Simple Models for Phosphorus Loss from Manure during Rainfall

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ABSTRACT

Mechanistic, predictive equations for phosphorus (P) transport in runoff from manure-applied fields constitute a critical knowledge gap for developing nonpoint-source pollution models. We derived two simple equations to describe the P release from animal manure during a rainfall event—one based on first-order P desorption kinetics and one based on second-order kinetics. The manure characteristics needed in the two kinetic equations are the maximum amount of water-extractable phosphorus (WEP) and a characteristic desorption time. Water-extractable P can be measured directly but currently the characteristic time can only be obtained by fitting experimental data. In addition, we evaluated two models usually used to estimate P loss from soil, the Elovitch equation and power function, both of which relate P loss to time. The models were tested against previously published data of P release from different manures under laboratory conditions. All equations fit the data well. Of the two kinetic equations, the second-order model showed better agreement with the data than the first-order model; for example, maximum relative differences between the model results and measured data were 2.6 and 4.7%, respectively. The characteristic times varied between 20 min for dairy manure and almost 100 min for poultry manure. The characteristic time did not appear to change with flow rate but decreased with smaller manure aggregates. The parameters for power-function relationships could not be related to measured manure characteristics. These results provide the first step to process-based approximations for predicting P release from manure with time during rainfall shortly after land application, when P losses are the greatest.

PUBLIC AWARENESS of eutrophication and its link to agriculture has lead to legislation encouraging agriculture to reduce its P contributions to streams (Sharpley et al., 2000). The primary pathway of P loss from the majority of agricultural soils is through surface runoff although loss from P can also occur through tile flow and interflow (Vadas et al., 2004). Traditionally, control of particulate P in runoff has been considered sufficient to improve water quality (Sharpley et al., 1994). Recently, however, research has shown that particulate P has a much smaller effect on eutrophication levels than dissolved P (Fozzard et al., 1999).

Given the need to reduce dissolved P losses from agricultural land, models using readily available data are seen as effective tools in predicting dissolved P losses from various parts of the landscape, allowing ranking of areas according to the dissolved P loss (Sharpley et al., 2002). These rankings can then be used to prioritize areas that should be treated first. Because manorial dissolved P loss can overwhelm all other P losses (Edwards and

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Daniel, 1993), accurate physical-based models predicting P release from manure are important.

Tools and models of various complexities are available to predict nonpoint-source P loss (Sharpley and Williams, 1990; Jarvis, 1994; Lewis and McGechan, 2002). These models address loss of P from the soil but not the leaching of dissolved P from manure. Vadas et al. (2004) recently developed a P loss regression type model for manure for total loss per rainfall event. Predicting the timing during the storm is, however, needed when the infiltration rate during the storm varies and part of the released P from the manure enters the soil (Steenhuis et al., 1981). Moreover, regression-based models do not give insight into the processes and may fail for situations outside the range for which they were tested.

Thus, our objective was to develop and evaluate relatively simple, mechanistically defensible mathematical expressions to predict the release of P from manure in rain or other leaching waters. This paper presents four analytical models that predict the release of dissolved P from manure with time. We used previously published laboratory data by Sharpley and Moyer (2000) to test the models' ability to predict total dissolved phosphorus (TDP) release from a variety of manure types. Total dissolved P is defined as the total P after filtration through 0.45-μm filter (Haygarth and Sharpley, 2000). Experiments by Muck (1978) were employed to further explain the dissolved P loss.

MODEL DEVELOPMENT

In this section we derive two kinetic models in the context of leaching dissolved P from manure and we present two other models that are commonly used to predict P loss from soils, namely, the Elovitch and power-function relationships. To derive kinetic models for TDP release from manure during rain or leaching, several simplifications are made. First, based on observations by Kleinman et al. (2002), we assume that only the WEP in manure is available for leaching. The magnitude of the WEP pool depends on the animal, diet, and amendments but can always readily be determined in the laboratory using methods of Sharpley and Moyer (2000) and Kleinman et al. (2002). Second, in the short time frame of a rain event, chemical and microbial transformations of TDP to non-water-extractable forms, and vice versa, are negligible. Third, during a rain and leaching event, TDP in solution is rapidly removed from the manure and, consequently, the TDP release from manure can be modeled as a net desorption process alone. Based on these assumptions, the TDP mass balance per unit mass of manure can be written as:

$$M(t) = M_0 - D(t) \qquad [1]$$

where $M(t)$ is the TDP in the WEP manure pool, M_0 is the initial P in the WEP pool, and $D(t)$ is the cumulative TDP release per unit mass of manure leached out in the rainwater (i.e., kg kg^{-1}).

