

MODELING SOLUBLE PHOSPHORUS DESORPTION KINETICS IN TILE DRAINAGE

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ABSTRACT: This paper describes a simple model for the desorption and transport of soluble reactive phosphorus (SRP) to subsurface drains. The model assumes first-order kinetically rate-limited desorption in a soil surface mixing layer over a soil profile layer that rests on an underlying, shallow restricting layer. Input data include precipitation, soil hydraulic properties, drain outflow, free water surface fluctuation, sorbed P concentrations for the mixing layer and profile, desorption rate and equilibrium soil-SRP partitioning. Model results are compared to data on flow and SRP concentrations in drain outflow collected during natural rainfall events under field conditions. The concentration time series simulated follow the sharp rise, peak, and gradual recession of the observed field data. Predicted event mass loads resulting from observed and simulated tile discharges differ from the observed load by +8.2% and -9.7%, respectively. Sensitivity analysis indicate that equilibrium assumptions would not provide satisfactory results and that mass transfer limits SRP release to the tile drain.

INTRODUCTION

The contribution of agriculture to the degradation of surface and shallow ground-water quality has become more apparent as point-source pollution identification and abatement measures have increasingly addressed those sources (Sharpley et al. 1994; Nair et al. 1998; Scott et al. 1998a). Subsurface tile drains have been shown to have a significant effect on the quality of receiving waters, particularly under storm event conditions (Kladivko et al. 1991). The transport of sorbed and nonadsorbed solutes from the soil surface to tile drains through preferential flow in structured soils has been observed and models have been developed to simulate such transport processes (Steenhuis et al. 1994; Boyer et al. 1996; Shalit and Steenhuis 1996; Stamm et al. 1998; Villholth and Jensen 1998). Several existing models assume saturation buildup in a surface mixing layer that results from precipitation at rates higher than saturated conductivity. For soils with restricting layers such as compacted glacial till and fragipans, saturation builds up from the profile below the mixing layer. Additionally, where desorption kinetics in the mixing layer limit the rate of solute release during relatively rapid transport events, equilibrium partitioning of sorbed and solute phases does not apply (Enfield et al. 1981; Beauchemin et al. 1996). Xue et al. (1998) present a model for the kinetics of dissolved P export with relation to tile flow. The objective of this paper is to present a model for soluble reactive phosphorus (SRP) transport from a soil surface mixing layer to tile lines, validated by field data. The mixing layer approach is advanced to account for the desorption kinetics of sorbed P under conditions of short duration precipitation events of low intensity. The model is compared to event-based data collected in a field drainage study of P transport in tile drains with saturation-excess runoff processes.

The present study was conducted as part of a cooperative program to preventively manage water quality in the Catskills Mountains watershed that supplies drinking water to New York City. The research focused on identifying and describing the hydrologic pathways for rapid transport of P and pathogens to

surface waters (Scott et al. 1998a). In the study area, tile lines are installed to drain the perched water table that occurs as a result of the shallow fragipan. The soils are structured and for most rainfall events, precipitation does not exceed saturated conductivity (except for crusted soils). Tile drainage is a significant contributor to water quality impairment for two reasons: (1) tiles are used to maintain accessibility to fields where manure is spread, and may act as "short circuits" for contaminant transport to streams; and (2) the prolonged duration of tile flow during the spring and fall seasons means that the total volume of drainage flow (and therefore contaminant mass load) is relatively high (Scott et al. 1998b).

MODEL DESCRIPTION

The concept of a surface mixing layer that acts as a linear reservoir with complete mixing and homogeneous solute concentration has been applied by Steenhuis et al. (1994). Solute is adsorbed to the soil prior to precipitation and subsequently desorbs once the mixing layer becomes saturated with water. Adsorption and desorption partition coefficients are different to account for hysteresis; however, solution concentrations are assumed to be at equilibrium with the sorbed phase.

For short-term events, the release of sorbed solutes is limited by the kinetics of desorption (Aharoni et al. 1991; Garcia-Rodeja and Gil-Sotres 1995; Beauchemin et al. 1996). The

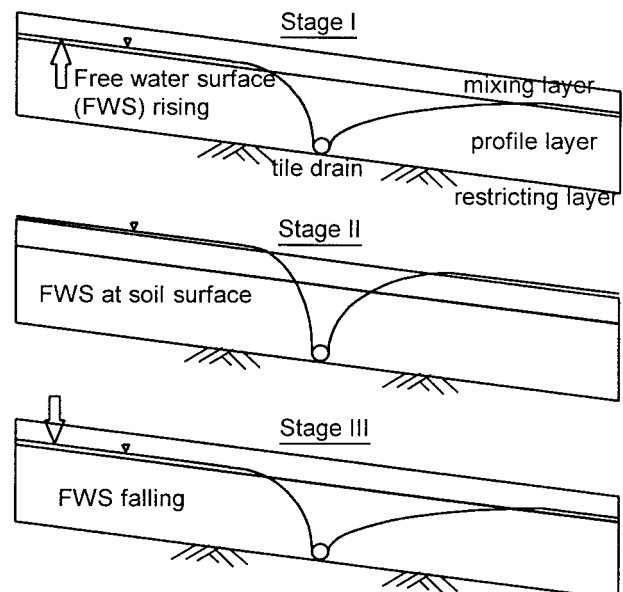


FIG. 1. Conceptual Model with Mixing Layer Buildup, Saturation, and Drainage Stages

