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A nested catchment approach for defining the hydrological controls on non-point phosphorus transport

Todd M. Scanlon[a,1], Ger Kiely[a,*], Qiushi Xie[b]

[a]Department of Civil and Environmental Engineering, University College, Cork, Cork, Ireland
[b]Aquatic Services Unit, Department of Zoology and Animal Ecology, University College, Cork, Cork, Ireland

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Abstract

Stream water phosphorus (P) concentrations for three nested pastureland catchments located in southern Ireland, having areas of 0.14, 2.11, and 15.24 km^2, were monitored for the purpose of defining the hydrological controls on the P transport. Concentration–discharge (C–Q) relationships were developed for total phosphorus (TP) and its two components, dissolved phosphorus (DP) and particulate phosphorus (PP), where Q is the area-normalized discharge. An analysis of covariance statistical test was applied to determine if any differences in C–Q relationships existed between sub-catchments. Significant differences ($p < 0.01$) between sites were found for the TP and PP C–Q relationships, but not for the DP C–Q relationships, indicating that phosphorus transport in its sediment-bound particulate form was alone responsible for the differences in overall P fluxes between sites. The intermediate-scale catchment possessed the highest discharge-specific PP and suspended solid concentrations. An analysis of catchment topography was undertaken in an attempt to explain the observed differences in the C–Q relationships for the individual sub-catchments. The distributions of the $\ln(A_s/\tan\beta)$ topographic index, where A_s is the upslope contributing area per unit contour width and β is the local slope, were first considered in order to test the conceptual model of variable saturated area control on the overland PP transport. Next, the distributions of the length–slope (LS) factor from the universal soil loss equation were evaluated as an index of erosion to describe PP transport. Neither topographic descriptor was found to satisfactorily conform to the C–Q observations, indicating that local catchment sediment delivery factors or in-stream channel processes are likely to be responsible for the observed differences.

Keywords: Phosphorus; Discharge; Sediment; Topography; Catchment

1. Introduction

Defining the hydrological processes involved in the transport of phosphorus (P) from soil to streams is a critical objective with regard to developing strategies for minimizing P loss and reducing the potential for the downstream eutrophication of freshwater bodies. The buildup of P in soils as a cumulative effect from fertilizer and manure application in excess of plant and animal demand has been observed on a widespread basis for both pastureland and agricultural areas alike (e.g. Sharpley et al., 1994; Sharpley and Rekolainen, 1997; Tunney, 2002). While effective strategies have

* Corresponding author. Tel.: +353-21-4902965;fax: +353-21-4276648.
E-mail address: g.kiely@ucc.ie (G. Kiely).
[1] Present address: Department of Civil and Environmental Engineering, Princeton University, Princeton, NJ, USA.

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been implemented to reduce point sources of P, such as the treatment of sewage, accelerated eutrophication as a result of P transport from such non-point sources as pastoral and agricultural soils has become an increasingly significant water quality issue (Sharpley et al., 1999; Brogan et al., 2002). Models to predict P loadings and mitigative initiatives designed to reduce these loadings must account for the factors controlling the transport of P from soils to surface water, which include soil type, soil chemistry, biotic processes, land use, and hydrological pathways. In this article, we focus on the last of these factors by constraining the analysis to a nested catchment setting in which the remaining factors are largely constant.

Total phosphorus (TP) measured in streams is partitioned in two principle forms: dissolved phosphorus (DP) and particulate phosphorus (PP). Studies have shown concentrations of DP in streams to be highly correlated with soil test P levels in the surface soil (Olness et al., 1975; Sharpley et al., 1986; Daniel et al., 1994; Sibbesen and Sharpley, 1997). Over short timescales such as single runoff events, the amount of DP available for transport exhibits an added dependency upon desorption kinetics, in which dissolved P in soil water generally increases with increased contact time with the soil surfaces (Sharpley et al., 1981). Groundwater concentrations of DP are typically low since, in contrast to nitrogen, P remains in the upper portions of the soil profile as a result of sorption onto amorphous oxides of iron and aluminum (Johnson et al., 1986).

Catchment areas that are subject to fertilization often exhibit a dominance of event-initiated transport of P in terms of the contribution to the overall flux (e.g. Pionke and Kunishi, 1992; Lennox et al., 1997; Grey and Henry, 2002). In many parts of the world, this increased flux during storm events is due disproportionately to the increased mobilization of P in its particulate form (Edwards and Owens, 1991; McDowell and Sharpley, 2002). Therefore, the identification of critical source areas and mechanisms associated with the transport of PP has become the subject of research interest, especially since remediative strategies designed to reduce total P transport by regulating soil P levels have met with only limited success (Daniel et al., 1994; Sharpley et al., 1994; Gburek and Sharpley, 1998). Attention is now focused on spatially explicit portions of catchments, specifically those areas with high soil P levels combined with a high potential for surface runoff and erosion (Gburek and Sharpley, 1998), as targeted areas for possible remedial initiatives.

