



Patterns and processes of phosphorus transfer from Irish grassland soils to rivers—integration of laboratory and catchment studies

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Abstract

The objectives of this research were to investigate the patterns of phosphorus (P) transfer from fertilised soils to streams and to investigate the processes responsible for such losses. The three lowland grassland catchments involved in the study were: the Oona Water, Co. Tyrone, the Dripsey, Co. Cork and the Clarianna, Co. Tipperary. In each catchment, three or four nested sub-catchments were monitored for flow and P fraction concentrations at scales from 0.15 to 88.50 km². The P sorption and desorption characteristics of soil samples from each catchment were also determined. Results for 2002 indicated that the reactive P transfer, especially at the small catchment scale, could be predicted by Langmuir soil P properties, especially in the non-calcareous soils. In these soils, although iron (Fe) was an important determinant of P sorption, the sorption sites were weakly bound and binding energy only increased with increasing aluminium (Al) concentration. In calcareous soils, the Langmuir model was not applicable and P retention in these soils, which resulted in low reactive P transfer to streams, was most likely linked to P and calcium (Ca) precipitation and dissolution reactions. Particulate P transfer from all soils reflected differences in soil hydrological properties when flow was summarised as the Q₅:Q₉₅ ratio, which is a metric of runoff flashiness. Reactive and particulate P patterns changed with increasing catchment area due to changing hydrology and the cumulative influence of point source inputs. The findings of this study, therefore, implicated soil type, flow regime and scale as the important factors when linking P transfer process to catchment patterns and will be central to developing monitoring and mitigation strategies for managing P transfers to freshwater.

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1. Introduction

Increased phosphorus (P) transfer to freshwater causes eutrophication and is one of the most pervasive

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water quality problems in Europe. While the extent of freshwater eutrophication in Ireland is not as great as in other countries, there has, nevertheless, been a decline in water quality over several decades (Earle, 2003; Foy et al., 2003). One of the principle causes of rural P transfer to freshwater is agriculture and, specifically, P losses from agricultural soils and direct losses from farmyards. While the latter point sources can cause local impacts it is the wider, hydrology driven diffuse sources that are predominantly linked to catchment scale P transfers in agricultural river basins (Withers et al., 2001).

Ireland has a maritime climate with annual rainfall varying between 800 and 1600 mm and the landscape is dominated by grassland agriculture that is managed over a range of soil types (Keane, 1986). The aim of this study was to assess soil as a pathway for P transfer under these soil and climate gradients using grasslands under similar landuse intensity and to assess whether management of agricultural soil P can be prioritised to soils, or catchments, of greater P transfer risk. The application of soil P chemistry has been widely researched and there has been a focus on developing P transfer risk assessment tools based on the P sorption and desorption properties of soils and their associated chemistry (Sharpley, 1995; Beauchemin and Simard, 1999). This type of assessment removes hydrological variability by reacting different soil type samples over similar time periods and with the same amount of water and energy in controlled laboratory conditions. Scale is an important issue as laboratory and/or plot scale P transfer studies have no upscaling theory to describe the subsequent delivery of mobilised nutrients to the small catchment scale. This limitation to providing catchment scale P risk estimates is largely due to the interaction of different hydrological processes within catchments, as scale increases, and also due to hydrological differences between catchments (Heathwaite, 2003; Sharpley and Tunney, 2000).

These considerations led to the following objectives for the investigation:

1. Use soil P chemical characteristics to determine the potential for P transfer in three major Irish soil types.
2. Investigate the limitations of objective 1, above, with up-scaled P transfer rates in nested catchments with different drainage pathways.

To place these objectives into the context of the needs of catchment managing authorities in Ireland, a requirement of this study was to demonstrate the link between laboratory P risk assessments and the confounding affects of scale and different hydrological regimes when actual P transfers were measured in 1st to *n*th order rivers. This is of significance as the requirement for river basin authorities to assess, monitor and manage river water quality at the catchment scale will often involve mitigation measures at smaller scales in order to meet the objectives of the European Union Water Framework Directive (Earle, 2003). Outside the terms of reference of this study was a more explicit investigation of the process between soil P mobilisation at the plot scale and P delivery to first order streams. This will be an important consideration for further process-based investigations that will, for example, aid in the physical modelling of P transfers. Differences in hillslope hydrology, as the driver between plot scale P mobilisation and P delivery to first order streams, was, however, an implicit aspect of the project and the catchments studied were regarded, a priori, as having different storm hydrological pathways.

The three catchments studied were the Dripsey, a tributary of the River Lee in Co. Cork, the Oona Water, a tributary of the Blackwater River in Co. Tyrone and the Clarianna, a tributary of the Nenagh River in Co. Tipperary (Fig. 1a and b).

The Dripsey extends to 88 km² before its confluence with the River Lee. Three gauging stations were situated at 0.17, 2.11 and 14.00 km² with elevations of 210, 160 and 80 mOD, respectively. The geology of the catchment is predominantly Old Red Sandstone and soils are brown podzols with some peaty brown podzols in the upper part of the catchment. The soil profile is a dark organic loam over an iron-enriched b-horizon. Topsoils are typically iron (Fe) rich with up to 12% organic matter content. Soil drainage in the Dripsey ranges from free to impeded with some areas prone to overland and near surface flow during storm events and other areas to deeper subsurface flow (Lewis, 2003).

The solid geology of the Oona Water catchment is dominated by Carboniferous series sandstone and limestone although some older Triassic sandstone is exposed in a small area in the south east of the catchment with some valley floor alluvial gravels.

