Changes in Water-extractability of Soil Inorganic Phosphate Induced by Sodium Saturation

A. N. Sharpley,* D. Curtin, and J. K. Syers

ABSTRACT

The effect of replacing indigenous exchangeable cations with Na on the subsequent release of inorganic phosphate (P) from 34 USDA-SCS benchmark soils representing nine soil orders was investigated by sequential extraction with distilled water. Sodium saturation substantially increased the water extractability of P regardless of whether Ca-P or sorbed P was the predominant form of inorganic P in the soil. On average, Na-saturated soils released about 2.5 times more P than the untreated soils. Sequential chemical extractions were used to identify the sources of P extracted. In soils that had not been Na saturated, water-extractable P appeared to originate largely from the NaHCO₃-extractable fraction. The additional P released following Na saturation was accounted for by a disappearance of Ca-P compounds (HCl-extractable) in soils where such entities were present or a decrease in the sorbed-P fraction extracted by NaOH. The results indicate that the distribution of P between solid and solution phases is strongly dependent on the nature of the exchangeable cation population. These results have important implications to soil fertility and P availability in irrigated soils influenced by Na.

Additional Index Words: Ca-P, P release, Saline soils, Sorbed P.

T HE P RELEASE characteristics of soils and soil components have been studied extensively (Barrow, 1979; Chien and Clayton, 1980; Kuo and Lotsi, 1974; Sharpley et al., 1981). Factors that influence the extent of P release to solution include: soil pH; solution composition, e.g., ionic strength and concentration of competing inorganic and organic anions; temperature; and duration of contact with added P (Barrow, 1983; Lopez-Hernandez et al., 1986; Ryden et al., 1977; 1987).

Recent studies (Curtin et al., 1987; Smillie et al., 1987) have produced evidence that the equilibrium between surface P and P in solution is influenced to a considerable degree by the nature of the exchangeable cation suite. For example, Curtin et al. (1987) found that when a group of New Zealand soils were Na-saturated, an average 2.6 times more P was released to distilled water (10 consecutive extractions), than from the original soils, where Ca was the dominant exchangeable cation. This effect may have an important bearing on the availability of P in soils that have become saline or receive saline irrigation water.

It has been suggested (Curtin et al., 1987) that P release induced by Na-saturation could be due to release of P associated with oxide surfaces or to dissolution of Ca-P phases. The relative importance of P desorption and Ca-P dissolution was not established, although such information is essential to understanding the role of exchangeable cations in the chemistry of soil P.

Sequential chemical extraction procedures have been widely used to characterize soil P and offer a means of quantifying changes in sorbed P and Ca-P. Hedley et al. (1982a) have developed a modification of the Chang and Jackson (1957) inorganic P fractionation procedure, which enabled the P fractions, depleted as a result of plant uptake, to be identified (Hedley et al., 1982b) and the transformations of soil P during long-term cultivation to be traced (Sharpley and Smith, 1985; Tiessen et al., 1983).

Because previous studies of the effect of Na saturation on P release (Curtin et al., 1987; Smillie et al., 1987) were confined to seven soil types with a narrow range of pH values, it is not known if the results are applicable to soils in general. Accordingly, one of the objectives of the present study was to quantify the effect of Na saturation on the release of P to distilled water in soils spanning a wide range of properties and pedogenic stages. A second objective was to identify the source(s) of P removed by water extraction with and without Na saturation by means of the procedure of Hedley et al. (1982a).

MATERIALS AND METHODS

Soils

Samples of the surface horizon (Al or Ap) of 34 soils from the Benchmark collection were obtained from the SCS, Lincoln, NE. These soils included representatives of all mineral soil orders; viz., two Alfisols (Amarillo and Holland series), three Andisols (Abasto, Sanpete, and Witt series), five Entisols (Avondale, Coly, Crofton, Lakeland, and Wayden series), four Inceptisols (Agawam, Leeper, Mardin, and Paxton series), seven Mollisols (Acuff, Grundy, Kidman, Macksburg, Muscatine, Shelby, and Uly series), one Oxisol (Catalina series), one Spodosol (Caribou series), one Vertisol (Houston Black), and 10 Ultisols (Appling, Bertie, Dothan, Millhopper, Norfolk, Rayburn, Ruston, Sassafras-like, Sosa, and Tifton series). Clay content and pH were obtained from published SCS soil survey reports and are given along with a full description of these soils in Sharpley et al. (1985). Exchangeable Ca and Mg were extracted by end-over-end shaking of 1 g of soil with 10 mL 1.0 M NH₄, OA for 2 h. Exchangeable Al was extracted from 1 g of soil by 10 mL 1.0 M KCl. Calcium, Mg, and Al were determined on filtered extracts by atomic absorption spectrophotometry.

