EFFECT OF EXTRACTABLE SOIL SURFACE PHOSPHORUS ON RUNOFF WATER QUALITY

T. C. Daniel, D. R. Edwards, A. N. Sharpley

ABSTRACT. Phosphorus (P) additions to surface water from agricultural nonpoint sources are of concern, because P often limits eutrophication of surface waters. Numerous sources of runoff P exist: indigenous soil and plant material, land-applied manure and sludge, and commercial fertilizer. In many soils receiving commercial fertilizer and manure, concentrations of P at the soil surface have been steadily rising due to either long-term or excessive applications of P. Critical levels of soil surface P may exist, above which runoff may promote eutrophication. Methods for rationally identifying these critical levels are needed to manage losses of P, which implies the need for accurate methods of relating soil surface P concentration (P_s) to runoff P concentration. A study was conducted on both pasture and tilled plots (with and without residue) to evaluate the relationship between P_s and dissolved reactive P in runoff (P_R) using simulated rainfall. The data indicated that even for comparable storms, P_s alone was not a satisfactory estimator of P_R. A model describing the kinetics of P release from surface soil to runoff was used to include additional variables in predicting P_R. When used with uncalibrated parameters, the model explained a significant proportion of the variation in observed P_R values for pasture plots (r^2 = 0.43) but was less successful in predicting P_R for tilled plots (with and without residue, r^2 = 0.13). Calibration of (adjustments to) the extraction coefficients resulted in an overall coefficient of determination between observed and predicted P_R values of 0.73. While the model was successful in describing how P_R and the independent variables are related for the pasture plots, the extraction coefficients should be calibrated to obtain best estimates of P_R. When used with calibrated extraction coefficients, the model provided realistic estimates of P_R over the range of experimental conditions. Keywords. Pollution, Runoff, Water quality.

Runoff from agricultural land is one of the major sources of nonpoint pollution responsible for accelerated eutrophication of surface waters. Noxious aquatic weed and algal growth can result from the addition of excessive amounts of nitrogen (N) and phosphorus (P) to bodies of water (Levine and Schindler, 1989). Phosphorus is usually the limiting nutrient for growth of aquatic weeds and algae in surface waters, because background levels of N are sufficiently high to meet needs, and because most filamentous blue-green algae fix atmospheric N. As a result, Sawyer (1947) and Vollenweider (1968) proposed critical dissolved P (DP) and total P (TP) concentrations of 0.01 and 0.02 mg/L, respectively, to limit surface water eutrophication. Thus, efforts designed to minimize eutrophication due to agricultural runoff should emphasize limiting P transport from fields to surface waters.

Many nonpoint sources of P exist, including runoff from land where commercial fertilizer, sludge, or manure has been applied (Baker and Laflen, 1982; Sharpley and Menzel, 1987; Logan, 1990). Phosphorus losses from such sources are often linearly related to source application rate with greatest losses occurring when the fertilizer or manure is not incorporated into the soil away from the zone of extraction and detachment by runoff (Mueller et al., 1984; Baker and Laflen, 1982). Accumulation of P near the soil surface due to previous P application also influences the concentration and loss of P in runoff (Oloya and Logan, 1980; Sharpley et al., 1981).