Kinetic reactions assume that the mass-release rate of TDP

per unit mass of manure, dD/dt, is related to the amount of TDP in the WEP pool (per unit mass of manure on a dry weight basis) remaining in the source matrix following:

$$\frac{dD}{dt} = k_D M^n \qquad [2]$$

where k_D is a reaction constant (kg^{n-1} kg^{1-n} min^{-1}), n is the order of the reaction, and t is time (min). For a first-order reaction $n = 1$ and for a second-order reaction $n = 2$. Substituting Eq. [1] into Eq. [2] gives:

$$\frac{dD}{dt} = k_D[M_0 - D(t)]^n \qquad [3]$$

The cumulative release for a first-order reaction kinetics (i.e., $n = 1$) is obtained by integrating Eq. [3] with time, using the initial condition, $t = 0$, $D = 0$:

$$D(t) = M_0[1 - \exp(-t/\tau_1)] \qquad [4]$$

where $\tau_1 = k_D^{-1}$ is a characteristic time. For a second-order kinetics, $n = 2$, the integration of Eq. [3] gives:

$$D(t) = M_0 \frac{t}{t + \tau_2} \qquad [5]$$

where $\tau_2 = (M_0 k_D)^{-1}$ is a characteristic time for the second-order kinetic reaction.

In Eq. [4] and [5], the mass of TDP released over time, $D(t)$, approaches the initial mass of WEP in manure, M_0. The parameters τ_1 and τ_2 correspond to the characteristic time of desorption, an indicator of how fast the cumulative TDP concentration reaches the maximum. In particular, τ_2 can be interpreted as the "half-life" of WEP in manure during the rainfall event. For large characteristic times the P is released more slowly than for short characteristic times.

Methods for predicting P loss from soils might be applicable to manure as well. The power-function relationship between the cumulative mass of P released, D, and time, t, are commonly assumed, for example, Kuo and Lotse (1973):

$$D(t) = At^B \qquad [6]$$

where A and B are fitted or calibrated parameters. Equation [6] is the starting point of the Vadas et al. (2004) analysis. Another equation that is often used to predict P release from soil is the semi-empirical Elovitch equation (Chien and Clayton, 1980) that can be expressed as:

$$D(t) = \alpha \ln(1 + \beta t/\alpha) \qquad [7]$$

where α ($kg\ kg^{-1}$) and β ($kg\ kg^{-1}\ min^{-1}$) are fitted parameters. The Elovitch equation has been successfully fitted to observe P data from soil data (Chien and Clayton, 1980; Hansen and Strawn, 2003).

MODEL APPLICATIONS

Two sets of published experiments were used to evaluate the P release models: Sharpley and Moyer (2000) and Muck (1978). These experiments are briefly described, followed by a discussion on how well the models fit the data. Full details of the experimental procedures can be found in the original publications.

Sharpley and Moyer (2000) Experiments

Experiments were performed to determine TDP release under artificial rain from six different manure-related products: three manure types (dairy, poultry, and swine), two composts (dairy and poultry), and poultry litter. Subsamples were analyzed within three days of collection. Phosphorus was sequentially extracted from the manures and composts by a modified Hedley fractionation. The total P and WEP for each material are given in Table 1. Dairy manure had the highest portion of WEP. In the experiments, 20 g of each material was uniformly spread over a 15-cm-diameter filter paper. Simulated rainfall was applied daily for five days

Table 1. Measured concentrations of total P and water-extractable phosphorus (WEP) in various types of manure and compost and fitted values of the parameters, M_0 and τ, for the first- and second-order models, Eq. [4] and [5], A and B for the power-function relationship, Eq. [6], and α and β for the Elovitch relationship, Eq. [7], for each material in the Sharpley and Moyer (2000) experiment. Data are fitted to total dissolved phosphorus (TDP).

