Available online at www.sciencedirect.com

ScienceDirect

Journal of Environmental Sciences 2013, 25(9) 1–11

JOURNAL OF ENVIRONMENTAL SCIENCES
ISSN 1001-0742
CN 11-2629/X
www.jesc.ac.cn

Seasonal exports of phosphorus from intensively fertilised nested grassland catchment

Ciaran Lewis[1], Rashad Rafique[2,*], Nelius Foley[1,6], Paul Leahy[1], Gerard Morgan[3], John Albertson[4], Sandeep Kumar[5], Gerard Kiely[1,5]

1. Department of Civil and Environmental Engineering, University College Cork, Ireland. E-mail: ciaran.lewis@gmail.com
2. Department of Microbiology & Plant Biology, University of Oklahoma, Norman OK, 73019, USA
3. Aquatic Services Unit, Environmental Research Institute, University College Cork, Ireland
4. Department of Civil and Environmental Engineering, Duke University, Durham, NC, 27708, USA
5. Department of Plant Science, South Dakota State University, Brookings, SD, 57007
6. Environmental Research Institute, University College Cork, Ireland

Received 04 December 2012; revised 18 February 2013; accepted 11 March 2013

Abstract

We carried out a one year (2002) study of phosphorus (P) loss from soil to water in three nested grassland catchments with known P input in chemical fertilizer and animal liquid slurry applications. Chemical fertilizer was applied to the grasslands between March and September and animal slurry was applied over the twelve months. The annual chemical P fertilizer applications for the 17 and 211 ha catchments were 16.4 and 23.7 kg P/ha respectively and the annual slurry applications were 10.7 and 14.0 kg P/ha, respectively. The annual total phosphorus (TP) export in stream-flow was 2.61, 2.48 and 1.61 kg P/ha for the 17, 211 and 1524 ha catchments, respectively, compared with a maximum permissible (by regulation) annual export of ca. 0.35 kg P/ha. The export rate (ratio of P export to P in land applications) was 9.6% and 6.6% from the 17 and 211 ha catchments, respectively. On average, 70% of stream flow and 85% of the P export occurred during the five wet Autumn/Winter months (October to February) indicating that when precipitation is much greater than evaporation, the hydrological conditions are most favourable for P export. However the soil quality and land use history may vary the results. Particulate P made up 22%, 43% and 37% of the TP export at the 17, 211 and 1524 ha catchment areas, respectively. As the chemical fertilizer was spread during the grass growth months (March to September), it has less immediate impact on stream water quality than the slurry applications. We also show that as the catchment scale increases, the P concentrations and P export decrease, confirming dilution due to increasing rural catchment size. In the longer term, the excess P from fertilizer maintains high soil P levels, an antecedent condition favourable to P loss from soil to water. This study confirms the significant negative water quality impact of excess P applications, particularly liquid animal slurry applications in wet winter months. The findings of this study suggest that the restricted P application in wet months can largely reduce the P losses from soil to water.

The specific objectives were: to determine the seasonal and annual exports in stream flow of total phosphorus (TP), total dissolved phosphorus (TDP) and particulate phosphorus (PP) and to examine the hydrological and chemical controls on P exports in the stream-flow.

Key words: phosphorus; fertilizer; slurry; exports; grassland; land management; water quality; eutrophication

DOI: 10.1016/S1001-0742(12)60255-1

Introduction

Phosphorus (P) is an essential element present in all living organisms. It is a non-renewable resource and plays an important role in food production. Agriculture is considered as the main consumer of mined P which is 80%–90% of the total world demands (Childer et al., 2011). However, approximately 20% of the P used in agriculture reaches the food consumed and most of the rest is lost in inefficient steps in the P cycle (Cordell et al., 2011). Phosphorus enriched runoff from agricultural land promotes eutrophication of rivers and lakes (Correll, 1998). A recent review of P losses from agriculture and eutrophication in north-west Europe (Norway, Sweden, UK and Ireland) showed that the several lake systems (e.g., Lough Lake in Ireland) have become eutrophic because of intensive agricultural practices (Ulén et al., 2007). In Ireland, the level of P in soils have increased tenfold over the past 50 years as a result of historical intensive use of

* Corresponding author. E-mail: rashidbao@gmail.com

fertilizers and grazing. Despite the significant reduction in P fertilizer use in last 10 years, there is still a surplus input of 8.3 kg P/(ha·yr). This high input is mainly associated with mineral P fertilizer and intensive grazing. The average mineral P fertilizer input on grasslands is 5 kg P/(ha·yr) which is much less than arable land (46 kg/ha). In most experimental studies, water from agricultural sector has more than 50% of P in the form of dissolved reactive P (DRP). This constant high level of P in Irish soils may be due to in appropriate accounting of P in animal manure and continuous intensity of slurry applications and grazing on grasslands. The total P loss to waterways from Irish agricultural land is estimated to be 0.5 kg P/(ha·yr) (Ulén et al., 2007). However, for good water quality in Irish waters, it is advised that P additions from all sources should not increase to a concentration greater than 0.035 mg P/L (Bowman, 2009).

Grasslands are an important part of Irish agriculture system in providing food for rapidly growing livestock industry (Rafique et al., 2011a, 2011b). The concentration of P in water bodies fed by runoff from grassland catchments is dependent on the climate, hydrology, geomorphology, soil chemistry, and farm management within the catchment. The climate and hydrology factors include: the rainfall amount and intensity; the antecedent soil moisture conditions; the extent of overland and sub-surface flows; the soil moisture status particularly in the near stream fields; the potential for erosion of the hill-slopes and the duration of high water flows (Tunney et al, 1997; Jordan et al., 2005). The geomorphology parameters include: the catchment size (scale); the soil type; the slope of the fields adjacent to the streams and the concavity or convexity of hill-slopes. The soil chemistry factors include: the magnitude of soil phosphorus especially in the top 10 cm of the soil profile and in particular the extractable phosphorus in the topsoil (Daly, 1999; Ulén et al., 2001) and the degree of soil P saturation (Hooda et al., 2000). The farm management factors include: the amount and seasonality of application of chemical fertilizer and animal slurry (Rafique et al., 2012); the phosphorus content in fertiliser; the animal stocking density; animal diet; the duration and timing of livestock in the fields and the phosphorus residue in grass after silage or hay harvesting and the contribution of farm yard runoff (Coulter et al., 2002).

The data collection of time series of stream P concentrations is an integral component of many monitoring programmes and water quality studies (Smith et al., 2001; Stow et al., 2001; Ulén et al., 2007; Csathó and Radimszky, 2009). Such data are required for estimating: the annual phosphorus export loads; the detection of trends in seasonal and annual transport rates; the identification of hydrologic controls on exports; assessing the efficacy of measures taken to reduce phosphorus loading to surface waters from diffuse agricultural sources; and modelling land use change scenarios (Scanlon et al., 2005; Nasr et al., 2007).