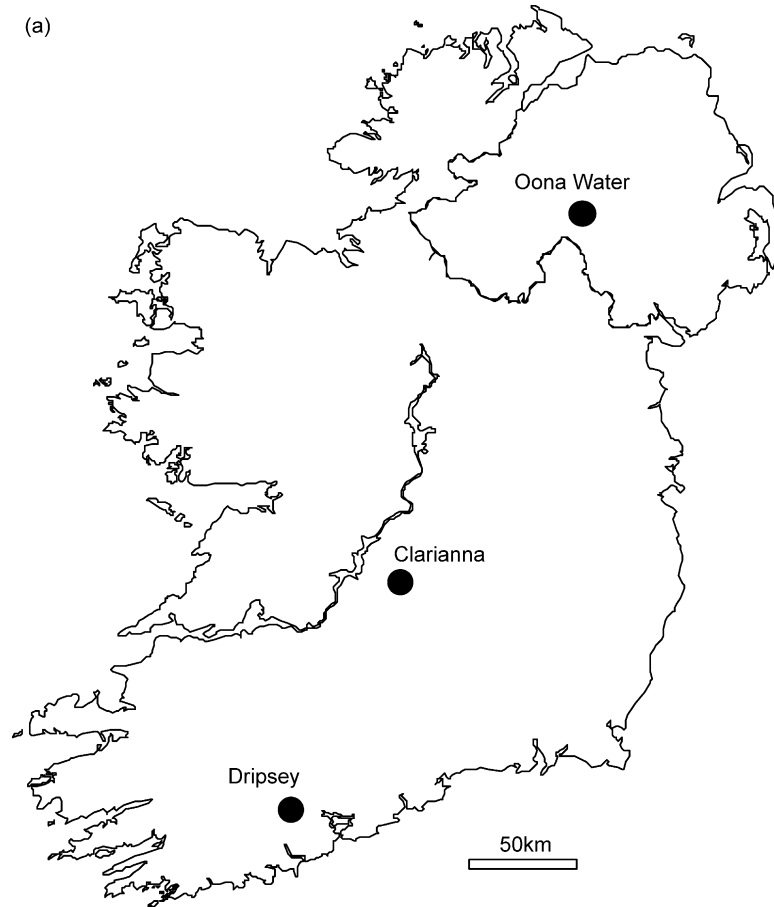


Fig. 1. (a) Ireland and the location of the three study catchments; the Dripsey (Co. Cork) and Clarianna (Co. Tipperary), Republic of Ireland and the Oona Water (Co. Tyrone), Northern Ireland. (b) The Dripsey, Oona Water and Clarianna study catchments showing hydrometeorological and water quality monitoring stations.

This part of Ireland is overlain by glacial till and is part of an extensive drumlin belt that forms soils which are clay rich and highly gleyed with low infiltration rates and have high Fe, aluminium (Al) and manganese (Mn) concentrations (Cruickshank, 1997). Storm runoff is dominated by overland flow and this is augmented with field and field-edge drainage. The three monitoring stations were installed at 0.15, 0.62 and 88 km² with elevations of 94, 79 and 51 mOD, respectively. Oona Water meteorological data was provided by CHASM infrastructure.¹

¹ The Oona Water is a Catchment Hydrology and Sustainable Management-CHASM study basin with hydrological infrastructure funded by the UK Natural Environment Research Council.

The Clarianna catchment is part of an Environmental Protection Agency monitoring programme in the larger Derg-Ree lake catchment system on the River Shannon and hydrochemistry monitoring stations were established at 0.80, 7.20, 13.60 and 29.80 km² with surface elevations of 90, 60, 50, and 45 mOD, respectively. The catchment is located within a Carboniferous limestone formation with depth to the bedrock varying from 2.7 to over 30 m of Quaternary gravels. The principal soil type in the catchment is grey brown podzol on gravelly limestone parent material. Other soil types include brown earth, gleys and peat. The soil is deep, well structured and freely draining during storm events (KMM, 1999).

