phosphorus from the soil than does a single extraction with fifth-normal nitric acid, which has been used to a considerable extent for this purpose in the past. This is true, not so much because one is a more powerful solvent than the other, but because a process of leaching tends to reduce to a minimum the reabsorption of phosphorus once dissolved. This phase of the subject has been studied at length by Prescott (6).

From data published in a former paper (7), it appeared that in the case of the soil then studied, inorganic phosphorus absorbed by the soil from acid solution was completely recovered as inorganic phosphorus in water washings and a subsequent ammonia extraction. Unfortunately, no work intended to confirm this point for the soils now under consideration has been done, so that in these cases there is no proof that the absorbed phosphorus is completely removed by a subsequent ammonia extraction. The most that can be said is that the phosphorus neither removed by acid leaching nor appearing in the ammonia extract is about the maximum amount which can be considered to be in a form very resistant to solvents, possibly because it is enclosed in mineral particles. If this last statement is true, it seems probable that there

would be evident, in many cases, a certain uniformity among figures so obtained for virgin and cultivated surface and subsurface soils of the same type, of similar origin and mineralogical composition. Such being the case, it would indicate that the figures for organic phosphorus are probably not grossly inaccurate by reason of incomplete extraction at least, since it is improbable that the surface and subsurface samples would contain the same amounts of organic phosphorus not extracted by ammonia. This phase of the subject will be dismissed with the statement that the percentages of insoluble phosphorus, calculated on the soil, do in most cases show a marked similarity. The variation between soil types is large, but several types show nearly as large differences between surface and subsurface of the same sample. As the percentages can readily be calculated from other data in table 1, they are not tabulated.

The total nitrogen contents of these samples are included, because these serve as indicators of the relative amounts of organic matter in the samples. The comparative color, total organic matter (humus) and humus ash in the ammonia extracts are included to establish their relation to the content of organic phosphorus.

DISCUSSION OF ANALYTICAL DATA

In nearly all cases the virgin surface sample contains more total phosphorus than the corresponding cultivated sample. The same is true of the subsurface samples also, although here the average difference is comparatively small.

The ammonia-soluble organic phosphorus of both depths averages higher with virgin samples than with cultivated. In each depth, the average percentage of the total phosphorus which is in the ammonia-soluble organic form is practically the same in the cultivated samples as it is in the virgin samples. One-third the total phosphorus of the average surface sample is organically combined, while in the subsurface samples the average proportion is one-fifth. As it happens, the extremes are in the cases of the two sandy soils, the Dunkirk fine sand having but 18 and 20 per cent of the total phosphorus in the surface depths of the cultivated and virgin samples, respectively, in the organic form, while the Clyde fine sand shows 52 and 50 per cent so combined in the corresponding samples. The lowest proportion of total phosphorus in organic form in the case of a subsurface sample is found in the case of the virgin Wooster silt loam, 6 per cent; the highest is 47 per cent in the virgin Clyde fine sand.

The proportion of the total phosphorus occurring as ammonia-soluble inorganic averages slightly higher in the subsurface than in the surface samples. The average figure is 11 per cent for both virgin and cultivated samples of this depth, but 8 and 9 per cent, respectively, for surface samples. The extremes are 2 per cent in the subsurface of the cultivated Clyde fine sand and the surface of the virgin Crosby silt loam and 20 per cent in the subsurface of the vir-