Decades of P fertilization at rates exceeding those of crop removal have resulted in widespread increases in levels of soil P as assessed by standard soil analysis methods (Sims, 1993). After high levels of soil surface P have been attained, considerable time is required for significant depletion (Daniel et al., 1991). For example, McCollum (1991) estimates that without further P addition, 8 to 10 years of cropping will be required to bring a Portsmouth sand from 54 mg/kg P (Mehlich-III extraction) to 20 mg/kg P. Pierzynski et al. (1990) examined several Midwestern soils and found 218 and 246 mg/kg P in a Plainfield sand (Wisconsin) and Blount silt loam (Illinois), respectively, and attributed these levels to addition of commercial fertilizer. Levels of soil surface P are also elevated by long-term land application of wastes. Application of dairy manure has contributed to 200 mg/kg soil surface P concentrations in Wisconsin (Motschall and Daniel, 1982), and Pierzynski et al. (1990) found levels of 613 mg/kg soil surface P in Illinois as a result of sludge additions. Sharpley et al. (1991) examined several Oklahoma soils receiving long-term application of poultry litter and found soil surface P concentrations of up to 279 mg/kg. Phosphorus may be transported in runoff from agricultural lands in either particulate or dissolved forms. Particulate P forms are generally associated with the eroded sediments. Thus, agricultural practices which are
effective in controlling erosion will likewise be effective in reducing particulate P losses. Since there are many proven technologies for erosion control (e.g., terracing and no-till production), losses of particulate P can be managed. Control of dissolved P forms may be a greater management challenge at present than control of particulate P forms, because there are relatively few economically feasible management options developed to minimize losses of pollutants in the solution phase. Also, as shown later in this article, measures which significantly reduce erosion can have practically no impact on losses of dissolved P. The issue of dissolved P control takes on greater importance in view of the previously noted nationwide increases (particularly in areas receiving long-term application of manures/sludges) and persistent nature of soil surface P.

The importance of managing dissolved P, as well as particulate P, losses is also highlighted by several studies which found little decrease in lake productivity with reduced total P inputs. Gray and Kirkland (1986), Logan (1982), and Young and DePinto (1982) attributed this to an increased bioavailability of P entering lakes as well as internal recycling of P.

Since previous work has shown that runoff dissolved P and soil surface P concentrations are related (e.g., Sharpley and Smith, 1989), it should be possible to identify critical soil surface P concentrations such that runoff dissolved P concentrations defined as critical are not exceeded. The critical runoff dissolved P concentration may be defined on a general basis, such as by Sawyer (1947) and Vollenweider (1968), or a case-by-case basis. In any event, corresponding critical levels of soil surface P concentration must be identified to ensure that runoff concentration of dissolved P are below values associated with eutrophication. Therefore, reliable methods of relating runoff dissolved P concentration to soil surface P concentration for a variety of soils are needed.

The objectives of this experiment were to (a) assess the usefulness of soil surface P alone as the sole estimator of runoff dissolved P concentrations for various management scenarios, and (b) evaluate the ability of current dissolved P predictive technology to determine critical soil surface P levels using a low level of data availability comparable to realistic conditions faced by action agencies. The results can be used by resource managers as a guide in selecting technology for identification of critical soil surface P concentrations.

**MATERIALS AND METHODS**

**SITE DESCRIPTION**

A total of 38 plots were constructed for the experiment at the University of Arkansas Main Agricultural Experiment Station, at Fayetteville, on a Captina silt loam soil. The area had previously been in unimproved pasture for approximately 10 years, during which time it received no fertilizer and the grass was intermittently mowed. Prior to that, approximately 15 to 20 years ago, the field was a common disposal area for animal manure (poultry and equine). All plots have dimensions of 1.5 x 6.0 m (long axis oriented downslope) and a uniformly graded slope of 5%. Runoff is isolated by individual plot borders and collected from an aluminum gutter installed at the lower end of the plot. Soil sampling was performed approximately two weeks prior to the experiment to determine the surface soil P concentrations of the plots. Three samples per plot (upper end, middle, and lower end) were taken over the 0 to 5 cm interval, mixed together, and analyzed for Mehlich 3 extractable P content (Mehlich, 1984).

Twenty-three plots were established and seeded with tall fescue in fall, 1990, to represent a pasture situation. Grass height at the time of the experiment (mid-August, 1991) was approximately 10 cm. An additional 15 plots were constructed in spring, 1991, but were kept bare to evaluate the effect of residue on P loss. Approximately four months prior to the experiment, corn stubble was spread over nine of the 15 bare plots to simulate tillage with residue (TR); the remaining six plots received no residue and represented tillage without residue (T).

**RUNOFF SAMPLING AND ANALYSIS**

Runoff was produced by simulated rainfall (Edwards et al., 1992) applied to all plots at an intensity of 5 cm/h. Total duration of simulated rainfall was varied from plot-to-plot to obtain a constant runoff duration of 0.5 h. A flow-weighted composite runoff sample (500 mL) for each plot was constructed from six individual samples (approximately 500 mL) collected at 5-min intervals during runoff. The times required to collect individual samples were recorded, which enabled computation of plot hydrographs.