The different fractions of P found in streams (Turner and Haygarth, 2000) include: total dissolved phosphorus (TDP), soluble reactive phosphorus (SRP) and total phosphorus (TP). The SRP is particularly important as it is immediately available for algal growth in rivers and lakes (Liu et al., 2012). Observations of the seasonal relationships between these fractions provide insight to the physical and chemical processes involved in the loss of P from soil to water. Particulate phosphorus (PP) concentration (mg/L) is defined in Eq. (1):

$$PP = TP - TDP \quad (1)$$

Annual TP losses from agricultural soils generally amount to 0.5–2.0 kg P/ha, which is between 1% and 5% of the P input from fertilizer and slurry (McDowell and Trudgill, 2000; Chapman et al., 2001; Ulén et al., 2001; McKergow et al., 2003). The maximum permissible mean annual concentration of TP in Irish rivers is 0.35 mg/L (Tunney, 2002). Assuming an annual stream runoff of say, 1000 mm, then the annual export of TP should not exceed 0.35 kg P/ha.

From fertilized grassland catchments, increases in concentration of phosphorus are positively correlated with stream flow (McDowell and Trudgill, 2000; Hooda et al., 2000; van Es et al., 2004; Warner et al., 2009). However, P concentration during a flood event is also dependent on antecedent flow conditions, for maybe several weeks prior to the flood event (Warner et al., 2009). The relationships between the different fractions of phosphorus in streams vary with season and with the type of fertiliser application. Catchments that are subject to P fertilization often exhibit a dominance of event-initiated transport of P in the overall annual P flux (Grey and Henry, 2002; Scanlon et al., 2004). This event initiated P flux may be dominated by either PP or TDP.

In Denmark, using four arable catchments, Grant et al. (1996) found that PP varied from 29%–71% of TP and that the PP fraction was lower for areas using manure fertilization. Brunet and Astin (1998) found for a large catchment (7840 km^2) in France that the annual flux of PP was 34% of TP and the ratio of PP to TDP increased significantly during flood events. For a 7.3 km^2 catchment over twelve years (Pionke et al., 1999) most TDP (66% of annual) was measured in winter and associated with storm flow while the concentration of DP remained almost constant for base flow throughout the year at about 0.01 mg/L. Surveys in the UK (HMSO, 1995) found that the average annual application of P (from chemical fertiliser) was 16 kg P/ha in Scotland, 14 kg P/ha in England and Wales and 13 kg P/ha in Northern Ireland. In Sweden, farmers are not allowed to apply more than 22 kg P/ha to ensure the good water quality (SBA, 2010). In Southern Ireland the estimated regional average for pasture was 12 kg P/ha and for silage field 15 kg P/ha (Coulter et al., 2002). The Irish values are estimated on regional sales of fertiliser and not on individual farm surveys.

In the context of promoting sustainable agriculture by understanding the processes of P loss from soil to water, we carried out a one year study of three nested grassland catchments with known fertilisation regimes for two of the three catchments (17 and 211 ha). The specific objectives were: (1) to estimate the annual export loads of TP, TDP and PP; (2) to examine the seasonal relationships between TP, TDP and PP; (3) to examine the contribution of fertiliser and animal slurry to the P export; and (4) to examine the hydrological controls on P export.

1 Site description

The study site is the upland Dripsey catchment, a sub-catchment of the river Lee in County Cork, Ireland. The nested grassland catchments with outfall weir controls at S1, S3 and S4 have areas of 17, 211, and 1524 ha, respectively (**Fig. 1**). The elevation of points S1, S3 and S4 are 210, 160 and 80 m above sea level (masl). The experimental catchments are located approximately 25 km northwest of Cork city (52°N, 08°44′W). **Figure 1** shows the shape, contours and site boundaries of the three nested catchments. A gauged point S2 exists (between S1 and S3) but no water chemistry analysis was carried out there. The stream runs from North to South and at S1 the stream is approximately 1 m wide.

The average annual rainfall recorded from a meteorological tower near S1 was 1472 mm for the six years 1997 to 2002. The monthly rainfall ranges from under 50 mm in the summer to approximately 200 mm in the winter. The mean monthly temperature is ca. 5°C in the winter and ca. 15°C in the summer. The geology of these nested catchments is old red sandstone. The topsoil at the higher elevations is peaty podzols and at the lower regions are brown podzols. The profile of the soil is characterised by a dark organic loam to a depth of 15 to 25 cm overlying a yellowish-red, iron enriched B-horizon of loam texture.

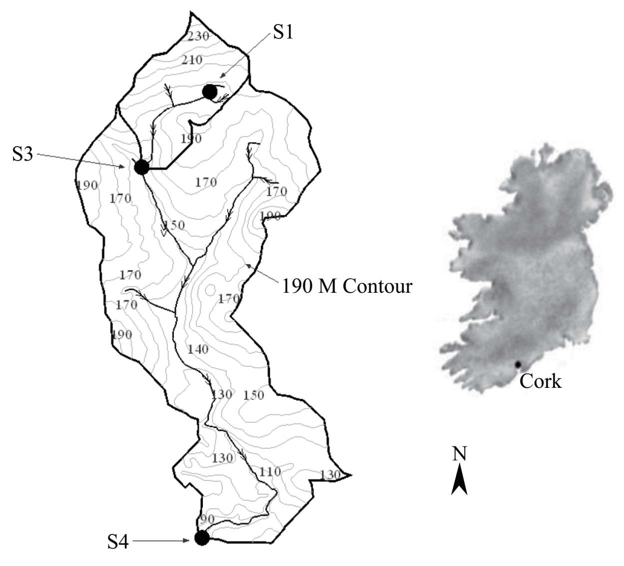

Fig. 1 Contour map of the three nested catchments: S1 (17 ha), S3 (211 ha) and S4 (1524 ha), showing the shape and location of the nested catchments in Cork, Ireland.

Approximately 45% of the total area of Ireland (85% of agricultural land) has a land cover of grassland (Coulter et al., 2002). Farming layout and practice in the study area of County Cork is a mix of dairy and beef cattle and is typical of Irish farming. The 211 ha catchment encompassing stream-flow station at Site 3 consists of seven dairy and beef farms and one sheep farm. Farm sizes range from approximately 10 to 40 ha. Land cover is dominated by agricultural grassland consisting of perennial rye-grass with some clover. The growing season in Ireland is weather dependant but generally it starts in early March and finishes in October. Stocking rates are expressed as livestock units (LU), which is equivalent to a mature (500 kg live weight) productive cow. The stocking rate in the study catchment for 2002 was 2.1 LU/ha compare to Irish national average stocking rate of 1.9 LU/ha (Rafique et al., 2011b). The cattle strip graze part of the farm during the eight-month growing season and the rest of the farm (typically approximately one-third to one-half) is closed off from cattle and kept for grass silage harvest and production. In the study catchments, there are normally two silage cuts, the first in May/June and the second about 6 weeks later. For the year 2002, cattle were housed indoors for approximately 4 months of the year.

Fertilizer was applied throughout the growing season at four to six week intervals with most applied in March and April and again after silage cuts. The chemical fertiliser type, Pasture Sward (N:P:K, 24:2.5:5, *m*/*m*/*m*) was applied to the pastures and Cut Sward (N:P:K, 24:2.5:10, *m*/*m*/*m*) was applied to the silage fields. Slurry was applied less often but throughout the twelve months. Data were collected on fertiliser and animal slurry applications for the eight farms of catchment 3 (this also includes catchment 1) but not for the 47 farms of catchment 4.

