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# Distributed hydrological modeling of total dissolved phosphorus transport in an agricultural landscape, part II: dissolved phosphorus transport

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**Abstract.** Reducing non-point source phosphorus (P) loss to drinking water reservoirs is a main concern for New York City watershed planners, and modeling of P transport can assist in the evaluation of agricultural effects on nutrient dynamics. A spatially distributed model of total dissolved phosphorus (TDP) loading was developed using raster maps covering a 164-ha dairy farm watershed. Transport of TDP was calculated separately for baseflow and for surface runoff from manure-covered and non-manure-covered areas. Soil test P, simulated rainfall application, and land use were used to predict concentrations of TDP in overland flow from non-manure covered areas. Concentrations in runoff for manure-covered areas were computed from predicted cumulative flow and elapsed time since manure application, using field-specific manure spreading data. Baseflow TDP was calibrated from observed concentrations using a temperature-dependent coefficient. An additional component estimated loading associated with manure deposition on impervious areas, such as barnyards and roadways. Daily baseflow and runoff volumes were predicted for each 10-m cell using the Soil Moisture Distribution and Routing Model (SMDR). For each cell, daily TDP loads were calculated as the product of predicted runoff and estimated TDP concentrations. Predicted loads agreed well with loads observed at the watershed outlet when hydrology was modeled accurately ( $R^2$  79% winter, 87% summer). Lack of fit in early spring was attributed to difficulty in predicting snowmelt. Overall, runoff from non-manured areas appeared to be the dominant TDP loading source factor.

## 1 Introduction

Water quality protection programs require the effective control of non-point source (NPS) pollution. Phosphorus (P) has been recognized as a key element controlling surface water eutrophication (Carpenter et al., 1998), and legislative measures have been taken to encourage the reduction of P loading on a watershed scale. In the New York City watersheds, maintaining low phosphorus levels is a challenge for the economic development of local communities. Phosphorus loss from dairy farms has been identified as a significant contributor of non-point-source P loading to Cannonsville Reservoir (Brown et al., 1989), the third largest of the reservoirs that supply New York City's drinking water. The New York City Watershed Agriculture Program has undertaken a program of Whole Farm Planning and Best Management Practice (BMP) implementation to reduce NPS pollution from regional dairy farms.

Modeling of P loss from watersheds is key to understanding the long term effects of agricultural BMPs (Sharpley et al., 2002). Once the significant mechanisms affecting the fate of soil P and its release to streams are identified, their relative importance can be estimated and cost-effective preventive or remedial management practices can be efficiently selected.

The fate and transport of P in the soil environment has been shown to be responsive to a broad range of abiotic and biotic processes (Frossard et al., 2000), including: soil test P (Cox and Hendricks, 2000; McDowell and Sharpley, 2001); landuse (Beauchemin et al., 1996); tillage (Kingery et al., 1996); soil mineralogy and particle size distribution (Cox and Hendricks, 2000); erosion (Sharpley et al., 2002); manure application (Beauchemin et al., 1996; Kleinman et al., 1999;

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Kleinman and Sharpley, 2003); grazing (Smith and Monaghan, 2003); plant uptake (Koopmans et al., 2004); P mass balance and soil accumulation (Cassell et al., 1989); soil moisture and hydrology (McDowell and Sharpley, 2002b); soil type (Needelman et al., 2004) and management (Ginting et al., 1998; Klatt et al., 2003; Sharpley and Kleinman, 2003); temperature and precipitation (Correll et al., 1999); sorption kinetics (Morel et al., 2000; Schoumans and Groenendijk, 2000); and preferential flow and soil structure (Akhtar et al., 2003).

Basically, phosphorus can be transported as particulate P, through erosion, or as dissolved P through leaching and overland flow. Traditionally, control of particulate P in runoff has been considered sufficient to improve water quality (Sharpley et al., 1994). However, recent research has shown that particulate P has a much smaller effect on eutrophication levels than dissolved P (Fozzard et al., 1999). This paper focuses only on the transport of total dissolved P (TDP).

The complexity of simulating P loading processes that vary spatially, temporally, and with management practices is amazing. A mechanistic modeling of the interaction of TDP with the environment would require an extensive set of input parameters which are not readily available. Therefore, a reasonable simplification consists in lumping the different biotic and abiotic processes, so that P loss is modeled using an export coefficient approach (Clesceri et al., 1986; Hanrahan et al., 2001; Sharpley et al., 2002), where flow volumes are combined with predicted P concentrations that are derived from soil-, environment-, and site-specific data. Such a lumped approach has the advantage of reducing the required number of parameters, thus limiting the risk of overparametrization described by Beven (1996), among others.

In order to apply the export coefficient approach, insight into the generation mechanisms of overland flow is needed (Gburek et al., 1996). Two main processes can be considered. Infiltration-excess overland flow occurs when rainfall intensity exceeds soil infiltration capacity (Horton, 1933, 1940). The resulting runoff volume generated depends on rainfall intensity, soil type and land cover. In the case of infiltration-excess runoff production, semi-distributed models, such as SWAT (Arnold et al., 1993, 1994; Neitsch et al., 2002; DiLuzio and Arnold, 2004) or GWLF (Haith and Shoemaker, 1987; Haith et al., 1992; Schneiderman et al., 2002), are sufficient to estimate streamflows and TDP loads. In contrast, saturation excess overland flow is generated by precipitation falling on already saturated areas, or when subsurface flows converge in a poorly drained area (Hewlett and Hibbert, 1967; Dunne and Black, 1970; Hewlett and Nutter, 1970; Dunne et al., 1975; Beven and Kirkby, 1979). Runoff volumes are then a function of topography and soil characteristics. In this case, fully distributed models preserving information about landscape position must be used. In addition, P loading processes are spatially heterogeneous, requiring the distributed estimation of above and below ground flow volumes and P loading pathways. In the Catskills re-

gion, where saturation-excess is the dominant process for runoff production, a fully distributed modeling approach is required to adequately characterize overland flow production from source areas that vary spatially and temporally.