TABLE 1
Data on soils investigated

DESCRIPTION	NUMBER	PHOSPHORUS										TOTAL NITROGEN	COMPARATIVE COLOR OF NH ₄ OH EXTRACTS	NH ₄ OH-SOLUBLE ORGANIC MATTER (HUMUS)	HUMUS ASH	ORGANIC P IN NH ₄ OH-SOLUBLE MATTER	REACTION OF SOIL
		Total	NH ₄ OH-soluble organic	Organic as per cent of total	NH ₄ OH-soluble inorganic	NH ₄ OH-soluble inorganic as per cent of total	HCl-washing-soluble	HCl-washing-soluble as per cent of total	HCl-washing-soluble								
									per cent	per cent							
Wooster loam.....	Cultivated {	4a	0.0530	0.0165	31	0.0045	8	0.0062	12	0.14	63	1.430	0.197	1.15	Acid		
	Virgin {	4b	0.0361	0.0058	16	0.0013	4	0.0015	4	0.06	18	0.444	0.213	1.30	Acid		
Wooster silt loam.....	Cultivated {	8a	0.0342	0.0108	31	0.0050	15	0.0028	8	0.12	52	1.048	0.169	1.03	Acid		
	Virgin {	8b	0.0307	0.0060	20	0.0033	11	0.0011	4	0.07	19	0.551	0.108	1.09	Acid		
Cincinnati silt loam.....	Cultivated {	9a	0.0520	0.0140	27	0.0063	12	0.0072	14	0.16	83	1.454	0.111	0.96	Acid.		
	Virgin {	9b	0.0348	0.0020	6	0.0063	18	0.0021	6	0.05	8	0.310	0.090	0.65	Acid		
Clermont silt loam.....	Cultivated {	19a	0.0613	0.0182	30	0.0056	9	0.0015	2	0.11	67	1.083	0.130	1.69	Acid		
	Virgin {	19b	0.0541	0.0038	7	0.0093	17	0.0014	3	0.06	9	0.355	0.069	1.06	Acid		
Clermont silt loam.....	Cultivated {	20a	0.0657	0.0202	31	0.0070	11	0.0062	9	0.15	91	1.403	0.171	1.44	Acid		
	Virgin {	20b	0.0534	0.0045	8	0.0095	18	0.0045	8	0.06	11	0.384	0.070	1.17	Acid		
Clermont silt loam.....	Cultivated {	21a	0.0437	0.0125	29	0.0048	11	0.0010	2	0.10	28	0.870	0.412	1.44	Acid		
	Virgin {	21b	0.0288	0.0040	14	0.0023	8	0.0010	3	0.04	5	0.352	0.470	1.14	Acid		
Clermont silt loam.....	Cultivated {	22a	0.0464	0.0140	30	0.0040	9	0.0016	3	0.14	40	1.247	0.359	1.12	Acid		
	Virgin {	22b	0.0294	0.0045	15	0.0025	9	0.0008	3	0.06	9	0.377	0.484	1.19	Acid		

Crosby silt loam.....	{ Cultivated }	34a	0.0312	0.0420	38	0.0018	6	0.0037	12	0.14	113	1.617	0.106	0.74	Acid
		34b	0.0221	0.0053	24	0.0020	9	0.0017	8	0.06	28	0.576	0.184	0.91	Acid
	{ Virgin }	35a	0.0522	0.0148	28	0.0013	2	0.0042	8	0.17	129	1.920	0.97	0.77	Acid
		35b	0.0242	0.0058	24	0.0008	3	0.0007	3	0.07	34	0.538	0.135	1.07	Acid
Fox silt loam.....	{ Cultivated }	59a	0.0442	0.0155	35	0.0050	11	0.0024	5	0.11	52	1.091	0.093	1.42	Acid
		59b	0.0472	0.0075	16	0.0063	13	0.0031	7	0.07	23	0.522	0.087	1.44	Acid
	{ Virgin }	60a	0.0524	0.0228	43	0.0048	9	0.0032	6	0.18	85	1.676	1.155	1.36	Alkaline
		60b	0.0451	0.0125	28	0.0040	9	0.0026	6	0.11	48	0.909	0.097	1.38	Alkaline
Dunkirk fine sand.....	{ Cultivated }	25a	0.0337	0.0068	18	0.0040	11	0.0084	22	0.10	63	1.169	0.085	0.58	Neutral
		25b	0.0200	0.0038	19	0.0025	13	0.0035	18	0.05	21	0.475	0.080	0.79	Neutral
	{ Virgin }	26a	0.0318	0.0065	20	0.0020	6	0.0024	8	0.10	66	1.147	0.061	0.57	Acid
		26b	0.0211	0.0025	12	0.0013	6	0.0011	5	0.04	11	0.371	0.056	0.67	Acid
Clyde (Maumee) fine sand...	{ Cultivated }	28a	0.0305	0.0160	52	0.0020	7	0.0053	17	0.16	250	2.356	0.345	0.68	Acid
		28b	0.0284	0.0088	31	0.0007	2	0.0025	9	0.06	68	0.820	0.303	1.07	Acid
	{ Virgin }	29a	0.0561	0.0283	50	0.0032	6	0.0071	13	0.19	185	2.127	0.684	1.33	Acid
		29b	0.0353	0.0165	47	0.0023	7	0.0048	14	0.08	70	0.929	0.244	1.78	Acid
Miami silty clay loam.....	{ Cultivated }	32a	0.0265	0.0095	36	0.0033	12	0.0020	8	0.12	54	1.136	1.195	0.84	Alkaline
		32b	0.0259	0.0043	17	0.0040	15	0.0017	7	0.08	14	0.475	0.129	0.90	Acid
	{ Virgin }	33a	0.0372	0.0138	37	0.0045	12	0.0060	16	0.18	122	2.097	0.285	0.66	Alkaline
		33b	0.0317	0.0063	20	0.0043	14	0.0021	7	0.08	24	0.614	0.129	1.02	Alkaline

