SOIL PHOSPHATE SORPTION AND SIMULATED RUNOFF PARAMETERS AS AFFECTED BY FERTILIZER ADDITION AND SOIL PROPERTIES

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ABSTRACT: Changes in soil phosphate (P) sorption properties, soil P availability and two runoff-related parameters, were determined on 32 Italian soils, following application of 100 mg P/kg soil. The ability of soil chemical and physical characteristics, in predicting the relative changes in soil P availability was investigated. Phosphorus Sorption Index (SI) gave the best estimate ($r>0.76; P<0.001$) of the potential for change in the studied P soil properties. Inclusion of SI into the fertilizer recommendation process using soil P availability, may improve fertilizer-use efficiency and reduce the potential for P loss in runoff.

INTRODUCTION

By necessity, soil testing programs must measure plant available P in soil through the use of rapid chemical extraction procedures to provide recommendations in a timely and cost-effective manner. From an environmental perspective, however, other tests for soil P may be more relevant. For example, if the environmental issue is eutrophication, an assessment of the desorption of soil (and sediment) P and subsequent bioavailability to aquatic organisms such as algae, is of greatest interest.

In this context, measurement of dissolved P and bioavailable P is considered of prime importance in controlling the eutrophication processes of fresh waters (Sharpley et al., 1994). Conversely, for a wastewater irrigation system, estimates of the long-term capacity of a soil profile to retain P against leaching will be needed.
Although it is unrealistic to expect that routine soil tests can provide the information required by all environmental management programs, a number of alternative tests for soil P are available that, while not as easily conducted as a routine soil test, can provide supplemental information on P sorption, desorption and bioavailability. A number of relatively rapid tests for available or labile P, for example, have been developed in recent years, such as the use of anion exchange resins (Abrams and Jarrell, 1992) and iron oxide-impregnated strips (Menon et al., 1990) in both laboratory extraction and in-situ field soils.

The long-term capacity of soils to retain P is commonly estimated by adsorption isotherms that can be used to derive adsorption maxima, equilibrium P concentration, standard P requirement, and P buffer capacity (Kuo, 1991). These isotherms require equilibration of soil with a series of P solutions of increasing P concentrations, normally for 24 hours, which are thus not well adapted to routine soil testing. However, Bache and Williams (1971) suggested that a single-point isotherm (P sorption index) could be used to estimate the P adsorption maxima of soils with reasonable accuracy. This was recently confirmed by Mozaffari and Sims (1994) for surface and subsoils horizons of four Atlantic Coastal Plain soils.

Although several studies have investigated the release of bioavailable P to runoff and several aspects of P sorption (Kuo, 1991; Sharpley et al., 1994), information is needed on the effect of soil P additions on bioavailable soil P and sorption capacity. This information should aid increasing the reliability of fertilizer recommendations from both agronomic and environmental standpoints. Thus, the objectives of this research were to compare the applicability of P sorption index relative to other P sorption parameters and some physical and chemical soil properties to provide information about changes in soil P extractability, soil P retention and release of P to simulated runoff, following P fertilizer application to 32 Italian soils.

**MATERIALS AND METHODS**

Thirty-two soils, both volcanic and alluvial, representing a wide range in physical and chemical properties and P adsorption capacity, were selected from several locations in the Southern Latium area of Italy, air dried, and screened through a 2-mm sieve.

Soil pH was determined with a glass electrode at a 2.5:1 water to soil ratio (v/w); clay content by pipet analysis following dispersion with hexametaphosphate.
carbonate content was determined by means a Dietrich-Fröhlig calcimeter; and organic carbon (C) by the wet oxidation procedure (Raveh and Avnimelech, 1972). Free iron and aluminium oxides were extracted with the citrate-dithionite-bicarbonate solution (Mehra and Jackson, 1960) and determined by atomic absorption spectrometry (AAS). The concentration of P in solution was measured by the ammonium molybdate method with ascorbic acid as the reducing agent (Murphy and Riley, 1962). All determinations were made in duplicate and results given as means.

**Soil Equilibration Procedure**

Soils were amended with soluble phosphate (as KH$_2$PO$_4$) at amounts equivalent to 100 mg P/kg soil and were incubated for 90 days at room temperature (20±3°C) in PVC Petri capsules left open during equilibration; soils were rewet to field capacity twice a week. Fertilization rate of 100 mg P/kg soil was seen by a preliminary study to cause appreciable change in P parameters, both for low- and high P-fixing soils.

