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An empirical model for dissolved phosphorus in runoff from surface-applied fertilizers

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ABSTRACT

Dissolved phosphorus (P) in runoff from surface-applied fertilizers can be relatively great, but commonly used, field or watershed-scale computer models often do not simulate direct transfer of fertilizer P to runoff. Using data from our own simulated rainfall experiments and published runoff studies, we developed a simple model to predict fertilizer P release during rain and the concentration of dissolved P in runoff. The model operates on a daily time-step and requires input data on the amount of fertilizer P applied, type of soil cover (bare, residue-covered, grassed), and amount of rain and runoff for each storm during the simulation period. The model applies fertilizer to the soil surface, adsorbs fertilizer P to soil before the first rain, releases P from fertilizer for each rain event, and distributes released fertilizer P between runoff and infiltration based on the runoff to rain ratio. Using data from 11 runoff studies, we validated that our model accurately predicts dissolved P in runoff from surface-applied fertilizers. Validation data represented a series of runoff events for a variety of fertilizer types, soil cover types and subsequent fertilizer P adsorption amounts, storm hydrology conditions (i.e., runoff to rain ratio), and plot or field sizes ($0.2 \, m^2$ to 9.6 ha). An analysis showed model predictions can be quite sensitive to rainfall and runoff data. However, the simplicity of our model should make it straightforward to incorporate into more complex P transport models, thus improving their ability to reliably predict P loss to the environment for a variety of agricultural land uses.

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1. Introduction

Non-point source pollution of fresh waters by agricultural P is a water quality concern because it contributes to accelerated eutrophication, which limits use of surface water resources for drinking, recreation, and industry (Carpenter et al., 1998; Gibson et al., 2000; Sharpley and Rekolainen, 1997). The major P transport pathway for most agricultural soils is surface runoff. Soil and plant material are significant sources of P to runoff, but their effect can be overwhelmed by P release from recently applied, inorganic fertilizers that are left unincorporated (Torbert et al., 1999; Withers et al., 2001). Hart et al. (2004) presents a comprehensive review of research that has investigated the nature of surface-applied fertilizer P transport in runoff. Studies reviewed in that paper consistently show that because P in commercially available fertilizers is formulated to be highly water-soluble, dissolved P concentrations in runoff in the first storm after fertilizer application can be orders of magnitude greater than P concentrations in runoff from unfertilized soils (Kleinman et al., 2002). Because a majority, but not all, of applied fertilizer P is likely released during this first storm, dissolved P concentrations in runoff from fertilized soils decrease rapidly for subsequent storms (McDowell et al., 2003; Shigaki et al., 2006). Runoff dissolved P concentrations may thus become dominated by soil P release again after only 4–5 storm events. Despite the relatively short-term effect of surface-applied fertilizers on runoff dissolved P, such transfer of fertilizer P in runoff can constitute the majority of annual dissolved P loss (Nash et al., 2000; Owens and Shipitalo, 2006). It is therefore important to be able to reliably predict direct loss of fertilizer P in runoff.

Computer models are often used to predict field or watershed-scale P transport, but commonly used models, such as EPIC (Williams et al., 1983), GLEAMS (Leonard et al., 1987), ANSWERS (Bouraoui and Dillaha, 1996), or SWAT (Arnold et al., 1998), do not simulate surface application of fertilizers or direct transfer of dissolved P from fertilizers to runoff. Instead, these models immediately incorporate P surface-applied as fertilizer into soil P pools and simulate loss of dissolved P to runoff from only these

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soil pools (Jones et al., 1984; Vadas et al., 2006). Thus, the models will likely poorly simulate the relatively great concentrations of dissolved P in runoff that can occur shortly after a surface fertilizer P application (Yuan et al., 2005). If such models are to be used in settings where surface-application of fertilizer is common, they should be modified to simulate such dissolved P transport in runoff.

Considerable research has been conducted to investigate and model the release of P from fertilizers, but mostly in regard to fertilizer dissolution in soils and P availability to plants (Di et al., 1994; Kirk and Nye, 1986; Sikora et al., 1991) or in regard to fertilizers of relatively low P solubility (Saggar et al., 1992). Little research has focused on modeling release of dissolved P from surface-applied fertilizer during rainfall and its subsequent transport in runoff. McDowell et al. (2005) have developed a model that estimates fertilizer P loss from pastures on a daily time-step, but presents the output as annual losses within the Overseer nutrient budgeting software. Our model presented here represents a substantial improvement because it also considers cropped soils and is designed for easy inclusion within mechanistic models like SWAT or EPIC. Our objectives were thus to develop a simple, empirical surface fertilizer and runoff dissolved P model and to validate the model with independent data.

