

Relating Soil Phosphorus Indices to Potential Phosphorus Release to Water

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ABSTRACT

Relationships between soil test phosphorus (STP) and release of P in surface and subsurface runoff are needed to help identify source areas for implementing management strategies to limit P loss to water. To determine whether soil P release could be predicted either by STP values, sorption-desorption indices, or the degree of soil saturation with phosphorus (DSSP), 11 sites with contrasting chemical properties and management histories were sampled from long-term field trials in the UK. Each site offered up to three treatments, resulting in a total of 29 soil samples. The results showed that the amount of P desorbed using a successive dilution procedure had no relationship with either total soil P content or P sorption capacity. The most significant property was the extent of P saturation. There was little desorption for DSSP values below 10%; above this point, the amount of P desorbed increased linearly with the DSSP. Five STP methods (Olsen, Mehlich-3, acidified ammonium oxalate-oxalic acid, Fe₂O₃-coated paper strip, and distilled water) were compared to predict their effectiveness in predicting potential P release to water. While STP values obtained using acidified ammonium oxalate proved to be least effective, those extracted with water correlated best with the amount of P desorbed, accounting for 96% of the variability in differential P release from the soils.

PHOSPHORUS transport in agricultural runoff can accelerate eutrophication in surface waters (Sharpley

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Published in J. Environ. Qual. 29:1166-1171 (2000).

and Menzel, 1987). The loss of P from agricultural soils in surface runoff or subsurface drainage therefore can have potentially serious implications for water quality. The magnitude of P loss from soils is influenced by various factors, including land use (Nearing et al., 1993), soil type (Miller, 1979; Hooda et al., 1997), soil P (Heckrath et al., 1995; Pote et al., 1996; Hooda et al., 1999), amount and intensity of rainfall (Edwards and Daniel, 1993), and time and rate of fertilizer and manure application (Edwards and Daniel, 1993; Hooda et al., 1999). However, soil P is the underlying source of P in agricultural runoff, and increases in soil P status due to surplus P inputs therefore represent a long-term eutrophication hazard.

The potential loss of P from soils has been assessed using STP methods (e.g., Olsen, Mehlich-3, and acetic acid) that were originally designed to estimate plant available P (Miller et al., 1993). A certain degree of relationship has been demonstrated to exist between STP and the loss of P in runoff. These relationships generally have been tested for situations having similar soil type (Heckrath et al., 1995; Austin et al., 1996; Pote et al., 1996; Hooda et al., 1999). However, recent research suggested that an approach based upon STP might lead to ambiguous conclusions, particularly when different soils are compared, due to differences in the nature of P-adsorbing surfaces. For example, Sharpley (1995), assessing P loss from a group of 10 soils amended with poultry litter, showed that two soils of 200 mg kg⁻¹

Abbreviations: STP, soil test phosphorus; DSSP, degree of soil saturation with phosphorus; DRP, dissolved reactive phosphorus; PSI, phosphorus sorption index; PSM, phosphorus sorption maxima.

Table 1. Land use, range of P inputs, and classification of the soils from 11 long-term field trials.

Soil series	Land use and management details	Range of P inputs	Texture	U.S. Classification
		kg P ha ⁻¹ yr ⁻¹		
Stirling	Grassland; fertilized and/or cattle slurry applied	45–75	Silty clay loam	Typic Haplaquept
Dess	Grass–barley rotation; no fertilizer or fertilized	0–50	Sandy clay loam	Alfic Fragiortod
Insch	Grass–barley rotation; no fertilizer or fertilized	0–40	Sandy loam	Typic Cryochrept
Foudland	Grass–barley rotation; no fertilizer or fertilized	0–40	Sandy loam	Typic Fragiortod
Stonehaven	Grass–arable rotation; no fertilizer or fertilized	0–40	Sandy loam	Typic Cryochrept
Bromyard	Cereals; no fertilizer, fertilized, or cattle slurry applied	0–82	Silty clay loam	Typic Hapludalf
Cuckney	Cereals; fertilized, no fertilizer, or poultry litter applied	0–300	Loamy sand	Typic Udipsamment
Beccles	Cereals; fertilized or no fertilizer	0–44	Clay loam	Typic Albaqualf
Peebles-1	Grassland; no fertilizer or sewage sludge applied	0–130	Sandy loam	Typic Dystrochrept
Caprington	Grassland; no fertilizer or sewage sludge applied	0–130	Clay loam	Typic Haplaquept
Peebles-2	Grassland; sewage sludge applied	115–355	Sandy clay loam	Typic Humaquept

