

Relationship between Phosphorus Levels in Three Ultisols and Phosphorus Concentrations in Runoff

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ABSTRACT

Soils that contain high P levels can become a primary source of dissolved reactive P (DRP) in runoff, and thus contribute to accelerated eutrophication of surface waters. In a previous study on Captina soil, several soil test P (STP) methods gave results that were significantly correlated to DRP levels in runoff, but distilled H₂O and NH₄-oxalate methods gave the best correlations. Because results might differ on other soils, runoff studies were conducted on three additional Ultisols to identify the most consistent STP method for predicting runoff DRP levels, and determine effects of site hydrology on correlations between STP and runoff DRP concentrations. Surface soil (0–2 cm depth) of pasture plots was analyzed by Mehlich III, Olsen, Morgan, Bray-Kurtz P1, NH₄-oxalate, and distilled H₂O methods. Also, P saturation of each soil was determined by three different methods. Simulated rain (75 mm h⁻¹) produced 30 min of runoff from each plot. All correlations of STP to runoff DRP were significant ($P < 0.01$) regardless of soil series or STP method, with most STP methods giving high correlations ($r > 0.90$) on all three soils. For a given level of H₂O-extractable STP, low runoff volumes coincided with low DRP concentrations. Therefore, when each DRP concentration was divided by volume of plot runoff, correlations to H₂O-extractable STP had the same ($P < 0.05$) regression line for every soil. This suggests the importance of site hydrology in determining P loss in runoff, and may provide a means of developing a single relationship for a range of soil series.

EUTROPHICATION of streams and lakes can be greatly accelerated by the influx of nutrients in surface runoff from agricultural land. Since P has been identified as the nutrient in runoff that is usually the most limiting to algal growth, control of P levels in runoff is often recommended as the best way to minimize the eutrophication of surface waters (Rohlich and O'Connor, 1980; Little, 1988; Breeuwsma and Silva, 1992; Sharpley et al., 1994). Phosphorus is often perceived to be so immobile in soil that losses from agricultural land are not usually considered to be agronomically important, but even small agronomic losses can have serious environmental consequences. In fact, soils that contain high levels of P from excessive fertilization can become a primary source of dissolved reactive P (DRP) in runoff (Edwards et al., 1993).

Other investigators have found direct correlations between soil P levels and P concentrations in runoff.

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Schreiber (1988) sampled soil and runoff from monocropped corn (*Zea mays* L.) or cotton (*Gossypium hirsutum* L.) research plots and watersheds in Mississippi, with various cropping practices for corn including conventional tillage, no-till, crop residue removed for silage, and crop residue left on the soil surface. Results showed that water-extractable soil test P (STP) was significantly correlated to annual discharge-weighted DRP in runoff. Yli-Halla et al. (1995) analyzed soil and runoff from eight cultivated field plots in southwestern Finland and concluded that mean DRP concentration in runoff depended on the water-extractable P level in surface soil. However, both of these studies relied on uncontrolled natural rainfall events to produce runoff, and combined a variety of cultivated crops and management practices, while neither study included uncultivated grassland.

In a previous study (Pote et al., 1996), we controlled the variability of field conditions as much as possible by using consistent dimensions, slope, soil, and grass cover for all plots, and using simulated rainfall to produce runoff. The study compared results from several soil test P (STP) extraction methods to determine which were most useful for predicting DRP levels in runoff from fescue (*Festuca arundinacea* Schreb.) plots on a Captina silt loam (fine-silty, siliceous, mesic Typic Fragiudult). Extraction of P in soil samples from the surface soil (0–2 cm depth) showed that the Mehlich III (Mehlich, 1984), Bray-Kurtz P1 (Bray and Kurtz, 1945), and Olsen (Olsen et al., 1954) extraction methods gave soil P levels with very significant correlations to DRP concentrations in surface runoff. The soil P-saturation method (Pote et al., 1996) also gave results that correlated very well to runoff DRP, but Fe-oxide strips (Sharpley, 1993), distilled water, and acidified ammonium oxalate (Pote et al., 1996) were the STP extractants that gave the best correlations to DRP in runoff. Since this study was only conducted on a single soil, we hypothesized that the results might be different for other soils of differing physical and chemical properties, even within the same soil order.