One mechanism that has been observed to produce surface runoff (or 'overland flow') is described by the variable saturated area (VSA) concept (Dunne and Black, 1970), in which a rising groundwater table can intersect the near-stream catchment surface, resulting in surface saturation. Rainfall landing on this area follows an overland pathway directly to the stream. This concept has been adopted to describe the transport of PP (Whelan et al., 2002) or TP (Pionke et al., 1997; Gburek and Sharpley, 1998) to streams during storm events. The catchment areas deemed critical for P transport based upon this approach are the low-slope, near-stream regions that possess large upslope contributing areas. A quantitative descriptor of the degree to which discrete areas within a catchment are prone to surface saturation is the topographic index used in the rainfall-runoff model TOPMODEL (Beven and Kirkby, 1979). Probability density function (PDF) statistics for this distributed index have been used to infer the hydrological pathways involved in streamflow generation on a comparative basis for multiple catchments (Wolock, 1995), and have been used to assess the impact of the flow pathways on geochemical transport to downstream receiving bodies (Wolock et al., 1989, 1990). With regard to P transport, catchments having a larger fractional area that can function as a VSA during storm events should be more effective in transporting P to streams, assuming similar land cover, land use, and land management amongst catchments.

Strong correlations between stream water PP and suspended solids (SS) concentrations (Grant et al., 1996; Kronvang et al., 1997; Brunet and Brian Astin, 1998; Owens and Walling, 2002) suggest that erosional processes can be important in shaping overall P fluxes. As inferred from the assumptions used by erosional models, infiltration excess overland flow is the hydrological process that would be implicated in the transport of PP to streams, as the energy associated with the overland flow acts as the driving force for the potential removal of soil particulate matter from the land surface. Thus, and in partial contrast to the VSA-related characteristics, the critical source areas that are specific to erosional processes correspond to steep hillslopes that posses large contributing areas. A quantitative way to describe the potential for erosion based upon the catchment topography is the length–slope (*LS*) factor from the universal soil loss equation (USLE) (Wischmeier and Smith, 1965, 1978) and the revised universal soil loss equation (RUSLE) (Renard et al., 1994) as calculated for three-dimensional terrain using the method outlined by Moore and Wilson (1992). Although originally developed to infer long-term soil erosion rates, this approach can be used to evaluate the erosional effects involved in PP transport that may be manifested on shorter timescales, especially when considered on a comparative, rather than absolute, basis for disparate catchment topographic profiles.

The nested catchment approach described in this article provides a structure for evaluating P transport mechanisms in terms of an assumed control of the catchment topographic characteristics on the flow pathways. In undertaking this analysis, our objectives are: (1) to define the differences in stream water P hydrochemistry that may exist amongst the nested catchments; (2) to differentiate between forms of P (DP and PP) that may have caused any observed differences; and (3) infer the hydrological flowpaths and associated critical source areas that are responsible for enhanced P losses to streams. In fulfilment of this last objective, two competing conceptual models (VSA vs. erosional controls) are tested for compatibility with the information revealed by stream water observations.

2. Site description

The study site is located near the town of Donoughmore in rural Co. Cork, Ireland, which receives an average of approximately 1400 mm of rainfall per year. The nested catchments examined in this study lie in the headwater region of the greater Dripsey River catchment, which ultimately drains into Inniscarra Lake, a freshwater lake that in recent years has shown increased signs of eutrophication. Fig. 1 depicts the relief and boundaries of the sub-catchments, which consist of the S1 catchment (0.14 km^2), the S3 catchment (2.11 km^2), and the S4 catchment (15.24 km^2). A gauged S2 catchment does exist, but this was not included in the present study because no stream chemistry measurements were taken at this site. The variation in scale amongst the three sub-catchments represents approximately order-of-magnitude differences in their respective areas.

The land use for the overall catchment area is largely uniform, consisting primarily of cattle grazing for dairy farming. As a consequence, the land cover is also similar throughout the study area, with pastureland, accounting for approximately 80% of the total area, segmented into individual farms. Other minor classifications of the land cover include small patches of broadleaf forest, clusters of houses, and roads. A 0.30 km^2 area used for sand and gravel mining is located in the S4 catchment, away from the vicinity of the stream. The topsoil of the study area 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. The underling bedrock consists of red sandstone. Perennial ryegrass is the dominant vegetation type for the pastureland.

Farm practice in this region involves regular applications of fertilizer and slurry in order to boost the yield of the grass with amended levels of nitrogen and phosphorus. The combined application per field in 2002 ranged from 0 to 92 kg P ha^{-1} yr^{-1} with a mean value of 28.2 kg P ha^{-1} yr^{-1}, based on data from farmer surveys. 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 over the years to levels that are well in excess of annual plant requirements. Morgans P in the fields ranged from 2.6 to 25.7 with a mean value of 10.2 mg P l^{-1} for 2002. The negative impact of this buildup, namely the loss of P to streams, is the topic of the present investigation.

3. Methods

3.1. Field methods

Stream discharge and water samples for chemistry measurements were collected at the outlets of the S1, S3, and S4 catchments within a 1-year period from August 1, 2001 to July 31, 2002. Stream stages were continuously measured by Thalimedes water level