Mehlich-3 P supported a dissolved reactive phosphorus (DRP) concentration of 0.28 mg L⁻¹ and 1.36 mg L⁻¹. Hooda et al. (1997), monitoring P outputs in six agricultural catchments in Scotland, provided a more tangible evidence of soil extractable P being an ambiguous index of assessing P loss in agricultural runoff. The P losses in runoff from well-drained podzols were more than four times smaller than those from the poorly drained gleysols, despite the fact that the former group of soils had four times larger 0.43 M acetic acid extractable-P. Standard soil extractable-P tests might not be expected to provide a good estimation of the P loss in runoff, because these (agronomic) tests extract a large pool of P accessible to growing plants rather than the P fraction that might be potentially released to draining water. Knowledge of the ease with which P is desorbed from different soils and the factors that affect the process therefore might help better assess the soils that are potentially vulnerable to P loss to water. For example, the amount of P that can be easily desorbed is more likely to be dependent on the DSSP than the extractable-P content, as the soil-specific soil-phosphate binding strength will decrease with increasing P loading (Ryden and Syers, 1977; Hooda et al., 1999). A measure of the DSSP therefore might provide a better estimate of the potential for P loss to water than soil total- and extractable-P or P sorption capacity (Sharpley, 1995); however, this approach has not been fully examined.

This paper reports a study designed specifically to test the relationships between a range of soil test methods with potentially desorbable P using soils collected from long-term field trials receiving fertilizer, cattle slurry, or sewage sludge as the source of P inputs. The specific objectives of the work were to (i) examine the relationship between soil total P, sorption-desorption indices, DSSP, and the amount of P that can be potentially released to water and (ii) determine which of the commonly used soil tests best predict potential loss of P to water, particularly when compared across a range of soils.

MATERIALS AND METHODS

Land Use, Soil Characteristics, and Analyses

A range of soils with contrasting chemical properties and management histories under both grassland and arable farming systems were collected from 11 long-term field trials from various locations in the UK. The land use, ranges of P inputs, management histories, and classifications of the soils are listed in Table 1. Some of the grassland sites had received cattle

slurry or superphosphate or a combination of the two; others had received P inputs through sewage sludge applications. The arable sites had either superphosphate, cattle slurry, or poultry litter as the source of P. Each soil offered up to three treatments, resulting in a total of 29 soil samples. Representative surface samples (0–20 cm) of the 11 sites (Table 1) were collected, air-dried, gently ground, and passed through a 2-mm sieve prior to use in these studies.

Particle size distribution, pH, organic matter, and calcium carbonate equivalent were determined using standard procedures given in Rowell (1994). For total P, soils were first digested in 60% HClO₄ followed by a mixture of concentrated HNO₃ and HClO₄ before being diluted with distilled water and filtered through acid-resistant filter paper. Inorganic P in the soils was extracted with 0.5 M H₂SO₄, and organic P was assumed to be the difference between total and inorganic P (Olsen and Sommers, 1982).

Extractable P in the soil samples was determined using five different methods and extractants: Mehlich-3 (Mehlich, 1984), Olsen (Olsen et al., 1954), iron oxide-impregnated paper strips (Sharpley, 1993), acidified ammonium oxalate-oxalic acid (Evans and Wilson, 1985), and distilled water (Sissingh, 1971). The Olsen and Mehlich-3 methods are commonly used for soil fertility advisory purposes. The ammonium oxalate method is designed to remove the P associated with amorphous oxides of Fe and Al (the two principal components of P sorption in non-calcareous soils) while iron oxide-impregnated strips act as a sink and have been shown to correlate with algal biomass (Sharpley, 1993). This method therefore may provide a measure of the potentially bioavailable P in runoff from soils. The distilled water method is designed to extract easily desorbable P (Sissingh, 1971). The extraction procedure involved adding 2 mL distilled water to each soil sample weighing 1.2 g in 50-mL centrifuge tubes. Following a contact time of 20 h, a further 25 mL distilled water was added and the mixtures were shaken for 16 h before centrifugation at 27 000 g and filtration through Whatman no. 42 filter paper.