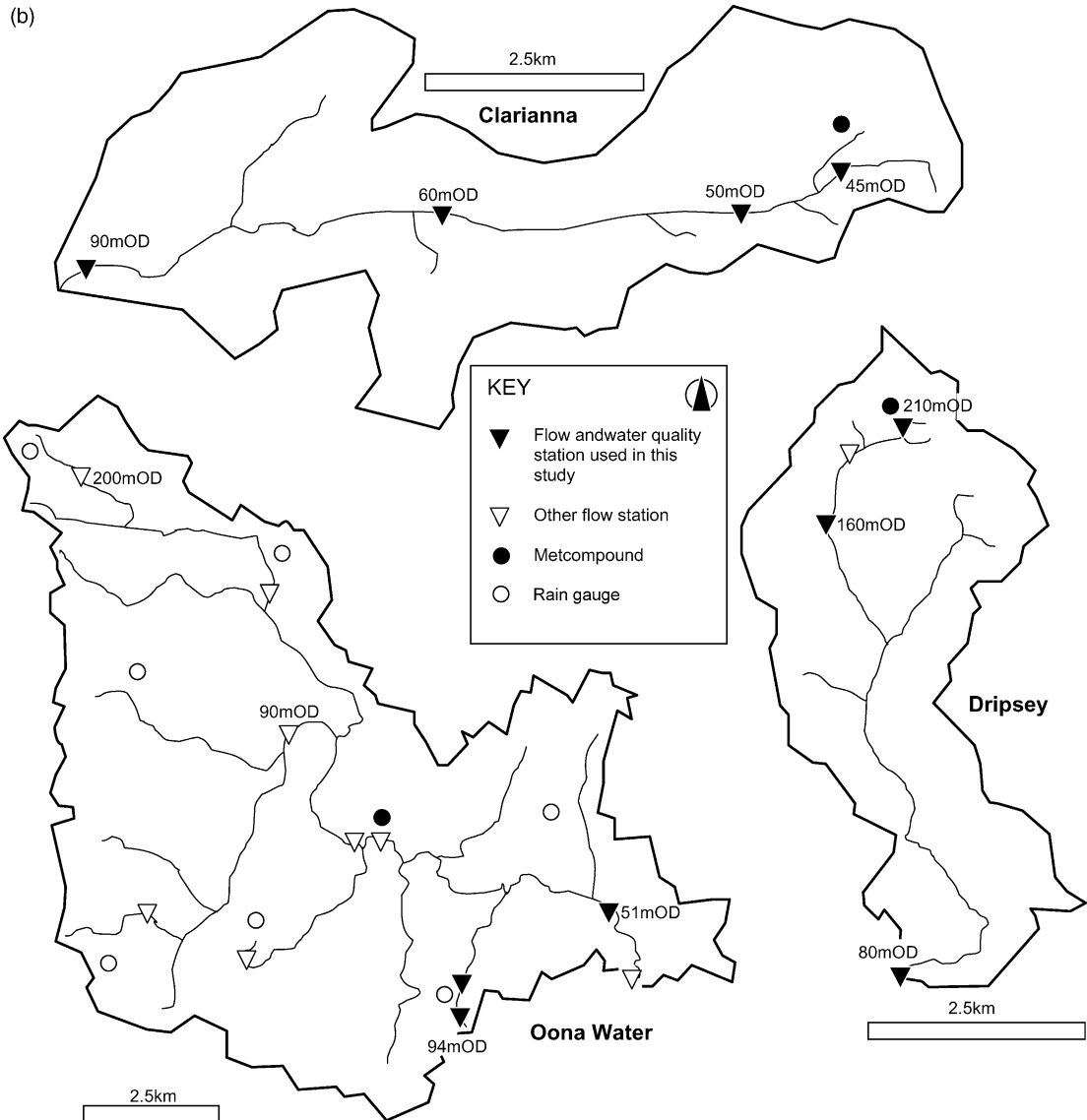


Fig. 1 (continued)

2. Methods

For objective 1 a series of soil P investigations were undertaken, which have been designed to forecast the risk of RP (<0.45) loss from agricultural soils via desorption (e.g. Paulter and Sims, 2000). Composite soil samples (0–10 cm soil depth) were collected from 7 to 12 fields in each catchment

that covered a Morgan soil P index of 1–4. Not less than 0.5 kg wet weight of soil was collected from each field and samples were air dried and sieved to 2 mm. Mehlich-3 P (P_{M3}), Fe, Al and calcium (Ca) were measured by adding 2 g soil to a solution of 0.2 M CH_3COOH , 0.25 M NH_4NO_3 , 0.15 M NH_4F and 0.013 M EDTA at a soil to solution ratio of 1:10, at room temperature, and shaken for 5 min

(Paulter and Sims, 2000). Chemical concentrations in filtered extracts were measured by ICP-MS. Morgan 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 (Morgan, 1941). Soil pH was determined on a 2:1 soil–water ratio paste and percentage organic matter (%OM) estimated as the loss-on-ignition of 5 g samples. Potential P sorption to soils was estimated using the Langmuir method (Paulter and Sims, 2000). Six solutions of P concentration 0, 5, 10, 15, 20 and 25 mgP/L were added to 2 g soil samples in 50 ml centrifuge tubes in duplicate. The suspensions were shaken at room temperature for 24 h, centrifuged and filtered, and the concentration of P in solution measured colorimetrically (John, 1971). Phosphorus sorbed to soil was calculated as the difference between initial concentration and P concentration measured at equilibrium. Phosphorus sorption isotherms were plotted for each soil using the Langmuir model and were used to derive sorption maximum (X_m , mg/kg), binding energy (b , L/mg) and maximum buffer capacity (MBC, L/kg) as the product of X_m and b . The X_m term referred to the maximum amount of P that could be sorbed by the soil and the b term referred to the intensity/stability of P sorption. Maximum buffer capacity in soils was defined as a measure of the ability of a soil to resist a change in the concentration of P in solution. A high MBC indicated a strong resistance to change in solution concentration and vice-versa (Bolland and Allen, 2003; Bertrand et al., 2003). All soils in the three catchments fitted the Langmuir model ($r^2 > 0.95$) with the exception of two peat soils, which were excluded from the analysis.

Potential phosphorus desorption from the soil samples was estimated by the Fe-oxide paper strip (Pfeo) method. One gram of soil was added to 50 ml centrifuge tubes and suspended in 40 ml of 0.01 M CaCl_2 with one Fe-oxide impregnated paper strip (Menon et al., 1990). The centrifuge tubes were shaken end-over-end for 16 h. After rinsing, the strips were eluted in 0.01 M H_2SO_4 for 1 h and the concentration of P in solution was measured colorimetrically (John, 1971).

For objective 2, above, all stream and river stations in the study used a combination of rated control structures, pre-calibrated flumes or weirs and water level recorders to monitor discharge. Storm water samples were taken by automatic sampler and, in the Dripsey and the Oona Water, a flow proportional composite sampling method was employed that concentrated the monitoring on storm events without generating prohibitively large numbers of samples in these flashy streams (Ulén and Mattson, 2003; Stone et al., 2000). As the Clarianna was considered to be a less flashy river, a flow proportional discrete method was chosen whereby a sample was taken and stored in isolation from the others over storm periods.

A method of grab sampling between storms was also undertaken at least once weekly to isolate nutrient and sediment concentrations during low flow periods.

The reactive P (RP (<0.45)) fraction² method is well documented and the procedure was followed in the current project by filtration to 0.45 μm and the measurement of P by solution spectrometry (Murphy and Riley, 1962). Total P (TP (unf)) and total dissolved P (TP (<0.45)) fractions were determined according to Eisenreich et al. (1975), and the particulate P (TP (>0.45)) fraction was calculated as the difference between TP (unf) and TP (<0.45). In so far as possible, samples were collected within 24 h (and never more than 36 h) of being taken and then prepared for P analysis. Periodic laboratory tests of RP (<0.45) decay from grab samples taken during storm events and analysed within 6 h of collection and up to 36 h of collection showed that no discernable RP (<0.45) decay occurred up to this longer time period. Subscription to the AQUACHECK accreditation scheme was a further aspect of laboratory quality assurance. Suspended sediment (SS) concentrations were calculated thermogravimetrically from the dried residue (105 °C) of samples filtered on GF/C filter papers (APHA, 1984; HMSO, 1985). Up to 40% of the annual discharge was successfully sampled using the flow proportional method and the remaining gaps in the data series were filled by the log-linear flow

² Phosphorus fraction nomenclature follows Haygarth and Sharpley (2000).

models described by Webb et al. (1997) and Lennox et al. (1997).

Tipping bucket raingauges, which were situated close to the smallest sub-catchments, monitored rainfall. In the Oona Water and Clarianna catchments, daily evapotranspiration was calculated by the Penman–Monteith equation using data generated from automatic weather stations. In the Dripsey, actual evapotranspiration was measured directly by the eddy-covariance method (Moehrlen et al., 1999; Jaksic, 2003).

