Journal of Hydrology xxx (2009) xxx–xxx

Contents lists available at ScienceDirect

Journal of Hydrology

journal homepage: www.elsevier.com/locate/jhydrol

Does quantifying antecedent flow conditions improve stream phosphorus export estimation?

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ARTICLE INFO

Article history:
Received 2 September 2008
Received in revised form 24 July 2009
Accepted 4 September 2009
Available online xxxx
This manuscript was handled by L. Charlet, Editor-in-Chief, with the assistance of Bernhard Wehrli, Associate Editor

Keywords:
Water quality
Phosphorus
Runoff
Model
Loads
Ireland

SUMMARY

A reliable and economical method for the estimation of nutrient export (e.g. phosphorus) in stream flow from catchments is necessary to quantify the impact of land use or land use change upon aquatic systems. The transport of phosphorus (P) from soil to water is known to impact negatively on water quality. A key observation from studies is that most P export occurs during high stream flow. However, it is not yet clear how flood-antecedent conditions affect the P export during flood events. In this study, the P loss from soil to water as represented by soluble reactive phosphorus (SRP) in stream waters from three different catchments, varying in land use, scale and location in Ireland was monitored over 1 year. This study examined the role of antecedent stream flow conditions on SRP export and identifies a catchment-specific relationship between SRP flood event load (EL) and a flow ratio (FR). The FR is defined as the ratio of the flood event volume (EV) to the pre-event volume (PEV). The latter is the cumulative flow volume for a number of days preceding the event. This PEV period was found to be longer (average 81 days) in the grassland catchments which were known to be saturated with soil P than in the forested catchments (average 21 days) with minimal soil P. This FR ratio is a measure of the antecedent hydrological state (wet or dry) of the catchment. For SRP for each catchment, a specific SRP EL:FR relationship was identified. The annual SRP export was estimated, using this ratio and compared with the concentration/discharge (C/Q) method. The new flow ratio method was used with data from 12 flood events during the year to estimate an annual export of SRP. For the two grassland catchments in the study, using the FR method, we estimated an SRP export of 1.77 and 0.41 kg ha^{-1} yr^{-1}. Using the C/Q method, for the same sites, our estimate of SRP export was 1.70 and 0.50 kg ha^{-1} yr^{-1} respectively. The C/Q method used SRP concentrations covering 40% of the year while the FR method used only 12 flood events covering less than 2% of the year. This new method which takes account of the antecedent flow state of the river is an alternative to and may be more promising than the traditional C/Q method, particularly when short duration or flood sampling of water quality is carried out.

Introduction

Diffuse phosphorus (P) transfer from agricultural soil to water has been the focus of much research during the last decade. The deleterious effects of eutrophication on water bodies are well known, but reliably quantifying P exports using intermittent water quality measurements with continuous discharge measurements is challenging due to the poor relationship between P concentration (C) and stream discharge (Q). Water quality monitoring programmes have, until recently, utilised fixed interval grab sampling techniques combined with continuous flow gauging or more usually single point flow measurements. This limited form of monitoring is appropriate for measuring broad trends in water quality and is beneficial for catchments dominated by relatively constant point-source contaminant discharges. However these approaches are limited and less valuable when trying to estimate the annual nutrient exports from rural catchments dominated by diffuse-source pollution and intermittent flood events (Haygarth et al., 2005).

Factors that affect the movement of phosphorus (P) from soil to water are a synthesis of hydrology, soil type, and land management (Haygarth and Jarvis, 1999). There is a need to quantify the impact of each of the above factors prior to examining mitigation measures for individual catchments. The movement of P from soil to water occurs by one of four routes: overland flow due to saturation

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0022-1694/$ - see front matter © 2009 Published by Elsevier B.V.
doi:10.1016/j.jhydrol.2009.09.009

Please cite this article in press as: Warner, S., et al. Does quantifying antecedent flow conditions improve stream phosphorus export estimation? J. Hydrol. (2009), doi:10.1016/j.jhydrol.2009.09.009

excess; overland flow due to infiltration excess; shallow subsurface flow or by groundwater. In catchments where the dominant flow path is overland flow due to saturation excess, Diamond and Sills (2001) observed a gradually increasing area contributing to stream flow as the rainfall–runoff event evolved. This is the basis of the variable source area (VSA) concept (Dunne and Black, 1970; Gburek, 1990; Pionke et al., 2000). The extent of catchment area contributing to runoff during an event is dependent on the intensity and magnitude of the rain event and the degree of soil saturation prior to the flood event. The effect of antecedent rainfall conditions on stream nutrient concentrations and loads can affect patterns in stream concentrations and loads. Morgan et al. (2000) reported a pattern of increased flood event concentration for soluble reactive phosphorus (SRP) after a dry spell and subsequent reductions in successive events following a prolonged wet period.

The rate of transfer of P from soil to water depends on soil P concentration, organic matter content (% OM), the P sorption capacity of the soil (Daly et al., 2001) and the presence of preferential routes for P transfer (Stamm et al., 1998). The % OM and sorption capacity of the soil is unlikely to change in the short term (i.e. over the duration of the flood event). The soil P status is a dynamic response to myriad biological, chemical and hydrological processes, which also has a seasonal variation (Sharpley, 1995). Land management within an agricultural catchment, including the application of chemical fertiliser, and farmyard liquid and solid wastes, impacts the soil P status. Similarly, management practices such as the cutting of drainage ditches or afforestation can alter the hydrological regime of a catchment (Allen and Chapman, 2001).

The current means of estimating P exports in streams is known as the concentration/discharge (*C*/*Q*) method or variants of it (Ferguson, 1986; Lennox et al., 1997; Webb et al., 1997; Coats et al., 2002). In experimental catchments the discharge is readily measured continuously. However, measurements of P concentration are usually intermittent, because of the high costs. Hence, it is usual to establish a relationship between discharge and P concentration (from a finite set of data points) and apply this relationship to the entire time-series of flow to estimate the annual P export. The method has been improved by resampling large datasets to optimise sampling strategy. Robertson (2003) highlights the need for 'storm-chasing' in conjunction with fixed-period sampling. Coats et al. (2002) found that due to a statistically insignificant relationship between *C* and *Q* for SRP that a Period-Weighted Sample method was least biased. In trying to quantify the required number of data pairs necessary to establish a relationship, Moosman et al. (2005), noted that any less than 30 points, leads to increases in errors of load estimation. Other authors also highlight that P concentration is weakly correlated with stream flow (House and Warwick, 1998; Smart et al., 1998; Pionke et al., 1999; Daly et al., 2002; Gächter et al., 2004; Haygarth et al., 2004;) and so the traditional *C*/*Q* method is not robust. Therefore, any method that could improve this correlation is desirable.

Part of the reason why C and Q are poorly correlated, relates to the fact that the method does not take into account hysteresis of concentration, whereby the concentration along the rising limb of the hydrograph exceeds the concentration along the falling limb for the same discharge. Furthermore the *C*/*Q* method does not account for the effects of flushing of nutrients in flood events prior to events being sampled. Wetter soils produce flow more quickly and in greater volumes (McDowell and Sharpley, 2002). It is therefore postulated that including information on the antecedent flow, as distinct to the instantaneous flow only, might improve the estimate of P exports.

The catchments studied are forest and agricultural grassland that are representative of the rural landscape in Ireland (Irvine et al., 2002). The Douglas River, County Cork, a tributary of the Munster Blackwater, is the largest (1623 ha) with heterogeneous land use. The Dripsey River, a tributary of the River Lee in County Cork, and the Oona River, a tributary of the Ulster Blackwater, which flows into Loch Neagh, are both on a smaller scale (17 and 15 ha) and are entirely agricultural grassland.

The aim of this study was to investigate if taking into account antecedent flow conditions might be used to improve the estimate of P export in streams. The effect of antecedent stream flow status of each of five catchments was quantified and related to P export loads, with the aim to formulate a predictive relationship between flow, antecedent flow and P loads. We examine the relationship between the SRP event load (SRP EL) and the catchment stream flow using continuous flow measurement in catchments of different land use and size. This approach is novel in water quality analysis, and no similar work has been reported in the literature.

Methods

Study catchments

We used flow and water chemistry data from two grassland catchments (the Dripsey in County Cork and the Oona River in Northern Ireland) and three forested sub-catchments in County Cork. The location of each is shown in Fig. 1.

Dripsey river

The Dripsey River is located approximately 25 km North West of Cork City. The study area is an upland sub-catchment covering an area of 17 ha at an elevation ranging from 190 to 210 m. Land use in the catchment is agricultural grassland for dairy and beef production. Old Red Sandstone underlies the entire area with overlying soils of peaty gleys on brown podzols. Fertiliser and slurry were regularly applied during 2002 when approximately 300 kg ha^{-1} of N and 15 kg ha^{-1} of P in chemical fertiliser and farmyard slurry were applied (Scanlon et al., 2004).

Oona river

The Oona River is a tributary of the Ulster Blackwater River, which is one of the influent rivers to Lough Neagh in Northern Ireland. The study catchment is 15 ha, at a mean elevation of 94 m. The land use is agricultural grassland. The geology is primarily Carboniferous sandstone and limestone with some Triassic sandstone evident in the south east of the catchment and in the valley floor alluvial gravels. The soils are rich in clay and highly gleyed with low infiltration rates and are high in iron, aluminium and manganese (Cruikshank, 1997). Fertiliser and slurry applications to grassland were applied but not quantified during the 2002 study period.

Douglas forested catchments

The River Douglas is situated about 30 km North East of Cork City, Ireland (Fig. 1). The study catchment covers an area of 1623 ha with an altitudinal range of 60–290 m. The land use composition is 41% plantation forest, 21% agricultural grassland and 38% moorland. The conifer plantation was established in 1924, and today Sitka Spruce (*Picea sitchensis*) and Douglas Fir (*Pseudotsuga menziesii*) comprise the majority of the area planted (Clenaghan et al., 1998). Brown podzol soils underlie most of the catchment with some blanket peat, peaty podzols, peaty gleys and lithosols at the upper altitudes (Giller et al., 1996). The moorland tributaries are approximately 1 m wide and the main channel is approximately 5 m, where it leaves the forest (Giller et al., 1992). Devonian Old Red Sandstone underlies most of the catchment with overlying yellowish Kiltorcan beds (Giller et al., 1996). The Douglas catchment is divided into three sub-catchments: Douglas; DougL

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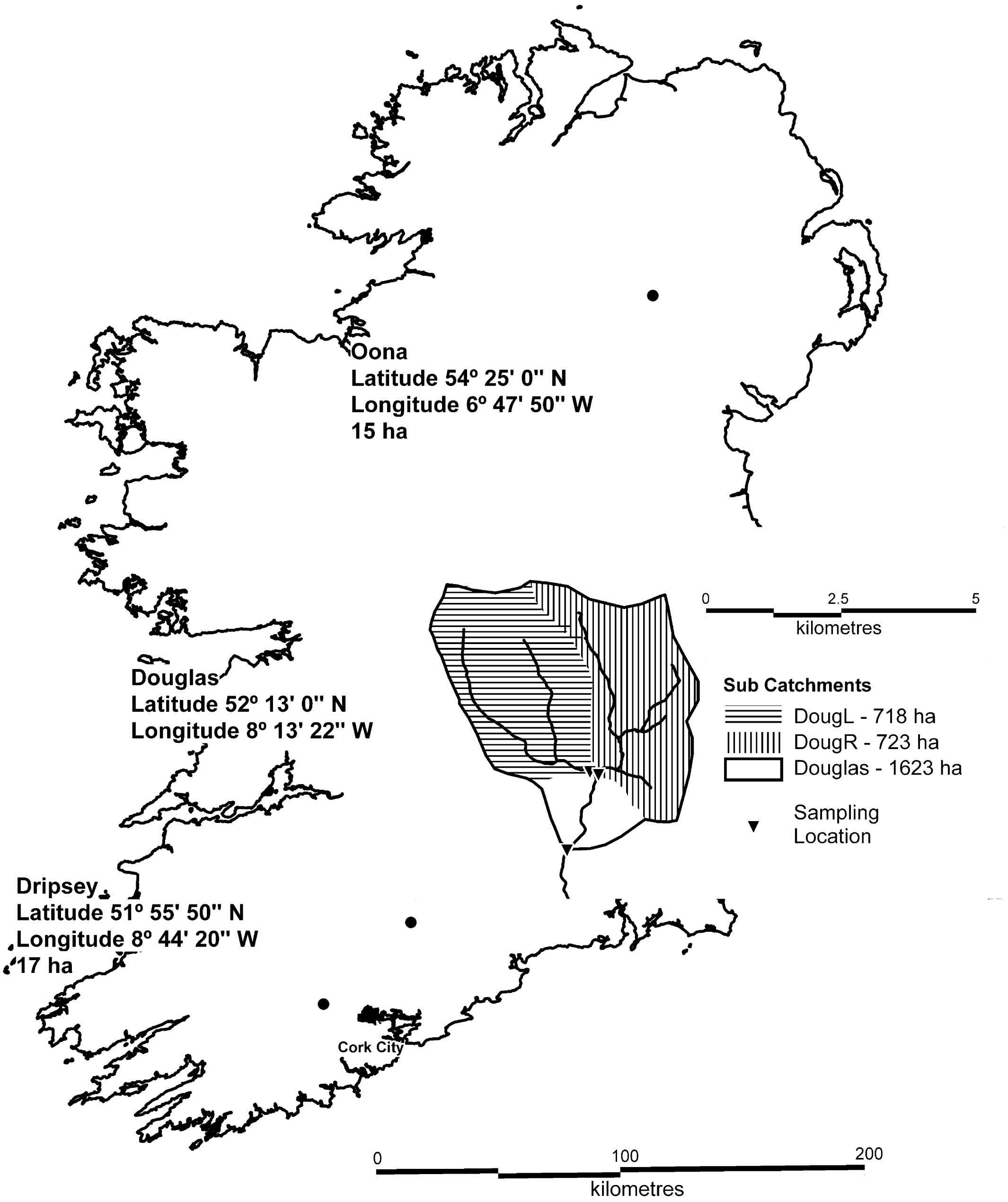

Fig. 1. Site location map for the three catchments: the 17 ha Dripsey grassland catchment in County Cork; the 15 ha Oona Water grassland catchment in Northern Ireland; and the 1623 ha forested Douglas catchment in County Cork with inset of the three sub-catchments of the Douglas. Only the Douglas sub-catchment outlines are shown to illustrate the relative size.

and DougR. The Douglas is downstream of DougL and DougR and encompasses both. The catchment layout is shown in the inset of Fig. 1. The Douglas catchment includes 21% grassland; the DougL sub-catchment has an area of 718 ha with no grassland; the DougR sub-catchment has an area of 723 ha including 35% grassland. No fertiliser was added to the forest during the study period. While fertiliser or slurry was applied to the grassland section of DougR, the amounts were not recorded.

In the case of the three forest catchments and the Dripsey grassland catchments, there was no known municipal waste streams. However in the Oona catchment, while there were no documented municipal waste streams, it was the considered view that there was some contribution from domestic septic tanks (Jordan et al., 2005).

Data collection

The data collection period for the Dripsey and Oona was January 1, 2002 to December 31, 2002. For the three sub-catchments of the Douglas the data collection period was August 1, 2002 to July 31, 2003.

Stream flow

In all catchments, stream discharge was estimated from the stream stage using calibrated rating curve relationships. For the Dripsey and Oona sites, stream stage was logged every 15 min using Thalimedes water level recorders (OTT Hydrometry, UK) which were installed upstream of a flow control structure (90° V notch weir). For the three Douglas river sampling sites, rectangular

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weirs were used and stream stage was logged every 45 min using a bubble meter integrated into an automatic water sampler (ISCO, USA. Model 730).

Water chemistry

In both the Dripsey and Oona streams, water samples were collected using flow-proportional composite samples. Following automatic sampler actuation by a preset exceeded stage height; sub-samples (200 ml) were collected after a known volume of water had passed the V-notch. Eighteen sub-samples were used to fill one 3.7 L bottle and an average storm event which was estimated from previous data was used to calculate the flow volume between each sub-sample. In addition to the event-flow samples, at least 10 baseflow samples were collected from each site during periods of low flow. Water samples from the automatic samplers were returned to the laboratory within 36 h of the first sample being taken, and were either analysed immediately or stored at 4 °C for no more than four days. All samples were analysed for SRP following filtration at 0.45 µm before measurement of P by solution spectrometry (Murphy and Riley, 1962). Using the flow-proportional composite sampling method, up to 42% of actual flow during the 2002 year was sampled for SRP in the Dripsey and up to 40% in the Oona site.

Data from the Douglas Catchment was recorded for 12 distinct flood events from the three sub-catchments (Douglas, DougL and DougR), between August 2002 and July 2003. Automatic water samplers (ISCO, USA. Model 6712) were used to collect 24 samples from each site in acid-washed bottles during each event with a 45-min interval between each sample. The sampling programme commenced after a 5 mm rise in stream height. Samples were collected from the site and returned to the laboratory within 16 h and analysed using the same method as for the Dripsey and Oona sites.

In Table 1, we show the range of SRP concentrations and annual average concentrations from all five sites. Gaps in the time-series of SRP were later filled using concentration-flow relationships using an adapted method described in Ferguson (1986) and Lennox et al. (1997).

The soil P concentrations were measured as chemical concentrations in filtered extracts by ICP-MS. Morgan's P (Pm) was determined by adding dried and sieved soil (6.5 ml) to 30 ml of Morgan's reagent (1480 ml of 40% NaOH and 1444 ml of glacial acetic acid to 20 L distilled water at pH 4.8) and shaken for 30 min. The filtered extracts were analysed colorimetrically for P (Jordan et al., 2005).

Estimation of phosphorus export

C/Q method

The instantaneous transport of a pollutant in a river is the product of its concentration *C* and the river discharge *Q*. The total load over a period *T* such as a year is

$$L = \int_0^T CQdt \tag{1}$$

Table 1
Range and mean SRP concentrations.

Catchment	Range of SRP (mg/l)	Annual concentration (mg/l)
Douglas	0.000*–0.110	0.019
DougL	0.000*–0.140	0.010
DougR	0.010–1.390	0.045
Dripsey	0.001–3.200	0.120
Oona	0.050–1.650	0.083

* Below the limit of detection (0.001 mg P/l).

Concentration measurements are typically intermittent whilst discharge measurements are often continuous. Therefore, to generate annual loads, the solute concentrations have to be estimated for periods of the year when concentrations are not available. The most common method of estimating river loads from continuous discharge data and intermittent measurement of solute concentration is to use a rating curve relationship (between discharge and concentration) to predict the unmeasured concentrations from the discharge at the time (Ferguson, 1986). This is the so-called concentration/discharge (*C*/*Q*) method. The concentration of a solute (e.g. P) in stream water is measured at the same time as the stream discharge and a relationship (e.g. a power or exponential) is built between *C* and *Q*. Detailed descriptions of the *C*/*Q* approach and variations of it can be found in Webb et al. (1997), Lennox et al. (1997), Coats et al. (2002), Robertson (2003). With an acceptable *C*/*Q* relationship, and a time-series of *Q* we can then assign a concentration to each instantaneous *Q*, which can then be used to estimate annual exports. However, it is widely reported that the *C*/*Q* method has limitations, particularly when the number of concentration measurements are limited or confined to periodic grab sampling (Ferguson, 1986; Stamm et al., 1998; Moosman et al., 2005).

Flow ratio method

Event load estimation. For the Dripsey and Oona streams, the flood flow event volume (EV) was estimated from the area under the stream-flow hydrograph. This volume was then multiplied by the composite sample concentration to obtain an EL. For the Douglas catchments, discrete samples were collected which produced instantaneous concentrations C_i (mg l^{-1}) at a number of points (N) along the stream-flow hydrograph. These values were used in conjunction with the instantaneous discharge Q_i (L s^{-1}) to estimate the export load for each event (e.g. flood hydrograph event)

$$EL = \sum_{i=1}^{N} C_i Q_i \Delta t \tag{2}$$

The different event load estimation methods between the grassland and forest sites were due to the different sampling regimes between the sites, i.e. composite sampling in the Dripsey and Oona; and discrete sampling in the Douglas.

Correlation of event load with the flow ratio. To include for the effect of antecedent flow conditions, we introduced a flow ratio (FR) which we defined as the current flow event volume (EV) divided by its pre-event flow volume; PEV*n*, where *n* is the number of days from 1 to 112. The export loads from the 12 Douglas river flow events, were correlated with the flow ratio (FR). The R^2 values of these correlations for all five catchments are shown in Table 2. The correlations for all five catchments along with the equation of best fit are shown in Fig. 2a–e.

Using correlations to estimate annual loads. The correlations (of SRP EL:FR) with the highest R^2 in addition to baseflow-load estimation were used to determine the annual export. This was performed by separating the time-series of the annual hydrograph into specific flood events and then estimating its EV and PEV. For the Dripsey catchment the optimum PEV had a duration of 91 days (see correlations in Table 2). For the DougR catchment, the optimum PEV had a duration of 42 days (see correlations in Table 2). For the DougR, the EV and PEV_{42} were then used in (3) to estimate an EL for unsampled events.

$$EL = 273.28\left(\frac{EV}{PEV_{42}}\right)^2 + 6.28\left(\frac{EV}{PEV_{42}}\right) \tag{3}$$

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Table 2
R^2 values of the correlations between SRP EL:FR correlations for each of the Douglas, DougL, DougR, Dripsey and Oona catchments, with the highest R^2 shown in bold.

	Douglas	DougL	DougR	Dripsey	Oona
EV	0.24	0.01	0.502	0.375	0.723
FR_1	0.75	0.643	0.306	0.004	0.873
FR_7*	0.506	0.537	0.64	0.004	0.055
FR_14	0.61	0.603	0.712	0.003	0.166
FR_21	**0.869**	**0.719**	0.75	0.006	0.751
FR_28	0.93	0.789	0.824	0.045	0.806
FR_35	0.929	0.688	0.91	0.16	0.825
FR_42	0.864	0.59	**0.953**	0.317	0.864
FR_49	0.779	0.543	0.949	0.515	0.949
FR_56	0.714	0.549	0.941	0.652	0.971
FR_63	0.676	0.538	0.936	0.721	0.978
FR_70	0.644	0.518	0.925	0.763	0.978
FR_77	0.601	0.494	0.907	0.791	**0.979**
FR_84	0.583	0.503	0.898	0.796	0.975
FR_91	0.583	0.504	0.9	**0.815**	0.969
FR_98	0.575	0.488	0.893	0.804	0.965
FR_105	0.558	0.458	0.878	0.778	0.955
FR_112	0.525	0.429	0.896	0.752	0.951

* FR_7 means the flood ratio (event volume/PEV_7) with 7 days volume preceding the event.

In Table 3, we include the best fit equations for all five catchments. The integration of these estimated ELs over the year was used to estimate the annual event load export. To include the baseflow export, the annual baseflow is multiplied by the mean baseflow concentration. The total base flow volume is taken as the annual flow volume (from the hydrograph) minus the summed event flow volume. The mean base flow concentration was estimated from ten base flow measurements for each site taken throughout the year.

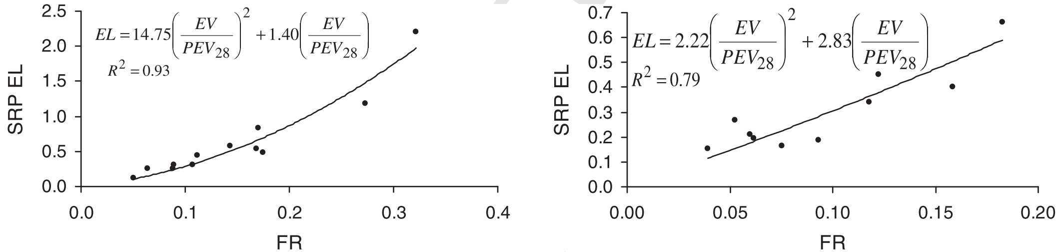
Dripsey and oona events

In the Dripsey (and Oona) streams, the use of composite flow proportional flow samplers enabled as much as 42% of the total year to be analysed for SRP. This allowed us to examine: (1) if the correlations of "Estimation of phosphorus export" could be verified and (2) to compare the new model of export estimation with the traditional C/Q model. To test whether event-selection affected the correlations from the Dripsey data, 34 flow events were sampled and events selected include the first flood event of every month, the third of every month, the last of every month and then all 34 events together. The resulting EL equations for the Dripsey and Oona sites are included in Table 3.