Phosphorus, iron, and aluminum concentrations in the ammonium oxalate extracts were determined using inductively coupled plasma atomic emission spectroscopy. Phosphorus concentrations in all other digests/extracts were determined using the colorimetric method of Murphy and Riley (1962). Where required, samples were neutralized prior to analysis. All results are the means of two individual digestions/extractions and are expressed on an oven dry (105°C) mass basis. The average values of selected soil properties are listed in Table 2. The DSSP was computed using the P, Fe, and Al contents (mmol kg⁻¹) extracted with the acidified ammonium oxalate-oxalic acid:

$$\text{DSSP (\%)} = \frac{[\text{P}] \times 100}{[\text{Fe} + \text{Al}]} \quad [1]$$

Breeuwsma and Silva (1992) calculated DSSP as a function of the ratio of [P]/0.5[Fe + Al]. They reported 0.5 mmol P as

Table 2. Selected physical and chemical characteristics of the studied soils.

Soil series	Clay	OM†	CCE‡	Fe _{ox} + Al _{ox} §	pH	Total P range
			g kg ⁻¹			mg P kg ⁻¹
Stirling	558	59.6	2.5	5.04	5.6	813–891
Dess	200	64.7	3.5	8.88	5.9	778–1042
Insch	370	67.2	2.0	13.25	5.2	944–1713
Fouldland	370	56.9	4.0	10.71	5.7	1685–2320
Stonehaven	400	50.0	2.5	8.90	5.5	938–1145
Bromyard	250	29.0	2.0	2.82	6.7	447–513
Cuckney	50	20.0	3.0	2.66	6.0	526–873
Beccles	270	22.0	1.5	6.93	6.3	464–642
Peebles-1	180	47.0	2.5	7.34	6.3	919–1094
Caprington	310	83.0	2.0	7.23	5.9	852–1088
Peebles-2	200	90.5	3.5	11.96	5.2	2042–3041

† OM, organic matter.

‡ CCE, CaCO₃ equivalent.§ Fe_{ox} and Al_{ox} = ammonium oxalate-extractable Fe and Al.

the maximum amount of P that can be sorbed per mmol of [Fe + Al]. However, this approach of calculating a sorption maximum as a function of 0.5[Fe + Al] is arbitrary, as P sorption maxima will increase with the time of equilibration and the initial concentration (W.J. Chardon, 1999, personal communication). Any such factor therefore should not be applied arbitrarily unless it has been pre-determined for individual situations (e.g., soil type, potential environmental impact).

Adsorption–Desorption Studies

Phosphorus sorption and desorption characteristics of the soils were studied using the equilibrium-based Freundlich and Langmuir models. Although these models are empirical in nature and cannot be used for delineating sorption or desorption mechanisms at soil surfaces (Sparks, 1995), they provide useful indices for comparing different soils. Phosphorus sorption characteristics of the soils were determined by shaking 3 g soil with 60 mL of 0.01M CaCl₂ containing varying concentrations of P (0 to 100 mg P L⁻¹) on an end-over-end shaker at 20 ± 2°C. After 24 h the soil suspensions were filtered through Whatman no. 42 filter paper and P concentrations in the filtrates were analyzed immediately. The sorption data were best fitted to the linearized Langmuir model (Sparks, 1995):

$$C/q = 1/kb + C/b \quad [2]$$

where C is the equilibrium concentration of P (mg L⁻¹) and q is the amount of P (mg kg⁻¹ oven-dried soil mass) sorbed. By plotting C/q against C , the slope is the value of $1/b$ and the intercept is equal to $1/kb$; k is a constant related to the binding strength and b is the maximum amount that can be sorbed, commonly known as phosphorus sorption maxima (PSM). A single-point P sorption index (PSI) is considered a suitable reference index to characterize the P-sorbing properties of soils. The PSI was determined using the procedure of Bache and Williams (1971). This involved shaking 1.5 g P kg⁻¹ soil for 40 h at a soil to solution ratio of 1:40 (w/w), all other conditions being similar to the sorption experiment. The initial P concentration of the solution was 37.5 mg P L⁻¹. The index was then calculated as the quotient of q (log C)⁻¹, where q and C are as previously defined.