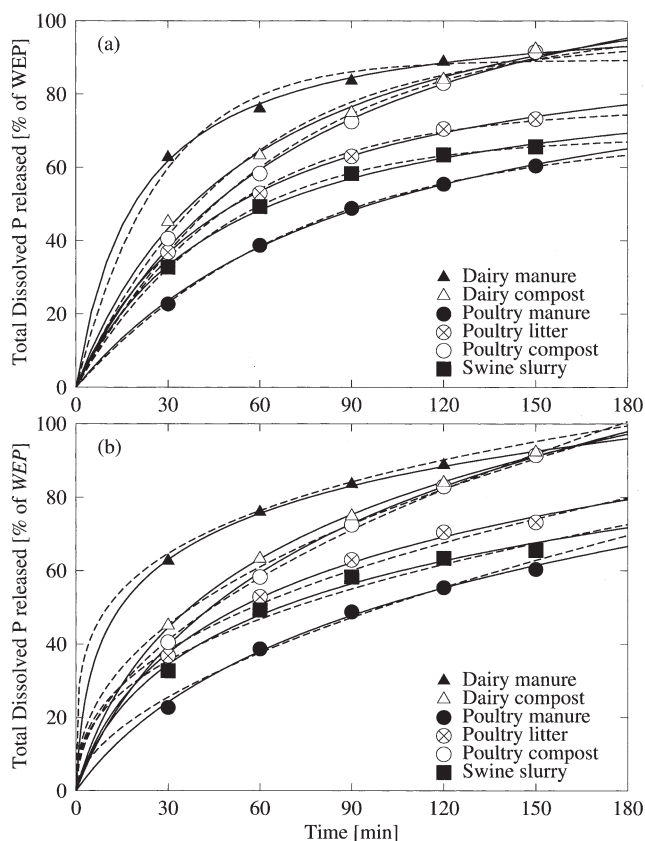|	Dairy manure	Dairy compost	Poultry manure	Poultry litter	Poultry compost	Swine slurry
Measured parameters						
Total P, mg kg^{-1}	3987	16 530	28 650	16 320	9440	32 950
WEP, mg kg^{-1}	2498	2 670	9 790	4 534	2090	7 571
Fitted parameters						
First-order model (Eq. [4])						
M_0, mg kg^{-1}	2231	2 527	6 818	3 456	2075	5 178
τ_1, min	27	52	75	49	65	47
R^2	0.932	0.975	1.000	0.993	0.985	1.000
RD†	0.044	0.047	0.007	0.025	0.042	0.004
Second-order model (Eq. [5])						
M_0, mg kg^{-1}	2584	3 318	9 818	4 493	2852	6 707
τ_2, min	20	56	97	51	77	49
R^2	0.992	0.992	0.998	0.998	0.994	0.995
RD†	0.015	0.026	0.017	0.014	0.026	0.021
Power function (Eq. [6])						
A, mg kg^{-1} min^{-1}	715	281	371	432	156	686
B, dimensionless	0.24	0.43	0.56	0.41	0.5	0.4
R^2	0.992	0.998	0.981	0.98	0.998	0.959
RD†	0.015	0.013	0.052	0.01	0.013	0.058
Elovitch function (Eq. [7])						
α, mg kg^{-1}	468	918	3 259	1 214	869	1 794
β, mg kg^{-1} min^{-1}	437	81	116	124	46	196
R^2	0.999	0.999	0.995	0.994	0.999	0.981
RD†	0.006	0.01	0.028	0.023	0.013	0.039

† Standard error/observed mean.

Fig. 1. Cumulative dissolved total P leached from manures and composts with time. Values are expressed as percentage of total water-extractable phosphorus (WEP). Data from Sharpley and Moyer (2000). (a) Comparison of first-order (dashed lines) and second-order (solid lines) kinetic models. (b) Comparison of power function (dashed lines) and Elovitch (solid lines) relationships.

Table 2. Coefficients of correlation (R^2) of measured water-extractable phosphorus (WEP) and total phosphorus (TP), and fitted parameters of the four models: M_0 and τ_1 (first-order kinetics), M_0 and τ_2 (second-order kinetics), A and B (power-function model), and α and β (Elovitch model).