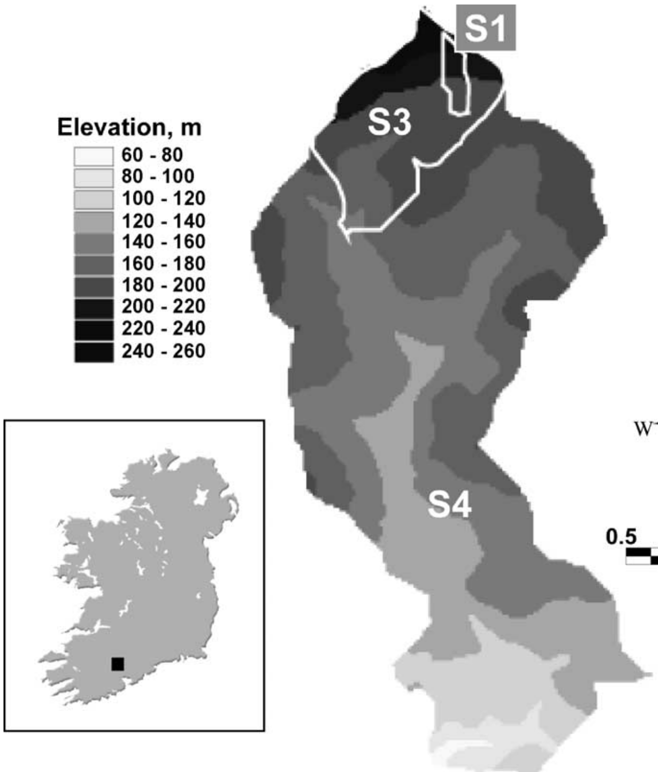

Fig. 1. Contour map showing the locations of the S1, S3, and S4 nested catchments in Co. Cork, Ireland.

recorders (OTT Hydrometry Ltd, UK) placed within stilling wells and situated several meters upstream from flow controls. The controls consisted of a v-notch weir (S1), a rectangular weir (S3), and a modified Crump weir (S4). Rainfall was measured by a gauge near the S1 outlet.

Composite, flow-weighted samples for the three sites were collected in flow-actuation mode by ISCO 6712 autosamplers at the catchment outlets. The intakes for the autosamplers were positioned approximately 0.25 m above the stream bed, 2 m upstream from the weirs at S1 and S3, and 5 m upstream from the weir at S4. Samples were left in the autosamplers for 1–4 days after collection, depending on the flow conditions and sampling frequency. During periods of elevated flow and frequent sampling, e.g. this time was usually on the order of 1–2 days. Most of the samples were collected during the cooler part of the year (January–May), when the air temperature was typically below 10 °C. Once collected, samples were refrigerated at 4 °C until analysis, which was conducted on either the same day or the following morning.

3.2. Laboratory methods

Phosphorus analyses for the stream water samples were performed manually by the colorimetric method 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 phosphorus, organic phosphorus, and complexed non-organic phosphorus, 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 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 neutralisation step. SS were measured following the method outlined in *Standard Methods* (Anon., 1985), with the modification of using pre-washed and dried Whatman GF/C filters followed by oven-drying (103–105 °C) to constant weight.

3.3. Analytical methods

Concentration–discharge (C–Q) relationships for the three sub-catchments were developed on an area-specific basis, with Q expressed in units of mm h^{-1}, which allows for direct comparison between the sites. Since composite sampling was performed, values of Q were taken as the mean discharge over the sampling time interval. A power relationship in the form of

$$C = aQ^b \tag{1}$$

where a and b are constants, was used to describe the observed variations in stream water phosphorus concentrations as a function of discharge. With C representing either TP, DP, or PP, the data from the three sub-catchments could be analysed simultaneously in order to identify any differences that may exist between their respective C–Q relationships. This was statistically evaluated through the use of an analysis of covariance (ANACOVA) test, which was applied to determine if there were any significant differences in the intercepts (a) or slopes (b) in the log-transformed C–Q data for the S1, S3, and S4 catchments.

Digital elevation model (DEM) data at a 10-m resolution was used to define the topography of the catchments. From this, a catchment topographic index was calculated according to $\ln(A_s/\tan\beta)$, where A_s is the upslope contributing area per unit contour width and β is the local slope. The 'D∞' method of Tarboton (1997) was used in the calculation of A_s. Grid points that corresponded to the mapped locations of perennial streams were not used in the analysis. Statistics of the $\ln(A_s/\tan\beta)$ probability distribution functions (i.e. mean, standard deviation, and skewness) for the sub-catchments were generated, which were then used on a comparative basis to infer catchment hydrological flowpaths, as in Wolock (1995). The VSA-based conceptual model for phosphorus transport was evaluated for its applicability to these catchments by checking for consistency in the information yielded by the observed $C-Q$ relationships and the $\ln(A_s/\tan\beta)$ distributions.

Another topographic factor that can be a potential descriptor of phosphorus transport, particularly in terms of the sediment-bound PP, is the LS-factor. Mean annual soil loss, E, is estimated from the series of multiplicative factors

$$E = RKLSCP, \tag{2}$$

where R is the rainfall erosivity factor; K, the soil erodibility factor; L, the slope length factor; S, the slope gradient factor; C, the crop management factor; and P, the erosion control practice factor. The L and S factors are often considered in a combined form, and when applied to three-dimensional terrain this can be calculated according to

$$LS = (A_s/22.1)^p(\sin\beta/0.0896)^q, \tag{3}$$

where the constants 22.1 and 0.0896 are specific to the reference hillslope considered in the original USLE (Wischmeier and Smith, 1965, 1978), and p and q are assumed to be 0.6 and 1.3, respectively (Moore and Wilson, 1992). Like in the calculation of $\ln(A_s/\tan\beta)$, the LS values that corresponded to the positions of streams were not considered. For the nested catchment experimental design, we take advantage of the similarities in rainfall rates, soil properties, land use, and land management for the different scales under consideration in order to assume that R, K, C, and P, respectively, are uniform. This leaves the topographically derived, distributed LS factor in Eq. (2) as the sole contributor to any proportional differences in E that may exist between the catchments. The observed high sensitivity of E to the LS factor (Risse et al., 1993) lends support to the suitability of this simplification.