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Note. Discussion open until September 1, 2001. To extend the closing date one month, a written request must be filed with the ASCE Manager of Journals. The manuscript for this paper was submitted for review and possible publication on March 9, 2000; revised October 3, 2000. This paper is part of the *Journal of Irrigation and Drainage Engineering*, Vol. 127, No. 2, March/April, 2001. ©ASCE, ISSN 0733-9437/01/0002-0070-0076/\$8.00 + \$.50 per page. Paper No. 22178.

model proposed in this paper accounts for kinetically limited solute release to water percolating through the mixing layer. Three stages are contemplated (Fig. 1). Prior to the first stage, the profile layer has become saturated (i.e., a perched water table has built up on the restricting layer). Stage I begins when the free water surface enters the mixing layer, and continues until the mixing layer is saturated. Stage II is the mixing layer saturation stage; the tile is flowing at maximum discharge and excess precipitation is lost as runoff. All subsurface lateral flow is assumed to be intercepted by the tile. Stage III is the desaturation stage, which occurs through drainage after rain has ceased. It should be noted in the conceptual depiction in Fig. 1 that the drain runs downslope; it is assumed that the slope of the free water surface along the drain is equal to the land slope. The model attempts to keep data requirements to a minimum, and as a result makes several assumptions that simplify the complexity observed in the field.

Buildup (Stage I)

This stage begins when the free water surface first encounters the mixing layer and starts to desorb solute. The inflow to the drain is given by the water balance

$$Q_i(t) = \frac{D_s K_s \phi + i(t) r_e}{r_e} = Q_u(t) + i(t) \quad (1)$$

where $Q_i(t)$ = inflow (flux units); D_s = total depth of the soil profile; K_s = saturated conductivity; ϕ = prevailing input slope; r_e = radius of influence of the tile line for both flow and solute; $Q_u(t)$ = lateral inflow from upslope; and $i(t)$ = time-dependent rainfall rate. Although (1) holds for a rainfall rate equal to zero, it assumes that the profile layer of the upslope contributing area is saturated, but neglects upslope runoff contribution to tile flow given that the field site has an upslope surface ditch to divert runoff. Conceptually, the inclusion of upslope runoff would produce a more initial rapid rise and prolonged decline of the mixing layer and result in a longer period of SRP desorption.

The total mass of solute in the mixing layer at any time, t , is given by the solute mass balance

$$M_m(t) = C_m(t) V_m(t) = C_m(t) A_c [d_m(t) \{ \theta_s - \theta_f \} + D_m \theta_f] \quad (2)$$

where $M_m(t)$ = total mass of solute in the mixing layer; $C_m(t)$ = its time-dependent concentration; and $V_m(t)$ = total flow volume, which is based on the area A_c that contributes to tile flow (assumed constant and equal to the total length of the tile drain times $2r_e$). $d_m(t)$ is the time-dependent depth of the free water surface in the mixing layer (with $t = 0$ when the free water surface enters the mixing layer), D_m is the total depth of the mixing layer, θ_s is the saturated moisture content, and θ_f is the field capacity moisture content.

In order to find the time-dependent depth of saturation in the mixing layer we solve the differential equation

$$\frac{d d_m(t)}{dt} = \frac{Q_u(t) + i(t)}{\theta_g} - \frac{Q_o(t)}{A_c \theta_g} \quad (3)$$

where θ_g = gravitational water content ($\theta_s - \theta_f$) that causes perched water; and $Q_o(t)$ = volumetric tile outflow rate. Solving (3) yields

$$d_m(t) = \frac{\Theta(t) + I(t)}{\theta_g} - \frac{\xi(t)}{A_c \theta_g} \quad (4)$$

where $\Theta(t)$ = cumulative upslope lateral influx; $I(t)$ = cumulative rainfall; and $\xi(t)$ = cumulative tile outflow since onset of the event (the start of stage I).

Based on first-order kinetics, the solute mass balance in the mixing layer is given by:

$$\frac{dM_m(t)}{dt} = -Q_o(t)C_m(t) + V_m(t)\beta_d C_m(t) \quad (5)$$

where all variables are defined as before and β_d = desorption kinetic rate constant, under the assumption that the desorption rate is limited by mass transfer and that for short-duration events total sorbed mass is not reduced appreciably enough to be considered explicitly. Substituting and arranging (2), (4) and (5) and collecting terms yields the differential equation for concentration:

$$\frac{dC_m(t)}{C_m(t)} = \frac{\beta_d \theta_g d_m(t) - i(t) + \beta_d \theta_f D_m - Q_o(t)}{\theta_g d_m(t) + \theta_f D_m} = \pi_1(t) dt \quad (6)$$