2 Methods

2.1 Field methods

Stream discharge and water chemistry samples were collected at the outfalls of the three nested catchments at the control points at S1, S3 and S4 for the calendar year 2002. At S1 the control point is a 90° v-notch weir; at S3, a rectangular weir; and at S4 a modified crump weir. Stream discharge was measured continuously (at 15 min intervals) using an OTT Thalimedes (OTT Hydrometry Ltd., UK) water level recorder at S1, S3 and S4. Composite, flow-weighted water samples for the three sites were collected in flow-actuation mode using an ISCO 6712 auto-samplers at S1, S3 and S4. The composite sampling regime ran for the year 2002 and covered 44% of the entire year at the three sampling locations. The composite samples were made up of a number of smaller samples. These were collected more often during periods of high flow and less frequently in periods of low flow. The samples were returned to the laboratory, from the auto-samplers and stored in refrigerators at 4°C until analysed. Weekly grab samples were taken to supplement the composite sampling strategy. Laboratory analysis was performed in the Aquatic Services laboratory of the Environmental Research Institute at University College Cork.

2.2 Laboratory methods

Phosphorus analyses for the stream-water were performed manually by spectrophotometer after Standard Methods (Anon and Mary, 1985), based on a molybdate/ascorbic acid method of Murphy and Riley (1962). For TDP, which is composed of dissolved reactive phosphorus and dissolved organic phosphorus, the samples were membrane filtered using 0.45 μm cellulose acetate filters and then digested using sulphuric acid/ammonium per sulphate in an autoclave. Filtering was not performed for the TP measurements.

2.3 Data analysis

One key objective of this study is to estimate the annual phosphorus export to the stream in kg P/ha (Ferguson, 1987). The instantaneous phosphorus export (e) for a given stream location is calculated as the product of the river's instantaneous discharge (q_i) and the concentration of phosphorus C_i (Webb, 1997).

$$e = q_i \times C_i \tag{2}$$

The phosphorus export load (L) for any time period is calculated from:

$$L = (Q_{i+1} - Q_i) \times \overline{C} \tag{3}$$

where, Q_i (L/sec) is cumulative flow at the start of the time period and Q_{i+1} (L/sec) is cumulative flow at the end of the period. $\overline{C}$ (mg/L) is the mean concentration of phosphorus during the time period. The cumulative flow in the stream for the year is computed from the observed 15-min flow data. The annual export (AE) of P (assuming the full year is sampled) is then

$$AE = \sum_{i=1}^{i=n} L_i \tag{4}$$

where, n is the number of composite sampling periods over the year and L_i is the P export of a given time period. The total export for the year is then normalized (per unit of catchment area) for comparison with other catchments.

$$NAE = \frac{AE}{A} \tag{5}$$

where, A (ha) is the area of the catchment and NAE is normalized annual export of total P. We have a detailed record of the river flow for the full year. The composite water chemistry samples cover 42%, 40% and 43% of the year at the three measuring locations S1, S3 and S4 respectively. Covering 100% of the year was not possible due to cost. There are gaps in the water chemistry data most frequently at low flows but not exclusively so. To estimate the annual export, we require a robust gap filling technique for the remainder of the year. We computed the export of phosphorus (kg P/ha) from S1, S3 and S4 using Eq. (3) above including only the time periods for which we had stream water phosphorus data. For S1 this is 42% of the total year. This is a lower bound estimate since it assumes that TP is zero for those time periods that we do not have TP data. We also estimate an upper bound of the export, by factoring the lower bound estimate. For S1 the lower bound was estimated using a time period of 42% of the year. The upper bound export is 2.38 times the lower bound estimate.

2.4 Gap filling

We used an empirical power law relationship between C and Q:

$$C = mQ^n \tag{6}$$

Where, C (mg/L) is the concentration of TP or TDP in any given sample, Q (L/sec) is the corresponding flow rate observed during sampling and m and n are catchment specific constants. This technique was to plot the C vs. Q for known data for the year and determine a single annual relationship as in Eq. (6). In a catchment with seasonal variation of flows and seasonal variation of application of fertiliser (and slurry) it may be more appropriate to plot the known data for each of the four seasons. This gives four empirical relationships for the year (for each of the three sites) rather than one relationship for the full year. We applied both sets (the single annual and the four seasonal curves) to estimate the annual export load of TP and TDP. We estimated the export of PP from Eq. (1).

3 Results

The annual rainfall at location S1 for 2002 was 1812 mm (see cumulative rainfall, **Fig. 2**), compared to the 1472 mm average for the period 1997–2002. Normalised stream flow (in mm/ha) for 2002 was measured as 1206 mm at S1, 1080 mm at S3 and 1035 mm at S4. The annual stream flow amounted to 66% of annual rainfall at S1 and 55% at S4. The reduced runoff at S4 was due to lower (not measured) rainfall averaged over S4 (1524 ha). The single rainfall measurement location is at an elevation of 190 m near S1

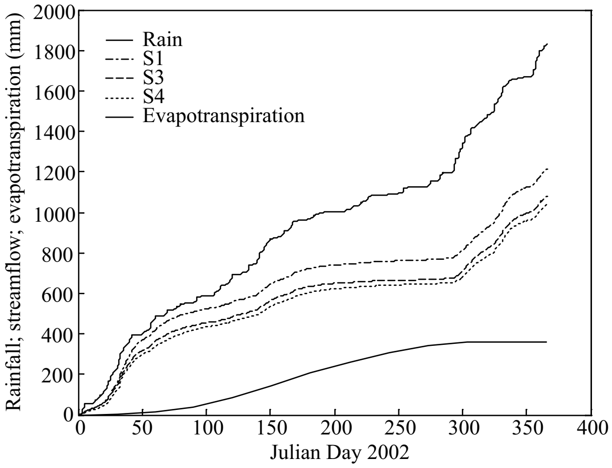

Fig. 2 For the year 2002, the cumulative rainfall recorded S1; stream flow at the outfall of the three catchments, normalized per unit area; and the evapotranspiration estimated by eddy covariance.

(**Fig. 1**). In **Fig. 2** we note that there are pulses of rainfall (and high stream flow) at the beginning of the year (Julian day 1 to 60) and again at the end of the year (Julian day 300 to 365). While there was rainfall in the summer months (Julian day 150 to 300), the evapotranspiration was of the same order as the summer rainfall with the result that the stream flow was composed mainly of groundwater, which is close to zero in P concentration.

Figure 3 shows the monthly chemical fertiliser and animal slurry applications area averaged for the S1 and S3 catchments. Chemical fertiliser was applied in each of the eight months, February to September and animal slurry was applied more randomly throughout the year. For S1 and S3, the phosphorus applied in chemical fertiliser was 16.4 and 23.7 kg P/ha respectively. The corresponding animal slurry P application was estimated at 10.7 and 14.0 kg P/ha. The magnitude of the combined P in fertiliser and slurry at S1 (26.7 kg P/ha) and at S3 (37.7 kg P/ha) exceeds the reported national averages of 12 and 15 kg P/ha for pasture and silage fields (Coulter et al., 2002) which was estimated from sales statistics of fertiliser.