As several states are attempting to define threshold STP levels above which DRP enrichment of runoff is unacceptable from a water-quality perspective, more information relating soil P to runoff P is needed (Sharpley et al., 1996). Such field data are essential to development of technically-sound STP levels that can be used to guide P management recommendations. Therefore, runoff studies were conducted on three additional Ultisols. The objectives were to determine (i) which STP method maintains the highest correlation to

Abbreviations: CV, coefficient of variation; DRP, dissolved reactive P; ICP, inductively coupled plasma spectrometer; M3, Mehlich III extraction method for soil P; PSI, P sorption index; SD, standard deviation; STP, soil test P.

Table 1. Soil characteristics (mean) and results of various soil test P (STP) methods from plots on three soils.

	Nella soil			Linker soil			Noark soil		
Clay content	10.5%			14.9%			7.4%		
Organic C content	3.8%			3.6%			4.6%		
pH	5.9			5.2			6.2		
Oxalate-Fe, mg kg ⁻¹	1909			1003			1043		
Oxalate-Al, mg kg ⁻¹	1504			1170			1643		
	Nella soil			Linker soil			Noark soil		
	Range	Mean	SD [†]	Range	Mean	SD	Range	Mean	SD
STP method	STP, mg kg ⁻¹								
Mehlich III	200-422	294	73	122-366	226	88	17-263	109	82
Olsen	79-166	115	28	61-162	104	31	7-103	44	30
Morgan	23-65	44	15	30-108	57	27	0-101	35	34
Bray-Kurtz P1	161-342	240	62	121-328	207	76	14-156	70	47
NH ₄ -oxalate	691-1127	900	129	315-707	492	144	210-613	406	140
Distilled H ₂ O	37-109	74	25	18-107	50	30	6-80	36	24

[†] Standard deviation.

DRP concentrations in runoff from a variety of soil series within the Ultisol order, (ii) whether STP levels affect DRP concentrations in runoff consistently across soil series and if not, (iii) what effect soil hydrology has on the relationship between STP and runoff DRP.

MATERIALS AND METHODS

Field Plots

Six field plots were constructed during the fall of 1993 on each of three soils in northwest Arkansas: Nella (fine-loamy, siliceous, thermic Typic Paleudult), Linker (fine-loamy, siliceous, thermic Typic Hapludult), and Noark (clayey-skeletal, mixed, mesic Typic Paleudult) (Table 1). All plots were constructed on well-established tall fescue pastures with approximately 7% slope and 100% ground cover as measured by the line-transect method (Lafren et al., 1981). These pastures had previously been amended with various combinations of swine manure slurry, commercial fertilizers, and/or manure from grazing cattle. Some plots had received swine manure the previous year, but no amendments were allowed on the plots for several months preceding this study. Vegetation height was maintained between 0.1 and 0.2 m throughout the study by mowing. Each plot (1.5 × 3 m) was fitted with aluminum borders (extending 5 cm above and 10 cm below the surface) for runoff isolation, a downslope trough for runoff collection, and a runoff sampling pit, as described by Edwards and Daniel (1993). Fences were constructed around the plots to prevent cattle from contributing P inputs or causing other damage during the study.

In May 1995, a simulator described by Edwards et al. (1992) was used to reduce antecedent moisture variability by applying rainfall (75 mm h⁻¹) to each plot until the surface layer was saturated. This simulator delivers rainfall at an exit pressure of 41.4 kPa from four VeeJet nozzles¹ elevated 3.05 m above the soil surface by an aluminum scaffold to obtain drop-size distribution and terminal velocity comparable to that of natural rainfall. Tarpaulins attached to the aluminum scaffold surround the plot to form wind screens. An electric motor drives the shaft to which the nozzles are attached, causing them to oscillate across openings in the simulator body, with the rainfall intensity dependent upon the frequency of oscillation.