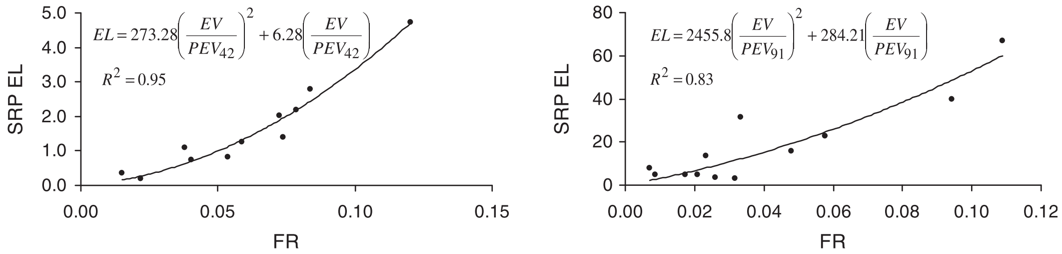
Results

Comparison of water quality results

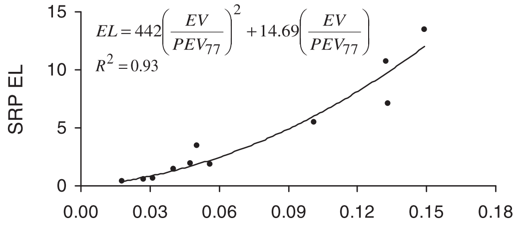
In Table 1 we include the range and annual concentrations of SRP at all five sites. The grassland sites of the Dripsey and Oona show the highest magnitudes with regards to both concentrations and annual mean concentrations. The SRP for the Dripsey and Oona were an order of magnitude higher than the forest sites of the



(a) Douglas (b) DougL



(c) DougR (d) Dripsey



(e) Oona

Fig. 2. (a) Correlation between SRP EL and EV/PEV_{28} for Catchments Douglas. (b) Correlation between SRP EL and EV/PEV_{28} for Catchment DougL. (c) Correlation between SRP EL and EV/PEV_{42} for Catchment DougR. (d) Correlation between SRP EL and EV/PEV_{91} for the Dripsey Catchment. (e) Correlation between SRP EL and EV/PEV_{77} for the Oona Catchment.

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Table 3
Comparison of catchment characteristics and correlations for the Douglas, DougL, DougR, Dripsey and Oona. R^2 values are also included.

Catchment	Area (ha)	Land use (Grassland %)	Optimum PEV duration (Days)	FR: SRP EL correlation	R^2	Range of EL (g ha^{-1})
Douglas	1623	21	28	$\mathrm{EL} = 14.75\left(\frac{\mathrm{EV}}{\mathrm{PEV}_{28}}\right)^2 + 1.40\left(\frac{\mathrm{EV}}{\mathrm{PEV}_{28}}\right)$	0.93	0.12–2.20
DougL	718	0	28	$\mathrm{EL} = 2.22\left(\frac{\mathrm{EV}}{\mathrm{PEV}_{28}}\right)^2 + 2.83\left(\frac{\mathrm{EV}}{\mathrm{PEV}_{28}}\right)$	0.79	0.15–1.03
DougR	723	35	42	$\mathrm{EL} = 273.28\left(\frac{\mathrm{EV}}{\mathrm{PEV}_{42}}\right)^2 + 6.28\left(\frac{\mathrm{EV}}{\mathrm{PEV}_{42}}\right)$	0.95	0.18–4.69
Dripsey	17	100	91	$\mathrm{EL} = 2455.8\left(\frac{\mathrm{EV}}{\mathrm{PEV}_{91}}\right)^2 + 284.21\left(\frac{\mathrm{EV}}{\mathrm{PEV}_{91}}\right)$	0.83	3.00–67.01
Oona	15	100	77	$\mathrm{EL} = 442\left(\frac{\mathrm{EV}}{\mathrm{PEV}_{77}}\right)^2 + 14.69\left(\frac{\mathrm{EV}}{\mathrm{PEV}_{77}}\right)$	0.93	0.38–13.5

Douglas catchment. The DougR catchment which has a 35% grassland cover also has concentrations approximately the same as the Dripsey and Oona.

Comparison of antecedent periods

In Table 2 we show the correlations between the FR and SRP ELs for different antecedent durations and identify the optimum correlation as that with the highest R^2. The PEV duration (or antecedent period) is that which best explains the relationship between the FR and the SRP EL. It is a measure of the number of antecedent days during which the flow has an impact on the subsequent flood event being considered. The forest sites of Douglas and DougL have the shortest antecedent period of 21 days, while the Dripsey and grassland sites (with 100% grassland land cover) have the longest antecedent period of 91 and 77 days respectively. The DougR catchment which has a 30% land cover with the remaining being forest and some moorland, had an antecedent period length of 42 days.

