Including Source-Specific Phosphorus Mobility in a Nonpoint Source Pollution Model for Agricultural Watersheds

Zachary M. Easton1; M. Todd Walter2; Elliot M. Schneiderman3; Mark S. Zion4; and Tammo S. Steenhuis5

Abstract: Most widely used nonpoint source models associate pollutant loads almost exclusively with land use via pollutant export coefficients and some kind of runoff coefficient. Not surprisingly, the range of management options suggested by such models’ simulations are largely linked to changes in land use. This problem is addressed by developing models of dissolved phosphorus (DP) mobility for specific agricultural sources: manure, fertilizers, soil/plant complexes, and impervious surfaces and those associated with baseflow P loads. These models are coupled with a spatially distributed hydrologic model, the variable source loading function model. The model was applied to a small (164 ha), upstate New York watershed and tested against 1996–2000 stream flow and DP data. The source-specific model required no direct calibration of parameters compared to eight parameters needed in a similar export coefficient type model. Both models predicted stream DP loads well but the source-specific model provided additional insights into, for example, how much DP in the stream was derived from accumulated soil P as opposed to direct leaching from manure. This type of information is necessary to develop and assess a full range of options for best management practices, especially those that involve nonstatic activities such as manure spreading.


CE Database subject headings: Phosphorus; Watersheds; Agriculture; Water pollution; Nonpoint pollution.

Introduction

In order to protect water quality, watershed managers tasked with implementing strategies for controlling nonpoint source (NPS) pollution need water quality models that can correctly identify both the locations where runoff is generated and contributions from specific pollutant sources. Here we will consider NPS phosphorus (P) loading to surface waters in agricultural watersheds, which is a considerable problem in many areas of the country (Allan 1995; DeLaune et al. 2004; Sharpley et al. 2004). Hamilton et al. (2004) found more than 70% of sampled agricultural streams exceeded the USEPA P goal for preventing nuisance plant growth. However, few, if any, of the currently used water quality models realistically model both hydrology and the processes governing pollutant mobilization.

Many current water quality models use some form of the Natural Resource Conservation Service (formerly the Soil Conservation Service) curve-number (CN) equation (USDA-SCS 1972) to predict storm runoff and use it in ways that implicitly assume an infiltration excess (or Hortonian) Horton (1933) response to rainfall (Walter and Shaw 2005); i.e., where storm runoff is only generated when the rainfall intensity exceeds the soil’s infiltration capacity. However, in humid, well-vegetated regions, particularly those with permeable soils underlain by a shallow restricting layer, rainfall intensity rarely exceeds infiltration capacity (Walter et al. 2003) and storm runoff is usually generated from parts of the landscape that are saturated, i.e., saturation-excess runoff (Dunne and Black 1970; Dunne and Leopold 1978; Beven 2001; Srinivasan et al. 2002; Needlemann et al. 2004). The extent of saturated, runoff source areas changes over time due to a suite of hydrological processes referred to en mass as variable source area (VSA) hydrology. Lyon et al. (2006) demonstrated that a substantial fraction of saturation-excess runoff is rapid, shallow subsurface flow from areas that are nearly saturated; thus, “saturation” does not necessarily mean “saturated-to-the-surface” as implied in many early works on VSA hydrology (as highlighted in Dunne and Leopold 1978).

Lyon et al. (2004), building on Steenhuis et al. (1995), showed how CN models can be used to predict the distribution of VSAs. Schneiderman et al. (2007) used this body of work to successfully modify a widely used water quality model, namely, the general watershed loading function (GWLF) (Haith and Shoemaker 1987), so that it explicitly simulated VSA hydrology; the resulting model is referred to as the variable source loading function (VSLF) model.

Although VSLF has been shown to correctly predict the distribution of VSAs in the landscape (Schneiderman et al. 2007) it retains the overly simple routines for predicting pollutant transport that are conceptually similar to those employed in the...
original GWLF model, namely, export coefficients that are either constant for a watershed or only dependent on land use (Schneiderman et al. 2002). An export coefficient simply relates the pollutant loading (kg day\(^{-1}\)) to discharge. Often the export coefficients are simple multipliers, such as the export coefficient Schneiderman et al. (2002) used to predict dissolved P (DP) load associated with basflow, \(D_B\) (kg day\(^{-1}\)).

\[
D_B = u_B B_i
\]

where \(u_B\)=basflow export coefficient (kg m\(^{-3}\)); and \(B_i\)=basflow (m\(^3\) m\(^{-2}\) day\(^{-1}\)). Sometimes modelers adjust the export coefficient to account for nonlinear relationships between pollutant load and discharge, such as the power function used by NYCDep (2007) to predict DP loads in runoff, \(D_R\) (kg day\(^{-1}\))

\[
D_R = E_{AC}(A + (BQ^C))Q
\]

where \(E_{AC}\) (kg m\(^{-1}\))=runoff export coefficient, a function a land use, \(A\), \(B\), and \(C\)=unitless calibration parameters; and \(Q\)=runoff (m\(^3\) m\(^{-2}\) day\(^{-1}\)).

Predictions based on export coefficients like these provide little insight into the processes controlling nutrient losses. In addition, when multiple export coefficients corresponding to differing land uses are simply calibrated to observed stream DP data, modelers are faced with the problem of equifinality (Beven 1996a,b). What is needed are models that require little or no calibration (i.e., the model parameters can be independently quantified) and can be used to predict nutrient contributions from multiple sources associated with a single land use. For example, it would be useful to separately predict phosphorus (P) loads from field-applied manure or fertilizer and P loads from the soil to make better judgments about the influence of agricultural land management on water quality.