The potential release of P to water was determined by a successive dilution method; this involved shaking a 3-g soil sample with 30 mL distilled water for 24 h at 20 ± 2°C. The soil–water mixtures were centrifuged and 15 mL of the solution was replaced by an equal volume of distilled water. In this way a total of seven desorption runs were carried out. The total amount of P desorbed is assumed to represent the potentially desorbable P that could be released in a series of

runoff events. Phosphorus desorption isotherms for individual soils were constructed by plotting the amounts of P desorbed against the equilibrium concentrations, which were best fitted to the linearized Freundlich equilibrium model (Sparks, 1995):

$$\log X_{s(or d)} = \log K + 1/n \log C \quad [3]$$

In a Freundlich sorption isotherm (by plotting the amount of P sorbed, log X_s , against the equilibrium, log C) the slope is the value of $1/n$ and the intercept is equal to log K . While the Freundlich distribution coefficient, log K , is indicative of the number of sorption sites, the slope ($1/n$) denotes the bonding energy. This implies that the energy of sorption decreases exponentially with increasing saturation of the surface (Eq. [3]). In a desorption phase, the reaction being backward, the slope (amount of P desorbed, log X_d , against the equilibrium concentration, log C) will signify the ease of desorption: the greater the slope the greater the ease with which P is desorbed.

The relationships of soil P, DSSP, sorption–desorption indices, and all the STP methods used with the potentially desorbable P were developed by linear regression analyses. The relationships were evaluated on the basis of statistical significance of the regression coefficients.

RESULTS AND DISCUSSION

Phosphorus Release vs. Soil Phosphorus and Sorption–Desorption Indices

The 11 soils with their contrasting chemical properties and management histories are representative of a relatively large area of agricultural land in the UK and provided a wide range of total soil P concentrations both within and between the soils (Table 2). The mean and range of PSM and PSI, together with those of STP values obtained using each of the five STP methods, are presented in Table 3, and cover a similar range to those reported for agricultural soils in the USA (Mozafari and Sims, 1994; Sharpley, 1995). The amounts of P desorbed from the soils were regressed against the soil P content, P sorption indices, and DSSP. The total P, organic P, and PSM (P sorption capacity) had no relation with the amount of P desorbed (Table 4). Although the inorganic P and PSI were significantly correlated to the amount of P desorbed, the relationships accounted for only 26 and 22%, respectively, of the variation in P desorption (Table 4). The correlation of desorbed P with soil inorganic P, however, may not necessarily imply that P desorption occurs largely from the inorganic pool, as

Table 3. Descriptive statistics for desorbed P and soil P extracted using five soil test phosphorus (STP) methods and the sorption indices.†

Variable	Range‡	Mean	SD
Desorbed P, mg kg ⁻¹ §	<1-55	9.8	13.3
Olsen P, mg kg ⁻¹	10-132	46.3	30.8
P _{ox} , mg P kg ⁻¹ ¶	25-2989	830.2	647.0
Fe strip P, mg kg ⁻¹	7-131	41.1	34.6
Water-soluble P, mg kg ⁻¹	<1-92	14.5	21.7
Mehlich-3 P, mg kg ⁻¹	10-567	149.3	163.2
P sorption maxima, mg kg ⁻¹ #	606-1400	938.9	224.9
P sorption index, L kg ⁻¹ #	208-654	369.9	112.9

† Data based on 29 soils from 11 locations.

‡ Values are rounded to the nearest whole number.

§ Total desorbed in seven desorption runs.

¶ P_{ox} = ammonium oxalate-extractable P.