Runoff samples were filtered (0.45 μm) within 2 h of collection and stored at 4° C until analysis. The colorimetric molybdenum-blue method of Murphy and Riley (1962) was used to determine dissolved reactive P on filtered runoff samples. Total suspended solids content was determined for unfiltered runoff samples by gravimetric analysis. Analyses were performed by the University of Arkansas Water Quality Laboratory.

**PREDICTION OF RUNOFF DISSOLVED REACTIVE P CONCENTRATIONS**

Runoff dissolved reactive P concentration (PR) was regressed against soil surface extractable P concentration (PS) to determine whether PS alone can be used as a reliable estimator of PR. Separate regressions were performed for the simulated pasture, tillage with residue, and tillage without residue treatments.

Methods described by Sharpley and Smith (1989) were also used to predict PR for each plot. This procedure is based on the kinetics of P desorption from the soil and incorporates previous work that demonstrated that variables other than PS directly influence PR (Sharpley et al., 1981). Runoff dissolved reactive P concentrations was predicted from:

\[ P_R = \left( K \ P_L \ E_D \ D_B \ t^\alpha \ W^\beta \right) / V \]  

(1)

where PR is the average runoff concentration of dissolved reactive P for an individual runoff event (mg/L), PL is labile P at the soil surface (0 to 5 cm) prior to the runoff event (mg/kg), ED is the effective depth of interaction between surface soil and over land flow or runoff (mm), DB is the soil bulk density (g/cm³) taken as 1.30 g/cm³ (Thiesse, 1985), t is the duration of soil/water interaction,
taken as the time from the beginning of rainfall to the onset of runoff (min), W is the runoff to interacting soil ratio (cm³/g), and V is runoff volume per unit area (mm). The extraction coefficient K and the exponents α and β are soil-dependent parameters.

Values of K, α, and β, which were applicable to all plots, were computed from (Sharpley, 1983):

\[
K = 1.422C^{-0.829} \quad (2)
\]

\[
\alpha = 0.815C^{-0.54} \quad (3)
\]

\[
\beta = 0.141C^{-0.429} \quad (4)
\]

where C is the ratio of proportions of clay to organic carbon. Using 15.96 as C (Marbun, 1991) resulted in K, α, and β values of 0.143, 0.183, and 0.463, respectively.

Values of labile P were computed from corresponding plot values of P₅ as (Sharpley et al., 1985):

\[
P_L = 0.134P_5 + 10.9 \quad (5)
\]

which is applicable to the slightly weathered grouping of the Captina soil.

Values of E_D were computed from associated values of sediment yield as (Sharpley, 1985):

\[
E_D = A + B \ln(Y) \quad (6)
\]

where A and B are soil-dependent parameters that are functions of degree of aggregation (ratio of proportions of soil particles < 2 μm in dispersed and undispersed soil), and Y is sediment yield (kg/ha). No aggregation data were available for the Captina soil, so values of -1.307 and 0.542 were assigned to A and B, respectively. These values have been previously reported for Kirkland silt loam soil (Sharpley, 1985) and were used because of similar textural properties between the Captina and Kirkland soils. Sediment yield was calculated for each plot from measured rates of runoff from the plots and total suspended solids concentrations of the composite runoff samples.

The ratio of runoff to mass of interacting soil W was computed:

\[
W = 100V/(E_D D_B) \quad (7)
\]

where the factor of 100 is necessary to ensure proper units. Runoff volume V was determined by integrating each plot hydrograph with respect to time and dividing by plot area.

RESULTS AND DISCUSSION

SOIL AND RUNOFF PARAMETERS

Table 1 provides Ps and PR values as well as other inputs required by equation 1. Statistics of the variables contained in table 1 are shown in table 2. As expected, average Y was lowest for the pasture plots, increasing by a factor of approximately 250 for the tillage with residue treatments (table 2). Average Y for the tillage without residue treatments was in turn more than an order of magnitude greater than for the tillage with residue plots. The duration of rainfall prior to runoff was lowest for the tillage without residue plots and highest for the pasture plots, reflecting increased dissipation of rain droplet kinetic energy, decreased soil dispersion and surface sealing, and increased infiltration with increased soil cover. Cover effects were also evident in V values, which were lowest for the pasture plots and highest for the tillage without residue plots, indicating high plot-to-plot variation in soil hydraulic characteristics.