The discharge Q and total phosphorus concentrations C for the composite samples at S1, S3 and S4 are shown in **Fig. 4**, respectively. Increases in TP concentration coincided with increases in flow at each of the three measuring sites. The peak concentrations at S1, S3 and S4 were measured on October 20 (Julian day 293) as 5.1, 2.8 and 0.55 mg/L, respectively (**Table 1**). These very high concentrations are the result of a combination of an animal slurry application and high rainfall. From **Fig. 4**, we note that the highest concentrations of TP were in winter and the lowest were in summer.

Figure 5 shows the annual CQ relationship for TP at S3 with an r^2 of 0.174. The C vs. Q relationships were estimated using best fit non-linear regression routines within the Matlab Curve Fitting Toolbox at the confidence level of $p < 0.05$. The weak correlation coefficient is due to the frequent application of animal slurry and chemical fertiliser.

The C vs. Q relationships for catchments S1, S3 and S4 are given in Eqs. (7), (8) and (9), respectively,

$$\text{at S1,} \quad C = 0.118Q^{0.422} \tag{7}$$

$$\text{at S3,} \quad C = 0.017Q^{0.59} \tag{8}$$

$$\text{at S4,} \quad C = 0.058Q^{0.174} \tag{9}$$

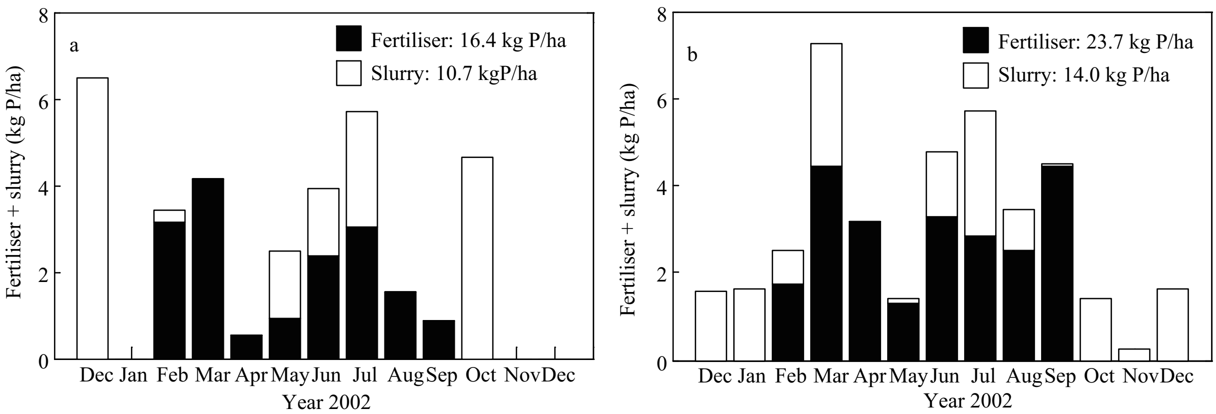

Fig. 3 Monthly applications of chemical fertilizer and slurry over the catchments areas. (a) S1 (17 ha) and (b) S3 (211 ha).

Table 1 Summary results of flows and measured TP concentrations at the three catchments in County Cork, Ireland

Catchment name	Area (ha)	Highest concentration (mg P/L)	Lowest concentration (mg P/L)	Range of flow rate (L/sec)	Range of flow rate (L/(sec·ha))
S1	17	5.1	0.019	0.25–140	0.01–8.28
S3	211	3.0	0.040	2.5–267	0.01–4.31
S4	1524	1.2	0.022	29–8100	0.02–5.31

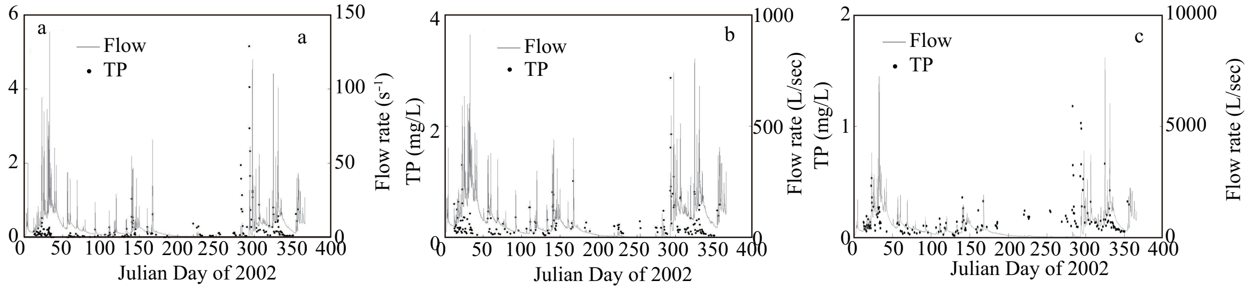

Fig. 4 Time series over the year 2002 of total phosphorus concentration and flow rate at S1 (17 ha) (a), S3 (211 ha) (b), and S4 (1524 ha) (c).

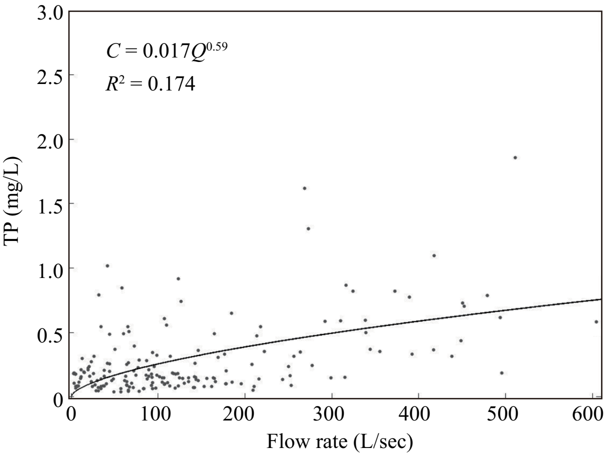

Fig. 5 Total phosphorus concentration vs. stream flow for catchment area S3 (211 ha) and the best fit equation ($C = 0.017Q^{0.59}$) used for gap filling.

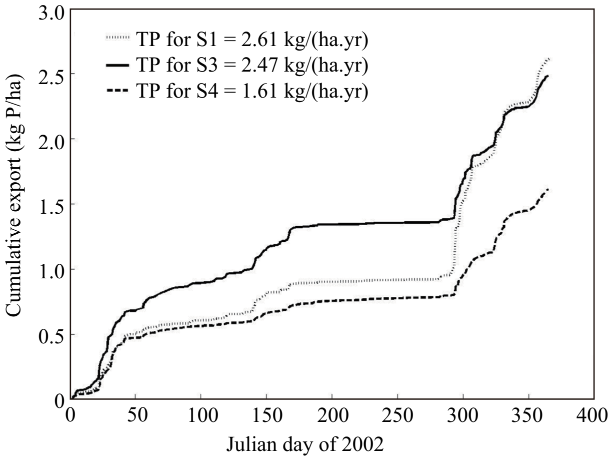

Fig. 6 Normalized cumulative TP export (kg/ha) at the three sites S1, S3 and S4.