Comparison of PEVs and ELs

The details for each catchment, including area and land cover are shown in Table 3. Also included are the optimum antecedent period (PEV duration) and its associated R^2, the SRP EL equation and the range of ELs. As with SRP concentrations, the grassland catchments of the Dripsey and Oona had ELs up to 67 g ha^{-1}, while those from the forested sites were an order of magnitude less. The Dripsey catchment recorded the widest range of ELs during the study period (3.00–67.01 g ha^{-1}), and the DougL the narrowest (0.15–1.03 g ha^{-1}). The higher ELs were associated with the smaller catchments dominated by grassland.

Testing the event selection used in the correlations

The identification of the SRP EL:FR correlation originally in the Douglas catchments and then in the Dripsey and Oona may be coincidental, therefore it was necessary to test this. The availability of the high frequency data covering 34 individual events in the Dripsey catchment were used to investigate the event-selection process. Initially, the 34 events were separated by size and season, then sequentially into groups of twelve according to position in the month: 1st, 3rd and last, and finally all 34 events were grouped together. The correlation was not identified in the seasonal and size separation, leading to the conclusion that the 12 chosen events were representative across all seasons and of events of all sizes observed in the catchment. With regard to the sequential separation, the correlation was identified in each case, with the exception of the 'last of month' group (Table 4). When all events were considered together again the correlation could be identified ($R^2 = 0.82$). To investigate why no correlation could be identified in the 'last of month' group, it was noticed the events from this group were representative of both season and magnitude, but were unrepresentative of SRP ELs calculated from samples with high SRP concentrations.

Table 4
Comparison of events selected from the Dripsey data to determine whether event selection altered the derived correlation. R^2 values are also included.

Subset of events	R^2 value	Event flow export (kg)	Annual baseflow export (kg)	Annual export (kg ha^{-1})
Original (12)	0.83	2.58	4.36	1.77
1st of month (12)	0.95	1.85	4.36	1.34
3rd of month (12)	0.83	2.09	4.36	1.49
Last of month (12)	0.17	2.18	4.36	0.38
All events (34)	0.82	2.24	4.36	1.58

Comparison of annual loads from C/Q method and FR method

In Table 5 we show the estimated annual SRP loads using the new FR method and the traditional C/Q method. For the Dripsey, the FR method produced an annual export 4% higher than the C/Q estimate. For the Oona, the FR estimate was 82% of the C/Q estimate. For the Douglas sites the FR estimate was approximately 60% of the C/Q method.

Discussion

It is widely recognised that C/Q method does not give the optimum estimate of export loads (Ferguson, 1986; Lennox et al., 1997; Coats et al., 2002; Robertson, 2003; Moosman et al., 2005). This is due to the fact that C/Q data tend to have a lot of scatter, and best fit relationships tend to have low R^2. For the C/Q method, the range of R^2 in our five catchments was between lows of 7% and highs of 23%. SRP concentrations increased with flow, but not consistently so. This is due to the dynamic nature of flow and transport of P from soil to water. Typically we found that the SRP concentra-

Table 5
Comparison of annual SRP loads estimated loads using the C/Q and the new FR methods.

Catchment	FR estimate (kg ha^{-1})	CQ estimate (kg ha^{-1})
Douglas	0.043	0.065
DougL	0.029	0.053
DougR	0.112	0.169
Dripsey	1.77	1.70
Oona	0.41	0.50

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tions were higher on the rising limb of the hydrograph than on the falling limb with SRP peaks occurring around the peak of the hydrograph. Ferguson (1986) noted that the *C*/*Q* method tended to underestimate loads due to this scatter and identified a correction to the method. In addition, intermittent sampling of water chemistry does not always catch the full range of concentrations, as high concentrations can come and go in short periods when sampling is not active.

This new FR method was identified from observations that similar size flow events often exhibit very different SRP concentrations and loads. Following dry periods, SRP loads were observed to be higher than after wet periods. This phenomenon has been reported previously (Morgan et al., 2000; Turner and Haygarth, 2001; Gächter et al., 2004; de Jonge et al., 2004; Oberson and Jones, 2005). It is the result of one or more possible phenomena including: sequential flood events flushing the available stored water-soluble P from the soil; the wetting and drying of soils increasing the release of soluble organic P from soil biomass; different flow paths for varying intensity of precipitation events. Gächter et al. (2004) noted that desorption sustains elevated SRP concentrations in the topsoil pore water, as long as the rate of desorption equals or exceeds the flushing or dilution rate of pore water by precipitation. Furthermore SRP remains relatively low on the rising limb of the hydrograph when the flushing rate of the soil pores is large, and hence residence time of rainwater in topsoil is short. The FR method uses this phenomenon and quantifies the time period prior to flood events and its associated volume (PEV) in order to develop a useful tool in estimating SRP export. In the Dripsey grassland catchment, the *C*/*Q* method was used to estimate the SRP export of 1.70 kg P ha^{-1} yr^{-1}, using the full available SRP data set of 34 events covering 42% of the year. Using the new FR method with the SRP data set of 34 events gave an export of 1.58 kg P ha^{-1} yr^{-1}; and with 12 events (covering approximately 2% of the year) gave an export of 1.77 kg P ha^{-1} yr^{-1}. Similarly, using SRP data for approximately 2% of the year, we estimated the SRP export for the Oona to be 0.41 kg P ha^{-1} yr^{-1}, by comparison with 0.50 kg P ha^{-1} yr^{-1} when using SRP data from 40% of the year. This suggests that the new FR method may be used to estimate exports with less SRP data than would be satisfactory for the *C*/*Q* method. It is unusual to have data covering 40% of the year as we had in Dripsey and in the Oona, and it is much more common that the available data is more intermittent and likely to cover only a fraction of the year. With such limited data, the new FR method is better than the flawed *C*/*Q* method as we have shown above. Considering that the FR ratio was derived from flow data only, the event volume divided by a pre-event volume, suggests that it is a catchment specific property and once established, can be used to estimate future SRP exports with minimal SRP sampling.

