Using Phosphorus Concentration in the Soil Solution to Predict Phosphorus Desorption to Water

José Torrent* and Antonio Delgado

ABSTRACT

The growing concerns about water eutrophication have made it urgent to restrict losses of phosphorus (P) from agricultural soils and to develop methods for predicting such losses. In this work, we used the paradigm of P sorption-desorption curves to confirm the hypothesis that the amount of dissolved reactive phosphorus (DRP) released to a dilute electrolyte tends to be proportional to the concentration of DRP in the soil solution raised to a power that decreases with increasing solution to soil ratio (W). The hypothesis was tested for a group of 12 widely ranging European agricultural soils fertilized with P in excess of crop needs. Phosphorus desorption was studied under near-static and turbulent conditions in laboratory experiments. The concentration of DRP in the 1:1 soil to water extract (P1:1) was used as a proxy for the DRP concentration in the soil solution. The amount of desorbed P was found to be correlated with P1:1 raised to a power that decreased from 0.7 to 0.9 at W = 100 to 0.2 to 0.4 at W = 10,000. Correlation was not improved by introducing additional variables related to P sorption-desorption properties. Olsen P was found to be of lower predictive value than P1:1. Also, the index of degree of soil saturation with phosphorus (DSSP) based on oxalate extraction failed to predict P desorption. The fact that P1:1 seemingly predicts P desorption accurately for a wide range of soils makes it potentially useful in areas of high soil diversity.

The risk of eutrophication of streams, lakes, and reservoirs has made it urgent to restrict the transport of phosphorus (P) from soils in many agricultural areas to surface waters. Substantial P losses via surface runoff or subsurface flow can occur when soils rich in P are fertilized with inorganic P or animal manure (Sharpley and Withers, 1994). It is thus crucial to predict the partitioning of applied P into solution P and P bound to the solid phase. Partitioning of P is described in terms of P sorption isotherms, also known as quantity–intensity (Q/I) relationships or P sorption curves.

Generally, the equations of Langmuir and Freundlich have been used to describe the shape of the sorption curves. For a soil with a well-defined phosphorus sorption capacity (PSC), large increases in solution P concentration are expected in response to small additions of phosphate as the PSC is approached. It therefore seems pertinent for practical purposes to determine the degree of soil saturation with phosphorus (DSSP), which is defined as the ratio of the amount of P already sorbed to the PSC of the soil (van der Zee et al., 1988; Breeuwsma et al., 1989; Schoumans, 1995). Thus, the DSSP may help predict the potential of soil to release P to water (Sallade and Sims, 1997).

Under a specific set of conditions (e.g., the solution to soil ratio, reaction time, and temperature), any soil possesses a characteristic sorption curve. The maximum ordinate of this curve is the PSC of the soil and each point of the curve represents a value of the DSSP and the corresponding equilibrium solution P concentration. If the sorption–desorption of P were reversible and the P already sorbed and the PSC of the soil could be determined accurately, predicting P desorption or partitioning of P added to the soil would be an easy task. Lack of reversibility (Barrow, 1983) and difficulties in determining the PSC and the P already sorbed by the soil make it difficult in practice to find an index for the DSSP that is universally valid to predict P desorbability. One useful DSSP index is the \( \frac{P_{ox}}{q(Al_{ox} + Fe_{ox})} \) ratio, where the subscript ox stands for acid oxalate-extractable and \( q \) is usually 1 or 0.5. This index, first proposed and used by authors from the Netherlands (van der Zee and van Riemsdijk, 1988; Breeuwsma et al., 1995; van der Zee et al., 1990a,b), is based on the assumption that oxalate extracts P sorbed by the soil and that \( (Al_{ox} + Fe_{ox}) \) is a proxy for the PSC. This is in turn based on the fact that \( (Al_{ox} + Fe_{ox}) \) provides a measure for the most active P-sorbing soil components (poorly crystalline Fe and Al oxides, organically complexed Al and Fe, and edges of silicate clays). Generally, this index exhibits good correlation with P dissolved in runoff or drainage water (Pote et al., 1999) and also with P released to various types of solutions in laboratory experiments (Beauchemin and Simard, 1999). However, in soils where P occurs in non–Fe and Al compounds (e.g., Ca phosphate), this index may not be effective in predicting P loss to water.

Other methods of assessing P loss to water are based on standard soil test phosphorus (STP) or on the ratio of STP to PSC. A number of STP methods, including Mehlich-3, Olsen, iron oxide–coated paper, and water-extraction P (Pote et al., 1996, 1999; Hooda et al., 2000) have been used.

