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Phosphorus Distribution in Calcareous Soil Profiles of the Central Plains

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ABSTRACT

Deep-rooted crops benefit from high subsurface P content. While some documentation exists for high levels of available inorganic P well below the soil solum, very little information exists on organic-P contents deep in the soil profile. This research was conducted to document the presence of large pools of available organic and inorganic P on top of a carbonate layer 2.2 m below the soil surface. Additionally, soil organic C, N, texture, and selected mineral concentrations were determined to assess their correlations with total P. Soil samples (Aridic Argiustolls) from two fields that have been out of cultivation for at least 10 yr were taken in 0.15-m increments to a depth of ≈2.5 m. The surface soils (0.0–0.3 m) were high in nutrients (11.0 g C and 1.1 g N/kg soil) and negligible in carbonates; the middle soil layers (0.30–0.25 m) were low in nutrients (4.0 g C and 0.3 g N/kg) and intermediate in carbonates (90 g/kg); and the deep soil layers (2.25–2.55 m) were high in available inorganic and total organic P, and very high in carbonates (>300 g/kg). The total P concentration in the profile was inversely correlated with the percentages of sand and Ca, and directly correlated with the total content of Fe and Al. Total organic C and N and, to a greater extent, total organic P accumulated near or on top of a carbonate layer. Most of the organic C and P below 0.45 m were soluble in 2 M HCl. For the surface soil (0.0–0.45 m), the bulk of the organic P was extracted only after 2 M HCl pretreatment. Alfalfa and similar deep-rooted crops may benefit from this large reserve of available P near the water table.

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K NOWLEDGE concerning the forms and amounts of P in a soil profile is important in both edaphic (fertility) and pedologic (genesis) studies (Walker and Syers, 1976). While the vertical distribution of nitrates has been extensively studied below the soil solum, less information is available on soil P distribution because of its relative immobility. Spencer and Stewart (1934), however, did report some early work on organic and inorganic P movement in soils. Hannapel and his coworkers (1964a,b) and Bowman et al. (1967) expanded on this earlier work with column studies. General consensus was that organic P moved more readily than inorganic P.

Deep-rooted crops such as alfalfa (*Medicago sativa* L.) have been shown to effectively assimilate below-solum P, especially the pool associated with capillary-fringe water near the water table (Lipps and Fox, 1956). Additionally, Murdock and Englebert (1958) reported significant uptake of P below the solum with corn (*Zea mays* L.), and Roscoe (1960) with grasses. Thus, knowledge of the form, location, and association of P with other soil parameters could be useful for site selection for deep-rooted crops.

Trierweiler (1961) studied the vertical distribution of available P along a Fort Collins to Denver transect. His documentation of large amounts of available inorganic P well below the soil solum led us to reexamine selected sites near Fort Collins. Results from a preliminary study in 1985 of a Fort Collins soil profile showed large amounts of not only NaHCO₃-extracta-

ble inorganic P, as was originally found by Trier-weiler, but also large amounts of total and acid-extractable organic P 2 m below the soil surface. Trierweiler was interested in plant-available inorganic P and did not measure organic P, so no documentation exists for large pools of organic P at this depth. A review of selected studies showing high subsurface available P indicated a probable association of this P with free carbonate contents, which were high in the Fort Collins soil (Fox et al., 1953; Lipps and Fox, 1956; Trierweiler, 1961). The purpose of this research, there-fore, was to reevaluate this phenomenon of high subsoil available inorganic P, and to document the distribution of even larger levels of subsurface organic P near a carbonate layer, and the implications for deep-rooted crops. A secondary objective was to assess the relation-ships between total P and soil texture, and total P and total Ca, Fe, and Al concentrations.

MATERIALS AND METHODS

Two sites were selected near Fort Collins, CO, for profile analysis based on information provided by Trierweiler (1961). The sites were separated by a natural drainage way, and were ≈50 m apart. The soils belong to a Nunn clay loam series (fine, montmorillonitic, mesic Aridic Argiustolls). Parent material is the Pierre shale. The A horizon is ≈0.2 m thick, and is essentially free of carbonates. Carbonates start to accumulate in the B horizon (0.2–0.8 m). Thickness of solum varies from 0.4 to 1.1 m.

The area receives ≈310 mm of rainfall annually, most of which occurs in the spring and early summer. One of the two profile sites selected was in an old alfalfa field that was abandoned at least 10 yr ago; the other site was in native shortgrass (predominantly *Bouteloua* spp. and *Stipa* spp.). This site was also in cultivation >20 yr ago.