Phosphorus Release Characteristics

The effect of Na saturation on the release of P to distilled H₂O was examined using a procedure similar to that described by Curtin et al. (1987). Duplicate soil samples were initially shaken with 1.0 M NaCl in preweighed centrifuge tubes at a solution/soil ratio of 40:1 for 24 h at 298 K. After separating the solution from the soil by centrifugation (266 km s⁻¹ for 5 min) and filtration (0.45 μm), distilled H₂O was added (40:1 water/solution ratio) and the suspension again shaken for 24 h. This procedure was repeated to give a total of nine extractions with H₂O. After each extraction cycle, the centrifuge tube and contents were weighed to determine the quantity of entrained solution and, thus, the amount of P carried over between extractions. Release of P from soil samples that had not been pretreated with NaCl was measured by 10 successive extractions (each of 24 h duration) with H₂O at a solution-to-soil ratio of 40:1.

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Phosphorus Fractionation Procedure

Following \( H_2O \) extraction, the soils were subjected to the inorganic P fractionation procedure described by Hedley et al. (1982a). This involved sequential extraction with 0.5 \( M \) NaHCO\(_3\), (pH 8.5); 0.1 \( M \) NaOH; a second extraction with 0.1 \( M \) NaOH following ultrasonic vibration to disrupt soil aggregates; and finally, 1.0 \( M \) HCl. Each extraction was of 16-h duration and the solution-to-soil ratio was 60:1. The inorganic P content was determined on each neutralized extract. Soil samples that had not been extracted with \( H_2O \) or NaCl/\( H_2O \) were also subjected to the P fractionation procedure, to enable estimation of the effect of \( H_2O \) and NaCl/\( H_2O \) extraction on the various P fractions. These fractions are subsequently referred to as NaHCO\(_3\)-P, representing the most biologically available fraction; NaOH-P, representing P associated with hydrous Al and Fe oxides; sorbic P, representing Al-P and Fe-P most likely located within soil aggregates broken down by sonication; and Ca-P, representing relatively stable Ca-P. The amounts of P extracted by NaOH following sonication were small relative to those removed by the first NaOH treatment. Consequently, the quantities of P extracted by the two NaOH treatments were combined, along with NaHCO\(_3\)-P, to give an estimate of sorbed P.

The P concentrations of all filtrates were determined by the method of Murphy and Riley (1962). The following data are in all cases reported as duplicate means, and differences between soil groups and properties indicated statistically significant refer to the 5.0% level as determined by analysis of variance.

**RESULTS AND DISCUSSION**

The soils were divided into two groups, each of 17 soils, on the basis of their P chemistry. In one group, Ca-P was a dominant P form (37-97% of total inorganic P) and included Absted, Acuff, Amarillo, Avondale, Coly, Crofton, Grundy, Houston Black, Kidman, Leeper, Macksburg, Muscatt, Sanpete, Shelby, Uly, Wayden, and Witt. The other group contained soils dominated by sorbed-P (79-97% of total inorganic P) and included Agawam, Appling, Bertie, Caribou, Catalina, Dothan, Holland, Lakeland, Mardin, Millhouse, Norfolk, Paxton, Rayburn, Ruston, Sassafras-like, Sosa, and Tifton. Within each of these groups, a considerable diversity existed with respect to soil chemical composition and P status (Table 1). As would be expected, the soils dominated by Ca-P generally had higher pH values; nine of the 17 soils in this group contained free CaCO₃.

