

1967

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Reprinted from SOIL SCIENCE SOCIETY OF AMERICA PROCEEDINGS

Vol. 31, No. 1, January-February 1967, pages 85-89

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Organic Phosphorus in Calcareous Colorado Soils¹

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ABSTRACT

Organic P in calcareous soils was determined by a modified 4N HCl-0.5N NaOH extraction procedure. Organic P averaged 23% of the total P in soils from 23 locations in Colorado, 26% for 3 irrigated rotation soils of 4 rotations each, and 27% in 4 virgin soils. Organic C, N, and P were highly correlated for all soil groups tested. Carbon-to-phosphorus ratios of 95:1, 72:1, and 128:1 were obtained for the Colorado, rotation, and virgin soils, respectively. Alfalfa (*Medicago sativa*) and manure in rotations increased the level of organic C, N, and P, and also the C/P and N/P ratios when compared with continuous row cropping without organic residues. Alfalfa was more effective than manure in maintaining organic C, N, and P. Nonvirgin soil contained less organic P, much less organic C and N, and lower C/P and N/P ratios than virgin soil. Organic P mineralized at an average of 3.6 ppm P for 13 Colorado soils when incubated for 21 days at 35C.

analysis in soil. Organic P in soil is usually determined by indirect methods. A number of techniques to determine organic P using various acid and base extracts have been developed in an effort to bring the maximum quantity of organic P into solution with minimum hydrolysis (4, 5, 8). Dormaar (4) investigated nine extractant and ignition methods for use on southern Alberta soils. Only four methods gave reproducible results, and he concluded that an accurate determination of organic P is still needed.

The method of determining organic P reported in this paper includes modifications of the procedure of Mehta et al. (8) for use on calcareous soils. This procedure does little to alleviate the time required for organic P analysis. The results did provide a means for analysis of organic P levels, C/P and N/P ratios, the effect of some cropping practices, and rate of mineralization for some calcareous soils.

MATERIAL AND METHODS

Soil Samples

Soils were collected from 3 irrigated sections of Colorado, from crop rotation plots at Huntley, Montana; Scottsbluff, Nebraska; and Belle Fourche, South Dakota, along with 4 pairs of virgin-nonvirgin soils from north-central Colorado. The sample locations for the irrigated soils are shown in Table 1. The virgin-nonvirgin soils were collected near Fort Collins, Colorado. Information concerning soils involving long-term rotations with organic treatments is given below:

- 1) No organic treatment—continuous cropping, all locations
- 2) Manure each year (5 tons)—continuous cropping, all locations
- 3) Alfalfa:
 - 50% of crop rotation time—Huntley, Mont., Scottsbluff, Nebr.
 - 100% of crop time—Belle Fourche, S. Dak.
- 4) Manure each year (5 tons) plus
 - Alfalfa 50% of crop rotation time—Huntley, Mont., Scottsbluff, Nebr.
 - Alfalfa 100% of crop time—Belle Fourche, S. Dak.

The virgin-nonvirgin soil samples represent composites of five

ORGANIC P CONSTITUTES a significant fraction of total P in many soils (1, 3, 9, 15). Most information to date regarding organic P has been obtained from acid soils. Much less is known concerning the role of organic P in calcareous soils (6, 16). Since field crops absorb only 22 to 54 kg/ha per year of P, only a small part of the total organic P needs to be mineralized in order to supply a significant part of crop requirements. The exact contribution of organic P to plant nutrition has been partially studied, but information gaps still exist (3, 14, 15).

In many studies of organic P, the tedious analytical procedures required have limited research for organic P

¹ Contribution from the Northern Plains Branch, Soil and Water Conservation Research Division, ARS, USDA, in cooperation with the Colorado Agr. Exp. Sta. Received May 24, 1966. Approved Aug. 2, 1966.

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drillings, each 6.1 m apart, and not exceeding 30.5 m between virgin and nonvirgin soil. The soils were sampled 0–15 cm in depth for both the organic treatment soils, and 0–5 cm for the virgin and nonvirgin soils.

