SOIL PHOSPHORUS SORPTION AND AVAILABILITY AS A FUNCTION OF HIGH PHOSPHORUS FERTILIZER ADDITIONS

R. Indiati, A. N. Sharpley, C. Izza, A. Figliolia, B. Felici, and P. Sequi

Istituto Sperimentale Per La Nutrizione Delle Piante, Via della Navicella 2, 00184 Roma, Italy

ABSTRACT: After a 3-months equilibration of soil with phosphorus (P) (up to four times the respective P sorption capacity), equilibrium P concentration (EPCo), standard P requirement (SPR), P sorption index (SI), and P availability by Bray I, Olsen, water and iron-oxide paper strip methods were determined on three soils of the Latium region of Italy, widely ranging in their affinity for P. Soil P addition increased EPCo and availability P content and decreased SPR and SI values for all soils with differences between soil types a function of P sorption maximum. The tractional increase of available NaHCO3-P with added P, i.e. P availability index (F) was 0.486 for the soil with the lowest P sorption maximum, 0.217 for the soil with the highest P sorption maximum, and 0.369 for the third soil presenting an intermediate P sorption (r = 0.997; P<0.01). The results indicate that soil type, in addition to the amount of P added, will determine the potential for a soil to release P to runoff.

INTRODUCTION

With the application of P in fertilizer or manure to soil, in excess of crop removal rates, soil P can accumulate to levels of environmental concern and the

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accelerated eutrophication of receiving fresh waters can be promoted by the
increased potential for P loss in agricultural runoff and drainage (Schindler, 1977;
Sharpley et al., 1994). Knowledge of the dynamics of P sorption and desorption
process for enriched P soils, may, therefore, be of prime importance in controlling
soil P bioavailability. This will be of particular importance if we consider that the
ability of heavily P-fertilized soils to retain further additions of P from loss in
runoff, will depend to a large extent on the sorption capacity of the soil. In fact, the
potential for P loss from Dutch soils is classified by the degree of saturation of P
sorption (Sharpley et al., 1994). Furthermore, as the traditional approach to soil
phosphate sorption study has involved use of low solution P concentrations,
relevant to plant availability of soil P, investigation of the effect of high P additions
to soil on soil P sorption and availability is needed.

The objective of this study was to investigate the effect of high soil P additions
(up to four times the P sorption maximum) on subsequent P sorption, desorption,
and availability for three Italian soils of differing physical and chemical properties.

MATERIALS AND METHODS

The surface horizon of three soils (Typic Xerorthents) were collected from the
Frosinone District in south-east Latium, Italy. The characteristics of the air dried
and 2 mm-sieved soils are reported in Table 1. Clay content of the soils was
determined by pipet analysis following dispersion with sodium hexametaphosphate
(Day, 1965), soil pH by a glass electrode at a 2:1 water/soil (v/w) mixture, and
organic C by the wet oxidation procedure (Raveh and Avnimelech, 1972). Free iron
oxide was extracted with citrate-dithionite-bicarbonate solution (Mehra and
Jackson, 1960) and determined by atomic absorption spectrometry.

Equilibration Procedure

Solution P (as KH2PO4) was added to soils at amounts equivalent approxi-
mately to 0, 1/8, 1/4, 1/2, 1, 2, and 4 times their P sorption maximum (Xmax)
estimated by a modified Langmuir isotherm (Kuo et al., 1988). La Bufola was
treated with 0 to 1,600 mg P/kg, Sornino with 0 to 800 mg P/kg, and Valle S.
Angelo with 0 to 3,200 mg P/kg. Soil-P mixtures were aerobically incubated for 90
days at 25°C in PVC Petri capsules. The soils were rewetted to field capacity twice
a week. After incubation, P sorption and availability were determined as described
below.
Table 1. Selected physical and chemical characteristics, Olsen available P and P sorption maxima for the studied soils.