		R^2	
Model	Fitted parameter	WEP	Total P
First-order	M_0	0.996	0.762
	τ_1	0.222	0.202
Second-order	M_0	0.975	0.723
	τ_2	0.263	0.210
Power function	A	0.054	0.021
	B	0.223	0.261
Elovitch	α	0.901	0.639
	β	0.015	0.115

and the experimental data does not necessarily mean that the results are physically realistic. A more discriminating evaluation consists of comparing the values of the fitted parameters with corresponding measured manure characteristics. To do this we linearly regressed the fitted values against the measured values (see Table 2). Only M_0 in both kinetic models and α in the Elovitch model had R^2 values greater than 0.25, indicating that only these parameters could be statistically related to a measured manure characteristic. They were related better to WEP ($R^2 > 0.9$) than to the total P in the manure ($R^2 > 0.64$). The values of M_0 and α as function of measured WEP are shown in Fig. 2 along with linear regressions. For the second-order kinetic models, the regression was not significantly different (at the 0.05 significance level) from the 1:1 line (slope = 0.88 ± 0.07). The regression slopes for the first-order kinetic model and the Elovitch model were both significantly (at the 0.05 significance level) less than unity, indicating that both models underestimated the TDP in the manure WEP pool. However, the first-order model gave significantly higher estimates of WEP than the Elovitch model. Although the power-function relationship, Eq. [6], has worked well in soil studies, it cannot be theoretically derived because the units of parameters are dimensionally meaningless, or, at least, their meaning is not clear.

We also analyzed the kinetic models with respect to organic and inorganic P data (also Sharpley and Moyer, 2000) and found the models fit these data similarly as well as they fit to the TDP data (data not shown). For inorganic P the R^2 values range from 0.97 (dairy manure) to 1.00 (poultry manure) and the organic P R^2 values range from 0.89 (poultry manure) to 1.00 (poultry litter). For the inorganic fraction, the kinetic models' M_0 values correlated with the inorganic WEP fraction (slope = 0.92 ± 0.14 and 1.01 ± 0.26 for the first- and second-order models, respectively). For the organic P fraction, the slope of the regression line between measured organic WEP and M_0 was significantly ($\alpha = 0.05$) less than 1 for both models (slope = 0.62 ± 0.22 and 0.75 ± 0.24 for the first- and second-order models, respectively), and estimated fractions were substantially lower than observed. This was not surprising because the assumption of an absence of transformation to non-water-extractable form is less likely to hold for the organic fraction. This was not problematic for the prediction of TDP from manure because the organic fraction was only a small fraction of the total dissolved P.
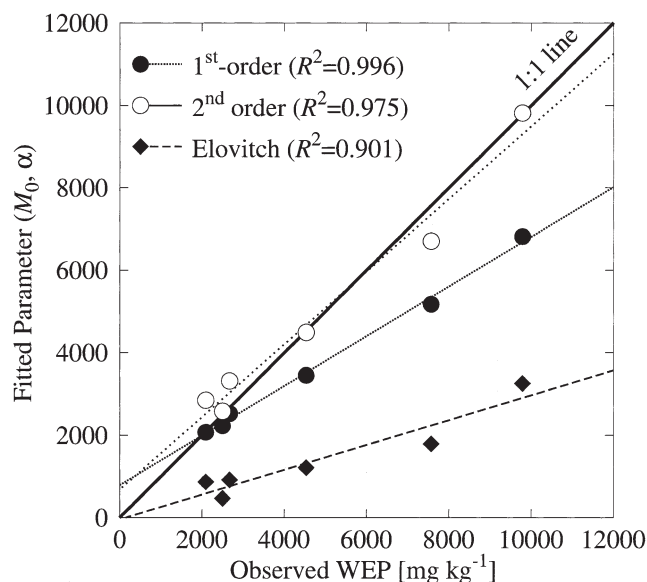
for 30 min, at a constant intensity of 70 mm h^{-1}; experiments were triplicated. For each event, water samples were collected, filtered, and analyzed for fractions of dissolved P. The samples were refrigerated between each event, minimizing the transformation of WEP into non-water-extractable forms between rainfall events.

Because the manure was refrigerated between simulated rainfall events and, consequently, P transformations were minimal, we merged Sharpley and Moyer's (2000) five 30-min events into a single 150-min event for the regression analyses. The first- and second-order kinetic models, Eq. [4] and [5], the power-function, Eq. [6], and the Elovitch model, Eq. [7], were fitted to the experimental data with the Levenberg–Marquardt least-squares method (Marquardt, 1963). Figure 1a shows the first-order (dashed lines) and second-order (solid lines) kinetic models and Fig. 1b show the power-function (dashed lines) and Elovitch model (solid lines). The experimental data normalized by the initial WEP mass are represented by symbols in Fig. 1. Table 1 presents the fitted parameter values and their standard errors for the four models and statistical evaluations of the model fits to the data, R^2 and relative difference (RD; standard error/mean). All R^2 values are near one and the relative differences are all small indicating that all the models performed similarly well.