¹ Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

Following the initial rainfall application, all plots were allowed to drain for 48 h before simulated rain was applied again at an intensity of 75 mm h⁻¹ to generate 30 min of runoff from each plot.

Sampling Methods

Runoff was sampled manually at 5-min intervals throughout the runoff event, beginning 2.5 min after initiation of continuous-flow runoff. For each discrete runoff sample, the volume and time required to collect it were recorded and used to calculate mean flow rate and total volume of runoff for the 5-min interval. Using these runoff data, the six discrete runoff samples from each plot were used to construct a flow-weighted composite sample to represent the total runoff from that plot. An aliquot of each composite runoff sample was filtered (0.45- μ m pore diameter) within 2 h of collection and stored in the dark at 4°C until analyzed for DRP by the molybdenum-blue method (Murphy and Riley, 1962). Total DRP mass loss from each plot was calculated as the plot's total runoff volume multiplied by DRP concentration in the flow-weighted composite runoff sample from that plot.

Just prior to applying simulated rainfall to a given plot, a representative composite soil sample was collected by combining 10 discrete soil cores (2.54 cm diam.) taken randomly from the surface layer (0-2 cm depth) of the plot. All composite soil samples were stored in the dark at 4°C until air dried and sieved (2 mm) to remove larger rock particles and most of the plant material.

Two complete runoff events were conducted on each plot, separated by a 2-d interval. For each separate runoff event, soil samples were collected just prior to simulated rainfall application.

Soil Analyses

Each soil sample was analyzed for extractable P by six methods: Morgan (Morgan, 1941), Mehlich III (Mehlich, 1984), Bray-Kurtz P1 (Bray and Kurtz, 1945), Olsen (Olsen et al., 1954), distilled water, and acidified ammonium oxalate. The Morgan, Mehlich III, Bray-Kurtz P1, and Olsen chemical extractants were selected because they are commonly used for STP analysis in soil testing laboratories. These methods were not originally developed to predict runoff water quality, but rather to assess the fertility status of soil for crop production. Distilled water most closely simulates actual runoff solution, and may thus be the most appropriate for predicting runoff DRP. One gram of soil was mixed with 25 mL of

distilled water, shaken end-over-end for 1 h, centrifuged for 5 min at 266 m s^{-1} ($27\,100 \text{ g}$), filtered ($0.45 \mu\text{m}$), and the supernatant analyzed for P by the molybdenum-blue method (Murphy and Riley, 1962). Acidified ammonium oxalate has been used in several previous studies (van der Zee et al., 1987; van der Zee and van Riemsdijk, 1988; Molina et al., 1991; Breeuwsma and Silva, 1992; Freese et al., 1992), theoretically to release into solution potentially desorbable P, as it dissolves the compounds (noncrystalline oxides of iron and aluminum) controlling P sorption in acid soils (Table 1). In our study, ammonium oxalate extractant was made by mixing 0.2 M oxalic acid with 0.2 M ammonium oxalate (approximately 535 mL of oxalic acid with 700 mL of ammonium oxalate) until the combined-solution pH was 3.0. A 20-mL aliquot of the ammonium oxalate solution was then mixed with 0.5 g of soil, shaken in the dark for 2 h, centrifuged for 20 min at 131 m s^{-1} ($14\,481 \text{ g}$), and decanted for P analysis. Oxalate-extractable P, Al, and Fe were also used to calculate the P sorption-saturation of each soil as described below. Mehlich III, Bray-Kurtz P1, and acidified ammonium oxalate extracts were analyzed for P by inductively coupled plasma spectrometer (ICP), while Morgan, Olsen, and distilled water extracts were analyzed colorimetrically by the molybdenum-blue method (Murphy and Riley, 1962).