The goal of this study is to develop and adapt a distributed watershed loading model for predicting DP export from agricultural watersheds. We use the previously tested, spatially distributed VSLF model (Schneiderman et al. 2007) to predict magnitudes and source areas of runoff. The mobility of DP is predicted separately for different sources: manure, chemical fertilizer, soil/plant complexes, and impervious surfaces, and DP associated with basflow conditions based largely on previous work by Gérard-Marchant et al. (2006), Hively et al. (2006), and Easton et al. (2007). The model is tested against 4 years of observed data from 164 ha agricultural watershed in the Catskill Mountains of New York state. For comparison purposes we also calibrated the traditional export coefficient version of VSLF and applied it to the same farm over the same period of time.

**Hydrologic Model Description**

The hydrologic model, VSLF, is described fully in Schneiderman et al. (2007), but briefly outlined here. VSLF is based on work by Steenhuis et al. (1995) and Lyon et al. (2004) who demonstrated how the CN (USDA-SCS 1972) method could be conceptualized to predict runoff from VSAs and used to identify where the VSAs are in the landscape. Steenhuis et al. (1995) showed that the fraction of the watershed saturated during a storm (\(A_i\)) can be estimated by taking the derivative of the CN equation for runoff (\(Q\)) with respect to effective precipitation (\(P_e\)). The CN equation is (USDA-SCS 1972) (all unit in mm)

\[
Q = \frac{(P_e)^2}{(P_e + S_e)}
\]

and

\[
A_i = \frac{dQ}{dP_e} = 1 - \frac{S_e^2}{(P_e + S_e)^2}
\]

where \(S_e\)=depth of effective available storage (or storage deficit) over the whole watershed. If we have a distribution of effective available storages, \(\sigma_e\), any location \(i\) will begin generating runoff when \(P_e = \sigma_e\). Thus, replacing \(P_e\) in Eq. (4) with \(\sigma_e\) results in a relationship for the percent of the watershed area, \(A_e\), which has an effective available soil water storage \(\leq \sigma_e\) for a given overall watershed storage of \(S_e\) (Schneiderman et al. 2007)

\[
A_e = 1 - \frac{S_e^2}{(\sigma_e + S_e)^2}
\]

Solving for \(\sigma_e\) gives the maximum effective local soil moisture storage deficit within any particular fraction, \(A_e\), of the overall watershed area (Schneiderman et al. 2007)

\[
\sigma_e = S_e \left( \frac{1}{(1 - A_e)} - 1 \right)
\]

In keeping with the original concept of the CN equation, we consider an initial abstraction, \(I_e\) which must be filled before runoff is initiated, i.e., \(P_e = P - I_e\), where \(P\)=total precipitation. Runoff at a location in the watershed, \(Q_e\), can now also be expressed for the saturated area simply as:

for saturated parts of the watershed

\[
Q = P_e - \sigma_e \quad \text{for} \quad P_e > \sigma_e
\]

for unsaturated parts of the watershed

\[
Q = 0 \quad \text{for} \quad P_e \leq \sigma_e
\]

Lyon et al. (2004) and Schneiderman et al. (2007) showed that the spatial distribution of the runoff response correlates to the distribution of an aerially weighted soil-topographic index (STI) (Beven and Kirkby 1979)

\[
\text{STI} = \ln \left( \frac{a}{T \tan \beta} \right)
\]

where \(a\)=upslope contributing area per unit of contour line (m); \(T\)=transmissivity (soil depth \times saturated hydraulic conductivity); and tan(\(\beta\))=local topographic slope. The watershed is divided into \(N\) equal areas along iso-STI lines and each area is assigned a wetness index ranking the propensity of each area to saturate. For each wetness index the local storage deficit, \(\sigma_{e,i}\), is determined by integrating Eq. (6) over the fraction of the watershed associated with what that wetness index represents (Schneiderman et al. 2007)

\[
\sigma_{e,i} = \int_{A_{i,j}}^{A_{i,j+1}} \sigma_{e,i} dA_i = \frac{2S_e \sqrt{1-A_{i,j}} \sqrt{1-A_{i,j+1}}}{(A_{i,j+1} - A_{i,j})} - S_e
\]

where each area, defined by a specific wetness index, is bounded on one side by the fraction of the watershed that is wetter, \(A_{i,j}\), and on the other side by the fraction of the watershed that is dryer, \(A_{i,j+1}\). VSLF requires daily temperature and precipitation data, land use distribution, the land-use-related runoff export coefficients, and the areas of individual hydrologic response units (HRU), defined by the intersection of land use and wetness class. Additional
Source-Specific Phosphorus Model

We developed our P model around the currently recognized sources of DP from agricultural watersheds, namely: animal manures, chemical fertilizers, soil/plant complexes, and impervious areas (e.g., barnyards). We also recognize that there is substantial DP transported under baseflow conditions, although the immediate source is not necessarily well identified. Source-specific DP models are described here.

Dissolved P Loss from Manure and Fertilizers

Manure and chemical fertilizers clearly contribute substantial amounts of DP to streams (Sharpley et al. 2001, 2002; Walter et al. 2001), and sometimes manure, in particular, is the dominant source (Gérard-Marchant et al. 2005). Based on published data, Gérard-Marchant et al. (2005, 2006) showed that available or mobile manure DP declined exponentially following field application

\[ M_{F,t} = M_{F,\Delta t} \exp \left( -\frac{\Delta t}{\tau} \right) - D_{F,t-\Delta t} \] (10)

where \( \tau \) = immobilization rate (day); \( M_{F,t} \) = available water-extractable P at time \( t \) per unit area (kg m\(^{-2}\) day\(^{-1}\)); \( M_{F,\Delta t} \) = water-extractable P on the previous time step (kg m\(^{-2}\) day\(^{-1}\)); and \( D_{F,t-\Delta t} \) = manure DP loss in runoff (kg m\(^{-2}\) day\(^{-1}\)) from the previous time step. Following manure application, the water initial extractable P in the manure [a fraction, \( \omega \), of the total manure P, \( M_T \), (kg m\(^{-2}\)) in the manure] is added to the amount already present on the soil surface. A time step, \( \Delta t \), of 1 day is used in the model.

