Phosphorus in Soils of Pasture Farms Subject to Chemical and Slurry Fertilization

by
Fahmida Khandokar
B.U.R.P, 2002

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To my Parents

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Statement of work

In this project, I was given all the data necessary. The hydrological and meteorological data was collected by **Professor. Gerard Kiely's** research group. The water chemistry data was collected by **Dr. Gerard Morgan** and the **Aquatic Services Unit**. I analysed the data using **Matlab** and present my work in this thesis.

Abstract

In areas of intensive agricultural production, phosphorous (P) is applied as chemical fertilizer and slurry in amounts which often exceeds agronomic requirements and thus leading to an increase of the soil P level. The cumulative effect of annual P surplus and elevated soil P can negatively impact stream water quality. As part of a project to understand the processes of P loss from soil to water, this study examines the phosphorous budget of eight farms within a 2.1 km^2 grassland catchment (Dripsey, County Cork) for one year (2002). We also examine the soil P index levels (based on Morgan's P) of 127 fields within the catchment (for 1993 and 2002). The results of the study show that 42% of the fields were at a soil P index of 4 (>10 mg l^{-1}) in 2002. The soil P analysis for the 127 fields for 1993 and 2002 shows clearly that the higher soil P concentrations are located close to the stream. We also examine the degree of soil phosphorous saturation (*DSSP*) and establish a pedotransfer function type relationship of soil P and *DSSP*. Using *DSSP*, and an upper threshold value of 25% we then examine which fields and farms are in excess of this threshold. The estimated annual soil P surpluses of the farms varied from 0 to 31 kg P ha^{-1} $year^{-1}$ (with a mean of 17 kg P $ha^{-1}year^{-1}$). The high percentage of fields with the elevated P index level in association with the surplus P on farms provides a suitable environment for P loss from the fields to the stream. In our study the mean annual total phosphorous concentration in the stream was 0.3 mg l^{-1} which is much higher than the TP concentration recommended of approximately 0.035 mg l^{-1}. The relative contributions of the yards and the fields were not taken into account in this study. It is likely that if there was no P in yard runoff, then the P concentration level in the stream would be less than what we found. A phosphorus export coefficient model was developed based on the farm management and hydrological parameters that significantly influence the phosphorous export process. The parameters include: fertilizer and slurry application rate; phosphorous uptake by grass; evapotranspiration; surface and sub surface runoff. Management strategies with a long-term perspective are now required to reduce this P accumulation in soil which is a threat to water quality.

***Key words**: Morgan's P, P index, degree of soil phosphorous saturation, P budget, phosphorous export coefficient model.*

Abbreviations

Al_{ox}	Oxalate extractable Aluminium
DP	Dissolved phosphorous
DSSP	Degree of soil P saturation
Fe_{ox}	Oxalate extractable Iron
EPA	Environmental Protection Agency
GIS	Geographical information system
p	Probability level
PP	Particulate phosphorous
Psat%	Phosphorous saturation percentage
PSC	Phosphorous sorption capacity
LU	Livestock unit
r	Correlation coefficient
r^2	Coefficient of determination
RMSE	Root Mean Squared Error
SSE	Sum of Squares Error
SRP	Soluble reactive phosphorous
STP	Soil test phosphorous
TP	Total phosphorous

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Chapter 1: Introduction

1.1. Introduction

In areas of intensive grassland production, phosphorous is applied as chemical fertilizer and as slurry to improve grass production and soil fertility. As there are no obvious adverse affects of high soil P concentrations on plant growth, farmers in neglecting the fertilizer value of slurry and manure often add P in fertilizer in amounts exceeding that required for optimum grass growth. Long term P surpluses in fertilizer and slurry application can lead to P accumulation in soil, (Hooda et al., 2001) thereby elevating the soil P test level (*STP*, e.g. Morgan's P). This causes a reduction in the soil P-sorption capacity and an increase in the degree of soil P saturation (*DSSP*), (Hooda et al., 2001). Furthermore since the soil P content can directly influence the concentration of P in surface (Pote et al., 1996) and subsurface runoff from artificially and naturally drained soils (Hooda et al., 1999), elevated soil P levels can result in increased P loss to water (Hooda et al., 2001) and may contribute to eutrophication of freshwaters (Sharpley et al., 1994).

The level of phosphorus in soil, especially in topsoil (0 to 10cm depth) is considered to play a major role in the process of phosphorus loss from soil to water (Daly, 1999; Edwards and Withers, 1998). In determining the level of phosphorus in soil, the most common approach has been to sample the soils and measure the soil test phosphorus (*STP*), e.g. Morgan's P, Olsen's P etc. Morgan's P is used in Ireland. Olsen's P is used in Northern Ireland (Tunney et al., 1997a). The *STP* was originally developed for agronomic purposes but has been adopted to environmental risk studies (Sims et al., 2000). Another method of risk assessment is to use a simple P-index approach categorising each field or farm as having a risk factor associated either with a single parameter, e.g. the *STP* value or with multiple parameters to include, *STP*, soil type, soil hydraulic conductivity, field distance from stream etc (Heathwaite et al., 2003). A more robust approach is to examine the degree of soil P saturation (*DSSP*), so that we can assess how saturated a soil is with regard to phosphorus (Kleinman, 1999). This is a more expensive test procedure than the *STP*, but a methodology using the concept of the pedotransfer function (from soil physics) may be used to estimate *DSSP* from known *STP* values (Kleinman, 1999). Furthermore, if the applications of fertilizer and slurry are recorded then it is possible to do soil P budget analysis (at field and farm scale) and assess if the soil has a surplus or deficiency of phosphorus (Haygarth et al., 1998). In an effort to understand the principle factors of P loss from grassland soil to water we study the *STP*, the *DSSP*, the P-index method and the farm soil P budgets of eight farms of an intensively grazed grassland catchment over a one year cycle. Furthermore a phosphorous export coefficient model is developed based on the significant management and hydrological factors.

1.2. Literature review

In recent years most of the phosphorous loss to water bodies is from agricultural sources (Tunney, 2002). Many studies document the P surpluses present is soils under intensive agricultural production and show that long-term applications of slurry and chemical fertilizer based only on grass nitrogen requirements have caused the soil test P values to increase beyond agronomic optima (Edwards and Withers, 1998; Klausner, 1997; Haygarth et al., 1998; Sims, 1997, 1998; Tunney et al., 1997a). The national P budget for Ireland shows a surplus of P of around 30,000 tonnes per year with a continued upward trend in *STP* magnitudes (Tunney, 1990). Furthermore from another study undertaken by Daly (1999) it was found that more than 60% of Irish grassland soils have *STP* levels higher than required for optimal grass production.

The Environmental Protection Agency (EPA) in its report on Water Quality in Ireland (Lucey et al., 1999) and the report on Ireland’s Environment (A Millennium Report) Stapleton et al. (2000) demonstrated that surface water in Ireland is continuing to deteriorate. Recently Phosphorous loss from agriculture, including farm yards has become the single biggest source of pollution problems in Irish rivers. The overview survey for 1998 – 2000 indicates that 30% of the Irish river channels are polluted to a greater or lesser extent, primarily due to phosphorous-driven eutrophication.

Within Europe and world wide there is growing evidence from nutrient budget studies on a range of catchments that diffuse losses of P from agriculture have been increasing in recent years and increasing eutrophication of many European rivers and lakes (Sharpley and Rekolainen, 1997; Foy and Bailey-Watts, 1998). About 50% of rivers in the United Kingdom, Poland and Belgium have mean annual phosphorous concentration exceeding 500 µg l^{-1} which is higher than the Irish standard (35 µg l^{-1}) set by the Local Government (Water Pollution) Act, 1977, (Water Quality Standards for Phosphorous) Regulations, SI. No.258 of 1998, for the control of eutrophication in rivers (Anon, 1998). Therefore it has become a long term process to control the water quality standard of rivers in these countries. In Ireland there remains a challenge to halt the trend of eutrophication.

1.3. Relationship between the phosphorous application to grass land and soil P

A long term study was undertaken in a grass sward area at Johnstown Castle, from three areas receiving an annual P application rate of 0, 15 and 30 kg ha^{-1}. The results of the study show that Morgan's P for various P application rates over a 20 year period caused a significant variability in building up P at different depths of soil (Figure 1.1).

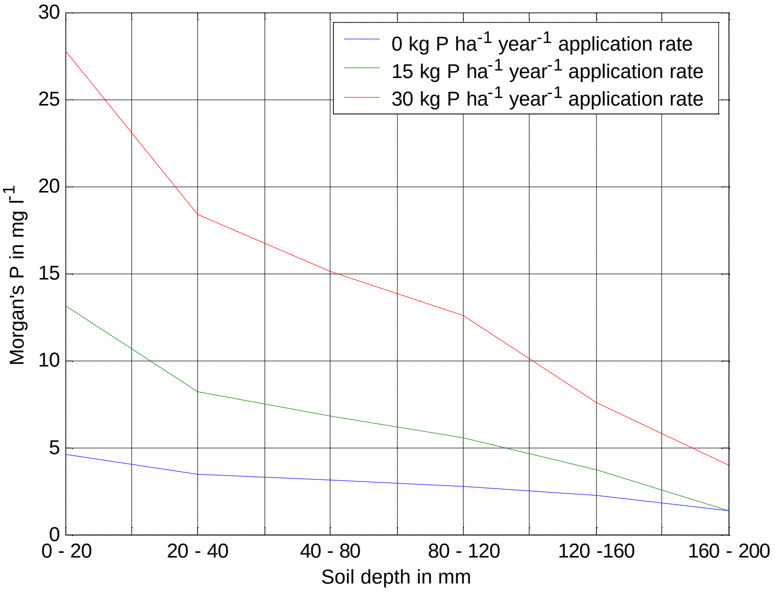

Figure 1.1 *Morgan's P at different depths within soil as a result of different P application rates for 20 years (adapted from Murphy and Culleton, 1997).*

Figure 1.1 shows that a 15 kg ha^{-1} P application rate over 20 years results in the P concentration (Morgan's P) at the top 0 - 20 mm of the soil to be doubled. Furthermore it shows that the soil P concentration decreases with the increase in the depth of soil. It should be noted that for an annual P application rate of 15 kg ha^{-1} the P concentration level remained the same as the 0 kg.ha^{-1} application rate at the 160 – 200 mm depth of soil. The 30 kg ha^{-1} annual application rate caused the soil P concentration at 160 – 200 mm depth to be doubled. This indicates an annual P application rate of 30 kg ha^{-1} caused a downward movement of P through the soil profile. The downward diffusive flux of P raises the question of risk of soluble P loss from soil in subsurface runoff (Morgan, 1997). This implies that apart from the risk of P loss from immediate P application, high fertilizer application generates the long term source of P loss at greater depth.

1.4. Relationship of soil P to water quality

Several studies have reported that the loss of dissolved phosphorous (DP) in runoff is dependent on the soil P content of surface soil. For example, a highly significant linear relationship was obtained between the DP concentration in runoff and soil P content (Mehlich-3 P) of surface soil (5 cm) from cropped and grassed catchments in Arkansas, Oklahoma and Texas (Sibbesen and Sharpley, 1997). A similar dependence of the DP concentration in runoff on Bray-1 P was found by Romkens and Nelson (1974) for a Russell silt loam in Illinois (r = 0.81) and on water extractable soil P (r = 0.61) of Mississippi catchments by Schreiber (1988) and 11 Oklahoma catchments by Olness et al. (1975) (r = 0.88). Moreover Sharpley and Lemunyon identified a close relationship between TP loss and soil P_index rating (based on soil P level) suggesting that the indexing procedure can give a reliable estimate of catchment vulnerability to P loss.

1.5. Previous studies undertaken in this catchment

A detailed study of the Dripsey catchment was undertaken from April, 1993 to March, 1994 which was stated in the Stride Report (1995). According to this report within the twelve months period: the stocking rate in the catchment was 2.04 LU ha^{-1}, the estimated slurry application based on the livestock number (for a four months storage period) was 19.57 kg P ha^{-1}, the chemical fertilizer application was 19.62

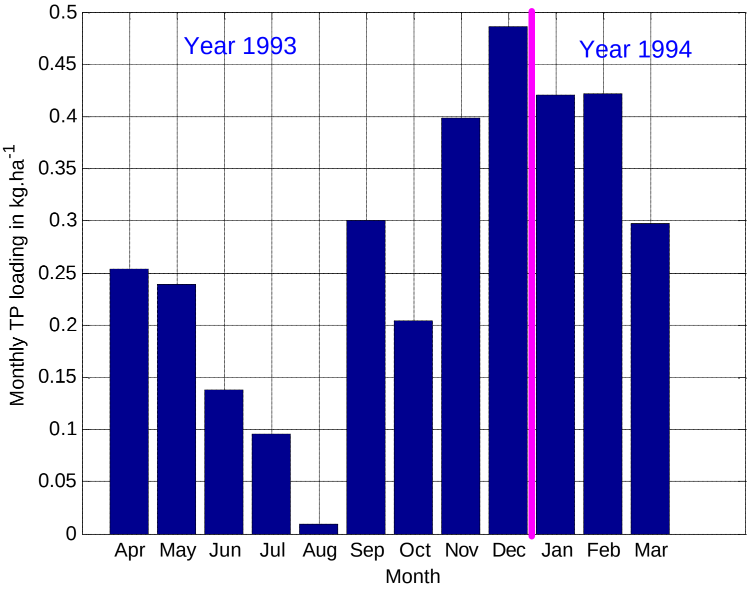

Figure 1.2 *Monthly TP export during the study period in the Dripsey catchment.*

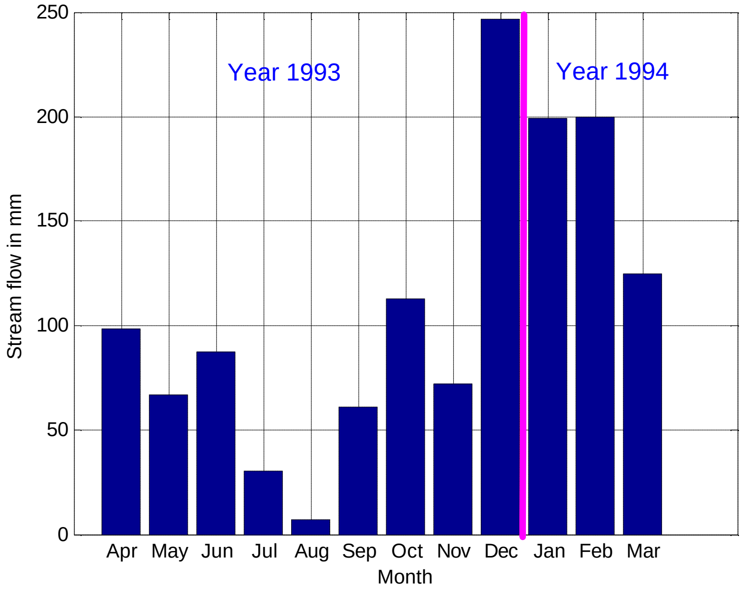

Figure 1.3 *Monthly stream flow during the study period in the Dripsey catchment.*

kg P ha^{-1}, the total estimated P application was 39.19 kg ha^{-1} and the estimated P loss to water was 3.26 kg P ha^{-1}.

The total flow of the catchment during this study period was 1306 mm. This study shows that there was an intensive use of agriculture (2.04 LU ha^{-1}) and a practice of high rate of P application within the catchment. This resulted in a high rate of TP export (3.26 kg ha^{-1}) from the soil to the stream (see Figure 1.2). The rate of TP export was high during the winter months when the rate of monthly flow was high (Figures 1.2 and 1.3).

1.6. Objectives

As part of a project to understand the processes of P loss from soil to water, this field study examines, in an intensively grazed (2.2 LU ha^{-1}) grassland catchment of area 211 ha, the P loading to the soil from chemical and slurry fertilization for one year, the *STP* levels in 117 fields (eight farms) and the annual phosphorus load exported in the stream. Our specific objectives are:

(1) to examine the *STP* (Morgan's P) in the 117 fields for the two years, 1993 and 2002;

(2) to examine the P-index as a tool for assessing the risk of P loss from soil to water;

(3) to investigate the degree of soil P saturation (*DSSP*);

(4) to estimate the surpluses (or deficits) of P in the soil for the eight farms;

(5) to study the impact of soil and water quality with the existing soil P level and use of fertilizer and slurry;

(6) to identify the parameters of the phosphorous export model.

1.7. Methodology

In this study firstly the existing soil phosphorous concentration level (based on Morgan's soil P test) of the fields is examined. Then based on the *STP* test of the fields the soil P index is developed to rank the risk of losing phosphorous from each field. To better understand the soil phosphorous a pedotransfer function is developed to estimate the degree of soil phosphorous saturation level with respect to the phosphorous sorption capacity of soils.

Secondly, phosphorous budgets of the eight farms are estimated based on available data. The phosphorous budget for pasture farms and silage farms are estimated based on two different conceptual model approaches. The catchment is assumed to be homogeneous in terms of hydrological factors (surface runoff, sub surface runoff, rainfall) and phosphorous uptake by grass. The phosphorous vulnerable fields are identified with the existing *STP* level and fertilizer application rate of each field.

The process of phosphorus export from the catchment is very complex which is yet not very clear. The variability of phosphorous export over the year may be caused by the simultaneous effects of local management, different natural and hydrological factors. Finally a simple model is developed using easily determined parameters to estimate the phosphorous export of the catchment on a monthly time step.

1.8. Statistical analysis used in this study

Statistical analysis of the data was carried out in Matlab using the curve fitting toolbox to derive correlation among variables. The correlation coefficient **r** and the coefficient of determination $\mathbf{r}^2$ refer to the measures of the linear and non linear relationships between variables respectively, the direction of which is denoted by positive (+) and negative signs (-) (Milewski, 1997). The correlation coefficient and coefficient of determination are a number between 0 and 1. If there is no relationship between the predicted values and the actual values the correlation coefficient/ coefficient of determination is 0 or very low (the predicted values are no better than random numbers). As the strength of the relationship between the predicted values and actual values increases so does the correlation coefficient/ coefficient of determination. A perfect fit gives a coefficient of 1.0. Thus the higher the correlation coefficient the better. In practice 90%, 95%, and 99% intervals (for probability values, $p<0.1$, 0.05 and 0.01 respectively) are often used, with 95% being the most commonly used. The values of Sum of Squares Error (SSE) and the Root Mean Squared Error (RMSE) less than 1.0 suggest a good numerical fit.

1.9. Layout of the thesis

The thesis consists of six chapters. Chapter 1 includes the introduction, literature review, objectives, methodology and structure of the thesis. A detailed description of the geological, topographical and hydrological characteristics of the catchment is given in chapter 2. Chapter 3 includes the study of two years (1993 and 2002) of soil P level data for 117 fields. Two methods (soil P_index and *DSSP*) were used to examine the risk potential of these fields to P loss. In chapter 4 the detailed estimation of phosphorous budget of eight farms is given. Chapter 5 illustrates the phosphorus export coefficient model. Finally chapter 6 includes summary, conclusions, recommendations and suggestions for further research. The presentation and analysis were done using GIS and MATLAB.