A single-point P sorption index (PSI) described by Mozaffari and Sims (1994) was also determined on each soil. A P sorption solution (containing 300 mg P per liter) was made by dissolving 1.318 g of KH_2PO_4 in enough distilled, deionized H_2O to make 1 L of solution. The PSI was determined by weighing 1.00 g of soil into a 50-mL centrifuge tube, adding 20 mL of $0.0125 \text{ M CaCl}_2 \cdot 2\text{H}_2\text{O}$, and adding 5 mL of P sorption solution to make a combined solution containing 0.01 M CaCl_2 and 60 mg P per liter. After two drops of toluene were added and the tubes sealed, the mixture was shaken for 18 h on a reciprocating shaker, centrifuged for 10 min at 266 m s^{-1} ($27\,100 \text{ g}$), filtered ($0.45\text{-}\mu\text{m}$), and analyzed for P by inductively coupled plasma spectrometer (ICP). The PSI was calculated as $X (\log P_f)^{-1}$ where

X is P sorbed (mg kg^{-1}) = $[(P_i)(V) - (P_f)(V)] (\text{kg of soil})^{-1}$

P_i is initial P concentration in sorption solution (mg L^{-1})

V is volume of P sorption solution (L)

P_f is final P concentration in solution (mg L^{-1})

Phosphorus Saturation of Soil

The P saturation (%) of each soil sample was calculated by two different methods; (i) oxalate-extractable P (mmol kg^{-1}) divided by the oxalate-extractable Al and Fe (mmol kg^{-1}) content, and multiplied by 100, and (ii) initial STP content (mg kg^{-1}) divided by P_{MAX} (mg kg^{-1}), and multiplied by 100. For this second method, the PSI value was used to approximate the maximum amount of P (P_{MAX}) that could be adsorbed by the soil. Mozaffari and Sims (1994) found that P_{MAX} can be estimated by the equation $P_{\text{MAX}} = (\text{PSI} + 51.9)/0.5$, given that $P_{\text{MAX}} < 1400 \text{ mg kg}^{-1}$. STP extractants selected to obtain the initial STP content were Mehlich III (M3-PSI method) and distilled H_2O (H_2O -PSI method).

Statistical Methods

For each soil, comparisons were made between STP methods by correlating STP results to DRP concentrations in runoff from the plots, developing a linear regression from the 12 data points, and calculating the sample correlation coefficient (r value) for each. For each soil test method, analysis of covariance was used to determine whether there were statistical

differences between regression slopes and intercepts of the three soils.

RESULTS AND DISCUSSION

Soil Phosphorus

For each of these soils, the range, mean, and standard deviation of STP contents are shown in Table 1. Distilled water, Morgan, and Olsen methods extracted the least amounts of P from soil, while Mehlich III and Bray-Kurtz P1 methods extracted larger amounts. NH_4 -oxalate extracted much larger amounts of soil P than did other extractants, suggesting that most of the P in these soils is sorbed or precipitated on amorphous oxides of Fe and Al.

Relationship between STP and Runoff DRP

For each soil, correlations of STP to runoff DRP were not significantly affected by the time interval (2 d) between the two runoff events. Therefore, the data from both runoff events were combined to give a total of 12 data points for each soil. The correlation coefficient (r) and linear regression equation are given in Table 2 for each STP correlation to DRP in runoff. For all soils, the STP values obtained by each method were significantly correlated ($P < 0.01$) to DRP concentrations in plot runoff. Yet, when the extraction methods were compared using r values to see how closely the data points fit the regression line, it was apparent that some STP methods were more closely related to DRP concentrations in runoff than other methods (Table 2). For example, the NH_4 -oxalate and Olsen methods each gave a weaker correlation ($r < 0.90$) to DRP concentrations in runoff from at least one soil, while all other STP methods gave correlations with $r > 0.90$ for all three soils (Table 2). However, if previous studies (Pote et al., 1996) are considered, the H_2O -extractable soil P has shown the most consistently high correlation to DRP concentrations in runoff, even when rainfall intensity, slope, and seasonal conditions varied.