<table>
<thead>
<tr>
<th>Soil</th>
<th>pH</th>
<th>Clay</th>
<th>Organic C</th>
<th>Free Fe₂O₃</th>
<th>NaHCO₃-P</th>
<th>Xmax</th>
</tr>
</thead>
<tbody>
<tr>
<td>La Bufola</td>
<td>6.6</td>
<td>30</td>
<td>1.32</td>
<td>1.65</td>
<td>10.8</td>
<td>408</td>
</tr>
<tr>
<td>Sornino</td>
<td>6.7</td>
<td>9</td>
<td>1.04</td>
<td>0.57</td>
<td>8.2</td>
<td>180</td>
</tr>
<tr>
<td>Valle S. Angelo</td>
<td>6.6</td>
<td>64</td>
<td>1.92</td>
<td>3.31</td>
<td>28.0</td>
<td>780</td>
</tr>
</tbody>
</table>

**Phosphorus Sorption**

Three g of incubated soil were shaken with 30 mL 0.01M CaCl₂ solution containing from 0 to 60 mg P/L for 24 hours at 25°C. After centrifugation and filtration (0.45 μm), solution P concentration was determined and the amount of P sorbed was calculated as the difference between added and solution P. Two sorption parameters, equilibrium P concentration (EFCO, solution P concentration at which there is neither sorption nor desorption of P) and standard P requirement (SFR P sorbed at solution P concentration of 0.2 mg P/L) were obtained by plotting sorbed P versus solution P. The amount of P sorbed, X (mg/100 g) from one addition of 1.5 g P/kg of soil was also determined after shaking for 24 hours at a water to soil ratio of 10:1. The P sorption index (SI) was calculated using the quotient X/log C, where C is the solution P concentration expressed as μmoles/L (Bache and Williams, 1971). This quotient has been found close correlated with P sorption maximum derived from a Langmuir sorption plot for a wide range of soils.

**Phosphorus Availability**

Ten g of incubated soil were shaken with 100 mL distilled water containing 0, 5, 10, and 20 mg P/L for 24 hours at 25°C. The suspension was filtered (0.45 μm) and the soil was washed five times with 20 ml of distilled water to give a final volume of 200 mL. Adsorbed P was calculated as the difference between added P and solution P.

Available P content was determined on air-dried soil (Bray I, Bray and Kurtz 1947, Olsen et al., 1954), water (two, 1 hour consecutive extractions at a soil to
water ratio of 1:40) (Ryden and Syers, 1977) and iron oxide impregnated paper strip (Fe-oxide strips) techniques (Menon et al., 1989). In all cases, P in solution or neutralized extracts was determined by the colorimetical molybdenum-blue method of Murphy and Kiley (1962). All determinations were made in duplicate and results given as means.

The employed extractants were chosen on the basis of their different aptitude to remove soil P: Bray I and Olsen solutions, very commonly used soil P tests for acidic and neutral and calcareous soils, respectively, are capable of extracting specific forms of P by increasing P solubilization by addition of dilute acids and complexing P with fluoride anion (Bray I) or hydrolysis of P-binding cations (Olsen). Conversely, water and Fe-oxide strip techniques are insensitive to soil properties. The former was seen to provide a reliable estimate of the amount of more-physically sorbed P (isotopically exchangeable P) (Ryden and Syers, 1977); the latter, analogously to anion resin, was described to act as a sink for soil solution P, the quantity of P removed by the strip depending on the process of mobilization from the solid phase and diffusion through the solution to the paper (Menon et al., 1989).

RESULTS AND DISCUSSION

Phosphorus Sorption

Soil P addition had a dramatic effect on P sorption isotherms for the three soils (Fig. 1). Following soil-P equilibration, EPCo increased for Valle S. Angelo from an initial level of 0.02 mg/L to 13 mg/L at the maximum P addition of 3,200 mg/kg, while slightly lower values were found for La Bufola and Sornino after additions of 1,600 and 800 mg P/kg, respectively (Table 2). A close linear relationship between EFCO and added P was obtained and the correlation coefficients were 0.98 for La Bufola, 0.99 for Sornino, and 0.94 for Valle S. Angelo (P<0.001). Conversely, SPR and SI decreased with added P but at different rates for the three soils. In fact, a P addition of 50 mg/kg reduced the SPR value of Sornino to 0 but 800 mg P/kg were needed to reduce the SPR value of Valle S. Angelo to the same level; La Bufola showing an intermediate behaviour.