### Table 1. Chemical and physical properties of the soils used.

<table>
<thead>
<tr>
<th>Property</th>
<th>Extraction</th>
<th>Mean</th>
<th>Min</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay, %</td>
<td>Sorbed-P (n = 17)</td>
<td>19.7a</td>
<td>0.4</td>
<td>75.8</td>
</tr>
<tr>
<td>pH</td>
<td>Sorbed-P (n = 17)</td>
<td>5.5a</td>
<td>4.4</td>
<td>5.6</td>
</tr>
<tr>
<td>Exch Ca, mg kg(^{-1})</td>
<td>Sorbed-P (n = 17)</td>
<td>1.299a</td>
<td>120</td>
<td>2400</td>
</tr>
<tr>
<td>NaHCO(_3)-P, mg kg(^{-1})</td>
<td>Sorbed-P (n = 17)</td>
<td>5.8a</td>
<td>3</td>
<td>755</td>
</tr>
<tr>
<td>NaCl-P, mg kg(^{-1})</td>
<td>Sorbed-P (n = 17)</td>
<td>350a</td>
<td>8</td>
<td>127</td>
</tr>
<tr>
<td>HCl-P, mg kg(^{-1})</td>
<td>Sorbed-P (n = 17)</td>
<td>350a</td>
<td>8</td>
<td>127</td>
</tr>
<tr>
<td>Total P, mg kg(^{-1})</td>
<td>Sorbed-P (n = 17)</td>
<td>572a</td>
<td>78</td>
<td>1317</td>
</tr>
</tbody>
</table>

**Fig. 1. Release of P in sequential extractions with either \( H_2O \) or 1.0 \( M \) NaCl (extraction no. 1) followed by \( H_2O \) (extraction no. 2-10).**

Pretreatment with 1.0 \( M \) NaCl increased water extractability of P, irrespective of whether sorbed- or Ca-P was the predominant form of inorganic P in the soil (Fig. 1). The effect of NaCl pretreatment on P release for the two groups of soils is represented by Agawam, a weakly acid (pH 6.1) Inceptisol, in which 77% of inorganic P is present in the NaOH-extractable form; and Coly, a calcareous Entisol with 93% of inorganic P occurring as Ca-P. The other soils in each group exhibited similar patterns of P release. For the Agawam soil, the release of P in 1.0 \( M \) NaCl was lower than in \( H_2O \) (Fig. 1), reflecting the well-known effect of ionic strength on the P sorption-desorption balance (Barrow and Shaw, 1979; Ryden et al., 1977). The absence of an ionic strength effect on P release from the Coly soil (Fig. 1) is probably partly due to the low level of sorbed P in this soil.

Following the NaCl wash, a large increase in water extractability of P was obtained in all soils (Fig. 1). Release of P was generally highest in the second or third water extraction following the NaCl wash and declined steadily thereafter.

**Table 2. Total amount of Ca, Al, and P released and decrease in P fractions during 10 water and one NaCl and nine water extractions.**

<table>
<thead>
<tr>
<th>Predominant inorganic P forms</th>
<th>Sorbed-P</th>
<th>Ca-P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Property</td>
<td>Extraction</td>
<td>Mean</td>
</tr>
<tr>
<td>Ca</td>
<td>Water</td>
<td>196a</td>
</tr>
<tr>
<td>NaCl-water</td>
<td>525c</td>
<td>94</td>
</tr>
<tr>
<td>Water</td>
<td>34a</td>
<td>13</td>
</tr>
<tr>
<td>NaCl-water</td>
<td>368b</td>
<td>76</td>
</tr>
<tr>
<td>P</td>
<td>Water</td>
<td>39a</td>
</tr>
<tr>
<td>NaCl-water</td>
<td>102b</td>
<td>8</td>
</tr>
<tr>
<td>NaHCO(_3)-P</td>
<td>Water</td>
<td>33a</td>
</tr>
<tr>
<td>NaCl-water</td>
<td>35a</td>
<td>0</td>
</tr>
<tr>
<td>NaOH-P</td>
<td>Water</td>
<td>19a</td>
</tr>
<tr>
<td>NaCl-water</td>
<td>89c</td>
<td>0</td>
</tr>
<tr>
<td>HCl-P</td>
<td>Water</td>
<td>3a</td>
</tr>
<tr>
<td>NaCl-water</td>
<td>3a</td>
<td>0</td>
</tr>
</tbody>
</table>

† For each soil property, means followed by the same letter are not significantly different (at the 5.0% level) as determined by analysis of variance for unpaired data between NaOH- and Ca-P soils and between water and NaCl/water extractions.