TABLE 1—Continued

DESCRIPTION	NUMBER	PHOSPHORUS										TOTAL NITROGEN	COMPARATIVE COLOR OF NH ₄ OH EXTRACTS	NH ₄ OH-SOLUBLE ORGANIC MATTER (SUMS)	SUMS ASH	ORGANIC P IN NH ₄ OH-SOLUBLE MATTER	REACTION OF SOIL
		Total	NH ₄ OH-soluble organic	Organic as per cent of total	NH ₄ OH-soluble inorganic	NH ₄ OH-soluble inorganic as per cent of total	HCl-washing-soluble	HCl-washing-soluble as per cent of total									
Lucas silt loam.....	Cultivated	38a	0.0448	0.0125	28	0.0030	7	0.0010	2	0.13	80	1.161	0.134	1.08	Alkaline		
		38b	0.0331	0.0050	15	0.0058	18	0.0007	2	0.06	19	0.455	0.293	1.10	Alkaline		
	Virgin	39a	0.0437	0.0118	27	0.0050	11	0.0054	12	0.14	82	1.226	0.202	0.96	Alkaline		
		39b	0.0407	0.0080	20	0.0080	20	0.0058	14	0.08	51	0.756	0.326	1.06	Alkaline		
Brookston silty clay loam.....	Cultivated	36a	0.0612	0.0270	44	0.0045	7	0.0061	10	0.20	165	2.224	0.170	1.21	Alkaline		
		36b	0.0505	0.0188	37	0.0053	11	0.0038	8	0.12	77	1.103	0.180	1.70	Alkaline		
	Virgin	37a	0.1145	0.0535	47	0.0050	4	0.0261	23	0.39	215	3.833	0.211	1.39	Alkaline		
		37b	0.0698	0.0235	34	0.0050	7	0.0229	33	0.23	96	1.208	0.139	1.94	Alkaline		
Newton loam.....	Cultivated	49a	0.0509	0.0198	39	0.0033	6	0.0191	37	0.24	214	2.678	0.513	0.74	Alkaline		
		49b	0.0368	0.0068	18	0.0033	9	0.0174	47	0.10	67	0.880	0.625	0.77	Alkaline		
	Virgin	50a	0.0604	0.0258	43	0.0023	4	0.0220	36	0.28	231	3.351	0.295	0.77	Alkaline		
		50b	0.0421	0.0100	24	0.0028	7	0.0209	50	0.10	59	1.000	0.597	1.00	Alkaline		
Average of 12 soil types.....	Cultivated	0-7	0.0433	0.0148	34	0.0039	9	0.0050	11	0.14	100	1.489	0.212	1.05			
		7-15	0.0345	0.0067	20	0.0038	11	0.0033	10	0.07	31	0.584	0.228	1.11			
	Virgin	0-7	0.0587	0.0205	34	0.0047	8	0.0104	15	0.19	118	1.931	0.233	1.05			
		7-15	0.0381	0.0083	21	0.0041	11	0.0061	14	0.08	36	0.642	0.211	1.18			

gin Lucas silt loam. It should be noted that the figure for ammonia-soluble inorganic phosphorus is to some extent influenced by the technique of the previous acid extraction, so that these data are of uncertain significance.