Integrating (6) results in

$$C_m(t) = C_o \exp \left[\int_0^t \pi_1(t') dt' \right] \quad (7)$$

The concentration $C_r(t)$ in the tile line during this stage results from the combination of flow and solute mass balances, and is calculated as the flow-weighted average of the ambient solution concentration C_p (constant) in the profile layer below the mixing layer and the calculated mixing layer concentration $C_m(t)$. Using the Dupuit assumptions of horizontal flow lines, this mixing takes the form

$$C_r(t) = \frac{d_m(t)C_m(t) + D_p C_p}{D_p + d_m(t)} \quad (8)$$

where D_p = profile depth. Eq. (8), which applies for all three stages given their respective $C_m(t)$ concentrations, is well defined at its temporal boundary conditions. If time is set to zero, $d_m(0) = 0$ and the concentration in the tile lines equals the ambient concentration C_p , determined by:

$$C_p = S_p / K_d \quad (9)$$

where S_p = sorbed concentration in the profile layer; and K_d = distribution, or desorption partition, coefficient assuming equilibrium linearity.

Saturation (Stage II)

Note that in the previous stage, surface runoff has not yet been initiated; however, there is no limitation in the theory put forth as to when the mixing layer becomes saturated. We do not attempt to predict surface runoff concentration. After the free water surface reaches the soil surface, the water balance is

$$Q_u(t) + i(t) = R(t) + Q_o(t) \quad (10)$$

where $R(t)$ is runoff. Substituting (10) into (6) with $d_m(t) = D_m$ yields the differential equation

$$\frac{dC_m(t)}{C_m(t)} = \beta_d - \frac{Q_o(t)}{\theta_s A_c D_m} \quad (11)$$

which yields the exponential

$$C_m(t) = C_o(t_r) \exp \left[\beta_d (t - t_r) - \int_{t_r}^t \frac{Q_o(t')}{\theta_s A_c D_m} dt' \right] \quad (12)$$

where t_r = time at which runoff is initiated. Again, the concentration in the tile line will be given by (8) with $d_m(t) = D_m$. It can be seen from (12) that the concentration in the mixing layer will decrease through dilution if the mass export rate in tile outflow exceeds the desorption-generated supply and will increase if desorption exceeds the rate of mass outflow. This equation is valid until the peak outflow from the tile lines begins to decline, at which point the profile begins to desaturate.

Drainage (Stage III)

The time dependence of $d_m(t)$, similar to (4), is given by

$$d_m(t) = D_m + \frac{\Theta(t - t_s)}{\theta_g} - \int_{t_s}^t \frac{Q_u(t') dt'}{A_c \theta_g}$$

$$= D_m + \frac{\Theta(t - t_s)}{\theta_g} - \frac{\xi(t - t_s)}{A_c \theta_g} \quad (13)$$

where the cumulative upslope influx $\Theta(t)$ is assumed to be based on constant $Q_u(t)$ with any temporal variation negligible compared to cumulative tile flow $\xi(t)$. Both $\Theta(t)$ and $\xi(t)$ are taken over the interval t since desaturation, t_s .

The mass balance, analogous to (6), is

$$\frac{dC_m(t)}{C_m(t)} = \frac{\beta_d \theta_g d_m(t) + \beta_d \theta_f D_m - Q_u}{\theta_f D_m + \theta_g d_m(t)} = \pi_m(t) \quad (14)$$

The fundamental difference between (14) and (6) is that (14) contains no dilution effect due to precipitation directly on the pollutant area, and $d_m(t)$ should generally be decreasing. Again, the mixing layer concentration is found using

$$C_m(t) = C_{s0} \exp \left[\int_{t_s}^t \pi_m(t') dt' \right] \quad (15)$$

where C_{s0} equals the final $C_m(t)$ concentration of the saturation stage as given by (12).

The resulting tile line concentration is then found by solving (8) with $C_m(t)$ determined by (7), (12), or (15) for the appropriate stage.

METHODS AND MATERIALS

The field study site is located in the Catskills region of New York state. A 2.24 ha field on a 10.8% slope is drained by a branched lateral-main tile line with total length of 504 m (Fig. 2). The soil series is a moderately well drained Willowemoc channery silt loam (coarse, loamy, mixed, frigid, typic fragi-ochrept) with an underlying fragipan at 550 mm depth. Upslope water from an adjoining 6 ha contributing area is intercepted in a surface ditch approximately 500 mm deep that diverts all upslope runoff and lateral flow away from the field. The tile line discharges into a holding tank where outflow is gauged using a 90° V-notch weir. The weir was calibrated at different discharges using a stopwatch and graduated cylinder; recorded flow matched observed flow within 8%. Depending on head in the holding tank, a maximum of 0.2 L s⁻¹ is lost