2. Model development

We investigated only widely used, highly water-soluble P fertilizers, such as superphosphate, triple superphosphate, and mono- and diammonium phosphate. We intended our fertilizer P and runoff model to be easily incorporated into more complex models that operate on a daily time-step and have only simple fertilizer characteristics and daily quantities of rain and runoff data available to predict fertilizer P transport in runoff. Examples of such models are EPIC, GLEAMS, ANSWERS, or SWAT. The intended use for our model thus precluded developing a fertilizer P runoff model that considers complex kinetics of fertilizer dissolution or hydrology. Our model relied on empirical relationships that can reliably predict fertilizer P loss in runoff with few input parameters. However, given that the above-mentioned models currently do not predict direct loss of surface fertilizer P in runoff, even such simple empirical routines should help improve these models. Finally, while P loss in runoff from fertilizers can occur in forms other than dissolved P (i.e., physical transport of fertilizer particles themselves, or loss of fertilizer P adsorbed onto suspended sediment or dissolved organics in runoff), our model simulates only loss of the dissolved P form. However, research consistently shows the vast majority of fertilizer P loss in runoff may indeed occur in the dissolved form (Greenhill et al., 1983; McDowell and Catto, 2005; Nash et al., 2004; Shigaki et al., 2007).

2.1. Reaction of applied fertilizer phosphorus with soil before rain

The first step in developing our model to predict loss of fertilizer P in runoff was to determine the extent of fertilizer P adsorption by soil after application and before any rain occurs. In our literature review, we found only studies by Williams (1969) and Kuczynski et al. (1968) that investigated short-term reaction of surface-applied P fertilizers with soil. In controlled laboratory experiments, Williams (1969) placed superphosphate fertilizer particles on the surface of ground soil packed into test tubes and measured the degree to which fertilizer P was adsorbed by the soil during 8 days. Williams (1969) found that 25–50% of applied fertilizer P had adsorbed to the soil the first day after application, and that 50–65% of applied P had adsorbed to soil after 2 days. The rate of fertilizer P adsorption declined greatly after 2 days. Kuczynski et al. (1968) obtained similar results in field experiments using superphosphate

fertilizer. Data from Williams (1969) in Fig. 1a show that the amount of fertilizer P remaining available on the soil surface decreased in an exponential manner with time after application. Extending the decreasing relationship beyond the measured time period of 8 days shows that the amount of fertilizer P adsorbed reaches a general maximum at about 75% of that applied (at about 25 days for these experimental conditions). Williams (1969) also observed that adsorption of fertilizer P by soil decreased as the soil moisture or degree of contact between fertilizer and soil decreased. Thus, adsorption of fertilizer P by soil after application will be greater for bare soils than for soils partially covered with crop residues or grassed soils.

Based on data from Williams (1969), we thus formulated our model so the amount of surface-applied fertilizer P that remains available for loss in runoff decreases with time (i.e., due to adsorption by soil), but does at a slower rate for grassed or residue-covered soils than for bare soils. Fig. 1b shows the equations our model uses to calculate the fraction of applied fertilizer P that remains available on the soil surface over time after application. We formulated our model so a maximum of 75% of applied fertilizer P can be adsorbed by soil and thus rendered unavailable for direct loss in runoff. Once this maximum 75% has been adsorbed, the model does not change the amount of fertilizer P on the soil surface until rain occurs (see discussion below). We also formulated our model so adsorption of fertilizer P by soil proceeds only between the time of application and the first rainfall. After the first rainfall, the model assumes all readily available fertilizer P (75%, see discussion below) has been leached and that adsorption
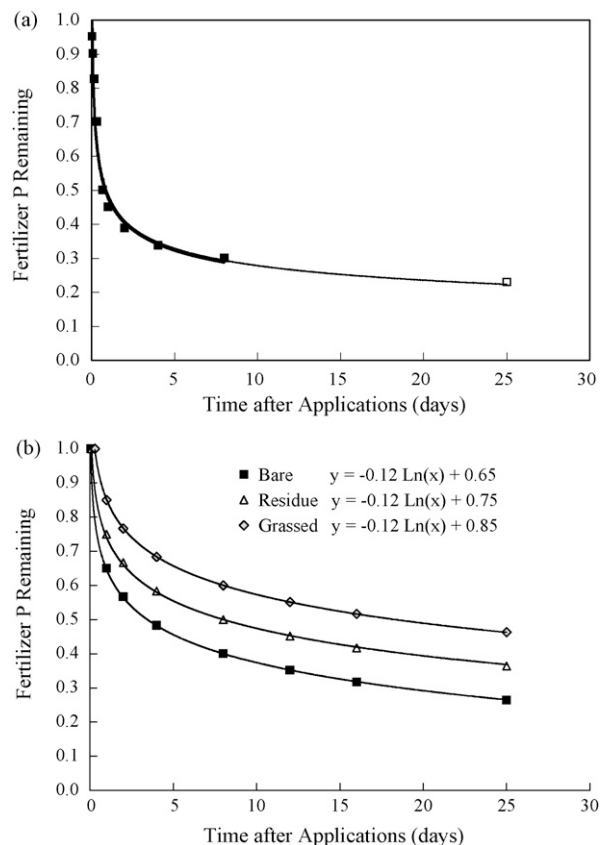