In developing the FR method, the significance of events needed to form the SRP EL:FR correlation was investigated. The need to include events representative of season, magnitude and sample concentration was imperative to form the relationship. The necessity to include events representative of all seasons is due to a number of variables which influence soil P concentration and P transfer, as well as seasonal effects upon precipitation patterns. During winter months Gächter (2004) suggests that due to absence of fertiliser applications and a higher groundwater to drainage water ratio, SRP concentrations were lower. Additionally, reduced mineralisation rates of organic P caused by low temperatures lead to depleted inorganic P in the soil matrix (Foster, 1978). Conversely, primary productivity is low, resulting in reduced uptake of inorganic P. During the summer months primary productivity is at its highest, but mineral fertiliser and manure applications resume. It is therefore necessary to include events that account for all seasons to ensure the relationship is identified.

In the catchments studied, the shorter PEVs of 21 days were associated with the two most forested catchments (which were also the largest in area) whilst the longer PEV periods of 77 and 91 were associated with the grassland catchments, which were two orders of magnitude smaller in area. The main reason for this is that both grassland catchments contain soils that are near saturated with P, as a result of many years of application of mineral fertilisers. The area-averaged levels of soil P in both catchments were approximately 10.0 mg l^{-1} (Morgans P) (Jordan et al., 2005). A P level of 6 mg l^{-1} is deemed optimum for grass growth, and any soils with values greater than 6 mg l^{-1} are vulnerable to P loss from soil to water (Jordan et al., 2005). Thus, in our two grassland catchments there was a significant reservoir of soil P, some of which was released in flood events causing high concentrations of SRP in the streams during flood events. By comparison, the levels of soil P in the forested catchments are minimal as no P in fertiliser was applied to these mature forest catchments. The result was a limited reservoir of soil P, producing small amounts of P loss from soil to water in flood events. This suggests that the PEV duration, or length of relevant antecedent period is independent of catchment size, but dependent on the degree of soil P.

Conclusions

This study examined the role of antecedent hydraulic conditions on P export and identified a catchment-specific relationship between SRP EL and a FR. The FR is the ratio of the EV to the PEV. The latter is the cumulative flow volume for a number of days (e.g. 28) preceding the event. This PEV period was found to be longer (average 81 days) in the grassland catchments saturated with soil P than in the forested catchments (average 32 days) with minimal soil P. This ratio is a measure of the hydrological state (wet or dry) of the catchment. For each catchment, a specific SRP EL:FR relationship was identified. For the two grassland sites, using the FR method, we estimated an SRP export of 1.77 and 0.41 kg ha^{-1}yr^{-1}. Using the *C*/*Q* method, for the same sites, our estimate of SRP export was 1.70 and 0.50 kg ha^{-1}yr^{-1} respectively. The *C*/*Q* method used SRP concentrations covering 40% of the year whilst the FR method used only 12 flood events covering less than 2% of the year. It is unusual to have data covering 40% of the year as we had in Dripsey and in the Oona, and it is much more common that the available data is more intermittent and likely to cover only a fraction of the year. With such limited data the new FR method is better than the flawed *C*/*Q* method as we have shown above. For the forested catchments (which received no P applications of fertiliser or slurry) the exports of SRP are an order of magnitude less than those of the fertilised grasslands. The *C*/*Q* estimated exports for the forested catchments range from 0.029 to 0.112 kg ha^{-1}yr^{-1} whilst the estimate using the new FR method ranges from 0.053 to 0.169 kg ha^{-1}yr^{-1}. This new method which takes account of the antecedent flow state of the river may be more promising than the traditional *C*/*Q* method, particularly when short duration or flood sampling of water quality is carried out.

Acknowledgments

We are grateful to the Irish Higher Education Authority who funded the initial study under the Programme of Research in Third Level Institutions (PRTLI2) 'Catchment management through real-time remote flow and water quality data acquisition: development of infrastructure.' Also to the Environmental Protection Agency, Republic of Ireland (2000-LS-2.1.1a_M1) for funding the research in the Dripsey and Oona catchments, and to Phil Jordan of the University of Coleraine for providing data from the Oona catchment.

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