The percentages of the total phosphorus removable by leaching with 1 per cent hydrochloric acid and washing with a saturated solution of carbon dioxide are on the average distinctly higher in the cases of both depths of virgin samples. This is in harmony with the results obtained for fifth-normal-nitric-acid-soluble phosphorus and is doubtless to be attributed to depletion of the more soluble forms of phosphorus as the result of cultivation. In the cases of several types, however, the cultivated sample contains the greater amount of acid-soluble phosphorus.

As might be expected, the data for total nitrogen show very distinctly the effect of cultivation upon the surface soil. The effect upon the subsurface is much less, in fact several samples show as much total nitrogen in the lower depth of a cultivated sample as in the virgin sample of the same depth, or still more. In general, within each type there is apparent a marked relation between total nitrogen and the ammonia-soluble organic matter, organic phosphorus and color. The Clyde fine sand is rather exceptional in the lack of such correlation. In comparing different types a similar, though commonly less exact relation between these constituents is observed. From the averaged data for all types, it was found that the ratio is such that if the ammonia-soluble organic matter of the surface soil is represented by 100, the total nitrogen will approximate to 10 and the organic phosphorus 1. For the subsurface samples, the ratio of soil nitrogen to organic phosphorus is slightly higher, and the relative amount of ammonia-soluble organic matter is somewhat less.

The percentage relations of the ammonia-soluble organic phosphorus to humus are included in table 1. From these, it may be observed that the least proportion of organic phosphorus to organic matter in ammonia solution is found in the case of the surface soil of the Dunkirk fine sand; the figure here is slightly less than 0.6 per cent for both samples, and the subsurface samples also show percentages but a trifle greater. The highest percentage of organic phosphorus in ammonia-soluble organic matter is found in the case of the virgin subsurface of the Brookston silty clay loam, the figure being 1.94 per cent. The percentage of organic phosphorus in the ammonia-soluble organic matter is distinctly higher in the case of the subsurface samples and in most cases the organic matter from the subsurface of virgin samples contains more than that from cultivated samples.

The comparative color of ammonia extracts is more nearly directly proportional to the organic matter in the extract than to organic phosphorus or total nitrogen in the soil. Considering the amount of the color due to ferric hydroxide, it could scarcely be expected to show any very close relations to other constituents of the solution.

The percentages of humus ash contained in the ammonia extracts of these soils do not exhibit any close relation to other constituents found in solution.

In general, it may be said that surface soils containing much organic matter soluble in ammonia run higher than the average in humus ash. Subsurface samples, however, sometimes furnish an extract with more ash than that from the corresponding surface soils. The percentage of ash in the ammonia extract is to a large extent dependent upon the effectiveness of the filtration procedure. It was found in a previous investigation (7) that the method of filtration employed for these samples affords an extract practically free from clay. With most samples ferric oxide is the predominant constituent of the ash.

REACTION OF SOIL AND ORGANIC PHOSPHORUS CONTENT

In so far as the data obtained permit any opinion to be formed, reaction of the soil is without influence upon the organic phosphorus. The soils included in this investigation are predominantly acid; there are but four types in which both cultivated and virgin samples are alkaline. Of these four types, the Miami silty clay loam and the Lucas silt loam are upland soils and the Brookston silty clay loam and Newton loam are representative of the dark-colored, often poorly drained neutral or alkaline soils so common in the northwestern quarter of the state, and formerly referred to the Clyde series of soils on account of their high content of organic matter, which is the distinguishing characteristic of the Clyde series. The soils first named are rather below the average of all the types here considered in total nitrogen, ammonia-soluble organic matter and organic phosphorus, while the second pair of soils are distinctly above the average in all these constituents.

The averaged percentages of organic phosphorus in ammonia-soluble organic matter of these soils are not markedly different from those of the other types considered, nor are the ratios of these constituents to total nitrogen dissimilar when averaged for the four types, although including samples which are near extremes in both directions with respect to ratios of nitrogen, humus and organic phosphorus.

It is true that the dark-colored alkaline soils under discussion are higher than the average in total phosphorus, and that an unusually large proportion of this is present in the organic form. But the Clyde fine sand, although lower in total phosphorus, has an even larger proportion of this in the organic state, and this soil is acid. The only relation existing between reaction and organic phosphorus content seems to follow from the fact that the chief factor favoring the accumulation of organic matter (and organic phosphorus with it) is poor drainage, and this also operates toward the conservation of bases, the soil remaining alkaline if it was well supplied with basic material at the beginning.