‡ Represents the decrease in amount of P in a given fraction, following extraction with water or NaCl/water.
The total amount of P released during the sequential NaCl/H₂O extraction (NaCl/H₂O-P) was significantly greater (2.5-fold) than that during H₂O extraction (H₂O-P) alone, for both groups of soils (Table 2). Sodium saturation, therefore, increased the extractability of both sorbed- and Ca-P. This is substantiated by the decrease in the amount of P in several fractions following extraction (Table 2). As expected, removal of Al and Ca was substantially greater in NaCl/H₂O than in H₂O alone (Table 2).

For both groups of soils, H₂O-P was closely related to the decline in NaHCO₃-P caused by extraction with H₂O (Fig. 2). Although the major proportion of H₂O-P appeared to be derived from the NaHCO₃-P fraction for both soils dominated by sorbed-P (85%) and Ca-P (67%), some depletion of NaOH-P and Ca-P occurred in the respective groups (Table 2). As expected, removal of Al and Ca was substantially greater in NaCl/H₂O than in H₂O alone (Table 2).

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Although a close linear relationship was found between the amount of NaCl/H₂O-P and NaOH/P in NaHCO₃-P and one NaCl/nine H₂O extractions and the decrease in NaHCO₃-P for soils containing predominantly sorbed-P (a) and Ca-P (b).

The extra P removed from the Ca-P dominated soils was closely related to the decline in HCl-soluble P (Fig. 3b), indicating a dissolution of Ca-P. Even so, only a small fraction of the total Ca-P was removed during the NaCl/H₂O extraction sequence (10% for Ca-P dominated soils), probably because the degree of Ca saturation increases as extraction proceeds, thereby reducing the effectiveness of the soil as a Ca sink. Smillie et al. (1987) found that when the level of P in the H₂O extracts declined, a further NaCl wash resulted in an increase in P release.

**CONCLUSIONS**

This study shows that in soils spanning a wide range of development, P release is stimulated when indigenous exchangeable cations are replaced by Na. The present results thus support and extend the work of Curtin et al. (1987) and Smillie et al. (1987).

It is clear from the results that Na saturation leads to both release of sorbed-P and dissolution of Ca-P compounds. While the effect on Ca-P is predictable, considerable uncertainty exists as to why changes in exchangeable cations have such a marked influence on P sorption/desorption. Smillie et al. (1987) suggested that their data were consistent with a chemical association between P and Ca at oxide surfaces, as previously suggested by Helyar et al. (1976). On the other hand, surface electrostatic potential becomes more negative when divalent and trivalent ions are replaced by Na and this would reduce the affinity of the surface for P, thereby leading to desorption of P (Barrow, 1983). The importance of surface electrostatic poten-
tial is recognized in the P sorption models of Barrow (1983) and Goldberg and Sposito (1984), although these authors differ as to the precise manner in which surface potential influences phosphate sorption. It cannot be established from the present data if the NaCl-induced desorption of P is due to changes in surface electrostatic potential or to destabilization of surface Ca-P complexes.

The soils used by Curtin et al. (1987) and Smillie et al. (1987) were weakly to moderately acid with little or no exchangeable Al. In contrast, several of the strongly acid soils used in the present study contained significant levels of exchangeable Al and its removal may be partly responsible for the enhanced release of P following NaCl washing. Syers et al. (1971) showed that sorption of added P decreased when exchangeable Al was removed by KCl extraction. Observations such as these are often interpreted as evidence of an aluminum-phosphate precipitation reaction (Sanchez and Uehara, 1980). An equally plausible explanation, however, is that P sorption was reduced because surface negative potential increases substantially when Al is replaced by a monovalent cation.

The present work has important implications to P fertility and P movement in irrigated soils influenced by Na. Irrigation of soils with water containing high salt concentrations is known to result in surface soils having high exchangeable Na percentages (McNeal, 1974). In addition to affecting the physical characteristics of a soil, this change in cation composition would be expected to shift the solid P–solution P equilibrium in favor of the latter, thereby increasing the availability of P to plants. Because the commonly used soil P tests involve concentrated solutions, it is doubtful if they are sensitive to the increased release of P from soils influenced by Na.

An increase in the use and reuse of water for irrigation will result in a gradual increase in the Na content of groundwater used for irrigation, as exemplified by data for the Colorado River (USEPA, 1978). Given that irrigation in semiarid areas is increasing (USDA, 1984) and nonarid areas may also be faced with a salinity problem as water use approaches available supply, the implications of the present findings to the availability of soil P requires further evaluation under field conditions.

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REFERENCES