While procedures based on DSSP (Pote et al., 1999) or STP (Pote et al., 1999; Sharpley, 1995) have correlated to P loss and/or release to water, current research suggests that these procedures may not be applicable to most soils (Beauchemin and Simard, 1999; Uusitalo and Tuukkanen, 2000). Consequently, lack of a universally appli-

Abbreviations: DRP, dissolved reactive phosphorus; DSSP, degree of soil saturation with phosphorus; \( P_{1:1} \), concentration of dissolved reactive phosphorus in the 1:1 soil to water extract; PSC, phosphorus sorption capacity; STP, soil test phosphorus. Subscripts for Al, Fe, and P extracted by different solutions: d, citrate–bicarbonate–dithionite; ox, oxalate.

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The equation can be expressed as

\[ X = A c^b \]  

where \( X \) is the amount of sorbed P, \( c \) is the equilibrium solution P concentration, \( A \) is the amount of P sorbed at unit solution P concentration, and \( b \) is a constant typical of each soil and experimental condition. The value of \( A \) varies widely depending on the PSC for the soil and \( b \) usually ranges from 0.25 to 0.65 (Barrow, 1980). Figure 1 shows the shape of a Freundlich equation with \( b = 0.4 \). This figure also includes the corresponding P desorption curve. Such a curve is assumed to conform to the Freundlich equation, consistent with the work of Le Mare (1982), Barrow (1983), and Okajima et al. (1983).

When a mass of soil contacts a mass of runoff or percolating water initially free of, or containing little, dissolved P, desorption of P occurs. Under specific desorption conditions (time of contact, degree of turbulence of the suspension, temperature, etc.), the concentration of dissolved reactive phosphorus (DRP) in solution or runoff/drainage, \( c \), is given by

\[ W_c = Y(c_0) - Y(c) \]  

where \( W \) is the water to soil ratio, \( W_c \) is the amount of desorbed P, \( Y \) is the equation of the desorption curve, and \( c_0 \) is the initial concentration of DRP in the soil solution.

Many studies have shown that the Freundlich equation provides a simple description of P sorption curves over a wide concentration range (\( 10^{-15} \) to \( 10^{-3} \) M) in the soil solution (Barrow, 1980; Torrent, 1987; Singh and Gilkes, 1991). The equation can be expressed as

\[ W_c = k A_i (c_0^b - c^b) \]  

where \( W \) is the water to soil ratio, \( W_c \) is the amount of desorbed P, \( A_i \) is the amount of P previously sorbed at unit solution P concentration, and \( k_i \) is the fraction of sorbed P that is desorbed.

\[ W_c = k A_i (c_0^b - c^b) \]
Table 1. Selected soil properties.†

<table>
<thead>
<tr>
<th>Soil</th>
<th>Origin</th>
<th>Soil unit (FAO, 1994)</th>
<th>Clay %</th>
<th>Organic carbon</th>
<th>CaCO3 equivalent</th>
<th>pH (CaCl2)</th>
<th>Fe (g kg⁻¹)</th>
<th>Fe ox (g kg⁻¹)</th>
<th>Al ox (g kg⁻¹)</th>
<th>Inorganic P (mg kg⁻¹)</th>
<th>Organic P (mg kg⁻¹)</th>
<th>Clay fractions §</th>
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<tbody>
<tr>
<td>D1</td>
<td>Germany Haplic Chernozem</td>
<td>200 24</td>
<td>0 6.4</td>
<td>6.0</td>
<td>2.0</td>
<td>1.4</td>
<td>670</td>
<td>205</td>
<td>LS,K,Q</td>
<td></td>
<td></td>
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<tr>
<td>D2</td>
<td>Germany Dystric Gleysol</td>
<td>150 18</td>
<td>0 6.7</td>
<td>8.6</td>
<td>3.1</td>
<td>1.2</td>
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<td>220</td>
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<tr>
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<td>0 7.8</td>
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<td>0.7</td>
<td>0.5</td>
<td>1050</td>
<td>100</td>
<td>IS,F,K,C,Q</td>
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<td></td>
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<td>0.8</td>
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<td>E3</td>
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<td>15.8</td>
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<td>0 4.6</td>
<td>12.7</td>
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<td>0 5.2</td>
<td>14.8</td>
<td>5.6</td>
<td>4.2</td>
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<td>550</td>
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<tr>
<td>H1</td>
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<td>0 5.2</td>
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<td>1.2</td>
<td>405</td>
<td>405</td>
<td>10</td>
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<tr>
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<td>595</td>
<td>65</td>
<td>L,Ch,F</td>
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</table>

† Data from Delgado and Torrent (1997).
‡ Subscripts: d, citrate–bicarbonate–dithionite extractable; ox, oxalate extractable.
§ From the Langmuir equations taking the isotopically exchangeable P at 14 d to be the P already sorbed by the soil (Delgado, 1996).
¶ Data from Ruiz et al. (1997).