Although the usefulness of an STP method for predicting runoff DRP concentrations depends largely on its ability to produce data points that closely fit a regression line on any given soil, it would also be very helpful to have an STP method that produces approximately the same regression for all soils (or at least a large group of soils). Such a method would eliminate the need to use soil series as the basis for maximum soil P recommendations, thus saving the time and expense of accurately identifying the soil series of each individual site. If the data points from all three soils are combined into a single data set, the P-saturation (oxalate method) might seem to be a good choice for this purpose because it gives a good linear correlation ($r = 0.887$), and the fit is even better for a second-order regression ($r = 0.931$ for the curve where $y = 0.3083 - 0.0353x + 0.0014x^2$). However, if the data points are separated into regression lines for each soil, differences between some slopes become apparent (Fig. 1). When the regression-line graphs of each method were compared visually, the P-satura-

Table 2. Results of soil test P (STP) methods correlated to dissolved reactive P (DRP) in runoff from three Ultisols.

STP method	Correlation coefficient (<i>r</i>) for STP (mg kg ⁻¹) correlated to DRP (mg L ⁻¹)†		
	Nella soil	Linker soil	Noark soil
Mehlich III	0.908	0.916	0.932
Olsen	0.869	0.864	0.935
Morgan	0.907	0.941	0.932
Bray-Kurtz P1	0.913	0.950	0.943
NH ₄ -Oxalate	0.806	0.914	0.908
Distilled H ₂ O	0.923	0.928	0.968
P saturation (oxalate method)	0.903	0.928	0.933
P saturation (M3-PSI method)	0.916	0.928	0.937
P saturation (H ₂ O-PSI method)	0.932	0.921	0.978

STP method	Regression line equation for STP (mg kg ⁻¹) correlated to DRP (mg L ⁻¹)		
	Nella soil	Linker soil	Noark soil
Mehlich III	$y = 0.0036x - 0.45$	$y = 0.0035x - 0.38$	$y = 0.0016x + 0.00$
Olsen	$y = 0.0088x - 0.43$	$y = 0.0093x - 0.56$	$y = 0.0043x - 0.02$
Morgan	$y = 0.0181x - 0.18$	$y = 0.0115x - 0.25$	$y = 0.0038x + 0.04$
Bray-Kurtz P1	$y = 0.0043x - 0.42$	$y = 0.0042x - 0.46$	$y = 0.0027x - 0.02$
NH ₄ -Oxalate	$y = 0.0018x - 1.03$	$y = 0.0021x - 0.63$	$y = 0.0009x - 0.19$
Distilled H ₂ O	$y = 0.0107x - 0.18$	$y = 0.0104x - 0.11$	$y = 0.0055x - 0.03$
P saturation (oxalate method)	$y = 0.0820x - 2.03$	$y = 0.0397x - 0.62$	$y = 0.0251x - 0.24$
P saturation (M3-PSI method)	$y = 0.0080x - 0.08$	$y = 0.0065x - 0.04$	$y = 0.0045x + 0.03$
P saturation (H ₂ O-PSI method)	$y = 0.0262x + 0.03$	$y = 0.0215x + 0.06$	$y = 0.0159x + 0.01$

† All correlation coefficients were significant ($\alpha = 0.01$).

tion (PSI methods), Mehlich III, Bray-Kurtz P1 (Fig. 2), and distilled H₂O (Fig. 3) methods each appeared to have regression lines that were relatively close together with similar slopes for all soils, but statistical analysis showed that none of the methods for correlating STP to DRP in runoff gave the same ($P < 0.05$) regression line for all three soils. This result was not surprising, given the differences in chemical and physical properties between soils.