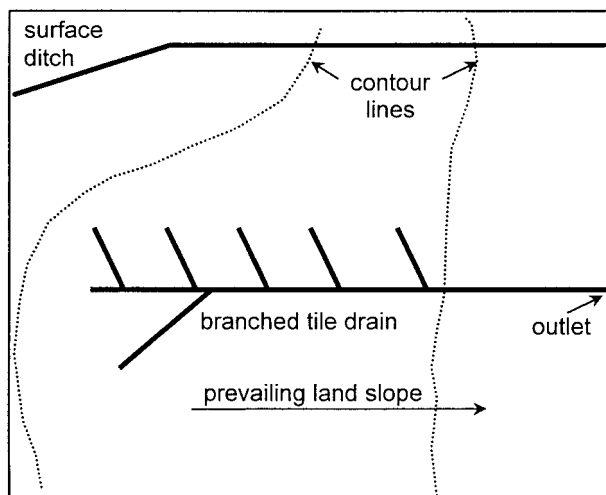


FIG. 2. Schematic Layout of Tile Drain

under the weir. Tile discharge, surface runoff and precipitation were datalogged on a 15-min interval (CR10, Campbell Scientific, Logan, Utah). Free water surface fluctuation was not monitored in the field; instead, this variable was simulated as described below. Tile outflow and runoff were sampled on a variable interval using automatic water samplers (ISCO 2800, Lincoln, Neb.). Dairy manure was liquid-applied on a variable interval during the course of the preceding summer season with the heaviest applications in June and August. Numerous rainstorm events were monitored; the representative event taken for the analysis in this paper took place over a 28-h period in November 1996, with total precipitation of 74.7 mm and peak 15-min intensity of 12.2 mm h⁻¹. Samples were collected hourly for the duration of the event; only the tile sample concentrations are presented because runoff concentration is not included in the present model.

Samples were filtered through Supor® 0.45 μm filters under a vacuum of 70 kPa or less to separate the soluble reactive phosphorus (SRP) fraction. P concentration of the filtrate was determined by measuring ascorbic acid-reduced phosphomolybdate using a Turner Instruments® 690 spectrophotometer at 440 nm following *Standard Methods* (1985).

Data on desorption kinetics and equilibrium distribution were developed using a field soil composite of 15 thoroughly mixed samples collected from the upper 150 mm of the mineral soil horizon, distributed over the entire tile contributing area. The desorption procedure used a 1:25 soil:solution ratio [following the standardized procedure of Nair et al. (1984), although this ratio may not be achieved under field conditions] with snowmelt water (<0.001 mg L⁻¹ SRP) and was mixed in a completely stirred reactor. Solution was removed from the reactor at approximately 2, 5, 10, 15, 30, 45, 60, 75, 90, 105, and 180 min after initial mixing and centrifuged at 6,000 rpm to achieve an initial soil-solution separation. Immediately thereafter, each sample was filtered (1.04 μm followed by 0.45 μm) and P concentration was determined as described above. Solution removed from the reactor for time $t > 180$ min was not used to determine the kinetics rate. All lab ware used was only for P analysis and was washed in concentrated acid for 24 h, soaked in distilled-deionized water and dried at 37°C prior to use.

Soil P was extracted with Morgan's solution (10% sodium acetate in 3% acetic acid buffered to pH 4.8, using a 1:5 w/v soil:solution ratio) as per New York state procedures, and measured colorimetrically by stannous chloride reduction.

Hydrological simulation of the event was performed using the Cornell Soil Moisture Routing (CSMR) model, a distributed parameter model in GRASS, run on 10 m resolution and 15-min time step. CSMR was designed to predict saturated areas on underlying restricting layers by routing moisture through the landscape (Frankenberger, 1999; Zollweg et al. 1996). Tile flow simulations were performed assuming r_c , tile radius of influence, to be 3 m. The free water surface elevation in the profile was determined by the model, assuming that the moisture content of the unsaturated layer was at field capacity. This procedure is recognized as a limitation for the validation of the analytical kinetics model.

RESULTS AND DISCUSSION

The desorption of SRP from the field soil produced concentrations in the range measured in the field (see Fig. 3). As a result, the measured value of the first-order kinetic release rate, $\beta_d = 0.00447 \text{ min}^{-1}$ (significant at $p < 0.01$), was used for both simulations. Several additional desorption runs suggest that a variable $\beta_d = f(S_m)$ relationship exists, where S_m is the sorbed mass [see also Sharpley (1983)].

Tile SRP concentrations were computed by solving for transport and concentration simultaneously using stepwise dis-