Chapter 2: Description of the catchment and farms

2.1. *Location of the catchment area*

The study area is located 25 km north-west of Cork, Ireland (Latitude: 52.14^{o}N, Longitude: 8.66^{o}W). The rural grassland catchment is at the upland region of the Dripsey tributary of the river Lee which flows through Cork city. The 0.17 km^2 (site 1) and 2.1 km^2 (site 3) catchments are nested within a 15 km^2 catchment (site 4), (see Figure 2.1).

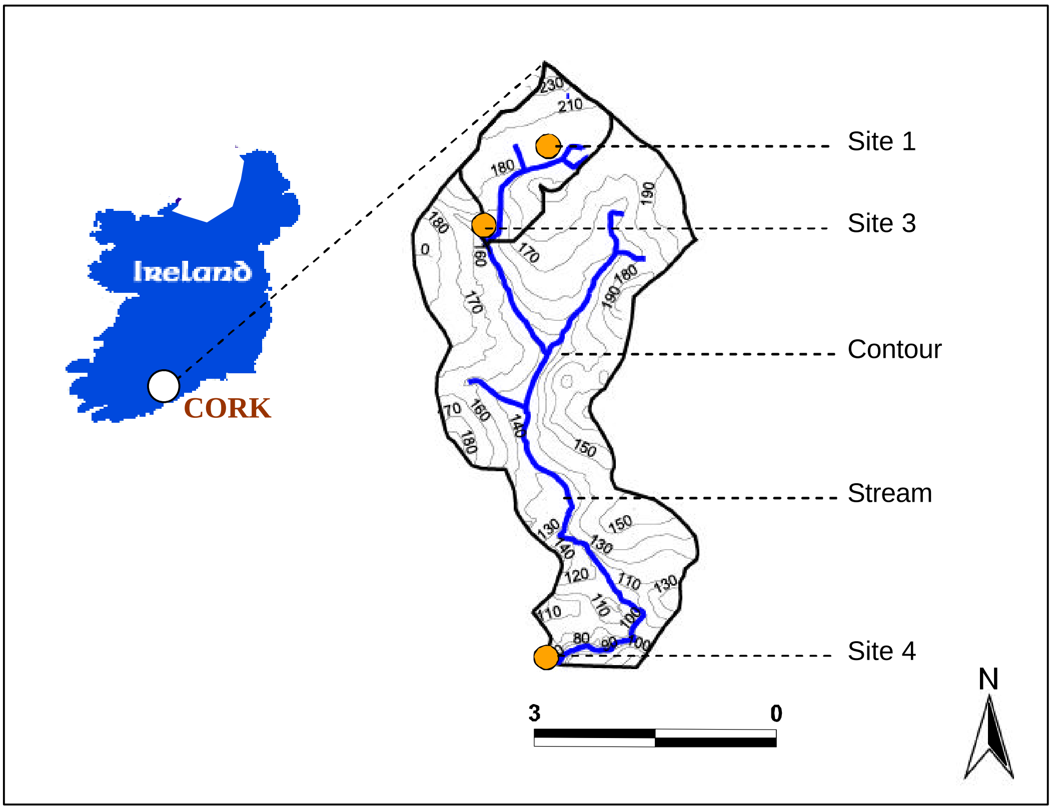

Figure 2.1 *Location map of the Dripsey catchment. The 2.1 km2 catchment is located at the top of a 15 km2 catchment. The stream is shown by blue line along with sampling stations of sites 1, 3and 4.*

2.2. *Site characteristics*

The catchment is considered homogenous with respect to geology, vegetation, hydrology and meteorology. The climate is temperate and humid. Hydrologically, the catchment area is 211 ha and soils were sampled in each of 117 fields covering 187 ha of the 211 ha. There are eight farms in the study catchment with areas varying from 10 to 37 ha. Of the eight farms in the catchment, six are primarily dairy (with some beef production), one is silage production for export and one farm is sheep only. The eight farms are outlined in Figure 2.2. The site is intensively grazed grassland with an average of 2.2 LU ha^{-1} (livestock units per hectare), (Lewis, 2003).

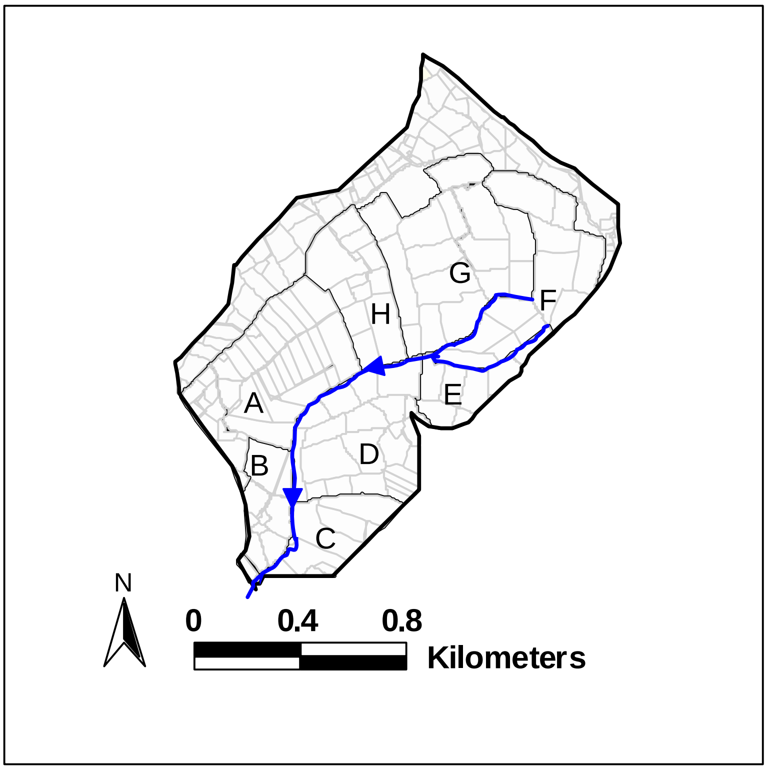

Figure 2.2 *The field boundaries are shown in ash lines. Boundary lines of farms A, B, C, D, E, F, G and H are shown by dark black lines. The stream is shown by the blue line.*

2.3. Topography

In the Dripsey catchment the hill slopes to the stream with gradients ranging from 1% to 7% (Figure 2.3). Approximately 20% of the area within the catchment has a slope of more than 5%. The elevation ranges from about 250 m (metres above sea level) in the upstream end to 160 m in the downstream end (Figure 2.4). About 50% of the area at the middle of the catchment is within 180 to 200 m elevation level (above sea level).

2.4. Vegetation

The grassland type is moderately high quality pasture and meadow, with perennial ryegrass being the dominant plant species. Cattle graze on alternate fields (rotation of about 3 to 5 weeks) from March to November. Grass is cut as silage once or twice a year, typically at the end of May and at the end of July. The height of grass varies from 5 to 50 cm depending on the land quality. The silage is used for winter feed of the cattle that are housed indoors for about 4 to 5 months of the year, from November to February. More than half the fields are grazed with the remainder retained for silage. This is representative of the land use and vegetation in this part of the county.

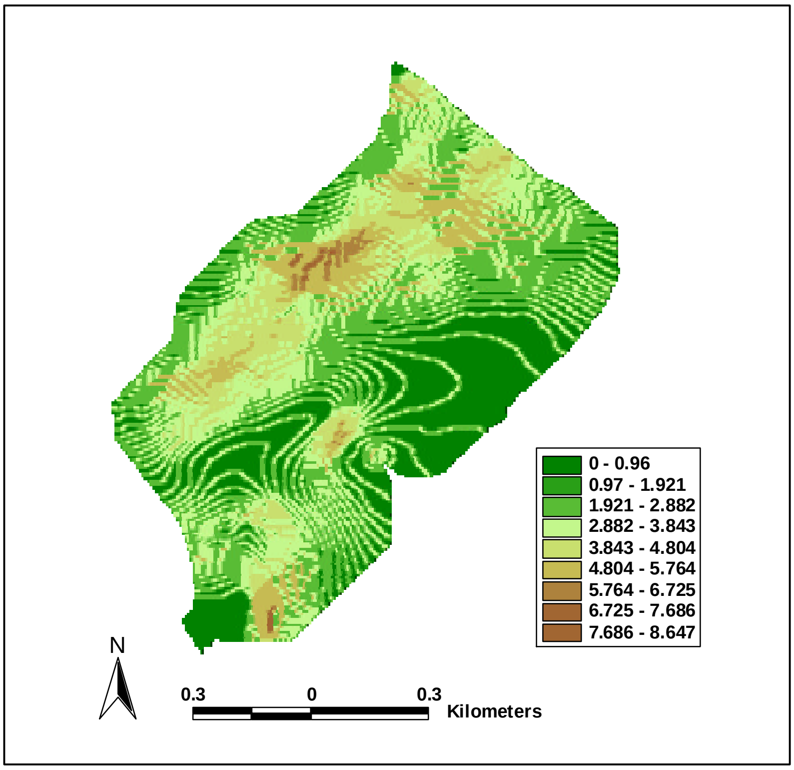

Figure 2.3 *Slope map of the catchment. The legend scale is in percentage.*

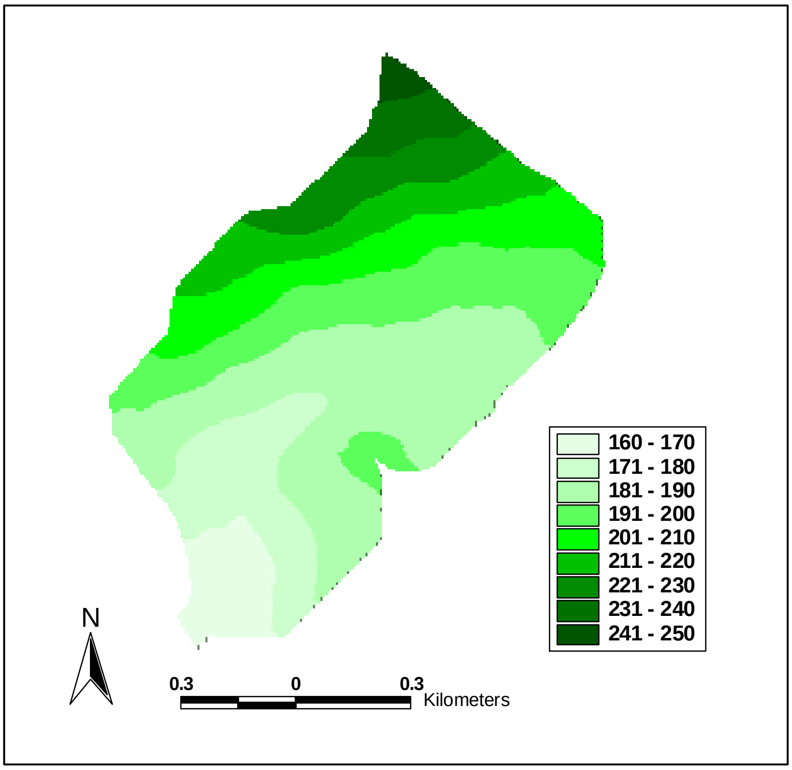

Figure 2.4 *Digital Elevation Model of site 3. The legend scale is meters above sea level. The upstream and downstream areas are shown by dark and light green colour respectively.*

2.5. *Soil description*

Soil texture determines to a large extent the hydrological properties of a soil. The soil type of our site is broadly classified as brown-grey podzols. This soil type is suited to agricultural use and in particular, pasture. When adequately supplemented with lime and fertilizer, this type of soil can sustain 1.85 livestock units per ha (Gardiner and Radford, 1980). This soil is generally well drained and has a good moisture holding capacity. The topsoil is rich in organic matter to a depth of about 10 cm (about 12% organic content, Daly, 1999), underlain by a dark brown A horizon of sandy gravel soil to a depth of 22 cm. Then a yellowish-red, iron enriched B horizon of loam texture to a depth of 75 cm. This layer of the soil progressively transformed into an old red sandstone parent material at about 75 cm depth (Figure 2.5).

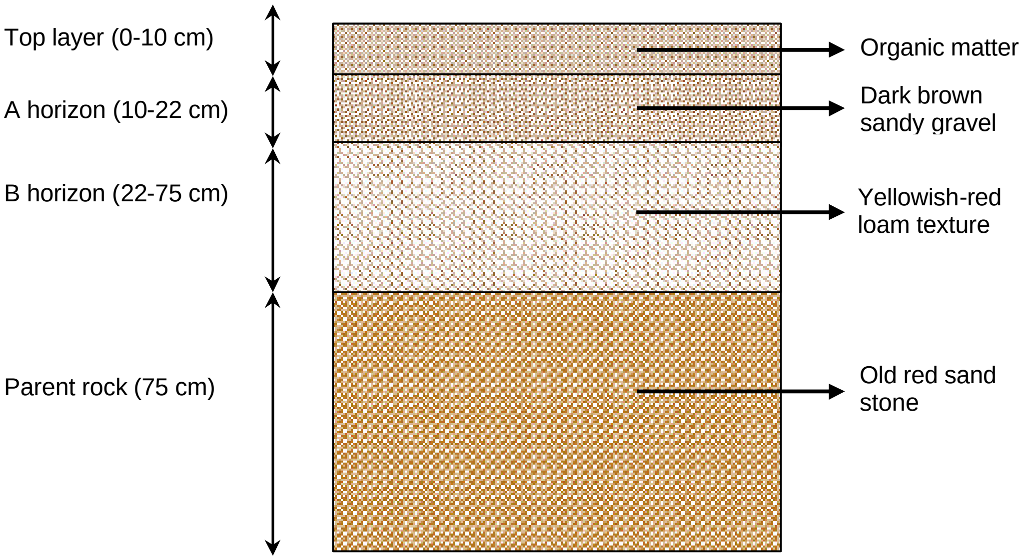

Figure 2.5 *Different layers of brown podzols soil (not to scale).*

2.6. *Temperature*

A meteorological tower near site 1 provides the time series of all the meteorological parameters. In the catchment, the air temperature was measured by a HMP45C temperature and relative humidity probe by Campbell Scientific. Two of these probes are located at 3 and 6 meter heights (Figure 2.6). The mean monthly temperature was positively skewed with a peak temperature of 14.5^{0}C in August (Figure 2.7). In the year 2002 the mean monthly temperature gradually increased from February to August and decreased from August to December. The mean annual temperature was 9.6^{0}C. The coldest month was December with an average temperature of 6^{0}C where August was the

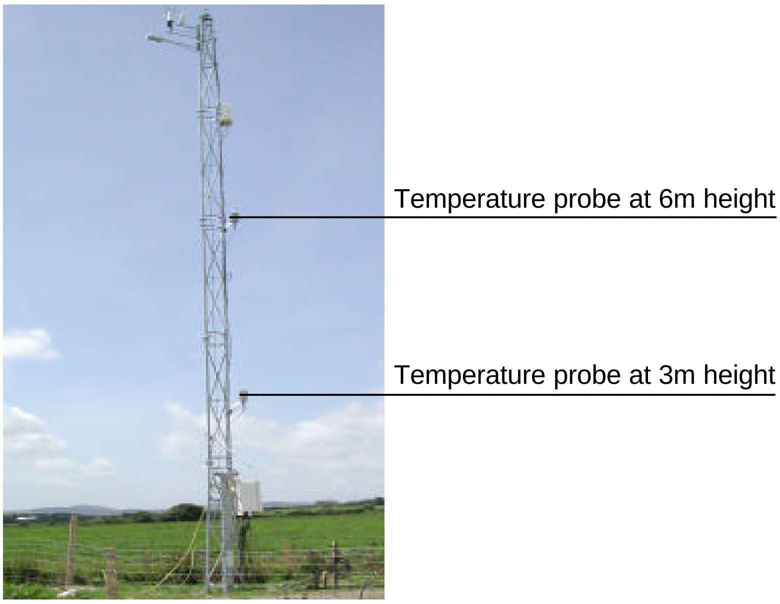

Figure 2.6 *The temperature probes in the 10 m meteorological tower.*

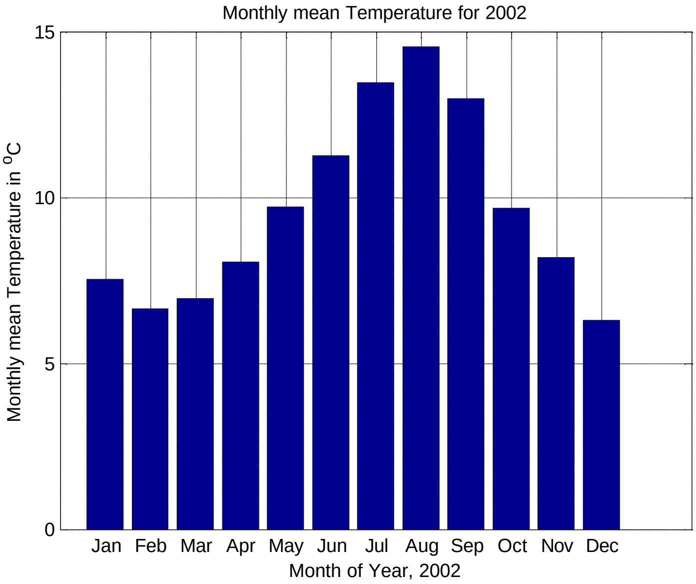

Figure 2.7 *The mean monthly temperature ranges from 6^{o}C in December to 14.5^{o}C in August.*

warmest month at 14.5^{0}C. During the winter months average temperature was around 7^{0}C.

It should be noted that the low air temperature permits the retention of water quality samples in the field for a few days where as at higher temperature the water quality samples should be analysed within one day.

2.7. *Precipitation*

The precipitation is the main driving force of phosphorous transport from the soil to water. A simple flow chart of the major components of water cycle is shown in Figure 2.8. The precipitation is distributed as surface runoff, infiltration to the unsaturated zone, changing its storage, sub surface runoff, deep percolation to the unsaturated zones, ground water flow and evapotranspiration (Kiely, 1997).

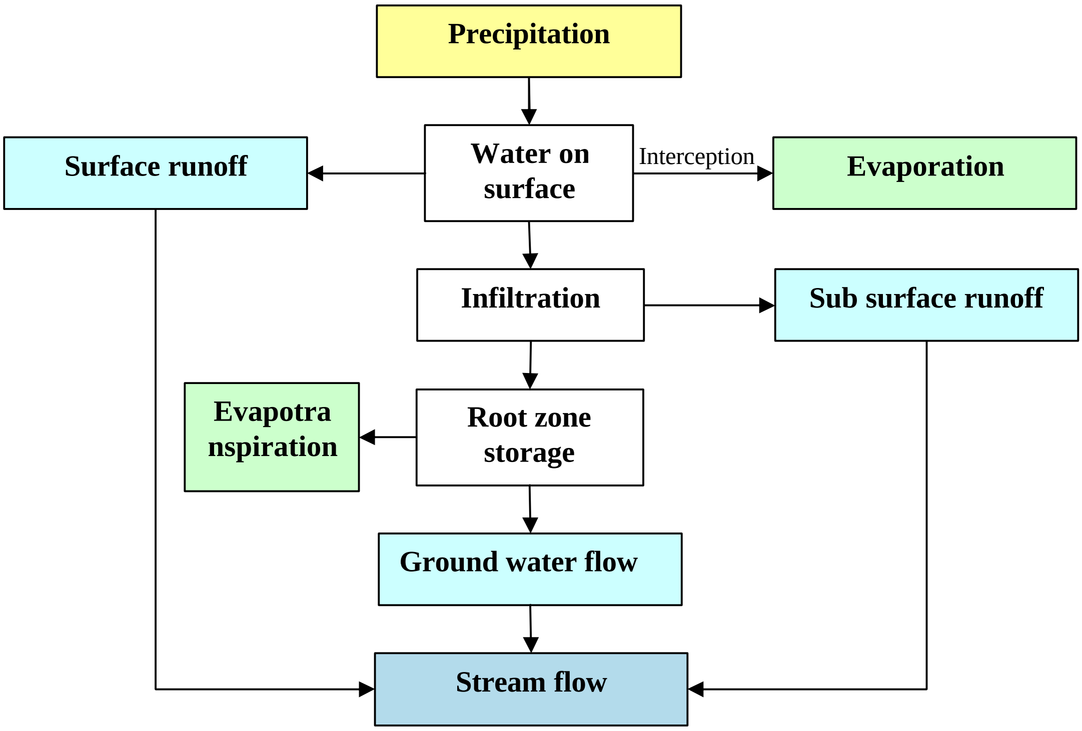

Figure 2.8 *The major components of hydrological cycle (adapted from Kiely, 1997, p.148).*

Over the long term (e.g. a year) there is normally little change in soil moisture and ground water status and so the precipitation or water balance equation for the catchment can be expressed as:

$$P = R + E \tag{2.1}$$

Where, P, R and E are precipitation, stream flow and evapotranspiration respectively.

Rainfall data had been collected over the study period from a tipping bucket rain gauge located near S1 at approximately 190 m elevation (above sea level). The amount of rainfall for each event is measured by counting the number of tips of the tipping bucket rain gauge (Figure 2.9) where each tip corresponds to 0.2 mm rainfall. The rain gauge is connected to a Campbell CR23X data logger recording rainfall at a 30 minute time interval. The mean annual precipitation (1997 to 2002) in the catchment is approximately 1470 mm. The annual precipitation for the study year 2002 was 1812 mm.

Figure 2.9 *The tipping bucket rain gauge.*

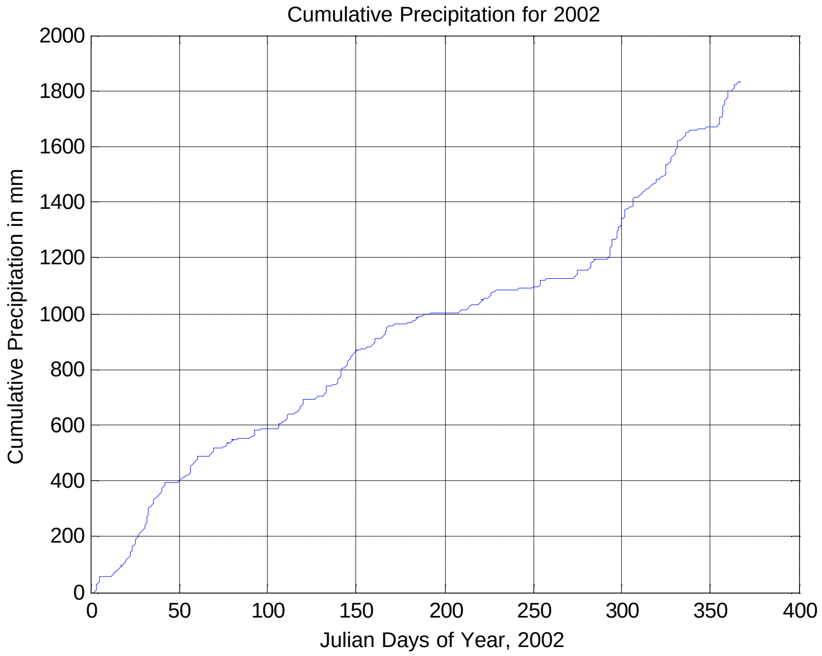

Figure 2.10 *The cumulative rainfall for 2002 was 25% higher than the annual average precipitation from 1997 to 2002.*

The cumulative precipitation for 2002 is shown in Figure 2.10. The monthly precipitation for the year 2002 is shown in Figure 2.11. The monthly precipitation varied from about 50 mm month^{-1} in the summer to as much as 250 mm month^{-1} in the winter. The daily precipitation was a maximum of 39 mm in November and 36 mm in February (Figure 2.12). In 2002 about 80% of the days were recorded as wet days.

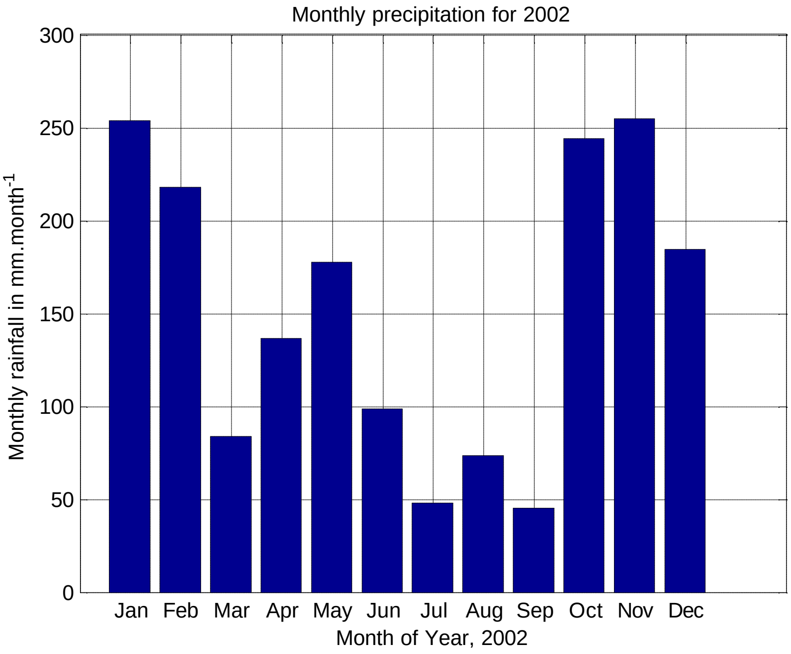

Figure 2.11 *The monthly precipitation over the year 2002.*

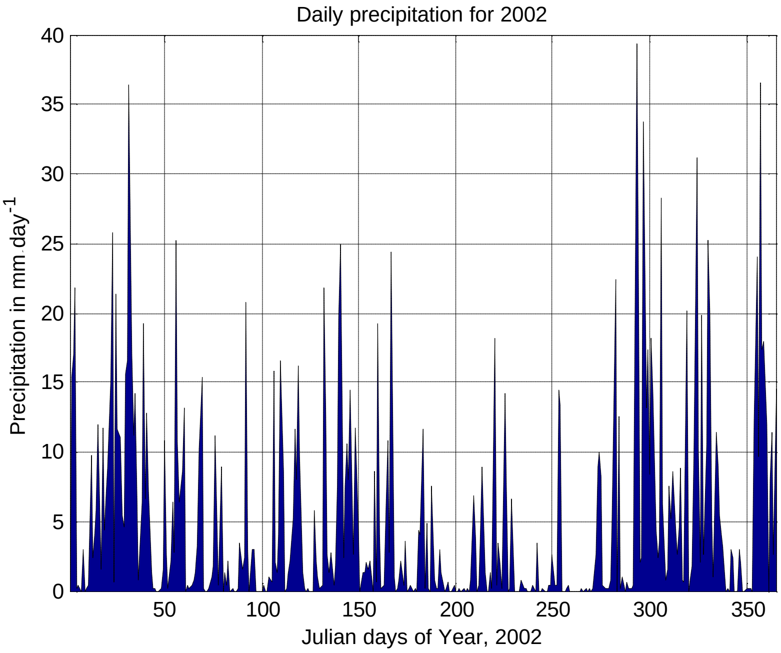

Figure 2.12 *The daily precipitation for the year 2002.*

2.8. Evapotranspiration

The annual evapotranspiration for grasslands in southern Ireland varies from 300 to 500 mm year^{-1} which is approximately 30% of the annual precipitation (Moehrlen et al., 1999). At our site evapotranspiration was estimated by the eddy covariance technique (Jaksic et al., 2004). The estimated annual evapotranspiration in our site for the year 2002 was 362 mm year^{-1} which corresponds to approximately 20% of the annual precipitation. This low value was likely due to the high amount of annual precipitation and cloudy weather during 2002. The monthly evapotranspiration ranged from 0.1 mm in December to 63 mm in June (shown in Figure 2.13).

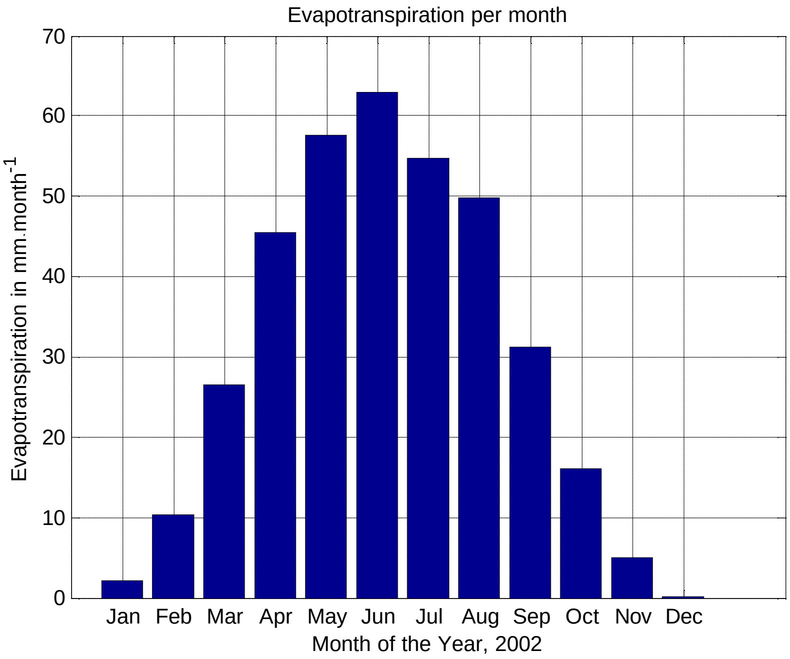

***Figure 2.13** The monthly evapotranspiration shows a positively skewed trend over the year.*

2.9. Stream flow

Stream discharge and water chemistry samples were collected at the outlets of the site 1 and site 3 (see Figure 2.1) for the one year period, January 1, 2002 to December 31, 2002. The stream flow at site 1 and site 3 were monitored by measuring the height of water at a 90^0 V notch weir and at a 1.5 m wide rectangular weir respectively. Stream stage was continuously recorded (15 minute intervals) by a Thalimedes water level recorder (OTT Hydrometry Ltd, UK), which was placed within a stilling well. The stream is at the headwater of the Dripsey river and at the sampling location the stream is less than 2 m wide.

Figure 2.14 *The 90^o V notch weir to measure stream flow at site 1.*

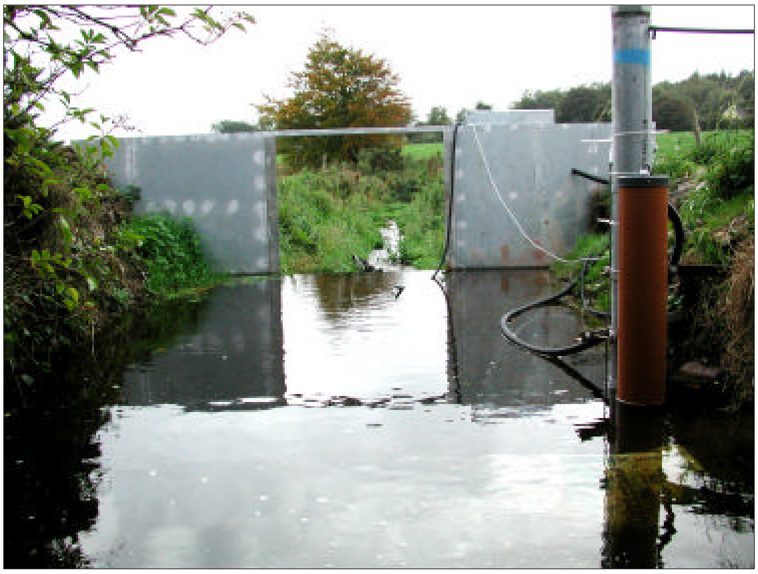

Figure 2.15 *The rectangular weir to measure stream flow at site 3.*

The stream flow of site 1 and site 3 were estimated by equations 2.2 and 2.3 respectively:

$$Q_1 = 1378 * h_1^{2.48} \tag{2.2}$$

$$Q_3 = 3011 * h_3^{1.4} \tag{2.3}$$

Where Q_1 and Q_3 are stream flow of site 1 and 3 respectively in l sec^{-1}; h_1 and h_3 are the heights of the V notch and rectangular weir respectively in m. Equation 2.2 is the classical V notch equation where 2.3 is a calibrated equation from a series of field measures of flow.

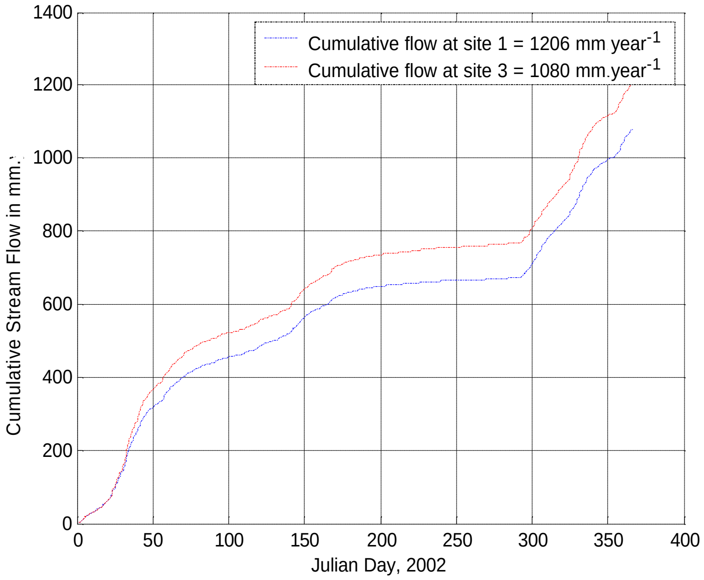

Figure 2.16 *Cumulative stream flow for 2002 at site 1 and 3.*

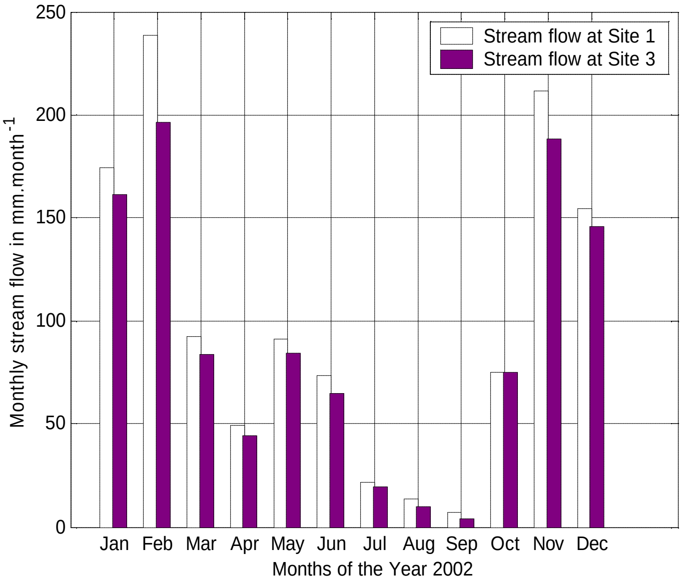

Figure 2.17 *Monthly stream flow for 2002 at site 1 and 3.*

The annual estimated stream flow for site 1 and 3 in 2002 were 1206 and 1080 mm year^{-1} respectively (Figure 2.16). It is revealed from Figure 2.17 that the stream flow was very low during summer months compared to rest of the months of the year. On the other hand stream flow was high during winter months. It is obvious from the previous discussions that the reasons for lower stream flow for summer months were lower precipitation and higher evapotranspiration during this time. The monthly stream flow in site 1 was higher than the site 3 over the full year.

2.10. Summary

The potential P loss from the agricultural land is dependent on weather, catchment characteristics and management practices. In the Dripsey catchment the major natural, hydrological characteristics within the context of phosphorous export can be illustrated as: firstly, the stream passes through the middle of the catchment and raises the potential of P loss from both sides of the catchment, the average number of livestock units is higher than the national average of 1.4 LU ha^{-1}, and there is no forest within the catchment. The soil texture in Dripsey is essentially a stony gravel loam which facilitates the rapid release of water (and nutrients) to watercourses. Several surveys of catchments in the USA have shown that P loss in runoff increases as the portion of the catchment under forest decreases and agriculture increases (Sharpley and Rekolainen, 1997). Secondly, the catchment is subject to very high rate of precipitation over the year which generates high amounts of stream flow. This can increase the loss of phosphorous from the catchment by surface and sub surface flow. Therefore, this catchment may be considered as having the potential for high rapid P loss.

Chapter 3: The Soil phosphorous test and degree of soil phosphorous saturation

3.1. Introduction

Soil P testing was originally developed for agronomic requirements. However, in the past two decades, the *STP* has been adopted for use in the environmental area of P loss from soil to water bodies. It is now generally accepted that there is a positive relationship between *STP* and P loss to water, as indicated by research in the USA, Denmark and Ireland (Tunney et al., 1997b). In the Netherlands, where P loadings to ground water are a national concern, the *STP* is used to regulate P additions to agricultural soils (Breeuwsma and Silva, 1992). In the determination of *STP*, there are more than ten different extraction procedures including: Morgan's-P; Mehlich-P (I and III); Bray-P; Olsen-P; water extractable P(H2O-P); double lactate P(Dl-P); Cottenie-P and Schaffer-P, all used for estimating the available soil P for plant uptake in the European Union. There is almost double that number of different extractant procedures worldwide. The Irish Agricultural Research Institute (Teagasc) use Morgan's soil P test in Ireland as it has been identified that soil P extracted by Morgan's extractant correlated well with nutrient response for the Irish soil types and simulates the amount of P removed by grasses. The results of *STP* using Morgan's extractant can be compared with the other *STP* tests, i.e. Olsen and Mehlich1; Olsen = 5.96* Morgan$^{0.773}$, r = 0.74 (Foy et al., 1997) and Morgan's P = 061* Mehlich1$^{.84}$ (Tunney et al., 1999). Where, Mehlich1 and Olsen P are used in USA and Northern Ireland respectively (Tunney et al., 1997a).

A P-index risk methodology is another tool used to examine the soil P accumulation and the potential of P loss from soil to water associated with agricultural practices. For example, a P-Index method, developed by Lemunyon and Gilbert (1993) was used to assess the risk of P loss from agricultural soils. This employs the soil test P as a source risk indicator and uses threshold levels derived from agronomic recommendations. In Ireland a four tier P-Index system, based on Morgan's P for soil analysis is used as the basis for P-fertilizer recommendations for grassland (Herlihy, 1996, Daly 1999). The P Index (Table 3.1) ranks a field to determine its risk to contribute P to surface water. Each category is assigned an interpretive rating with a corresponding numerical value: No risk - (1) ,Low risk - (2), Medium risk - (3), and High risk - (4), based subjectively on the potential for P loss from a field. A soil P at Index 4 is considered as high risk to contaminate surface water even if no manure or fertilizer is added. A soil at category 4 is considered to have exceeded the requirement for optimum grass growth. Teagasc advises that optimum live weight gain for cattle can be attained from grass grown on soils at P index 3 (Teagasc, 2003).

The soil test phosphorus (*STP*) alone is not the most effective means to identify the risk of agricultural P loss to water as a high soil P in peaty soils may have a lower P sorption capacity than a lower soil P in podzols. Another indicator of environmental risk is soil P saturation and research has shown that the degree of soil P saturation (*DSSP*) can better predict the potential for P loss to surface and ground waters than the traditional agronomic soil P tests (Sims et al., 2000). Kleinman (1999) noted that "soil P saturation relates the sorbed P load of a soil to its phosphorous sorption capacity (*PSC*), or its maximum ability to adsorb and/or precipitate P. As P accumulates in a soil, the difference between the sorbed P and PSC decreases and the soil loses its ability to remove additional P from the soil solution. Ultimately the build up of sorbed P relative to PSC augments equilibrium solution P to the point that P is readily removed in runoff and leachate". Different soils have different values of the degree of soil P saturation (*DSSP)* which is dependent on the soil pH, soil minerals and the organic matter content. Peat soils have high *DSSP* values while podzols have low values (Daly, 2003). Soil P saturation can be viewed as a measure of a soil's remaining capacity to bind soluble P additions. The theoretical foundation of soil P saturation, rests in the concept that the upper root zone of a soil (upper 2 cm to 30 cm), has a finite P sorption capacity (*PSC*). As P is added, the soil's capacity to adsorb additional inputs of soluble P diminishes. The most widespread measure of the degree of soil P saturation (*DSSP*) for non-calcareous soils is $Psat_{ox,}$ (Breeuwsma et al., 1991) and is defined as:

$$P_{sat_{ox}}\% = 100 * P_{ox}\left(0.5 * \left(Fe_{ox} + Al_{ox}\right)\right)^{-1} \qquad \% \qquad \textbf{(3.1)}$$

Where P_{ox} is the oxalate extractable *P* representing the *P* load or *P* already sorbed. Fe_{ox} and Al_{ox} are the extractions of *Fe* and *Al* representing the precipitate-*P* sorption capacity (*PSC*). The application of $Psat_{ox}$ to water quality protection was reported by Sharpley (1995) who identified a single linear relationship between $Psat_{ox}$ and the dissolved P concentrations in runoff under a variety of soil conditions. Pote et al. (1996) reported that $Psat_{ox}$ as the best indicator of P runoff concentrations. For use in the Netherlands, van der Zee et al. (1990) estimated that above the critical P saturation value of 24%, the P equilibrium concentrations in groundwater are believed to rise above 0.1 mg l^{-1} P (Lookman, 1995). In the Netherlands, the critical *Psat%* value was found to be 25% (Breeuwsma et al., 1991). In a Delaware study it was 32% (Kleinman, 1999) and in Belgiam study it was 35% for grassland (Lookman, 1995).

3.2. Method

3.2.1. Methods of determining Morgan's P

The soil test P is determined from field sampling and is related to the amount of soil P that is readily available for crop uptake. The soil test P is a historical indicator of the net accumulation of P based on previous manure and fertilizer additions, crop removal rates and loss to the stream. The Bray–Kurtz P1 (Bray–Kurtz, 1945), Mehlich I (Mehlich, 1953), Mehlich III (Mehlich, 1984), Oslen (Oslen et al., 1954) and Morgan's (Morgan, 1941) soil P tests are widely used to measure soil P. All the above soil P tests are based on agronomic requirements and not on environmental risk requirements.

In the Dripsey catchment study soil samples were collected from 117 fields (fields range from about 1 to 5 ha in area) throughout the 2.1 km^2 catchment to a depth of 10 cm during January 1993 and February 2002. Fertilizer and slurry had not been applied for two months prior to sampling. This is standard practice so as to characterize more accurately the environmentally important forms of available soil P for plants. Samples were collected from 12 to 15 locations within each field in a zigzag pattern across the field. These samples were then composited to produce one sample per field that was analysed in the laboratory (at Teagasc, Johnstown Castle, Wexford) for Morgan's P and other parameters.

After collection, soil samples were placed in a forced draught oven and dried for 60 hours at 40^{o}C. Samples were rolled by hand, thoroughly mixed and passed through a 2 mm sieve. 10 cm^3 of air dried sieved soil was extracted using 50 ml of Morgan solution (10% CH_3COONa buffered at pH 4.8) mechanically for 30 minutes at constant temperature (20^{o}C). Finally the sample was filtered through a medium porosity filter paper and filtrates were analysed for P.

3.2.2. Method of determining degree of soil phosphorous saturation

Acid oxalate extracts amorphous Fe and Al [mmol kg^{-1}] minerals, which, in acid soils account for the *PSC* or the bulk of P sorption. Soil P saturation is typically expressed as $Psat_{ox}$ and is determined using the P, Fe and Al contents [mmol kg^{-1}] extracted with the acidified ammonium oxalate oxalic acid. It was first proposed by Dutch scientists (van der Zee and van Riemsdijk, 1988). The *PSC* and $Psat_{ox}$ (Lookman, 1995; Kleinman, 1999; Hooda et al., 2001) are calculated as:

$$PSC = a * (Fe_{ox} + Al_{ox})/100 \qquad \% \qquad \textbf{(3.2)}$$

$$Psat_{ox} = P_{ox} / PSC \qquad \% \qquad \textbf{(3.3)}$$

The PSC and $Psat_{ox}$ (or $DSSP$) are represented as a percentage, with P_{ox} accounting for the quantity of P in the soil. The coefficient a estimates the fraction of Fe_{ox} and Al_{ox} dedicated to P sorption (van der Zee and van Riemsdijk, 1988). The value of a varies between 0.3 to 0.7 depending on the soil type, texture, pH etc (Paulter and Sims, 2000). To enable comparison of data from this study with the critical $Psat_{ox}$ level identified in other research, we adopt an a value of 0.5 as in other studies.

3.3. Results

3.3.1. Soil phosphorous test (Morgan's P)

Morgan's P was determined for the soil (10 cm depth) for each of 117 of the fields in the catchment in January 1993 and January 2002. The results for 1993 and 2002 are shown in Figures 3.1 and 3.2 respectively and Table 3.1.

For 1993 the range of Morgan's P for the fields was 3.3 to 25.7 mg l^{-1}. The range of Morgan's P for the eight farms was 5.1 to 12.6 mg l^{-1}. The catchment area weighted average for 1993 was 10.3 mg l^{-1} (see Table 3.1). For 2002 the range of Morgan's P for the fields was 1.9 to 22.8 mg l^{-1}. The range of Morgan's P for the eight farms was 6.6 to 12.7 mg l^{-1}. The catchment area weighted average for 2002 was 9.98 mg l^{-1}. This implies that the area weighted average soil P in 1993 remained almost same in 2002.

Table 3.1 *For each farm, the Morgan's P value (mg* l^{-1}*) for soils sampled in 1993 and 2002. (The hydrologic catchment area is 211 ha. The area that was sampled for soils common to both years was 187 ha).*

Farm Code	**Area ha**	**Dominant Farm Activity**	**Morgan's P mg** l^{-1} **1993**	**Morgan's P mg** l^{-1} **2002**
A	34.1	Dairy	8	7.3
B	9.8	Dairy	5.1	6.6
C	20.7	Dairy	10.1	8.5
D	31.7	Dairy	12.8	12.2
E	15.6	Silage	9.0	9.6
F	23.9	Dairy	12.6	12.7
G	36.8	Dairy	10.6	10.7
H	15.6	Sheep	11.1	9.8
Total	187		Average =10.3	Average = 10.0

We assume site 3 has received a surplus of about 10 kg P ha^{-1} $year^{-1}$ on average over the past nine years (1993 – 2002). This indicates that even after a total soil P surplus of about 100 kg ha^{-1} $year^{-1}$ over the past nine years (a surplus of over 20000 kg P for the 211 ha catchment) there was no significant change in the area average soil P in 2002. It appears that the STP is not sensitive enough to pick up this level.

3.3.2. Soil P_index of 1993 and 2002

We converted Morgan's P to the soil P Index scale of 1 to 4 is shown in Table 3.2. The P index provides a relative ranking of the risk of P loss from individual fields, which can also be used to prioritize phosphorous requirement.

The use of the soil P index provides a means of identifying fields that have a low or moderate potential for P loss to surface water, as well as fields that have a high risk of P loss which require limiting the slurry and fertilizer application. The soil P index of the individual fields within the catchment (for 1993) is shown in Figure 3.1 and those for the year 2002 are shown in Figure 3.2. In both years, some of the higher Morgan's P values are in fields adjacent to the stream.

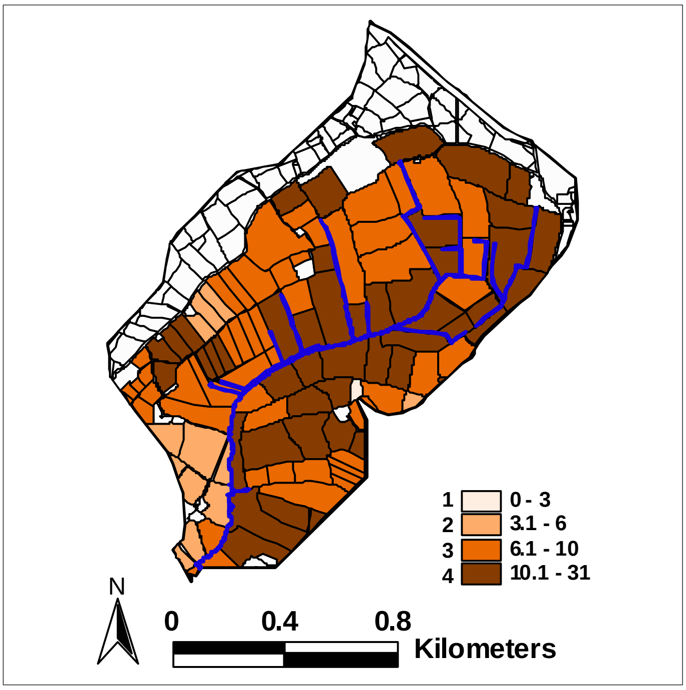

Figure 3.1 *1993 - The Soil P Index based on Morgan's P (mg l^{-1}) at (10 cm) depth of soil showing the fields under different categories. The Soil P level varies between 3.3 to 25.7 mg l^{-1}. The stream and the field drains are shown in blue.*

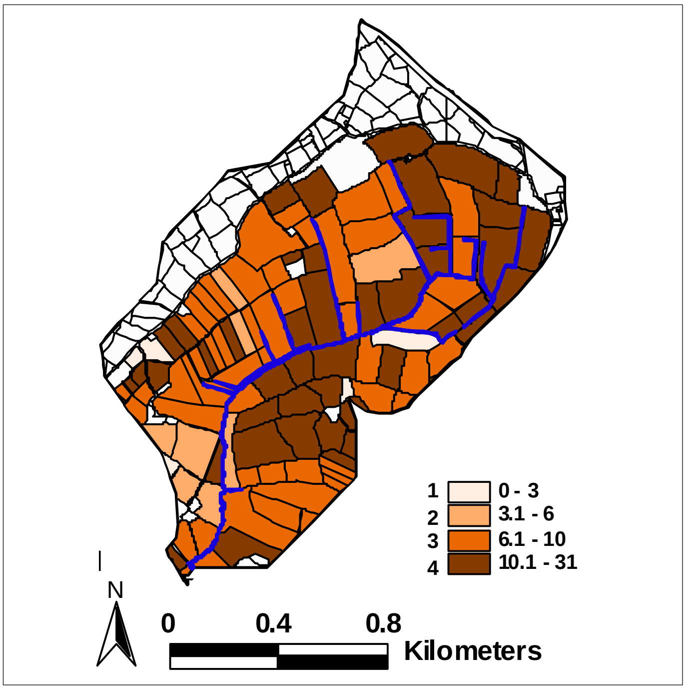

Figure 3.2 *2002 - The Soil P Index based on Morgan's P (mg l^{-1}) at (10 cm) depth of soil showing the fields under different categories. The Soil P level varies between 1.9 to 22.8 mg l^{-1}. The stream and the field drains are shown in blue.*

Table 3.2 *A four category soil phosphorous index developed by the Agricultural Research Institute Ireland, (Teagasc), for Irish soils to estimate the potential risk of agricultural farm areas (Herlihy, 1993; Daly, 1999).*

Level of Risk	**P-index Rank**	**Morgan's P mg l^{-1}**
No risk	1	0 - 3
Low risk	2	3.1 - 6
Medium risk	3	6.1 - 10
High risk	4	Above 10.1

In the 1993 soil P survey, there are no fields at Index 1 and about 10% of the fields are at index 2. Approximately 42% of the fields (Table 3.3) have a soil P index 3 which is considered optimum for grass growth (Teagasc, 2001).

In 1993 almost half of the fields (48%) have a P index of 4 which is above the agronomic requirements and has potential to cause P loss from soil to water. It is noted in Figure 3.1 that there is a trend of high soil P index close to the stream. This may be the result of a combination of factors including: topography, soil type and runoff mechanisms. As the land slopes towards the stream (1 to 6% gradient), the wetter zones of the catchment are closer to the stream. Runoff and phosphorus from upslope regions are likely to direct towards the stream edge, concentrating the soil P in the fields closest to the stream.

Table 3.3 *The P index values and their respective percentage of areas for soils sampled in 1993 and 2002.*

P Index	**Morgan's P(mg l^{-1})**	**Area_1993 (ha)**	**% of Area**	**Area_2002 (ha)**	**% of Area**
1	0 - 3	0	0	6.3	3.35
2	3.1 - 6	18.6	9.94	15.0	8.04
3	6.1 - 10	79.4	42.46	86.5	46.30
4	10.1 - 31	89.0	47.60	79.1	42.30
		187	**100**	**187**	**100**

It is notable that the soil P Index in 2002 (Figures 3.2), has a similar spatial distribution to that of 1993. There is a slight decline in the percentage of fields at index 2 (10% to 8%). The soil P level at index 4 has fallen by 5% (47.6% to 42.3%) suggesting a minor improvement of P application over the intervening nine years. Comparing Figures 3.1 and 3.2 it is seen that that the decrease in percentage soils in index 4 (from 1993 to 2002) is compensated by the rise in percentage in P index 3 (46%). The improvement in soil P in the nine year period is measurable but not significant.

3.3.3. Degree of soil phosphorous saturation

Previous research (Breeuwsma and Silva 1992; Kleinman, 1999) has shown that the P-sorption capacity of acidic sandy loam soils is primarily due to its oxalate extractable *Fe* and *Al* content. A 25% value of *PSC* for this catchment has been assumed based on the international studies. It is important to note here that, for a given field, the P-retention capacity and the amount of surplus P will together determine the number of years required to reach the saturation limit (e.g. 25%). As a measure of soil P build-up relative to P sorption capacity, the soil P saturation value is a key indicator of pollution potential (Behrendt and Boekhold, 1994). Hooda et al. (2001) showed a linear relationship between *Psat* and the amount of P that can be potentially released to runoff water. The main advantage of the P saturation approach comparing to the *STP* is that it not only describes the potential for P loss from the soil but also indicates how close the P-sorption fields of a soil are to being saturated. In other words, the degree of P soil saturation describes the potential of soil to DP loss in runoff and also helps to predict how much of the P added in fertilizers and slurry will be retained by the soil in a form that is resistant to loss in surface runoff (Sibbesen and Sharpley, 1997). At present, the major limitation to the application of *Psat* to environmental risk assessment is the scarcity of *Psat* data. One way of using *Psat* as a risk assessment tool is to develop a pedotransfer function that links soil test data (e.g. Morgan's P) to *Psat*.

In our study, a significantly correlated ($r = 0.94$, $p < 0.05$) relationship between the *Psat* and Morgan's soil P was derived based on soil samples from ten fields in the catchment (Daly, 1999) is shown in Figure 3.3 and takes the form of:

$$Psat = 6.87 + 1.36P_m \qquad (r = 0.90) \qquad \textbf{(3.4)}$$

The *PSC* value of 25% corresponds to a Morgan’s P value of 13.3 mg l^{-1}, (see Figure 3.3).

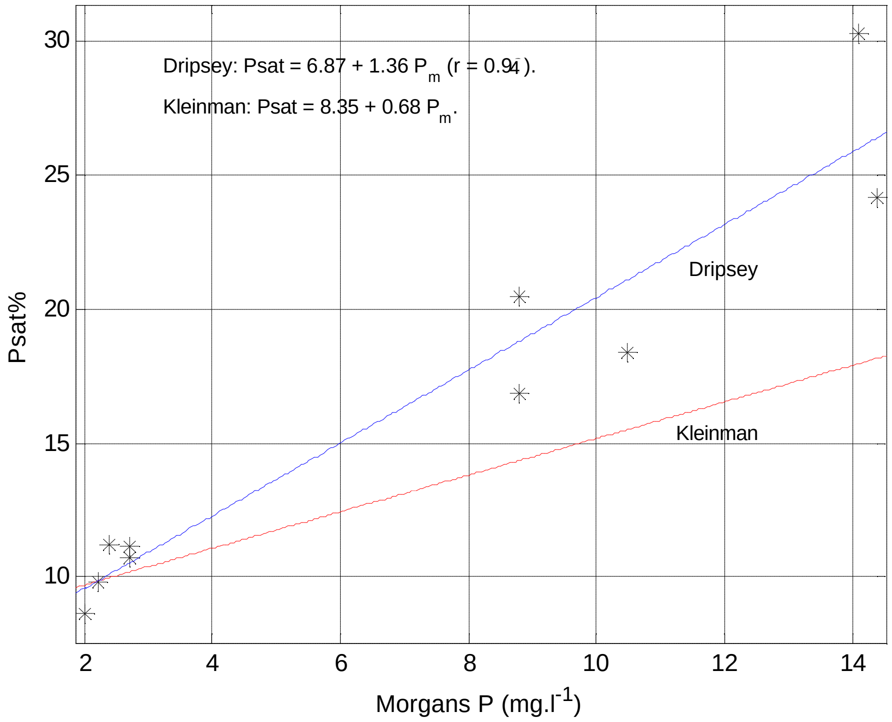

Figure 3.3 *Relationship between the soil P saturation (Psat %) with Morgan’s P in mg* l^{-1}*. The pedotransfer function, Psat = 6.87 + 1.36* P_m *with a correlation coefficient of 94%* ($p < 0.05$)*. The Soil P sorption capacity of 25% corresponds to a Morgan’s P of 13.33 mg* l^{-1}*. The ‘Kleinman’s relationship’ is shown (by the red line) for comparison.*

Kleinman (1999) investigated 59 soil samples from the Delaware river watershed (New York state). He developed a pedotransfer function relationship for computing *Psat* from the more easily measured soil P test (Morgan’s P). Kleinman’s (1999) pedotransfer function for his soil samples, took the form of:

$$Psat = 8.35 + 0.68P_m \qquad (r = 0.88) \qquad \textbf{(3.5)}$$

The degree of soil P saturation (*DSSP*), estimated from equation (3.4 and 3.5), is shown in Figure 3.4 for the year 1993 and in Figure 3.5 for the year 2002. Comparing the different soil P saturation levels of 1993 and 2002 very slight changes were found. In 2002, about 79% of the fields within the catchment are in a progressive stage (12.1% to 25%) of P saturation indicating the probability of exceeding the P saturation limit of these fields unless there is a proper P application.