All catchments were monitored concurrently for 12 months so that the full agricultural cycles of grazing, stock housing, silage cutting, fertilising and wet and dry periods of the hydrological cycle were included.

3. Results

The concentrations of P, Fe, Al, Ca, organic matter, pH and P sorption and desorption characteristics are presented in Table 1. The range of pH was 4.8–7.3 and %OM was 5.3–14.2%, excluding the two peat samples in the Clarianna. Acidic–neutral soils were represented by the Oona catchment, neutral soils in the Dripsey and neutral–alkaline soils were typical of soils sampled from the Clarianna catchment. A correlation matrix is presented in Table 2 and shows that there was a positive correlation between extractable Ca and soil pH for all soil samples (excluding the two peat samples) while Fe and, particularly, Al were negatively correlated with soil pH.

The Fe and Al concentrations in the soils were strongly correlated with the Langmuir sorption maximum, X_m , but only Al positively correlated with binding energy, b , and MBC. In comparison, soil Ca was negatively correlated with all Langmuir parameters.

The P_f desorption term increased with pH up to 5.5. This was a particular feature of the soils taken from the Dripsey catchment. As pH increased further, from 6.0 to 7.5, i.e. the Clarianna soils, P_f decreased to levels comparable to those in acidic soils, i.e. the Oona soils, possibly due to the insolubility of calcium and magnesium phosphates at high pH (Morgan, 1997).

Iron provided sites for P sorption, but the Fe concentration was also positively correlated with P_f and %OM.

This suggests that OM was associated with Fe as a complex or it maintained Fe in an amorphous form more suitable for sorption in the non-calcareous soils. Despite, however, OM being positively correlated with X_m , it was negatively correlated with binding energy, b . In summary, although OM associated with Fe may have provided sites for P sorption (e.g. Maguire et al., 2001), P was weakly bonded and so at risk of rapid P desorption and this was a feature of the Dripsey soils. This risk of P desorption was decreased in the non-calcareous soils as the Al concentration increased and this was a feature of the Oona Water soils.

The key hydrometeorological and hydrochemical characteristics for the three catchments are presented in Table 3. The distribution of rainfall across the three catchments during 2002 was very similar and most storms were recorded concurrently (± 1 to 2 days) in all three catchments despite the distance between them (Fig. 2).

The data in Table 3 show that the Dripsey received more rainfall than the other two catchments. Runoff, normalised to catchment area, was also higher in the Dripsey than elsewhere and especially so from the headwater catchment, 0.17 km², which discharged 1206 mm. Despite similar normalised runoff from the 2.11 and 14.00 km² catchments, the discharge frequency percentile Q5:Q95 ratios show that the 2.11 km² catchment (78) was a flashier system than the other two catchments in the Dripsey. This dimensionless ratio summarises the magnitudes of the infrequent fifth percentile (high flow) discharges and the frequent 95th percentile (low flow) discharges and so is a practical way of comparing the runoff response between gauged catchments. Catchments with a higher ratio have flashier responses to rainfall due primarily to a predominance of faster runoff flowpaths (Ineson and Downing, 1965; Wilcock, 1997).

The Oona Water 0.15 km² catchment is in a steeper part of the 0.62 km² catchment. The latter has a lower gradient and the Q5:Q95 ratios reflect this at 96 and 49, respectively. Very low base flows in the 0.15 km² catchment are also reflected by overall less normalised runoff, 611 mm, than from the larger Oona Water catchments. The Clarianna headwater catchment at 0.80 km² is situated almost entirely on peat and the stream was diverted during the peat-cutting season in

Table 1
Soil chemistry results from sample soils in the three catchments with Langmuir parameters

Catchment	Soil type	Xm (mg/kg)	b (L/mgP)	MBC (L/kg)	Pm (mg/L)	P _{M3} (mg/kg)	Pfeo (mg/kg)	pH	OM (%)	Ca (mg/kg)	Fe (mg/kg)	Al (mg/kg)
Clarianna	Gley	323	0.66	213	11.8	56.1	38	6.8	12.7	4635	399	69
Clarianna	Gley	333	1.25	417	3.2	24.3	24	6.8	8.7	3737	305	379
Clarianna	Gley	263	0.93	244	6.8	50.2	32.8	6.4	8.7	2925	362	471
Clarianna	Peat	^a		^a	3.6	11.3	34.8	7.3	30.5	23008	177	^b
Clarianna	GBP	323	1.19	385	3.9	45.2	31	6	6.4	2430	323	686
Clarianna	GBP	263	0.81	213	4.5	47.4	35.4	6	10.7	2391	252	778
Clarianna	Peat	^a		^a	2.5	3.9	27	7.2	21.8	32104	75	^b
Clarianna	BE	323	1.48	476	2.4	25.6	21.6	6.6	6.9	3543	222	435
Clarianna	BE	333	1.15	385	13	51.4	37.2	6.7	7.5	3185	215	548
Oona	Gley	588	2.13	1250	25.8	285	113	6.3	10.9	3566	422	931
Oona	Gley	476	4.2	2000	8.4	96.9	41.8	4.9	7.9	913	411	1265
Oona	Gley	455	2.2	1000	7.9	71	34.2	5	7.5	681	468	1075
Oona	Gley	385	1.86	714	4.8	64.3	31	5.1	6.5	1136	407	971
Oona	Gley	417	6	2500	4	40.7	18.4	5.2	5.3	953	446	1225
Oona	Gley	500	1.43	714	22.3	204.8	128	5.2	7.8	1127	537	925
Oona	Gley	417	4.8	2000	2.8	46.1	15.4	4.9	6.6	427	390	1102
Oona	Gley	417	4.8	2000	1.8	18.4	16.2	4.8	6.2	781	419	1070
Oona	Gley	455	3.14	1429	10.4	70.2	51.2	4.9	7.8	1041	571	901
Oona	Gley	435	2.56	1111	8.6	90	47.2	5.1	7.4	1468	473	1042
Oona	Gley	435	7.67	3333	5.7	49.9	23.6	4.8	6.9	465	464	1231
Oona	Gley	556	4.5	2500	2.9	38.1	18.8	4.8	7.9	284	397	1330
Dripsey	BP	500	2.5	1250	8.9	99.5	39.8	5.1	8.9	894	619	880
Dripsey	Gley	270	0.54	147	13.7	102.6	53.6	5.4	8.9	1656	454	612
Dripsey	BP-Gley	500	1.82	909	10.2	141.4	64.8	5.5	10.1	1974	527	940
Dripsey	BP	476	1.75	833	8.6	133.4	57.2	5.7	8.3	1858	498	901
Dripsey	BP	526	2.71	1429	6.6	101.8	71.6	5.3	8.6	1187	524	1068
Dripsey	BP	556	2.57	1429	14.6	211.7	70.4	5.2	9.3	1021	612	^b
Dripsey	BP	625	2	1250	13.5	192	83.2	5.6	14.2	1666	561	1054

Xm, P sorption maximum; b, binding energy; MBC, maximum buffer capacity ($Xm \times b$); Pm refers to Morgan soil P test and P_{M3}, Fe, Al and Ca are all Mehlich-3 extracts. Pfeo refers to P desorption as determined by iron-oxide paper strips. OM is the percentage soil organic matter as estimated by loss-on-ignition; BE, brown earth; BP, brown podzolic; GBP, grey brown podzolic.

^a No fit to Langmuir model.

^b Not enough sample for analysis.

Table 2
Pearson's *r* correlation matrix of soil parameters

	Pm	P _{M3}	Pfeo	Xm	<i>b</i>	MBC	pH	OM	Ca	Fe
pH	0.14	-0.04	0.03	-0.48*	-0.66**	-0.70**				
OM	0.48*	0.50**	0.48*	0.25	-0.46*	-0.34	0.38			
Ca	0.21	0.01	0.08	-0.45*	-0.66**	-0.69**	0.97**	0.43*		
Fe	0.38	0.55**	0.48*	0.70**	0.22	0.33	-0.61**	0.21	-0.54**	
Al	-0.09	0.18	0.05	0.66**	0.73**	0.80**	-0.86**	-0.32	-0.87**	0.46*

Al and Ca indicate strong retention of P when compared to the desorption term, Pfeo, but Ca was negatively correlated with the Langmuir terms. Fe concentrations, while providing a high degree of sorption sites (Xm), bind P weakly and so positively correlates with the Pfeo term. Significance levels are denoted by * for $p < 0.05$ and ** for $p < 0.01$.

Table 3
Hydrochemistry results from the three catchments from 1 January 2002 to 31 December 2002

	Catchment area (km ²)	Rain (mm)	ET (mm)	Runoff (mm)	Q5/Q95	TP (unf)		TP (>0.45)		RP (<0.45)		SS (mg/L)
						mg/L	kg/ha	mg/L	kg/ha	mg/L	kg/ha	
Dripsey	0.17	1833	362	1206	51.85	0.220	2.658	0.049	0.596	0.153	1.847	6.053
	2.11			1080	77.53	0.230	2.480	0.099	1.071	0.105	1.138	13.241
	14.00			1037	40.75	0.154	1.599	0.057	0.591	0.078	0.812	13.115
Oona water	0.15	1366	352	611	95.80	0.393	2.403	0.239	1.461	0.083	0.506	73.682
	0.62			894	48.85	0.269	2.408	0.157	1.404	0.060	0.536	34.933
	88.50			817	67.43	0.382	3.125	0.203	1.656	0.111	0.904	50.184
Clarianna	0.80	1091	493	603	410.84	0.114	0.685	0.078	0.472	0.024	0.146	67.024
	7.30			435	12.72	0.069	0.298	0.049	0.212	0.013	0.058	7.126
	13.60			416	20.92	0.040	0.165	0.021	0.089	0.014	0.057	12.163
	29.80			434	13.67	0.053	0.232	0.021	0.089	0.025	0.109	19.355

The very high Q5:Q95 ratio from the 0.80 km² Clarianna was due to a stream diversion during summer 2002 and so does not reflect the wider catchment flow statistics.