The loss of manure DP at time \( t \) in runoff \( (D_{F,t}) \) on each manured/fertilized location in the watershed is modeled as a second-order kinetic reaction (Easton et al. 2007)

\[ \frac{dD_{F,t}}{dQ_t} = k_f(M_{F,t} - D_{F,t})^2 \] (11)

where \( k_f \) (m\(^3\) kg\(^{-1}\)) = reaction constant. Eq. (11) is modified from Gérard-Marchant et al. (2005), who considered the derivative with respect to time under steady-state rainfall, i.e., \( dD_{F,t}/dt \). Here we transposed their model, replacing time with runoff, \( Q_t \), (m\(^3\) m\(^{-2}\) day\(^{-1}\)) (Easton et al. 2007). In fact, reducing the available DP simply as a function of time results in overpredictions of available P when large events remove much of the available DP (data not shown). Integrating Eq. (11) results in a function of DP loss from manured/fertilized areas as a function of runoff

\[ D_{F,t} = \left[ M_{F,t} \left( \frac{k_f M_{F,t} Q_t}{1 + k_f M_{F,t} Q_t} \right) \right] \] (12)

Note, although this discussion has focused on DP from manures, chemical fertilizers can be modeled the same way, albeit with appropriate model parameters (Easton et al. 2007). Chemical fertilizers were not significant in our test system so we will not discuss them further.

P Loss from Impervious Surfaces

In agricultural watersheds, barnyards serve as concentrated sources of P and are often completely impervious to facilitate ease of maintenance, or nearly so from heavy traffic. Hively et al. (2005) report steady-state runoff rates from a barnyard at 100% of precipitation from a simulated event. We use an accumulation/wash-off equation to model the contribution of DP from barnyards and similar “impervious” areas. Because the contribution of the barnyard to DP stream loads varies temporally (e.g., in northern latitudes, there is higher contribution in the winter when cows are confined and lower in the summer when they are pastured) the modeled rate of P buildup may vary seasonally. Accumulation is modeled with an exponential buildup equation (Easton et al. 2007)

\[ M_{I,t} = M_{I,\text{Max}} - \left( M_{I,\text{Max}} - M_{I,t-\Delta t} \right) \exp \left( -k_I \Delta t \right) \] (15)

where \( M_{I,t} \) = DP load (kg m\(^{-2}\) day\(^{-1}\)) in the barnyard; \( M_{I,\text{Max}} \) = maximum DP load (kg m\(^{-2}\)) from the previous event; \( M_{I,\text{Max}} \) = maximum DP load (kg m\(^{-2}\)) in the barnyard; and \( k_I \) = exponential buildup rate factor (day\(^{-1}\)). Wash-off of DP from the barnyard is estimated using a first-order relationship with respect to runoff, \( Q_t \).
\[ D_{t,j} = M_k [1 - \exp(-k_{i,j}Q_{i,j})] \] (16)

where \( D_{t,j} \) = DP load (kg m\(^{-2}\) day\(^{-1}\)) in runoff from the impervious surface; \( k_{i,j} \) = wash-off coefficient (m\(^2\) m\(^{-3}\)); and \( Q_{i,j} \) = runoff (m\(^3\) m\(^{-3}\) day\(^{-1}\)). \( D_{t,j} \) is subtracted from \( M_{k,i} \) before the next day is calculated.

**P Loss in Baseflow**

Baseflow, although it does not generally contain high P concentrations, acts as a constant background source of P (McDowell et al. 2001), and may contribute substantially to cumulative P loads (Caruso 2000; Maguire and Sims 2002; Hively et al. 2006). We have a poor understanding of where the baseflow-associated P is derived. Some researchers suggest prolonged transport via preferential flow paths, including tile drains, contribute substantially to baseflow P loads (Hooda et al. 1999) and others attribute baseflow P to a suite of factors including subsurface geology, climate, land use, and land management (Wayland et al. 2003). In-stream processes constitute another likely source of baseflow P. In light of the unresolved controlling processes, a lumped export coefficient approach is used to model baseflow P loss

\[ L_{B,t,j} = \mu_{B,B}B_t \] (17)

where \( L_{B,t,j} \) = DP load (kg day\(^{-1}\)) in baseflow; \( B_t \) = baseflow at the watershed outlet (m\(^3\) day\(^{-1}\)); and \( \mu_{B,B} \) = baseflow DP export coefficient adjusted for temperature with an Arrhenius equation similar to soils [Eq. (14)]

\[ \mu_{B,B} = \mu_{T,B}Q_{100}(T - T_b)/10 \] (18)

where \( \mu_{T,B} \) and \( Q_{100} \) = parameters. Since baseflow originates from deeper in the soil profile than surface runoff, we assume the \( T_b \) parameter should reflect the greater temperature damping observed at a greater soil depth, \( Z_t \) (m). Thus, we vary temperature at a depth \( Z_T \) in the soil using a sine function (Brutsaert 1982; Hively et al. 2006)

\[ T(t,Z_t) = T_{AVG} + \Delta T \sin[t \omega(t - t_b) - Z_t/Z_c] \] (19)

where \( T_{AVG} \) (°C) = annual average temperature at the soil surface; \( \Delta T \) (°C) = maximum temperature deviation from the average; \( \omega = 2\pi/365 \) = radial frequency (day\(^{-1}\)); \( t_b \) = time lag (day), so that \( \omega t_b = t_b \) when \( T(t,0) = T_{AVG} \); and \( Z_c \) (m) = equivalent dampening depth. Since the baseflow coefficient, \( \mu_{B,B} \), integrates the effects of the entire watershed on DP loss it is taken directly from observed baseflow DP concentrations.