Chemical Analysis

The pH of soil was measured on a 1:1 soil-to-water mixture and CaCO₃ content of the soil samples was analyzed by the method of Peterson and Goodding (10). Organic C was determined by the wet combustion method of Smith and Weldon (13). The Kjeldahl distillation method was used to determine organic N.

Method Used for Organic P Determination

Extraction of P—A soil sample of 2.0 g was transferred into an 80-ml centrifuge tube. Then 50 ml of 4*N* HCl was added, the CO₂ allowed to evolve, and the solution was warmed for 10 min at 70 to 80°C. The extract was centrifuged until clear and filtered into an Erlenmeyer flask calibrated for 500 ml total extract volume. The acid-treated soil was washed with 30 ml of distilled water and by stirring the soil with a glass rod. This second extraction was also centrifuged and filtered into the Erlenmeyer flask. The filter paper was washed several times with distilled water and the washings were added to the acid extract.

The soil was then washed with small increments of 0.5 *N* NaOH into another Erlenmeyer flask and 0.5*N* NaOH was added to bring the extracting mixture to 200 ml. This extract mixture was allowed to stand 16 hours at 20 to 30°C. After 16 hours, most of the extract was decanted into the Erlenmeyer flask calibrated at 500 ml which contained the acid extract. The remaining NaOH extract and soil was transferred into a centrifuge tube and after centrifuging the extract clear, the supernatant solution was added to the combined acid-base extract. An additional 50 ml of 0.5 *N* NaOH was added to the soil in the centrifuge tubes, the soil was loosened by stirring and this mixture was digested for 2 hours at 80 to 90°C. After cooling, the mixture was centrifuged and the NaOH extract was decanted to the acid-base extract. The acid-base extract was then brought to a 500-ml volume with distilled water.

Inorganic P determination—An aliquot (5 to 10 ml, dependent upon P content) of the clear acid-base extract was transferred into a 125-ml capacity separatory funnel. The extract was then neutralized by adjusting with 0.5*N* NaOH and 1*N* H₂SO₄ to the fade point of yellow color of 2, 4 dinitrophenol indicator. Dis-

tilled water was added to the extract to bring the extract volume to 15 ml. Organic P content of the extract was determined by the Pons and Guthrie (11) method.

Total P in extract—The acid-base extract was shaken vigorously to bring the floccules of organic matter into a fine state of suspension. Then a 25-ml aliquot of the extract was rapidly taken with a pipette and transferred to an evaporation dish. A 5-ml quantity of 10% Mg(NO₃)₂ solution was added to the extract and the mixture was evaporated to dryness on a steam bath. After drying, the mixture was heated for several minutes at 450°C in a muffle furnace. After the ash had cooled, 15 ml of 1*N* HNO₃ was added to bring the ash into solution. The evaporation dish was then covered with a watch glass and heated to 60 to 80°C for 1 hour. The solution was transferred to a 25-ml capacity volumetric flask and diluted to 25 ml with distilled water. An aliquot (5 to 10 ml, dependent upon P content) was transferred into a 125-ml capacity separatory funnel and the analysis for P was made as before (11).

Method of Incubation

Several methods for measuring mineralization of organic P have been designed (3, 14, 15). For this study the differences in 1% K₂CO₃-soluble P after a 21-day incubation at 35°C and at 20°C were used as a measure of mineralized organic P. Duplicate 100-g soil samples were placed into each of two sets of mason jars. Water was added to bring the soil up to field capacity. The mason jars, with lids loosely attached, were placed in incubators with one set at 35°C and the other set at 20°C. Open jars of concentrated NaOH were also placed in the incubators to absorb CO₂. The jars were aerated and the soil brought back to field capacity every third day. At the end of 21 days the soils were air-dried and passed through an 18-mesh sieve. Soluble mineralized organic P was extracted with 1% K₂CO₃ at a 1:50 soil-to-solution ratio at 85°C for 1 hour (17) and determined colorimetrically by the Pons and Guthrie method (11).