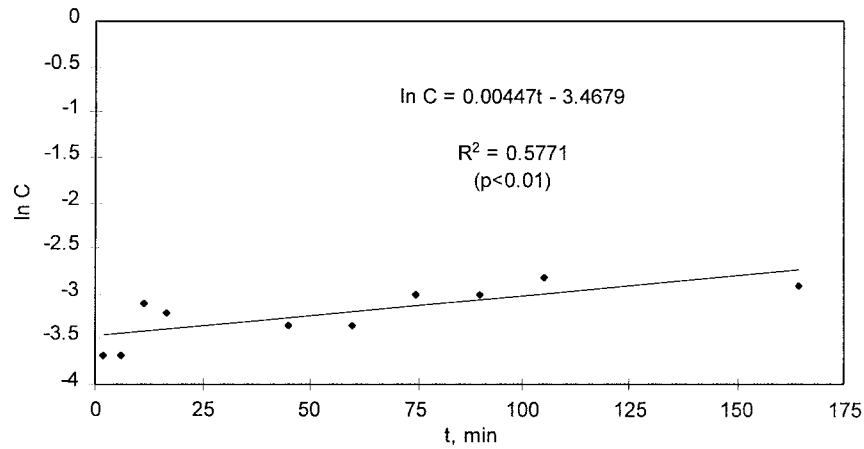


FIG. 3. Desorption from Field Soil Using Snowmelt Water ($\beta_d = 0.00447 \text{ min}^{-1}$)

TABLE 1. Simulation Parameter Values

Parameter (1)	Simulation 1 (2)	Simulation 2 (3)
Mixing layer depth, D_m (mm)	200	200
Profile layer depth, D_p (mm)	350	350
Distribution coefficient, K_d (L kg^{-1})	143.8	143.8
Kinetic rate constant, β_d (min^{-1})	0.00447	0.00447
Profile S_p (mg kg^{-1})	2.1	2.1
Observed rainfall rate, $I(t)$, stage I average (mm h^{-1})	3.3	3.3
Observed rainfall rate, $I(t)$, stage II average (mm hr^{-1})	4.2	4.2
Tile discharge	Observed field data	Simulated
Free water surface	Rise and fall rates assumed constant	Simulated (assuming field capacity unsaturated moisture content)

crete (15-min) time intervals. Sequential solutions have been proposed and applied by Yeh and Tripathi (1991), and Tebes-Stevens et al. (1998). The model was used to generate event SRP time series for the tile, $C_T(t)$, as well as cumulative mass loads and discharge-weighted event mean concentrations resulting from observed and simulated discharge time series, $Q_o(t)$. The respective parameter values for the two simulations are presented in Table 1. The 200 mm mixing layer depth, D_m , agrees with reported values of 200 to 250 mm (Steenhuis et al. 1994) and 155 mm (Shalit and Steenhuis 1996). This layer corresponds to a plow layer, as bulk densities are 1.1 Mg m^{-3} in the mixing layer, 1.4 Mg m^{-3} in the profile layer, and 1.8 Mg m^{-3} in the fragipan.

Tile discharge and free water surface fluctuation were the only parameters altered for the two runs. The initial rise in $C_T(t)$ is driven by desorption after the free water surface enters the mixing layer. Fig. 4 shows the assumed and simulated water surface time series $D_p + d_m(t)$ plotted with observed and simulated tile discharge $Q_o(t)$. Note that the assumed water surface leads the simulated water surface by several time steps; this is an artifact of the routing algorithm employed by the hydrologic model, in which lateral flow is routed to the adjoining cell (10 m) once every time step (15 min). The lag has

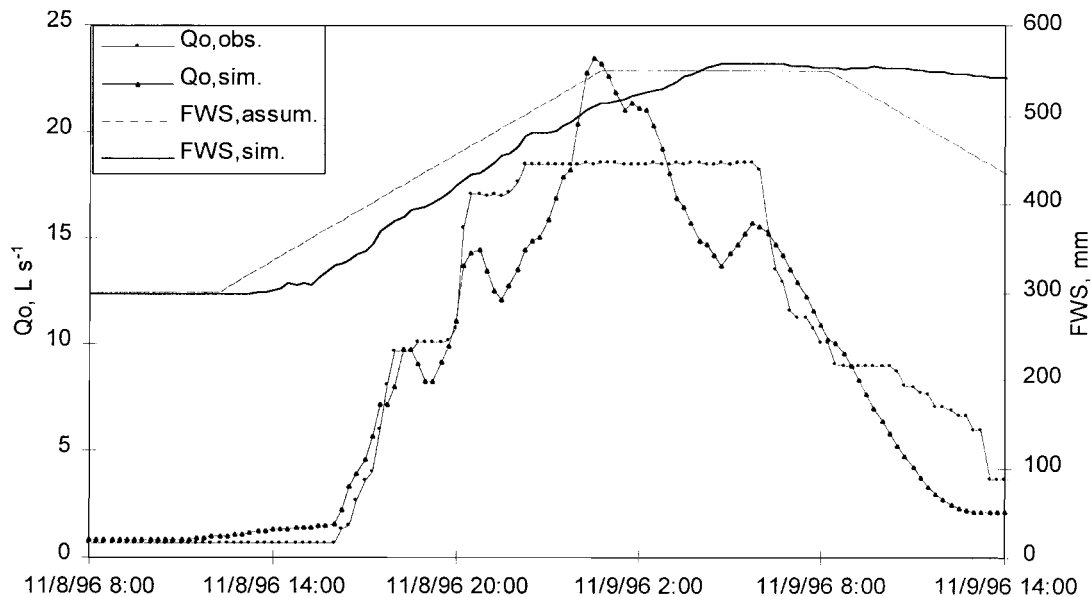


FIG. 4. Observed and Simulated Tile Discharge, Assumed and Simulated Fluctuation of Free Water Surface (FWS, Height above Fragipan)

