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Model determination of non-point source phosphorus transport pathways in a fertilized grassland catchment

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Abstract:

A modified version of TOPMODEL was developed and applied to a 14·26 ha grassland catchment in Ireland in order to infer the significant pathways of soil-to-stream phosphorus transport. The physically based hydrological model generated pathway-specific information for three components of discharge: overland flow, shallow subsurface flow, and groundwater discharge. Shallow subsurface flow in this model consisted of lateral, unsaturated discharge and relied upon the same hydraulic conductivity versus depth profile used by groundwater discharge, thereby limiting the number of additional parameters that were required. Model output compared favourably with both observed stream discharge and a soil moisture time series that was measured at a location within the catchment. By bringing together, on an independent basis, model results with in-stream measurements of total phosphorus (TP) concentration, we found that the fraction of modelled stream discharge deriving from overland flow and shallow subsurface flow was a reliable descriptor of the observed TP concentrations. The analysis revealed shallow subsurface flow to be the dominant P transport mechanism, primarily because volumetric contributions to stream discharge from this zone were much greater than those from overland flow. Since the source area associated with shallow subsurface flow covers the entirety of the catchment, in contrast to only the near-stream area for variable saturated area overland flow, a catchment-wide strategy for managing fertilizer and slurry inputs for this grassland setting may have a greater potential for effectively reducing P export than would the implementation of targeted strategies alone. Copyright © 2005 John Wiley & Sons, Ltd.

INTRODUCTION

Fertilizer phosphorus (P) applications in excess of plant demand have had the cumulative effect in many agricultural and pastureland areas of creating significant non-point sources for the hydrological transport of P. The main environmental risk associated with this transport is the eutrophication of freshwater bodies, since P is the limiting nutrient in many of these systems (e.g. Daniel *et al.*, 1993). Efforts to address this issue require a catchment-level understanding of the transport processes involved in the mobilization of P from its source (i.e. soil) to output destination (i.e. stream). In this study, we develop a hydrological model in order to infer the dominant transport mechanisms that produce the observed stream water P concentrations and to assess whether there are specific areas within a grassland catchment that may be prone to P losses. Our overall aim is to generate findings that are relevant towards guiding future fertilizer application and remedial initiatives.

The scarcity of mechanistic models heretofore employed to simulate P transport at the catchment level is likely attributable to the non-ideal vertical distribution of P in the soil profile with respect to the location of the hydrological flow pathways considered in most physically based models. In other words, existing catchment models are least proficient at simulating the hydrological transport that occurs in the portions of the subsurface where P is most prevalent. When applied in chemical fertilizer or slurry form, P becomes bound to amorphous aluminium and iron oxides in the upper portions of the soil, thereby impeding its vertical

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mobility via leaching (Johnson *et al.*, 1986). High concentrations of soil P available for lateral transport to the stream are thus situated in the macroporous shallow subsurface, a potential conduit for rapid hydrological transport during and shortly following precipitation events, but one that can be problematic in terms of explicit model representation.

The modelling approach used here extends from that of Scanlon *et al.* (2000), who, in keeping with the TOPMODEL conceptual framework (Beven and Kirkby, 1979), added a shallow subsurface zone that contributed to stream discharge by routing water through this layer of high permeability. Also present in this model implementation were the traditional TOPMODEL flow-generating mechanisms, namely groundwater discharge from a permanent water table and overland flow from a variable saturated area (VSA). Inclusion of the shallow subsurface zone was shown to be important for simulating variations in stream hydrochemistry (Scanlon *et al.*, 2001). Mathematical development for discharge from this zone was predicated on the formation of transient, perched water tables, separate from the underlying permanent water table, which were observed at the study location and have been documented elsewhere (e.g. Hammermeister *et al.*, 1982a,b; Mulholland *et al.*, 1990; Wilson *et al.*, 1990). Walter *et al.* (2002) noted that unsaturated flow through the macroporous shallow subsurface could be a more apt description of the discharge mechanism in some settings and developed an alternative TOPMODEL expression for this.

The VSA concept, a feature of TOPMODEL, has been used in efforts to identify critical source areas (CSAs) that are vulnerable to P transport (e.g. Heatwole *et al.*, 1987; Grubek and Sharpley, 1998; Pionke *et al.*, 2000; McDowell *et al.*, 2002). Overland flow, which originates from rainfall incident upon near-stream areas that are prone to saturation, has been regarded as the principle mode of P transport for both of its principle forms, i.e. dissolved P (DP) and sediment-bound particulate P (PP) (e.g. Rode and Lindenschmidt, 2001). Recommended management strategies for controlling P loss have, as a consequence, focused on these near-stream areas with regard to monitoring soil P status and reducing fertilizer/slurry inputs (e.g. Pionke *et al.*, 2000). It is this VSA-centred conceptual model of P transport that is evaluated in this paper by independently comparing the flow pathway information yielded by a hydrological model with observations of in-stream P concentrations. Our specific aims are (1) to develop a physically based catchment hydrological model that will accurately reproduce stream discharge and soil moisture time series, (2) identify the primary P transport pathways through an inverse model evaluation, and (3) provide spatial information related to P transport with the catchment that may aid future water quality protection strategies for grassland settings.

SITE DESCRIPTION

The 14·26 ha 'S1' study catchment is located near the town of Donoughmore in rural Co. Cork, Ireland, in the headwater region of the Dripsey River catchment. The river ultimately drains into the freshwater Inniscarra Lake, which in recent years has shown increased signs of eutrophication (Reynolds and Petersen, 2000). Rainfall measured at the site from 1997 to 2002 averaged approximately 1470 mm per year. The S1 catchment is the smallest in a sequence of nested catchments that have been monitored for P loss (Scanlon *et al.*, 2004), and its relative size was the basis of selection for the present study in order to minimize the in-stream particulate mobilization, deposition, and P sorption/desorption. In larger catchments, these processes can exert a greater influence on the P concentrations at the outlets, thereby obfuscating the analysis of the soil-to-stream transport processes. As shown in Figure 1, the S1 catchment consists of a hillslope with steeper gradients in the upper portions that give way to more gentle terrain near the perennial stream at the base of the slope. Several fields and portions of fields fall within the topography-defined boundaries of the catchment.

Land cover within S1 catchment, like much of the surrounding rural landscape, is primarily pastureland. Perennial ryegrass is the dominant vegetation type. The land is grazed by cattle, used for dairy and meat production, and land management includes regular applications of fertilizer and slurry in order to boost the grass yield with amended levels of nitrogen and P. Application of P in 2002 was 7·7 kg ha^{-1} in the form of fertilizer and 6·6 kg ha^{-1} in the form of slurry, based on farmer surveys. Morgan's P measurements for

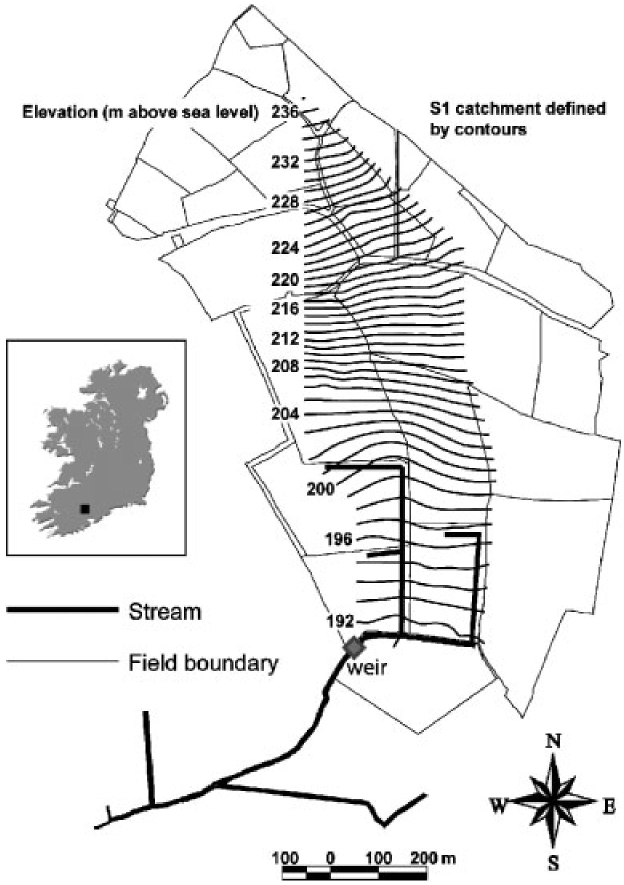

Figure 1. Contour map of the S1 catchment, showing field boundaries and the stream channels. The study site is located in southern Ireland (inset)

the fields within the S1 catchment ranged from 7·6 to 13·3 mg l^{-1}, with a mean value of 10·6 mg l^{-1} in 2002. Although P is necessary for grass growth, the soil P levels in the study area, like throughout much of Ireland (Tunney, 2002), have built up through decades of fertilization to levels that are well in excess of plant requirements (e.g. 3–6 mg l^{-1}).

The topsoil of the S1 catchment is primarily organic to a depth of 0·05–0·10 m, overlying a dark brown A horizon of sand texture. A yellowish-brown B horizon of sand texture progressively changes into a brown, gravelly sand, which constitutes the parent material, at a depth of about 0·30 m. Visual surveys have noted an abundance of macropores in the soil horizons above the parent material, with the highest concentration of grass roots also corresponding to depths of approximately 0–0·30 m below the surface. The underlying bedrock consists of red sandstone.

METHODS

Field methods

Stream discharge and chemistry measurements were collected at the outlet of the S1 catchment throughout 2002. Stream stage was continuously measured by a Thalimedes water level recorder (OTT Hydrometry Ltd, UK) placed within a stilling well situated several metres upstream from a v-notch weir. Stage measurements were converted to discharge based on the weir equation, which was checked for accuracy with manual stage–discharge measurements. Composite, flow-weighted water samples were collected in flow-actuation mode by an ISCO 6712 autosampler, with the intake positioned approximately 0·25 m above the stream bed, 2 m upstream from the weir. Samples were left in the autosamplers for between 1 and 4 days after collection, depending on the flow conditions and sampling frequency. During periods of elevated flow and frequent sampling, for example, this time was usually on the order of 1–2 days. Once collected, samples were held at 4 °C until analysis, which was conducted on either the same day or the following morning.

A meteorological station positioned approximately 5 m from the weir recorded a variety of variables used in the modelling effort. Among these were air temperature and relative humidity (HMP45C, Campbell Scientific, Inc.) and rainfall (TE525, Campbell Scientific, Inc.). An eddy covariance (EC) system, consisting of a three-dimensional sonic anemometer (model 81 000, R.M. Young Co.) working in tandem with an open-path gas analyser (model Li-7500, Li-Cor, Inc.), was used to measure evapotranspiration E directly. The height of these instruments was 6 m above the land surface. Net radiation R_n was also measured (model CRN-1 radiometer, Kipp and Zonen), along with the soil heat flux G (model HFT3, Campbell Scientific, Inc.) at a depth of 0·05 m. Root-zone volumetric soil moisture θ_{rz}, taken as the average over a depth of 0–0·30 m, was measured by three time-domain reflectometry (TDR) probes (model CS615, Campbell Scientific, Inc.) oriented parallel to the surface at depths of 0·05, 0·15, and 0·25 m.