Soils with and without added P were then air dried, sieved (2-mm), and analysed for P sorption properties, Mehlich and water P extractability, and potential release of P by a simulated runoff procedure.

**Phosphorus Sorption Studies**

Three g of soil were shaken with 30 mL 0.01M CaCl$_2$ solution containing from 0 to 60 mg P/L, for 24 hours at 25°C. Two drops of toluene were added to minimize microbial activity. After centrifugation and filtration, P concentration in solution was determined and the amount of P sorbed was calculated as the difference between added and solution P. Readily desorbable P was represented by the amount extracted by 0.01M CaCl$_2$ following equilibration without P (Reddy et al., 1980).

By plotting sorbed P versus solution P, the following sorption P parameters were calculated: i) the equilibrium phosphate concentration (EPC$_0$), defined as the soluble P concentration that is supported by a soil sample at which no net sorption or desorption take place (White and Beckett, 1964; Taylor and Kunishi, 1971); ii) the standard P requirement (SPR), defined as the amount of P sorbed in correspondence of a solution P concentration of 0.2 mg P/L (Fox and Kamprath, 1970; Juo and Fox, 1977); iii) a modified standardized P buffer capacity (SBC), calculated as the ratio of the change in quantity of P sorbed to the change in solution P concentration from 0.15 to 0.25 mg P/L (Holford, 1979; Ozanne and Shaw,
In addition, the amount of P sorbed, X (mg/100 g), from one addition of 1.5 g P/kg of soil was 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/logC, where C is the solution P concentration expressed as μmoles/L (Bache and Williams, 1971).

EPCo is a parameter related to soil P intensity, important in determining amount and direction of the changes between soluble P and particulate P that can take place during transport of sediment in a stream flow; SPR, the quantity of P retained at a specified concentration of P in soil solution, represents the soil P capacity factor and SBC gives an index of the soil buffering capacity as the quantity of P sorbed per unit increase of P solution concentration (Kuo, 1991). Lastly, SI has been found close related with P sorption maxima derived from Langmuir sorption plot for a large range of soil.

**Simulating Runoff Procedure**

Simulated runoff samples were obtained by shaking 5 g of soil with 200 mL deionized water for 24 hours. The suspension was then diluted to 500 mL with distilled water; the 20-μm soil suspension fraction was decanted after an appropriate settling time adjusted for water temperature (Gee and Bauder, 1986). The suspended sediment samples resulting from this extraction and separation procedure were used for the immediate determination of both dissolved P (DP), after centrifugation and filtration at 0.45 μm and bioavailable P (BAP), or Fe-oxide strip P, after immersion of one strip in unfiltered runoff (50 mL) for 16 hours (Sharpley, 1993).

**Phosphorus Availability Studies**

Extractable P was determined by: i) Mehlich 3 solution (mixture of 0.2M CH₃COOH, 0.25M NH₄NO₃, 0.015M NH₄F, 0.013M HNO₃, and 0.001M EDTA), with 5 minutes extraction at a soil to solution ratio of 1:10 (Mehlich, 1984), and ii) two-1 hour consecutive extractions of soil with distilled water at a soil to water ratio of 1:40. The amount of P removed in the last extraction procedure resulted in a linear and approximately 1:1 relationship with the amount of physically sorbed P for a range of soils (Ryden and Syers, 1977). It represents an estimate of the quantity of soil P that can be readily released to solution (Sharpley, 1981).

**RESULTS**

Some physical and chemical characteristics of the studied soils are reported in Table 1 while the original values of the soil P properties are shown in Table 2. It is
TABLE 1. Selected Physical and Chemical Properties of the Soils Studied.

<table>
<thead>
<tr>
<th>Soil property</th>
<th>Min.</th>
<th>Max.</th>
<th>Mean</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5.6</td>
<td>8.0</td>
<td>7.0</td>
<td>0.7</td>
</tr>
<tr>
<td>Clay, mg/kg</td>
<td>40</td>
<td>780</td>
<td>280</td>
<td>190</td>
</tr>
<tr>
<td>Org. C, mg/kg</td>
<td>2.0</td>
<td>58.3</td>
<td>14.4</td>
<td>11.3</td>
</tr>
<tr>
<td>Al₂O₃, mg/kg</td>
<td>0.5</td>
<td>13.7</td>
<td>6.2</td>
<td>3.8</td>
</tr>
<tr>
<td>Fe₂O₃, mg/kg</td>
<td>4.6</td>
<td>51.9</td>
<td>21.4</td>
<td>13.9</td>
</tr>
<tr>
<td>CaCO₃, mg/kg*</td>
<td>22</td>
<td>344</td>
<td>137</td>
<td>113</td>
</tr>
</tbody>
</table>

* Values are referred to soils effectively presenting a CaCO₃ content (n=10).