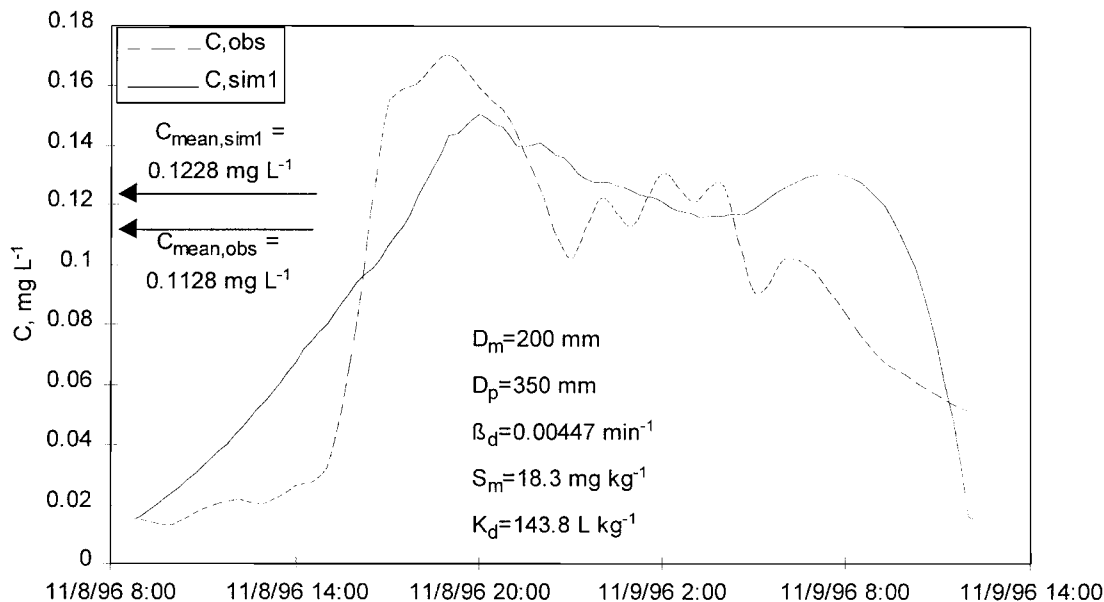


FIG. 5. Soluble Phosphorus, Observed, and Simulation 1 (Observed Q_o , Assumed FWS with Constant Rates of Rise and Fall)

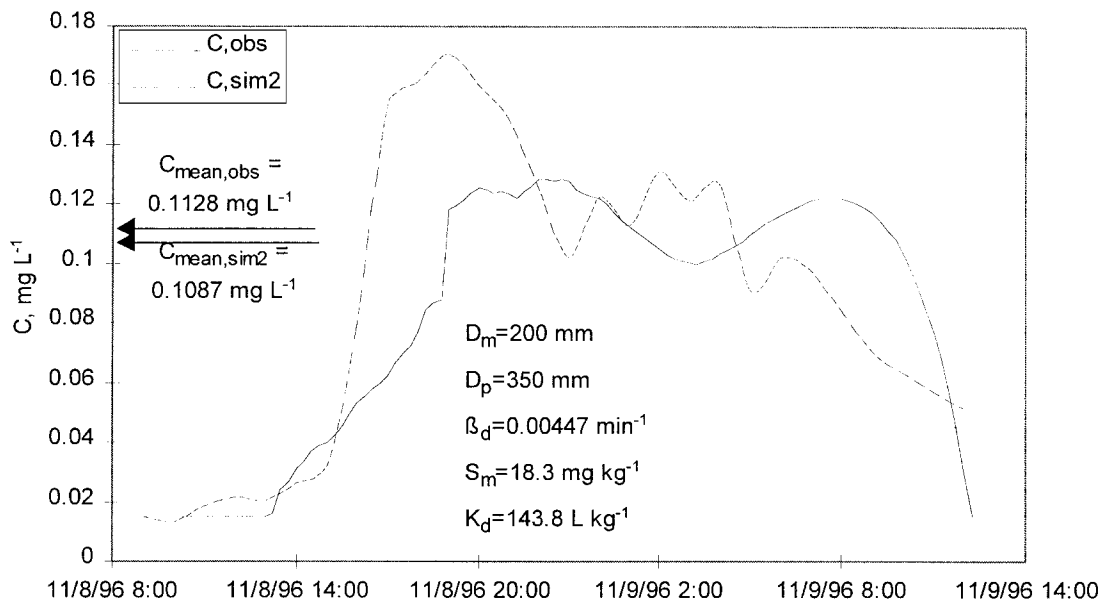


FIG. 6. Soluble Phosphorus, Observed, and Simulation 2 (Simulated Q_o and FWS)

a minimal effect on simulated tile flow during this stage of high precipitation rate, a parameter to which the hydrologic model is sensitive given its assumption of complete moisture redistribution in the soil. Simulated tile flow peaks higher than observed, although the mass error in predicted event total tile volume is -10.1% . This error will be shown to affect the calculated solute mass error and the event mean concentration for the second simulation.