**Stream Dissolved P Loss**

The total load of DP to the stream (\( L_{T,t,j} \)) (kg day\(^{-1}\)) = sum of the contributions from manure/fertilizers (\( D_{F,F,j} \)), the plant/soil complex (\( D_{S,j} \)), the barnyard (\( D_{I,j} \)), and in baseflow (\( L_{B,t,j} \))

\[ L_{T,t,j} = L_{B,t,j} + \sum_{j=1}^{N} A_j(D_{F,j,t} + D_{S,j} + D_{I,j}) \] (20)

where \( A_j \) = area of each wetness index class.

**Model Application and Test**

**Watershed Description**

We applied our model to a 164 ha dairy farm watershed in the Cannonsville basin in Delaware County, New York. The farm watershed drains into the West Branch of the Delaware River above the Cannonsville reservoir. The climate is humid continental, with an average temperature of 8°C, and an average precipitation of 1,123 mm year\(^{-1}\) (NCDC 2005). The topography is steep and winter snow accumulation and spring snowmelt dominate the hydrology (Bishop et al. 2005). The farm has 102 milking cows and over 70 heifers. Land use on the farm consists of deciduous forest (52.2%), brush/shrub (2.6%), pasture (8.7%), permanent hay (23.7%), cropland (7.4%), water (0.7%), barnyard/impervious surfaces (1.7%), and buffer (3.2%) (Fig. 1). Daily stream flows were recorded on a 10-min basis by a gauge at the watershed outlet, and integrated over each day (Bishop et al. 2003, 2005, and 2006). Observed DP concentrations were derived from flow-weighted sampling at the watershed outlet, as described in Bishop et al. (2003, 2005, and 2006). Dissolved P is defined as molybdate reactive orthophosphate in filtered (45 μm) Kjeldahl digested water samples. Daily minimum and maximum temperatures were obtained from a weather station located in Delhi, N.Y., about 20 km southwest of the watershed (NCDC 2005).

**Input Data**

All data correspond to the 1996–2001 period. Weather data included daily precipitation and minimum and maximum temperature. Watershed data included land use (Fig. 1), topography [10 m horizontal, 0.1 m vertical digital elevation model (DEM)], (NYCDEP 2007), and soils (SSURGO soil database), (USDA-NRCS 2000). The \( \alpha \) and \( \beta \) values used to calculate STIs [Eq. (8)] were derived directly from a 10 m DEM of watershed, while \( T \) (soil depth × saturated hydraulic conductivity) is extracted from the SSURGO soil database (USDA-NRCS 2000) for each 10 m cell. Plant/soil complex export coefficients are distributed according to STP values [Fig. 2(b)]; the parameter estimation section explains how coefficients were quantified. Agricultural best management practices (BMPs) were implemented on this farm as part of comprehensive nutrient management plan (NMP). Some consisted of a variety of land use changes (e.g., riparian buffer areas, barnyard realignment, etc.), which are reflected in the land use map (Fig. 1). BMPs also included a specific manure spreading.
and fertilizer application schedule for farm fields, precision feeding, and exclusionary fencing to prevent livestock from direct stream access. The producer for this farm kept records of manure and fertilizer applications over the test period that we used in our model.

Parameter Estimation

Calibration of the VSLF hydrology and stream flow was performed during the 1996–1998 period (Fig. 3). Details of the calibration procedure are described in Schneiderman et al. (2002). Calibration was completed with a multistep process to minimize bias and maximize the Nash–Sutcliffe (Nash and Sutcliffe 1970) efficiency (E) as follows. Briefly, the effective storage \( S_e \) (or CN) for pervious land was calibrated to cumulative runoff for the non-growing season, the runoff recession coefficient was calibrated to baseflow-separated runoff, and the snowmelt factor was calibrated to streamflow. Next, a soil moisture adjustment factor (Saxton 1982), which adjusts the \( S_e \) and \( \sigma \) values based on soil moisture, was calibrated to cumulative runoff during the growing season. Finally, the baseflow recession coefficient was optimized to measured baseflow.

For the P model, the variables that affect DP concentration in the surface runoff are land use, STP, time since fertilizer/manure application, and temperature. Twelve parameters are needed for the DP model, all of which were independently quantified a priori (Table 1). These variables are: the immobilization rate (\( \tau \)) [Eq. (10)], the reaction constant (\( k_r \)) [Eqs. (11) and (12)], water extractable P (\( \omega M_P \)), base temperatures for soil (\( T_b \)) [Eq. (14)], and baseflow (\( T_B \)) [Eq. (18)], the maximum DP load that can accumulate on in the barnyard (\( M_{I,M\alpha} \)) [Eq. (15)], the exponential buildup factor (\( k_L \)) [Eq. (15)], the wash-off coefficient (\( k_{L,D} \)) [Eq. (16)], the base coefficients for soil (\( Q_{100b} \)) [Eq. (14)] and baseflow (\( Q_{100b} \)) [Eq. (18)], and the reference export coefficient for baseflow (\( \mu_{F, b} \)) [Eq. (18)] and soil (\( \mu_{F, S} \)) [Eq. (14)]. All 12 of these parameters were determined from field measurements, published values, or logical a priori criteria. Table 1 summarizes the parameter values. Below the sources are discussed in some detail.