Spatially-distributed hydrological modeling of small, upland watersheds is possible using the Soil Moisture Distribution and Routing model (SMDR). In SMDR, the watershed is divided into a continuous grid of square cells of 10 to 30 m side. At each time step, a water balance is computed on each gridcell of the watershed. Overland flow is generated mainly by saturation excess. Infiltration excess is taken into account on impervious areas such as roads and barnyards. Details of the water balance components are presented in a companion to this paper (Gérard-Marchant et al., 2006). The model has been successfully applied to several New York and Pennsylvania watersheds (Frankenberger et al., 1999; Kuo et al., 1999; Johnson et al., 2003; Mehta et al., 2004; Srinivasan et al., 2005). The model is designed to simulate sloping areas, and does not work in flatter areas such as alluvial floodplains, nor does it account for infiltration excess runoff that can be produced on dry soils by brief, intense summer rainstorms.

The objective of this paper is to develop and test a fully distributed model that can predict total dissolved P (TDP) transport from small watersheds where saturation-excess runoff production is the dominant hydrological process.

## 2 Description of the total dissolved P transport model

Four transport processes are considered in the various model components of the SMDR TDP load model: (i) TDP loss from non-manure covered soils in overland flow, (ii) TDP loss in base flow, (iii) TDP loss from manure-covered areas in overland flow, and (iv) TDP loss from impervious areas (roads, farmstead). The four processes are modeled separately, on a daily basis, for each gridcell, and summed to estimate daily TDP loads from the entire watershed.

### 2.1 Component 1. Overland Flow from non Manure-covered Soils

Management history, including manure and nutrient application, crop removal, and tillage, can have a significant effect on soil P content, with repeated manure application leading to nutrient accumulation and increased risk of leaching. Sharpley et al. (1996); Maguire and Sims (2002) and McDowell and Sharpley (2003), among others, have demonstrated that TDP concentrations in overland flow and in base-flow are positively correlated to the quantity and extractability of P in the top layer of soil. Although more complex relationships have been suggested (Kleinman et al., 2000; McDowell and Sharpley, 2001), a simple linear relationship between soil test P and TDP in runoff is generally valid for soils with P concentrations below a critical P saturation threshold

(Kleinman et al., 1999; Sharpley et al., 2002), and can be expressed as:

$$D_{<S>}(t) = \mu STP(t)SE(t) \quad (1)$$

where  $D_{<S>}$  is the loss of TDP in overland flow per unit area [ $\text{kg m}^{-2}$ ],  $STP$  the amount of extractable soil P as estimated by soil test P [ $\text{kg m}^{-3}$ ],  $SE$  the overland flow volume per unit cell area [ $\text{m}^3 \text{m}^{-2}$ ], and  $\mu$  a soil-specific coefficient determined from rainfall simulation (Schroeder et al., 2004) or laboratory extraction (Beauchemin et al., 1996; Pote et al., 1996) at a specific temperature. Equation (1) can be simplified to:

$$D_{<S>}(t) = c_S(t) SE(t) \quad (2)$$

where  $c_S(t) = \mu STP(t)$  is the TDP export coefficient [ $\text{kg m}^{-3}$ ], corresponding to the average predicted TDP concentration in runoff from a particular cell. This coefficient depends thus partly on soil properties, through the coefficient  $\mu$ , and partly on land use and management practices that affect the concentration of P in soils,  $STP$ . Potential release of TDP from soils, as reflected in the export coefficient, depends on both abiotic factors (soil moisture, temperature, precipitation, de/sorption and transport), and biotic factors (decomposition, mineralization, plant uptake) that vary with climate and season (Frossard et al., 2000; Hansen et al., 2002).

In order to reflect the temporal nature of TDP availability, the export coefficients associated with each combination of soil and land use are modified with an Arrhenius type of equation (Bunnell et al., 1977; Johnsson et al., 1987; Kuo, 1998):

$$c_S(t) = c_{S\text{ref}} Q_S^{\left[\frac{T(t,0)-T_S}{10}\right]} \quad (3)$$

where  $T(t, 0)$  is the mean temperature at the soil surface at time  $t$  [ $^{\circ}\text{C}$ ],  $T_S$  the base temperature at which the reference export coefficient  $c_{S\text{ref}}$  was estimated [ $^{\circ}\text{C}$ ], and  $Q_S$  the factor change (range 1 to 5) for a  $10^{\circ}\text{C}$  change in temperature. Soil surface temperatures can be approximated from long term climate records, as

$$T(t, 0) = T_{\text{avg}} + \Delta T \sin[\omega(t - t_\phi)] \quad (4)$$

where  $T_{\text{avg}}$  is the annual average temperature of the soil surface [ $^{\circ}\text{C}$ ],  $\Delta T$  the maximum temperature deviation from the annual average [ $^{\circ}\text{C}$ ],  $\omega = 2\pi/365$  the radial frequency [ $\text{d}^{-1}$ ] and  $t_\phi$  a lag time [d] so that  $\omega t = t_\phi$  when  $T(t, 0) = T_{\text{avg}}$ .

## 2.2 Component 2. Baseflow

Although transport in overland flow is the predominant P loading mechanism in many watersheds (Randall et al., 2000), subsurface transport can often be substantial (Maguire and Sims, 2002; Ryden et al., 1973). In particular, soils exhibiting preferential flow through macropores can quickly

transport a significant amount of P to deeper soils (Gächter et al., 1998; Stamm et al., 1998; Gupta et al., 1999; Akhtar et al., 2003) and to subsurface drains (Hooda et al., 1999; Geohring et al., 2001). Baseflow chemistry has been shown to vary temporally and spatially with changes in land use, representing an integrated signal of climate, geology, and historical land use (Wayland et al., 2003).

Once again, the complexity of mixing and equilibrium interactions between P forms in the soil and soil-water solution advocates implementing an export coefficient approach. Loads of TDP in baseflow  $D$  [ $\text{kg d}^{-1}$ ] are thus calculated as:

$$D_{<BF>}(t) = c_{BF} BF(t) A \quad (5)$$

where  $c_{BF}$  is the baseflow export coefficient [ $\text{kg m}^{-3}$ ],  $BF(t)$  the predicted daily baseflow volume delivered over the watershed (per unit area) [ $\text{m}^3 \text{m}^{-2} \text{d}^{-1}$ ], and  $A$  is the watershed area [ $\text{m}^2$ ].