Fig. 1. (a) Shows data from Williams (1969) of the fraction of applied fertilizer P remaining available on the soil surface with time after application. The dashed line extends the relationship beyond the measured data of Williams (1969). Applied fertilizer P not remaining on the surface was adsorbed by soil. (b) Shows the equations used in our model to predict the decrease in applied fertilizer P remaining on the soil surface after application and before the first rain event for bare, residue-covered, and grassed soils.

of the remaining 25% of fertilizer P by soil is slow enough to be considered inconsequential (Williams, 1969). However, the remaining 25% of applied fertilizer P is still available to be leached by rain and transported in runoff.

2.2. Rain-induced phosphorus release from fertilizer

The second step in developing our fertilizer P runoff model was to predict the release of fertilizer P on the soil surface when rain falls. We found only two published laboratory studies that investigated fertilizer P release to water using flow-type experiments similar to fertilizer leaching by rain. Williams (1969) placed superphosphate fertilizer on Whatman no. 42 filter paper in a circular holder, leached it with finely sprayed water at a rate of 2.5 cm h^{-1}, and analyzed successively collected leachate volumes for dissolved P. Ramakrishnan and Perrott (2004) continuously leached superphosphate fertilizer with water though ion-exchange columns that measured P release.

To further investigate the nature of fertilizer P release with rain, we conducted fertilizer leaching experiments with an indoor rain simulator. We spread duplicate samples of a triple superphosphate fertilizer onto coarse filter paper in 7.5 cm diameter funnels at rates of 2.5, 5.0, 10.0, and 20.0 g. We then rained on the funnels at a rate of 7.5 cm h^{-1} for 45 min using a rain simulator based on the design of Miller (1987). We conducted three successive rainfalls at one rainfall per day for 3 days. We also conducted the same rainfall experiments with 20 g of fertilizer and a rain rate of 4.8 cm h^{-1}. During the 45 min simulations, we collected all leachates at intervals of 5 or 10 min for a total of seven discrete samples per simulation. We analyzed all samples for volume and dissolved P using the method of Murphy and Riley (1962).

Our rainfall simulation data showed that relative fertilizer P release was consistent regardless of the amount of fertilizer used or the amount of rain added (Fig. 2). Relative fertilizer P release data from the laboratory experiments of Williams (1969) and Ramakrishnan and Perrott (2004) in Fig. 2 agreed well with our data. Because we did not intend for our model to describe fertilizer P release using complex kinetic equations, we had to simply describe our observed patterns of fertilizer P release. Our data showed that consistently about 75% of original fertilizer P was released during the first rain simulation. For the second rain simulation, consistently about 40% of fertilizer P remaining after the first rain simulation was released. For the third simulation, consistently about 7.5% of remaining fertilizer P was released. Our rainfall simulations of 4.8 or 7.5 cm h^{-1} followed the protocol of the National P Research Project (2007), which is intended to represent storm return periods of 5–10 years. Our simulations thus represent significant storm events and magnitudes of fertilizer P release.
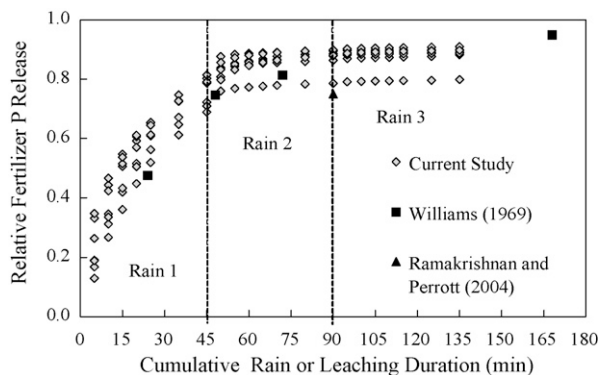

Fig. 2. Data from our simulated rainfall and fertilizer P dissolution experiments showing relative P release from fertilizer with time after the start of rain for the three rain events. Included are published data from two flow leaching experiments.