Figs. 5 and 6 compare observed and simulated SRP time series $C_T(t)$ in tile flow for the first and second simulations. The time durations of the three stages in the model were the same for both simulations. Simulation 1 in Fig. 5 uses the observed tile flow to saturate and drain the profile; as a result, the shape of the simulated $C_T(t)$ matches that of the observed data well although the observed data demonstrate a more pronounced breakthrough. It can be seen that the event-mean concentration is overpredicted, particularly as a result of the high $C_T(t)$ values predicted for the saturation stage, i.e., when flow and solute flux are highest. By contrast, in the second simulation using simulated flow (Fig. 6), the start of solute desorp-

tion from the mixing layer is delayed and solute loss through tile drainage is less rapid, allowing a more rapid rise in $C_T(t)$. The water surface lag mentioned above also introduces a discontinuity in $C_T(t)$ at the transition from stage I to II (build up to saturation). Because simulation 2 is based on a volume of total tile outflow that is 10% less than observed, the simulated event mean concentration underpredicts the observed.

Sensitivity analyses were performed for kinetic release, the basic process assumed to limit SRP transport to tile drain outflow, in order to demonstrate that equilibrium assumptions would not provide satisfactory results. Accordingly, the kinetic rate constant β_d was varied for both simulations by a factor of $\pm 5\%$, with the results shown in Figs. 7 and 8. It should be noted in both cases that the most significant differences are observed for stages II and III as a function of (11) and (14), respectively. As noted above, the physical process assumed to account for this is limited mass transfer, indicating that kinetic release is a crucial process for transient events of the type described and simulated using the model.

The mass of solute lost through the tile is the product of

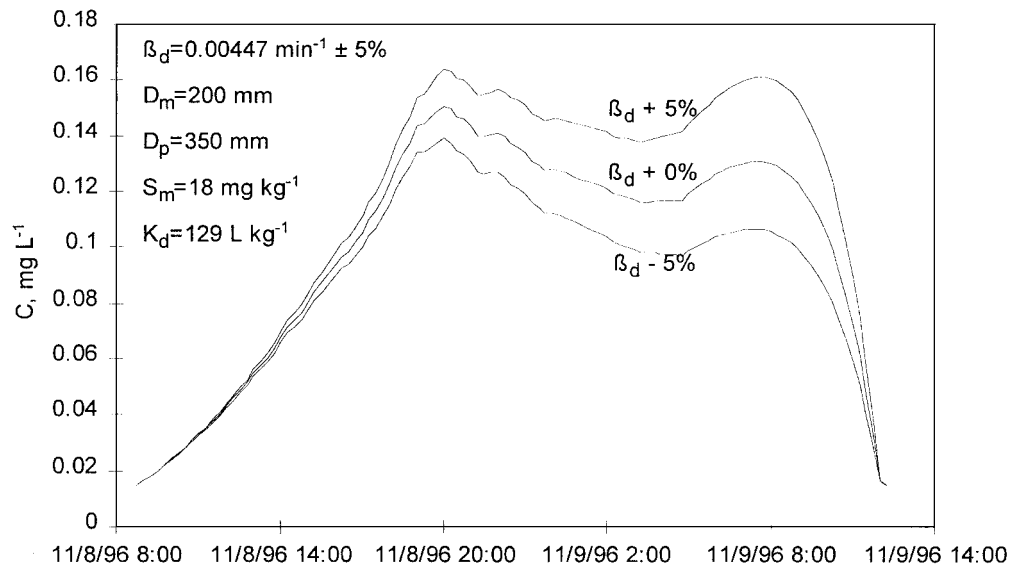


FIG. 7. Sensitivity Analysis, Simulation 1 (Kinetic Rate Constant β_d Varied $\pm 5\%$)