P sorption maxima estimated from Langmuir equation, and P sorption index estimated from a single point sorption isotherm.

the molybdate blue method (Murphy and Riley, 1962) is not necessarily exclusive to inorganic P.

The P desorbed was best related ($P < 0.001$) to the degree to which the soils were saturated with P (DSSP), accounting for 94% of the variation in the amount of P desorbed. Breeuwsma and Silva (1992) suggested a relationship between the concentration of P in soil solution and the DSSP. This approach (Eq. [1]) seems logical particularly in non-calcareous soils where oxalate-extractable Fe and Al contents are the principal components of P retention. Sharpley (1995) observed that the P concentration in runoff from 10 soils freshly amended with poultry litter was better correlated to the DSSP than Mehlich-3 or Fe strip STP values. Pote et al. (1996) found a good correlation between the DSSP and DRP in runoff from grass plots on a Captina silt loam, but concluded that the correlation may not hold true for other soils. The results of our study provided a clear evidence of DSSP being the most significant soil property for predicting water desorbable P from contrasting soils (Table 4). There was little desorption for DSSP values below about 10%; above this point, the amount of P desorbed increased linearly with the DSSP (Fig. 1). Some recent work from the Broadbalk Experiment at Rothamsted showed little P leaching below 60 mg Olsen P kg⁻¹; above this, P leaching increased linearly with Olsen P (Heckrath et al., 1995). It appears that the 60 mg Olsen P kg⁻¹ point probably represented a critical DSSP value similar to our work (Fig. 1). We further investigated this relationship between the DSSP and P desorption by constructing P desorption isotherms of the data collected in seven desorption runs. Since in a sorption phase the slope ($1/n$, Eq. [3]) of the Freundlich

Table 4. Results of soil P contents and sorption indices correlated to the amount of P desorbed ($n = 29$).

Variable	Intercept	Slope	r ²	P value
Soil total P	2.86	0.006	0.091	NS
Soil total organic P	10.38	0.001	0.0005	NS
Soil total inorganic P	0.19	0.018	0.267	<0.01
P sorption maxima†	6.52	0.003	0.003	NS
P sorption index†	30.50	-0.056	0.225	<0.01
DSSP‡	-12.41	1.458	0.942	<0.001

† As in Table 3.

‡ Degree of soil saturation with phosphorus. NS, nonsignificant ($P > 0.05$).

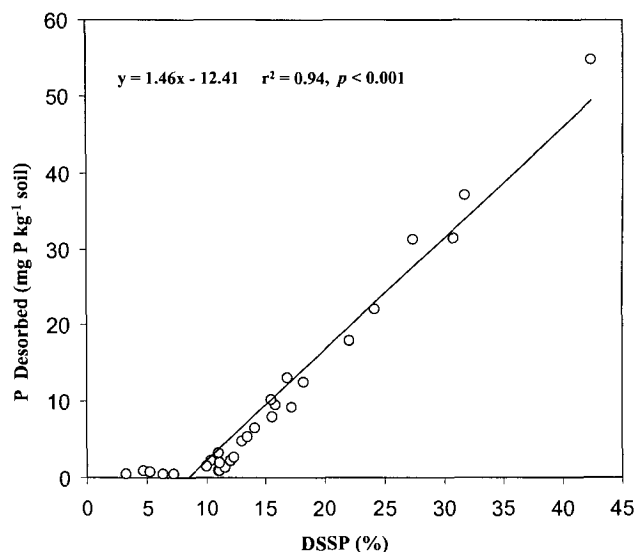


Fig. 1. Relationship between the degree of soil saturation with phosphorus (DSSP) and the amount of P desorbed.

model denotes the bonding energy that decreases with increasing sorption, the slope in a P desorption phase therefore would be a measure of the “ease” with which P is desorbed (Eq. [3]). The results clearly showed that the ease with P desorbed increased with the DSSP (Fig. 2). These results are consistent with the relationship between the amount of P desorbed and the DSSP (Fig. 1), showing some uncertainty in the relationship until DSSP reaches about 10%, that is, no definite change in desorption. The relationship between DSSP and the slope of the P desorption isotherm (Fig. 2) confirms earlier findings that showed that soil-phosphate binding strength decreases as P loading (DSSP) increases due presumably to a corresponding decrease in high energy binding sites (Ryden and Syers, 1977; Hooda et al., 1999), with a consequent ease in desorption. The 10% DSSP point (Fig. 1 and 2) reflects a marked change in