The link between the PP fluxes observed in the stream and the erosional potential given by the LS factor is not a direct one, even when assuming that the stream water PP:sediment ratio is constant. This is because sediment yield, or the amount of sediment transported through the catchment outlet, is highly dependent upon the sediment delivery processes within the catchment (Wolman, 1977; Walling, 1983, 1988; Ferro and Minacapilli, 1995; Ferro, 1997). For example, the degree of concavity associated with the flowpath from a particular location within the catchment to the stream plays a role in determining if the soil particles eroded at that location will reach the stream or be deposited downslope on the land surface. The areas of net erosion and net deposition are not properly distinguished with application of Eq. (2). Nevertheless, as a topographic descriptor, the *LS* factor can be useful for identifying catchment areas that have the potential for erosion, and we therefore adopt this as a quantitative index for evaluating the influence of topography on the stream water PP observations, while keeping in mind the abovementioned caveats.

4. Results

The time series of composite stream water TP sample concentrations is shown in Fig. 2a, with the corresponding stream discharge for the three sub-catchments shown in Fig. 2b. The stream water chemistry sampling program was initiated in January 2002 and captured many of the significant storm events over the course of the one-year period. Area-specific discharge, Q, displays consistency between the sites (Fig. 2b), which indicates that the nested catchments have similar water balance characteristic as well as similar hydraulic conductivity profiles as a function of depth for their respective groundwater reservoirs.

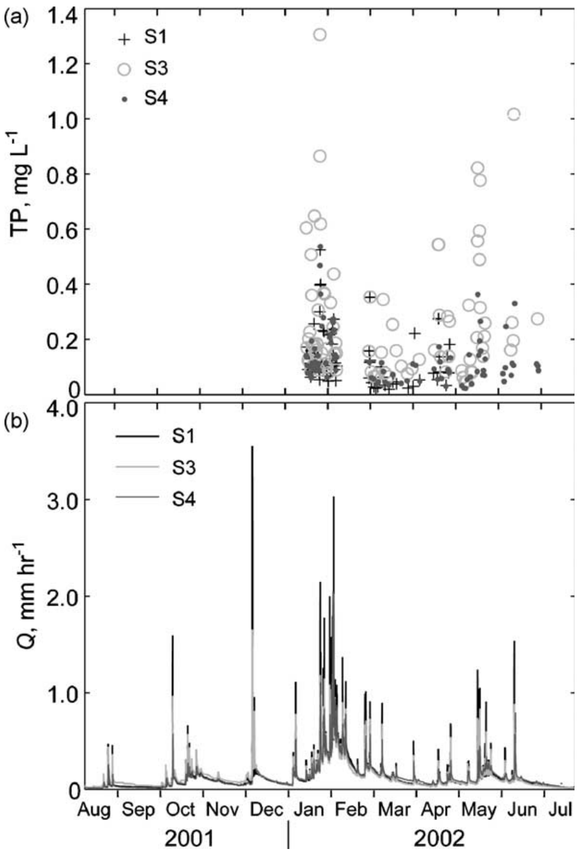

Fig. 2. (a) Stream water composite samples of total phosphorus (TP) concentrations, and (b) the discharge hydrographs for the three sub-catchments.

Observed relationships between stream water phosphorus concentrations and stream discharge are illustrated in Fig. 3a–c for TP, DP, and PP, respectively. The C–Q plots are shown on logarithmic axes in order to linearize the relationship described by Eq. (1). The data encompass a wide range of initial conditions for individual storm events and incorporate the effects of hysteresis, both of which contribute to the scatter of the C–Q data. In the present context, the term 'initial conditions' refers to the timing of fertilizer application to the pastureland, as well as to the soil moisture conditions and associated sorption/desorption kinetics that affect the amount of P available for transport to the streams. 'Hysteresis' describes the phenomenon of different P concentrations on the rising and receding limbs of the hydrograph for like levels of discharge. Positive C–Q relationships are exhibited for all of the catchments in terms of the TP (Fig. 3a) as well as for the individual phosphorus phases (Fig. 3b and c), indicating that the catchment soils contain very high levels of P that can be mobilized. The dilution effect does not dominate in this case; instead, the increased flow activates increased concentrations of P in the stream water.

In the case of TP (Fig. 3a), the C–Q relationships for the individual catchments appear to be stratified, with S3 having the highest average concentration, followed by S4, and then S1 for any given value of Q. The stratification effect is not as clear in the case of DP (Fig. 3b), but once again becomes evident for PP (Fig. 3c). If the data are indeed stratified in this manner, the slopes of the log-transformed C–Q relationships, b, should not differ between sites, but the intercepts, a, should have significant differences. The ANACOVA statistical test was applied to the data and the results are shown in Table 1. With regard to differences between sites, no significant ($p < 0.01$) differences in the slopes of the C–Q relationships were observed for any of the forms of P. Significant