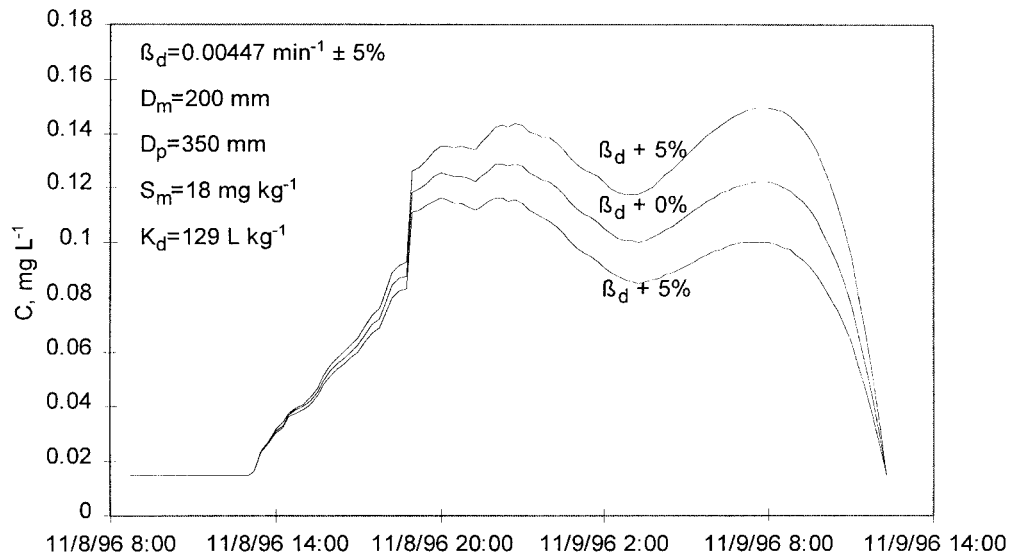


FIG. 8. Sensitivity Analysis, Simulation 2 (Kinetic Rate Constant β_d Varied $\pm 5\%$)

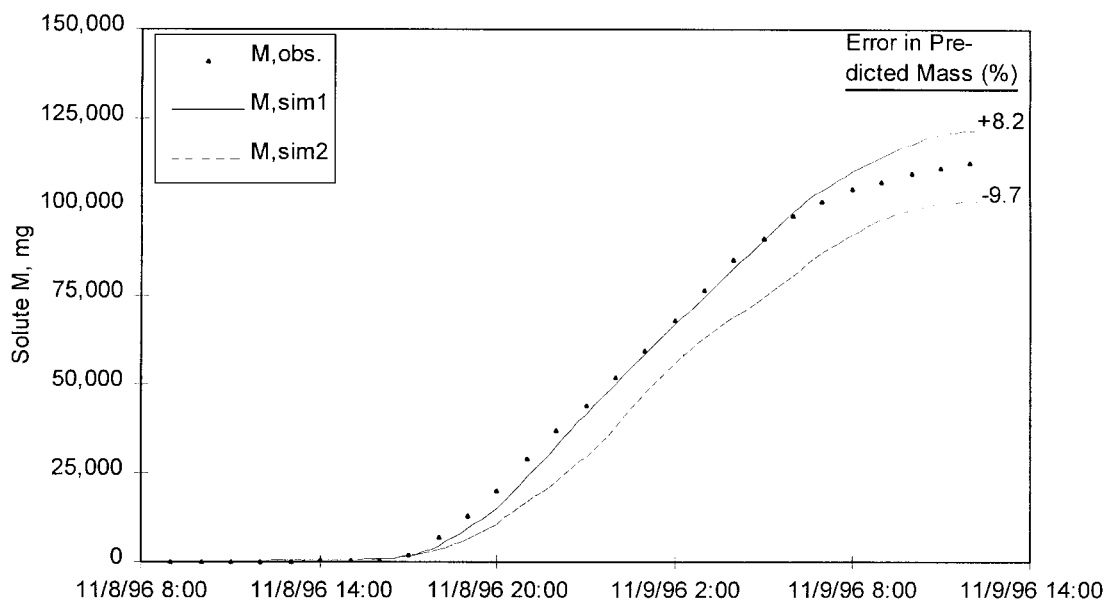


FIG. 9. Soluble Phosphorus Cumulative Mass Load in Tile Outflow (Observed and Simulations 1 and 2)

flow volume and concentration for each time step. The cumulative mass export for the event is depicted in Fig. 9 for observed data, and simulations 1 and 2. Both simulations underpredict solute mass for the buildup in stage I. This may be due to the fact that the lower part of the field has already saturated, and that macropore flow transports surface water of higher concentration to the tile (with the mixing used in this paper). This raises the possibility of a three layer model, i.e., a surface layer above the mixing layer, which interacts with surface runoff (Zhang et al. 1997; Wallach and van Genuchten 1990) and entrains sediment. The depth of the surface layer for runoff desorption is on the scale of millimeters (Sharpley 1985).

CONCLUSIONS

We presented a simple mixing layer model for kinetic desorption of strongly sorbed solutes and their transport to tile drains. The analyses attempt to minimize the requirement for extensive data; nevertheless, the model requires two laboratory-derived variables: the kinetic desorption rate and the equilibrium distribution coefficient. The model was applied to data collected as part of a field drainage study. Sensitivity analysis indicates that desorption kinetics do limit SRP delivery to the tile drain. The results indicate a better correlation between observed and simulated values for event mass export ($\pm 10\%$) than for concentration time series, essentially because concentration is better predicted at high flow when most export takes place. A limitation of the model is its sensitivity to free water surface fluctuation during the course of the event. Further work is required to investigate the interaction of surface runoff with the mixing layer and the effect this has on tile line concentrations. Finally, the approach developed provides a conceptual framework to explain the variability observed in solute transport through drainage water and has potential applications for other sorbed solutes including pesticides.

ACKNOWLEDGMENTS

The research reported on in this paper was supported by the Watershed Agricultural Council and the New York City Department of Environmental Protection. The writers would like to thank Jan Boll, Tammo Steenhuis, and Michael Walter for their comments on earlier drafts.

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