Seasonal variability of the baseflow export coefficient  $c_{BF}$  is modeled similarly to the soil export coefficient  $c_S$ , as :

$$c_{BF}(t) = c_{BF\text{ref}} Q_{BF}^{\left[\frac{T(t)-T_{BF}}{10}\right]} \quad (6)$$

where  $Q_{BF}$  and  $T_{BF}$  are two calibration parameters. The difference with Eq. (3) is that base flow originates from deeper in the soil, and therefore uses an estimated below-ground soil temperature. The soil temperature at a depth  $z_T$  [m] is calculated assuming that the annual surface temperature varies as a sine wave (de Vries, 1963; Brutsaert, 1982):

$$T(t, z_T) = T_{\text{avg}} + \Delta T e^{-z_T/z_e} \sin[\omega(t - t_\phi) - z_T/z_e] \quad (7)$$

where  $z_e$  the equivalent damping depth [m], which is directly related to thermal diffusivity. It should be noted that the baseflow export coefficient  $c_{BF}$  is calculated for the entire watershed, rather than on a gridcell basis, and should be calibrated from observed base flow streamwater concentrations of TDP. This direct calibration also serves to account for in-stream processes particular to the watershed, including in-stream manure deposition, stream bank erosion, algal growth, and the effects of hydric soils and sediments. This approach is consistent with the assumption in the hydrology model that all the water percolating out of the topsoils enters a subsurface reservoir. Ideally one would link P concentration in the baseflow directly to the average DP concentration of the percolating water or to the soil TDP export coefficients. These processes are currently being investigated but results are not conclusive yet. Therefore, for this paper, simulated DP baseflow concentrations are calibrated with observed DP values.

## 2.3 Component 3. Overland Flow from Manure-Covered Areas

Surface application of manure can lead to large TDP losses in overland flow (e.g., Sharpley et al., 1998; Haygarth and Sharpley, 2000; Kleinman, 2000) if the nutrients are not incorporated and runoff production is large. In some circumstances, P loading from manured areas can be several orders

of magnitude larger than loads produced from non-manured soils (Edwards and Daniel, 1993b). The SMDR TDP model calculates TDP losses from surface applied manure using an extraction coefficient approach, where the coefficient is modified by cumulative runoff and elapsed time since manure application, on a semi-distributed basis.

Sharpley and Moyer (2000) observed from laboratory experiments that the concentration of manure TDP (both organic and inorganic forms) in leachates decreased rapidly during simulated rainfall events. A re-examination of their data shows that during a rainfall event of duration  $\delta t$  [d] with an average rainfall rate  $R$  [ $\text{m}^3 \text{m}^{-2} \text{d}^{-1}$ ], the load of TDP leached from manure,  $D_{<M>}(\delta t)$ , can be expressed as (G erard-Marchant et al., 2005):

$$D_{<M>}(\delta t) = M(t) \exp(-k_D \delta V / R) \quad (8)$$

where  $M(t)$  is the amount (per unit area) of water-extractable P available in manure at time  $t$  [ $\text{kg m}^{-2}$ ],  $k_D$  the reaction constant [ $\text{d}^{-1}$ ], and  $\delta V = \delta t / R$  is the volume of precipitation during the time interval  $\delta t$ .

G erard-Marchant et al. (2005) did not observe any clear correlation between the reaction constant  $k_D$  and simulated rainfall rate. Therefore, it can be assumed in a first approximation that the ratio  $k_D / R$  is independent of time and rainfall rate, so that in Eq. (8), the event duration  $\delta t$  can be replaced by the time step  $\Delta t$ , the volume  $\delta V$  by the volume of runoff (per unit cell area) generated during the time step,  $\Delta V$ , and the ratio  $k_D / R$  by a constant characteristic volume  $V_m$ . Equation (8) then becomes:

$$D_{<M>}(\Delta t) = M(t)[1 - \exp(-\Delta V / V_m)]. \quad (9)$$

If no runoff is generated on the cell during the time step, the volume  $\Delta V$  is identified with the amount of rainfall or snowmelt, but  $D_{<M>}$  does not contribute to stream loads.

After application, manure P interacts with soil between rainfall events and is transformed to forms less and less available for transport (Edwards and Daniel, 1993a). Based on the findings of Gascho et al. (1998) and Nash et al. (2000), the decline in availability of manure water-extractable P,  $M$ , is modeled as an exponential decay:

$$M(t) = M(t_o) \exp[-(t - t_o) / \tau] \quad (10)$$

where  $M(t_o)$  is the initial content of water-extractable P in manure applied at time  $t_o$ , and  $\tau$  the characteristic decay time [day]. For lack of additional data,  $\tau$  is considered a constant, independent of temperature.

A fully distributed modeling requires knowledge not only of the amount of manure applied, but also of the location and method of the application. Unfortunately, the location information is usually not available on a gridcell basis, and a semi-distributed approach must be followed. The watershed is divided in “manure application zones”, corresponding to the smallest area for which information about manure

application is available, such as a field, or a group of adjacent fields. Each manure application zone is then subdivided in elementary “spreading plots”, with an area equal to that covered with a single load of manure. At each time step, manure is first distributed on each application zone following farmer’s information, then randomly on each spreading plot within each application zone, so that no plot can receive manure again before all plots of the zone are covered. Manure TDP losses in runoff are then computed with Eqs. (9) and (10) for each spreading plot, using precipitation data and saturation excess overland flow volumes simulated by SMDR. The simulated overland flow is averaged over each manure application zone, i.e., each spreading plot of one zone receives the average of the estimated runoff volumes for the gridcells within each manure application zone.

#### 2.4 Component 4. Impermeable areas

Overland flow from heavily-manured impervious source areas, including barnyards, roadways, and cowpaths, can play a significant role in delivering water and TDP to the stream (Robillard and Walter, 1984; McDowell and Sharpley, 2002a; Hively, 2004), particularly during dry summer periods when the extent of saturated soils is small. Ideally, TDP loads in overland flows from manure-covered impervious areas could be simulated using the same approach as for manure-covered soils described in Eq. (9). However, the temporal dynamics of barnyard and roadway P availability are not yet well characterized. Therefore, a more generic “export coefficient” approach is followed, similar to the modeling of TDP release from soils to overland flow. The overall extents of manured and non-manured impervious areas are estimated from fine-scale land use mapping and an equivalent number of gridcells are established as impervious, with extraction coefficients chosen for periods of active grazing (spring to fall) and animal confinement (winter).