Sorption index values decreased logarithmically with an increase in P added with r values of 0.990 for La Bufola, 0.962 for Sornino, and 0.962 for Valle S. Angelo (P<0.001). For the same P addition (200 mg/kg soil), La Bufola had an
FIGURE 1: Isotherm sorption curves for the three soils-La Bufola, Valle S. Angelo, and Sornino—amended with several rates of P expressed as a function of P sorption maxima (A=0 Xm, B=1/8 Xm, C=1/4 Xm, D=1/2 Xm, E=1 Xm, F=2 Xm, G=4 Xm).
Table 2. Soil P sorption parameters, EPC0 (mg/L), SPR (mg/Kg) and SI in function of added P (expressed as a fraction of P sorption capacity, Xmax).

<table>
<thead>
<tr>
<th>Soil</th>
<th>P sorption parameter</th>
<th>0</th>
<th>1/8 Xmax</th>
<th>1/4 Xmax</th>
<th>1/2 Xmax</th>
<th>Xmax</th>
<th>2 Xmax</th>
<th>4 Xmax</th>
</tr>
</thead>
<tbody>
<tr>
<td>La Bufola</td>
<td>EPC0</td>
<td>0.03</td>
<td>0.05</td>
<td>0.07</td>
<td>0.20</td>
<td>0.62</td>
<td>4.20</td>
<td>10.00</td>
</tr>
<tr>
<td></td>
<td>SPR</td>
<td>115.0</td>
<td>83.0</td>
<td>55.0</td>
<td>&lt;0</td>
<td>&lt;0</td>
<td>&lt;0</td>
<td>&lt;0</td>
</tr>
<tr>
<td></td>
<td>SI</td>
<td>30.5</td>
<td>27.3</td>
<td>23.7</td>
<td>22.1</td>
<td>16.3</td>
<td>12.7</td>
<td>7.5</td>
</tr>
<tr>
<td>Sornino</td>
<td>EPC0</td>
<td>0.07</td>
<td>0.16</td>
<td>0.35</td>
<td>1.15</td>
<td>3.60</td>
<td>5.50</td>
<td>11.80</td>
</tr>
<tr>
<td></td>
<td>SPR</td>
<td>8.1</td>
<td>2.0</td>
<td>&lt;0</td>
<td>&lt;0</td>
<td>&lt;0</td>
<td>&lt;0</td>
<td>&lt;0</td>
</tr>
<tr>
<td></td>
<td>SI</td>
<td>9.6</td>
<td>5.5</td>
<td>3.8</td>
<td>3.2</td>
<td>2.6</td>
<td>2.4</td>
<td>1.4</td>
</tr>
<tr>
<td>Valle S. Angelo</td>
<td>EPC0</td>
<td>0.02</td>
<td>0.04</td>
<td>0.06</td>
<td>0.09</td>
<td>0.52</td>
<td>2.30</td>
<td>13.00</td>
</tr>
<tr>
<td></td>
<td>SPR</td>
<td>275.0</td>
<td>235.0</td>
<td>180.0</td>
<td>98.0</td>
<td>&lt;0</td>
<td>&lt;0</td>
<td>&lt;0</td>
</tr>
<tr>
<td></td>
<td>SI</td>
<td>51.6</td>
<td>48.3</td>
<td>45.6</td>
<td>42.9</td>
<td>35.7</td>
<td>26.6</td>
<td>16.2</td>
</tr>
</tbody>
</table>

EPC0 of 0.20 mg/L (1/2 Xmax), 3.60 mg/L (1 Xmax) for Sornino, and 0.06 mg/L (1/4 Xmax) for Valle S. Angelo (Table 2).

**Phosphorus Availability**

The amount of P desorbed by Olsen, Bray-I, water, and Fe-oxide strips increased with an increase in the amount of P sorbed (P desorbed from the samples was corrected for that from the control receiving no P) (Fig. 2). Although the amount of P extracted varied considerably among the three soils, trends in P availability behaviour, were similar for the four extractants in spite of the remarkable difference in their acidity, ionic strength, and ability to desorb P.