Given our need for model simplicity and the relatively intense nature of our rain simulations, we thus formulated our model so that in the first rain event after fertilizer application, 75% of available fertilizer P is released regardless of how much rain falls. This leaves 25% of applied fertilizer available for leaching during the second rain event. During the second event, 40% of this fertilizer P remaining on the soil surface is released. For all subsequent rain events, 7.5% of remaining fertilizer P is released. These 75%, 40%, and 7.5% values thus ensure that a majority, but not all, of fertilizer P is released during the first storm after application and is available for transport if runoff occurred. During the second storm, not only has the amount of fertilizer P on the soil surface declined due to leaching by the first storm, but the rate of P release from remaining fertilizer during the second storm is less than during the first storm. The same trend follows for the third rain event, but the rate of fertilizer release is constant after the third event. Thus, our model predicts a continuous decrease in fertilizer P availability and rate of release (up until the third rain event) across a series of storms. However, fertilizer continues to be a significant source of P to runoff for several rain events after application. This is consistent with observed patterns of fertilizer P loss in runoff over a series of rain events after application (McDowell et al., 2003; Shigaki et al., 2006).

We also formulated our model to account for previous soil adsorption of fertilizer P when predicting fertilizer P release during the first rainfall after application. Our rainfall simulation data described above showed that consistently about 75% of original fertilizer P was released during the first rain simulation. As also discussed above, Williams (1969) similarly observed that a maximum of about 75% of applied fertilizer is adsorbed by soil during several weeks after application. Given the consistency of the 75% value, we thus theorized that about 75% of fertilizer P is in a readily available form that can either be adsorbed by soil or leached by the first rain. However, any fertilizer P adsorbed by soil would no longer be available for leaching by rain. We thus formulated our model so that 75% of applied fertilizer P is either adsorbed by soil or released by rain by the end of the first rainfall after application. For example, if rain occurs on the day of application, then the full 75% of applied fertilizer P is released by rain and 0% is adsorbed by soil. If rain occurs 5 days after fertilizer application, the model predicts that 46% of applied fertilizer has already been adsorbed by soil (according to the bare soil equation in Fig. 1b) and only 29% (75–46%) is thus leached by rain. If the maximum allowable 75% of applied fertilizer P is adsorbed by soil before any rain occurs, our model assumes only the 25% of applied fertilizer P remaining on the soil surface is available for leaching by rain. The model then predicts leaching from this remaining fertilizer P the same as for any second rain event after application (i.e., 40% of remaining fertilizer P is released, as discussed above).

2.3. Distribution of released fertilizer P between infiltration and runoff

The final step in developing our model was to predict dissolved P concentrations in runoff from soils where fertilizers have been surface applied. In our model, P is released from fertilizer for any rain event regardless if runoff occurs. If no runoff occurs, all released fertilizer P infiltrates into the soil. In reality when runoff occurs, some of the fertilizer P infiltrates into soil and some is transported in runoff. We sought a simple method to predict the proportion of released fertilizer P that would be transported in runoff. To do this, we first examined the fertilizer P runoff data from Kleinman et al. (2002). In that study, diammonium phosphate fertilizer was surface applied to small boxes that were 20 cm wide by 100 cm long and packed with soil to a depth of 5 cm. Simulated rain was applied to boxes at 7 cm h^{-1} until 30 min of runoff was collected. Because the time between initiation of rainfall and
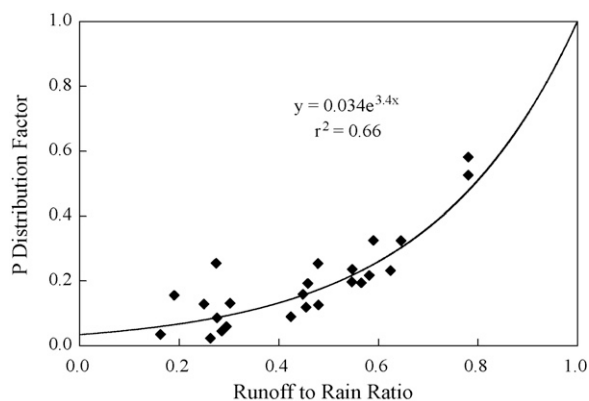
Fig. 3. Data from published studies showing the empirical relationship between measured runoff to rain ratios and calculated P distribution factors, which are measured dissolved P concentrations in runoff divided by calculated concentrations of fertilizer P released during a rain event.

initiation of runoff and also the volume of runoff varied from box to box, the subsequent ratio of runoff volume to rain volume also varied (from 0.16 to 0.65). Ultimately, there was a strong, empirical relationship showing dissolved P concentrations in runoff increased as the runoff to rain ratio increased (see Fig. 3 and the associated discussion below). Greater runoff to rain ratios reflected conditions where greater amounts of rain were converted to runoff earlier during the rain event. Because the rate of P release from fertilizer decreases with time during a rain event (see Fig. 2), earlier occurring runoff results in more fertilizer P being transported in runoff. This is consistent with storm-event data showing that dissolved P concentrations in runoff from surface-applied fertilizers decrease with time as a storm progresses (Tarkalson and Mikkelsen, 2004; Torbert et al., 1999; White et al., 2003).

We combined data from Kleinman et al. (2002) with data from six other studies (Daverede et al., 2004; Franklin et al., 2006; Gascho et al., 1998; Gaudreau et al., 2002; Romkens et al., 1973; Tarkalson and Mikkelsen, 2004) to develop a simple, empirical method to predict dissolved P concentrations in runoff from surface-applied fertilizer. The six studies surface-applied superphosphate or triple superphosphate fertilizer to field plots that

ranged in size from 4 to 84 m^2. Most studies used simulated rainfall to generate runoff, except for Gaudreau et al. (2002) who monitored natural storms. Studies represented a variety of soil cover conditions and times between fertilizer application and the first runoff event (Table 1). All data represented the first rain event following fertilizer application, but the time between fertilizer application and rain ranged from 1 h to 1 month. All studies reported the rate of P applied to field plots, total rain that was applied to or fell on soils, total runoff measured, and the flow-weighted dissolved P concentration in runoff for the entire runoff event.

For all seven runoff studies, we first predicted the amount of fertilizer that was adsorbed by the soil after application and before the first rain event using equations in Fig. 1b. We then predicted the mass (mg) of remaining fertilizer P that was released during the first rain event. We then calculated a concentration of P released from fertilizer (mg L^{-1}) by dividing the mass of fertilizer P released (mg) by the total rain for the event (L). These calculated fertilizer P release concentrations theoretically represent the maximum runoff P concentration that could possibly occur if all rain was converted to runoff. We then compared these calculated fertilizer P release concentrations with measured runoff dissolved P concentrations. Measured runoff P concentrations were always less, which shows that only a portion of the fertilizer P released was actually transferred in runoff. We then divided measured runoff dissolved P concentrations by our calculated fertilizer P release concentrations to quantify the fraction of released fertilizer P that was transferred to runoff. We called the resulting quotients P distribution factors, as they represented distribution of released fertilizer P between runoff and infiltration. Data in Fig. 3 show that across all seven studies there was a consistent, empirical relationship between runoff to rain ratios and P distribution factors. This relationship essentially shows that as more rain was converted to runoff, a greater proportion of fertilizer P released during a storm was transferred to runoff. Interestingly, if all rain were converted to runoff during a storm, the empirical relationship in Fig. 3 would calculate a P distribution factor of about 1.0. This means a predicted dissolved P concentration in runoff would be equal to the concentration of released fertilizer P dissolved in the total rain volume for the event, which is what should theoretically occur. However, we formulated our model so that a P distribution

Table 1
Data for fertilizer type, soil cover type, days from application to the first rain/runoff event, measured runoff to rain ratios, and measured runoff dissolved P concentrations for studies used for model development and validation

Source	Fertilizer P applied (kg ha^{-1})	Plot size (m^2)	Fertilizer type	Soil cover type	Days from application to first rain/runoff	Runoff to rain ratio	Runoff dissolved P (mg L^{-1})
Data used for model development							
Daverede et al. (2004)	54	3	Triple super P	Residue	30	0.27	5.5
Franklin et al. (2006)	39	20	Triple super P	Grassed	0	0.46–0.57	16.3–16.8
Gascho et al. (1998)	45	622	Super P	Residue	1	0.19–0.25	5.8–7.0
Gaudreau et al. (2002)	25–50	6	Triple super P	Grassed	3	0.78	16.6–30.0
Kleinman et al. (2002)	100	0.2	Diammonium P	Bare	3	0.16–0.65	1.3–22.0
Romkens et al. (1973)	56	8.4	Triple super P	Residue	0	0.48–0.69	2.6–16.8
Tarkalson and Mikkelsen (2004)	11–110	4	Super P	Bare	0	0.27–0.30	1.9–6.6
Data used for model validation							
McDowell and Catto (2005)	30	0.2	Super P	Grassed	1	0.82	0.1–70.0
McDowell et al. (2003)	18–32	0.2	Super P	Grassed	7	0.32	0.1–5.4
Nichols et al. (1994)	87	9	Diammonium P	Grassed	7	0.48	24.9–27.3
Olness et al. (1980)	75	78000	Monoammonium P	Grassed	3	0.38–0.57	4.9–6.5
Pote et al. (2006)	76	4	Monoammonium P	Grassed	4	0.09–0.53	3.5–15.0
Seo et al. (2005)	51	158	Not reported	Residue	4	0.05–0.20	0.5–4.8
Shigaki et al. (2006)	100	2	Triple super P	Grassed	0	0.35–0.60	1.7–125.0
Shigaki et al. (2007)	100	0.2	Triple super P	Grassed	1	0.2–0.7	0.8–32.7
Timmons et al. (1973)	35	900	Super P	Residue	0	0.01	0.3–1.3
Warren et al. (2006)	24–116	3	Triple super P	Residue	2	0.47–0.67	0.3–73.2
Withers et al. (2001)	60–90	32	Triple super P	Bare	1–18	0.01–0.04	0.5–74.0

factor can have a maximum value of only 1.0, which is unlikely to ever occur under natural soil conditions.

Thus for any rain event, our model calculates a dissolved P concentration in runoff (mg L^{-1}) from surface-applied fertilizer as:

$$\text{Runoff dissolved P} = [\text{available fertilizer P (mg)}]$$
$$\times [\%\text{fertilizer P released}]$$
$$\times \frac{[\text{P distribution factor}]}{[\text{total rain during the event (L)}]} \quad (1)$$

The unitless P distribution factor is calculated as (Fig. 2a):

$$\text{P distribution factor} = 0.034 \, \exp[(3.4)(\text{runoff to rain ratio})]. \quad (2)$$

The available fertilizer P in Eq. (1) is for fertilizer P on the soil surface at the beginning of the rain event and not the amount of fertilizer P initially applied. Only on the day of fertilizer application will the pool of available fertilizer P be equal to the amount of fertilizer P applied. Thereafter until the first rain event, available fertilizer P will decrease due to soil P adsorption according to equations in Fig. 1b. When a rain event occurs, the pool of available fertilizer P will decrease due to leaching by rainfall. If no runoff occurs for a given storm event, all fertilizer P released infiltrates into soil. The amount of fertilizer P remaining on the soil surface after one rain event will be available for infiltration into soil or transport in runoff for the next rain event. As discussed above, the %fertilizer P released value is 75% for the first rainstorm after application, 40% for the second storm after application, and 7.5% for all subsequent storms.

3. Model validation

We validated our fertilizer P runoff model using data from 11 independent runoff studies (Table 1). The 11 studies surface-applied superphosphate or ammonium phosphate fertilizer to field plots or indoor soil boxes that ranged in size from 0.2 m^2 to 9.6 ha. Nine studies used simulated rainfall to generate runoff, while three monitored natural storms. Studies varied in soil cover types, including grassed, residue-covered, and bare soil. The studies also varied in the time between the application of fertilizer and the first rain/runoff event from a few hours to 18 days. These variations in soil cover types and times between fertilizer application and the first rain/runoff event enabled us to validate our model's ability to adequately account for adsorption of fertilizer P by soil before the first rain/runoff event. Data from two studies were from only the first rain event following fertilizer application, while data from 10 studies were from a series of rain events as long as 42 days after fertilizer application. These longer studies enabled us to validate our model's ability to track the decrease in available fertilizer P across a series of rain events. It also enabled us to validate if our fertilizer P release rates of 0.75 (first event after application), 0.40 (second event after application), and 0.075 (all subsequent events) resulted in reliable runoff P predictions. All studies reported the rate of fertilizer P applied to field plots, total rain that was applied to or fell on soils, total runoff measured, and the flow-weighted dissolved P concentration in runoff for the entire runoff events.

For all studies, we first predicted the amount of fertilizer adsorbed by the soil after application and before the first rain event using equations in Fig. 1b. For the first rain event in all studies, we used Eqs. (1) and (2) to predict the amount of P released from fertilizer and the dissolved P concentrations in runoff. We then subtracted the amount of released fertilizer P from the available fertilizer P pool to calculate the amount of fertilizer P available for transfer to runoff for the next storm event. We carried this process through for all runoff events in the 11 studies. For the majority of studies investigated, dissolved P concentrations in runoff from soil or plant materials (as indicated by data from unfertilized plots or

soil boxes) was one to two orders of magnitude less than runoff dissolved P concentrations from fertilized plots or soil boxes. Therefore, we did not correct observed runoff P data for fertilized plots or boxes for apparent dissolved P loss from soil or plant material.

Data in Fig. 4a show measured and predicted runoff dissolved P concentrations for only the first runoff events after fertilizer application for all 11 studies. An analysis using the PROC REG function in SAS (SAS, 1999) showed the slope and intercept of the regression line relating predicted and measured values were not significantly different ($p = 0.01$) from unity or zero. We also calculated a Nash–Sutcliffe model efficiency of 0.89 (Nash and Sutcliffe, 1970) for the data. Nash–Sutcliffe efficiencies can range from $-\infty$ to 1. An efficiency of 1 corresponds to a perfect match of modeled and observed data. An efficiency of 0 indicates model predictions are as accurate as the mean of observed data, whereas an efficiency less than zero occurs when the observed mean is a better predictor than the model. Essentially, the closer the model efficiency is to 1, the more accurate the model is. Thus, our model was able to accurately predict dissolved P in runoff during the first storm event after fertilizer application. These results demonstrate the ability of our model to reliably account for a variety of fertilizer types, soil cover types and subsequent fertilizer P adsorption for a variety of times between application and the first runoff event, the amount of fertilizer P released during the first storm event, and the effect of variable storm hydrology (i.e., runoff to rain ratio) on fertilizer P transport in runoff.

Data in Fig. 4b show measured and predicted runoff dissolved P concentrations for all runoff events after the first runoff event. An analysis using the PROC REG function in SAS (SAS, 1999) showed the slope and intercept of the regression line relating predicted and measured values were not significantly different ($p = 0.01$) from unity or zero. The Nash–Sutcliffe efficiency for these data was 0.75. These results demonstrate the ability of our model to reliably account for a decrease in the amount fertilizer P available for runoff through time, and the decreasing rate of fertilizer P release for the
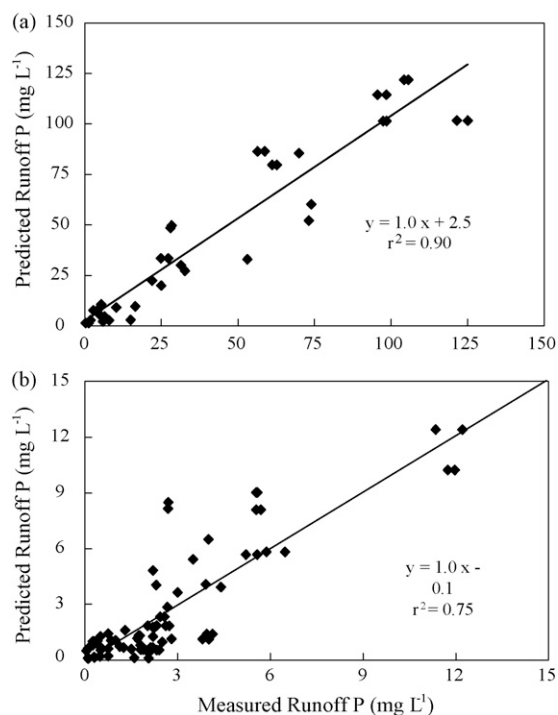

Fig. 4. The relationship between measured and predicted dissolved P concentrations in runoff for (a) the first runoff event after fertilizer application and (b) all other runoff events from 11 published studies.

second and all subsequent rain events after application. Data in Fig. 4b further demonstrate the ability of our model to account for variable storm hydrology on fertilizer P transport in runoff. Results in Fig. 4 also demonstrate the ability of our model to reliably predict dissolved fertilizer P in runoff across a wide range of plot and field sizes up to 9.6 ha.

4. Sensitivity analysis and model limitations

Our model is relatively simple and requires input data for only the amount of fertilizer P applied, the type of soil cover at the time of application, and the amount of rainfall and runoff for each storm event. Other variables or calculations important to the prediction of dissolved P in runoff from fertilizers include only the adsorption of fertilizer P by soil before the first rain event, the fraction of available fertilizer P on the soil surface predicted to be released by rain during any given event, and the P distribution factor, which is calculated from the runoff to rain ratio. Using data from our model validation exercise, we conducted a sensitivity analysis of our model by determining the percent change in runoff dissolved P predictions when increasing and decreasing the values of the following parameters by 10% and 25%: the amount of fertilizer P adsorbed by soil before the first rain event, the fraction of available fertilizer P on the soil surface predicted to be released by rain during any given event, and the P distribution factor, which reflects changes in runoff and rain data.

Sensitivity analysis results showed that predictions of dissolved P in runoff from fertilizer increased or decreased in the same proportion as the change in the amount of fertilizer P adsorbed by soil before the first rain event. This proportional change is expected given the linear nature of model calculations using this parameter. Because adsorption of fertilizer P occurs in our model only before the first rain event, changes in this parameter had no effect on model runoff P predictions for any rain event after the first. Futhermore, if no runoff occurs during the first rain event, then changes in the P adsorption parameter would have no effect at all on model runoff P predictions. Therefore, of the parameters included in the sensitivity analysis, model predictions were least sensitive to the fertilizer P adsorption by soil parameter.