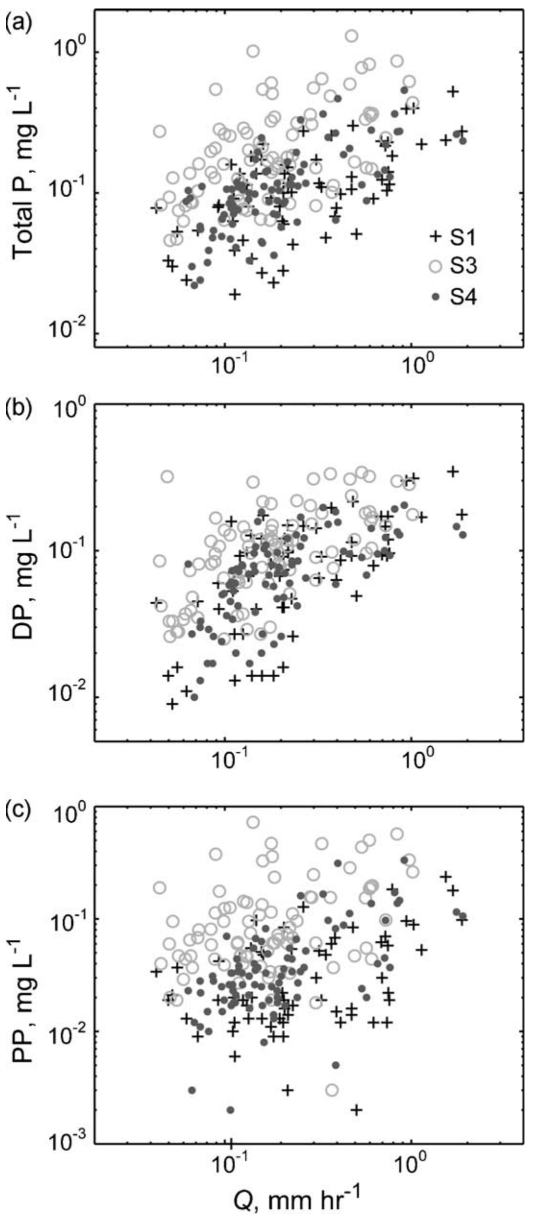

Fig. 3. Concentration–discharge (C–Q) plots for (a) total phosphorus (TP), (b) dissolved phosphorus (DP), and (c) particulate phosphorus (PP).

differences in intercepts, however, were found for TP and PP. Since there were no significant differences in slopes or intercepts for the DP C–Q relationships, this implies that the observed stratification in the TP C–Q relationships is due almost entirely to PP. Phosphorus transport in its particulate phase is thereby identified

Table 1
Analysis of covariance (ANACOVA) test results

Type of P	Significant difference in slopes ($p < 0.01$)?	Significant difference in intercepts ($p < 0.01$)?	Ranks in intercepts (highest–lowest)
Total P	none	S1 from S3	S3
		S3 from S1	S4
			S1
Dissolved P	none	none	S3
			S4
			S1
Particulate P	none	S1 from S3, S4	S3
		S3 from S1	S4
		S4 from S1	S1

as the cause of the differences in the TP loadings between the three nested catchments.

Additional analysis is required in order to determine if the observed differences in PP between the sites is a function of the PP sediment-binding characteristics or the PP transport processes. Stream water PP concentration is plotted as a function of the SS, concentration for the three sites in Fig. 4. The slope of the regressed lines, forced to have intercept at the origin, is a measure of the phosphorus enrichment of the SS. The S3 catchment, which has the highest levels of the PP per unit Q, also has the highest levels

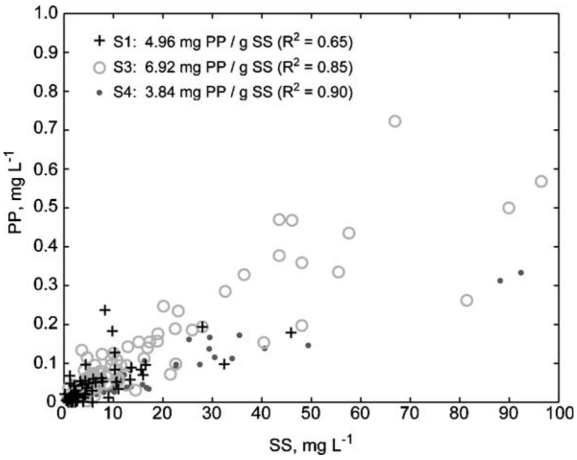

Fig. 4. Particulate phosphorus (PP) concentrations as a function of the suspended solid (SS) concentrations measured in the streams. The slope of the regression line is a measure of the phosphorus enrichment of the suspended solids.

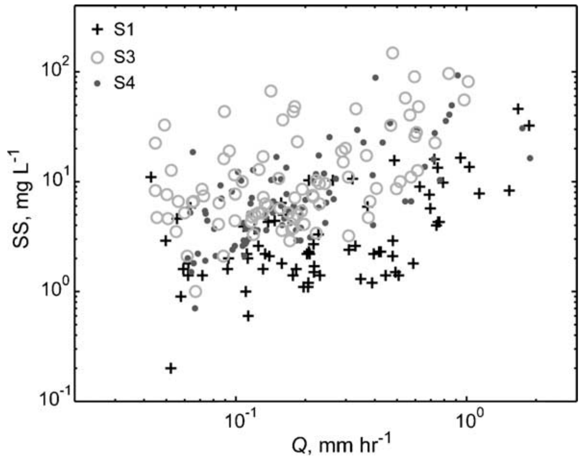

Fig. 5. Suspended solids (SS) as a function of discharge (Q), showing stratification of the data according to site.

of enrichment, 1.4 times the level of S1 and 1.8 times that of S4. These differentials are small, though, compared with the differentials in the concentrations of SS measured at the outlets of the catchments. As shown in Fig. 5, the discharge-specific SS concentrations for the sites are stratified much like those for the PP $C-Q$ relationships, with order-of-magnitude differences in SS concentrations, e.g. between sites S3 and S1. These results point to the sediment-generating processes as the cause of the observed differences in PP concentrations for the different sites.