According to Kuo et al. (1988), the recovery of sorbed P by the several extractants was highly dependent on P sorption capacity and in particular more P tended to be desorbed from soils with a lower P sorption capacity. This is also consistent with P fertilized soils in this study, as shown in Table 3 for four selected rates of added P. The amount of Olsen P increased linearly with an increase in the amount of P added:

- \( \text{NaHCO}_3\text{-P} = 13 + 0.369P \text{ added} \) \((R^2 = 0.99; P<0.001)\) for La Bufola
- \( \text{NaHCO}_3\text{-P} = -9 + 0.486P \text{ added} \) \((R^2 = 0.97; P<0.001)\) for Sornino
- \( \text{NaHCO}_3\text{-P} = 30 + 0.217P \text{ added} \) \((R^2 = 0.99; P<0.001)\) for Valle S. Angelo
FIGURE 2: The amount of phosphate extracted by NH$_4$F-HCl, NaHCO$_3$, H$_2$O and paper-strips as a function of the amount of P sorbed for the three soils.
Table 3. Parameters of the regression equation relating sorbed P to P desorbed by the used extractants (P extr. = a + b x P sorbed; r²) for the three soils and four selected rates of added P (expressed as a fraction of P sorption capacity, Xmax). P extracted and P sorbed are expressed as mg/Kg.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Added P</th>
<th>Bray 1-P</th>
<th>Olsen-P</th>
<th>Water-P</th>
<th>Paper-P</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a</td>
<td>b</td>
<td>r²</td>
<td>a</td>
</tr>
<tr>
<td>La Bufola</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>7.9</td>
<td>0.269</td>
<td>0.998</td>
<td>22.9</td>
<td>0.293</td>
</tr>
<tr>
<td>1/4 Xmax</td>
<td>24.1</td>
<td>0.368</td>
<td>0.996</td>
<td>50.5</td>
<td>0.389</td>
</tr>
<tr>
<td>Xmax</td>
<td>105.8</td>
<td>0.551</td>
<td>0.995</td>
<td>154.6</td>
<td>0.505</td>
</tr>
<tr>
<td>4 Xmax</td>
<td>598.2</td>
<td>0.930</td>
<td>0.993</td>
<td>684.7</td>
<td>0.937</td>
</tr>
<tr>
<td>Sornino</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>12.0</td>
<td>0.505</td>
<td>0.998</td>
<td>7.7</td>
<td>0.412</td>
</tr>
<tr>
<td>1/4 Xmax</td>
<td>35.8</td>
<td>0.690</td>
<td>0.993</td>
<td>32.4</td>
<td>0.507</td>
</tr>
<tr>
<td>Xmax</td>
<td>105.2</td>
<td>0.827</td>
<td>0.984</td>
<td>76.6</td>
<td>0.778</td>
</tr>
<tr>
<td>4 Xmax</td>
<td>460.2</td>
<td>0.904</td>
<td>0.952</td>
<td>450.3</td>
<td>0.902</td>
</tr>
<tr>
<td>Valle S. Angelo</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>4.5</td>
<td>0.093</td>
<td>0.985</td>
<td>44.8</td>
<td>0.258</td>
</tr>
<tr>
<td>1/4 Xmax</td>
<td>18.1</td>
<td>0.173</td>
<td>0.955</td>
<td>82.9</td>
<td>0.282</td>
</tr>
<tr>
<td>Xmax</td>
<td>96.8</td>
<td>0.350</td>
<td>0.993</td>
<td>223.5</td>
<td>0.366</td>
</tr>
<tr>
<td>4 Xmax</td>
<td>733.2</td>
<td>0.496</td>
<td>0.973</td>
<td>789.2</td>
<td>0.678</td>
</tr>
</tbody>
</table>
where the slope of the linear regression represent the fertilizer availability index (F) values for the studied soils. Clearly, a higher P value or P availability was obtained for soils with lower P sorption. In fact (Fig. 3) the change in F value was closely related to P sorption index \( r = 0.99 \), clay \( r = 0.99 \), and Fe-oxide content \( r = 0.99 \) of the original soils.

**CONCLUSIONS**

Following high P additions, soil P sorption and availability were influenced to different degrees as a function of soil physical and chemical characteristics. As a result, high P additions influenced P sorption parameters related to a soil’s pollution potential. However, differences in the magnitude of change in EPCo, SPP, SI, and P availability between soils, indicates soil type, in addition to the amount of P added, will determine a soil potential to release P to runoff and drainage water. Further studies of the differences in the magnitude of change in P sorption and availability in response to soil P amendments, to a greater soil population and soil
types, will improve our ability to ass the potential risk of a soil to release P to runoff and drainage water.

REFERENCES:


