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Importance of spatial and temporal patterns for assessment of risk of diffuse nutrient emissions to surface waters

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Abstract

The relationships between catchment characteristics, management and ecological response of receiving waters categorise risk of impact from diffuse pollution. We investigated spatiotemporal patterns in area-weighted nutrient loads and nutrient–flow relationships at 14 locations on 11 rivers in the catchment of Lough Mask in the west of Ireland. Relationships between river flow and the concentrations of a number of fractions of phosphorus and nitrogen differed significantly among the rivers, suggesting that risk is not static, but varies over short timescales and among catchments. Further, the relative magnitude of the nutrient–flow relationship was found to vary seasonally for both phosphorus and nitrogen. Nutrient concentrations during high flows in summer and autumn were significantly higher than during winter and spring, suggestive of disproportionate risk to surface water quality during summer high flow events owing to high potential growth rates of algal communities. Significant positive associations were found between extent of high productivity grasslands and urban areas with nutrient loads, slopes of nutrient–flow relationships and the most biologically available fractions of nutrients. These findings are important for the implementation of the European Water Framework Directive, as defining risk to degradation of ecological quality of waters from catchment activities will drive programmes of measures. Insufficient or inappropriate risk assessment will likely inhibit or prevent effective implementation.

Keywords: Nutrients; Catchment management; River dynamics; Risk; Diffuse pollution

1. Introduction

Characterisation of river basins, required for the implementation of the European Water Framework Directive (CEC, 2000), provides an assessment of risk to degradation of surface waters arising from anthropogenic activities. Diffuse nutrient pollution has been shown many times to provide a substantial risk to the quality of surface waters (e.g. Sharpley et al., 1994; Foy et al., 1995; Haygarth and Jarvis, 1999). In Ireland, this is primarily from grassland agriculture (Allott et al., 1998; Lennox et al., 1998). Assessment of risk is an important part of the characterisation process of catchments and is important for making judgements of the likelihood that water bodies will

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fail to meet defined environmental objectives. Diffuse nutrient emissions vary with season and management (Jennings et al., 2002) and the appropriate resolution of the source—pathways link is important to both understand and manage pollution transport (Heathwaite et al., 2003). In this paper, we investigate the importance of spatial and temporal controls on the diffuse emission of nutrients from catchments through the examination of both linkages between catchment attributes and nutrient loads, and spatio-temporal variation in nutrient–flow relationships in a number of rivers in the Mask Catchment in the west of Ireland.

2. Study site

The 859 km^2 catchment of Lough Mask (Fig. 1) contains two relatively large lakes; Lough Carra (16 km^2; max depth 20 m; mean total phosphorus (TP, ±95% C.I.) from July 2001 to July 2002 was 10.4 ± 1.3 μg L^{-1}) and Lough Mask (82 km^2; max depth 60 m; mean TP 12.8 ± 2.7 μg L^{-1}; Irvine et al., 2003). Metamorphic and igneous rocks, in combination with some shales and sandstones, underlie the more mountainous western side of the catchment. The relatively flat and low-lying eastern side of the catchment is underlain almost entirely by Carboniferous limestone. Agricultural grasslands, which dominate the eastern side of the catchment, are used mostly for production of cows, with some farming of sheep and pigs. The western side, which is covered mostly by peat bogs, with some agricultural grassland on the lower slopes, is used mostly for extensive sheep grazing. Two small towns, Ballinrobe and Claremorris (populations of both approximately 2500), are located on the eastern side of the catchment. Wastewater treatment plants servicing

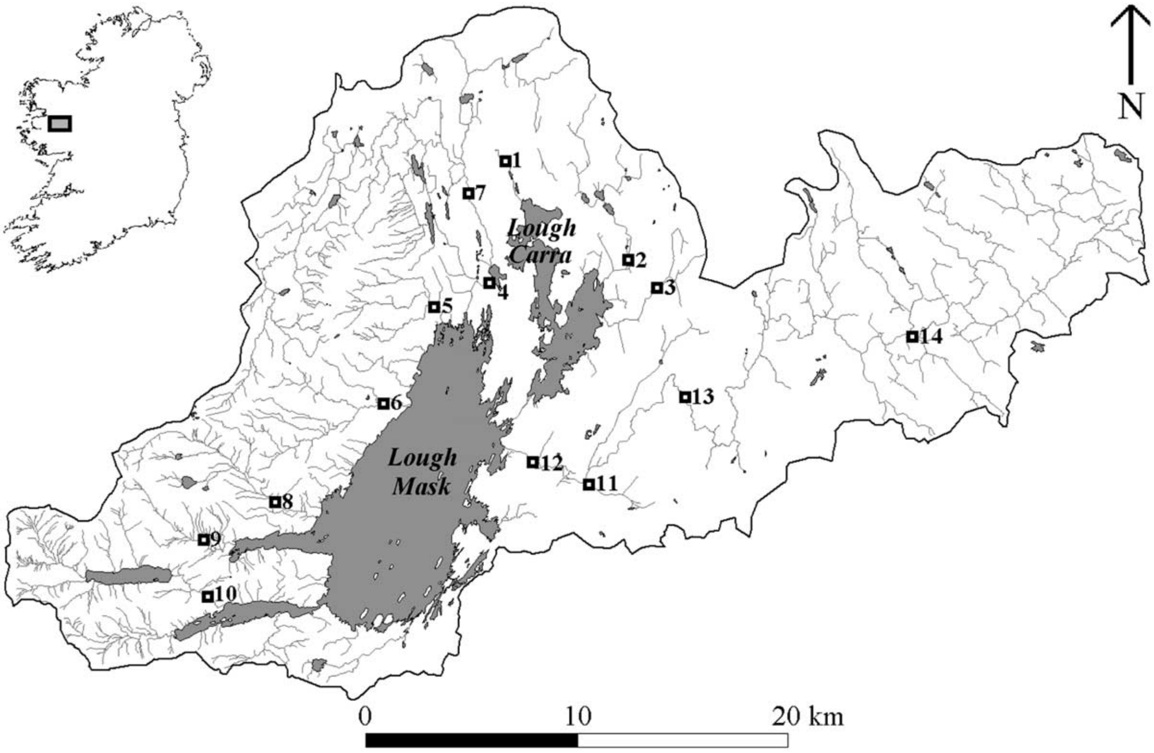

Fig. 1. The Lough Mask catchment and its drainage network, showing the locations of the river sampling sites used in this study. Site numbers correspond to: (1) Carra Bridge; (2) Clooneen; (3) Mullingar Bridge; (4) Cloon; (5) Srah; (6) Glensaul; (7) Cartron Bower; (8) Owenbrin; (9) Srahnalong; (10) Finny; (11) Cornaroya; (12) Curragh; (13) Foxhill Bridge; (14) Christina's Bridge.

these towns contribute relatively minor quantities of nutrients to the River Robe (comprising <5% of total annual loading of phosphorus and nitrogen; unpublished data), which drains the eastern part of the catchment. Mean annual rainfall at Claremorris (Grid reference: 52° 48.73′ N, 8° 58.29′ W) is 1143 mm and tends to fall consistently throughout the year. Mean annual evapotranspiration is 415 mm (Rohan, 1986).

3. Methodology

3.1. Water sampling and analysis

From July 2001 to July 2003, water samples were taken from 14 locations on 11 rivers in the catchment (Fig. 1). Sampling was done biweekly until November 2002 and continued monthly thereafter. River flows at the time of sampling were calculated using well-established stage–discharge relationships for all sites except for Carra Bridge, Clooneen and Mullingar Bridge (Sites 1–3; Fig. 1), where no river gauges were installed. Flow was measured from February 2003 at these sites using an Ott Kempten® Z30 current meter. Water samples from each monitoring station were analysed, in triplicate, for molybdate-reactive phosphorus (MRP), total dissolved phosphorus (TDP) and total phosphorus (TP) following Murphy and Riley (1962). Samples for MRP and TDP analysis were filtered through 0.45 μm Whatman® cellulose acetate membrane filters. Samples for quantification of TDP and TP were digested following Grasshoff et al. (1999). Dissolved inorganic nitrogen (DIN, filtered through Whatman® GF/C filters) and total nitrogen (TN, digested following Grasshoff et al. (1999)) were measured from triplicate samples following Grasshoff et al. (1999) in a Bran and Luebbe® AutoAnalyzer 3. Dissolved non-molybdate-reactive phosphorus (DnMRP), particulate phosphorus (PP) and total organic nitrogen (TON) were calculated as the differences between, respectively, TDP and MRP, TP and TDP, and TN and DIN (Johnes and Heathwaite, 1992). Quality control standards were used in all analyses, and were within acceptable ranges (±3% of target concentrations) in each case. All filtering was done immediately upon sample collection.

3.2. Statistical methods

Spatiotemporal variability in riverine nutrient concentrations was analysed with analysis of covariance (ANCOVA), with river, site, season and flow as independent variables. Site was nested within river and (log-transformed) flow was included as a continuous variable. Interaction terms between each of flow, river and season were included to test for spatial and temporal differences in nutrient–flow relationships. Owing to the design of these analyses, it was not possible to calculate post-hoc tests. Analysis of spatial and seasonal variability in river flow was analysed with analysis of variance (ANOVA), with river, season and site as independent variables. Site was nested within river. Spearman Rank correlation analyses were used to test for association between variables. The slope of the least-squares regression of flow to nutrient concentration estimated the magnitude of nutrient–flow relationships for each river, with differences between summer and winter slopes used as a metric of the extent of seasonality in nutrient–flow relationships. Slopes for Carra Bridge, Clooneen and Mullingar Bridge were not used in the seasonal analysis owing to the small number of flow measurements taken at these sites. Area-weighted nutrient loads were calculated by interpolation following Method 2 of Walling and Webb (1981) and using data from July 2001 to July 2002, reflecting the period of biweekly sampling. Hydrological loads for Carra Bridge, Clooneen and Mullingar Bridge for this period were estimated using rainfall data. All statistical tests were done with Data Desk® Version 6.

3.3. Data sources

Morphological aspects of catchments and catchment boundaries were calculated using a digital elevation model digitised from 1:50000 Discovery Series maps published by Ordnance Survey Ireland Land cover maps were compiled from CORINE land coverage data. Digital soil Morgan P maps were provided by Teagasc and rainfall data were supplied by Met Éireann. The Irish Environmental Protection Agency and the Office of Public Works provided river flow calculations. ArcView® Version 3.2 was used as the GIS interface.

4. Results

4.1. Spatial controls on area-weighted nutrient loads

Area-weighted nutrient loads (Table 1) varied considerably among catchments. Further, ranking of catchments by area-weighted phosphorus loading differed considerably from that for nitrogen. Area-weighted nutrient loads were significantly and consistently associated with morphological and land cover attributes of catchments (Table 2). Except for TON, all significant relationships between area-weighted nutrient loads and metrics of catchment morphology (mean slope and elevation) were negative. The DnMRP:TP ratio was, however, also related positively to catchment elevation. Extent of high productivity grassland and urban areas were associated positively with area-weighted loads of MRP, DIN and TN, and with the ratio of DIN:TN. Extent of high productivity grasslands was also related positively with area-weighted loads of TDP and with the ratio of MRP:TP, and inversely with the ratio of DnMRP:TP. All significant associations found between extent of high productivity grasslands and urban areas and area-weighted nutrient loads were inverse of those for peat bogs.

4.2. Spatio-temporal variability of nutrient–flow relationships

River flows (log-transformed) varied significantly both among and within rivers ($F_{10,424}=52.54$ and $F_{3,424}=5.86$; $P<0.0001$ and $P=0.001$, respectively) and with season ($F_{3,424}=5.1$; $P=0.002$). Flows in winter and spring were significantly higher than those during summer and autumn (least significant difference post-hoc tests, $P<0.05$ in each case).

Concentrations of each of the analysed phosphorus fractions except for DnMRP varied significantly both among and within rivers, and with season (Table 3). Significant variation of DnMRP was found among rivers and with season, but not within rivers. Although both PP and TP were affected positively by flow, no significant effect of flow per se on the concentrations of any of the dissolved P fractions was found. Whereas no significant differences were found in seasonal patterns of P fractions among the rivers, significant spatial variation in short-term flow-related patterns was found for dissolved, but not particulate, P fractions. Significant interactions between flow and season on PP and TP suggest significant seasonal variability in riverine phosphorus-flow dynamics. While overall concentrations of each P fraction were similar across all seasons during low flows,

Table 1
Median flow, area and area-weighted loads (kg km^{-2} a^{-1}) of each fraction of phosphorus and nitrogen for each subcatchment (see Fig. 1) for July 2001–July 2002