<table>
<thead>
<tr>
<th>Parameter</th>
<th>Min.</th>
<th>Max.</th>
<th>Mean</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolved P (DP), µg/L</td>
<td>6.8</td>
<td>125.4</td>
<td>35.6</td>
<td>26.5</td>
</tr>
<tr>
<td>Bioavailable P (BAP), µg/L</td>
<td>46.1</td>
<td>901.4</td>
<td>162.2</td>
<td>168.1</td>
</tr>
<tr>
<td>Water extractable P (Water-P), mg/kg</td>
<td>0.8</td>
<td>12.5</td>
<td>2.9</td>
<td>2.5</td>
</tr>
<tr>
<td>Mehlich available P (Mehl-P), mg/kg</td>
<td>0.1</td>
<td>36.2</td>
<td>6.8</td>
<td>8.0</td>
</tr>
<tr>
<td>Readily desorb. CaCl₂ P (CaCl₂-P), mg/kg</td>
<td>0.140</td>
<td>0.860</td>
<td>0.375</td>
<td>0.183</td>
</tr>
<tr>
<td>Equilibrium P Concentration (EPC₀), µg/L</td>
<td>14</td>
<td>90</td>
<td>39</td>
<td>19</td>
</tr>
<tr>
<td>Standard P Requirement (SPR), mg/kg</td>
<td>8</td>
<td>355</td>
<td>133</td>
<td>104</td>
</tr>
<tr>
<td>Standardized Buffer Capacity (SBC), L/kg</td>
<td>60</td>
<td>1100</td>
<td>407</td>
<td>303</td>
</tr>
<tr>
<td>P Sorption Index (SI)</td>
<td>4.3</td>
<td>54.2</td>
<td>28.2</td>
<td>15.9</td>
</tr>
</tbody>
</table>
evident that the selected soils ranged widely in physico-chemical parameters which were reflected in the variation in the P sorption properties. In fact, SPR, SBC, and SI resulted closely related to clay and free iron and aluminium oxides ($r = 0.84$ to 0.92; $P<0.001$). In addition, SPR, SBC, and SI were also related ($r>0.95$; $P<0.001$), and at a lesser degree, to Mehlich-P, CaCl$_2$-P, water-P, and EPCo ($r = 0.36$ to 0.51; $P<0.05$). No relationship was found with data resulting from the simulating runoff parameters, DP and BAP.

After addition and equilibration of the soils with 100 mg P/kg, wide soil-dependant changes resulted for the several studied P properties (Table 3).

**Phosphorus Availability**

The observed increases for the estimates of P availability ranged for Mehlich-P from 3.9 to 72.8 mg P/kg of soil, and for water extractable-P from 0.7 to 40.4 mg P/kg. In particular, for soils with very low P retention (SI<10, $n = 5$), the mean increases were 63 mg P/kg and 33 mg P/kg for Mehlich-P and water-P, respectively. Corresponding values for soils highly fixing P (SI>30, $n = 15$), approximate mean were much lower; 12 mg P/kg for Mehlich-P and 3.5 mg P/kg for water-P.

**Phosphorus Adsorption**

After P application, SPR and SBC decreased for all soils, but for soils with the lowest P fixation power (i.e., for soils with SI less than 13), these changes could not to be quantified. In fact, no P adsorption occurred at the solution P concentration at which these parameters were determined (0.2 µg P/L for SPR and 0.15 to 0.25 µg P/L for SBC). For soils with higher P retention capacity, SPR and SBC decreases varied from 37 to 74 mg/kg and from 0 to 150 L/kg, respectively. The generally negligible changes for SBC shown by most of the soils, resulted from the fact that the addition of P preferentially induced a translation of the isotherms downwards rather than a variation of the slope.

Furthermore, P applied to soils decreased SI from 0.5 to 3.9. Finally, EPCo increases ranged from 7 to 1,100 µg P/L and for readily desorbable-P (CaCl$_2$-P) from 0.07 to 7.63 mg/kg. The mean increase for soils with SI<10 was 942 µg P/L for EPCo and 6.6 mg/kg for CaCl$_2$-P, while for soils with SI>30, $\Delta$EPCo was 19 µg P/L and $\Delta$CaCl$_2$-P was 0.19 mg/kg.