Table 2. Extractable forms of phosphorus.

<table>
<thead>
<tr>
<th>Isotopically exchangeable P</th>
<th>Mixed resin–extractable P</th>
<th>P uptake by plants</th>
<th>P buffering capacity</th>
<th>P sorption maximum</th>
<th>P ox</th>
<th>P / (Al ox + Fe ox)</th>
<th>DRP in the 1:1 soil to water extract</th>
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<tr>
<td>Soil</td>
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<td>200</td>
<td>299</td>
<td>621</td>
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<td>186</td>
<td>300</td>
<td>119</td>
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<td>308</td>
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<td>882</td>
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<td>600</td>
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<td>953</td>
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<td>185</td>
<td>182</td>
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<td>128</td>
<td>301</td>
<td>62</td>
<td>71</td>
<td>355</td>
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</tbody>
</table>

† Data from Delgado and Torrent (1997).
‡ Calculated as the slope of the Temkin equation fitted to the plant P desorption curves (Delgado and Torrent, 1997).
§ From the Langmuir equations taking the isotopically exchangeable P at 14 d to be the P already sorbed by the soil (Delgado, 1996).
¶ Data from Ruiz et al. (1997).

SOILS AND METHODS

The P desorption data for 12 soils from European agricultural areas having a long history of fertilization with P were examined. About 50 kg were collected by the end of the winter of 1995 from the Ap horizons of single soil pits, air-dried, sieved through a 2-mm screen, and stored at room temperature in air-tight plastic sacks, from which subsamples were taken for analysis. The properties of the soils and the methods used to characterize them were reported by Delgado (1996), Barberis et al. (1996), Ruiz et al. (1997) and Delgado and Torrent (1997, 1999, 2000). General soil data for the soils are given in Table 1, and data on P forms and P sorption–desorption properties in Table 2. In particular, two commonly used STPs were considered: the Olsen P (Olsen et al., 1954), which is a good index for the plant-available P, and the oxalate-extractable P (van der Zee and van Riemsdijk, 1988), which provides a measure of the P associated with P-reactive Al and Fe components in many soils.

Data from experiments where P was desorbed to 0.002 M CaCl₂ were used. The Ca concentration and ionic strength of this solution are within the ranges expected for the solution of agricultural soils (Helmke, 2000) and that observed for the saturation extract of the 12 soils studied (data not shown); on the other hand, this Ca concentration does not differ excessively from the average Ca concentration of continental ground and surface waters (Stumm and Morgan, 1970). De-
Sorption experiments were conducted at solution to soil ratios ranging from 10 to 10,000 under near-static and turbulent conditions. In the former, suspensions were allowed to stand for different times up to 340 days and shaken only before each sampling. In the latter, suspensions were stirred vigorously (20 rad s\(^{-1}\)) on a rotating rod–blade assembly for 2 hours. Samples of the suspensions were taken at different times, filtered through a 0.22-μm membrane, and analyzed for DRP in the filtrate. The concentration of DRP in the 1:1 soil to water extract (P\(_{1:1}\)) was determined in the supernatant obtained by centrifugation (acceleration, 1.1 \times 10^5 ms\(^{-2}\)) of the suspension previously shaken on a reciprocating shaker oscillating at 2.5 Hz at 298 K for 16 hours. The saturation extract was prepared according to Rhoades (1996). Dissolved reactive P was analyzed by the molybdenum-blue method (Murphy and Riley, 1962). All determinations were done in duplicate.

Regression analyses were performed with Costat (CoHort Software, Monterey, CA). The significance of the differences between the slopes of the regression lines was tested by analysis of variance, which was based on comparing the sum of separate regressions with the joint regression (Quenouille, 1966).

**RESULTS AND DISCUSSION**

**Properties of the Soils**

The soils studied ranged widely in physical and chemical properties (Tables 1 and 2). Evidence for application of fertilizer P in excess of crop requirements was provided by Olsen P values, which were all higher than the critical levels for most field crops (10–15 mg kg\(^{-1}\)) (Kamprath and Watson, 1980). The values of Olsen P, as well as those of mixed resin-extractable P and isotopically exchangeable P (IEP), were rather divergent, and so was plant P uptake in a pot experiment with eight successive crops. Differences in P contents and forms among soils were reflected in the P\(_{1:1}\), which ranged from 0.09 to 10.4 mg L\(^{-1}\). There was no significant (P > 0.05) correlation between P\(_{1:1}\) and the other P-related properties listed in Tables 1 and 2.