After completing the 'gap filling' exercise for TP and TDP, we estimated the total export per unit area for the three catchments. Catchment 1 has the highest annual export of total phosphorus at 2.61 kg P/ha (**Fig. 6**) with 45% of the annual export in the three wet winter months (October, November and December). This is due to a combination of October animal slurry applications and heavy monthly rainfall after October (**Figs. 2** and **3**). S1 is also the most upland of the three catchments. The export of TP at sites 3 and site 4 were 2.5 and 1.61 kg P/ha respectively. For the 17 ha catchment (S1), the TP export rate was 9.6% of the combined P in chemical fertilizer and animal slurry. For the 211 ha catchment (S3), the TP export rate was 6.6% of the combined P in chemical fertiliser and animal slurry. These export rates are high by comparison with reported rates of 1% to 5% in the literature. From January to mid-October the export at S1 and S4 were 0.8 and 0.9 kg P/ha, respectively. There was a significant slurry application in three fields (consisting of 35% of the area) of S1 on October 15. In combination with heavy rainfall on October 20, this caused a significant increase in export load at S1 and S3 but not at S4 (9.5 km downstream). This suggests that as catchment size increased, dilution increased. At S1, the cumulative TP export rose from 0.9 kg/ha at October 15 to 2.61 kg/ha on December 31 (**Fig. 6**). At S3 the export rose from 1.5 kg/ha on October 15 to 2.5 kg/ha on December 31. At S4, the export rose from 0.8 kg/ha at October 1 to 1.61 kg/ha on December 31. The animal slurry application on October 15 in catchment 1 (S1) caused a pulse of phosphorus export at S1 with decreasing impacts as the catchment scale increases. S3 had higher exports than either S1 or S3 for the first nine months of the year. The difference between the S1 and S3 may be due to presence of point sources from farmyards. S1 had one farm but no farmyards and S3 consisted of eight farms and two farmyards. For S3 and S4, increasing the catchment (scale) size by one order of magnitude reduces the annual exports by approximately 50%. It is noticeable from **Figs. 4** and **6** that much of the phosphorus export is in pulses, coincident with high stream flow rate. **Table 2** summarises the exports at the different sites. This shows that as the catchment scale increases, the export rate decreases, confirming dilution with increasing catchment size. There are no urban areas in the catchments, and the low density of individual houses suggests virtually no human wastewater influences on the stream water quality.

The different fractions of phosphorus (dissolved and particulate) were analysed for the full year. At S1 (**Fig. 7a**) the PP was approximately 25% of TP for most of the year. At S3 (**Fig. 7b**) the PP was approximately 50% of TP for the first 100 days of the year and an end of the year cumulative PP was 43% of TP. At S4 (**Fig. 7c**) the pattern of PP vs. TP was similar to S1.

In **Fig. 8a** we show the monthly flows and the monthly exports of TP at S3 and note that months with high flows

Table 2 Summary of phosphorus exports at the three sites in County Cork, Ireland

Catchment name	Area (ha)	Cumulative export of TP (kgP/ha)	Cumulative export of TDP (kg P/ha)	Cumulative Export of PP (kg P/ha)	Cumulative Export of SRP (kg P/ha)	Cumulative Export of TP (g P/(ha·mm rain))
S1	17	2.61	2.01	0.60	1.7	1.44
S3	211	2.48	1.45	1.03	1.18	> 1.37
S4	1524	1.61	1.05	0.56	0.82	> 0.90

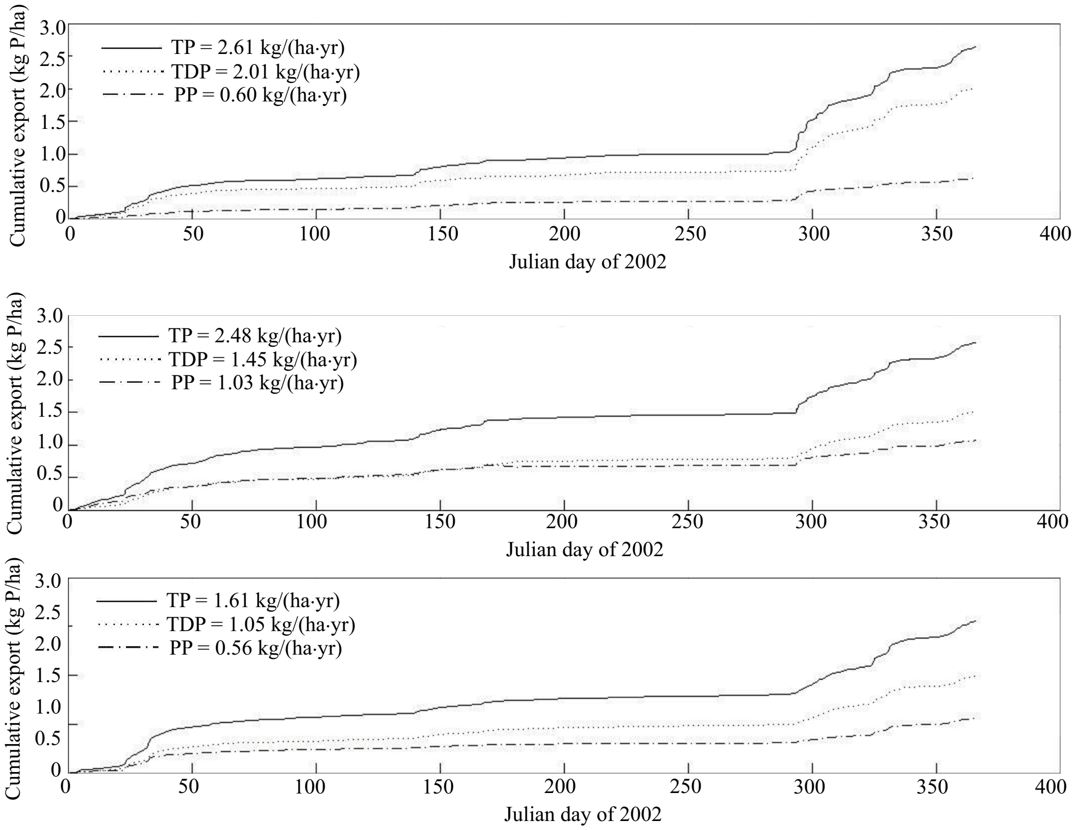

Fig. 7 Normalized export (kg/ha) of TP, TDP and PP at site 4 (1524 ha) (a), site 3 (211 ha) (b), site 1 (17 ha) (c).

also have high export of TP. This trend is observed for all three catchments. In **Fig. 8b** we show the monthly chemical fertiliser applications and the monthly export of TP. As the fertiliser was spread between February to September, the large exports of TP did not coincide (nor have a short lag time) with fertiliser applications. In Figure 10c we show the monthly slurry application and the monthly exports of TP with the months of significant exports of TP coinciding or lagging (by about one month) the months of animal slurry applications. **Figure 8** suggests that exports of TP were dependent on high flows suggesting that high rainfall rates produces surface runoff bearing phosphorus. Monthly exports of phosphorus are exacerbated by animal slurry applications especially when those applications occur in high flow months such as late autumn or winter. The chemical fertiliser applications appear to have less of an immediate impact on exports of phosphorus than animal slurry applications.

In **Fig. 9**, we examine the hydrological controls on phosphorus export. For 2002, we show the monthly phosphorus export along with the monthly precipitation and the monthly evapotranspiration. Monthly evapotranspiration has a clear pattern ranging from approximately 5 mm per month in January to 60 mm per month in midsummer. Precipitation is more erratic, ranging from 40 mm in July to greater than 200 mm per month in the five months January, February, October, November and December. In **Fig. 9b** we include the effective precipitation (precipitation–evapotranspiration) and monthly TP exports. In summer TP exports were negligible while in the winter exports were significant. This suggests that TP exports are directly proportional to effective precipitation.

4 Discussion

The application rates of P in fertilizer for 2002 were 16.7 and 23.7 kg P/ha at the farm scale (17 ha) and at the eight farms scale (211 ha), respectively. The slurry P application was 10.7 and 14.0 kg P/ha. The combined fertilizer and slurry P, was 27.1 and 37.7 kg P/ha. This

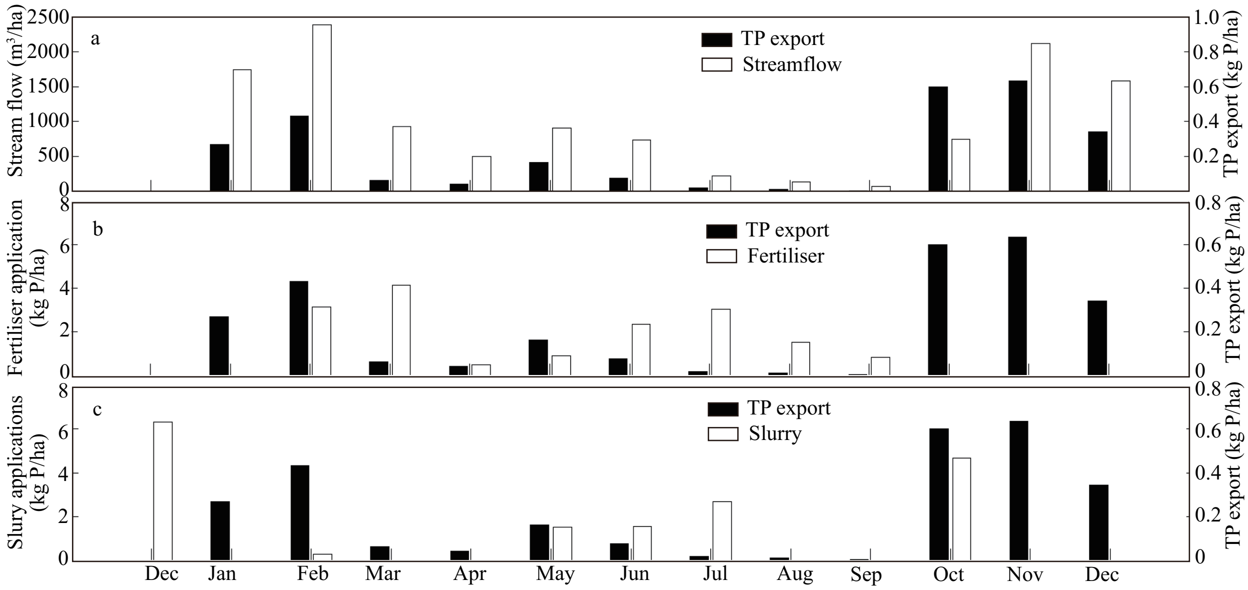

Fig. 8 Monthly TP export and monthly stream flow (a), monthly fertiliser applications (b), and monthly slurry applications (c) at S1.

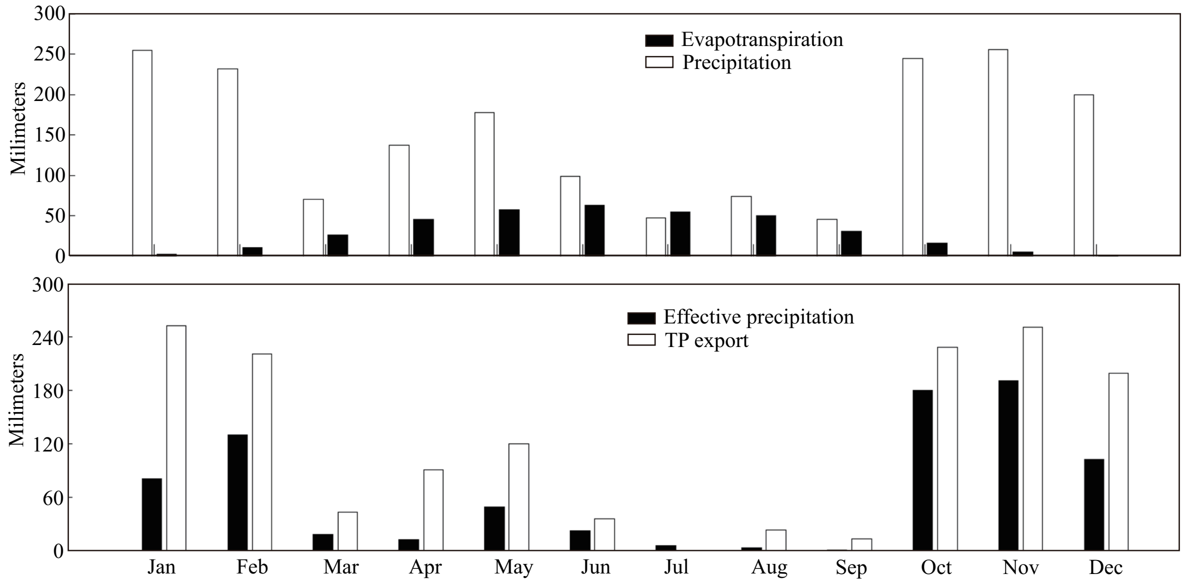

Fig. 9 Monthly precipitation and measured evapotranspiration (a), and monthly TP exports and effective precipitation (b) at S1.

compares to the Irish national average of 12 and 15 kg P/ha for pasture and silage fields respectively. The P application rates in the study areas were much higher than the national estimates determined from fertiliser sales. The annual exports of TP were 2.61, 2.48 and 1.61 kg P/ha for the 17 ha, 211 ha and 1524 ha catchments respectively, compared with a maximum permissible regulatory annual export of 0.35 kg P/ha. The corresponding exports of TDP were 2.01, 1.45 and 1.05 kg P/ha. The particulate fraction was approximately 25% of TP for the 17 ha farm scale, approximately 50% for the eight farm scale (211 ha) and approximately 25% for the 47 farm scale (1524 ha). At the 211 ha scale, the presence of two farmyards and some rutted fields near S3 contributed to the higher PP. As the catchment scale increases from 211 ha (S3) to 1524 ha (S4), there is a dilution in phosphorus export from 2.48 to 1.61 kg P/ha. This dilution effect was also noticeable in the concentrations of TP and its different P fractions during the year.

The annual export of TP was 15.9% and 10.6% (of chemical and slurry P applied) for the 17 ha and 211 ha catchments, respectively. This is high compared to values in the international literature of 1% to 5%. The amounts of fertiliser applied were higher than the Irish averages reported by Coulter et al. (2000). The land use history showed large impact on the P export which is due to large amount of animal slurry or inorganic fertilizer applied before the one year experiment. However, the interaction of slurry and inorganic P applications is very difficult to determine in controlling P leaching (Liu et al., 2012). Exports of phosphorus were negligible in the summer months and in months where effective precipitation was low (< 60 mm per month). Exports of phosphorus were highest in the wet winter months and in wet months outside of winter which is consistent with the results found by van Es et al. (2004). The amounts of fertilizer applied and the monthly amounts were not always coincident with the timing requirement of optimum grass growth (Khandokar, 2003) though this response also depends on the climatic conditions, fertilizer application rate and grass growth rate. Slurry applications were carried out at random times throughout the year with some applications in the wet winter months. Slurry applications were responsible for significant excursions of monthly phosphorus export, particularly at the smallest scale (17 ha). The months (October to February) where the effective rainfall exceeds 120 mm per month, provide enabling environmental conditions for phosphorus export, particularly if applied as liquid slurry.

In general animal slurry tends to be applied in large quantities and at inappropriate times because farmers underestimate the potential of P pollution from manure via surface run off and erosion. Therefore, practices to avoid P losses should aim for a low application rates with best timing of the year. For example, application of both inorganic P and slurry should be avoided during heavy rainfall as observed in this study (Syer et al., 2008; Elser and Bennett, 2011). Schröder et al. (2011) reported that the placement of fertilizer as close as possible to where the roots of the plants are growing can also significantly reduce nutrient (P) losses. Major losses of P along with other nutrients from soil are strongly related to the status of soil organic matter level. According to an estimate, about half of the P applied to farm soils is lost due to wind and water erosion. Therefore maintaining high organic matter in soils is crucial in holding P in soils (Blanco-Canqui et al., 2009). The maintenance of high SOM enhances the micro-organism activities and increases the nutrient cycling for best use of P reuse (Soil Association, 2010). The animal diet also plays an important role in preserving the P losses through manure application. Livestock farmers usually supply extra mineral P in the animal's diet as "cheap productivity" and which leads to overfeeding beyond the levels that could be utilized by animals (Knowlton et al., 2004). Thus, adjusting P requirements in diets to the animal needs is the first step in reducing P losses through farming system. However, there is a strong need to conduct a modelling study to look in detail at P balance from different Irish farm management practices. This study will help in quantifying the import and export of P at the farm and small catchment scale.

5 Conclusions

This study examined the export of P over one year from three nested grassland catchments. We found that the annual export of TP and TDP decreased as the catchment size increased. However PP increased from 0.6 kg P/ha for the 17 ha catchment to 1.03 kg P/ha for the 211 ha catchment and decreased to 0.56 kg P/ha for the 1524 ha catchment. The anomaly in PP may be due to the presence of farmyard runoff and some rutted (caused by winter cattle traffic) steep fields near the weir at S3. At S1, PP was approximately 25% of TP for most of the year while at S3, PP was approximately 50% of TP for the first 300 days, reducing to 40% for the last 2 months of the year and at S4, PP was approximately 30% of TP for most of the year.

At S1 the combined P in chemical and animal slurry was approximately twice the regional average and at S3 was approximately three times the regional average. The regional average estimate was based on fertilizer sales and is guided by amounts necessary for agronomic requirements. Chemical fertilizer was applied in the drier months between February and September, while animal slurry was applied over the full year. The animal slurry applied in the winter had significant impact on the concentrations of TP in the stream and boosted the TP exports for the year 2002. The high TP exports between October and December 2002 were due to the slurry applications in October and later. It is likely that if liquid slurry was not applied after October, that the TP exports would have been reduced. Effective precipitation is the hydrological driver enabling phosphorus loss from soil to water from soils saturated or near saturated with phosphorus. As effective precipitation is close to zero or sometimes negative in summer, phosphorus loss at this time is also close to zero. In winter (and to a lesser extent autumn and spring) effective precipitation is close to actual precipitation causing surface runoff leading to elevated stream flow. Applications of phosphorus at this time entered the stream and contributed significantly to large annual exports of phosphorus measured. The results of this study suggest that the restricted P application in heavy rainfall can largely reduce the P losses from soil to water.

Acknowledgments

This work has been prepared as part of the Environmental Research Technological Development which is managed by the Environmental Protection Agency and financed by the Irish Government under the National Development Plan 2000–2006 (No. 2000-LS-2.1.1A-M1). We appreciate the contributions to the experimental work by Orla Kingston, Xie Quishi and Stewart Warner of the Aquatic Services Unit at University College Cork and Adrian Birkby of the Civil and Environmental Engineering Department at University College Cork. We appreciate the co-operation of the landowners. We further appreciate the discussion and helpful comments of Dr. Hubert Tunney and Dr. Owen Carton of Teagasc, Johnstown Castle, Wexford, Ireland.

References

Anon D, Mary A D, 1985. Standard Methods for the Examination of Water and Wastewater (16th ed.). American Public Health Association, Washington, DC.

Bowman J, 2009. New Water Framework Directive environmental quality standards and biological and hydromorphological classification systems for surface waters in Ireland. *Biology and Environment: Proceedings of the Royal Irish Academy*, 109(3): 247–260.

Brunet R C, Astin K B, 1998. Variation in Phosphorus flux during a hydrological season: The River Adour. *Water Resources Research*, 32(3): 547–558.

Chapman A S, Foster I D L, Lees J A, Hodgkinson R A, Jackson R H, 2001. Particulate phosphorus transport by sub-surface drainage from agricultural land in the UK. Environmental significance at the catchment scale and national scale. *Science of the Total Environment*, 226(1-3): 95–102.

Childers D L, Corman J, Edwards M, Elser J J, 2011. Sustainability challenges of phosphorus and food: solutions from closing the human phosphorus cycle. *Bioscience*, 61(2): 117–124.

Cordell D, Rosemarin A, Schröder J J, Smit A L, 2011. Towards global phosphorus security: A systems framework for phosphorus recovery and reuse options. *Chemosphere*, 84(6): 747–758.

Correll D L, 1998. The role of phosphorus in eutrophication of receiving waters: a review *Journal of Environmental Quality*, 27(2): 261–266.

Coulter B S, Murphy W E, Culleton N, Finnerty E, Connolly L, 2002. A Survey of Fertiliser Use in 2000 for Grassland and Arable Crops. Teagasc Report 4729, Johnstown Castle, Ireland.

Csathó P, Radimszky L, 2009. Two worlds within the EU27: Sharp contrasts in organic and mineral nitrogen-phosphorus use, nitrogen-phosphorus balances, and soil phosphorus status: widening and deepening gap between western and central Europe. *Communications in Soil Science and Plant Analysis*, 40(1-6): 999–1019.