In August, 1988, two profile samples were taken at each site, ≈100 m apart. A previous profile sample had been taken in 1985 at the grass site. A bucket auger (5-cm diam.) was used to sample the profile down to a depth of 2.5 to 3.0 m. Samples were taken in increments of 0.15 m, placed in clear plastic bags, and transported back to the laboratory the same day. In the laboratory, the soil samples were air dried for 1 wk, mixed, passed through a 2-mm screen, and then stored at room temperature for analysis.

Analyses — Total Pools

Organic C was determined by the Walkley-Black chromic acid digestion (Nelson and Sommers, 1982) with a colori-metric adaption by Heanes (1984). Total N was determined by standard Kjeldahl digestion procedure without inclusions for nitrates, total P was determined by digestion with con-centrated acids (Bowman, 1988), and total organic P by an acid–base sequential extraction (Bowman, 1989). Total Ca, Na, Fe, and Al were determined from the total P extracts by inductively coupled plasma atomic emission spectros-copy at the Colorado State University Soil Testing Labo-ratory. Content of free lime (weight loss) of sand, clay, and silt (hydrometer), and pH (1:2 in water) were also determined.

Available Phosphorus Pools

Plant-available P wa determined by anion-exchange resin in the Cl form (Amer et al., 1955), and by the NaHCO$_3$ procedure (Olsen et al., 1954). Organic P in the NaHCO$_3$ extracts was determined by wet digestion of an appropriate aliquot (usually 5 mL) with 1 mL of 5.5 M H$_2$SO$_4$ and 0.50 g (calibrated scoop) of solid K$_2$S$_2$O$_8$. Extracts were heated

on a hot plate for ≈30 min at ≈150°C, or until essentially only H$_2$SO$_4$ remained (boiling of water ceased). The inor-ganic-P concentration of all extracts and digests was deter-mined by a colorimetric procedure (Watanabe and Olsen, 1965).

For selected surface (0.00–0.45 m), middle (0.90–1.35 m), and deep profile layers (2.25–2.55 m), an estimate of acid-extractable organic P was determined on 2.00 g of soil leached directly into 100-mL volumetric flasks with four, 10-mL portions of 2 M HCl. Soil residues were then washed with ≈30 to 40 mL of distilled water. Extracts were made to 100 mL. Organic P was determined by difference from the inorganic P, and the total P determined by persulfate oxidation of an appropriate aliquot. Organic C and total N were determined on the ground, dried, acid-leached residue to evaluate the organic C and total N associated with the organic P once carbonates had been removed.

Statistics

Values for the cores at each site were averaged (three for the grass site and two for the alfalfa site). As a measure of P associations within the profile, regression analyses were determined between total soil P and selected cations and particle size.
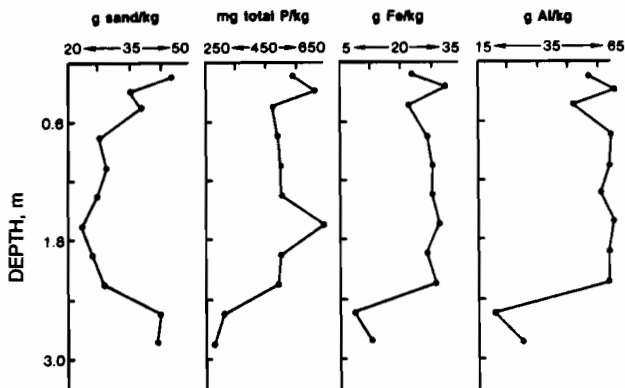
RESULTS AND DISCUSSION

Although there were significant spatial vertical var-iabilities between the two sites, in general, three dis-tinct zones could be discerned: (i) a zone of topsoil with high organic C, high available nutrients, and rel-atively low carbonates; (ii) a middle zone low in or-ganic C and nutrients and intermediate in carbonates; and (iii) a large carbonate barrier zone (at >1.8-m depth) on top of which organic C and nutrients ap-peared to have accumulated during pedologic time. The purpose of the separate corings was to document the existence of these three zones, especially the high organic-P concentration well below the soil solum, and not so much to document statistical differences between each depth increment, or differences in the surface soil that may have occurred because of dif-ferences in rooting patterns between grass and alfalfa.

Results from total C, N, and P analyses varied widely among depth increments for the profiles. All five pro-files showed the presence of three distinct zones. In the top 0.15 m, total organic C (range) varied by 30% (13.7 ± 3.0 k/kg), total N (range) by 22% (1.1 ± 0.2 g/kg), and total P (range) by 25% (540 ± 100 mg/kg). Because of smaller pool sizes (except for total P), middle layers were even more variable. The zone of nutrient accumulation in the deep layers only varied by one depth increment (data not shown) among all five corings, and this depth variation coincided with the presence of a carbonate layer.