Dissolved reactive P concentrations from the tillage with residue and tillage without residue plots were approximately five times lower than from the pasture plots.
Table 2. Statistics of soil and runoff parameters

<table>
<thead>
<tr>
<th></th>
<th>Tillage</th>
<th>Tillage</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>With Residue</td>
<td>Without Residue</td>
</tr>
<tr>
<td>Mean</td>
<td>CV*</td>
<td>Mean</td>
</tr>
<tr>
<td>(P_t) (mg/kg)</td>
<td>155</td>
<td>103</td>
</tr>
<tr>
<td>(Y) (kg/ha)</td>
<td>0.6</td>
<td>1.17</td>
</tr>
<tr>
<td>(t) (min)</td>
<td>13.9</td>
<td>0.51</td>
</tr>
<tr>
<td>(V) (mm)</td>
<td>3.2</td>
<td>0.78</td>
</tr>
<tr>
<td>(P_R) (mg/L)</td>
<td>1.01</td>
<td>0.50</td>
</tr>
</tbody>
</table>

* Coefficient of variation.
† \(P_t\) = extractable soil surface phosphorus.
‡ \(Y\) = sediment yield.
§ \(t\) = time from beginning of rainfall to beginning of runoff.
‖ \(V\) = unit runoff volume.
# \(P_R\) = runoff dissolved reactive P concentration.

(Tables 1 and 2). The higher concentration of \(P_R\) from the pasture plots can be explained in part by the presence of the dense fescue sod, some of which is in a continuing process of decomposition. Timmons et al. (1970) were some of the first in a series of investigators (Wendt and Corey, 1980) to demonstrate the role of decomposing surface residue in elevating \(P_R\) concentrations in the runoff. Lower runoff \(P_R\) concentrations from the tillage plots compared to the pasture plots may have also been due in part to greater dilution by the larger runoff volumes (Table 2) from the tillage with and without residue treatments. In addition, resorption of P by suspended sediment and differing degrees of interaction between soil surface and runoff may also contribute to the differences of \(P_R\) at similar \(P_s\) levels from pasture and the tillage treatments with and without residue.

It is interesting to note that when mean \(P_R\) levels between tillage with and without residue treatments are compared, no difference was evident (by t-test with \(p = 0.05\)) even though the mean \(Y\) for the tillage with residue treatment was reduced by an order of magnitude (significant by t-test with \(p = 0.05\)). This may appear contradictory from expected results; however, it may be explained in part by the desorption of P from soils enriched in P. Generally, the \(P_s\) level for Captina soils having received no manure or fertilizer P is in the range of 10 to 20 mg/kg. Captina soils with \(P_s\) levels of 100 mg/kg could be considered enriched and contain P in excess of the P saturation level. Desorption of P would be expected to occur from such soils if high erosion rates occurred concomitant with high runoff volumes. The tillage without residue treatment produced the highest mean runoff volume and sediment loss (Table 2) of all treatments evaluated; resulting in the greatest opportunity for desorption of P due to interaction between soil enriched in P and runoff water. As pointed out by Sharpley et al. (1992), this clearly indicates that measures which reduce sediment and particulate P losses can have a negligible effect on losses of dissolved reactive P.