The P\(_{1:1}\) differed little from, and was highly correlated with, the DRP concentration in the saturation extract (P\(_{1:1}\) = 0.10 + 0.93 × DRP in the saturation extract; \(R^2 = 0.99\)). For this reason, and because the 1:1 extract is more readily prepared than the saturation extract, P\(_{1:1}\) can be used as a proxy for the DRP concentration in the saturation extract.

**Phosphorus Desorbed to 0.002 \text{M} \text{CaCl}_2**

The loss of P from agricultural soils in subsurface flow or surface runoff can occur under diverse conditions. Generally, one can assume the ratio between soil mass and water (dilute electrolyte) mass in contact with it, time of contact, and degree of mixing of soil and water to be the most important factors influencing soil P loss. It is assumed here that the effect of these factors (related to the different soil loss scenarios) can be elucidated from simple laboratory experiments. For instance, the loss of P in runoff can be somewhat mimicked by experiments involving mixing soil under turbulent conditions with a dilute electrolyte (e.g., 0.002 M \text{CaCl}_2) at W values of 50 to 2500, which approximately represent...
In order to develop an approach effective in all these situations, \( W \) from a few hours to a few days. Also, release of \( P \) from sediments on the bottom of a lake to a relatively still mass of water above it can probably be predicted using large \( W \) values (\( >1000 \)) and times of contact ranging from a few hours to a few days. Figure 5 shows similar plots obtained in experiments under turbulent conditions, using two different times (5 min and 2 h) and four \( W \) values (100, 800, 2500, and 10 000). Correlation between variables was always significant (\( P < 0.05 \)), with \( R^2 \) values ranging from 0.40 to 0.92 (Table 3). As in Fig. 4, the slope of the regression lines decreased with increasing \( W \), with an average value of \( \approx 0.65 \) at \( W = 100 \), \( \approx 0.50 \) at \( W = 800 \), \( \approx 0.48 \) at \( W = 2500 \), and \( \approx 0.23 \) at \( W = 10 \ 000 \). The slope and \( R^2 \) values increased significantly if the soil with the highest \( P_{1:1} \) (D3, 10.4 mg L\(^{-1} \)) was excluded (Table 3). This soil

Table 3. Values of \( R^2 \) for the regressions of the logarithm of the amount of desorbed \( P \) against the logarithm of different \( P \) saturation indices.

<table>
<thead>
<tr>
<th>Index</th>
<th>Time, ( W )</th>
<th>( P_{1:1} )</th>
<th>( P_{1:1} )</th>
<th>( P_{1:1} )</th>
<th>Olsen ( P )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Static systems</td>
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<td></td>
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<tr>
<td>1 d</td>
<td>30</td>
<td>0.96***</td>
<td>0.25NS</td>
<td>0.72**</td>
<td>0.65**</td>
</tr>
<tr>
<td>100</td>
<td>0.89***</td>
<td>0.16NS</td>
<td>0.60*</td>
<td>0.71***</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>0.89***</td>
<td>0.21NS</td>
<td>0.60*</td>
<td>0.72***</td>
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<tr>
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<td>0.14NS</td>
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<td>0.60**</td>
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</tr>
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<td>2 500</td>
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</tr>
<tr>
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</tr>
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<td>0.29NS</td>
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<tr>
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<tr>
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<td>0.83***</td>
<td>0.32NS</td>
<td>0.46*</td>
<td>0.45*</td>
</tr>
<tr>
<td>2 500</td>
<td>0.51**</td>
<td>0.71*</td>
<td>0.52*</td>
<td>0.40*</td>
<td></td>
</tr>
<tr>
<td>10 000</td>
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<td>0.53*</td>
<td>0.19NS</td>
<td>0.28NS</td>
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</tr>
<tr>
<td>2 h</td>
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<td>0.92***</td>
<td>0.95**</td>
<td>0.26NS</td>
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</tr>
<tr>
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<td>0.83**</td>
<td>0.90***</td>
<td>0.28NS</td>
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<tr>
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<td>0.72*</td>
<td>0.36*</td>
<td>0.50*</td>
<td>0.58**</td>
</tr>
</tbody>
</table>

*, **, *** Significant at the 0.05, 0.01, and 0.001 probability levels, respectively. NS = not significant.
† Solution to soil ratio.
‡ Excluding soil D3.
§ Excluding the three calcareous soils (E1, E2, and I3).
exhibited an anomalous behavior under turbulent conditions, with unexplained erratic changes in the concentration of DRP in solution. With D3 excluded, the slope was $-0.78$ at $W = 100$, $-0.64$ at $W = 800$, $-0.65$ at $W = 2500$, and $-0.52$ at $W = 10000$.