The excellent agreement between the model results

Fig. 2. Comparison between Sharpley and Moyer's (2000) observed water-extractable phosphorus (WEP) in the manure and fitted parameter M_0 for the first- and second-order kinetic models, and the parameter α for the Elovitch model. The dashed lines are the best-fit linear regressions lines. The solid line is the 1:1 line.

Muck (1978) Experiments

The Sharpley and Moyer (2000) experiments were limited in the range of physical manure and leaching characteristics they evaluated, especially with respect to characteristics other than manure type that might influence the characteristic time parameter in the kinetic models (Eq. [6] and [7]), that is, the two most promising of the four tested for both TDP and inorganic P. We fitted the kinetic models to the dissolved orthophosphate concentration leached from poultry manure by Muck (1978); these experiments used various-sized manure aggregates and several leaching-flow rates. Total dissolved P was not measured. In the Muck (1978) experiments, poultry manure samples were collected from the Cornell Animal Waste Management Laboratory. The samples were air-dried to a moisture content of about 10% on a mass basis, and fractionated using standard U.S. soil sieves, 1/4", #4, #8, #16 and #30, with mesh gaps equal to 6.25, 4.75, 2.36, 1.18, and 0.60 mm, respectively. Ten grams of each size of manure aggregate were oven-dried at 104°C for 10 min and then placed in a laboratory column. Distilled water was leached upward through the columns at different flow rates through the bottom of the column. Flow rate occasionally varied during the experiments (Muck, 1978). In total, 23 experiments were run. Leachate was collected at regular time intervals, centrifuged, and filtered, and the concentration of soluble orthophosphate was measured by the stannous chloride method (American Public Health Association, 1978) after filtering through a 0.45-μm filter. The initial mass of soluble orthophosphate and total orthophosphate was measured (Table 3) but, according to Muck (1978), some of values are probably underestimated.

The two kinetic models, Eq. [6] and [7], were fitted, again using the Levenberg–Marquardt least-squares

Table 3. Concentration of soluble and total orthophosphate in air-dried poultry manure (Muck, 1978).

	Sieve size (mm)				
	0.60	1.18	2.36	4.75	6.25
	mg kg^{-1}				
Soluble orthophosphate	2740	2 640	2 720	2 910	3 280
Total orthophosphate	–	19 320	18 960	25 650	20 860

method, to the orthophosphate data for each experiment. As with the Sharpley and Moyer (2000) analysis, the two fitted parameters were the initial mass of dissolved orthophosphate, M_0, and the characteristic time, τ.

The kinetic models again fit the Muck (1978) data very well, in almost all but three cases, the R^2 is greater than 0.99. The lowest value was 0.97 for aggregate size #30 with a flow rate 935 mm h^{-1} for the first-order kinetic model. As an example, in Fig. 3, the observed data for one aggregate size, diameter 4.75 mm, and different flow rates, 203, 218, 920, and 935 mm h^{-1}, are compared with fitted curves using the first- and second-order models (dashed lines and solid lines, respectively).

To check that the fitted results were physically realistic, the fitted initial mass, M_0, was compared with the measured initial mass. There was no apparent trend in M_0 with either flow rate or aggregate size. However, the average values of M_0 for the first-order model are closer to the measured initial soluble orthophosphate concentration (Table 3) than the average M_0 value. For the second-order model M_0 values are consistently higher than the measured initial soluble orthophosphate concentrations.