**Regression Analysis**

The relationship between \(P_s\) and \(P_R\) is shown in figures 1 and 2 for the pasture, tillage with residue, and tillage without residue treatments, respectively. Figure 1 demonstrates that \(P_s\) alone is not a reliable estimator of \(P_R\) because of the very low coefficient of determination \(r^2 = 0.05\), not significantly different from zero based on t-test with \(p = 0.05\). The \(P_s\) and \(P_R\) data from the tillage with residue and tillage without residue plots are combined in figure 2 and have a coefficient of determination of 0.02, again not significantly different from zero. Coefficients of determination obtained from analyzing separate data sets from the tillage with residue and tillage without residue plots are even lower. These findings indicate that even for simulated rainfall events with equal intensities and similar total runoff durations, a linear relationship between \(P_s\) and \(P_R\) does not adequately reflect how the two variables are

![Figure 1](image1.png)

**Figure 1**—Relationship of runoff dissolved reactive phosphorus (\(P_R\)) to extractable soil surface phosphorus (\(P_s\)) for the pasture (P) plots.

![Figure 2](image2.png)

**Figure 2**—Relationship of runoff dissolved reactive phosphorus (\(P_R\)) to extractable soil surface phosphorus (\(P_s\)) for the tillage with residue (TR) and tillage without residue (T) plots.
related for the experimental variables. Other variables should therefore be considered to increase prediction accuracy.

**PREDICTED \( P_R \) FROM EQUATION 1**

Prediction of \( P_R \) from equation 1 increased the explained variation in observed \( P_R \) values for the pasture plots by threefold, but the coefficient of determination (0.17) was still not significant at the \( p = 0.05 \) level. Omission of data from the three plots with runoff below 1.2 mm (plots 4, 18, and 20) greatly improved agreement between predicted and observed \( P_R \) and resulted in a coefficient of determination of 0.43, significant at the \( p = 0.05 \) level (fig. 3). The deletion of these data may be justified by noting that at lower flows, the degree and time of surface soil-runoff interaction will differ from those of higher flows. As several parameters in equation 1 are included as logarithmic functions of factors affected by runoff volume, predicted values will be affected more at low than high flows. In fact, the value of \( E_D \) has been found to be particularly sensitive to runoff volume for larger watersheds (2 to 100 ha) (Sharpley and Smith, 1989). In addition, at low flow the contribution of \( P \) released from surface vegetative material is greater than that from soil material, due to less interaction of runoff of low energy and surface soil (Sharpley, 1981; Sharpley and Smith, 1989). At the present time, neither equation 1 nor other \( P \) transport models account for \( P \) release from vegetation to runoff.

The significant coefficient of determination obtained without the low flow data is quite encouraging, because it indicates that equation 1 can be applied even with uncalibrated parameters and still reflect relative changes in \( P_R \) as a function of the dependent variables. The fact that half the variation in \( P_R \) values was unexplained by the model suggests that accurate \( P_R \) prediction is very sensitive to variables which were taken as constant across all plots.

Variability in inputs such as bulk density, clay content, and organic carbon content could have been significant, and \( P_R \) predictions might therefore have suffered by not accounting for differences in these variables. Previous success with equation 1 for \( P_R \) prediction (Sharpley and Smith, 1989) suggests that this may have been the case, particularly since plot size in the present study was relatively small. It is also possible that values of variables such as \( P \), which was determined for a 5 cm depth, should have been determined for a much shallower depth since \( E_D \) values were computed as only a few millimeters.

On average, \( P_R \) was overpredicted by a factor of 1.7 as evidenced by the slope of the regression line in figure 3. This suggests that the value used for \( K \) may have been inappropriately high. However, since a constant value of \( D_B \) was used in equation 1, \( K \) is indistinguishable from \( D_B \) from the standpoint of parameter calibration. Thus, it is not possible to say whether the overestimation of \( P_R \) that occurred with an uncalibrated \( K \) was due to an inappropriately high estimate of \( K \), \( D_B \), or some combination of both. In addition, the lower interaction between runoff and surface soil in pasture (due to grass cover) relative to the tilled plots, will reduce the contribution of runoff \( P \) from surface soil compared to vegetation. As vegetative \( P \) release is not accounted for in equation 1, over-prediction of \( P_R \) may result from simulation of excessive \( P \) release from the pasture soils which also have a greater average \( P \) value (155 mg/kg) than tilled (109 mg/kg) (table 1).