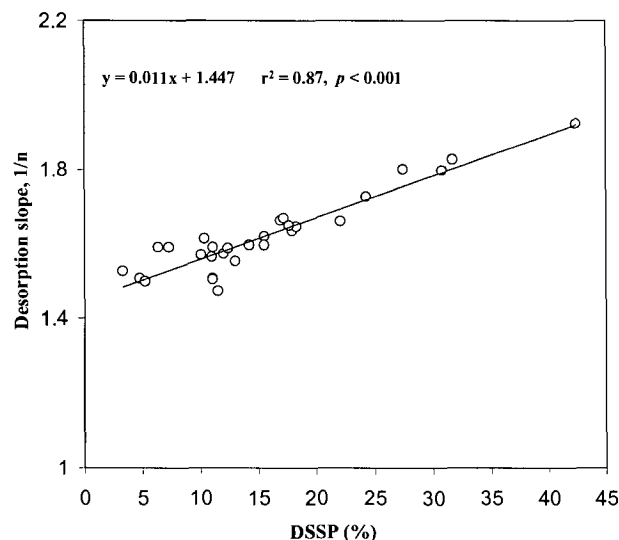


Fig. 2. Relationship between the degree of soil saturation with phosphorus (DSSP) and slope of the desorption phase Freundlich model.

Table 5. Results of soil P (mg kg⁻¹ soil) extracted using five soil test phosphorus (STP) methods correlated to the amount of P desorbed (mg kg⁻¹).†

STP method	Intercept	Slope	r ²	P value
Olsen	-7.085	0.365	0.72	<0.001
Mehlich-3	-1.095	0.073	0.81	<0.001
NH ₄ -oxalate	2.302	0.009	0.19	<0.05
Fe ₂ O ₃ coated paper	-4.378	0.346	0.81	<0.001
Distilled water	1.142	0.599	0.96	<0.001

† Number of soils = 29.

soil-phosphate binding strength, presumably related to the saturation of all or a certain proportion of high energy binding sites on soil surfaces. It would therefore appear that little P desorption is expected before about 10% saturation of the P sorption capacity is attained. In soils with calcium phosphates being the dominant forms of P, the ammonium oxalate-based DSSP approach may not provide a good estimation of the potential P release from such soils (e.g., calcareous soils). However, using an appropriate P extractant such as dilute acid-fluoride (HCl-NH₄F) or sodium bicarbonate (Olsen and Sommers, 1982), and an estimation of P sorption capacity, for example, by PSM, a similar DSSP approach for calcareous soils could also be developed.

The P desorption experiment in this study may not precisely reflect what may be expected to occur in the field, as other factors such as runoff P retention in the subsoil or other surface runoff pathways and amount of rainfall are also likely to influence runoff P concentration. However, a good correlation of runoff P with DSSP found in recent studies (e.g., Sharpley, 1995; Pote et al., 1996) suggests that our work (Fig. 1 and Fig. 2) does have relevance to field conditions.

Soil Phosphorus Release vs. Soil Test Phosphorus

The amounts of P desorbed from the soils were regressed against STP values obtained using each of the five STP methods; the results of regression analyses are summarized in Table 5. Although the STP values extracted using acidified ammonium oxalate-oxalic acid were significantly ($P < 0.05$) related to the desorbed P, the extraction method accounted for only about 20% of the variability in the amount of P desorbed. With such a large uncertainty, the oxalate method is unlikely to provide a reliable estimate of P that can potentially be released to water, particularly when comparing contrasting soils. The ammonium oxalate reagent is designed primarily to release P associated with Fe and Al, the two principal P-sorbing compounds in non-calcareous soils. Averaged across all soils, the ammonium oxalate-extracted P content amounted to a large proportion (76%) of the total soil P. Phosphorus content extracted with the ammonium oxalate reagent therefore provides an index of total P in non-calcareous soils, not an estimate of potentially desorbable P. In a study of 54 grass plots on Captina silt loam, ammonium oxalate-extractable STP values were highly related ($r^2 = 0.84$) to runoff DRP (Pote et al., 1996). However, for the purpose of comparing different P levels within a given soil where DSSP increases with increasing P inputs, even total P