Manured landscapes were identified from the NMP of the farm. Based on these records, the average P application rate was \( 78 \times 10^{-4} \) kg m\(^{-2} \) year\(^{-1} \) but varied between 57 and 115 \( 10^{-4} \) kg m\(^{-2} \) year\(^{-1} \). Individual application rates varied between \( 8 \times 10^{-4} \) and \( 19 \times 10^{-4} \) kg P m\(^{-1} \). In each application, the initial water extractable P (\( \omega \)) was set to a priori to 65% of (\( M_P \)), i.e., \( 5.2 \times 10^{-4} \) to \( 12.4 \times 10^{-4} \) kg DP m\(^{-2} \) and the immobilization rate (\( \tau \)) [Eq. (12)] was set to 7 days based on data from Gérard-Marchant et al. (2005).

The plant/soil complex export coefficients, \( \mu_{F, S} \), for each field on the farm as directed by the NMP, were based on STP values from the top soil (Sharpley et al. 2002; Maguire and Sims 2002; McDowell and Sharples 2003; DeLaune et al. 2004) and rainfall simulations performed in the watershed by Hively et al. (2005). A soil test on P was determined using the Morgan soil test extract (McIntosh 1969) and ranged from 1 to 385 mg kg\(^{-1} \), i.e., low to very high on the Morgan scale. Measured STP values from the rainfall simulation sites performed by Hively et al. (2005) were found to be well correlated with observed DP concentrations in runoff (mg L\(^{-1} \)) from these events. For low STP soils (\( STP<25 \) mg kg\(^{-1} \)) the relationship was \( D_{S_P}=0.0056+0.0180 \) (STP) \( (r^2=0.84) \) and for high STP soils (\( >25 \) mg kg\(^{-1} \)) it was \( D_{S_P}=0.4735+0.0065 \) (STP) \( (r^2=0.84) \) (Hively et al. 2006). The STP/runoff DP regressions were used to back-calculate the DP export coefficients (\( \mu_{S} \)) [Eq. (13)] in overland flow for the remaining soils in the watershed by using the measured STP values measured as part of developing the farm’s NMP. Results were
interpolated incorporating this information to assign reference P export coefficients (μT,i) [Eq. (14)] for all plant/soil complexes in the watershed.

The contribution of the barnyard was estimated using the simulated runoff data from Hively et al. (2005). They measured flow-weighted DP concentrations of 11.6 mg L−1 from a 30 min, 38 mm simulated rainfall event, with a subsequent DP loss of 56 mg m−2. We selected model runoff events from the barnyard with similar runoff losses (i.e., 35–40 mm), and set the parameters to return a concentration of 11.6 mg P L−1 and 56 mg P m−2. Accumulation in the barnyard (M1/Max) [Eq. (15)] was set at 12 × 10−4 kg m−2 from qualitative observations. The wash-off coefficient (k1) [Eq. (16)] was set to 0.25 m2 m−3. The exponential buildup factor (k5) [Eq. (15)] varied between 3 days−1 for the growing season to 1 day−1 during the winter, to reflect the threefold increase in time cows spent in the barnyard (see Easton et al. 2007).

By considering summer baseflow data we were able to determine the parameters for Eqs. (17) and (18) a priori or at least independently from the rest of the VSLF model. To do this, we set TB [Eq. (18)] to the average summer temperature at the mean watershed soil depth (60 cm) and fit a linear regression to (T-TB)/10 as a function DP concentrations measured during summer baseflow conditions; the y intercept of this regression is the log of μB and the regression slope is the log of Q10B. To develop this regression we used ~50 measurements of μB taken during summer, low flow (<1 mm day−1) periods. The same method was used to determine Q10S [Eq. (14)], from direct measures of μT,i from Hively (2004) and Hively et al. (2005) (Table 1).

To highlight some of the benefits of our proposed source-specific model, we also applied the more traditional export coefficient version of VSLF to this watershed and optimized (calibrated) all eight export coefficients to achieve the best fit between modeled and measured stream DP over the period of 1996–1998 (Table 1). See Schneiderman et al. (2002, 2007) for details on parameter optimization. Note that both the export coefficient and new source-specific models used the same underlying hydrological model (VSLF) as drivers for the P models.

Results and Discussion

Hydrology

Streamflow and landscape runoff losses were modeled in VSLF and used as drivers for the DP loading model. As with Schneiderman et al. (2007), the modeled stream flow was in good agreement with the measured stream flow (E=0.82) (Fig. 3), but perhaps more important is the spatial distribution of runoff (Fig. 4). The reconceptualization of the CN-based runoff predictions based on a VSA-hydrology predicts the greatest runoff