Daly K, 1999. An environmental appraisal of the phosphorus of the Irish Grassland Soil. Ph. D. thesis, Trinity College Dublin, Ireland.

Elser J, Bennett E, 2011. P cycle: A broken biogeochemical cycle. *Nature*, 478(7367): 29–31.

Ferguson R I, 1987. Accuracy and precision of methods for estimating river loads. *Earth Surface Processes and Landforms*, 12(1): 95–104.

Grant R, Laubel A, Kronvang B, Andersen H E, Sevedsen L M, Fuglsang A, 1996. Loss of dissolved and particulate phosphorus from arable catchments by subsurface drainage. *National Environmental Institute, Department of Streams and Riparian Areas*, 11(30): 2633–2641.

Grey M, Henry C, 2002. Phosphorus and nitrogen runoff from a forested watershed fertilized with biosolids. *Journal of Environmental Quality*, 31(3): 926–936.

HMSO, 1995. Statistical Review of Northern Ireland Agriculture, 1994. HMSO, Norwick, UK.

Hooda P S, Truesdale V W, Edwards A C, Withers P J A, Aitken M N, Miller A et al., 2000. Manuring and fertilization effects on phosphorus accumulation in soils and potential environmental implications. *Advances in Environmental Research*, 5(1): 13–21.

Jordan P, Menary W, Daly K, Kiely G, Morgan G, Byrne P et al., 2005. Patterns and processes of phosphorus transfer from Irish grassland soils to rivers-integration of laboratory and catchment studies. *Journal of Hydrology*, 304(1): 20–34.

Khandokar F, 2003. Phosphorus in Soils of Pasture Farms subject to Chemical and Manure Fertilisation. Master of Engineering Science Thesis. University College Cork, Ireland.

Knowlton K F, Radcliffe J S, Novak C L, Emmerson D A, 2004. Animal management to reduce phosphorus losses to the environment. *Journal of Animal Science*, 82(13): 173–195.

Liu J, Aronsson H, Ulén B, Bergstron L, 2012. Potential phosphorus leaching from sandy topsoils with different fertilizer histories before and after application of pig slurry. *Soil Use Management*, 28(4): 457–467.

McDowell R, Trudgill S, 2000. Variation of Phosphorus loss form a small catchment in south Devon. UK. *Agriculture Ecosystems and Environment*, 79(2): 143–157.

McKergow L A, Weaver D M, Prosser I P, Grayson R B, Reed A E G, 2003. Before and after riparian management: sediment and nutrient exports from a small agricultural catchment, Western Australia. *Journal of Hydrology*, 270(3-4): 253–272.

Murphy J, Riley J P, 1962. A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta*, 27(1): 31–36

Nasr A, Bruen M, Jordan P, Kiely G, Moles R, Byrne P, 2007. A comparison of SWAT, HSPF, and SHETRAN/GOPC for modelling phosphorus export from three catchments in Irish. *Water Research*,41(5): 1065–1073.

Pionke H B, Gburek W J, Schnabel R R, Sharpley A N, Elwinger G F, 1999. Seasonal flow, nutrient concentrations and loading patterns in stream flow draining an agricultural hill-land watershed. *Journal of Hydrology*, 220(1-2): 62–73.

Rafique R, Hennessy D, Kiely G, 2011a. Nitrous oxide emission from grazed grassland under different management systems. *Ecosystems*, 14(4): 563–582.

Rafique R, Mathias P, Hennessy D, Kiely G, 2011b. Evaluating management effects on nitrous oxide emissions from grasslands using the process-based denitrification-decomposition (DNDC) model. *Atmospheric Environment*, 45(33): 6029–6039.

Rafique R, Robert A, Hennessy D, Kiely G, 2012. What are the impacts of grazing and cutting events on the N_2O dynamics in humid temperate grassland? *Geoderma*, 181-182(2): 36–44.

SBA, 2010. Foreskrifter om andring I Statens jordbruksverks foreskrifter och allmanna rad (SJVFS 2004: 62) om miljohansyn I jordbruket vad avser vaxtnaring. SVFS 2010. Swedish Board of Agriculture.

Scanlon T M, Kiely G, Xie Q S, 2004. A nested catchment approach for defining the hydrological controls on Non-Point phosphorus transport. *Journal of Hydrology*, 291(3-4): 218–231.

Scanlon T M, Kiely G, Amboldi R, 2005. Model determination of non-point source phosphorus transport pathways in a fertilised grassland catchment. *Hydrological Processes*, 19(14): 2801–2814.

Schröder J J, Smit A L, Cordell D, Rosemarin A, 2011. Improved phosphorus use efficiency in agriculture: A key requirement for its sustainable use. *Chemosphere*, 84(6): 822–831.

Soil Association, 2010. A rock and a hard place: peak phosphorus and the threat to our food security. Soil Association UK, Bristol.

Smith K A, Jackson D R, Withers P J A, 2001. Nutrient losses by surface run-off following the application of organic manures to arable land, 2. Phosphorus. *Environmental Pollution*, 112(1): 53–60.

Stow C A, Borsuk M E, Stanley D W, 2001. Long term changes in watershed nutrient inputs and riverine exports in the Neuse river, north Carolina. *Water Resources Research*, 35(6): 1489–1499.

Syers J K, Johnston A E, Curtin D, 2008. Efficiency of soil and fertilizer phosphorus use: reconciling changing concepts of soil phosphorus behavior with agronomic information. FAO Fertiliser and Plant Bulletin 18. Food and Agricultural Organization of the United Nations. Rome, 2008. ISBN 978–92-5–105929-6.

Tunney H, Carton O T, Brooks P C, Johnston E E, 1997. Phosphorus Loss from Soil to Water. CAB International, Wallingford, UK.

Tunney H, 2002. Phosphorous needs of grassland soils and loss to water. *Irish Journal of Agricultural Research*, 272(1): 63–69.

Turner B J, Haygarth P M, 2000. Phosphorus Forms and concentrations in leachate under four grassland soil types. *Soil Science Society of America Journal*, 64(3): 1090–1099.

Ulén B, Bechmann M, Fölster J, Jarvie H P, Tunny H, 2007. Agriculture as a phosphorus source for eutrophication in the north-west European countries, Norway, Sweden, United Kingdom and Ireland: a review. *Soil Use and Management*, 23(S1): 5–15.

Ulén B, Johansson G, Kyllmar K, 2001. Model predictions and long-term trends in phosphorus transport from arable lands in Sweden. *Agricultural Water Management*, 49(3): 197–210.

van Es H M, Schindelbeck R R, Jokela W E, 2004. Effect of manure application timing, crop and soil type on phosphorus leaching. *Journal of Environmental Quality*, 33(3): 1070–1080.

Warner S, Kiely G, Morgan G, O'Halloran J, 2009. Does quantifying antecedent flow conditions improve stream phosphorus export estimation? *Journal of Hydrology*, 378(1-2): 97–104.

Webb B W, Phillips J M, Walling D E, Littlewood I G, Watts C D, Leeks G J L, 1997. Load estimation methodologies for British rivers and their relevance to the LOIS RACS(R) programme. *Science of the Total Environment*, 19(2): 379–389.