Fitted values for the characteristic time, τ, for the first- and second-order models with respect to flow rate and aggregate size are reported in Fig. 4. It appears that τ, the characteristic time, decreased slightly with increased flow rates; however, the trend is not strong or particularly obvious (Fig. 4a). The characteristic time, τ, was strongly correlated with the aggregate size for both models (Fig. 4b). Smaller aggregate sizes were associated with smaller characteristic times. Note that because the leaching of P was done with upward flowing water, the
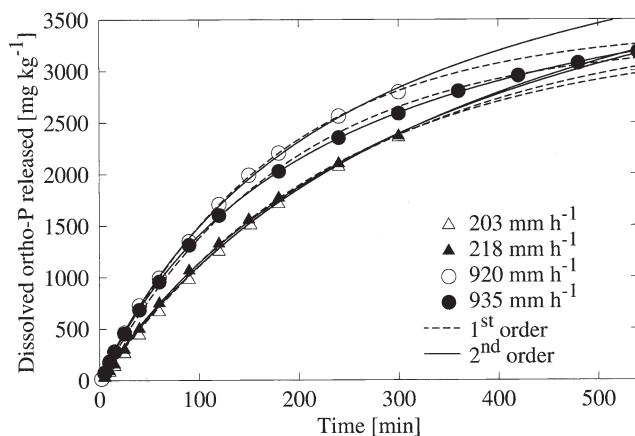

Fig. 3. Comparison of Muck's (1978) observed orthophosphate release from the manure data (symbols) and predictions using the first- (dashed lines) and second-order models (solid lines) for different flow rates and an aggregate size of 4.75 mm.
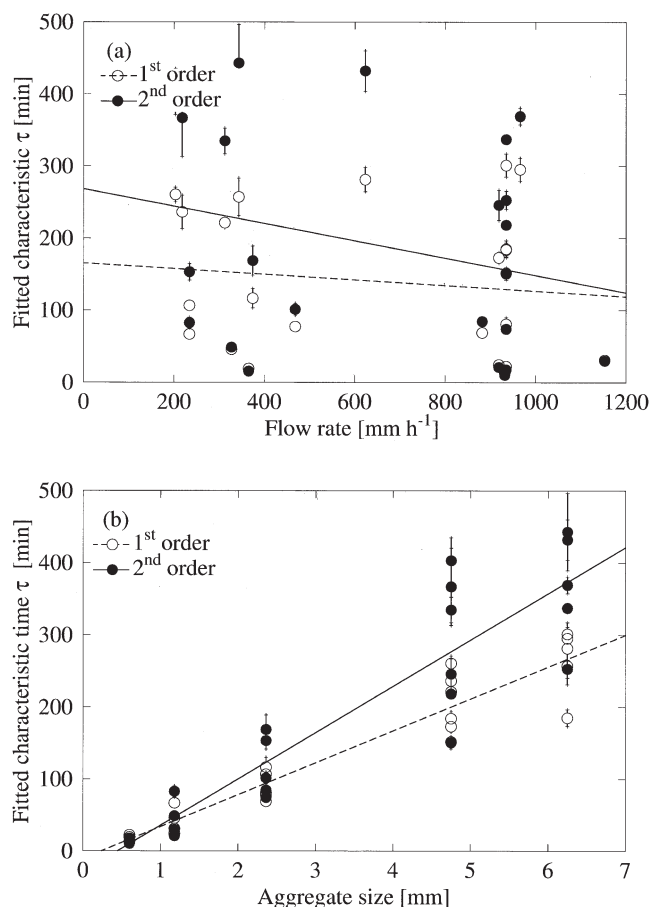
Fig. 4. Comparison between the estimates of characteristic time τ for each model, applied to the Muck (1978) experimental data: (a) relative to experimental flow rates and (b) relative to aggregate sizes. Open symbols are first-order results; solid symbols are second-order results; dashed line is regression for first-order results; solid line is the regression for second-order results. Error bars are $\pm 95\%$ confidence interval.

ately after application, M_0, can be calculated by functions given in Vadas et al. (2004). We expect that general expression for characteristic time can be derived also from the same set of experiments on which Vadas et al. (2004) based their regression model for P loss. While their equation is intended to be used in simple P index type of calculations, ours is more suitable for computer models.

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results are only qualitative indicators for rainfall. More experiments with rainfall are needed to quantitatively develop this relationship.

CONCLUSIONS

The two kinetic models for release of P from the manure are ideal candidates to be used in the new hybrid models to predict the P movement in the landscape such as proposed by Lewis and McGechan (2002). The kinetic equations can predict the concentration of TDP and orthophosphate release from manure as a function of time during a rainfall. This allows one to use these equations to calculate the P loss in runoff in situations where, for example, the infiltration is high in the beginning of the storm and decreases toward the end, by simply multiplying the concentration of P in the rain by the portion of runoff. The only input data that is required is the initial amount of water-extractable P in the manure at the time of rainfall, M_0, and the characteristic time. In a field situation, where it does not rain immedi-