CULTIVATION, SOIL REACTION AND NATURE OF ORGANIC PHOSPHORUS

The data in table 1 show that the organic phosphorus content of virgin surface soils is in general considerably greater than that of the corresponding cultivated samples; it has just been said that the reaction of the soil appears

to be without marked influence upon its content of organic phosphorus. The question of the influence of these factors upon the nature of the organic phosphorus compounds of the soil remains to be answered. As a means for detecting any difference in composition which might exist between the organic phosphorus compounds of different soils, the procedure of hydrolysis with 5 per cent sulfuric acid, as used by Jones (3) in his studies of the nucleotides and by Potter and Snyder (5) for ammonia extracts of soil, seemed promising.

The experiment was conducted in the following manner. Eight-hundred-cubic-centimeter portions of the ammonia extracts from the surface soil, both virgin and cultivated, of the pronouncedly acid Wooster loam, the very slightly acid or nearly neutral Clermont silt loam and the alkaline Newton loam were

TABLE 2

Decomposition of organic phosphorus compounds by boiling 5 per cent H_2SO_4

TIME OF HEATING	SAMPLE 4A			SAMPLE 21A			SAMPLE 49A		
	Inorganic P found	Increase due to hydrolysis	Per cent of organic P decomposed	Inorganic P found	Increase due to hydrolysis	Per cent of organic P decomposed	Inorganic P found	Increase due to hydrolysis	Per cent of organic P decomposed
	mgm.	mgm.	per cent	mgm.	mgm.	per cent	mgm.	mgm.	per cent
0	2.2	(0.8*)	(15)	1.8	(0.3*)	(8)	1.5	(0.5*)	(8)
$\frac{1}{2}$	2.6	0.4	9	2.2	0.4	11	1.8	0.3	5
1:05	2.9	0.7	16	2.3	0.5	14	2.1	0.6	10
2	3.1	0.9	20	2.5	0.7	19	2.4	0.9	15
4	3.3	1.1	24	2.7	0.9	24	2.9	1.4	24
	SAMPLE 5A			SAMPLE 22A			SAMPLE 50A		
	Inorganic P found	Increase due to hydrolysis	Per cent of organic P decomposed	Inorganic P found	Increase due to hydrolysis	Per cent of organic P decomposed	Inorganic P found	Increase due to hydrolysis	Per cent of organic P decomposed
	mgm.	mgm.	per cent	mgm.	mgm.	per cent	mgm.	mgm.	per cent
0	4.5	(1.0*)	(15)	2.3	(1.0*)	(22)	1.9	(1.2*)	(14)
$\frac{1}{2}$	4.8	0.3	5	2.5	0.2	6	2.1	0.2	3
1	4.9	0.4	7	2.6	0.3	9	2.5	0.6	8
2	5.1	0.6	11	2.8	0.5	14	2.8	0.9	13
3 $\frac{1}{2}$	5.6	1.1	19	3.1	0.8	23	Lost		

* Increase over that contained in the original solution, due to decomposition during preparation for experiment, including momentary boiling.

allowed to stand in large porcelain dishes for several days, in a place protected from dust but exposed to a constant current of air, until the ammonia had evaporated and the volume was reduced about one-half. The solutions were then transferred to 500-cc. flasks and made to volume with washings from the dishes. Aliquots of 100 cc. were transferred to 200-cc. extraction flasks, sufficient dilute sulfuric acid added to make the solution 5 per cent by weight and reflux condensers attached. The flasks were set, three at a time, upon an electric hot plate and heated as rapidly as possible to boiling, each time starting with the plate cold. After the solutions had boiled the stated time, the flasks were immediately cooled with water, the contents poured into centrifuge bottles, made alkaline with ammonia and treated in the usual manner for the

inorganic phosphorus determination. The results obtained are presented in table 2, also in graphic form in figure 1.