The P saturation status of each soil in this study was significantly ($P < 0.01$) related to DRP concentrations in runoff, regardless of the method used to calculate P saturation. All three methods gave high correlations to DRP in runoff but none gave the same regression line on all three soils, so their value as universal predictors of DRP concentrations in runoff is questionable.

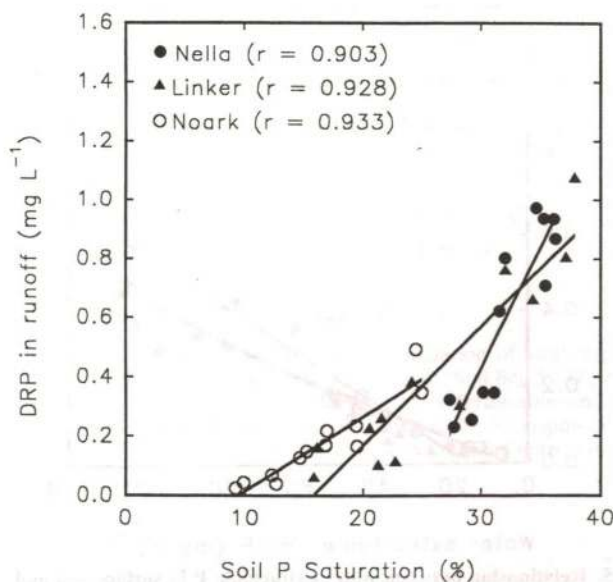


Fig. 1. Relationship between P saturation (oxalate method) of surface soil and dissolved reactive P (DRP) in runoff from three soils.

Effects of Runoff Volume

Because site hydrology of each soil is likely to impact the relationship between soil P and runoff P (Gburek and Sharpley, 1998), the effect of runoff volume on P transport from our plots was evaluated. The average rainfall application required to produce 30 min of continuous runoff is included in Table 3, along with mean runoff volume for each soil. Runoff from the Nella and Linker soils averaged about the same volume and the variability was also similar, while the Noark soil had the lowest amount of runoff and the least variability.

The differences in runoff among soils are reflected in the correlations of water-extractable STP to runoff DRP. For example, when water-extractable STP was correlated to mass losses (loads) of DRP in runoff (Fig.

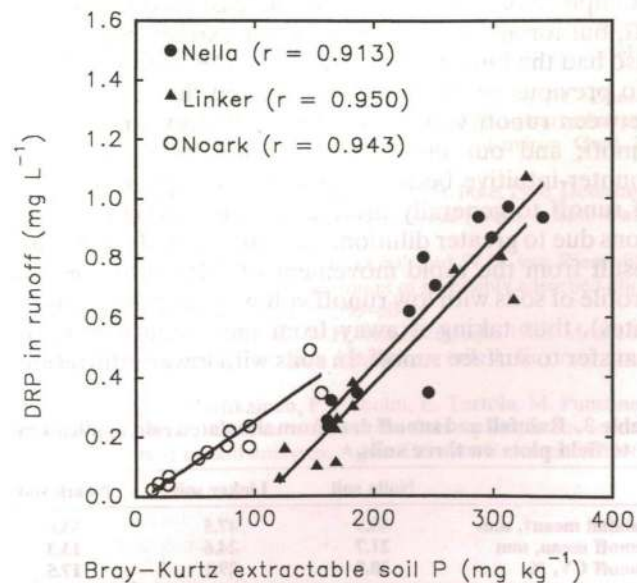


Fig. 2. Relationship between Bray-Kurtz P1 extractable P in surface soil and dissolved reactive P (DRP) in runoff.