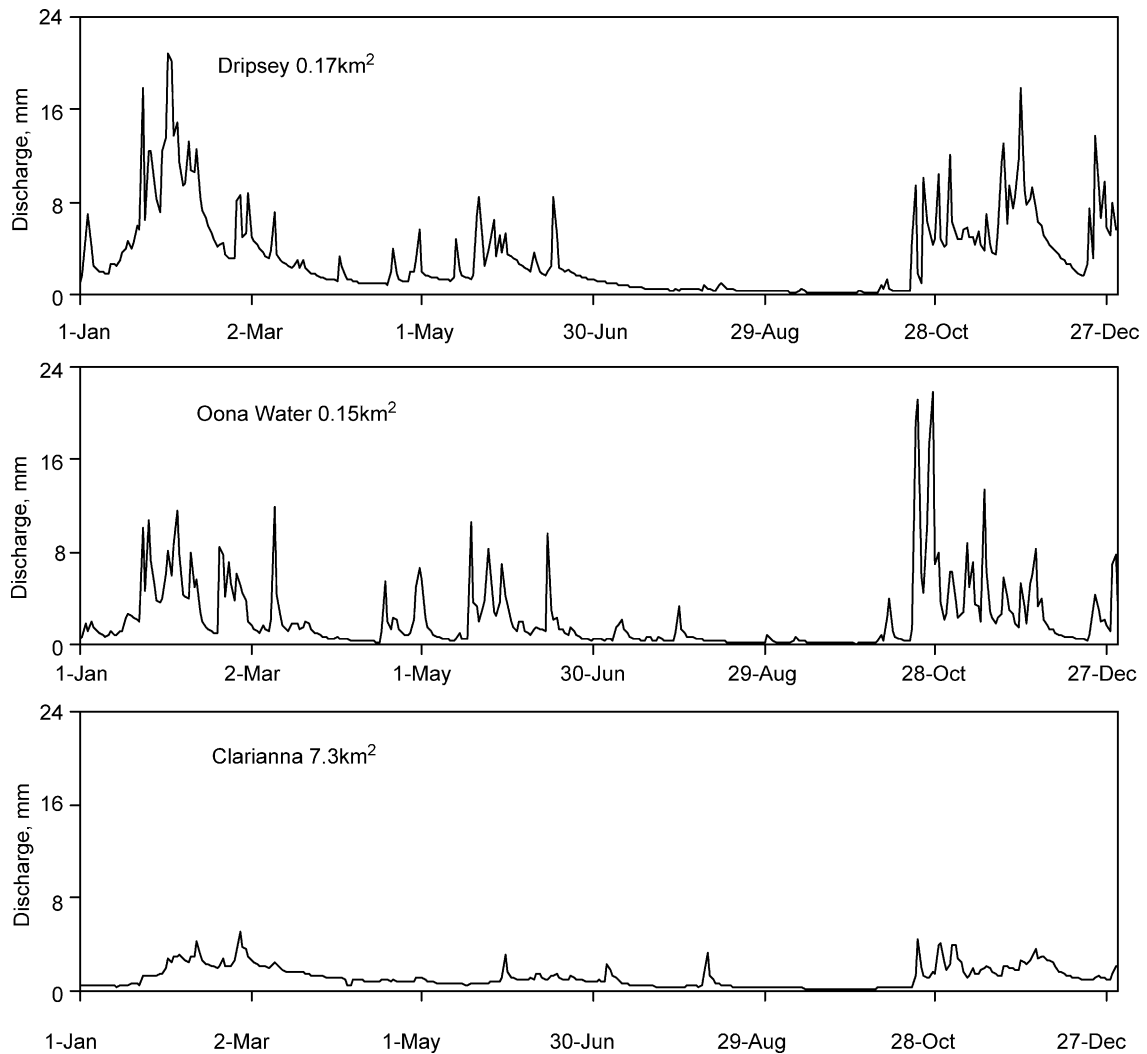


Fig. 2. Normalised daily discharge hydrographs for the three catchments from 1 January 2002 to 31 December 2002. The discharge statistics reflect increasing base flow contributions in the order Oona Water, Dripsey and Clarianna. The pattern of hydrograph peaks is very similar despite the geographical disparity of the catchments and indicates the dominance of frontal precipitation across Ireland.

2002. The resulting high Q5:Q95 ratio at 411 is due to this stream diversion and does not represent the wider catchment. The larger gauged catchments have ratios between 13 and 21 and reflect the low gradient and permeable nature of the wider catchment. Fig. 2 shows the response to rainfall from the two smallest catchments in the Dripsey and Oona Water and in the catchment below the peat catchment of the Clarianna. The shape of the hydrographs matches the discharge statistics with a dampening of storm response in the order Clarianna, Dripsey and Oona Water.

Hydrochemical results are presented as flow-weighted average concentrations and catchment exports for 2002 in Table 3. Despite similar annual exports from the Dripsey and Oona Water headwater catchments (2.66 and 2.40 kg/ha/yr respectively), the TP (unf) losses per unit of runoff were higher in the Oona Water. The TP (>0.45) fraction was dominant in the Oona Water and the Clarianna but not the Dripsey. At the largest scales, an increase in TP (unf) was a feature of Oona Water exports (3.13 kg/ha/yr) and a decrease was observed in Dripsey and Clarianna

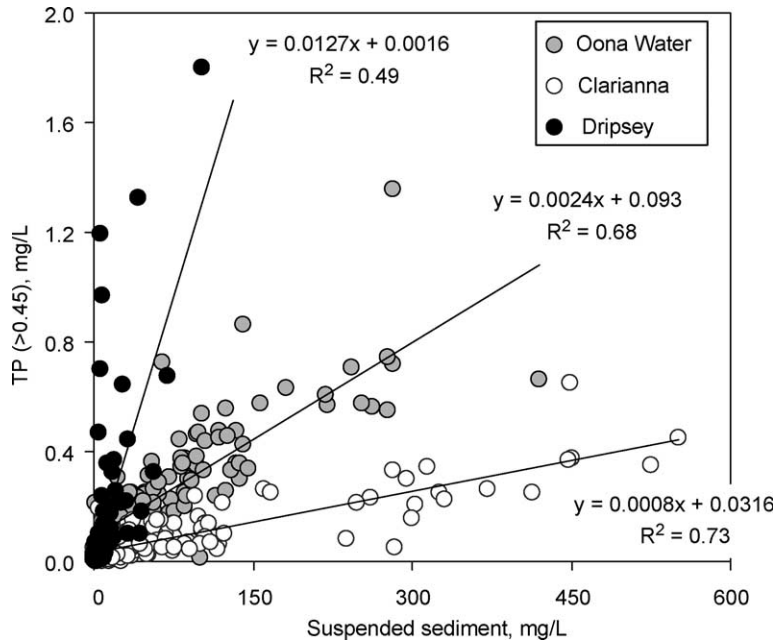


Fig. 3. Suspended sediment (SS) and particulate phosphorus (TP (>0.45)) concentrations in the headwaters of the three catchments. The differences are probably due to grain size (not measured). The Dripsey recorded higher TP (>0.45) concentrations although these were infrequent and the Oona Water recorded the higher flow-weighted concentration for 2002 (0.239 mg/L). The higher SS concentrations in the Clarianna were probably caused by a period of bed disturbance (dredging) for a short period along the whole channel.

exports (1.60 and 0.23 kg/ha/yr, respectively). These changes were observed despite very small differences in catchment normalised runoff depths and so can be considered a concentration of P load in the Oona Water and a dilution of P load in the Dripsey and Clarianna. The concentration of load with increasing catchment area in the Oona Water was also found in discretely sampled sub-catchments at scales from 9 to 48 km² owing to chronically high background (non-storm) P concentrations up to 0.3 mg/L (not presented here). The Clarianna catchment had much lower P exports than the Dripsey and Oona Water catchments with all except the peat headwater catchment exporting less than 0.5 kg/ha/yr TP (unf). The RP (<0.45) concentrations were less than 0.02 mg/L in all sub-catchments of the Clarianna and were below those considered to pose a eutrophication threat in freshwaters (Gibson, 1997).

Suspended sediment (SS) concentrations were positively correlated with the TP (>0.45) fraction in samples from all catchments and sub-catchments (Fig. 3) although higher concentrations in the Dripsey were infrequent and associated with low storm SS

concentrations of less than 150 mg/L. Without particle size measurements it is difficult to interpret these sediment associated P data although the higher SS concentrations in the Clarianna, for example, may be due to bed disturbance during the study period. Even with such disturbance, TP (>0.45) concentrations were still low compared with the other catchments.

4. Discussion

The soil chemistry results from the Dripsey and Oona Water soils, predict a higher desorption risk from the Dripsey soils. This is principally due to the dominance of highly adsorptive and strongly binding Al concentration in the Oona Water soils and of highly adsorptive but weakly binding Fe concentration in the Dripsey soils. The two soil samples from the Oona Water that do not conform to this model desorbed higher P concentrations but were also from Oona Water soils with the lowest Al concentrations. It is unclear as to whether the additional pH effect on P

desorption rates and the nature of Fe–OM sorption sites with low binding energies, were mutually exclusive. These were, however, the two principal effects observed in the data that may account for higher P desorption potential from soils in the Dripsey catchment.

For the Dripsey and Oona Water soils a comparative summary of adsorptive saturation potential is presented in Fig. 4 as Degree of Phosphorus Saturation (DPS), calculated using the ratio of Mehlich-3 extractable P (P_{M3}) and the Langmuir X_m after Sharpley (1995), and the Morgan P concentration (Kleinman et al., 1999). The intersect of the trend line in each dataset with the 25% DPS, above which RP (<0.45) losses from soils are proposed to increase (Sharpley, 1995; Beauchemin and Simard, 1999), is shown. The intersect corresponds to index 3 for Dripsey soils and index 4 for Oona Water soils and indicates that P saturation is likely to be greater in the Dripsey soils per unit concentration of soil P test.

Calcium concentrations in the Clarianna catchment soils were higher compared to the other two catchments. Calcium concentration was negatively

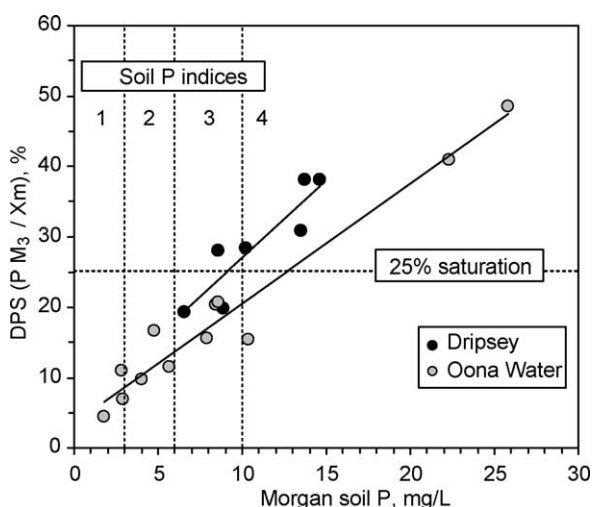


Fig. 4. Degree of phosphorus saturation (DPS) and soil P test (Morgan) for the Dripsey ($y = 2.22x + 4.75$, $r^2 = 0.81$) and Oona Water ($y = 1.70x + 3.57$, $r^2 = 0.95$) soils using the Langmuir X_m as the denominator and shows that the Dripsey soils were more P saturated for a given soil P test concentration compared with the Oona Water soils. The relationship is less clear with the Clarianna soils as P retention is probably dominated by precipitation/dissolution processes rather than adsorption/desorption processes and so the Clarianna data are omitted.

correlated with the Langmuir adsorption parameters and this might suggest that Clarianna soils would have the greatest desorption levels but there was no correlation between Ca and the Pfeo term. This may indicate that the process of uptake and release of P with Ca involved precipitation/dissolution reactions rather than adsorption/desorption sites. Kleinman and Sharpley (2002) have developed a DPS tool specific to calcareous soils in the US and it appears, from this work, that it will be appropriate to develop a DPS tool for Irish calcareous soils in addition to non-calcareous soils.

If soil chemistry is a determinant of the soils' ability to retain P against desorption (or dissolution), particularly at low and high pH, then the erosive effects of runoff may similarly provide the means to gauge whether the particulate TP (>0.45) fraction is at risk of transfer from fertilised soils (Foster et al., 2003; Hutchins et al., 2002). The Q5:Q95 ratio is a summary of flashiness in any stream system and high Q5 discharges or low Q95 discharge (or a combination of both) will yield a high ratio. Soil permeability, land drainage, topography and landuse should all affect the flashiness of a stream system (Ineson and Downing, 1965) and is caused by the faster water transfer flowpaths. These faster flowpaths may be responsible for greater erosivity, even on grassland catchments, and especially on impermeable soils and those subject to overgrazing and poaching (Heathwaite, 1994). Fig. 5 shows the relationship between Q5:Q95 ratio and TP (>0.45) export in all three catchments as a power relationship ($r^2 = 0.81$). The highest Q5:Q95 ratio and TP (>0.45) export in the Dripsey is from 2.11 km² catchment. Scanlon et al. (2004) could not find any relationship between this export and indices of catchment topography compared with the other Dripsey catchments and assumed that P and SS exports at 2.11 km² were driven by channel erosion and instream enrichment. It may be that other catchment factors including land-drainage density and/or local impermeability could be contributing to the high Q5:Q95 discharge ratios and that this is transporting eroded P more efficiently. Some caution must, however, be applied to this interpretation. There were no quantitative estimates of flow or P transfer in overland flow or under-field drainage to the smallest catchment outlets and so the link cannot be made between whether TP (>0.45) was from eroded soil

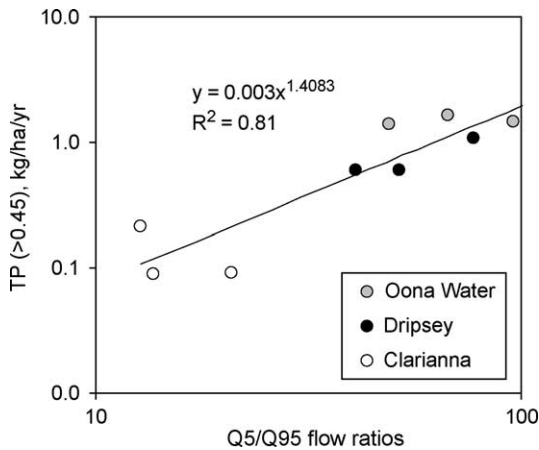


Fig. 5. Flow statistics using the ratio of high, infrequent flows (Q5) to low, frequent flows (Q95) in all sub-catchments compared with particulate P (TP (>0.45)) load. The relationship shows that, despite less runoff, the potential for the TP (>0.45) fraction to be transferred from fertilised soils in the Oona Water is greater due to runoff flashiness.

surfaces or was due to the enrichment of streambed sediments by soil-desorbed RP (<0.45). The nature of the impermeable clay soils in the Oona Water soils are, however, conducive to erosive overland flow and this was observed on several occasions when field visits coincided with storm events. The fact that soil chemistry tests indicated that the Oona Water soils were efficient at retaining soluble P is perhaps evidence that transfer following erosion is more likely than transfer following desorption. This TP (>0.45) erosion-enrichment question is, nevertheless, an important aspect of understanding the scale link between field surface P mobilisation to first order stream P delivery and will merit further investigation.

At the larger catchment scale, and particularly comparing the Dripsey and Oona Water P exports, there was evidence of changing hydrological and hydrochemical influences. In the larger Dripsey catchment outlet, P transfer decreased when expressed as an areal load from TP (unf) export of 2.65 kg/ha/yr at 0.17 km² with no point sources to 1.60 kg/ha/yr at 14.00 km² and this decrease in P load also took place despite the cumulative effects of potential inputs from eight farmyards. Sharpley and Tunney (2000) indicated that this phenomenon is most likely due to the cumulative input of groundwater, which is generally not associated with P

transfer in mineral soils, as catchment area increases. The fact that P concentrations in streams were very low between storm-events and during periods of baseflow in the Dripsey does indicate that there was little P transfer to groundwater.

In the larger Oona Water catchment, the TP (unf) transfer was increased (and not diluted) to 3.12 kg/ha/yr at 88.50 km² from 2.40 kg/ha/yr at 0.62 km². This increase in P load was associated with chronically high P concentrations throughout at low flow the main channel and has also been observed in other river systems in Northern Ireland (Stewart, 2000; Wood and Fallon, 1997). In the Oona Water, groundwater aquifers are largely isolated from the surface hydrology due to the impermeable till layer that forms the gleyed drumlin soils (Ó Dochartaigh, 2003) and so P inputs to river baseflows from groundwater transfers can be discounted. A more likely source is the cumulative affect of many discrete point sources that are not diluted in the low baseflows that are associated with flashy rivers during non-storm periods. In English rivers, similar findings of increased P load with increasing catchment area in rural catchments have been associated with sewage inputs from the rural population and specifically chronic P transfer from septic tanks (Bowes et al., 2003; Cooper et al., 2003). Census and Water Service statistics from the Oona Water catchment showed that only 630 population equivalents were connected to secondary wastewater treatment works from a population of 3300, with the remainder using septic tanks. Even with normal soil percolation from septic tanks, the final effluent from such a high rural density would be enough to elevate P concentrations at low flow (Foy et al., 2003).

5. Conclusions

The terms of reference for this study were to assess the potential for P transfer from Irish soils based on laboratory studies and integrate with the patterns observed at the river catchment scale and how these patterns might be confounded by variations in runoff response (climate and hydrology) and scale. The Dripsey soils were characterised in laboratory studies as having a higher potential for P desorption and a higher potential for soil P saturation per unit soil P test

when compared with Oona Water soils. Both soil types were non-calcareous and the major differences appeared to be Al concentration, which was higher in Oona water soils, and Fe–OM complexes in the Dripsey. These results reflected the magnitude of RP (<0.45) transfer as measured over 1 year in headwater catchments.

Particulate P transfer (TP (>0.45)) from fertilised soils was predicted by the flashiness of streams and rivers using the Q5:Q95 ratio of discharge statistics and this was higher in the catchments of the Oona Water despite having almost 50% less runoff. It is proposed that hydrological (groundwater influence) and hydrochemical (background P loading) changes influenced P loads with increasing catchment area by decreasing or increasing the P load in the Dripsey and Oona Water catchments, respectively.

It is clear from this work and from research elsewhere (McDowell and Sharpley, 2003; Withers and Bailey, 2003; Tunney, 2002; Laubel et al., 1999) that fertilised non-calcareous soils can be a major source for P transfer. In this study, at the smaller catchment scale, there were no point sources and P transfers (up to 2.5 kg/ha/yr) during normal runoff could be considered to be from soils subjected to normal grassland agricultural management over a 12-month cycle.

Lower soil Al appears to be a factor for potentially transferring the RP (<0.45) fraction in runoff water from fertilised non-calcareous soils by reducing the P binding energy and P adsorption maxima in soils and this would fit with other European studies (e.g. Lookman et al., 1996; Freese et al., 1992). Clarianna calcareous soils appear able to retain P although the precise mechanism and the extent of retention require further investigation (e.g. Kleinman and Sharpley, 2002). In any event, the transfer of TP (>0.45) with suspended sediment is more likely to be related to the flashiness of water runoff, independent of runoff volume, and the Q5:Q95 ratio is a practical summary of these runoff patterns between catchments. Combining the catchments' results, but bearing in mind the requirement for further work on the dissolution potential from calcareous soils, this study indicates that agricultural areas with mineral soils and catchments with (firstly) low Al concentration and

(secondly) high Q5:Q95 ratios are at the greatest risk of transferring reactive P (via desorption) and particulate P (via erosion or enrichment) to freshwater. These two variables are examples of minimum information requirements (e.g. Brazier et al., 2001) and could help managers to prioritise efforts that aim to reduce excessive P transfer from soils within large agricultural river basins.

Upscaling laboratory soil P risk assessments to river basins would appear possible in headwater streams. The changing influences of hydrological flowpaths at larger catchment scales, however, which may dilute or concentrate field scale soil P transfers, will require consideration when assessing the contribution of agricultural soil P and monitoring the effects of field scale mitigation.

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