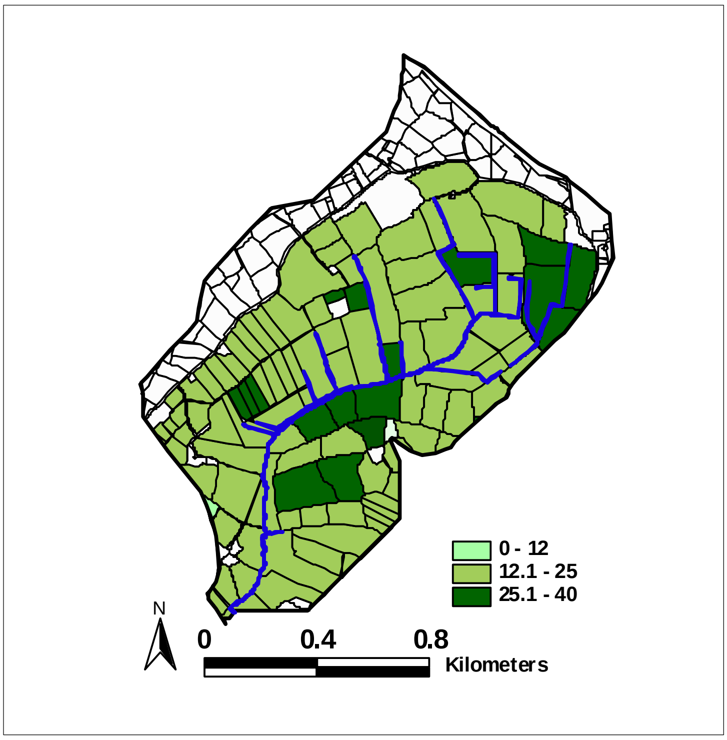

Figure 3.4 *GIS map showing the degree of soil P saturation of the fields in 1993.*

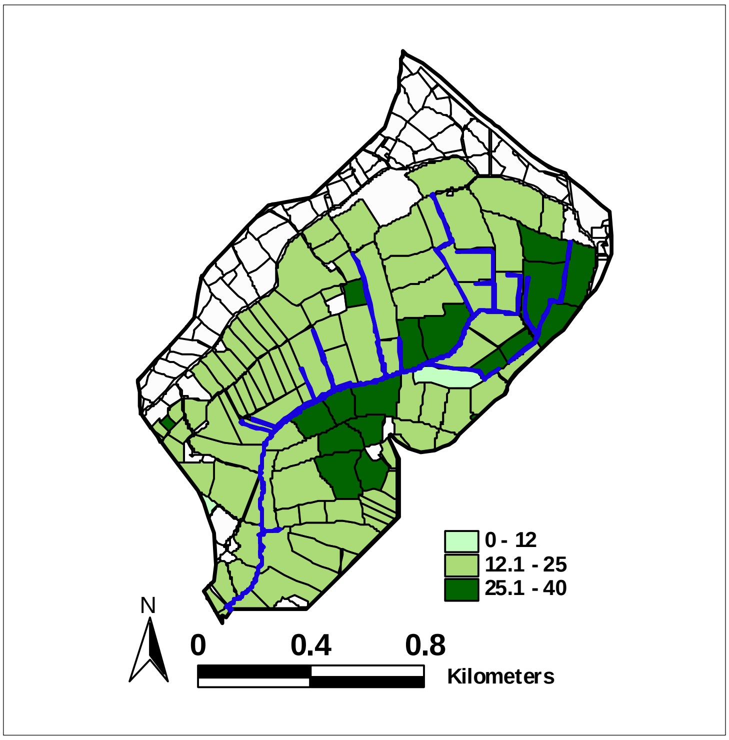

Figure 3.5 *GIS map showing the degree of soil P saturation of the fields in 2002.*

About 17% of the fields exceeded the 25% P saturation limit. Since more P is released from soil to solution as the degree of P saturation increases (Breeuwsma and Silva, 1992), more P is likely to be lost during runoff events from the fields exceeding 25% *DSSP*. The *DSSP* values (Figures 3.4 and 3.5) show that there are several fields adjoining the stream where the *DSSP* value is in excess of the threshold value of 25%. In 1993 most of the fields were in the range of 12% to 25% which implies a gradual state to reach the 25% P sorption capacity level. However, in 2002 there is a slight decline in the percentage of saturated fields most of the fields remains under the range of 12% to 25% saturation level.

3.4. Discussion

In an effort to understand phosphorus loss from soil to water, we determined the soil phosphorus level (Morgan's P) in 117 fields constituting six dairy farms, one silage farm and one sheep farm. We also examined the spatial distribution of a phosphorus loss index (P-Index, scaled from 1 to 4), based on a single parameter, Morgan's P. We then examine the degree of soil phosphorus saturation for all fields based on the pedotransfer relationship with Morgan's P.

From Figures 3.1 and 3.2 (and 3.4 and 3.5) we note that the highest soil test P results are in the fields closest to the stream. The stream runs along a valley with hill slopes on either side, varying in slope from 1 to 6%. The spatial distribution of high soil P and the topography, suggest that phosphorus is transported down the hill slope towards the stream edge. Topography and rainfall runoff patterns contribute to high soil P in the near stream fields. The existence of high soil P in the fields near the stream is likely to be one of the contributing causes of high P loss from soil to water.

The degree of soil P saturation is a more meaningful indicator of potential losses to the water than the soil P Index since it describes the soil P saturation limit with respect to its P saturation capacity. The P saturation approach has the potential to describe the capability for a wide range of soils to release P into the stream (Howard et al., 1999 A value of 25% degree of soil P saturation has been assumed based on the international studies, above this saturation value, the potential of P movement in surface and ground water becomes unacceptable (Breeuwsma and Silva, 1992).

Chapter 4: The soil phosphorous budget of the eight farms

4.1. *Introduction*

Another method of examining the potential of soils to lose phosphorus to water is to determine the budget of soil P at the field or farm scale. In examining the P budget of soils, we can estimate the P surplus or deficiency (in kg P ha^{-1} year^{-1}) in the soil at field (or farm) scale from:

$$P_{surplus} = P_{input} - P_{output} \tag{4.1}$$

Where the P inputs to the soil include: the P in fertilizer and slurry; the P in cattle food concentrate and the P in excreta from the grazing cattle. The P outputs are: the P lost to the stream; the P exported from the farm in meat and milk and the P export (off - farm) in silage and hay. In intensive grazed grassland systems, higher soil P levels often result from the use of excess inputs of P in fertilizer and P in animal feed concentrates (Tunney et al, 2000). Depending on the crop species and soil-P status, the recommended P-fertilizer application for permanent pastures in the UK varies between 20 to 40 kg P ha^{-1} year^{-1} (MAFF, 1994). According to HMSO (1993, 1995) the average annual field fertilizer P application rates were 16 kg ha^{-1} in Scotland, 14 kg ha^{-1} in England and Wales and 13 kg ha^{-1} in Northern Ireland. In Southern Ireland the estimated regional average fertilizer P application for dairy and cattle pasture is 12 kg P ha^{-1} and for silage fields is 15 kg P ha^{-1} (Coulter et al., 2002). These values are based on fertilizer receipts on a regional scale. A significant variation in these values may exist in farm scale study. Plant uptake of P by grasses generally varies between 10 to 25 kg P ha^{-1} year^{-1} (Sharpley et al., 1994). The literature on P budgets shows that the applications of P in fertilizer often exceeds the P requirement by grass (Edwards et al., 1998; Haygarth et al., 1998; Sims, 1997, 1998; Tunney et al., 1997b). Haygarth et al. (1998) estimated an annual P surplus of 24 kg ha^{-1} for a dairy farm in south-west England and Brouwer et al. (1995) found a P surplus of 14 kg ha^{-1} from a P balance for dairy farms in the west of England (Haygarth et al., 1998). A surplus of about 10 kg ha^{-1} year^{-1} is acceptable where *STP* is low and values greater than 10 kg P ha^{-1} year^{-1} is known to be excessive and lead to P loss from soil to water where *STP* level is high (Teagasc, 1999). In intensive agricultural farm areas, the P surpluses are high because slurry and manure application rates are usually based on the N needs of the grass, and the slurry contribution to P tends to be neglected in determining the P requirement in chemical fertilizer. Furthermore the P/N ratio found in slurry is usually much higher than the P/N ratio required by plants (Pote et al., 1996).

4.2. Concept of the phosphorous budget model

The annual phosphorous budgets for each of the farms are estimated based on a conceptual soil phosphorous balance model by Haygarth and Jarvis, (1998). Figure 4.1 is the outline of the soil P balance for the pasture grassland system and Figure 4.2 is the outline for the grassland silage system. Chemical fertilizer is as “Pasture Sward” and “Cut Sward” applied to the grazing and silage fields respectively. Also slurry is only applied to the silage fields (both in pasture and silage systems). The main difference in concept is that we assume that cattle excreta (grazing cattle dung plus slurry from winter housing) are applied to the pasture grassland but not to the silage system.

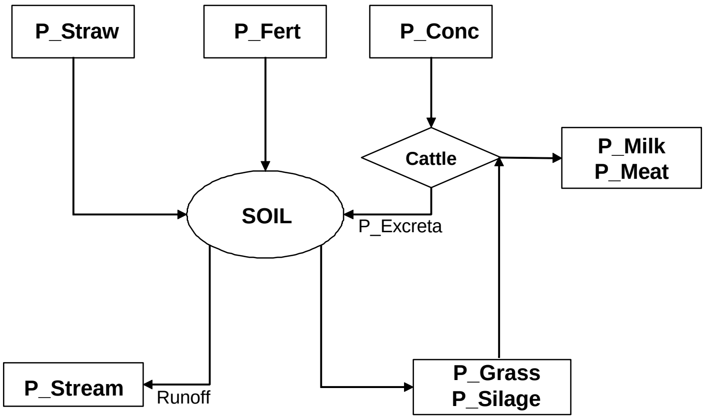

Figure 4.1 *Conceptual Model of Soil P Balance based on the Phosphorous input, output and recycling pathways for pasture farms, where cattle are grazed outdoors for eight months of the year and fed indoors for the four winter months.*

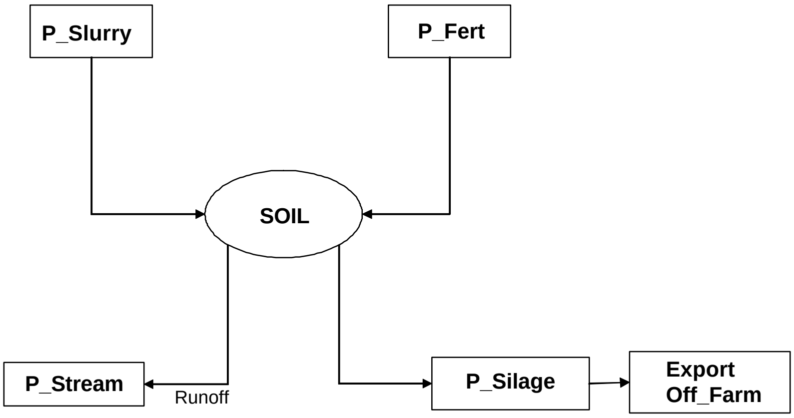

Figure 4.2 *Conceptual Model of Soil P Balance for silage farms with no cattle on these farms.*

Farms A, B, C, D, F and G (see Figure 2.2) are a combination of pasture fields and silage fields in a ratio of approximately two thirds pasture and one third silage. Cattle do not graze the silage fields (except in the early Spring or Autumn or a short period after a silage cut). The phosphorus inputs are in fertilizer, slurry, excreta (including food concentrates) and the phosphorus outputs are in grass (or silage), in meat and milk and in stream flow. It is assumed that 70% of the total P consumed (grass, fodder and food concentrate) by the animals becomes excreta and the rest of the P (30%) is exported off the farm as milk and meat (Simons et al., 1981). The contribution of atmospheric inputs is ignored in this study. The difference between the phosphorus inputs and outputs is defined as a surplus/deficiency.

4.3. Methodology

4.3.1. Collection of fertilizer application data

Data on chemical fertilizer and manure fertilizer application rates, timing and composition over the year 2002 were recorded for the seven cattle farms while the eight, a sheep farm uses no chemical or manure fertilizers. This data was collected from the farmers by **Dr. Gerard Morgan** and his team in the Aquatic Services Unit. Chemical fertilizer, mainly “Cut Sward” (N: P: K, 24:2.5:10) for silage fields and “Pasture Sward” (N: P: K, 24:2.5:5) on non-silage fields or after silage, was normally spread from February to September at intervals of about four to six weeks (Different types of fertilizer applied over the year is given in appendix D). Slurry was applied at a rate and frequency that was more random than the chemical fertilizer application (see Figure 4.3).

4.3.2. Water chemistry data

4.3.2.1. Water flow and phosphorous water chemistry

Stream discharge and water chemistry samples were collected at the outlet of the catchment (see Figure 2.1) for the one-year period, January 1, 2002 to December 31, 2002. Stream stage was continuously recorded (15 minute intervals) by a Thalimedes water level recorder (OTT Hydrometry Ltd, UK), which was placed within a stilling well and situated 2 m upstream of flow control structure. The latter was a 1.5 m wide rectangular weir. The stream is at the headwater of the Dripsey river and at the sampling location the stream is less than 2 m wide.

Composite, flow-weighted water chemistry samples were taken in flow-actuation mode with ISCO 6712 auto samplers. The intakes for the auto samplers were positioned approximately 0.25 m above the stream-bed and 2 m upstream of the weir. During periods of low flow, samples were collected from the auto samplers within 1 to 2 days after sampling. The duration of composite samples, from beginning to end of filling of the bottles varied from 1 hour for very high flows to 2 days for low flows. Grab samples were collected weekly at some specific points of the stream over the one year period to supplement the composite sampling strategy and to enable the annual P load to the stream to be estimated. Samples were held at 4^oC in the laboratory until analysis within about 6 hours after receipt at the laboratory.

The stream water chemistry data is an integrator of both field and farmyard runoff. In this study, we did not measure any farmyard runoff. Therefore, the relative contributions of the yards and the fields were not taken into account in this study. It is likely that if there was no P in yard runoff, then the P concentration level in the stream would be less than what we found.

4.3.2.2. Phosphorous in water samples

The water samples were analyzed according to Standard Methods (Anon, 1985) for Total Phosphorous (TP), Total Dissolved Phosphorous (TDP) and Soluble Reactive Phosphorous (SRP). For TP, sulphuric acid (H_2SO_4), and ammonium persulfate ($[NH_4]_2S_2O8$) were added to 50 ml of the unfiltered sample and boiled to convert phosphorous present in organic and condensed forms to reactive orthophosphate before analysis. After boiling down to approximately 10 ml, the sample was cooled and the phenolphthalein indicator was added. The sample pH was adjusted to 8.3 using sodium hydroxide (NaOH) and sulphuric acid (H_2SO_4). The sample was then brought back up to total volume. The Revised Standard Method by Murphy and Riley (1962) was used to measure TDP and SRP. Particulate phosphorus (PP) was estimated with:

$$PP = TP - TDP \qquad \textbf{(4.2)}$$

4.3.2.3. Gap filling analysis

Flow measurements were recorded at 15 minute intervals for the calendar year 2002. Composite water samples were taken throughout the year and covered 43% of full year Phosphorous concentrations in streams for the remaining time period of year (57%) were estimated from a rating curve relationship estimated from the concentration-discharge (C-Q):

$$C = aQ^{b} \tag{4.3}$$

Where, C and Q represent TP concentration (mg l^{-1}) and discharge (l sec^{-1}) respectively. The constants a and b were used to describe the observed variations in stream water phosphorous concentrations as a function of discharge. Different equations are used to measure stream flow of site 1 and 3 (see chapter 2). Since composite water samples were analysed, values of Q were taken as the mean discharge over the sampling time period. The detail on gap filling is reported in Lewis (2003).

4.3.2.4. Annual Soil Phosphorous Budget (surplus or deficit) of farms

Figure 4.1 is a sketch of the conceptual annual soil P balance for the pasture farms, where cattle are grazed on the fields for eight months of the year and are housed and fed indoors for four months of winter. The inputs are: annual P applied in fertilizer; P in straw; P in excreta (assumed equal 70% of cattle food consumption, including grass, silage food concentrates and imported fodder, e.g. maize). We assume that the other 30% of phosphorus is exported off-farm in meat and milk.

$$P_{excreta} = 0.7(P_{grass} + P_{concentrate} + P_{fodder}) \tag{4.4}$$

The phosphorus outputs are: P loss from soil to stream water and P uptake in the grass. The soil phosphorus balance for pasture farms is expressed as:

$$Pp = \left(P_{fert} + P_{exctreta} + P_{straw}\right) - \left(P_{stream} + P_{grass}\right) \tag{4.5}$$

Where *Pp* is the annual soil phosphorous surplus (or deficiency) in the pasture farms in kg P ha^{-1}. P_{fert} and $P_{excreta}$ are the phosphorus inputs to the soil of chemical fertilizer and cattle excreta respectively. For the pasture farms, we do not include slurry in the computation of the P budget. The P in the excreta is simply taken as 70% of the total animal food consumption for the year. P_{stream} and P_{grass} are the phosphorus output to the stream and the P removal by grass. Food supplements include food concentrates and fodder, the latter was imported maize (to two of the eight farms).