Our sensitivity analysis showed that predictions of dissolved P in runoff also increased or decreased in the same proportion as the change in the fraction of available fertilizer P on the soil surface predicted to be released during a rain event. However, these parameters are constants in the model; and our rainfall simulation data discussed above and our model validation exercise suggest these constants should provide reliable runoff P predictions.

Model runoff P predictions were most sensitive to changes in the P distribution factor, which distributes fertilizer P released by rain between runoff and infiltration during a storm event. Furthermore, because the relationship used to calculate P distribution factors from runoff to rain ratios is non-linear, the effect of changes to the P distribution factor on model runoff P predictions increased as runoff to rain ratios increased (Fig. 5). For example, at a runoff to rain ratio of 0.1, a 10% change in runoff or rain data would cause only about a 3.5% change in runoff P predictions. However, at a runoff to rain ratio of 0.6, a 10% change in runoff or rain data would cause a 23% change in runoff P predictions. A 25% change in runoff or rain data would cause a 66% change in runoff P predictions. This clearly indicates that our model predictions can be quite sensitive to changes in rain or runoff data. Thus, our model will require accurate estimates of rain and runoff input data to reliably predict runoff dissolved P from fertilizer.

Our model currently accounts for soil adsorption of fertilizer P after application according to the type of soil cover (Fig. 1), but considers only widely used, highly water-soluble P fertilizers, such
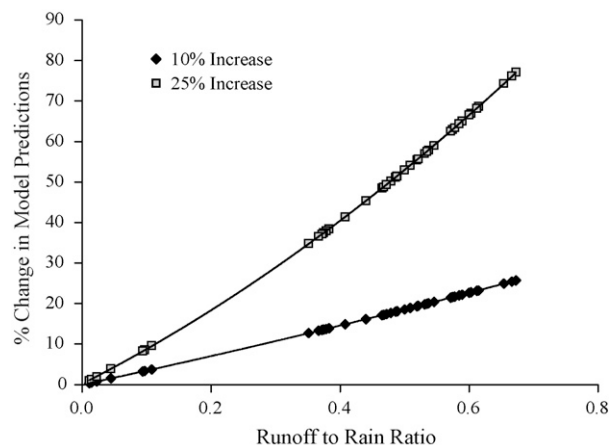

Fig. 5. Model sensitivity analysis results showing the relationship between the change in model runoff P predictions at various runoff to rainfall ratios when increasing runoff to rain ratios by either 10% or 25%.

as superphosphate, triple superphosphate, and mono- and diammonium phosphate. It does not consider poorly soluble or liquid P fertilizers. The model does not account for fertilizer P adsorption variability due to soil properties, such as clay, Fe, Al, or Ca content, or pH. The model also does not account for varying degrees of soil coverage by crop residues or soil moisture content when determining fertilizer P adsorption after application. Finally, our model uses only the runoff to rain ratio to partition fertilizer P released during a storm between infiltration and runoff. This method may not capture the effect of more dynamic storm hydrology, such as when runoff actually occurs during a storm, which is in turn a function of variable rainfall rate during a storm and antecedent soil moisture. Another source of model error may occur when runoff is caused by more than rainfall, such as when re-emergent interflow occurs.

5. Conclusions

Using data from our own simulated rainfall experiments and data from runoff studies reported in the literature, we developed a simple, empirical model to predict the release of P from surface-applied fertilizer during rain and the concentration of dissolved P in runoff when runoff occurs. Our model accounts for adsorption of fertilizer P by soil after application and before the first rain, for the decreasing availability of fertilizer P over consecutive rain events, for the decreasing rate of fertilizer P release through a series of rain events, and for the variable effect of runoff hydrology on the how much fertilizer P released during a storm is actually lost in runoff. Using data from 11 independent runoff studies, we validated that our model can reliably predict dissolved P in runoff from a variety of plot and field sizes, fertilizer types, and types of soil cover and subsequent fertilizer P adsorptions, and across a series of rain and runoff events through time. A sensitivity analysis showed that reliable model runoff P predictions will require accurate runoff and rainfall input data.

Our model requires input data for only the amount of fertilizer P applied, the type of soil cover at the time of application, and the amount of rainfall and runoff for each storm event. These minimal data requirements should make our model fairly straightforward to incorporate into more complex, field or watershed-scale P transport models, such as EPIC, GLEAMS, ANSWERS, or SWAT. Given these models do not currently simulate a pool of fertilizer P on the soil surface or direct loss of fertilizer P in runoff, incorporation of our model should help improve their ability to

reliably predict P loss to the environment for a variety of agricultural land uses.

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