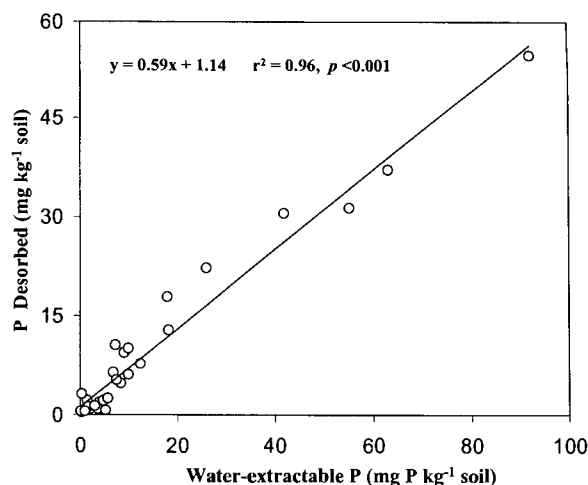


Fig. 3. Relationship between water-extractable soil test phosphorus (STP) and the amount of P desorbed.

content correlates to runoff P outputs and concentrations (Hooda et al., 1999). The Olsen and Mehlich-3 P contents, on average, were 4.2 and 13.6%, respectively, of the total soil P and were significantly correlated to the amount of P desorbed; Mehlich-3, however, proved a better method for assessing potential P loss from the soils than Olsen P, as indicated by greater r^2 value for the former STP procedure (Table 5). Pote et al. (1996), however, observed identical correlations ($r^2 = 0.72$) between P contents obtained using the two STP methods and DRP in runoff from a Captina silt loam. The STP values obtained by the Fe strip method accounted for 3.7% of the total P content, and were significantly ($P < 0.001$; $r^2 = 0.81$) related to the desorbed P. The Mehlich-3 and Fe strip STP values had identical correlations with the amount of P that can be desorbed from the soils (Table 5), which is consistent with other recent work (Sharpley, 1995).

The P contents extracted with distilled water represented only 1.3% of the total soil P, and provided a better estimation of the desorbed P than the other four procedures tested (Table 5). The distilled water extracted STP values accounted for 96% of the variability in P desorption (Fig. 3). As water is the solvent and transport medium for P loss from soils, it was not unexpected that estimates of water-soluble P proved to be best related to the amount of P desorbed from the soils.

CONCLUSIONS

The results of this study clearly showed that the amount of P that can be potentially released to water had no or a poor relationship with either soil P content or P sorption capacity (i.e., capacity factors). The most important property was the extent to which the soils were saturated with P. Relationships between loss of P in surface runoff or subsurface leaching through field drains and soil extractable-P often become inadequate when different soils are compared (Hooda et al., 1997). This is because such relationships do not integrate differential P release that is dependent on soil characteristics (e.g., P sorption capacity). The DSSP approach, on

the other hand, describes soil P content in relation to P sorption capacity, bringing together both P management- and soil type-associated factors, that is, independent of soil type. This approach has potential to identify soils that are likely to become diffuse source of P and thus will help in better targeting of management strategies to minimize the risk of P loss to water. Our work also demonstrates that the potential release of P in runoff from a range of soils is better estimated by extracting soils with water than other standard soil tests. However, further research is needed to test the relationship between desorbable P and P transfer in leaching and runoff.

ACKNOWLEDGMENTS

Thanks to Dr. Ivo Svoboda of SAC, Ayr for making one of the grassland soils available; to Dr. Mark Shepherd and Damien Hatley of ADAS, UK for providing information on two of the arable sites; and to Dr. Hamish Anderson of MLURI, Aberdeen for his help in soil classification. The Macaulay Land Use Research Institute receives funding from the Scottish Executive, Rural Affairs Department.

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