Similarly, Figure 4.2 is a sketch of the conceptual soil P balance on farms where grass is produced for silage only and is then exported off-farm. On these farms, there are no grazing cattle. The soil phosphorus balance for silage farms is expressed as:

$$Ps = \left(P_{fert} + P_{slurry}\right) - \left(P_{stream} + P_{silage}\right) \tag{4.6}$$

Where, Ps is the annual soil phosphorous surplus. P_{fert} and P_{slurry} are the phosphorus inputs of chemical fertilizer and slurry respectively. The slurry in the computation of the budget in the silage farms is that imported from outside farms (to which the silage has been exported). P_{stream} and P_{silage} are the phosphorus output to the stream and the P removal by silage (that is exported off-farm) respectively.

4.4. Results

4.4.1. Chemical fertilizer and slurry application rate

Phosphorous in fertilizer is a nutrient that promotes grass growth. The timing (and rates of application) of fertilizer is important in intensive agricultural systems so as to

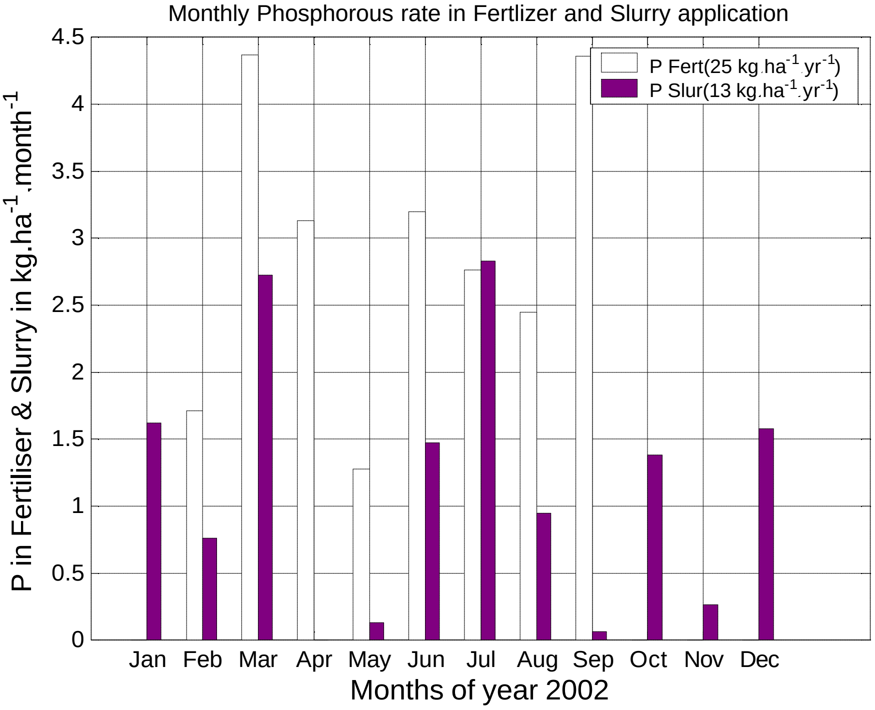

Figure 4.3 *The monthly P inputs in the form of fertilizer and slurry in 2002. The fertilizer is spread from February to September. The slurry was applied between January and December.*

optimise grass growth. For the year 2002 the chemical fertilizer was applied from February to September with a range of monthly application from 1.3 to 4.4 kg P ha^{-1} (Figure 4.3).

In addition to chemical fertilizer, slurry has also been applied throughout the year except in April. The estimated monthly slurry application rate ranges from 0.1 to 2.8 kg P ha^{-1} (Figure 4.3). A small amount of slurry was applied during March, September and November. The total phosphorous application in fertilizer and slurry was highest in May (7 kg P ha^{-1}). The maximum amount of fertilizer was applied in September, a risk time, considering that the winter rainfalls usually begin in October. Slurry was applied also in the risk winter months of October to February.

The annual P loading in chemical fertilizer on the 117 fields ranges from 0 to 55 kg ha^{-1} (Figure 4.4). The annual P loading in slurry on the 117 fields ranges from 0 to 25 kg ha^{-1} (Figure 4.5). The catchment average (area weighted) annual phosphorous from chemical fertilizer is 25 kg P ha^{-1} which is approximately two times higher than in that of slurry (13 kg P ha^{-1}). Only three fields received fertilizer higher than 30 kg P ha^{-1}. The catchment average total P (in fertilizer and slurry) is 38 kg P ha^{-1}. Only seven fields received slurry more than 15 kg ha^{-1}. In Figures 4.4 and 4.5 we observe that those fields

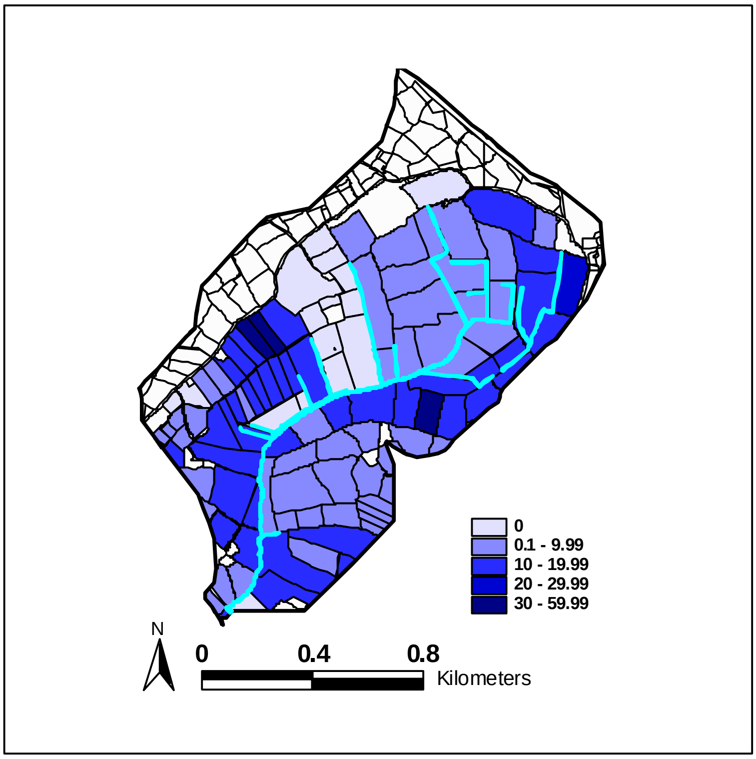

Figure 4.4 *GIS map of annual Chemical Fertilizer application (kg P ha^{-1}) of 117 fields in 2002.*

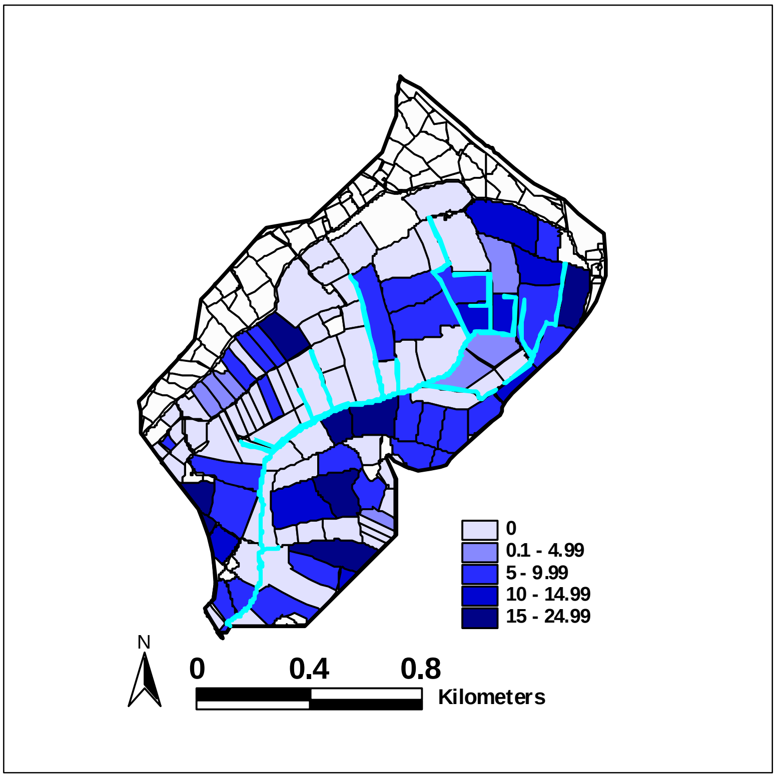

Figure 4.5 *GIS map of annual slurry application (kg P ha^{-1}) of 117 fields in 2002.*

receiving high fertilizer also receive high slurry applications. Also from Figure 4.5 it is noted that slurry applications were not restricted to fields away from the streams.

The national average values (Coulter et al, 2002) of P fertilizer application rates for pasture and silage fields are 12 kg ha^{-1} and 15 kg ha^{-1} respectively. Our estimates of 25 kg P ha^{-1} in fertilizer for the Dripsey catchment is approximately twice the value of national average.

4.4.2. Phosphorous uptake by grass

The monthly P requirement of grass over the year is presented in Figure 4.6. These results are based on data from a similar grassland ecological site (Teagasc, Moorepark, County Cork, 40 km, East of Dripsey) for the year 2002. The data included weekly biomass yields in kg of dry matter per hectare, from February to November (nitrogen fertilizer application rate of 150 kg N ha^{-1}). The phosphorous content in grass is assumed constant throughout the year at 0.4% P (Fleming and Murphy, 1968). The monthly P uptake by grass varied from 0 to 7.5 kg P ha^{-1} (depending on the season). The annual average P uptake is estimated at 32 kg P ha^{-1}. This value is higher than that estimated as 15 to 25 kg P ha^{-1} year^{-1} by Sharpley et al. (1994). The highest monthly phosphorous requirement was in April (23.5% of annual) and the lowest was in November (0.6% of annual). Approximately 94% of the annual phosphorous requirement by grass is between March and September. Phosphorous uptake gradually increases from February to April and gradually decreases from April to November.

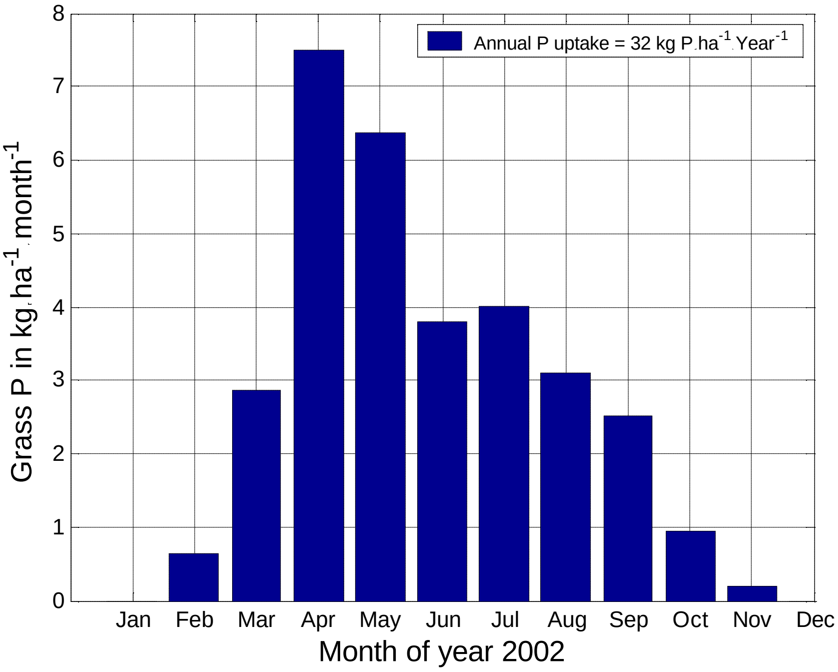

Figure 4.6 *Monthly Phosphorous uptake (kg P ha^{-1}) by grass over the year 2002 at the Teagasc research station at Moorepark, Fermoy, County Cork, Ireland*

4.4.3. P loss to the stream

The cumulative total phosphorus (TP) export to the stream is shown in Figure 4.7 for the year 2002. The annual export was estimated as 2.48 kg P ha^{-1}. This is higher than many other international studies (Lewis, 2003). The year 2002 was wet with an annual rainfall of 1812 mm by comparison with a six year average at this site of 1470 mm. Furthermore, there were slurry applications outside the preferred spreading period of March to September. The monthly TP loadings exports to the stream (Figure. 4.8) range from 0 to 0.48 kg P ha^{-1} (with a mean monthly loading of 0.2 kg ha^{-1}). About 76% of the phosphorous loss occurs during the five months October to February. It is important to note that there is no significant amount of fertilizer application during the winter five months. The export of TP of 2.48 kg P ha^{-1} is 9.9% of the chemical fertilizer application rate (25 kg P ha^{-1}) or 6.6% of the chemical fertilizer plus slurry application rate of 38 kg P ha^{-1}. High flows coincide with high TP exports. Low flows result in negligible TP exports. This suggests that P applied in the summer (Figure 4.3) if not taken up in grass growth is held in 'reservoir status' until winter when the rains mobilise the P out of the

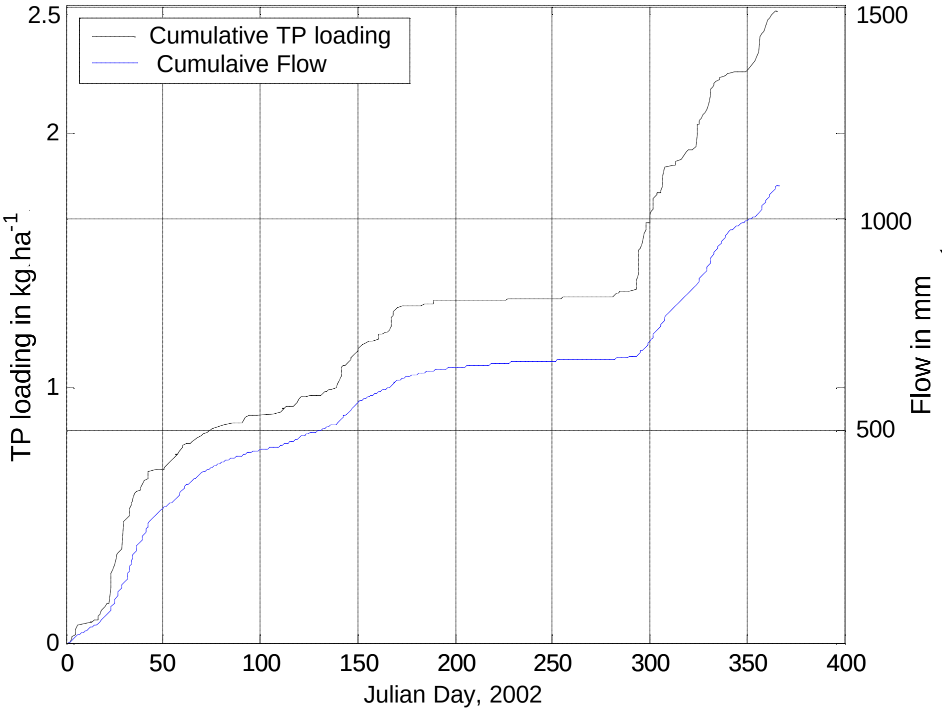

Figure 4.7 *Cumulative TP export load was 2.48 (kg P ha^{-1}) in the stream in 2002 from site 3. Here cumulative phosphorous followed the similar trend of the cumulative stream flow.*

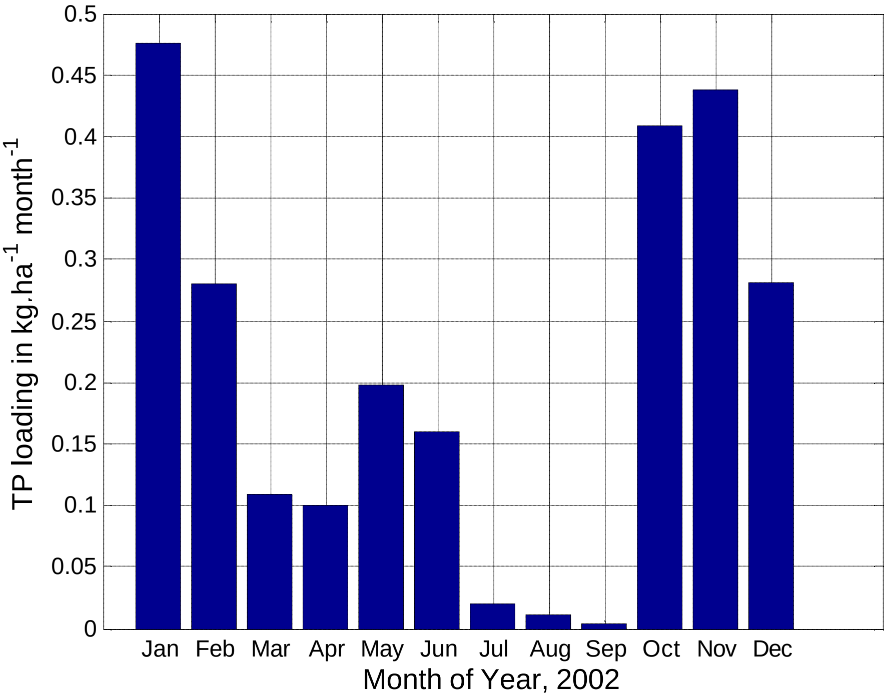

Figure 4.8 *Monthly TP export load to the stream at Site 3 in 2002.*

soil and into the stream. It is important that this reservoir of potentially mobile P in the soil be minimised before the onset of winter.

4.5. Annual phosphorous budget of the eight farms

The phosphorous budgets for the eight farms are estimated for year 2002 and shown in Table 4.1. The phosphorous budgets for the six cattle farms (A, B, C, D, F, and G) and one sheep farm (H) are estimated based on the pasture balance model, (4.5). The budget for the silage farm (E) is based on the silage balance model, (4.6). Farm E is the only grassland farm within the catchment which exports most of its silage and imports slurry from an outside farm. In both models we exclude any P uptake from the existing soil P pool.

In Table 4.1, we see that the annual chemical fertilizer application rates of the dairy and silage farms vary from 14 to 41 kg P ha^{-1} year^{-1}. The corresponding slurry application rates vary form 8 to 17 kg P ha^{-1} year^{-1}. The total amounts of phosphorous received from these two main sources, range from 22 to 55 kg P ha^{-1} yr^{-1}. The total annual P application in the seven farms (A to G inclusive) exceeds the annual grass/silage growth requirements of 32 kg P ha^{-1} year^{-1}. We assume for simplicity that

Table 4.1 Annual soil phosphorous balance (kg P ha^{-1}) for eight farms within the catchment showing the annual surplus (kg P ha^{-1}) for each farm. *We assume annual TP export rate was equal for the whole catchment.*

Farm	**Phosphorus Inputs (kg P ha^{-1} yr^{-1})**						**Phosphorus Outputs (kg P ha^{-1} yr^{-1})**			**Surplus (kg P ha^{-1} yr^{-1})**
	Fertilizer	Slurry	Concentrate	Fodder	Straw	Excreta	Grass	Stream	Silage Export.	
A	26.7	17.0	5.1	0	1.4	26.0	32	2.5	0	**22.9**
B	25.9	11.1	0.5	0.5	0	12.0	32	2.5	15.9	**3.4**
C	26.2	9.6	24.5	0.1	0.1	39.6	32	2.5	0	**31.4**
D	17.6	12.1	17.8	0.1	0.2	34.9	32	2.5	0	**18.3**
E	40.8	14.2	0	0	0	0	32	2.5	32	**6.3**
F	32.1	17.4	8.8	1.8	0.6	29.8	32	2.5	0	**28.0**
G	13.8	7.7	5.3	0	0	26.1	32	2.5	0	**5.4**
H	0	0	0	0	0	11.2	16	2.5	0	**-7.3**

the silage uptake of P is similar to the grass uptake of P. The six pasture farms all have some fraction in silage (farm E which is silage only). The range of input from excreta is 0 to 40 kg P ha^{-1}.