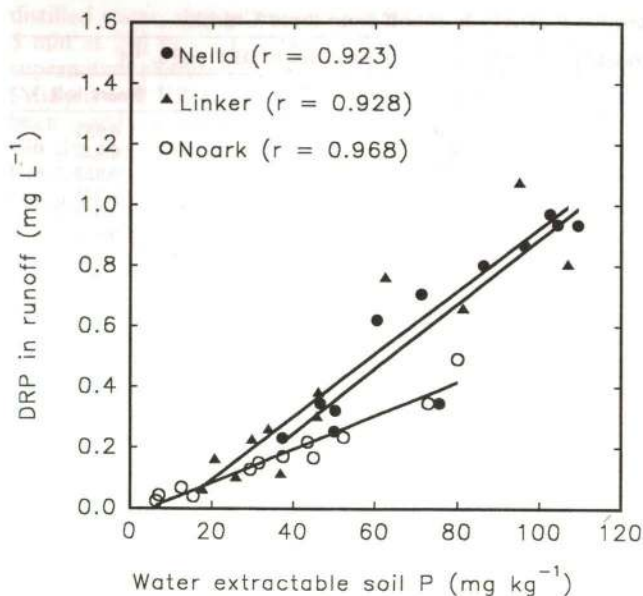


Fig. 3. Relationship between water-extractable P in surface soil and dissolved reactive P (DRP) in runoff.

4), the Noark correlation was best (r value = 0.963) because mass losses depend on both the P concentration and the volume of runoff (which was highly consistent for the Noark soil). Runoff volumes were more variable for the other two soils, and therefore mass losses of runoff DRP show a poorer correlation to STP (Fig. 4).

The variability of runoff volume is also reflected in the r values for the correlation of water extractable STP to DRP concentrations in runoff (Fig. 3). For example, Nella soil had the most variable runoff volume, and it also had the lowest r value, while Noark soil had the least variable runoff volume and the highest r value.

Finally, for a given level of water-extractable STP, soils with the lowest mean runoff volume also had the lowest concentration of DRP in runoff (Fig. 3). For example, Noark soil produced the least amount of runoff, but for any given level of water-extractable STP, it also had the lowest concentration of DRP in the runoff. No previous studies have investigated the relationship between runoff volume and DRP concentration in the runoff; and our observations at first seemed rather counter-intuitive because we expected higher volumes of runoff to generally produce lower DRP concentrations due to greater dilution. This unexpected trend may result from the rapid movement of DRP into the soil profile of soils with low runoff volumes (high infiltration rates), thus taking it away from the primary zone of transfer to surface runoff. In soils with lower infiltration

Table 3. Rainfall and runoff data from simulated rain application to field plots on three soils.

	Nella soil	Linker soil	Noark soil
Rainfall mean [†] , mm	48.9	47.5	53.6
Runoff mean, mm	21.7	24.6	13.3
Runoff CV, %	30.0	29.1	17.5

[†] Amount required to produce 30 min of runoff. Each mean represents 12 runoff events.

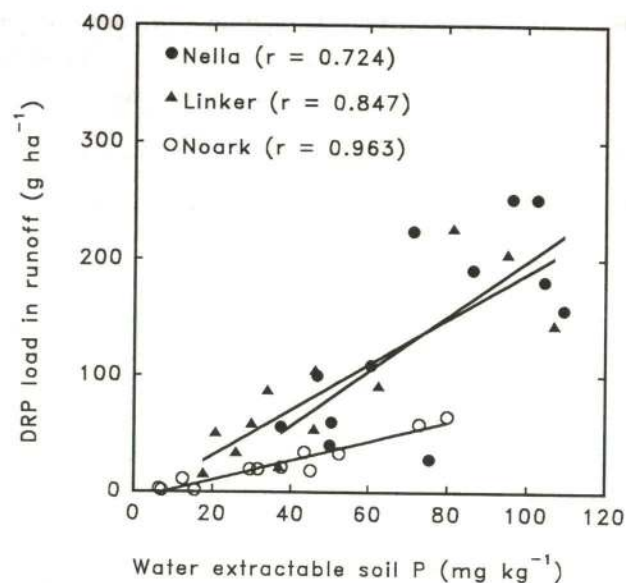


Fig. 4. Relationship between water-extractable P in surface soil and dissolved reactive P (DRP) load in runoff.

rates, much more of the dissolved P may remain near the soil surface long enough to be lost in runoff water.