RESULTS AND DISCUSSION

The procedure for the analysis of organic phosphorus in calcareous soils was used for several reasons. The strength of HCl in the extract is an excess strength of acid to prevent precipitation of insoluble calcium phosphates as are commonly found in calcareous soils. Although the acid causes partial flocculation of organic matter, this is easily separated by

Table 1—Chemical characteristics of 23 Colorado soils

Sample location	pH	CaCO ₃	Total P	Organic P	Organic P*	Organic N	Organic C	Ratio C/P	Ratio N/P
		%	ppm	ppm	%	ppm	%		
Rocky Ford	7.9	7.1	930	190	20	1,180	1.47	77	6.2
Center	8.1	0.7	990	130	13	760	0.99	76	5.9
Longmont	7.5	2.9	650	180	28	1,360	1.53	85	7.6
Montrose A	7.8	7.0	560	160	29	770	0.84	52	4.8
Montrose B	7.8	3.8	670	130	19	970	1.09	84	7.5
Brighton	6.9	0.1	330	80	24	460	0.67	84	5.7
Greeley	7.3	0.2	430	110	26	610	0.72	66	5.5
Grand Junction	8.1	6.6	850	100	12	900	1.11	111	9.0
Ovid	7.6	0.3	450	150	33	1,030	1.19	79	6.9
Trinidad	7.8	5.0	800	210	26	1,560	1.98	94	7.4
Salida	7.6	5.1	990	270	27	3,090	5.07	186	11.4
Monte Vista	8.8	0.7	800	60	8	510	1.07	180	8.5
Sterling	7.8	0.3	610	150	25	1,280	1.59	106	8.5
La Junta	8.1	5.0	840	120	14	850	0.95	79	7.1
Steamboat Springs	6.7	0.3	890	330	37	3,080	4.16	126	9.3
Delta	8.2	0.4	810	160	20	1,060	1.14	71	6.6
Durango A	7.4	3.9	350	90	26	620	0.67	75	6.9
Durango B	7.7	3.4	370	130	35	1,080	1.28	94	8.3
Fort Collins	7.7	10.6	450	160	36	1,130	1.59	99	7.1
Harmony	7.9	11.1	560	200	36	1,320	1.57	79	6.6
Fort Collins	8.0	7.1	610	100	16	820	0.79	79	8.2
Fort Collins	8.1	7.5	480	100	21	660	0.64	64	6.6
Fort Collins	7.7	0.9	740	210	28	1,300	1.23	58	6.2
Means	7.7	3.9	660	150	23	1,150	1.45	95	7.5

* % of total P.

centrifuging for inorganic P determination and easily dispersed by shaking for obtaining an aliquot for the total P analysis. None of the inorganic P was absorbed by the organic matter as indicated by a test for P^{32} exchange in a 20-hour period. The test of inorganic P showed no difference in quantity when the acid and base extracts were freshly mixed or mixed after 24 hours had elapsed. A preliminary test showed it required 16 hours at room temperature for the first NaOH extraction to obtain maximum solution of P. The second NaOH extraction did cause some hydrolysis of organic P if more than 2 hours extraction time was used at 85C.

The results for soil organic C, N, and P, and total P in the Colorado, rotation, and virgin-nonvirgin sampling groups are shown in Tables 1, 2, and 3.

Organic P content of 23 Colorado soils (Table 1) varied from 60 to 330 ppm, or from 8 to 37% of the total P content. About half of the soils contained between 20 and 30% of total P in the organic form. The C/P ratio varied from 52:1 to 186:1 and averaged 95:1 for the group. The N/P ratio was reasonably constant and averaged 7.5:1.

Analysis of soils from long-term rotations at three locations clearly showed the effect of organic matter treatments on the improvement of organic C, N, and P content of soil (Table 2). Organic P varied from 17 to 40% of total P and averaged 26% for the soil organic treatment rotation group. The C/P and N/P ratios of this group were lower than the Colorado soils and averaged 72:1 and 6.3:1 respectively. Both the C/P and N/P ratios tended to increase with increased use of manure and alfalfa in the rotations.

Cultivated nonvirgin soil had a slightly higher pH and contained more $CaCO_3$, less organic P, and much less organic C and N than did paired virgin soils (Table 3). Organic P averaged 27 and 26% of total P for the virgin and nonvirgin soils, respectively. The C/P ratio was reduced from 128:1 to 80:1 and the N/P ratio was lowered from 10.0:1 to 7.1:1 of the 4 virgin soils compared with the nonvirgin soils. This occurred because of a large reduction of both organic C and N in the nonvirgin soils.

A highly significant correlation was found between the

various organic constituents of C, N, and P for both the Colorado and rotation soils from other states (Table 4). A high correlation of C to N would be expected, but the correlation of organic P to organic C and N was also significant at the 1% level and r values were above 0.86 in all cases. These results give confidence in the reliability of the method for organic P analysis. Although any indirect procedure for determining organic P has limitations, the method employed was reproducible to 20 ppm for samples averaging 200 ppm of organic P.

The mineralization potential of organic P by incubation of soil for 21 days at 35C for the 13 Colorado soils was relatively low, as shown in Table 5. Only about 2% of organic P was mineralized for the Colorado soils tested. In seven of the samples the organic P mineralized was 2.0 ppm or less, and the four highest samples averaged 8.0 ppm. The results of mineralization of P with manured soil compared with non-manured soil were inconclusive. Only one of three manured soils gave a significant increase in mineralized organic P.

The results of this study showed a somewhat higher organic P content for calcareous soils than the 8 to 20% of the total P reported for Utah soils by Thorne and Peterson (16), but lower than the 31% obtained for Arizona soils (6). Nevertheless, the information implies that there is considerably less organic P in calcareous soils than has been found in acid soils. Organic P analysis from soils of the central USA have shown approximately 50% of the soil P being organically combined (1, 9, 15).

The C/P ratios obtained here are lower than the 150-100:1 established by Kaila (7) and higher than the 65-13:1 obtained by Fuller and McGeorge (6). In Colorado, however, the C/P ratios were much higher for mountain meadow soils from Salida, Monte Vista, and Steamboat Springs, and also for the virgin soils than for cultivated soils of the lower altitude valleys (Table 1). These findings agree with Bower (3) and Thompson and Black (15) who concluded that organic N and P become more resistant to decomposition as the degree of decomposition advances. Thus, the C/P ratio becomes narrower on more intensely cultivated soil, provided that

Table 2—Relationship of organic P to organic C and N in soils from long-term rotation plots of variable organic treatments

Sample location	Organic treatment	pH	CaCO ₃	Total P	Organic P	Organic P*	Organic N	Organic C	Ratio C/P	Ratio N/P
			%	ppm	ppm	%	ppm	%		
Huntley, Montana	none	8.0	9.5	650	110	17	890	0.95	87	8.1
Scottsbluff, Nebr.	none	7.7	0.4	380	120	32	500	0.48	40	4.2
Belle Fourche, S. Dak.	none	7.7	2.7	730	140	19	590	1.00	71	4.2
	Means			590	120	20	660	0.81	66	5.5
Huntley, Montana	manure	8.0	1.2	770	170	22	1,140	1.18	70	6.7
Scottsbluff, Nebr.	manure	7.7	0.1	470	140	30	850	0.75	53	6.1
Belle Fourche, S. Dak.	manure	7.7	4.3	870	200	23	940	1.31	66	4.7
	Means			700	170	24	980	1.08	63	5.8
Huntley, Montana	alfalfa	8.0	1.2	660	130	20	1,020	1.16	89	7.8
Scotts bluff, Nebr.	alfalfa	7.7	0.1	350	120	34	750	0.71	59	6.3
Belle Fourche, S. Dak.	alfalfa	7.7	1.3	750	300	40	1,690	2.20	73	5.6
	Means			590	180	31	1,150	1.36	74	6.6
Huntley, Montana	m + a†	8.0	1.0	730	190	26	1,170	1.33	78	6.1
Scottsbluff, Nebr.	m + a	7.7	0.1	380	110	29	920	0.91	83	8.4
Belle Fourche, S. Dak.	m + a	7.7	1.8	990	300	30	2,130	2.82	94	7.1
	Means			700	200	29	1,410	1.69	85	7.2

* % of total P. † manure plus alfalfa.

Table 3—Relationship of organic P to organic C and N on four virgin and nonvirgin Colorado soils

Soil type	Treatment	pH	CaCO ₃	Total P	Organic P	Organic P*	Organic N	Organic C	Ratio C/P	Ratio N/P
			%	ppm	ppm	%	ppm	%		
Laramie loam	virgin	7.5	3.4	490	170	35	1,640	2.73	160	9.7
	nonvirgin	7.7	10.6	450	160	36	1,130	1.59	99	7.1
Fort Collins clay loam	virgin	7.7	1.3	710	270	39	2,930	4.10	151	10.9
	nonvirgin	7.9	11.1	560	200	36	1,320	1.58	79	6.6
Weld loam	virgin	7.9	2.1	680	120	18	1,260	1.41	117	10.5
	nonvirgin	8.0	7.1	610	100	16	820	0.79	79	8.2
Terry fine sandy loam	virgin	8.1	3.5	550	100	18	900	0.82	82	9.0
	nonvirgin	8.1	7.5	480	100	21	660	0.64	64	6.6
Means	virgin			610	165	27	1,690	2.26	128	10.0
	nonvirgin			530	140	26	980	1.15	80	7.1

* % of total P.

Table 4—Correlation of organic C, N, and P in Colorado and soils from long-term rotations of organic treatments

Colorado soils	23	Organic P vs. organic N	0.914
		Organic P vs. organic C	0.866
		Organic C vs. organic N	0.972
		Total P vs. organic N	0.484
Organic treated soils*	12	Organic P vs. organic N	0.890
		Organic P vs. organic C	0.934
		Organic C vs. organic N	0.964
		Total P vs. organic N	0.675
<i>r</i> value needed for significance		1%	5%
Colorado soils		0.526	0.413
Rotation soils		0.708	0.576

* Huntley, Mont., Scottsbluff, Nebr. and Belle Fourche, S. Dak.; 4 each.

Table 5—Organic P mineralized from Colorado and soils from long-term rotation of organic treatments during 21 days incubation at 35C

Sample location	Organic P	Mineralized organic P	
	ppm	ppm	
<i>Colorado soils</i>			
Rocky Ford	190	5.0	
Longmont	180	2.0	
Montrose	160	1.3	
Greeley	110	1.0	
Grand Junction	100	1.3	
Trinidad	210	0.8	
Salida	270	3.2	
Monte Vista	60	4.0	
Sterling	150	0.0	
LaJunta	120	1.4	
Steamboat Springs	330	10.6	
Delta	160	6.0	
Fort Collins	270	10.5	
Means	180	3.6	
<i>Organic treated soils</i>			
Huntley, Mont.	O*	110	1.6
	m†	170	2.0
Scottsbluff, Nebr.	O*	120	3.0
	m†	140	0.5
Belle Fourche, S. Dak.	O*	140	0.0
	m†	200	8.0
Means	O*	120	1.5
	m†	170	3.5

* No organic additive. † Manure in rotation.

large amounts of organic materials are not added as part of the cultural practice.

The mineralized portion of organic P for calcareous soil was much lower than values obtained by others (3, 15). Yet, the contribution of 10 to 15 kg P/ha during the growing season should not be overlooked. This could be especially important on those soils containing marginal amounts of available P.

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