The effect of catchment topography on the phosphorus transport was examined by calculating the distributed values of $\ln(A_s/\tan\beta)$ and LS-factor for the nested catchments. The PDFs of the $\ln(A_s/\tan\beta)$ values are shown in Fig. 6 and the statistics of these distributions are provided in Table 2. The mean, variance, and skewness for the $\ln(A_s/\tan\beta)$ distributions all increase with increase catchment size.

Since the LS-factor tends to be log-normally distributed, the catchment fractional area was binned as a function of the natural logarithm of LS for display in Fig. 7. The statistics of the LS-factor reported in Table 3 show a decease in the mean value with increasing catchment area: S1 has the highest mean value of 1.79, followed by S3 at 1.72, and S4 at 1.69. The variances of the LS factor increase with increased catchment area, indicating that while there may be a larger percentage of high LS values in the S4 catchment than the S1 catchment, there are also many more very low LS values in the S4 catchment.

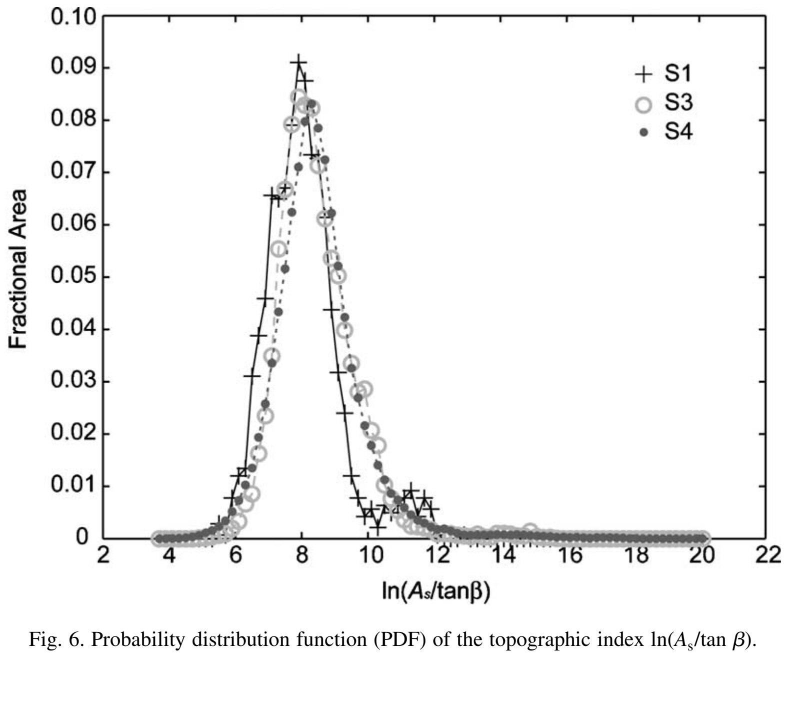

Fig. 6. Probability distribution function (PDF) of the topographic index $\ln(A_s/\tan\beta)$.

Table 2
Statistics for $\ln(A_s/\tan\beta)$ probability distribution functions

Catchment	Mean	Variance	Skewness
S1	8.05	1.28	1.01
S3	8.45	1.37	1.33
S4	8.48	1.75	1.42

5. Discussion

Joint analysis of stream discharge and phosphorus concentrations in the nested catchment setting provides an observational basis for characterizing the hydrological processes that control the transport of phosphorus from the soil to catchment outlets. The plot of TP concentrations as a function of area-specific stream discharges (Fig. 3a) shows that the $C-Q$ relationship vary according to site, a finding that is confirmed to be statistically significant (Table 1). The fact that the intermediate-scale catchment, S3, possesses the highest TP concentrations per unit discharge points to something other than a simple scale-dependent control on the P transport. In order to further explore why the TP $C-Q$ relationships are stratified according to site, it is instructive to look at the individual components of TP that are associated with differing flow pathways.

The shallow sub-surface is most likely the dominant conduit for the transport of DP to the stream. Soil water concentrations of DP are the highest in this zone, and the observed increase in DP concentrations with increased Q for all of the sites (Fig. 3b) indicates that more of the soil water becomes mobilized when this zone begins to fill during storm events. In the case of DP, there are no statistically significant differences between the $C-Q$ relationships of the three catchments (Table 1). This lends support to the assumption of similarity between the land use and cumulative effects from fertilizer/manure applications to the pastureland within the nested catchments.

Differences in the TP loadings for the individual sub-catchments are therefore explained by differences in the PP, which is primarily transported to streams via overland flow. This is shown by the significant differences that exist for the PP $C-Q$ relationships amongst catchments (Fig. 3c, Table 1). This observation raises the question as to how PP concentrations can be elevated for a particular catchment without similar increases in the DP concentrations. By looking at a single storm event, as shown in Fig. 8 for the S3 catchment, we find that the degree of hysteresis for PP is much greater than that for DP. Before the onset of the precipitation, the stream water concentration of