In Table 4.1, we show that for all farms except the sheep farm, the soils have a surplus of phosphorus. The range of surplus is 3.4 to 31.5 kg P ha^{-1} year^{-1}. The literature suggests that grasslands with a surplus greater than about 10 kg P ha^{-1} are at risk of P loss from soil to water (Teagasc, 1999). For four of the eight farms, the soil P surplus is greater than 18 kg P ha^{-1}. This suggests that a reduction of the volumes of fertilizer and slurry should be considered.

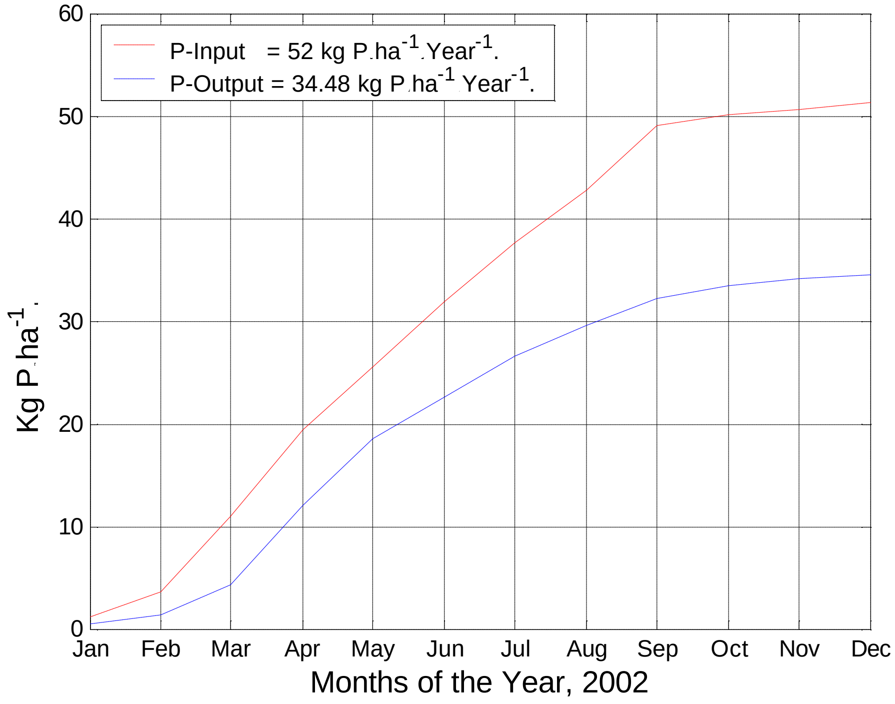

Figure 4.9 *The cumulative phosphorous input and output of the catchment over the year 2002. The cumulative input is 54 kg P ha^{-1} year^{-1} and cumulative output is 34.5 kg ha^{-1} year^{-1}.*

In Figure 4.9, we show the cumulative phosphorus inputs and outputs to the soil of the total catchment. We see that as the year goes on, the P inputs exceed the P outputs and the difference (surplus) between inputs and outputs grows. By the beginning of autumn, we note the maximum difference. This difference or surplus is likely to be partitioned between phosphorus that has entered the soil profile (and increased the soil Morgan's P level) and phosphorus that has built up in the soil water solution. The latter is then readily available for loss from the soil to the stream water. The timing of this maximum surplus is ominous, coming at the beginning of the 'wet season' which starts in October.

4.6. Relationship between the area average soil P and P surplus of the farms

In Table 4.2 we show the soil Morgan's P and the corresponding soil P surplus for each of the eight farms. It is of interest to note that the sheep farm with no fertilizer applications still has a Morgan's P higher than three of the dairy farms which have significant fertilizer applications, suggests that high fertilizer application in the past may have been raised the soil P level (not included in the computations for Table 4.1).

Table 4.2 *For each farm, the soil test P - as Morgan's P value (mg l^{-1}) for 2002 and the surplus phosphorus in the soil.*

Farm Code	**Dominant Farm Activity**	**Morgan's P** (mg l^{-1}) 2002	**Surplus** kg P ha^{-1} 2002
A	Dairy	7.3	22.9
B	Dairy	6.6	3.4
C	Dairy	8.5	31.4
D	Dairy	12.2	18.3
E	Silage	9.6	6.3
F	Dairy	12.7	28.0
G	Dairy	10.7	5.4
H	Sheep	9.8	-7.3
Total		Average = 10	

The scatter plot of each farm area average Morgan's P and farm surplus is shown in Figure 4.10. No relationship has been found between the area average soil P (Morgan's P level) and one year phosphorous surpluses of the eight farms. This may be since the soil P builds up is a long term process and one year surplus data is not enough to understand the relationship between soil P level and P surplus.

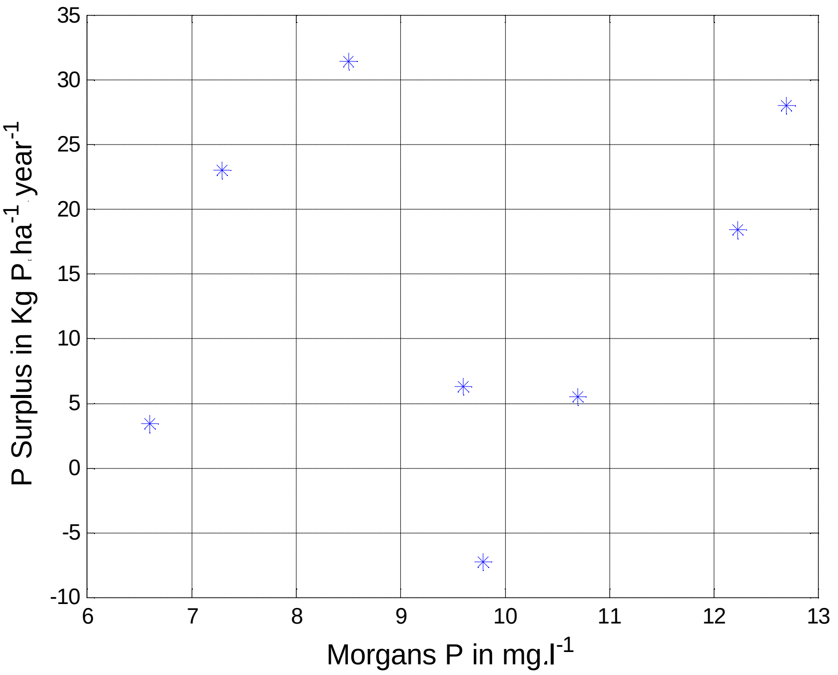

Figure 4.10 *The scatter plot of area average Morgan's P vs. and P surplus of the eight farms. Morgan's P reflects the past 40 years of surplus P inputs and will not be significantly influenced by one year's surplus.*

4.7. Phosphorous application in the fields with a P_index of 4

The fields with a soil P_index of 4 pose a high risk to the water quality. According to Teagasc no fertilizer application is recommended in these fields (Poulton et al., 1997). Any fertilizer application in these fields can cause a greater loss of P from these fields. The location of the fields with a P_index of 4 is shown in Figure 4.11. The relative risk of P loss from these fields is examined by partitioning the annual P application rate in these fields into four categories (0 to 10, 10.1 to 20, 20.1 to 30 and more than 30.1 kg ha^{-1}year^{-1}).

Figure 4.12 shows that about 24% of the fields with a P_index of 4 received an annual P application of less than 10.1 kg ha^{-1}. About 34% and 20% of the fields (with a P_index of 4) received an annual P application of more than 10 kg ha^{-1} and less than 20.1 kg ha^{-1}; and more than 20 kg ha^{-1} and less than 30.1 kg ha^{-1} respectively. A small percentage (6%) of the fields (with a P_index of 4) received an annual P application of more than 30 kg ha^{-1}.

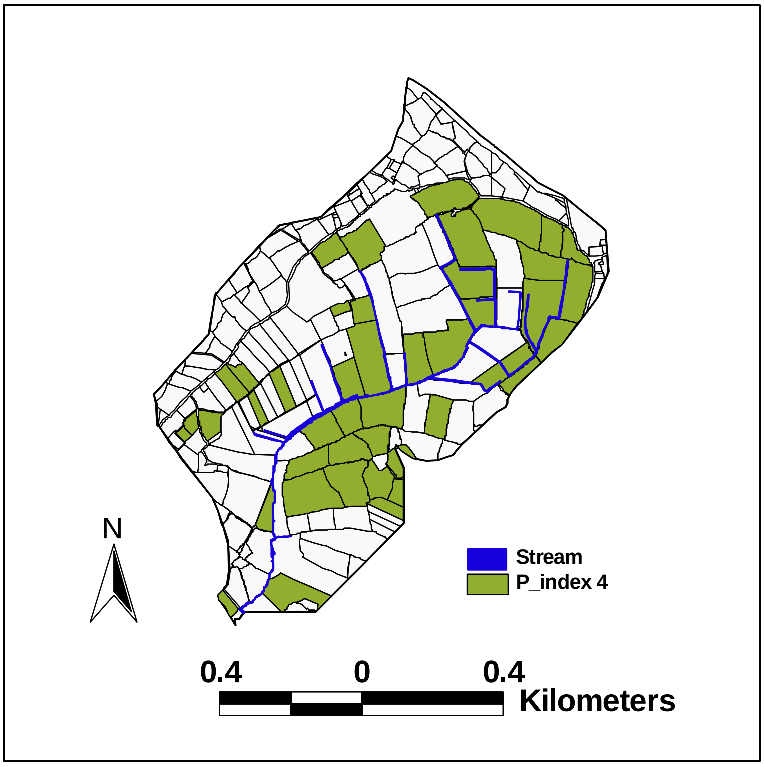

Figure 4.11 The location of the fields with a P-index of 4 in 2002.

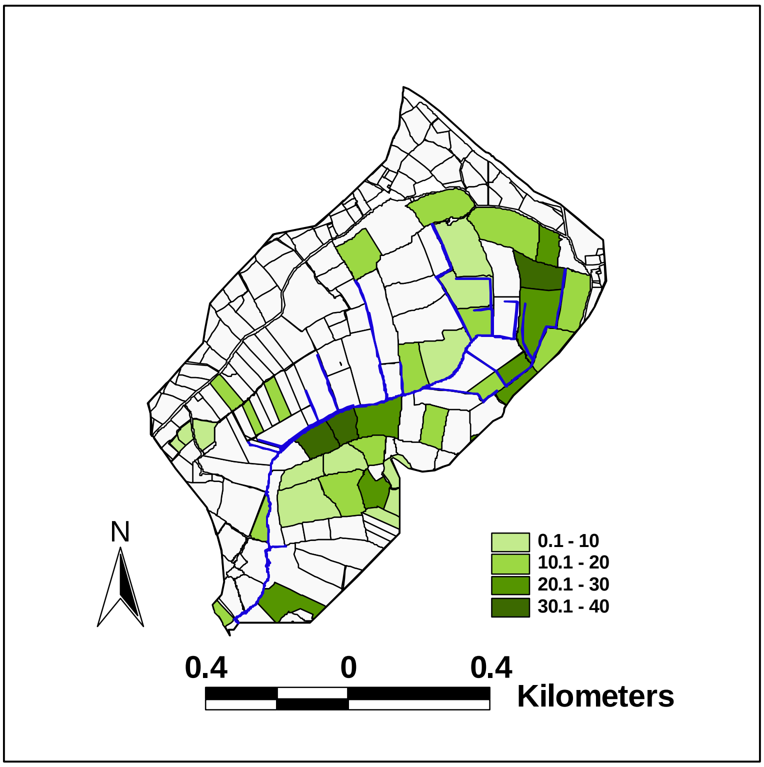

Figure 4.12 The annual P application rate (from fertilizer and slurry) in 2002 in the fields with a P_index of 4. The legend scale is kg P ha^{-1} $year^{-1}$.

4.8. Summary

The national average values (Coulter et al, 2002) of P fertilizer application rates for pasture and silage fields are 12 kg ha^{-1} and 15 kg ha^{-1} respectively. Our estimates of 25 kg P ha^{-1} in fertilizer for the Dripsey catchment is approximately twice the value of national average. In the soil P budget analysis for farms, we found that four of the eight farms had annual P surpluses greater than 18 kg ha^{-1}. These surpluses are likely to increase the vulnerability to P loss from the soil to the water bodies as well as leading to additional increases of Morgan’s P in the soil.

Chapter 5: Modelling of phosphorous export

5.1. Introduction

In our study the annual total phosphorous export for 2002 was 2.48 kg ha^{-1}. Generally TP loss in runoff exceeding 2 kg ha^{-1} year^{-1} classifies a catchment as having a high vulnerability of P loss (Sharpley and Lemunyon, 1997). Moreover to maintain the standard total Phosphorous concentration (35 µg l^{-1}) of the stream set by the Local Government (Water Pollution) Act, 1977 (Water Quality Standards for Phosphorous) Regulations, SI. No.258 of 1998 (Anon, 1998), the annual phosphorous export has to be reduced significantly. With an annual stream flow of 1080 mm, to maintain the mean annual TP concentration of less than 0.035 mg l^{-1} the annual TP export from the catchment should be 0.35 kg P ha^{-1}. Therefore the reduction from 2.48 kg P ha^{-1} to less than 0.35 kg P ha^{-1} is a great challenge (Lewis, 2003). In these circumstances significant progress in reducing P losses to the stream will require long term management strategies. To develop and implement any management strategies the major controlling factors of phosphorous export should be better understood. The major hydrological factors are: precipitation, surface runoff, sub surface runoff and evapotranspiration. The management factors include: fertilizer, slurry application rate and timing, phosphorous surplus and stocking density. The other factors are: P uptake by grass, soil texture etc. In previous chapters of this study, the TP export trend has been discussed in relation to the different components of the phosphorous budget model. In this chapter the management and the hydrological factors are examined.

The aim of this chapter is to develop a simple phosphorous export coefficient model based on the significant parameters influencing phosphorous loss. From the earlier discussions a significant seasonal dependence in TP export has been found in our study. The monthly time step has been chosen to illustrate the change in seasonal TP export with the seasonal change in the parameters.

5.2. Base flow separation

The surface and sub surface runoff (base flow runoff) are two components of hydrological cycle. An empirical method is used to separate base flow from the stream flow hydrograph. This method of hydrograph separation is from the British Low Flow Studies (Institute of Hydrology, 1980). A simple qualification algorithm is used to select the points of base flow hydrograph (see Appendix B for Matlab program). Surface runoff is estimated by deducting base flow from the stream flow. The daily base flow and surface run off for site 3 is shown in Figure 5.1.

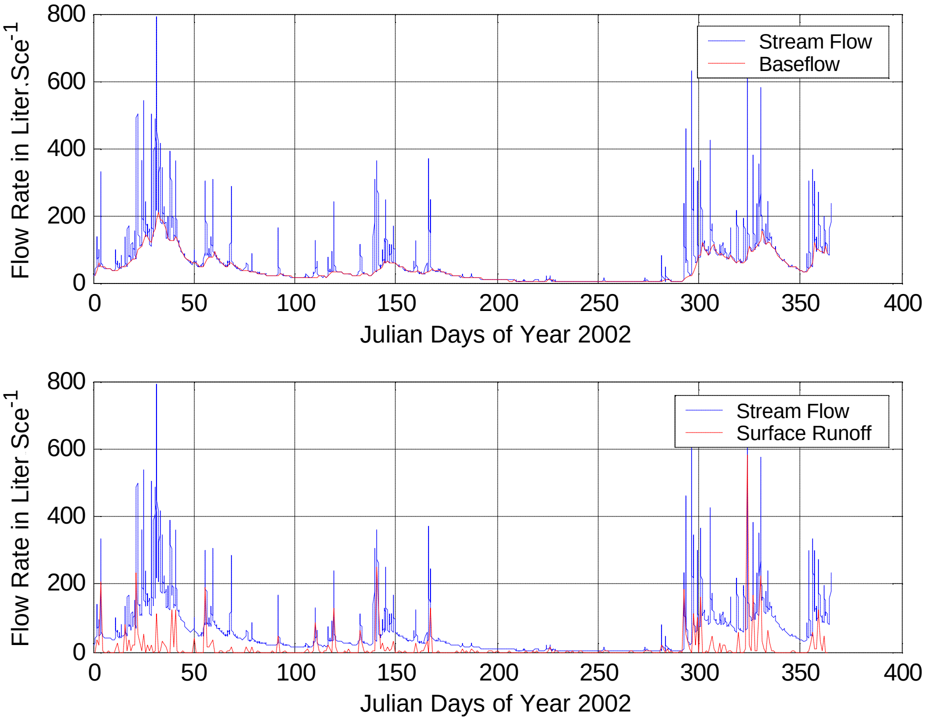

Figure 5.1 *The daily base flow and surface runoff for year 2002 at site 3.*

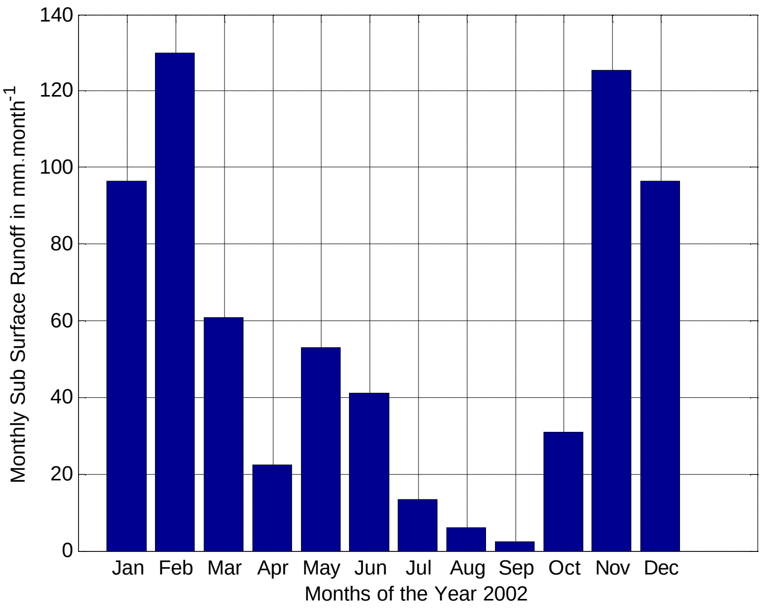

Figure 5.2 *Monthly base flow for 2002.*

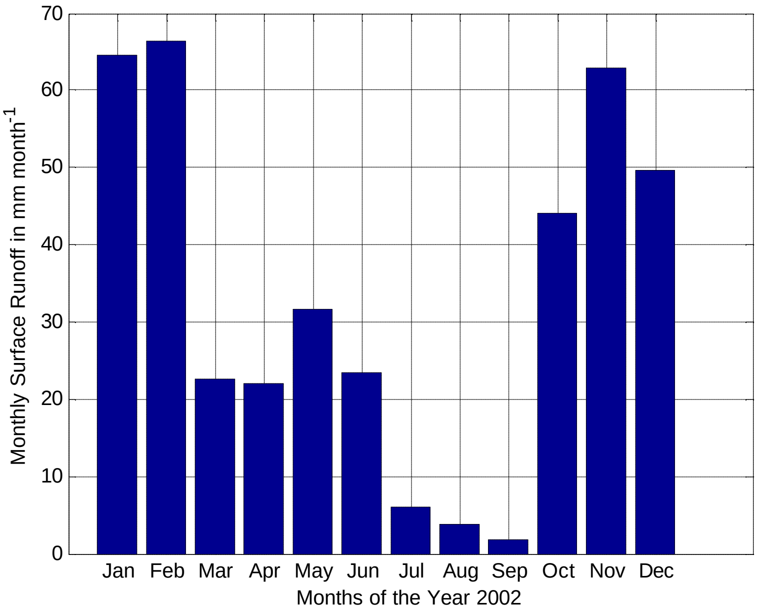

Figure 5.3 *Monthly surface runoff for 2002.*

Monthly base flow and surface runoff for site 3 are shown in Figures 5.2 and 5.3 respectively. These two components of stream flow show similar trend over the year. The annual base flow in site 3 for 2002 was 67% of the stream flow. These high magnitudes imply the significance of base flow in possibly controlling TP transport from the sub surface layers of the soil.