Laboratory methods

P analyses for the streamwater samples were performed manually by spectrophotometer after *Standard Methods* (Anon., 1985), based on the molybdate/ascorbic acid method of Murphy and Riely (1962). For DP, which is comprised of dissolved reactive P, organic P, and complexed non-organic P, the samples were membrane filtered using 0·45 μm cellulose acetate filters and then digested using sulphuric acid–ammonium persulphate in an autoclave. Filtering was not performed for the total P (TP) measurements. The test was somewhat modified from *Standard Methods* (Anon., 1985), in that the acid levels in the combined reagent were reduced in order to eliminate the NaOH neutralization step.

Modelling methods

Since perched water tables have not been observed to form in the pastureland setting of the present study, unsaturated flow is a more likely contributor to the storm hydrograph response. Soil moisture, therefore, is the state variable of interest for capturing the shallow subsurface hydrological dynamics. In an earlier study at the Co. Cork site, Albertson and Kiely (2001) were able to model the time evolution of the root-zone soil moisture θ_{rz} (dimensionless) at a position in the catchment by

$$\frac{d\theta_{rz}}{dt} = \frac{1}{d_{rz}}(I_o - E_{tr} - q_{rz}) \tag{1}$$

where d_{rz} [L] is the depth of the root zone, I_o [LT^{-1}] is the rate of infiltration, E_{tr} [LT^{-1}] is the water loss via transpiration, and q_{rz} [LT^{-1}] is the drainage across the bottom of the root zone. A unit head gradient was assumed for the drainage, in the form of

$$q_{rz} = K(\theta_{rz}) = K_{sat}\left(\frac{\theta_{rz}}{\theta_{rz,max}}\right)^{2b+3} \tag{2}$$

where K_{sat}, $\theta_{rz,max}$, and b are soil-specific properties, which can be derived from textural information (Cosby *et al.*, 1984).

Note that Equation (1) ignores lateral drainage, and is correct only for the positions in the catchment where lateral unsaturated flow is at steady state, i.e. the lateral drainage entering a unit volume is equivalent to the lateral drainage that leaves this volume. At the catchment scale, lateral drainage must affect the root-zone water balance, in that the contribution to stream discharge from this zone must be compensated for by a decrease in the catchment-average root-zone soil moisture $\overline{\theta_{rz}}$. The simple drainage term q_{rz} given in Equation (1) must be replaced by vectorized components representing vertical and lateral drainage, q_v [LT^{-1}] and q_l [LT^{-1}] respectively. The average soil moisture balance for the catchment then becomes

$$\frac{d\overline{\theta_{rz}}}{dt} = \frac{1}{d_{rz}}(\overline{I_o} - \overline{E_{tr}} - q_v - q_l) \tag{3}$$

The terms q_v and q_l are sought, in this paper, to be defined in a manner that is consistent with TOPMODEL assumptions.

By casting the unsaturated hydraulic conductivity $K(\theta)$ in the form of

$$K(\theta) = K_{sat}\exp(-\kappa\Omega)$$
$$\Omega = 1 - \frac{\theta - \theta_d}{\theta_s - \theta_d} \tag{4}$$

where K_{sat} [LT^{-1}] is the saturated hydraulic conductivity, κ is a soil-specific constant, θ_d is the soil moisture at which the conductivity is near zero, and θ_s is the soil moisture at saturation, Walter *et al.* (2002) generated an alternative expression for shallow subsurface flow based on soil moisture that is equivalent to

$$\overline{q_l} = T_{max}\exp(-\overline{\lambda})\exp(-\overline{\kappa\Omega}) \tag{5}$$

where T_{max} [L^{2}T^{-1}] is the maximum transmissivity and $\overline{\lambda}$ is the mean of the ln(a/tan B) topographic index distribution (Beven and Kirkby, 1979) for the catchment, with a [L] defined as the contributing area per unit contour width and B (dimensionless) the local slope. The original TOPMODEL configuration assumes that K declines exponentially with depth z according to the equation

$$K_{sat}(z) = K_o\exp\left(\frac{-\theta_n z}{m}\right) \tag{6}$$

where K_o [LT^{-1}] is the saturated hydraulic conductivity at the surface, θ_n is the drainable porosity (taken as $\theta_s - \theta_d$), and m [L] is a parameter that defines the exponential decay. We assume in our model that unsaturated discharge is confined to the root zone, with relatively insignificant amounts deriving from the region between this zone and the level of the permanent water table (this is due to a combination of low K_{sat} and low θ here, although the assumption is qualified according to the value of m). The maximum transmissivity the root zone is

$$T_{rz,max} = \int_0^{d_{rz}} K_o\exp\left(\frac{-\theta_n z}{m}\right)dz \tag{7}$$

Solving for Equation (7), substituting this into Equation (5), and assuming that the soil-specific parameter κ is independent of depth gives

$$q_l = \frac{K_o m}{\theta_n}\left[1 - \exp\left(\frac{-\theta_n d_{rz}}{m}\right)\right]\exp(-\overline{\lambda})\exp(-\kappa\overline{\Omega_{rz}}) \tag{8}$$

the equation for lateral root-zone discharge. Discharge deriving from the permanent groundwater table, q_{gw} [LT^{-1}], takes its traditional TOPMODEL form:

$$q_{gw} = K_o m\exp(-\overline{\lambda})\exp\left(-\frac{\overline{d_{wt}}\theta_n}{m}\right) \tag{9}$$