Site no.	Subcatchment	Median flow (m^3 s^{-1})	Area (km^2)	MRP	DnMRP	TDP	PP	TP	DIN	TON	TN
1	Carra Bridge	0.04[a]	3.5	4.7	3.3	8.0	10.0	18.0	265.6	207.4	473.0
2	Clooneen	0.9[a]	25.7	15.6	7.7	23.4	25.0	48.4	2142.9	691.9	2834.8
3	Mullingar Br.	0.2[a]	8.4	19.7	9.8	29.4	20.6	50.1	1246.8	555.7	1802.6
4	Cloon	2.7	121.5	7.6	12.7	20.3	30.9	51.2	489.9	670.8	1160.7
5	Srah	0.2	14.1	10.1	18.7	28.7	55.8	84.5	425.7	952.8	1378.5
6	Glensaul	0.4	23.9	6.0	10.1	16.1	26.9	43.0	170.9	983.8	1154.7
7	Cartron Bower	2.7	113.6	7.5	13.8	21.3	42.0	63.3	480.4	727.9	1208.3
8	Owenbrin	0.8	22.9	8.1	10.1	18.2	18.5	36.7	234.7	1198.4	1433.1
9	Srahnalong	0.2	8.9	6.2	5.6	11.8	20.6	32.4	104.7	950.2	1054.9
10	Finny	2.2	38.4	7.1	7.8	14.9	14.9	29.8	324.8	925.7	1250.5
11	Cornaroya	0.8	22.5	9.3	4.8	14.1	16.1	30.2	1687.7	292.5	1980.2
12	Curragh	6.7	284.7	15.8	15.9	31.7	38.7	70.5	1160.9	609.0	1769.9
13	Foxhill Br.	5.9	215.3	20.6	21.3	41.9	48.7	90.6	1256.3	881.0	2137.3
14	Christina's Br.	2.7	97.1	31.6	23.8	55.4	70.7	126.1	1300.6	1080.4	2381.1

[a] Median measured flows from February 2003 to July 2003.

Table 2
Spearman rank correlation coefficients (r_s) for associations between selected subcatchment characteristics and area-weighted loadings of each fraction of phosphorus and nitrogen ($df = 12$)

Subcatchment variable	MRP	DnM-RP	TDP	PP	TP	MRP:TP	DnMRP:TP	PP:TP	DIN	TON	TN	DIN:TN
Catchment morphology												
Mean slope	**−0.67***	−0.2	−0.503	−0.266	−0.389	−0.525	0.508	0.253	**−0.833*****	**0.556***	**−0.648***	**−0.899*****
Mean elevation	−0.38	0.196	−0.222	0.042	−0.059	**−0.692****	**0.684****	0.323	**−0.745****	**0.758****	−0.468	**−0.934*****
Land cover												
Peat bogs	**−0.578***	0.116	−0.305	0.099	−0.073	**−0.789****	**0.758****	**0.578***	**−0.785****	**0.684****	**−0.622***	**−0.903*****
High productivity grassland	**0.743****	0.194	**0.547***	0.275	0.405	**0.542***	**−0.549***	−0.320	**0.865*****	−0.439	**0.732****	**0.821*****
Urban areas	**0.562***	0.281	0.369	0.251	0.328	0.284	−0.289	−0.146	**0.581***	−0.217	**0.553***	**0.553***

Significant values in bold. *$P < 0.05$, **$P < 0.01$, ***$P < 0.001$.

inter-season differences were apparent during high flows, with highest concentrations during autumn and summer, and lowest concentrations during winter and spring (Fig. 2).

Although concentrations of different N fractions varied significantly in space and with season (Table 4), no significant effect of flow per se on the concentration of any of the analysed N fractions was found. Both short-term and seasonal patterns of DIN and TN, but not TON, differed significantly among the rivers, while significant interactions were found between flow and season for each of the analysed N fractions. Seasonal patterns of TON (Fig. 3) were similar to those of phosphorus. Whereas overall concentrations of TON were similar over the year at low flows, those of DIN and TN differed considerably among seasons (Fig. 3). At low flows, concentrations of DIN and TN were highest during winter and lowest during summer, while concentrations were particularly high during autumnal high flows.

Significant associations between aspects of catchment soil cover, land cover and morphology and the slope of the nutrient–flow relationship, irrespective of season, were found for fractions of both phosphorus and nitrogen (Table 5). Importantly, the extent of high productivity grassland in catchments was correlated positively with DIN, and with the ratios of both MRP:TP and DIN:TN, and inversely with the ratio of DnMRP:TP. The extent of urban areas were also associated positively with MRP and the ratio of MRP:TP, and inversely with the ratio of DnMRP:TP. Seasonal differences in the slope of the nutrient–flow relationship for phosphorus fractions were, however, associated solely with morphological characteristics of catchments. Both total catchment area and total length of river channel were associated positively with extent of seasonal differences in MRP ($r_s = 0.682$ and 0.736, respectively; $P < 0.05$) and the ratio of MRP:TP ($r_s = 0.809$ and 0.827, respectively; $P < 0.01$), and inversely with the ratios of PP:TP ($r_s = -0.745$ and -0.791; $P < 0.05$ and < 0.01, respectively) and DnMRP:TP ($r_s = -0.791$ and -0.755, respectively; $P < 0.01$).

5. Discussion

Significant linkages found between morphological and land cover characteristics of catchments and

Table 3
Results of ANCOVA analyses investigating spatiotemporal variability in each (log-transformed) fraction of phosphorus, with significant *P*-values in bold

Source	d*f*	MRP		DnMRP		TDP		PP		TP	
		F	*P*	*F*	*P*	*F*	*P*	*F*	*P*	*F*	*P*
River	10,371	13.35	**<0.0001**	13.88	**<0.0001**	30.76	**<0.0001**	18.27	**<0.0001**	43.26	**<0.0001**
Site	3,371	6.76	**0.0002**	2.28	0.08	9.21	**<0.0001**	5.37	**0.001**	14.73	**<0.0001**
Season	3,371	6.01	**0.0005**	5.98	**0.0005**	3.66	**0.013**	5.1	**0.002**	4.99	**0.002**
Flow	1,371	0.1	0.75	2.31	0.13	0.97	0.33	9.88	**0.002**	8.1	**0.005**
River*flow	10,371	4.68	**<0.0001**	1.52	0.13	3.45	**0.0002**	1.39	0.18	3.76	**<0.0001**
River*season	30,371	1.34	0.11	1.38	0.09	0.27	1	1.17	0.25	0.67	0.91
Flow*season	3,371	0.56	0.64	2.51	0.06	0.33	0.8	6.53	**0.0003**	2.63	**0.05**

area-weighted nutrient loads highlight the importance of both natural spatial patterns and human land uses on the movement of nutrients from land to water. Area-weighted nutrient loads indicated an importance of high productivity grasslands and urban areas for the diffuse transfer of nutrients to surface waters. Further, risk to water quality from these areas appears disproportionately high owing to a significantly greater proportion of biologically available emissions of both phosphorus and nitrogen. Risk may also vary considerably between catchments owing to significant seasonal and spatial variation in the potential for ecological impact from different nutrients.

The significant interactions found between flow and season on the particulate—containing fractions of phosphorus, and on each of the analysed fractions of nitrogen, suggest that the nutrient–flow relationship varies considerably over the year throughout the Lough Mask catchment. In particular, for each of the analysed nutrient fractions except for DIN, the risk of excessive nutrient transfer during high flow events was greatest during summer and autumn, and lowest during spring and, especially, winter. While concentrations of each P fraction and TON were similar across all seasons at low flows, considerable seasonal differences in the concentration of DIN and TN at low flows were likely caused by variability in the relative contribution of groundwater to river discharge; low flow concentrations were highest in winter and spring, concurrent with peak groundwater levels.

Seasonal variability in the nutrient–flow relationship for particulate–containing fractions of both phosphorus and nitrogen (i.e. PP, TP, TON and TN), with highest concentrations during high flows in summer and autumn, was likely caused primarily by the retention of particulates during low flows and subsequent resuspension during flood events. That river flows were lowest during summer and autumn supports this. Further, data from a continuous flow recorder on the River Robe (Grid reference: 53° 39.47′ N, 9° 9.26′ W; Office of Public Works, unpublished data) shows that high flow events occurred throughout the year. Abundance of macrophytes in river channels during summer and early autumn may also influence the retention of particulates considerably (Schulz et al., 2003). Our results suggest strongly that the extent of seasonal differences in nutrient–flow relationships is controlled mainly by natural morphological characteristics of catchments. Even though the interaction between flow and season was not significant in the ANCOVA for any of the dissolved fractions of phosphorus, seasonal patterns of these fractions were similar, but of lower amplitude, to those of particulate P. These patterns may be related to the lower water content of soils throughout the catchment in summer compared with winter. Dry soils have been shown to release significantly greater quantities of phosphorus upon rewetting compared with wet soils (Bartlett and James, 1980; Pote et al., 1999; Turner et al., 2003). Field evidence suggesting the importance of this for the transfer of P to surface waters has been found in the Lough Mask catchment (Styles, unpublished data).

The significant among—river differences in the magnitude of the nutrient—flow relationship found in the ANCOVA for a number of fractions of phosphorus and nitrogen suggest strongly that risk of pollution from diffuse sources varies across catchments, driven

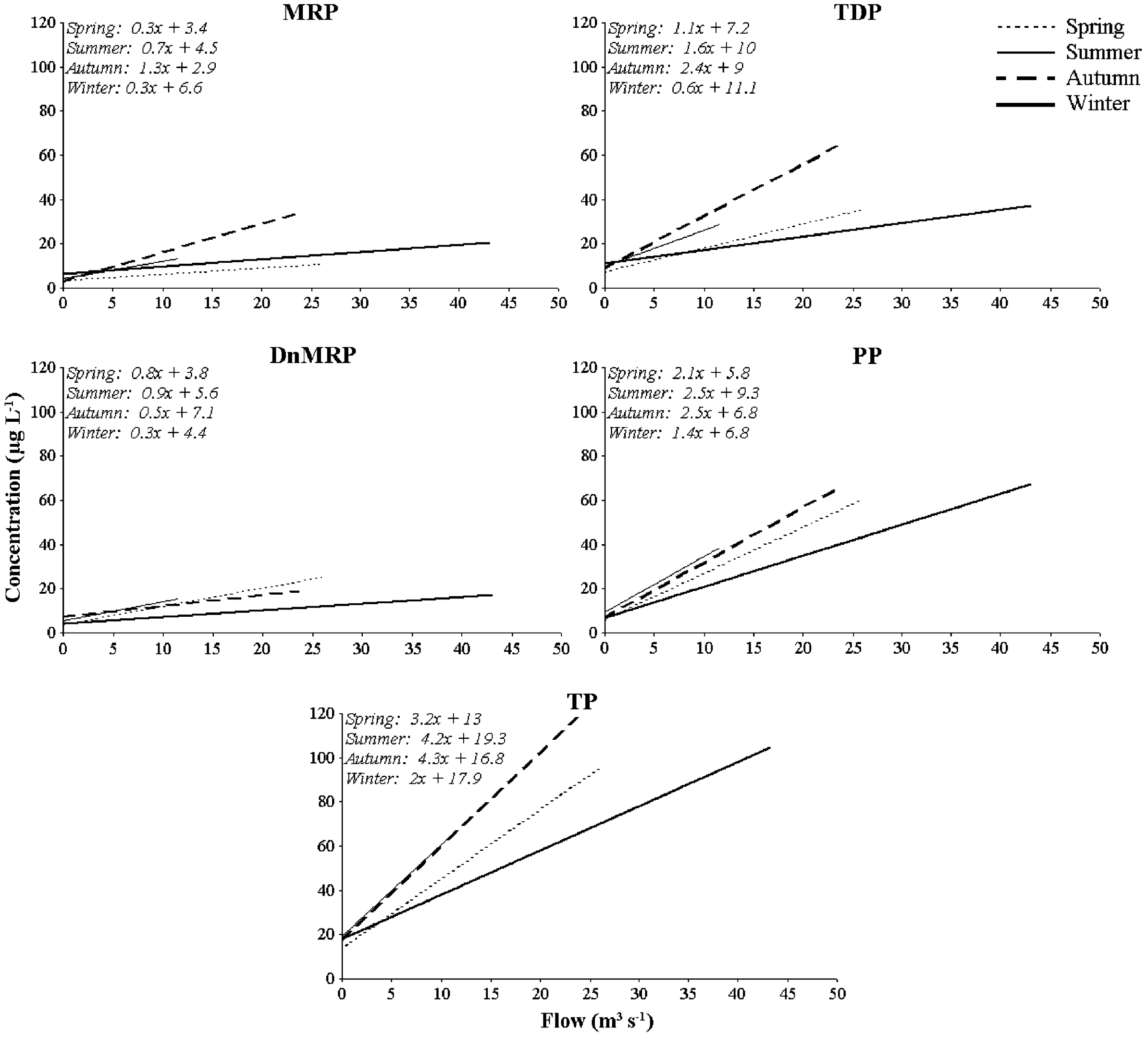

Fig. 2. Seasonal variability in the relationship between river flow ($m^3\ s^{-1}$, data from all rivers are included) and concentrations of each of the measured fractions of phosphorus ($\mu g\ L^{-1}$). For clarity, only least-squares regression lines and their coefficients are shown for each season.

by rainfall and associated significantly with land use. The importance of particulate retention in these rivers is supported by the significant and strongly inverse correlations between the slope of the PP:TP–flow relationship and both catchment area and total river length. A significant positive association between soil Morgan P and the magnitude of the MRP–flow relationship (Table 5) supports further the linkage between intensity of agriculture and increased transfer of nutrients. Further, the significant correlations of the slope of nutrient–flow relationships with both soil Morgan P concentrations and land cover characteristics suggest strongly that changes in the magnitude of nutrient–flow relationships may be used both in risk assessment and as an indicator of the effectiveness of catchment management plans.