**Phosphorus Bioavailability in Runoff**

Addition of P resulted in DP increases ranging from 5 to 357 µg P/L and for BAP from 5.7 to 504 µg P/L. The mean increases were 325 µg P/L for DP and 401
TABLE 3. Changes in the Selected Runoff-Related and P Availability Data, and P Sorption Parameters of the Studied Soils, following P Application (100 mg/kg).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Min.</th>
<th>Max</th>
<th>Mean.</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolved P (DP), µg/L</td>
<td>5.0</td>
<td>357.5</td>
<td>132.3</td>
<td>108.5</td>
</tr>
<tr>
<td>Bioavailable P (BAP), µg/L</td>
<td>5.7</td>
<td>504.0</td>
<td>217.0</td>
<td>127.5</td>
</tr>
<tr>
<td>Water extractable P (Water-P), mg/kg</td>
<td>0.7</td>
<td>40.4</td>
<td>12.8</td>
<td>11.3</td>
</tr>
<tr>
<td>Mehlich available P (Mehl-P), mg/kg</td>
<td>3.9</td>
<td>72.8</td>
<td>30.0</td>
<td>20.9</td>
</tr>
<tr>
<td>Readily desorb. CaCl₂ P (CaCl₂-P), mg/kg</td>
<td>0.070</td>
<td>7.630</td>
<td>1.660</td>
<td>2.375</td>
</tr>
<tr>
<td>Equilibrium P Concentration (EPC₀), µg/L</td>
<td>7</td>
<td>1100</td>
<td>218</td>
<td>341</td>
</tr>
<tr>
<td>Standard P Requirement (SPR), mg/kg</td>
<td>-34</td>
<td>-74</td>
<td>-52</td>
<td>10</td>
</tr>
<tr>
<td>Standardized Buffer Capacity (SBC), L/kg</td>
<td>0</td>
<td>-150</td>
<td>-35</td>
<td>46</td>
</tr>
<tr>
<td>P Sorption Index (SI)</td>
<td>-0.5</td>
<td>-3.9</td>
<td>-2.2</td>
<td>0.8</td>
</tr>
</tbody>
</table>

µg P/L for BAP, for soils with SI<10. In contrast, the increases for soils with SI>30 were 46 µg P/L for DP and 135 µg P/L for BAP.

In Table 4, the correlation coefficients of the regressions between the changes of each soil P property (Mehlich-P, Water-P, Readily desorbed-P, DP, BAP, and EPC₀) as a function of the selected physical and chemical characteristics and P sorption parameters (clay, free iron and aluminium oxides, SI, SPR, and SBC), are shown. The Sorption Index was the parameter closest linearly related to the variation of P soil properties following P addition, the correlation coefficients (r) being 0.94 with Mehlich-P, 0.92 with water extractable-P, 0.79 with CaCl₂ desorbed-P, 0.91 with DP, 0.86 with BAP, and 0.76 with EPC₀. Clay was the least related parameter presenting the following correlation coefficients: 0.74 with Mehlich-P, 0.71 with water extractable-P, 0.57 with CaCl₂ desorbed-P, 0.71 with DP, 0.74 with BAP, and 0.55 with EPC₀. Intermediate r values were shown by free iron and aluminium oxides, SPR, and SBC.
TABLE 4 - Correlations Coefficients (r) between Physical and Chemical Properties and P Sorption Parameters Changes in Runoff-Related and Availability Data, Following P Application. (All Data Are Significant at 0.001 Probability Level).

<table>
<thead>
<tr>
<th></th>
<th>ΔDP</th>
<th>ΔBAP</th>
<th>ΔWater-P</th>
<th>ΔMehl-P</th>
<th>ΔCaCl2-P</th>
<th>ΔEPC0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay</td>
<td>0.709</td>
<td>0.743</td>
<td>0.711</td>
<td>0.738</td>
<td>0.571</td>
<td>0.554</td>
</tr>
<tr>
<td>Al2O3</td>
<td>0.847</td>
<td>0.843</td>
<td>0.834</td>
<td>0.867</td>
<td>0.737</td>
<td>0.715</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>0.818</td>
<td>0.836</td>
<td>0.815</td>
<td>0.875</td>
<td>0.666</td>
<td>0.635</td>
</tr>
<tr>
<td>SPR</td>
<td>0.835</td>
<td>0.845</td>
<td>0.832</td>
<td>0.877</td>
<td>0.674</td>
<td>0.645</td>
</tr>
<tr>
<td>SBC</td>
<td>0.793</td>
<td>0.797</td>
<td>0.794</td>
<td>0.832</td>
<td>0.637</td>
<td>0.610</td>
</tr>
<tr>
<td>SI</td>
<td>0.907</td>
<td>0.855</td>
<td>0.918</td>
<td>0.942</td>
<td>0.792</td>
<td>0.762</td>
</tr>
</tbody>
</table>