Our results are basically consistent with the relationship illustrated in Fig. 3, that is, the amount of desorbed P is a function of the concentration of DRP in the soil solution raised to a power that decreases with increasing $W$, from $-0.9$ at $W = 30$ to $-0.4$ at $W = 10000$. Because the soils studied were heterogeneous in P sorption-desorption properties, one should expect the amount of desorbed P to be dictated not only by the DRP in the soil solution (according to Fig. 3), but also by the desorption capacity of the soil, at least at high $W$ values (as suggested by Fig. 2). However, the variance in the amount of desorbed P accounted for did not increase significantly when various P sorption and desorption properties of the soil (e.g., the P sorption maximum or the P buffering capacity measured in experiments of P uptake by plants) were added to $P_{1:1}$ in the regression analysis. The fact that DRP concentration in the soil solution seems to influence the amount of P desorbed to a dilute electrolyte more than other P sorption and desorption-related soil properties is certainly intriguing. The fraction of sorbed P that is desorbable may decrease with increasing P sorption capacity of the soil because higher P sorption capacities may be related to higher proportions of soil components with a high affinity for phosphate.

Good correlation between water-soluble P (Sissingh, 1971) and P desorbed to water in successive extractions was found previously by Hooda et al. (2000) for a relatively heterogeneous soil group; these authors only used a narrow water to soil ratio, not very different from that of the water-soluble P method. By contrast, Pote et al. (1999) found the correlation between concentration of DRP in runoff and water-soluble P to differ among soil series. These results do not contradict our conclusions because these authors found that, for any given level of water-extractable P, soils that produced the least volume of runoff (i.e., with the lowest $W$ values) also had the lowest loads of DRP in the runoff. So, if a plot of the type shown in Fig. 4 were used, the points corresponding to the soils associated with low $W$ values would lie lower than those corresponding to the soils associated with high $W$ values, consistent with our hypotheses.

Correlation between the amount of desorbed P and the $P_{soil}/(Al_{ox} + Fe_{ox})$ ratio was significant ($P < 0.05$) in only 9 of the 26 desorption experiments illustrated in Fig. 4 and 5 (Table 3). This is probably the result of acid oxalate dissolving P forms that are unlikely to be released in significant amounts to a dilute electrolyte because of their low solubility or slow dissolution kinetics; such forms must include detrital apatite (Uusitalo and Tuhkanen, 2000) and much of the poorly soluble Ca or Ca-rich pedogenic phosphates in calcareous and limed acid soils (Delgado and Torrent, 2000). When the calcareous soils (E1, E2, and I3) were removed from the regression, the correlations between desorbed P and $P_{soil}/(Al_{ox} + Fe_{ox})$ became significant ($P < 0.05$) in all cases except for the experiment under turbulent conditions at $W = 10000$ at $t = 5$ min (Table 3). In summary, the $P_{soil}/(Al_{ox} + Fe_{ox})$ index seems useful for acidic soils where the P sorption-desorption properties are largely determined by the poorly crystalline Al and Fe compounds, as was the case with the soils studied by Hooda et al. (2000).

The amount of desorbed P was correlated to Olsen P in all but one of the desorption experiments illustrated in Fig. 4 and 5 (Table 3). Olsen P accounted for less variance in desorbed P than did $P_{1:1}$ in all cases but two. Thus, even though Olsen P is useful to predict plant P uptake over a wide range of soils, it is clearly inferior to $P_{1:1}$ in predicting P environmental risks.

**CONCLUSIONS**

This study provides evidence that the concentration of DRP in the 1:1 soil to water extract ($P_{1:1}$) is a useful index for predicting the potential release of P from soil to water in different P desorption scenarios and across a wide range of soils. The amount of P desorbed to a dilute electrolyte under different desorption conditions was correlated with $P_{1:1}$ raised to a power that decreases with increasing water to soil ratio. The predictive value $P_{1:1}$ was higher than that of Olsen P. A DSSP index based on oxalate extraction of P, Al, and Fe had no significant predictive value unless the calcareous soils were not considered. Even in this case, this index had a lower predictive value than $P_{1:1}$.

Future use of the proposed index, like that of STP- or DSSP-based indices, will require careful calibration for each desorption scenario. However, the proposed index seems relatively insensitive to soil type, which makes it potentially useful in areas with high soil diversity. One added advantage of this index is that its determination is quite simple and requires little laboratory time.

**ACKNOWLEDGMENTS**

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