Table 4
Results of ANCOVA analyses investigating spatiotemporal variability in each (log-transformed) fraction of nitrogen, with significant *P*-values in bold

Source	d*f*	DIN		TON		TN	
		F	*P*	*F*	*P*	*F*	*P*
River	10,366	134.83	**<0.0001**	4.49	**<0.0001**	58.17	**<0.0001**
Site	3,366	0.79	0.5	4.04	**0.008**	3.2	**0.024**
Season	3,366	37.57	**<0.0001**	6.65	**0.0002**	1.37	0.25
Flow	1,366	0.9	0.34	1.25	0.26	1.72	0.19
River*flow	10,366	11.87	**<0.0001**	0.91	0.52	2.63	**0.004**
River*season	27,366	3.18	**<0.0001**	1.12	0.31	1.9	**0.005**
Flow*season	3,366	5.58	**0.0009**	5.88	**0.0006**	10.44	**<0.0001**

6. Implications

The transfer of nutrients in catchments is highly dynamic, affected by spatial pattern and operating at timescales of hours to seasons. To be effective, catchment management plans should recognise the importance of this in assessing the risk of excessive nutrient transfer from land to water. Further, monitoring programmes need to be at high resolution in both space and time in order to account for natural spatiotemporal variability in nutrient transfer (Irvine, 2004). Our data indicate that overall risk to water quality is disproportionately high during large summer rainfall events, when the slope of the nutrient–flow relationship is greatest and because of highest annual potential growth rates of algal communities in

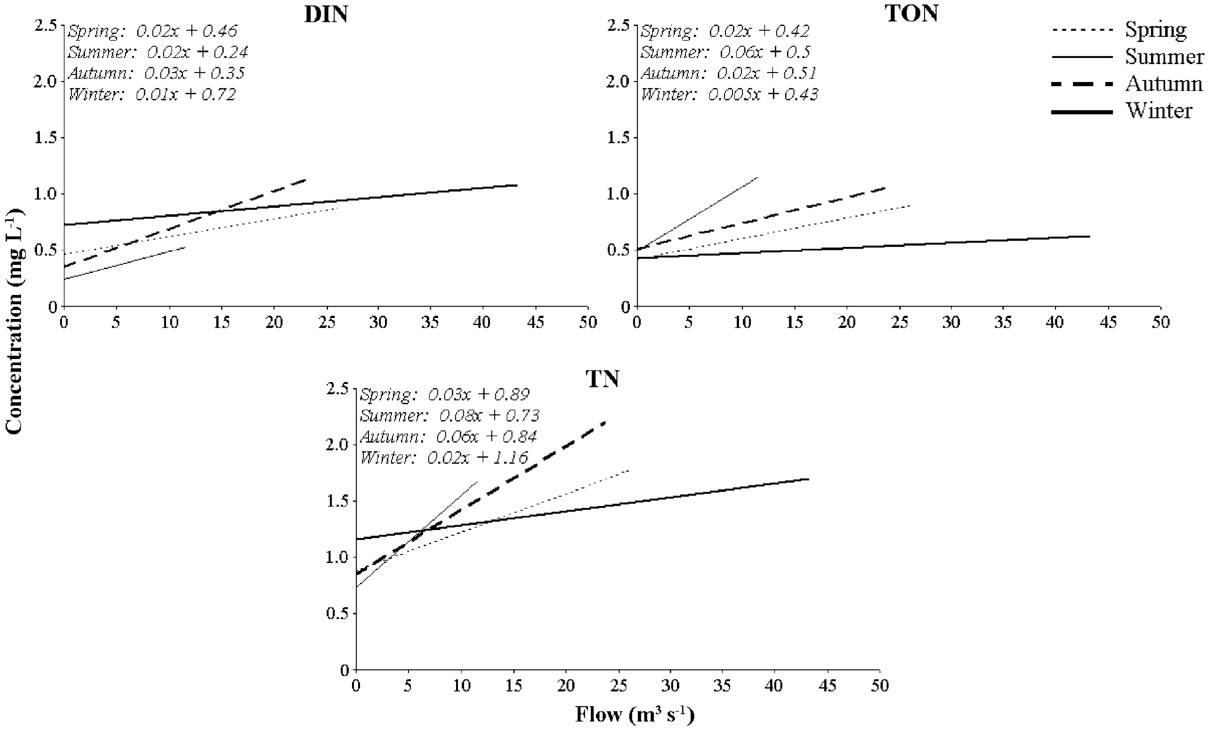

Fig. 3. Seasonal variability in the relationship between river flow ($m^3 s^{-1}$, data from all rivers are included) and concentrations of each of the measured fractions of nitrogen ($mg L^{-1}$). For clarity, only least-squares regression lines and their coefficients are shown for each season.

Table 5

Spearman rank correlation coefficients (r_s) for associations between selected subcatchment characteristics and the slope of the nutrient–flow relationship (irrespective of season, $df=12$) for each fraction of phosphorus and nitrogen

Subcatchment variable	MRP	DnMRP	TDP	PP	TP	MRP:TP	DnMRP: TP	PP:TP	DIN	TON	TN	DIN:TN
Catchment morphology												
Catchment area	0.429	0.438	0.503	−0.499	0.389	**0.679****	−0.204	−**0.912*****	−0.068	−**0.591***	−0.275	0.015
Mean slope	−0.429	−0.029	−0.116	−0.420	−0.200	−**0.600***	0.530	0.235	−**0.758****	0.327	−0.512	−**0.732****
Mean elevation	−0.143	0.095	0.055	−**0.670***	−0.046	−0.363	0.156	−0.196	−**0.908*****	0.262	−0.371	−**0.943*****
Total channel length	0.262	0.419	0.473	−0.530	0.292	0.468	−0.152	−**0.930*****	−0.169	−0.389	−0.248	−0.116
Soil characteristics												
Soil morgan P	**0.613***	0.031	0.156	−0.429	0.152	0.534	−**0.705****	−**0.631***	−0.002	−0.218	0.301	−0.125
Land cover												
Peat bogs	−0.415	0.216	0.077	−0.292	0.086	−0.490	**0.657***	0.055	−**0.846*****	0.270	−**0.547***	−**0.789****
High productivity grassland	0.490	−0.018	0.064	0.263	0.172	**0.611***	−**0.791****	−0.201	**0.663***	−0.323	0.448	**0.576***
Urban areas	**0.688****	0.128	0.262	0.019	0.284	**0.685****	−**0.628***	−0.485	0.377	−0.339	0.468	0.322

Significant values in bold. $^{*}P<0.05$, $^{**}P<0.01$, $^{***}P<0.001$.

receiving waters. Water quality in catchments with a large extent of grassland and urban areas appears to be at greatest risk. The catchment characterisation process required under Article 5 of the Water Framework Directive (CEC, 2000) needs to be at a sufficient resolution to identify the risk that landuse patterns have for the likelihood that waterbodies will fail to meet the defined environmental quality objectives. The extent of risk depends on both pathway susceptibility to pollutant mobility (Heathwaite et al., 2003) and receptor sensitivity to impact (Håkanson, 2001). These need to be incorporated in measurements, modelling and management of diffuse nutrient loads to surface waters.

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