Most of the coefficient of correlation improved when a non-linear relationship was used:

ΔMehlich-P  $e^{-0.016-0.049\times \text{SI}}$  $r = 0.96 \ (P<0.001)$

ΔDissolved-P = $e^{-0.062-0.055\times \text{SI}}$  $r = 0.98 \ (P<0.001)$

ΔBioavailable-P = $e^{6.128-0.028\times \text{SI}}$  $r = 0.94 \ (P<0.001)$

ΔWater extr.-P = $e^{3.910-0.065\times \text{SI}}$  $r = 0.96 \ (P<0.001)$

ΔCaCl2 Desorb.-P = $e^{8.875-0.088\times \text{SI}}$  $r = 0.95 \ (P<0.001)$

ΔEquil.P Conc. = $e^{6.845-0.096\times \text{SI}}$  $r = 0.94 \ (P<0.001)$

In Figure 1 and Figure 2, the changes in Mehlich-available P, water-extractable P, readily-desorbable P, equilibrium-P concentration, DP, and BAP, were plotted as in function of the SI. From these figures, a threshold level for SI can be extrapolated above which the addition of P to soils caused negligible variations for all the P soil properties examined, such a value for SI was 25 to 30.
FIGURE 1. Changes in Mehlich Available P, Water Extractable P and Readily Desorbed CaCl$_2$-P Following P Application (100 mg/kg) to 32 Soils as a Function of Soil Sorption Index (SI).
FIGURE 2. Changes in Dissolved-P (DP), Bioavailable P (BAP) and Equilibrium P Concentration (EPC₀) Following P Application (100 mg/kg) to 32 Soils, as a Function of Soil Sorption Index (SI).
DISCUSSION

The main challenges facing the establishment of economically and environmentally sustainable agricultural P management are the development of soil test methods and establishment of P levels that can identify soils of environmental concern (Sharpley et al., 1994). In relation to this, information is needed to develop methods which can identify soils that currently do not have P levels high enough to unacceptably enrich runoff P, but have the potential to do so with further P amendments. Current soil test P methods alone, cannot assess the potential of soil P for a given site to play a significant role in nonpoint-source pollution. Thus, we have to expand their traditional role from agronomic to “environmental tests” by including measures of other pools of P that offer an environmental interpretation of the analytical results (Gartley and Sims, 1994).

In this study, the determination coefficient (R²) values relative to the curvilinear functions of Figures 1 and 2, indicate that soil P Sorption Index explained 92% of the variation in the changes of Mehlich-P and Water-P, 96% for ADP, 88% for ΔBAP and ΔEPCo, and 90% for ΔReadily desorbable-P for 32 Italian soils. In this way, SI appears to be a simple soil P parameter to characterize the potential of a given soil for available P increase and release to runoff as a result of P amendments. Several other studies have suggested a measurement of soil P-sorption capacity may improve the P fertility recommendation process in terms of plant availability and crop response (Fox and Kamprath, 1970; Kuo, 1991; Yli-Halla, 1991).

CONCLUSIONS

The ability of several soil chemical and physical properties (clay and free iron and aluminium oxides) and P sorption parameters (SBC, SPR, and SI) in predicting changes in soil P availability, water P extractability, CaCl2-desorbable P, Equilibrium-P concentration and two parameters related to runoff-Dissolved P, and Bioavailable P, was analyzed for 32 soils from Latium (Italy). These soils were selected on the basis of their widely ranging P retention characteristics.

The P Sorption Index (SI) gave the best indication of the potential for change in soil-available P and transport or retention of P in soil runoff following P additions. Such simple and rapid estimates of soil P sorption appear to be of value to incorporate into traditional soil test programs in order to identify soils presenting problems if further P is added, and thus, aid development of environmentally sound fertilizer and manure P management.
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