<table>
<thead>
<tr>
<th>Parameter (source-specific model)</th>
<th>Equation</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>M_f Initial water extractable phosphorus in manure</td>
<td>(10), (11)</td>
<td>6.4 × 10−4</td>
<td>kg m−2</td>
</tr>
<tr>
<td>τ DP immobilization rate</td>
<td>(10)</td>
<td>9</td>
<td>day</td>
</tr>
<tr>
<td>T_s Base temperature, soil</td>
<td>(14)</td>
<td>20.5</td>
<td>°C</td>
</tr>
<tr>
<td>T_B Base temperature, baseflow</td>
<td>(18)</td>
<td>17</td>
<td>°C</td>
</tr>
<tr>
<td>M_{1,max} Maximum DP accumulation in barnyard</td>
<td>(15), (16)</td>
<td>12 × 10−4</td>
<td>kg m−2</td>
</tr>
<tr>
<td>( k_1 ) DP exponential buildup factor</td>
<td>(15)</td>
<td>1.3</td>
<td>day−1</td>
</tr>
<tr>
<td>( k_{1,0} ) DP wash-off coefficient</td>
<td>(16)</td>
<td>0.02</td>
<td>m−3</td>
</tr>
<tr>
<td>( \mu_s ) Plant/soil export coefficient</td>
<td>(13)</td>
<td>1–385</td>
<td>mg kg−1</td>
</tr>
<tr>
<td>( k_F ) Reaction constant</td>
<td>(11), (12)</td>
<td>1.7 × 10−2</td>
<td>m−1 kg−1</td>
</tr>
<tr>
<td>( Q_{10B} ) ( Q_{10} ) base coefficient, baseflow</td>
<td>(18)</td>
<td>2.50</td>
<td>—</td>
</tr>
<tr>
<td>( \mu_{T,B} ) Reference DP baseflow export coefficient</td>
<td>(18)</td>
<td>55 × 10−5</td>
<td>—</td>
</tr>
<tr>
<td>( Q_{10S} ) ( Q_{10} ) base coefficient, soil</td>
<td>(14)</td>
<td>1.70</td>
<td>—</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter (export coefficient)</th>
<th>Estimated a posteriori (calibrated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mu_B ) Reference DP baseflow export coefficient</td>
<td>(1)</td>
</tr>
<tr>
<td>( A ) Runoff concentration parameter A</td>
<td>(2)</td>
</tr>
<tr>
<td>( B ) Runoff concentration parameter B</td>
<td>(2)</td>
</tr>
<tr>
<td>( C ) Runoff concentration parameter C</td>
<td>(2)</td>
</tr>
<tr>
<td>( E_{C_{ah}} ) Reference land-use export coefficient</td>
<td>—</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Equation</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deciduous forest</td>
<td>(2)</td>
<td>0.015</td>
<td>g m−3</td>
</tr>
<tr>
<td>Shrubland</td>
<td>(2)</td>
<td>0.100</td>
<td>g m−3</td>
</tr>
<tr>
<td>Pasture</td>
<td>(2)</td>
<td>0.250</td>
<td>g m−3</td>
</tr>
<tr>
<td>Hay</td>
<td>(2)</td>
<td>0.250</td>
<td>g m−3</td>
</tr>
<tr>
<td>Cropland</td>
<td>(2)</td>
<td>0.290</td>
<td>g m−3</td>
</tr>
<tr>
<td>Buffer</td>
<td>(2)</td>
<td>0.080</td>
<td>g m−3</td>
</tr>
<tr>
<td>Barnyard</td>
<td>(2)</td>
<td>5.100</td>
<td>g m−3</td>
</tr>
<tr>
<td>Impervious</td>
<td>(2)</td>
<td>0.120</td>
<td>g m−3</td>
</tr>
</tbody>
</table>

Note: Exponential buildup factor varied based on season from 1 during the winter to 3 during the summer.
losses in near stream areas (or areas with a large upslope contributing area, flattened slope, shallow soils, or combinations of the three). The impact on surface topology by human manipulations, like drainage ditches, creates more runoff in these areas as well (Fig. 4). The drainage ditches effectively reduced the surface runoff losses in the down gradient areas by preventing upslope interflow from saturating the soil (Fig. 4). The barnyard had high runoff losses owing to its impervious nature (Fig. 4). See Schneiderman et al. (2007) for a more complete analysis of how well the VSLF spatially distributes runoff generation.

**Stream Phosphorus**

As expected, both the export coefficient and source-specific models predicted the stream DP export similarly well with little bias (Fig. 5). From Fig. 3 it is clear that snowmelt events dominate runoff generation and produce the majority of the DP loss seen in Fig. 5. However, it is also clear that the magnitude of P export varies substantially from season to season and year to year (Fig. 5, Table 2). Predicted daily average DP export was 0.130 kg day\(^{-1}\) for the export coefficient model and 0.123 kg day\(^{-1}\) for the new, more source-specific model, both mimicking the measured P export (0.120 kg day\(^{-1}\)) rather closely (Table 2, Fig. 5).

The export coefficient model poorly predicted DP for several events [Fig. 5(a)] despite accurate streamflow predictions (Fig. 3). The most notable are the snowmelt events in 2000 and, somewhat less so, in 1997 and 1999 [Fig. 5(a)]. Although the errors may be the result of unpredicted runoff distributions within the watershed during the winter, as frozen soil and snow are difficult to model, it is notable that the more source-specific model [Fig. 5(b)] did not experience these problems. The new, source-specific model’s better DP predictions during winter events is likely a result of

---

**Table 2. Modeled and Measured Stream P Export by Time Period for Source-Specific and Export Coefficient Models**

<table>
<thead>
<tr>
<th>Period</th>
<th>Modeled</th>
<th>Measured</th>
<th>(E^b)</th>
<th>(r^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source specific</td>
<td>0.123</td>
<td>0.120</td>
<td>0.86</td>
<td>0.81</td>
</tr>
<tr>
<td>Summer</td>
<td>0.100</td>
<td>0.102</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Winter</td>
<td>0.144</td>
<td>0.137</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Export coefficient</td>
<td>0.134</td>
<td>0.120</td>
<td>0.81</td>
<td>0.79</td>
</tr>
<tr>
<td>Summer</td>
<td>0.060</td>
<td>0.102</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Winter</td>
<td>0.208</td>
<td>0.137</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

\(a\)Coefficient of determination.  
\(b\)Nash–Sutcliffe efficiency.