Soil pH and texture varied widely with depth (Table 1). Soil reaction was slightly acidic at the surface, grading toward calcareous ≈1 m, and approaching sodic at ≈2 m. These soil reaction trends were also reflected in the quantities of total Ca and Na in the soil profile. The high Na content in the lower profile depths probably contributed to the slow movement and accumulation of nutrients in the bottom layers (Richards, 1954). Although the Na concentrations in the deep layers dropped because of the high carbonate content (400 g/kg, and hence, high total Ca concen-

Table 1. Average physical and chemical properties at selected depths in a profile of Nunn clay loam soil.

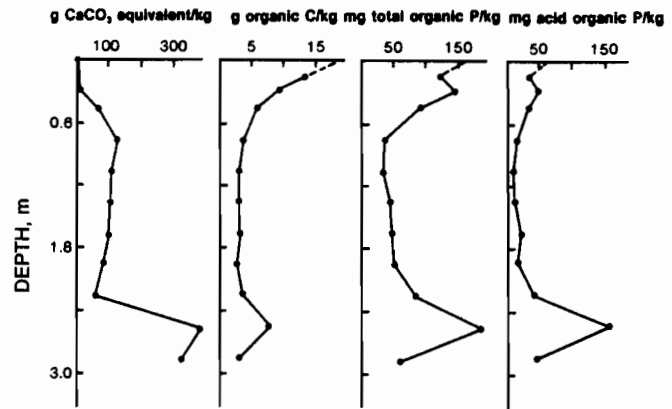| Soil depth	pH	Silt	Clay	Ca	Na
m		%		g/kg	
0.00–0.15	6.7	20	35	21.6	33.8
0.15–0.30	7.2	17	48	81.6	89.2
0.30–0.45	7.6	28	45	93.6	73.6
0.60–0.75	7.8	26	47	92.6	74.8
0.90–1.05	7.9	25	46	91.4	85.0
1.20–1.35	8.2	31	42	49.0	27.0
1.50–1.65	8.3	35	43	69.4	79.0
1.80–1.95	8.3	23	42	61.4	60.4
2.10–2.25	8.5	32	40	39.6	30.0
2.40–2.55	8.6	19	39	113.0	53.4
2.70–2.85	8.7	19	40	111.0	18.0

Fig. 1. Relationship between sand content and total P, Fe, and Al contents.

Fig. 2. Relationship between $CaCO_3$-equivalent content and total organic C, total organic P, and acid-extractable organic P contents.

Table 2. Average total organic N and available P indices properties at selected depths in a profile of Nunn clay loam soil.

Soil depth	Total N	NaHCO₃		Resin
		Inorganic P	Organic P	Inorganic P
m	g/kg		mg/kg	
0.00–0.15	1.09	14.2	4.8	27.5
0.15–0.30	1.03	3.8	4.0	7.6
0.30–0.45	0.65	2.4	2.2	4.3
0.60–0.75	0.42	3.1	0.8	6.6
0.90–1.05	0.30	5.4	0.4	14.7
1.20–1.35	0.29	8.9	0.8	23.1
1.50–1.65	0.27	9.3	0.4	31.2
1.80–1.95	0.27	12.2	0.6	34.1
2.10–2.25	0.37	20.9	0.7	39.8
2.40–2.55	0.58	36.8	3.0	18.8
2.70–2.85	0.18	8.2	1.0	8.9

trations), the pH remained high since the theoretical soluble-Ca concentrations (solubility of $CaCO_3$ at high pH) remained low. Soil texture was sandy clay loam at the surface grading to clay loam in the B horizon, then to clay below 0.3 m. Silt and clay decreased again at the carbonate interface.

A strong correlation existed between total soil P concentration and the sand content (inverse of silt and clay), and total Fe and Al concentrations (Fig. 1). The quantity of sand was greater in the top and bottom depths, and lower in the middle depths. The percentage of sand was inversely correlated ($r = -0.70$; $P < 0.05$) with total soil P. Other researchers have found similar associations between total soil P and clay content (Lekwa and Whiteside, 1986), and between silt and clay content (Day et al., 1987). Total soil P concentration was also directly correlated with total Fe and Al concentrations ($r > 0.9$; $P < 0.01$), and inversely correlated with total C concentration ($r = -0.52$; $P < 0.05$). The depth of maximum total soil P concentration (1.20–1.35 m) contained the most silt and clay, and the highest amounts of Fe and Al.