It could be argued that shallow lateral transport of P in the vadose zone is an important factor that should be modeled explicitly. However, the spatial heterogeneity of macropore flow processes makes this inherently difficult. Although the SMDR model does route water horizontally in the vadose zone, it was elected to confine the P routing model to the aforementioned four pathways because there is no data available to independently verify P concentrations in macropore flow. Furthermore, water transported horizontally through macropores can be expected to have one of four possible fates: 1) percolation into the subsoil, 2) contact with tile drainage, 3) conversion to surface runoff in the form of seepage and springs, and 4) direct transport into the stream channel. In the case of percolation, this is accounted for in the baseflow component. Tile drainage, however, might be a confounding factor. During grabsampling of runoff on the study watershed (Hively, 2004) P concentrations in flow from tile drains were consistently elevated in comparison to concentrations observed in overland flow from field areas.

Additional work that was done on the farm (Scott et al., 1998) observed that approximately 1/3 of total annual P lost from a grazed pasture was transported through tile drains. Accordingly, it might be worth while to attempt to incorporate tile drainage pathways into future versions of the model. In the case of conversion to surface runoff, which we believe to be the dominant fate of vadose zone macropore flow, this will tend to occur at slope breaks, toe slopes, and areas of converging groundwater flow pathways. In this case, it is assumed that soil P concentrations and land use at the point of surface runoff production control the concentration of P in runoff, as accounted for in the overland flow model component. It is worth while to note, however, that hydrologically active areas such as springs have unique P source area properties, related in part to the frequency of runoff production (Hively et al., 2005). Unfortunately, simulating the spatial distribution of permanent wet areas consisting of springs originating from faults in the bedrock is only possible with prohibitively intensive data collection. Finally, in the case of direct flow from the vadose zone into the stream, this is expected to comprise a small portion of the total flow from the watershed, and it is accounted for by the calibrated baseflow concentration used in the model.

### 3 Input data and parameter estimation

The SMDR model and the SMDR TDP transport model were applied to a 164-ha rural watershed that hosts a third-generation dairy farm with approximately 80 milking cows and 35 replacement heifers. The study watershed is located in the Catskills region of New York State, within the Cannonsville Reservoir basin. Since 1993, the study watershed has been the subject of a long term monitoring study conducted by the New York State Department of Environmental Conservation (Bishop et al., 2003) that demonstrated a 43% reduction in TDP loads delivered during runoff events since the implementation of BMPs in 1995 (Bishop et al., 2005). The extensive stream quality dataset and detailed management records available for this farm provided an ideal context for application of the models and verification of results. A detailed description of the study watershed, and a description of the raster maps for land use, soil type, and manure spreading zones, are given in Bishop et al. (2003, 2005), Gérard-Marchant et al. (2006), and Hively (2004). Total dissolved P (TDP) is defined as molybdate reactive orthophosphate found in filtered (45  $\mu\text{m}$ ) digested (Kjeldahl) water samples. The SMDR model was applied to the study watershed for a ten year period (1 January 1993–31 October 2001) of input data. The calibration process and validation results of this model are presented in a companion paper (Gérard-Marchant et al., 2006). Manure application records were available for a two year period (1997–1998) and the TDP transport model was therefore applied for the same two year period only.

#### 3.1 Climate

The climate of the study area is humid continental, with an average temperature of 8°C. Annual average precipitation for the year is 1120 mm. Daily minimum and maximum temperatures were obtained from a nearby weather station located at Delhi, New York, 438.9 msl, (National Weather Service (USDC NOAA) cooperative observer station #302036, “Delhi 2 SE”), located about 20 km SW of the site (NCDC, 2000). Temperatures were corrected by  $-1.2^\circ\text{C}$  to account for the difference in elevation from the study watershed.

#### 3.2 Land use

A spatially justified aerial photograph provided the basemap for on-screen digitization of land cover, manure application zones, impermeable areas, streams, artificial drainage, and other important landscape features (Hively, 2004). Combination of this information with field observations, field collection of GPS data, farm planning records, and farmer interview provided sufficient detail to produce 10-m land use raster maps reflecting annual changes in crop rotation. The resulting land use maps for 1997 and 1998 are presented in Fig. 1.

On-site GPS data collection (Hively, 2004) was used to map the extent of manured and non-manured impermeable areas within the watershed. Because the scale of the impermeable features was not adequately captured by the translation to 10-m gridcells, the area of each impermeable landuse type was first calculated, and the landuse raster map was subsequently hand-edited to reflect appropriate area distribution of each near-barn source area type.

#### 3.3 Observed streamflow and chemistry

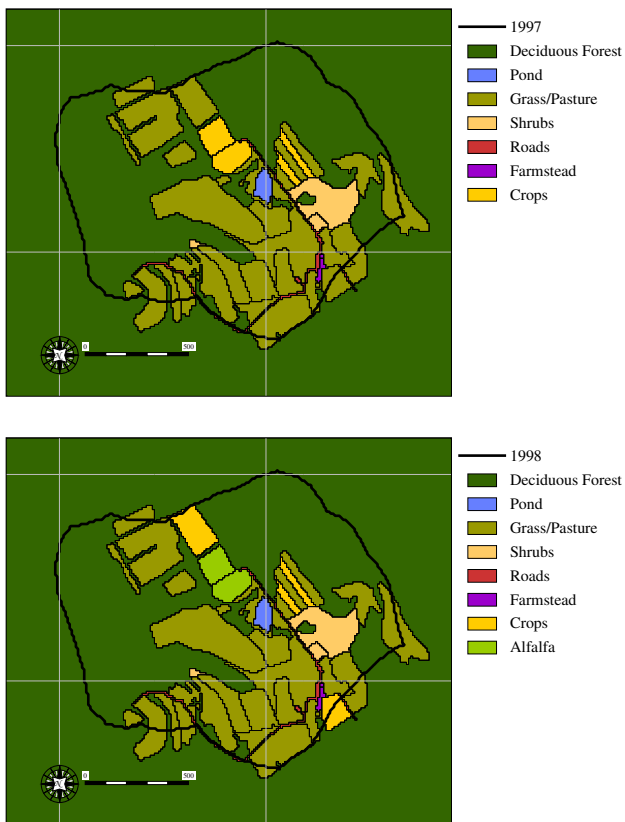
Daily stream flows were recorded on a 10-min basis by a gauge on the watershed outlet, and integrated over a day. Observed TDP concentrations were derived from flow-weighted automated sampling at the watershed outlet, as described in Bishop et al. (2003).

#### 3.4 Parameters estimation and calibration

The parameters that must be estimated for the TDP transport models are: export coefficients  $c_{S\text{ref}}$  for each combination of soil and land use (Eq. 3); base temperature  $T_s$  and  $Q_s$  coefficients (Eq. 3); reference base flow concentration over the watershed  $c_{BF\text{ref}}$  (Eq. 6); base temperature  $T_{BF}$  and  $Q_{BF}$  coefficient (Eq. 6); initial TDP mass in manure  $M(t_0)$  per load (Eq. 10); manure decay time  $\tau$  (Eq. 10); and manure characteristic volume  $V_m$  (Eq. 9). As detailed below, most of these parameters are estimated a priori from field measurements or data reported in the literature. However, some parameters are obtained a posteriori by calibration. Values of the parameters are summarized in Table 1.

**Table 1.** Model parameter values.

Parameter		Eq.	Value	
<b>Parameters estimated a priori</b>				
$T_{avg}$	Annual average temperature	(4)	6.3	[°C]
$\Delta T$	Annual temperature amplitude	(4)	12.8	[°C]
$t_{\phi}$	Time lag (from Jan., 01)	(4)	113	[d]
$T_S$	Reference temperature, soil	(3)	19.1	[°C]
$T_{BF}$	Reference temperature, baseflow	(6)	15.6	[°C]
$z_e$	Annual damping depth	(7)	1.87	[m]
$z_T$	Average depth to low-permeability layer	(7)	0.6	[m]
$M(t_0)$	Initial amount of water-extractable P	(9)	14	[kg ha <sup>-1</sup> load <sup>-1</sup> ]
$\tau$	Exponential decay characteristic time	(10)	7	[d]
$V_m$	Manure TDP release characteristic volume	(9)	25	[m <sup>3</sup> m <sup>-2</sup> ]
<b>Parameters estimated a posteriori</b>				
$Q_S$	Q10 base coefficient, soil	(3)	1.5	[-]
$c_{BFref}$	Baseflow reference export coefficient	(6)	60	[μg l <sup>-1</sup> ]
$Q_{BF}$	Q10 base coefficient, baseflow	(6)	2.5	[-]

**Fig. 1.** Land uses and field boundaries for 1997 (top) and 1998 (bottom).

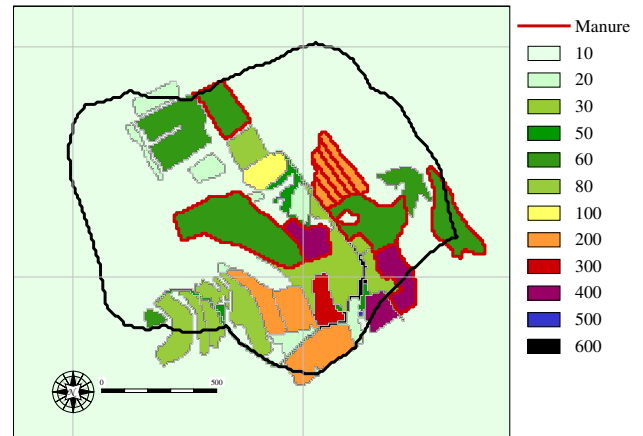
Concentrations of TDP in overland flow were measured using simulated rainfall application at nine locations within the study watershed (Hively et al., 2005). The observed concentrations,  $c_{Sobs}$  [mg l<sup>-1</sup>] were found to correlate well to Morgan's soil test P (Lathwell and Peech, 1965) for soils with low to moderate soil test P [ $c_{Sobs}=0.0056+0.0180$  STP, adjusted  $R^2=0.84$ ] and for manured areas exhibiting excessively high soil test P [ $c_{Sobs}=0.4735+0.0065$  STP, adjusted  $R^2=0.84$ ]. These equations, in combination with soil test P data collected throughout the watershed, provided initial estimations of TDP export coefficients for overland flow from non-manured soils. These values were subsequently rounded and adjusted to reflect TDP concentrations observed in samples of overland flow and other data collected on the study farm (Hively, 2004). When soil test P data were not available for a field, a TDP export coefficient was assigned by comparison with other fields sharing the same management history. Export coefficients were also estimated for impervious areas, such as barnyard and roadways, from the relationship derived for high soil test P soils, subsequently modified to reflect TDP concentrations observed in grab samples of surface runoff during rainfall and snowmelt events (Hively, 2004). Eventually, a 10-m raster map gathering all this information was produced, so that each land use category was assigned an estimated TDP release concentration  $c_{Sref}$ . The resulting map is presented Fig. 2.

Annual average temperature  $T_{avg}$ , temperature deviation  $\Delta T$ , and time lag  $t_{\phi}$  in Eq. (4) were estimated a priori from monthly averages of minimum, maximum and mean temperatures obtained for a 80-year period (1924–2004) from the Delhi, NY weather station. The reference temperature  $T_S$  for the soil export coefficient in Eq. (3) was set a priori to the amplitude of the sine wave temperatures at the soil

surface (20°C). The parameter  $Q_s$  for soil export coefficients introduced in Eq. (3) was obtained a posteriori by calibration with observed TDP loads. The parameters  $c_{BFref}$  and  $Q_{BF}$  of the baseflow export coefficient, Eq. (6), were also obtained a posteriori by calibration for winter and summer low flow events. The equivalent annual damping depth introduced in Eq. (7) to compute soil temperatures was set a priori to  $z_e=1.87$  m using average thermal diffusivities over a wide range of soils at field capacity (de Vries and Afgan, 1975; Kuo, 1998). The depth  $z_T$  at which soil temperatures were computed was set a priori using SSURGO data equal to the average depth of the soils in the watershed (60 cm). Reference temperature  $T_{BF}$  for the baseflow export coefficient, Eq. (6), was set a priori to the amplitude of the sine wave temperatures at depth  $z_T$  (11°C).

Records kept by the collaborating farm supplied the number of manure loads applied on each field and each day for 1997 and 1998. While the data are the best available, the records were frequently vague, and the information somewhat approximate. Manure spreading was therefore simulated on a semi-distributed basis, as described above. According to the manure spreader calibration record, one load represents 7670 kg of manure and covers approximately 2000 m<sup>2</sup> of land surface, or an application amount of 38 350 kg ha<sup>-1</sup>. Analysis of manure samples gave an average manure concentration of 0.56 gP/kg manure, hence about 4.3 kg per load or 21.5 kg ha<sup>-1</sup>. The average fraction of water-extractable P available just after application was estimated a priori at 65%, in accordance with Sharp-ley and Moyer (2000). Therefore, each load of manure corresponded to an initial mass of 2.8 kg of water-extractable P, or 14.0 kg ha<sup>-1</sup>. Following Nash et al. (2000), the exponential decay time  $\tau$  in Eq. (10) was set a priori to 7 days. The characteristic manure TDP release volume  $V_m$  was estimated a priori as 25 mm from Sharp-ley and Moyer (2000) and (Gérard-Marchant et al., 2005).

In translating hydrology to P transport we have attempted to rely on relationships derived from physical processes, in order to make the model have the largest range of possible application. However, each landscape behaves in its own particular way according to the highly variable nature of soil, bedrock, topography, vegetation, and farm management that control hydrologic and P loading processes. The manure-related P loading function is expected to be transferable, and is in fact based upon data from manure extraction studies in Pennsylvania. Users must estimate an initial manure P concentration and monitor the amount of rainfall and timing of application. In the case of surface runoff, the initial relationship between soil test P and P concentrations in runoff was derived on a site specific basis from simulated rainfall data (Hively et al., 2005). Considerable research has demonstrated that the relationship between soil test P and P in runoff is consistent, but only within soil types, and it is recommended that this relationship be established on a local basis (Kleinman et al, 2000; Sharp-ley et al., 2002, 2003). Such,



**Fig. 2.** Extraction coefficients map of the study watershed. Units: [ $\mu\text{g l}^{-1}$ ]. Regularly manured areas outlined in red. Watershed boundary outlined in black.

unfortunately, appears to be the nature of soil P loading processes, due to the inherent effects of particle size distribution and iron/aluminum content upon soil charge and P sorption capacity. That said, the coefficients derived in this model are likely applicable to soils throughout the Catskill landscape that comprises the New York City watersheds.

#### 4 Results and discussion

Daily predicted TDP loads for the watershed were calculated as the sum of TDP transported in flow from each gridcell via the four model components (non-manure covered soils, baseflow, manure-covered areas, and impermeable near-barn areas). These values were subsequently compared to the daily observed loads that were recorded at the watershed outlet. Tables 2 and 3 compare the observed and simulated TDP loads over the simulated period, along with the values of various efficiency criteria: standard Nash-Sutcliffe efficiency criterion NS (Nash and Sutcliffe, 1970), modified Nash-Sutcliffe criterion MSN (Chiew and McMahon, 1994), mean absolute error MAE (Ye et al., 1997), and correlation coefficients  $R^2$ .

As shown in Fig. 3, the timing of the load peaks was in most cases well reproduced, except on some winter dates (e.g. 15 January 1997, 6 February 1997, 17 January 1998) where flow and load peaks were missed. This discrepancy was attributed to imperfect modeling of snowmelt events, and to the use of offsite climate input data that did not reflect the actual localized on-site precipitation. During the winter, TDP load peaks were usually underestimated but overall flow volumes were generally correct. The simulated TDP loads matched well with the observed data during winter low flow events. During summer, however, loads corresponding to low-flow events were underestimated. It should be



**Table 2.** Comparison of annual, summer and winter values of observed and simulated daily TDP loads and efficiency criteria for the simulated period (1 January 1997–31 December 1998).

	With $Q_{10}$ correction			No $Q_{10}$ correction		
	All	1997	1998	All	1997	1998
<b>All data</b>						
Obs. Loads [g]	58 213	20 306	37 907	58 213	20 306	37 907
Sim. Loads [g]	44 645	20 483	24 162	98 200	45 491	52 709
Obs. Flows [mm]	976	424	552			
Simul. flows [mm]	944	424	520			
NS <sup>1</sup>	0.39	−0.22	0.48	−0.02	−3.01	0.46
MNS <sup>2</sup>	0.51	0.30	0.58	0.15	−0.59	0.46
MAE	0.38	0.20	0.47	0.01	−0.55	0.28
R <sup>2</sup>	0.40	0.30	0.54	0.49	0.38	0.60
<b>Summer data (1 May–31 Oct.)</b>						
Obs. Loads [g]	18 597	5191	13 406	18 597	5191	13 406
Sim. Loads [g]	17 839	7655	10 184	24 166	10636	13 530
Obs. Flows [mm]	236	73	163			
Sim. flows [mm]	197	76	121			
NS <sup>1</sup>	0.42	−1.36	0.67	0.20	−3.03	0.67
MNS <sup>2</sup>	0.57	0.08	0.71	0.43	−0.35	0.68
MAE	0.45	0.05	0.56	0.28	−0.43	0.50
R <sup>2</sup>	0.50	0.51	0.69	0.48	0.58	0.67
<b>Winter data</b>						
Obs. Loads [g]	39 616	15 115	24 502	39 616	15 115	24 502
Sim. Loads [g]	26 806	12 828	13 978	74 034	34 856	39 179
Obs. Flows [mm]	740	351	389			
Sim. flows [mm]	747	348	399			
NS <sup>1</sup>	0.36	−0.02	0.41	−0.12	−3.48	0.38
MNS <sup>2</sup>	0.40	0.16	0.49	−0.12	−1.32	0.31
MAE	0.32	0.14	0.41	−0.17	−0.84	0.16
R <sup>2</sup>	0.39	0.23	0.51	0.47	0.26	0.60

1. Nash-Sutcliffe criterion (Nash and Sutcliffe, 1970)

2. Modified Nash Sutcliffe criterion (Chiew and McMahon, 1994)

3. Mean Absolute Error (Ye et al., 1997)

noted that when the calculation of efficiency criteria was restricted to days when predicted flow matched observed flow by  $\pm 25\%$ , then the model accuracy improved substantially (e.g.,  $R^2$  values increased from 0.39 to 0.62 on the total period), as presented in Table 3, reflecting the fact that if the hydrology is not accurately modeled, the P loading will be in error.

Implementing the  $Q_{10}$  temperature modification to the estimated TDP export coefficients resulted in noticeable improvements in the predicted TDP load values, as illustrated in Fig. 3 and Table 2. In particular, the decrease of baseflow concentration  $c_{BF}$  and soil release concentrations  $c_S$  with decreased temperature substantially improved the match between predicted and observed TDP loads during winter low-flow events. However, this improvement had little effect on the various efficiency criteria, suggesting that these criteria may not be very effective for evaluating model performance.

The first difficulty of validation is that if hydrology is not accurately simulated, P loading, which is directly de-

pendent on hydrologic estimates, will be inaccurate. Therefore, the derived measures of fit were significantly better for days when hydrology was simulated within 25% of measured flow. The observed dataset is one of the most complete available in the nation, and provides an excellent daily estimate of actual P loads. Although it is difficult to aggregate landscape source factors for comparison with loads measured at a single outlet, this is a difficulty faced in common by all models. The main of the SMDR P Load Model in this case is that the estimated concentrations were carefully derived from a wide variety of on site measurements (Hively, 2004), and the validation data is therefore as good as any.

#### 4.1 Relative importance of model components

The relative contributions of each TDP transport component (baseflow, overland flow from soils, from manured areas, and from impervious areas) are reported in Table 4. Overall, predicted total TDP loads delivered from the watershed were

**Table 3.** Comparison of efficiency criteria of the temperature corrected simulations, for (a) simulated flows matching observed flows  $\pm 25\%$ ; (b) all flows.

	Well-simulated flows <sup>1</sup>			All flows		
	All	1997	1998	All	1997	1998
<b>Annual</b>						
Number of data points	209	124	85	730	365	365
NS <sup>2</sup>	-0.67	-0.07	-0.83	0.39	-0.22	0.48
MNS <sup>3</sup>	0.34	0.28	0.37	0.51	0.3	0.58
MAE <sup>4</sup>	0.13	0.15	0.14	0.38	0.2	0.47
R <sup>2</sup>	0.62	0.25	0.71	0.4	0.3	0.54
<b>Summer (1 May–31 October)</b>						
Number of data points	73	44	29	368	184	184
NS <sup>2</sup>	0.86	0.43	0.96	0.42	-1.39	0.67
MNS <sup>3</sup>	0.77	0.55	0.92	0.57	0.08	0.71
MAE <sup>4</sup>	0.62	0.42	0.76	0.45	0.05	0.56
R <sup>2</sup>	0.87	0.5	0.96	0.5	0.51	0.69
<b>Winter (1 January–31 March, 1 November–31 December)</b>						
Number of data points	136	80	56	362	181	181
NS <sup>2</sup>	-2.79	-0.76	-3.32	0.36	-0.02	0.41
MNS <sup>3</sup>	-0.23	-0.12	-0.32	0.4	0.16	0.49
MAE <sup>4</sup>	-0.49	-0.25	-0.61	0.32	0.14	0.41
R <sup>2</sup>	0.79	0.2	0.94	0.39	0.23	0.51

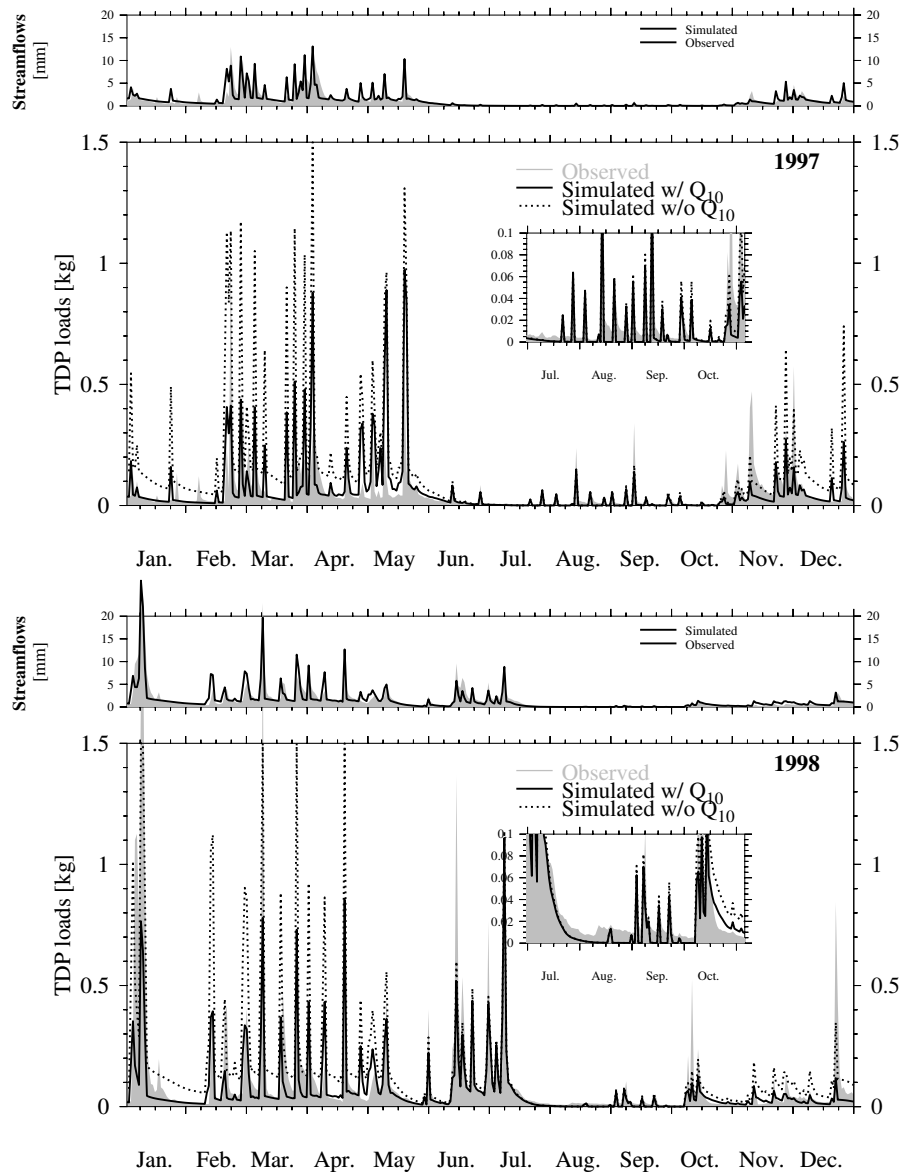
<sup>1</sup>  $|1 - Q_{sim}/Q_{obs}| < 0.25$ <sup>2</sup> Nash-Sutcliffe criterion (Nash and Sutcliffe, 1970)<sup>3</sup> Modified Nash Sutcliffe criterion (Chiew and McMahon, 1994)<sup>4</sup> Mean Absolute Error (Ye et al., 1997)**Table 4.** Contributions of each TDP transport component to the total TDP load.

	TDP loads [g]		Contributions [%]			
	Observed	Total	D <sup>2</sup> <sub>&lt;BF&gt;</sub>	D <sup>2</sup> <sub>&lt;S&gt;</sub>	D <sup>2</sup> <sub>&lt;IA&gt;</sub>	D <sup>2</sup> <sub>&lt;M&gt;</sub>
1997+1998	58213	44645	30.1	48.1	13.9	07.9
Summer <sup>1</sup>	18597	17839	33.4	31.4	18.4	16.8
Winter <sup>1</sup>	39616	26806	27.8	59.3	11	01.9
1997	20306	2048	27.5	45.2	13.1	14.2
Summer	5191	7655	24.5	27.2	16	32.3
Winter	15115	1828	29.2	56	11.4	03.4
1998	37907	24162	32.3	50.6	14.6	02.5
Summer	13406	10184	40.1	34.6	20.2	05.1
Winter	24502	13978	26.6	62.3	10.5	00.6

<sup>1</sup> Summer: 1 May–31 October; Winter: 1 January–30 April, 1 November–31 December<sup>2</sup> BF: baseflow; S: Soils; IA: Impervious areas; M: Manure covered areas

dominated by the effect of overland flow from soils without recent manure application (48% of total loading). The greater contribution of soils during winter vs. summer (Table 4) is likely attributable to the greater extent of saturated areas during winter months, while in summertime runoff pro-

duction is often concentrated in non-field areas such as slope-breaks, groundwater springs, and impervious areas (Hively et al., 2005). The predicted contribution of TDP from manure-covered soils was overall less than 10% of total loads for the entire simulation period. However, the relative contribution



**Fig. 3.** Comparison of observed and simulated total dissolved phosphorus (TDP) loads. For a description of the  $Q_{10}$  modification, see Eq. (6).

of manured areas varied greatly with time, with almost no contribution during most of the year, to a monthly average of 25% in April and May, with maximum contributions up to 90% on some days of these months. This “encouraging” observation may reflect the efficiency of the manure best management practices implemented on the farm, with no manure spread from November to April and reduced spreading on hydrologically sensitive areas. The estimation of P contribution from manured areas could be improved by field testing the algorithm for modeling TDP loss from manure, since it was derived from off-site experimental results (Sharpley and Moyer, 2000; Gérard-Marchant et al., 2005). Moreover, TDP losses from manure are modeled on a semi-distributed basis:

a fully distributed modeling of manure application could be attained if GPS data were recorded by the spreader unit.

Predicted contributions from the impervious areas accounted for about 15% of the total loads over the 2-year simulation period, although the areas were of minor spatial extent (<2% of total watershed area). Here again, the contributions varied greatly with time. In summer and fall, transport of TDP from impervious areas represented up to 95% of the daily loads. During this period, the watershed tends to be dry, and most runoff occurs from direct precipitation on roads and near barn area. Reciprocally, during winter, when the contribution of roadways to runoff production is small compared to saturation-excess and when cows did not travel

to pastures, the relative contribution of impervious areas to TDP transport was small.

#### 4.2 A call for further improvements

The preliminary model results are encouraging, because the model performed well with minimal calibration. However, there is room for improvement. First, a considerable amount of error in TDP load prediction resulted from error in SMDR-predicted flow volumes. The summer baseflows were underestimated (Gérard-Marchant et al., 2006), resulting in the underestimation of TDP loads during summer. Better results could be achieved with improvements in the hydrology of SMDR itself.

Some aspects of the TDP transport model itself could be improved as well. For example, summertime manure deposition on fields, or directly in streams, by the grazing herd is not currently considered, although results of rainfall simulation have indicated increased P loss following intensive grazing (Hively, 2004; Hively et al., 2005). If accurate grazing records were available, pasture and impervious area manure deposition could be directly implemented into the current model, using a modification of the algorithm currently used for manure-covered soils. A simpler approach would consist of allocating a variable release coefficient to each grazed cell. Finally, improved characterization of P loss from near-barn impervious areas could be attained through monitoring of manure deposition and roadway STP.

### 5 Summary and conclusion

A distributed model for the simulation of total dissolved phosphorus (TDP) in watershed runoff was developed and implemented. The Soil Moisture Distribution and Routing model (SMDR) provided daily estimates of distributed runoff production. Estimated TDP concentrations in base flow and runoff from non-manured fields were simulated with extraction coefficients adjusted for temperature with an Arrhenius type of equation. Estimated TDP concentrations from manured fields were simulated based on water soluble P in the manure. Estimated TDP losses from impervious areas with manure were simulated with seasonal extraction coefficients. The model was tested for a two year period when the manure spreading schedule was known for a watershed dairy farm. Observed TDP loads at the watershed stream outlet were reasonably well simulated when the temperature correction was taken into account. The TDP losses were largely controlled by transport of soil P by overland flow from non-manure covered soils. Phosphorus loss from manured fields was about 10% of total TDP losses on average, with the greatest contributions occurring in April and May, during the period that the winter-stored manure was spread and the extent of runoff producing areas was large.

Most of the differences between observed and simulated loads were attributed to an imperfect reproduction of the hydrological components. Improvements in the estimation of percolation and snowmelt would improve predictions during summer and winter periods respectively.

Although the actual implementation of the soil TDP extraction model relies strongly on the accurate spatial distribution of runoff generating areas, the model performance was evaluated by comparing simulated and observed flows and TDP loads summed over the entire watershed. Limitations in experimental data prevent the validation on a distributed basis. Despite this limitation, this simple P loading model provides an adequate starting point for the estimation of lumped TDP losses for various landscape areas and land uses and can be used in realistic manner to evaluate the effects of best management practices.

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