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**Fig. 4.** Average runoff loss for period 1996–2001; drainage ditches and barnyard are indicated on map with arrows.

**Fig. 5.** Measured and modeled DP export with: (a) traditional export coefficient DP model; (b) new, more source-specific P model. Adjacent graphs show 1:1 correspondence; period=1996–2001.
The Arrhenius temperature adjustment in the model. The source-specific DP model’s most noticeable errors were underpredicted stream DP in October–November 1998 and September 2000. Again, the streamflow for these periods was well predicted (Fig. 3). The 1998 error could be associated with inaccurate NMP input regarding manure applications since both models underpredict the same period. Both the 1998 and 2000 problem periods span times of the year when the landscape is rapidly rewetting due to reduced evapotranspiration when the trees lose their leaves and crops are harvested. Thus, the observed underprediction in Fig. 5(b) may be a result of erroneously predicting the distribution of runoff source areas in the fall.

**Landscape Phosphorus**

Table 3 best illustrates the extra details the source-specific model provides relative to the land use based export coefficient model, especially with respect to manured/fertilized fields, which constitute the largest farm-managed areas and potential NPS source areas. Both models predicted similar contributions from the major land uses, e.g., manured areas contributed 70.0% of the total DP for the export coefficient model and 72.3% for the source specific (Table 3). However, with the source-specific model we can see that most of this load (56.1% of the total from the watershed) was from the soil/plant complex and a much smaller fraction (16.2% of the total load) was from manure itself. The high contribution from the soil/plant complex is expected because of high soil P levels due to long-term continued manure applications. The spatial distributions of DP source areas in the watershed are shown for the simple export coefficient [Fig. 6(a)] and new, source-specific [Fig. 6(b)] DP models, respectively. As anticipated, the distribution of predicted DP source areas for both models reflects the imposed topographical controls on VSA hydrology such that higher runoff is associated with HRUs with higher wetness index classes, i.e., areas closer to the stream [Figs. 6a and b]. However, there are some differences between the two distributions.

The spatial distribution of DP loading predicted by the source-specific model reflects both the runoff distribution and the specific P source distribution, whereas the spatial distribution of DP loading predicted by the export coefficient model is more reflective of runoff losses and land use. As mentioned earlier, the row crop, pasture, and hay lands tended to be the largest source areas of DP for both models [Figs. 6(a and b)] (see Fig. 1 for land uses). However, their contribution varies considerably throughout the watershed, largely as a result of the drainage ditches, which is reflected in the predictions by both models [Figs. 6(a and b)], and NMP manure spreading schedules, which is probably better captured by the source-specific model. This is because the export coefficient treats each land use equally all the time, e.g., row cropland has the same export coefficient, irrespective of location timing of manure spreading or fertilization, thus differences in DP loss are introduced by variations in runoff [Figs. 4 and 6(a)].

Although difficult to see in Fig. 6, the barnyard is the largest concentrated source of P for both models, but at the watershed scale, it contributes relatively little to total DP export (Table 3). During the summer the source-specific model predicts substantially less DP loss (0.002 kg day\(^{-1}\)) reflecting the lesser amounts of time livestock spend confined in the barnyard, while more P loss is predicted during the winter (0.005 kg day\(^{-1}\)), which more accurately reflects the greater time livestock spend confined during the winter.

The higher losses during the winter are a result of increased hydrological sensitivity, i.e., larger extent of saturated or nearly saturated, runoff generating areas (Walter et al. 2000), and both models capture this. However, biogeochemical processes are suppressed by the cold temperatures and DP mobilization due to

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**Table 3. Phosphorus Contribution from Model Components as Well as Percentage of Total P Loss by Component and the Percentage of Watershed Represented by Component**

<table>
<thead>
<tr>
<th>Period</th>
<th>Basflow</th>
<th>Nonmanured soil</th>
<th>Manure(^a)</th>
<th>Manured soil(^b)</th>
<th>Barnyard/impervious</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source specific (1996–2001)</td>
<td>0.024</td>
<td>0.006</td>
<td>0.020</td>
<td>0.069</td>
<td>0.004</td>
</tr>
<tr>
<td>Summer</td>
<td>0.021</td>
<td>0.004</td>
<td>0.015</td>
<td>0.057</td>
<td>0.003</td>
</tr>
<tr>
<td>Winter</td>
<td>0.027</td>
<td>0.007</td>
<td>0.025</td>
<td>0.080</td>
<td>0.005</td>
</tr>
<tr>
<td>Percent of total DP loss (%)</td>
<td>19.5</td>
<td>4.8</td>
<td>16.2</td>
<td>56.1</td>
<td>3.2</td>
</tr>
<tr>
<td>Export coefficient (1996–2001)</td>
<td>0.024</td>
<td>0.008</td>
<td>0.091</td>
<td>0.007</td>
<td></td>
</tr>
<tr>
<td>Summer</td>
<td>0.009</td>
<td>0.004</td>
<td>0.037</td>
<td>0.007</td>
<td></td>
</tr>
<tr>
<td>Winter</td>
<td>0.039</td>
<td>0.012</td>
<td>0.145</td>
<td>0.007</td>
<td></td>
</tr>
<tr>
<td>Percent of total DP loss (%)</td>
<td>18.4</td>
<td>6.2</td>
<td>70.0</td>
<td>5.4</td>
<td></td>
</tr>
<tr>
<td>Percent of watershed (%)</td>
<td></td>
<td>58.4</td>
<td>39.9</td>
<td>1.7</td>
<td></td>
</tr>
</tbody>
</table>

Note: Land use is shown in Fig. 1.