In an attempt to define these processes, we normalized DRP concentration for each plot. When the DRP concentration in runoff from each plot was divided by the depth of runoff from that plot, and related to the water extractable STP level, regression lines for all soils were statistically the same line ($P < 0.05$) (Fig. 5). Thus, by combining water-extractable STP data with hydrologic data, it may be possible to make reasonably accurate predictions of DRP levels in runoff from a range of soils. Acquiring the necessary hydrologic data on runoff volumes from a soil may sometimes be just as difficult as accurately identifying the soil series of each specific site, but this at least provides an alternate

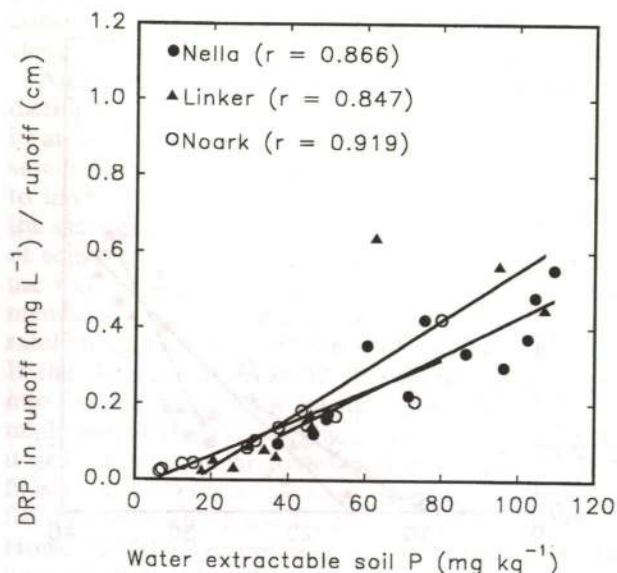


Fig. 5. Relationship between water-extractable P in surface soil and the ratio of dissolved reactive P (DRP) in runoff to the total amount of runoff.

method for predicting DRP concentrations in runoff. For water-quality modelers, it also supplies important information concerning the relationship between volume of runoff and DRP concentration in runoff. Most importantly, it shows the strong influence of site hydrology on processes controlling P loss in surface runoff.

CONCLUSIONS

The results of this study reinforce previous evidence of a linear relationship between P levels in surface soil (0–2 cm deep) and DRP concentrations in runoff from the soil surface, but this study also extends our knowledge by showing that such a relationship exists on a variety of Ultisols. On each soil that was tested, a significant ($P < 0.01$) linear relationship was apparent, regardless of the method used to determine STP. Because most STP extractants gave results that were highly correlated ($r > 0.90$) to DRP in runoff from all three soils, this study did not clearly identify any particular STP method for maintaining the highest correlation to DRP concentrations in runoff from all soils tested. However, the study did show that several STP extractants may be useful for predicting DRP concentrations in runoff, including extractants such as distilled water that were supported by the results of previous work (Pote et al., 1996) conducted under different rainfall intensity, slope, and seasonal conditions.

This study showed that effects of STP levels on DRP concentrations in runoff are not always consistent across soil series, and much of the difference can be attributed to soil hydrology. The fact that total plot runoff was much more variable on some soil series than on others was apparently reflected in correlations between STP and runoff DRP, as soils with the most consistent volume of plot runoff had the best correlations of water-extractable STP to both concentrations and mass losses of DRP in runoff. Also, for any given level of water-extractable STP, soils that produced the lowest volumes of runoff also had the lowest concentrations of DRP in the runoff. When this information was used to normalize the data for DRP concentrations in runoff (divide each DRP concentration by the volume of runoff from that plot), the resulting correlations to water-extractable STP had statistically the same ($P < 0.05$) regression line for every soil. This implies that knowledge of site hydrology can improve the usefulness of STP data for predicting DRP concentrations in runoff.

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