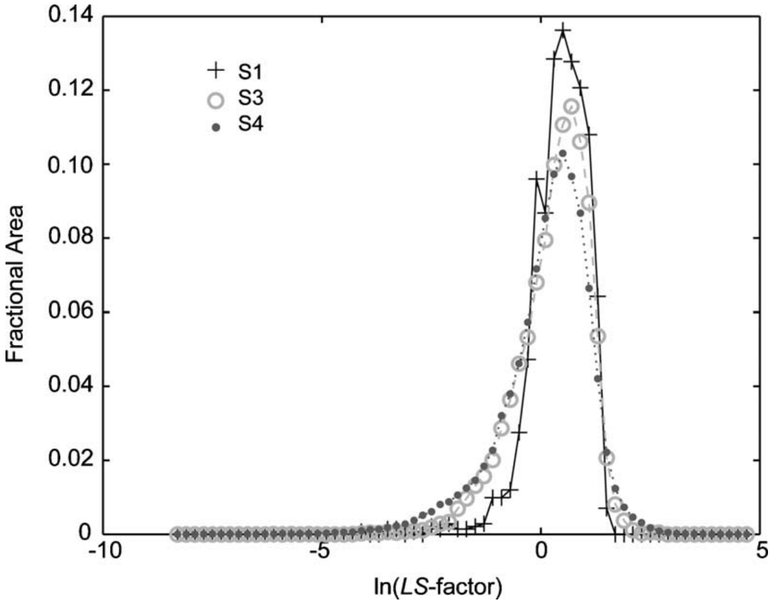

Fig. 7. PDF of the natural logarithm of the length–slope (LS) factor, which is used as a descriptor of erosion potential for the sub-catchments.

Table 3
Statistics for the *LS* and ln(*LS*) probability distribution functions

Catchment	Mean *LS*	Variance *LS*	Skewness *LS*	Mean ln(*LS*)	Variance ln(*LS*)	Skewness ln(*LS*)
S1	1.79	0.83	0.52	0.42	0.42	− 1.66
S3	1.72	1.42	1.82	0.27	0.69	− 1.02
S4	1.69	2.92	7.47	0.11	1.09	− 1.27

DP is higher than that of PP, but on the rising limb of the hydrograph, when overland flow becomes active, the concentrations of PP become greatly increased while the concentrations of DP increase much more gradually. On the receding limb of the hydrograph, when overland flow is not occurring, the concentrations of PP follow a different trajectory on the $C-Q$ plane, having much lower concentrations compared with those on the rising limb. In-stream processes are most likely responsible for maintaining the levels of PP that are measured at the catchment outlet after overland flow has ceased. The differences in the flowpaths associated with the two forms of P allows for separate flow responses of their individual concentrations.

The relatively similar PP-enrichment of the SS for the three sub-catchments (Fig. 4), weighed with the substantial differences in discharge-specific SS between the sub-catchments (Fig. 5), points to a differential in erosion rates as the cause of the observed differences in PP loss amongst the sites. Therefore, the identification of catchment surface source areas that contribute to sediment loss via overland flow is necessary in order to develop targeted strategies to reduce P mobilization. With different processes and source areas associated with the overland flow for VSA vs. erosional conceptual models, we apply topographic analysis to the nested catchments in an attempt to determine which is the most appropriate model for explaining the observed differences in the $C-Q$ relationships between the sites.

In an investigation on the impact of the ln(As/tan β) index on catchment hydrological pathways, Wolock (1995) reported that catchments with higher means and variances of this index had a higher percentage of overland flow in the total streamflow, as simulated by TOPMODEL. Since the PDFs of ln(A_s/tan β) are typically positively skewed, as in the case of the three nested catchments examined in the present

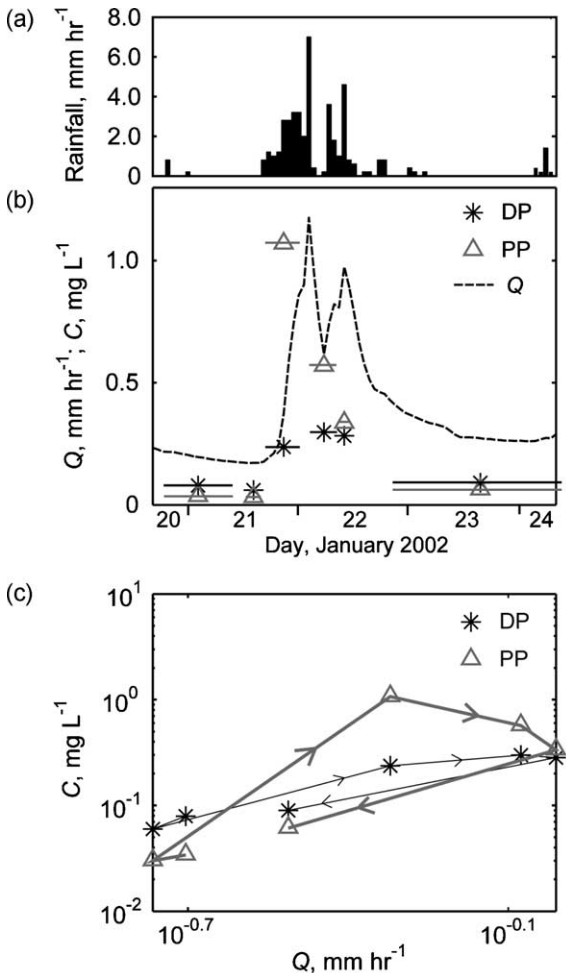

Fig. 8. An individual storm event, showing (a) rainfall, and (b) discharge and concentrations of dissolved phosphorus (DP) and particulate phosphorus (PP) in the stream water. The bars associated with the concentrations represent the span of time over which the composite sampling took place, and (c) $C-Q$ plot for DP and PP, with PP exhibiting the greatest degree of hysteresis. Arrows represent the direction of the sequence through time.

study, a higher mean and variance would result in a larger proportion of high values, which refer to the near-stream areas that more frequently reach surface saturation. If this VSA-based conceptual model were to successfully capture the P transport dynamics for the nested catchments, the expected result would be that the catchment with the highest mean and variance in $\ln(A_s/\tan\beta)$ would have: (1) the highest levels of PP due to the enhanced proportion of overland flow, and (2) the highest levels of DP due to the groundwater table intersecting the P-rich surface soil layer for a larger proportion of the catchment area. In the case of the three nested catchments, we find that S4, which has the highest mean and variance of $\ln(A_s/\tan\beta)$, does not exhibit either of the expected characteristics relative to the other catchments. The significant differences in the observed PP $C-Q$ relationships, in particular, must be explained by another factor apart from the potential extent of the catchment VSAs.

The other topographic descriptor that is examined in an attempt to explain the differences in PP between the catchments is the *LS*-factor. The interpretation of the *LS*-factor distribution is less straightforward than that for $\ln(A_s/\tan\beta)$, in that the spatial arrangement of the *LS* values within a catchment are relevant in determining how these *LS* values translate into actual sediment yield. This has been basis of criticism for erosion models such as the USLE (e.g. Trimble and Crosson, 2000). A method has recently been developed to take this spatial arrangement, along with slope curvatures, into account (Di Stefano et al., 2000a,b). However, it involves dividing the catchment into 'morphological units', which has been described as a more or less arbitrary process that can significantly affect the sediment yield predictions (Rompaey et al., 2001). Other distributed models that can potentially circumvent the spatial problem are data intensive, such as WEPP (Nearing et al., 1989) or EUROSEM (Morgan et al., 1998), or require calibration, such as SEDEM (Rompaey et al., 2001). In the absence of any promising alternatives, the *LS*-factor distribution was ultimately used.

With the highest mean *LS* values belonging to the S1 catchment (Table 3), these results do not conform to the expectation of the S3 catchment having the highest index of erodibility. Based on the form of the *LS* PDF for S3 (Fig. 7), there is nothing to indicate that this catchment would have the highest stream water SS and PP levels relative to the others. Perhaps this is not surprising, since a general descriptor for relating the physical properties of a catchment to specific sediment yield (SSY, dimensions of $ML^{-2}T^{-1}$) has remained elusive. For instance, in a recent study of 26 cultivated catchments in central Belgium, Verstraeten and Poesen (2001) found no significant correlations between SSY and seemingly important factors as mean slope, percentage of the catchment with erodible slopes ($>2\%$, $>4\%$ grade), and proportion of the catchment under agricultural production. Catchment area was found to be the dominant control on SSY, with this parameter masking a number of relevant factors thought to control the sediment transport. The observed decrease in SSY with increasing catchment area was attributed to the fact the proportion of the catchment area acting as a sediment sink, i.e. low-slope valley bottoms, is increased for larger-scale catchments. In the case of the nested catchments examined in the present study, other, possibly localized, factors must override this area-related effect in order to cause the intermediate-scale S3 catchment to have the highest SSY.

Aside from the catchment topographic factors, in-stream processes could also cause differences in PP transport between sub-catchments. Physical factors such as entrainment and deposition of sediment, as well as transformations of P from particulate to dissolved forms as a result of sorption/desorption reactions, occurring within the stream all shape the transport of P from field to catchment outlet (Jakeman et al., 1999; McDowell et al., 2001; Cooper et al., 2002) to some degree. These in-stream factors have the potential to override the effects of the catchment-scale controls on P transport for stream reaches that are not at steady-state with respect to sediment delivery.

6. Conclusions

By analysing the $C-Q$ relationships for three nested catchments, we found that the only significant differences between the sites were in the form of the PP transport. This was primarily a function of the differences in SS mobilization, which suggests that strategies for reducing the TP loads for this pasture-land catchment setting should target those areas within the catchment that possess both high erosion potentials and high potentials for sediment delivery to the stream. Although PP is not as effective as DP in promoting short-term algal growth since only a portion of it is immediately available for biological uptake (Sharpley, 1993), PP presents a long-term risk to lake eutrophication as a result of the gradual release of soluble P from lake-bottom sediment (Knuuttila et al., 1994). Any enduring remedial strategy must also include, as a long-term goal, the reduction in soil P levels that act as a source for the hydrological transport. Due to the buildup in soil P caused by years of fertilizer application, this can be accomplished with little cost to pastureland production. For example, a study in Ireland by Tunney et al. (1999) showed that 90% of optimum grass yield was obtained after 10 years without any fertilizer P added to soils that initially had moderate P levels.

Catchment topography is known to influence the hydrological flowpaths and degree of erosion. However, for the analysis of the three nested catchments, the PDFs of $\ln(A_s/\tan\beta)$ and the *LS*-factor did not exhibit the characteristics that would explain the observed stream water $C-Q$ relationships. In the case of the $\ln(A_s/\tan\beta)$ distribution, this may be because the VSA is not the dominant mechanism involved in the transport of sediment and associated PP to the stream, and DP transport could be insensitive to the extent of the VSA. With regard to the *LS*-factor distribution, the differences in the sediment delivery processes for the individual catchments could outweigh the significance of the observed differences in erosion potentials. A more advanced, spatially explicit model would be required in order to capture the erosion and sediment delivery dynamics of the overland flow. The results from the joint $C-Q$ analyses for the pastureland catchments indicate that the development of a physically based P transport model for this setting must account for the flow-activated transport of DP via the shallow sub-surface and should ideally include spatially explicit information for the transport and delivery of PP in overland flow as well as transport and transformation within the stream channel.

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