\(^a\)It is not possible to separate the contribution from manure and manured soil using export coefficients.

\(^b\)Represents the contribution from soil under manured areas.

---

*Fig. 6. Average landscape distribution of 1995–2001 DP loss predicted: (a) by VSLF export coefficient model; (b) for new VSLF model with more source-specific DP mobilization model*
processes like iron reduction is decreased, which is only considered in the new source-specific model. Thus, winter loads are generally predicted to be lower by the source-specific model than by the export coefficient model (Table 3).

Management Implications

While the new, source-specific model presented here is slightly more complex than export coefficient models, it has almost the same number of parameters and potentially requires much less direct calibration (Table 1). In fact, because published export coefficients vary by as much as an order of magnitude (Wickham et al. 2003; Haggard et al. 2003; Salvia-Castellvi et al. 2005), substantial data are required to empirically calibrate these coefficients (Sharpley et al. 2001). Thus, it is arguable that the source-specific approach presented here requires substantially less data input than export coefficient models because most of the parameters could be independently quantified, largely through published literature or field research. In a similar vein, other advantages to the modeling approach we have presented are that underlying processes governing DP transport can be more specifically identified and, more importantly, sources of error or knowledge gaps become more obvious. For example, this study showed that more work is needed to better understand the mechanisms that contribute to baseflow DP loads.

Ultimately, this type of modeling presents a more complete picture of P sources as well as insights into particularly sensitive times of the year such as right after manure spreading. It also potentially includes some indicators of underlying biogeochemical processes, which vary throughout the year, largely with respect to temperature. Thus, this modified VSLF model that includes more source-specific information might prove valuable in assessing management scenarios (Sharpley et al. 2001). For instance, with the new model, we can develop recommendations for the quantity of manure or fertilizer applied to a given field. Most export coefficients are static and cannot reflect the impacts of these kinds of day-to-day management activities. Furthermore, we can include the effect of continued manure application on soil P accumulation through periodic STP measurements and appropriately adjusting $M_S$ [Eq. (13)]. While the P losses predicted from the plant/soil complex and in baseflow still, basically, use export coefficient approaches, the incorporation of temperature adjustments probably improves results such that they realistically respond to temperature (Hively et al. 2006).

In Fig. 7 we show the model results for individual land uses, as opposed to specific DP sources. Both models predict similar magnitudes for each land use. The differences arise primarily from considering more dynamic DP availability or mobility in the new, source-specific model. Perhaps most surprising is the predicted P loss from hay field, which was much lower with the export coefficient model than the source-specific model (Fig. 7). The similarity between the export coefficient predicted hay land DP loss and the source-specific soil/plant complex loss from hay suggests that application of manure to the hay fields, particularly following harvesting practices, may be contributing DP to the streams.

The analysis of the source-specific model results suggests that, to improve water quality, P applications should be reduced or eliminated in near stream or saturated areas. By comparison, the export coefficient model simply suggests that pasture, hay, and crop lands should be eliminated near streams. This is probably achieved by conversion of farm land to buffer areas, i.e., taking land out of production, which may be unfeasible or unacceptable since there is a finite amount of land available for farm production. Additionally, because there is a finite amount of land on which to spread manure, excluding areas from production will force more intensive P applications to the remaining land, which may ultimately pose a threat to water quality. Note, contrary to historical agronomics, livestock producers generally have to deal with their manure as a waste product more so than a fertilizer. In short, a more source-specific NPS model, like the one presented here, provides information that allows for considering a wider range of NPS mitigation solutions than traditional export coefficient models.

Conclusions

Correctly predicting the spatiotemporal patterns of runoff generation in landscapes dominated by VSA hydrology provides valuable insights into locations that contribute NPS pollution to streams. The VSLF model has been shown to be a good predictor of VSA behavior and retains the CN equation (USDA-SCS 1972) that is commonly used in NPS models and, thus, retains a familiar modeling foundation for water quality practitioners (Schneiderman et al. 2007). Here we attempted to further improve our ability to predict locations that contribute NPS pollution, and their relative loading magnitudes, by developing a model that simulates the DP mobility for various specific sources: manure, fertilizers, soil/plant complexes, and impervious areas and those associated with baseflow. We applied our new model, which uses VSLF to simulate the underlying VSA hydrology, to a small agricultural watershed in upstate New York. The model predicted stream DP loads well, although only slightly better than a model using more traditional static, land-use-dependent export coefficients (both used VSLF to simulate hydrology). However, the source-specific model required less calibration than the export coefficient model. But most importantly, by modeling specific sources rather than by associating loads with land use, the source-specific model provides additional insights into where and when DP is transported to streams, which allows managers to consider a wider range of options for protecting water quality. Additionally, export coefficients only reflect land use, thus, the only

Fig. 7. Daily contributions normalized by area of dissolved P from watershed land uses for export coefficient model (light grey) and contributions from both soil P for pervious land uses (white) and manure P (dark grey) for mechanistic model. Contributions from impervious areas and barnyard are shown in white for mechanistic model. Standard deviations of average daily P loss across the ten wetness index classes are shown as bars.
changes that can be made are changes in land use. In contrast, models such as the one described here, can be used to analyze the impact of a wide range of field or farm level BMPs, e.g., changes in manure spread scheduling, on watershed-scale water quality.

References


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