The relationship between predicted and observed \( P_R \) values for the tillage with and without residue plots is shown in figure 4. Data from the tillage with residue and tillage without residue treatments were lumped together because there were no apparent differences in relationships between predicted and observed \( P_R \) values. The model was less successful in predicting \( P_R \) for the tillage plots as
noted by the low coefficient of determination (0.13, insignificant at the p = 0.05 level). The lack of agreement between predicted and observed \( P_R \) values is most likely due in part to plot-to-plot variability in inputs which were assumed constant. It may also suggest that the dynamics of \( P \) transport are quite different for the tillage treatments with and without residue than for the pasture treatments. Additional investigation over a greater range of observed \( P_R \) values will be necessary to explain the discrepancies between observations and predictions.

Figure 5 demonstrates the effect of calibrating the extraction coefficient \( K \) on the relationship between observed and predicted \( P_R \) for the experimental conditions. Multiplying \( K \) by 0.60 for the pasture plots and 0.01 for the tillage plots produced an overall coefficient of determination between observed and predicted \( P_R \) values of 0.73, significant at the p = 0.05 level. This demonstrates the benefit of calibration in obtaining realistic absolute estimates of \( P_R \) concentration as a function of the independent variables in equation 1.

**SUMMARY AND CONCLUSIONS**

This study was performed to assess the impact of varying \( P_e \) on runoff \( P_R \) from pasture, tillage with residue, and tillage without residue plots. Durations of runoff were held constant, and durations of rainfall were comparable (particularly for the tillage plots). The data showed that \( P_e \) alone was not a reliable estimator of \( P_R \) for either the pasture or tillage (with and without residue) plots. The equation presented by Sharpley and Smith (1989) was used with uncalibrated parameters to predict \( P_R \) and accounted for significant variation in \( P_R \) values for the pasture plots \((r^2 = 0.43)\) but not for the tillage (with and without residue) plots \((r^2 = 0.13)\). The unexplained variation could have been due in part to significant plot-to-plot variability in inputs that were assumed constant (e.g., \( D_B \), clay content, and organic carbon content), lumping inputs over too great a soil depth, and different transport dynamics between the pasture and tillage plots. Dissolved reactive \( P \) was overpredicted by a factor of 1.7 for the pasture plots and 100 for the tillage plots when uncalibrated parameters were used, pointing out the benefit of calibration if the model is to be used for identification of critical \( P_s \) levels. When used with calibrated extraction coefficients, the equation produced realistic predictions \((r^2 = 0.73)\) of \( P_R \) over the range of experimental conditions. The use of many water quality models is limited by data availability, the present simulation approach assumed a low level of data availability, as is often the case. Clearly, more detailed soil information will provide more accurate \( P_R \) estimates, but even routine soil properties such as clay, organic C, and aggregation may not be directly available to many action agency personnel who will use such modeling approaches, nor will they often have the resources to have these analyses conducted.

Given the increasing emphasis on surface water \( P \) contributions from agricultural nonpoint sources, it is apparent that reliable models for estimating these loading rates are needed. These models might enable identification of critical levels of \( P_s \) above which no \( P \) additions would be recommended. Critical \( P_s \) identification is logical from the standpoint of crop production but also from the perspective of water quality since \( P_R \) depends at least in part on \( P_s \). As discussed earlier, however, \( P_e \) alone is not a reliable estimator of \( P_R \), implying that more complex models than equations I might be necessary in some applications.

The results of this article can be helpful in the development and testing of \( P \) transport models because they suggest that even for small source areas, variability in causative soil properties may be quite significant. Use of distributed, more physically-based models may be justified in some cases, with inputs determined from thorough field reconnaissance. The results also point out some of the pitfalls which may be associated with establishing critical \( P_s \) levels with uncalibrated model parameters, since calibration was essential for realistic prediction of \( P_R \) values. In addition, there will always be a need for accurate runoff models, because the transport of \( P \) is governed in large part by hydrologic processes, and quantities such as \( V \) and \( t \) in equation 1 usually will not be observed in practical applications.

**REFERENCES**


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Figure 5—Overall relationship between observed runoff dissolved reactive phosphorus concentration \((P_{R,0})\) to predictions using equation 1 with calibrated extraction coefficients for pasture (P), tillage with residue (TR), and tillage without residue (T) plots.