Results of soil organic C (Fig. 2) and total N (Table 2) exhibited typical surface buildup from litter and root activity. These values declined exponentially in the middle depths, probably due to a decrease in rooting density. At about the 2.4-m depth, however, there was a significant accumulation of organic C, total N, and total organic P, and organic P soluble in 2 M H_2SO_4. While organic C and total-N values at the bottom layer were ≈50% of the surface values, total organic-P concentrations were higher than surface

concentrations, probably indicating an in situ development from marine shale or eluviation and accumulation of these nutrients with water or clay during pedologic time. The latter conjecture appears more probable since organic C, total N, and total organic P were high at the carbonate interface and much lower within the carbonate layer.

Available-P pools (Table 2) were large at the surface soil because of organic-matter cycling. Again values declined at the middle depths from lack of rooting volume ($NaHCO_3$ P more so than resin-extractable P). The bottom layers contained significant amounts of inorganic P. The increase in readily extractable inorganic P ($NaHCO_3$, resin) at the carbonate later may have arisen because this layer is sandier than the middle depths, and also lower in Fe- and Al-associated clays than the middle depths (Fig. 1). Thus, adsorption of P was at a minimum. Additionally, the large pool of acid-extractable organic P may be preferentially adsorbed compared with orthophosphate (McKercher and Anderson, 1989). Thus, organic P could conceivable increase the plant-available P at these depths.

Organic P at the deep profile extracted through leaching with acid was essentially equal to 60 to 75% of the total organic P. In the soil surface, this organic P readily extracted in acid represented only ≈30% of the total organic P. The rest of the organic P was extracted in base. The conventional HCO_3 (a measure of labile organic P) or OH extractions released lower

amounts of this large organic-P pool at the carbonate-interface layers. This differential extractability at the deep and surface layers suggests a class of compounds at the deep layers that are not as readily associated with humic materials, but perhaps one associated more with physical adsorption on carbonates, thus becoming available on dissolution of the carbonates with strong acid. Although the inositol phosphates (phytates) contain some similar characteristics (Jackman and Black, 1951; Anderson, 1975), we were unable to confirm definitively the presence of these compounds by nuclear magnetic resonance spectroscopy (data not shown).

Ratios of organic C to total organic P in the whole soil varied from 110 in the top 0.15 m to 36 in the high-organic-P (2.40–2.55-m) depth (Table 3). General ratios of $\approx 100{:}1$ in topsoils are well documented (Stevenson, 1986). Essentially 75% of the total organic P was associated with $\approx 30\%$ of the total organic C. Additionally, the surface 0.3 m contained significant amounts of organic P extractable in base, and the base extracts from the surface 0.45 m showed significant color (data of color absorbance at 550 nm not shown). The base extract from the profile at 2.40- to 2.55-m depth where some organic C was found showed less color, indicating less association of the organic P with humic materials or with buried soils. The data also indicated that the organic C–organic P pool at this depth was low in N (most of the N remained in the soil acid-leached residue, and not in the acid extract where organic P was high).

The data appeared to indicate that low levels of organic C and P, especially those pools associated with the carbonate and, therefore, soluble in acid, have eluviated and accumulated during pedologic times. Mechanistically, organic and inorganic P may have eluviated with clay into the B horizon (Smeck and Runge, 1971). Below the B horizon, movement was probably restricted to selective conditions that may have caused slow organic P desorption from carbonates. This, conceivably, could have occurred during saturated periods where organic P (assuming an anionic form) may have moved sparingly in association with the ferrous ion. Thus, while soil inorganic and organic P can be essentially considered immobile in the short term, translocation, both vertically and horizontally, can be significant during the long term necessary for soil development (Smeck and Runge, 1971).

It is conceivable that deep-rooted crops such as alfalfa and certain grasses could readily use this large pool of inorganic and organic P during times of favorable water supply.

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Table 3. Average organic C, and total organic P in surface, middle, and bottom profile depths for whole soil and acaid-leached soil residue.

Depth	Whole soil Organic C/ Total organic P	Soil residue		
		Organic C	Total N	Total organic P
m		g/kg		
0.00–0.15	110	9.5	1.1	0.010
0.15–0.30	60	6.0	1.0	0.010
0.30–0.45	68	3.5	0.6	0.005
0.90–1.05	91	3.5	0.3	0.003
1.20–1.35	67	2.0	0.2	0.003
2.40–2.55	36	3.5	0.4	0.005
2.70–2.85	43	3.5	0.2	0.003