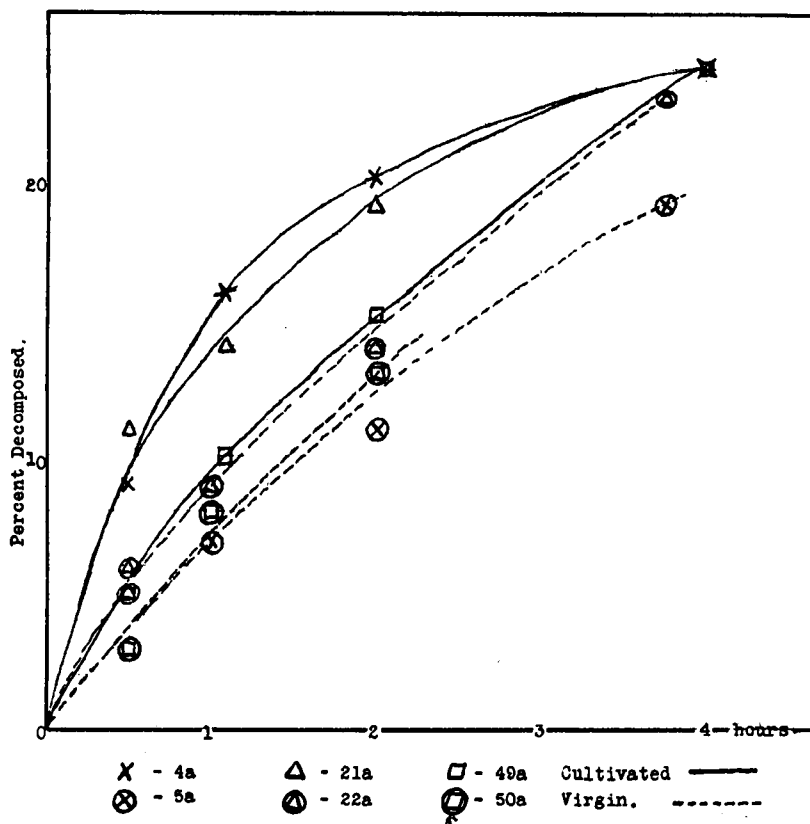


FIG. 1. HYDROLYSIS OF ORGANIC PHOSPHORUS COMPOUNDS BY 5 PER CENT H_2SO_4 AT BOILING TEMPERATURE

In explanation of table 2, it should be recalled that the samples represent 160 cc. of the original extract, and the original contents of inorganic and organic phosphorus were as follows:

SAMPLE	INORGANIC PHOSPHORUS	ORGANIC PHOSPHORUS
	mgm.	mgm.
4a	1.4	5.3
5a	3.5	6.7
21a	1.5	4.0
22a	1.3	4.5
49a	1.1	6.3
50a	0.7	8.3

The figures in table 2, enclosed in parentheses, represent increases over the corresponding original amounts of inorganic phosphorus as given above, and the percentage relation of the same to the original organic phosphorus contents. These indicate the amount of decomposition during preparation of the solutions for the experiment, including momentary heating to boiling temperature with immediate cooling, and serve as blank determinations with the time of hydrolysis at zero. Elsewhere in table 2, the amounts of inorganic phosphorus found after boiling for a stated time have been reduced by the corresponding quantities to which reference has been made and the percentages of decomposition have been calculated on the basis of the organic phosphorus remaining undecomposed after this preliminary treatment. These percentages of decomposition are plotted as ordinates in figure 1, while the periods of boiling, in hours, are abscissae.

The data presented in table 2 and plotted in figure 1 indicate that the organic phosphorus compounds of all the cultivated soils are somewhat less resistant to hydrolysis than are those of the virgin soils. It is noteworthy that decomposition during 4 hours' boiling has been precisely the same in the cases of all the cultivated soils, 24 per cent, although the percentages at intermediate periods do not coincide. Of the cultivated samples, the curves representing the acid Wooster loam, 4a, and the slightly acid Clermont silt loam, 21a, show considerable resemblance. Among the virgin samples, the Wooster loam, 5a, shows the greatest divergence from the other two, and also the greatest difference between a virgin and cultivated sample. The alkaline Newton loam shows greatest resemblance between data for virgin and cultivated samples, possibly because its extracts contain most organic phosphorus and any percentage errors are thus smaller. The results of this experiment are so indecisive that extended comment does not seem to be warranted. Neither striking resemblances nor marked dissimilarity among the organic phosphorus compounds of virgin and cultivated soils, both acid and alkaline, is indicated.

AVAILABILITY OF PHOSPHORUS IN ORGANIC COMPOUNDS

While it was not intended to include in this study any reference to the question of the amount of phosphorus supplied to vegetation from that stored up in the organic form, this being a subject for more extended investigation, it may be well to direct attention to some facts disclosed by the data obtained and which seem to furnish indications regarding this phase of the subject. The general relation found to exist between the humus, total nitrogen and organic phosphorus of the soils investigated and the marked similarity of the ratios between these constituents in virgin and long cultivated soils of the same type has been pointed out. The considerable resistance to decomposition by hydrolysis with boiling 5 per cent sulfuric acid shown by the organic phosphorus compounds of all the samples in which this was determined, has been demonstrated. The ready response to phosphorus fertilization shown by

practically all the soils of the state on which fertility experiments have been conducted has been shown by the work of the Ohio Station. Considered together, these facts do not indicate that the phosphorus in organic combinations becomes available very rapidly, certainly not at a generally greater rate than the organic nitrogen associated with it in the soil. Further, it seems altogether probable that the various agencies, including liming and frequent cultivation, known to result in a more rapid utilization of the soil's store of nitrogen, will have a similar effect upon the phosphorus in organic combinations.

SUMMARY

A study of the organic phosphorus content of samples from 12 representative types of Ohio soils, and the relation of the same to other soil constituents, is reported. The observations made have been based upon the examination of virgin and cultivated samples, surface and subsurface, from each soil type considered.

Averaged figures indicate that virgin surface samples are considerably richer in total phosphorus than the corresponding cultivated samples of the same type, and that virgin subsurface samples contain slightly more total phosphorus than cultivated soils at the same depth.

The organic phosphorus contents of the several samples from the average soil type stand in the same order as the contents of total phosphorus.

The organic phosphorus bears very nearly the same percentage relation to the total phosphorus in cultivated soils as in virgin soils at the same depths, in the greater number of cases.

From averaged data, one-third the phosphorus in the surface and one-fifth that in the subsurface samples of both virgin and cultivated soils is in the organic form.

The organic phosphorus and humus soluble in ammonia are shown to be closely related to each other, to total nitrogen in the soil and, to a less extent, the color of the ammonia extract. From averaged data, if 100 represents the percentage of ammonia-soluble humus obtained from a soil, the total nitrogen in the soil is 10, and the organic phosphorus in the ammonia extract is 1. Except as noted, there does not appear to be any connection between other soil constituents and organic phosphorus content.

Reaction of the soil appears to be without influence upon the quantity and nature of the organic phosphorus present.

There is some evidence that the organic phosphorus compounds of cultivated soils are decomposed slightly more readily than are those of the virgin soils examined.

From general considerations, it is thought that the phosphorus in organic combinations in the soil is not of a very high order of availability.

REFERENCES

- (1) AMES, J. W., AND SCHOLLENBERGER, C. J. 1919 Calcium and magnesium content of virgin and cultivated soils. *In* Soil Sci., v. 8, p. 323-335.
- (2) Association of Official Agricultural Chemists 1916 Committee on Editing Tentative and Official Methods of Analysis. Williams & Wilkins Co., Baltimore.
- (3) JONES, W. 1916 An indirect method of determining pyrimidine groups in nucleotides. *In* Jour. Biol. Chem., v. 24, no. 3, p. 3-10.
- (4) POTTER, R. S., AND BENTON, T. H. 1916 The organic phosphorus of soil. *In* Soil Sci., v. 2, p. 291-298.
- (5) POTTER, R. S., AND SNYDER, R. S. 1918 The organic phosphorus of soil. *In* Soil Sci., v. 6, p. 321-332.
- (6) PRESCOTT, J. A. 1916 The phenomena of adsorption in its relation to soils. *In* Jour. Agr. Sci., v. 8, pt. 1, p. 111-130.
- (7) SCHOLLENBERGER, C. J. 1918 Organic phosphorus of soil: Experimental work on methods for extraction and determination. *In* Soil Sci., v. 6, p. 365-395.