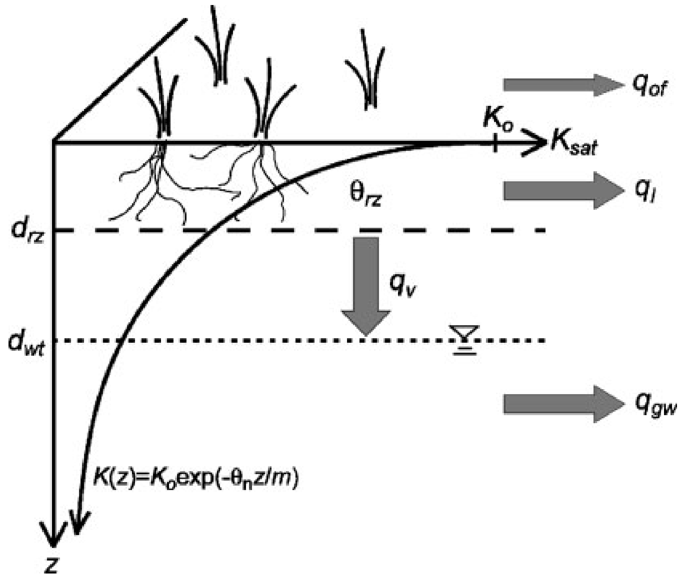

Figure 2. Cross-sectional diagram of the soil profile illustrating the exponential decrease in hydraulic conductivity as a function of depth, along with the modelled components of stream discharge (q_{of}, q_l, and q_{gw})

where state variable $\overline{d_{wt}}$ [m] is the average depth to the groundwater table. Note that the equations for q_l and q_{gw} rely upon the same $K_{sat}(z)$ profile (Figure 2).

Localized depth to the permanent water table d^i_{wt}, specific to the binned topographic index λ^i, is calculated by

$$d^i_{wt} = -\frac{\lambda^i m}{\theta_n} + \frac{\overline{\lambda} m}{\theta_n} + \overline{d_{wt}} \tag{10}$$

Similarly, the local soil moisture θ^i_{rz} can be expressed as

$$\theta^i_{rz} = \left(\frac{\lambda^i}{\kappa} - \frac{\overline{\lambda}}{\kappa} + \overline{\Omega_{rz}}\right)(\theta_s - \theta_d) + \theta_d \tag{11}$$

after Walter *et al*. (2002). The local variables d^i_{wt} and θ^i_{rz} are conceptualized to interact such that the soil moisture levels are accordingly augmented when the water table rises to within the root zone. This interaction is an important consideration for the calculations of overland flow q_{of} [LT^{-1}] and infiltration $\overline{I_o}$. Taking into account the distributed soil moisture and water table depth, the total localized root-zone soil moisture $\theta^i_{rz,tot}$ [L] is calculated by

$$\theta^i_{rz,tot} = \left[\left\{\begin{array}{ll} \theta^i_{rz} & d^i_{wt} \geq d_{rz} \\ \min\left\{\begin{array}{c} \theta^i_{rz} + \dfrac{(d_{rz} - d^i_{wt})\theta_n}{d_{rz}} \\ \theta_s \end{array}\right\} & d^i_{wt} < d_{rz} \end{array}\right.\right] d_{rz} \tag{12}$$

Average infiltration rate, which adjusts $\overline{\theta_{rz}}$ in the manner described by Equation (3), is found by

$$\overline{I_o} = \frac{1}{\Delta t}\sum_{i=1}^{N} \left\{\begin{array}{ll} \max[(P - \mathrm{sil}_{max}), P]A^i & P - \mathrm{sil}_{max} \leq (\theta_s - \theta^i_{rz,tot})d_{rz} \\ (\theta_s - \theta^i_{rz,tot})A^i & P - \mathrm{sil}_{max} > (\theta_s - \theta^i_{rz,tot})d_{rz} \end{array}\right. \tag{13}$$

where Δt [T] is the time step, A^i (dimensionless) is the fractional area corresponding to each topographic index bin i, P [L] is the rainfall, and $\mathrm{sil}_{\mathrm{max}}$ [L] is the surface interception store that is lost to direct evaporation. Overland flow is calculated by

$$q_{\mathrm{of}} = \frac{1}{\Delta t}\sum_{i=1}^{N}\begin{cases} 0 & P - \mathrm{sil}_{\mathrm{max}} \leq (\theta_{\mathrm{s}} - \theta^{i}_{\mathrm{rz,tot}})d_{\mathrm{rz}} \\ [P - \mathrm{sil}_{\mathrm{max}} - (\theta_{\mathrm{s}} - \theta^{i}_{\mathrm{rz,tot}})]A^i & P - \mathrm{sil}_{\mathrm{max}} > (\theta_{\mathrm{s}} - \theta^{i}_{\mathrm{rz,tot}})d_{\mathrm{rz}} \end{cases} \tag{14}$$

Calculation of the three discharge components, as outlined in Equations (8), (9), and (14), leaves only the variables q_{v} and $\overline{E_{\mathrm{tr}}}$ to be defined. Given the exponential decline in K_{sat} with depth, this makes q_{v} especially difficult to formulate properly, and simple equations such as Equation (2) are not suitable. A more detailed vertical drainage model has been developed for this conductivity profile (Montaldo and Albertson, 2001), but it is not readily compatible with the catchment model framework presented here. What can be reasonably assumed about q_{v} is that it is maximal when $\overline{\theta_{\mathrm{rz}}} = \theta_{\mathrm{s}}$, is near zero when $\overline{\theta_{\mathrm{rz}}} = \theta_{\mathrm{d}}$, and varies in an approximately exponential manner when $\overline{\theta_{\mathrm{rz}}}$ is between these two extremes. In other words, it behaves similar to q_{l}; therefore, the proportional relationship

$$q_{\mathrm{v}} = \chi q_{\mathrm{l}} \tag{15}$$

is adopted, where the coefficient of proportionality χ is, in an operational sense, a calibrated parameter. Finally, the transpiration term in the root-zone water balance is estimated using the Priestley and Taylor (1972) relationship with a coefficient β that represents a potential limitation imposed by the status of the soil moisture:

$$\overline{E_{\mathrm{tr}}} = \sum_{i=1}^{N}\alpha\beta(\theta^{i}_{\mathrm{rz,tot}})(R_{\mathrm{n}} - G - E_{\mathrm{b}})\frac{\Delta}{\Delta + \gamma}A^i \tag{16}$$

where α is the Priestley–Taylor coefficient (taken as 1·26), R_{n} and G [LT^{-1}] are measured variables, E_{b} [LT^{-1}] is the energy used for direct evaporation from the surface interception store, Δ is the slope of the saturation water vapour pressure curve, γ is the psychrometric constant, and β is defined by

$$\beta(\theta^{i}_{\mathrm{rz,tot}}) = \begin{cases} 1 & \theta^{i}_{\mathrm{rz,tot}} \geq \theta_{*} \\ \dfrac{\theta^{i}_{\mathrm{rz,tot}} - \theta_{\mathrm{wilt}}}{\theta_{*} - \theta_{\mathrm{wilt}}} & \theta_{\mathrm{wilt}} < \theta^{i}_{\mathrm{rz,tot}} < \theta_{*} \\ 0 & \theta^{i}_{\mathrm{rz,tot}} \leq \theta_{\mathrm{wilt}} \end{cases} \tag{17}$$

where the parameters θ_{*} and θ_{wilt} respectively represent the points at which soil moisture limits transpiration and where soil moisture causes transpiration to cease (Jacquemin and Noilhan, 1990; Avissar and Peilke, 1991; Albertson and Kiely, 2001). These are estimated from the joint analysis of the EC flux and soil moisture observations.

Of the parameters required to run the model, several can be reasonably estimated through direct and indirect observations and are, therefore, held constant throughout the model calibration procedure. For instance, the estimate of d_{rz} (0·3 m) comes from field observations of the soil profile, while $\mathrm{sil}_{\mathrm{max}}$ (0·001 m) is an approximation based on the grass vegetation cover. Soil moisture parameters θ_{s} (0·49) and θ_{d} (0·25) are deduced from the characteristics of the soil moisture time series measured at the study site, and m (0·0786 m) is defined on the basis of groundwater recession analysis, as outlined in Scanlon *et al.* (2000). Three parameters, κ, K_{o}, and χ, were adjusted during the model calibration, and the optimal set of these was selected based on minimizing the squared error between the modelled discharge q_{tot} ($= q_{\mathrm{gw}} + q_{\mathrm{l}} + q_{\mathrm{of}}$) and the observed stream discharge q_{obs}. The model runs on 0·5 h time steps.

Output from the hydrological model and stream water P measurements were brought together on an independent basis in order to test for the efficacy of the model and to gain insight into the controls on the stream chemistry. Since the concentrations of DP and PP measured at the S1 catchment outlet were highly correlated with one another ($R^2 = 0{\cdot}70$), we do not distinguish between the two forms in the present analysis and instead report the stream water concentrations in terms of TP. The flow-weighted composite sampling method for stream chemistry means that the measurements represent the average concentration over a period of time that depended on stream discharge. For the data presented in this study, this period ranged between 1 h during peak flow conditions and 145 h during low flow. Therefore, the modelled discharge associated with the TP concentrations was likewise averaged over the timeframe defined by the sampling interval. Analysis of the model-generated flow data focuses on the fraction of discharge that emerges from the specific flow pathways, since this, along with the concentrations associated with each pathway, governs the variation in stream water TP levels.

RESULTS

Stream discharge is not a reliable predictor of the stream water TP concentration, as indicated by the scatter in Figure 3. In general, there is a positive correlation between TP and q_{obs}, but there are instances in which the TP concentrations are high at low discharge and relatively low at high discharge. This points to controls on P transport that are related to the temporal dynamics associated with the specific flow pathways, information that we seek to obtain with the model application. With the model constructed as described in the Methods section, the calibration procedure for matching the observed hydrograph determined the optimal set of values for κ (12), K_o (150 m h^{-1}), and χ (1·5) that were ultimately used in the model analysis.

The 1785 mm of rainfall received at the S1 catchment during 2002 was well above the annual average. According to the model results, 1257 mm of the water left the catchment in the form of stream discharge, 407 mm was lost to evapotranspiration, and the remaining 121 mm went into soil moisture and groundwater storage. These modelled components of the water balance compare favourably with the direct measurements of total stream discharge (1214 mm) and EC-measured cumulative evapotranspiration (381 mm). In terms of the percentage of the modelled discharge that derives from the individual flow pathways, groundwater discharge accounted for 54·1%, shallow subsurface flow via the root zone contributed 41·3%, and overland flow provided the remaining 4·6%. Although the latter pathway did not generate a substantial amount in terms of the cumulative catchment discharge, it was important in defining the episodic stream response and contributed as much as 66·4% to the instantaneous discharge during one event in 2002. The maximum expanse of the VSA during the period modelled was 11·8% of the catchment area.

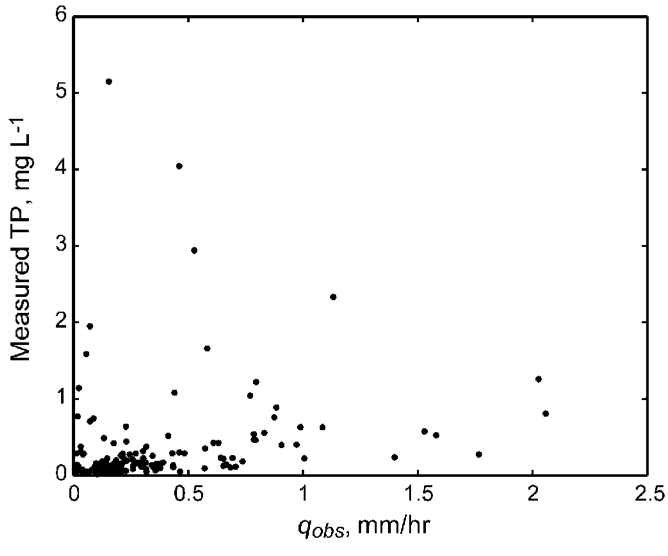

Figure 3. Measured TP as a function of the measured stream discharge q_{obs}

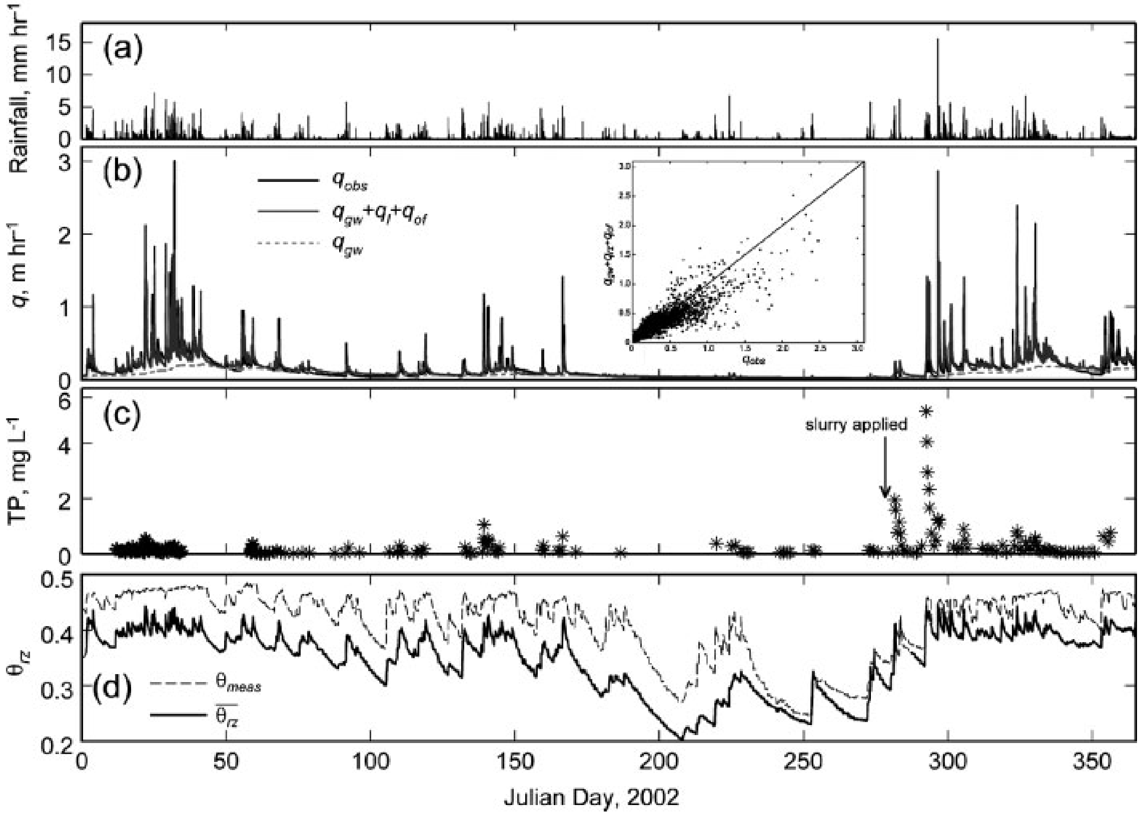

Figure 4. Time series of (a) measured rainfall, (b) measured and modelled components of stream discharge with the modelled total discharge plotted against observed discharge (inset), (c) measured stream water TP concentrations, and (d) locally measured and modelled catchment average root-zone soil moistures

Time series of modelled and observed data are shown in Figure 4. Rainfall was generally not of high intensity but was persistent, especially during the winter months (Figure 4a). Compaction of the time scale makes somewhat difficult the comparison between the modelled and observed hydrographs (Figure 4b), so these time series are also plotted against one another on a half-hourly basis with the 1 : 1 line given as a reference (Figure 4b, inset). Measured stream water concentrations of TP are also shown (Figure 4c), with the temporal position of the composite samples given as the midpoint of the sample collection period. Note the influence on the TP concentrations from a slurry application to several fields near the base of the S1 catchment on Julian day 280. Following the spreading, the TP concentrations during periods of peak discharge were greatly in excess of those observed during the remainder of the year, yet the concentrations were similar to background levels during low flow conditions.

Soil moisture is a state variable that is tracked by the simulation, and the modelled and observed time series for this are shown (Figure 4d). Whereas $\overline{\theta_{rz}}$ is the catchment mean for the soil moisture, θ_{meas} refers to the TDR measurements of the root-zone soil moisture at a single location near the base of the catchment. The corresponding topographic index λ^i is greater than the catchment mean $\overline{\lambda}$, so it is apparent from Equation (11) that these should be offset in a manner similar to that observed.

Model results were generated according to only hydrological considerations, and so when brought together with the stream chemistry measurements in Figure 5, this is done on an independent basis. If the TP concentrations associated with a particular pathway are much higher relative to the others, then the stream TP

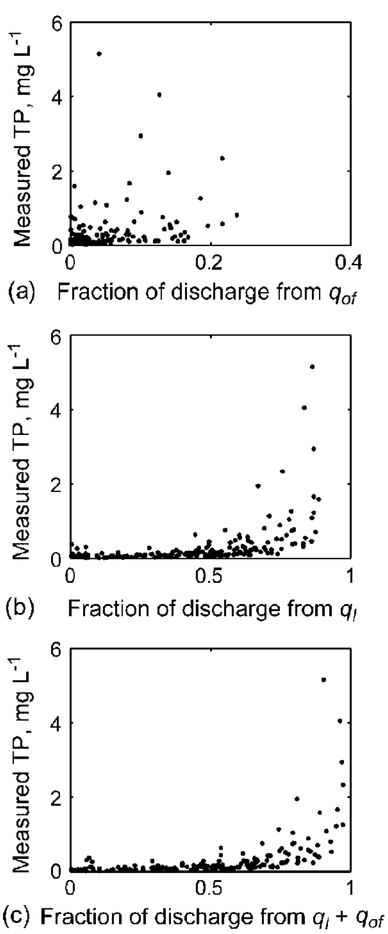

Figure 5. Measured stream water TP concentrations as a function of the modelled fraction of stream discharge deriving from (a) overland flow, (b) lateral shallow subsurface flow, and (c) overland plus lateral shallow subsurface flow

concentrations should increase when the fraction of the discharge deriving from that pathway is increased. In the case of overland flow (Figure 5a), there is no clear trend that would indicate that input from this pathway dominates the stream chemistry signal. The highest portion of discharge that derives from overland flow is only about 25% during the intervals over which the composite samples were collected. Shallow subsurface flow contributes a much greater proportion of the stream discharge, and its influence on the TP concentrations is readily apparent (Figure 5b). The organization of the data according to the fractional contribution is even more structured when overland flow and shallow subsurface flow are considered together (Figure 5c), exhibiting approximately exponential dependence upon the input fraction. The imprint from the land management within the catchment (i.e. slurry spreading) does, of course, remain, but it does not significantly alter the overall relationship. Much of the variability in the stream water TP concentrations that could not be accounted for by the magnitude of the discharge (Figure 3) can be explained by the modelled pathway-specific results.

DISCUSSION

Many studies have reported that a large portion of P that is exported from a catchment can be attributed to a limited number of discharge events within a rather short timeframe (e.g. Grant *et al.*, 1996; Kronvang *et al.*, 1997; Brunet and Brian Astin, 1998; Pionke *et al.*, 2000). This was also observed in the present study, as the major flux events possessed the combination of high P availability due to a recent slurry application and relatively large amounts of discharge that derived from surface and shallow subsurface flow pathways. The assessment that these conditions are favourable for generating a high P flux is fairly intuitive, but what requires greater clarification is how P reaches the stream in this grassland catchment. What may seem like a trivial distinction between overland flow and shallow subsurface flow as the dominant P transport pathway is, in fact, a significant one, owing to the differential source areas possessed by each. VSA overland flow is confined to an area near the base of the hillslope, whereas shallow subsurface flow is potentially active throughout the entirety of the catchment. The hydrological model presented in this paper aids in evaluating the relative contributions to the P flux from the distinct flow pathways.

The modified version of TOPMODEL used in this application was relatively parsimonious with regard to the number of calibrated parameters, considering that an extra discharge pathway (shallow subsurface) was included along with the traditional two (overland, groundwater). This was accomplished by using a single $K_{\mathrm{sat}}(z)$ profile (Figure 2), such that the unsaturated and saturated zone discharge equations, Equations (8) and (9) respectively, were influenced by the same values of m and K_{o}. The use of an EC system to measure E fluxes directly was helpful in assigning values to several root-zone parameters which would otherwise have had to have been calibrated. The general agreement between the cumulative E measured by the EC system and that simulated by the model, along with the consistency between cumulative measured and modelled discharges, is a positive outcome of the simulation. Another encouraging result was that the model state variable $\overline{\theta_{\mathrm{rz}}}$ tracked well with the measured root-zone soil moisture, especially considering that the model was calibrated on the basis of reproducing stream discharge alone. An effort was made to construct and parameterize the hydrological model properly, since an accurate representation of the catchment hydrological dynamics is a necessary prerequisite to inferring the P transport mechanisms.

The lack of a substantial correlation between the stream TP concentration and the fraction of the discharge deriving from overland flow (Figure 5a) is likely due to the fact that (1) this modelled component of discharge is typically less substantial than the modelled shallow subsurface flow, and (2) the TP concentration associated with the q_{of} must not be significantly higher than that for q_{l}. The first point suggests that overland flow is not the dominant volumetric contributor to the storm response, an outcome of the model that would be in agreement with findings from isotopic studies that have repeatedly shown the prevalence of pre-event water in the storm hydrograph for humid, temperate regions (e.g. Buttle, 1994; Dewalle and Pionke, 1994; Burns, 2002). The second point, which implies that shallow subsurface discharge can possess concentrations of TP on a par with those associated with overland flow, has been supported by recent field measurements in a managed grassland setting. Heathwaite and Dils (2000) found through direct sampling that TP concentrations in overland runoff and shallow subsurface macropore flow were essentially of the same magnitude, with PP in organic or colloidal form accounting for a large portion of the TP composition in the latter discharge component. They suggested that pathways other than the commonly assumed overland flow could be important conduits for P loss, especially in settings such as grassland catchments where soil erosion rates are relatively low.

The distribution of soil P within a catchment can provide clues as to how P is transported from soil to stream. If VSA overland flow were the dominant P transport mechanism, then it would be expected that the near-stream areas would be depleted in soil P. This would be the case because the removal of P from these areas via overland transport would occur at rates faster than those associated with downslope P mobilization to these areas via other, presumably less efficient pathways. Figure 6 is a map of the 211 ha S3 catchment, within which the S1 catchment is nested, showing the Morgan P levels that were measured in the fields at the beginning of 2002, several months before fertilizer application. No relationship was found between these soil P levels and the 2002 fertilizer/slurry P applications to each of the fields that were reported in farmer surveys, meaning that these soil P levels are reflective of historic application amounts and the redistribution processes within the catchment. The spatial distribution exhibited in Figure 6 does not conform to the pattern that would be expected if VSA overland flow was the dominant P transport mechanism. The near-stream areas are not depleted in soil P, and there is no evidence that soil P preferentially builds up

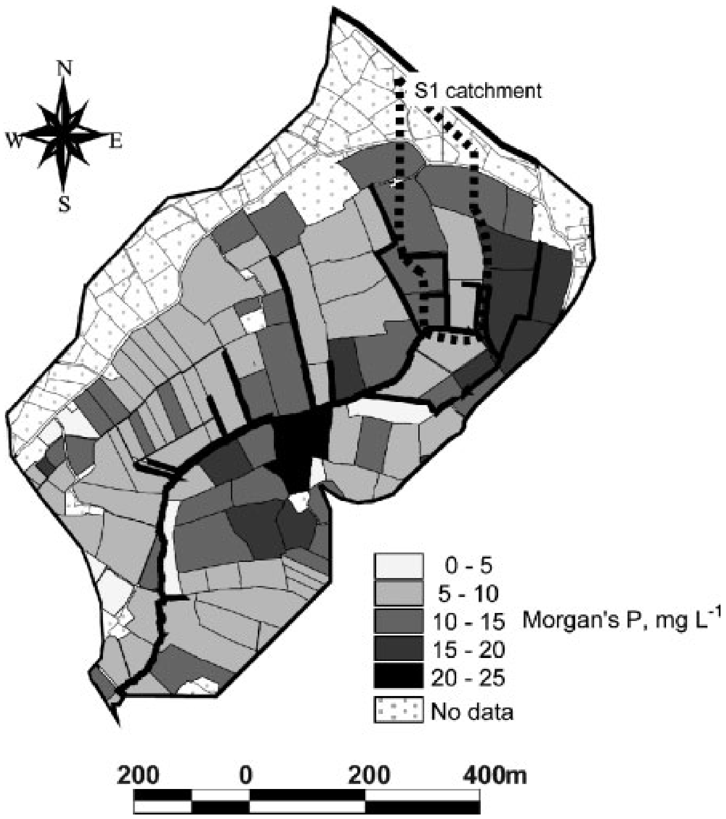

Figure 6. Morgan's P levels measured in 2002 for the fields within the S3 catchment. The boundary of the S1 catchment is noted by the dotted line

in the fields near the catchment perimeter, never to be mobilized by overland flow. The soil P pattern in Figure 6 imparts a more complex picture of the within-catchment P transport processes than can be accounted for by the VSA conceptual model. Significantly, both the model results and the soil P observations indicate that the source area for P that ultimately reaches the stream is not necessarily confined to the near-stream locations.

Shallow subsurface flow can potentially mobilize P throughout the entire catchment; therefore, fertilizer/slurry applications to fields even in the upper portions of the catchment can eventually contribute to the P flux in both direct and indirect ways. Direct transport of P from upslope fields to the stream is attenuated by sorption/desorption reactions that occur with the soil along the flowpath, and this transport is ultimately consequential in affecting the long-term P flux. Upslope portions of the catchment could also exert an indirect influence on the short-term, high-magnitude flux events, such as those associated with the Julian day 280 slurry spreading, by reducing the binding capacity of the soils in the near-stream areas due to the additional P that derives from non-local sources. The existence of connectivity between upslope and downslope areas of a catchment as a result of shallow subsurface transport should be factored into management strategies. While common-sense recommendations such as avoiding fertilizer/slurry applications to near-stream areas shortly before the onset of seasonal rainfall would go a long way toward reducing short-duration, high-intensity P fluxes, the land management practices in the areas further away from the stream should not be treated as inconsequential in shaping the magnitude of the catchment P yield. A catchment-wide approach for managing P application would, therefore, be needed for catchments that have been identified as being vulnerable to P loss.

The model result indicating that P transport at the study site is predominantly subsurface could help to explain interesting findings from another location. McKergow *et al.* (2003) found that riparian buffers, which were installed in an agricultural catchment with the intent of trapping sediment and nutrients in runoff and displacing sediment- and nutrient-producing activities away from the stream, were largely ineffective in reducing TP export. Shallow subsurface transport of P could largely circumvent the potentially beneficial aspects provided by these riparian buffers, a possibility that was not speculated upon earlier. Findings from field-based studies that have challenged the commonly held assumption that the majority of P transport occurs via surface runoff (e.g. Heathwaite and Dils, 2000), confirmed here by the model results, could have important implications for the design and implementation of remedial initiatives.

CONCLUSIONS

An independent comparison between measured stream water TP concentrations and model-generated discharge data from a modified version of TOPMODEL demonstrated that the flow pathway information yielded by the model is an organizing feature for describing the observed variability in stream water TP. Based on this analysis, we were able to infer the relative contributions from the individual pathways to the overall P transport. Whereas overland flow and shallow subsurface flow together provided the best qualitative descriptor of the stream water TP observations (Figure 5c), shallow subsurface flow was inferred to be the dominant transport mechanism in the grassland catchment setting. This was primarily due to much greater volumetric contributions to stream discharge deriving from the shallow subsurface flow than from overland flow, whereas their respective TP concentrations were presumably similar.

The source area associated with shallow subsurface flow basically covers the entirety of the catchment, meaning that fertilizer/slurry applications even to the upslope areas of the catchment could eventually impact water quality. Strategies for reducing the export of P from catchments such as the one examined in this study must, as a foremost goal, aim to reduce inputs of P throughout the catchment. In Ireland, this could be accomplished with little impact on grassland yield. As reported by Tunney *et al.* (1999), 90% of optimum yield was achieved after 10 years of no fertilization for soils with moderate Morgan's P in the range of 3–6 mg l^{-1}. In the S1 catchment, where soil P levels are much higher than this, there is little need to add fertilizer and slurry with the intent of boosting P availability, since risks associated with downstream eutrophication far outweigh any potential agronomic benefits.

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