5.3. Parameters estimation

The parameters of the phosphorous export coefficient model are given below:

1. Grass P uptake,
2. Slurry application rate,
3. Chemical fertilizer application rate
4. Phosphorous surplus
5. Evapotranspiration
6. Surface runoff and
7. Sub surface runoff.

These parameters were estimated from the data gathered over the year 2002 from the Dripsey catchment using very simple methods which will make the practical application of this model amenable to examining different possible scenarios of land management (see section 5.6).

5.3.1. Relationship between the Grass P uptake and TP export

The monthly data of grass P uptake is plotted against the monthly TP loading in Figure 5.4. A significantly related ($r^2 = 0.90$, $p < 0.05$) negative relationship is observed between these components. The exponential relationship can be denoted by (5.1):

$$Y_{TP\_Export} = 0.378 * \exp(-0.342 * X_{P\_Grass}) \tag{5.1}$$

Where, Y_{TP_Export}, X_{P_Grass} are the monthly TP export coefficient rate in kg ha^{-1} $month^{-1}$ and grass Phosphorous uptake kg ha^{-1} $month^{-1}$ respectively. The Sum of Squares Error (SSE) and the Root Mean Squared Error (RMSE) of this equation are 0.015 and 0.039 respectively and suggests a good numerical fit. The relationship shows an increase of P uptake by grass corresponds to an exponential decrease in P loss from the soil to the water body. Figure 5.4 suggests that the risk of TP loss dropped dramatically during monthly high P uptake for grass growth (e.g. May, June etc).

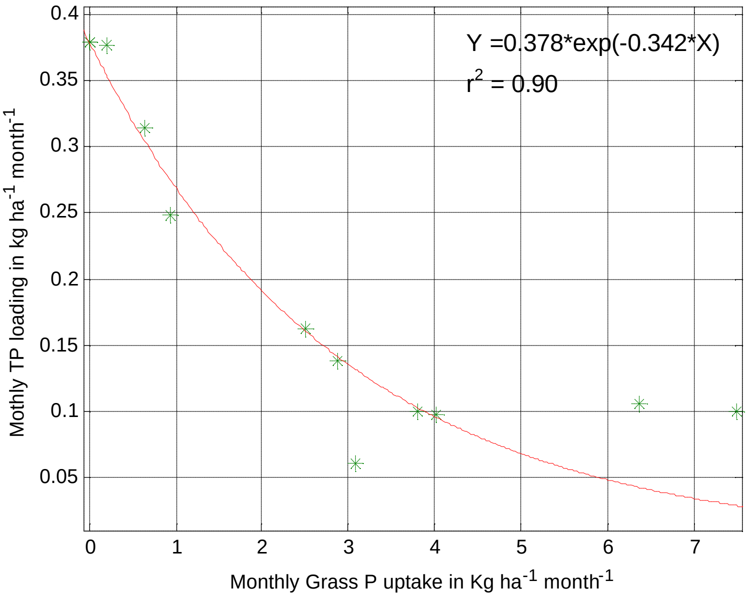

Figure 5.4 Relationship between monthly the P uptake by grass rate and TP export.

5.3.2. Relationship between the monthly Slurry application rate and TP export

A linear relationship is derived from a scatter plot between the monthly slurry application rate and TP export (Figure 5.5). The TP export is estimated from the equation below:

$$Y_{TP\_Export} = 0.152 + \left(0.118 * X_{P\_Slurry}\right) \qquad \textbf{(5.2)}$$

Here X_{P_Slurry} denotes the monthly slurry application rate in kg ha^{-1} month^{-1}.The monthly TP export rate is positively correlated with the slurry application rate. The correlation coefficient is 57% ($p < 0.05$). This can be illustrated as a relatively low increase of TP export with the increase of slurry application rate.

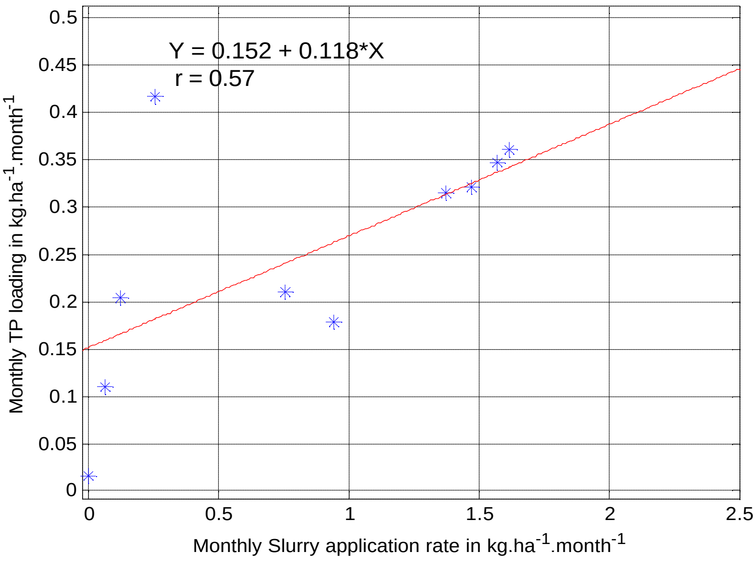

***Figure 5.5** Relationship between the monthly slurry application rate and TP export.*

5.3.3. Relationship between the monthly fertilizer application rate and TP export

No significant relationship was found from the scatter plot diagram of monthly fertilizer application rate vs. TP export (Figure 5.6). Here the most ambiguous thing is the TP export rate was more than 0.25 kg ha^{-1} month^{-1} during three months when there was no fertilizer application within the catchment. This suggests that there was a lag after the fertilizer application before its effects was noticeable in the stream. This is probably due to the fact that the losses of applied P in runoff are generally less than 10% of that applied, unless rainfall immediately follows application (Sharpley and Rekolainen, 1997).

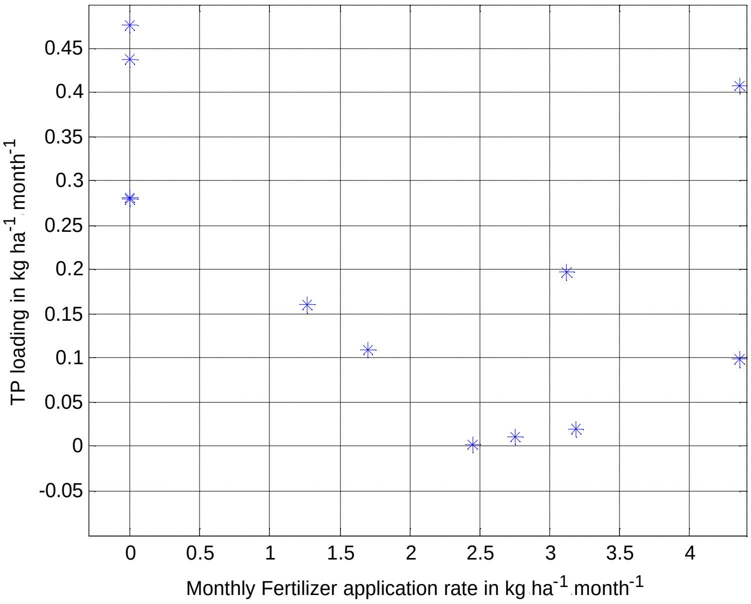

***Figure 5.6** Relationship between the monthly fertilizer application rate and TP export.*

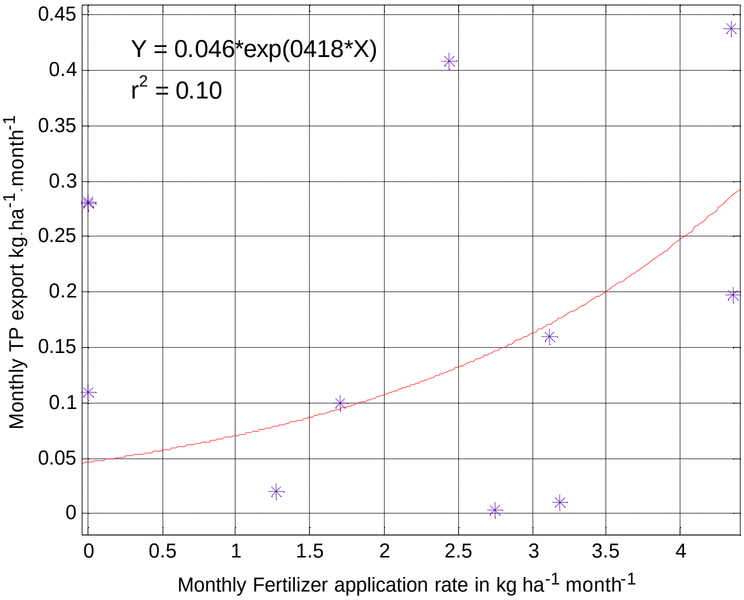

***Figure 5.7** Relationship between the monthly fertilizer application rate and TP export of the next corresponding month of fertilizer application.*

An exponential less significantly correlated relationship ($r^2 = 0.10$, $p < 0.05$) is derived from the scatter plot of the monthly fertilizer application and the corresponding next month TP export. This relationship is given as:

$$Y_{TP\_Export} = 0.046 * \exp(0.418 * P_{Fert}) \qquad \textbf{(5.3)}$$

Where P_{Fert} is the monthly fertilizer application rate in kg ha^{-1} $month^{-1}$.

5.3.4. Relationship between the monthly phosphorous surplus and TP export

The data of monthly phosphorous surplus is plotted against the data of monthly TP export and is shown in Figure 5.8. The graph shows no significant relationship between the two components. However a few points of this graph shows an increase of TP export with the increase of P surplus most of the points does not follow this trend. Furthermore, no relationship has been found between the cumulative monthly P-surplus and TP-export (Figure 5.9).

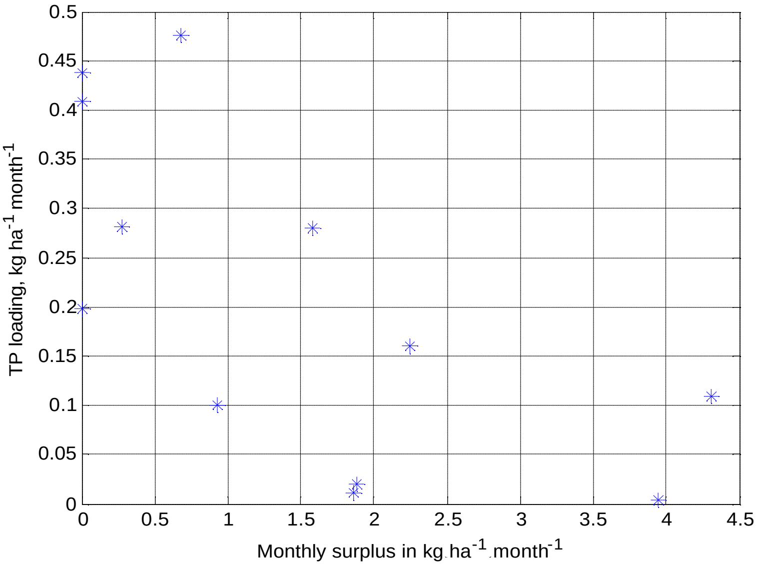

Figure 5.8 *Scatter plot diagram of the monthly P surplus. vs. TP export.*

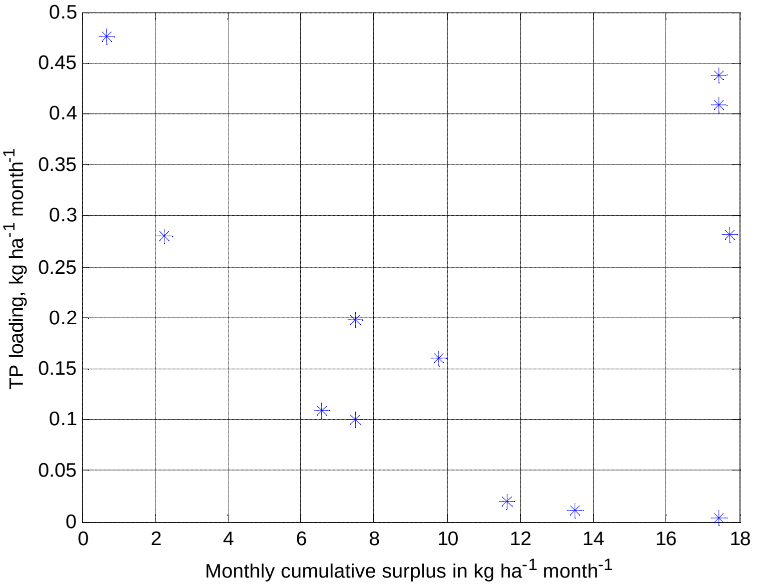

Figure 5.9 *Scatter plot diagram of the monthly cumulative P surplus vs. TP export.*

5.3.5. Relationship between the monthly evapotranspiration and TP export

The relationship between monthly evapotranspiration and TP export can be defined by an exponential fitting shown in Figure 5.10. The monthly TP export is negatively correlated with the evapotranspiration (($r^2 = 0.74$, $p < 0.05$)). The expression between these components is given below:

$$Y_{TP\_Export} = 0.402 * \exp\left(-0.038 * X_{Evap}\right) \quad \textbf{(5.4)}$$

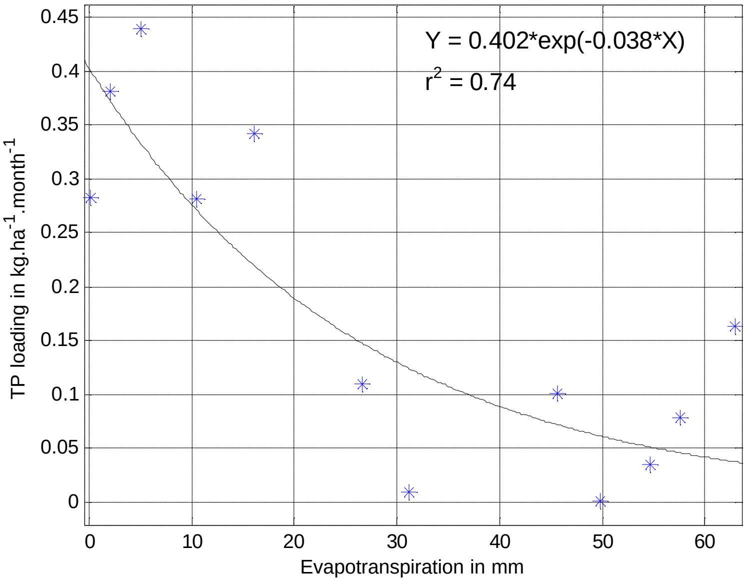

Figure 5.10 *Relationship between the evapotranspiration and TP export.*

Where X_{Evap} is the monthly evapotranspiration in mm

Here the monthly TP export decreases exponentially with the increases of evapotranspiration (Jaksik, 2004).

5.3.6. Relationship between the monthly surface runoff and TP export

The transfer of phosphorous from the grassland to the stream has in the past been considered to be dominated by surface runoff (Sharpley and Rekolainen, 1997). The scatter plot of monthly surface runoff and TP export is shown in Figure 5.11. The monthly TP export is significantly correlated (($r^2 = 0.73$, $p < 0.05$)) with the surface runoff. The exponential relationship derived from these two components can be shown by the expression given below:

$$Y_{TP\_Export} = 0.071 * \exp\left(0.027 * X_{Sruface\_Runoff}\right) \quad \textbf{(5.5)}$$

Where $X_{Sruface\_Runoff}$ is the monthly surface runoff in mm month^{-1}.

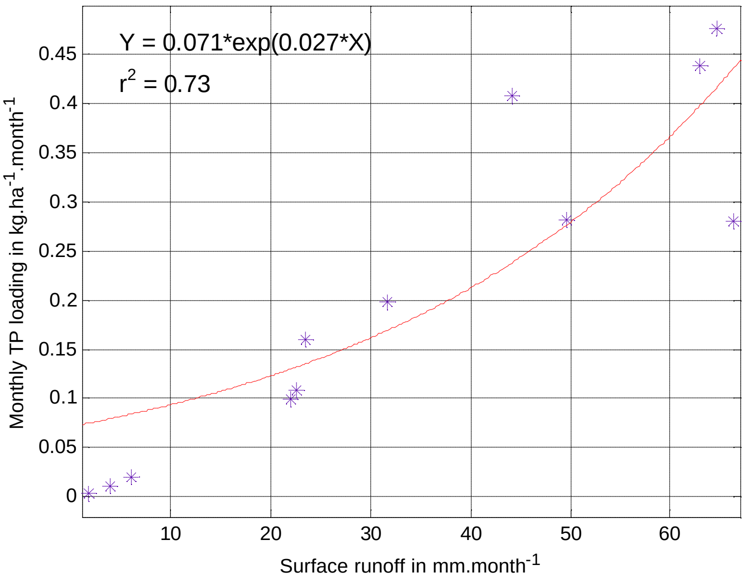

Figure 5.11 *Relationship between the monthly surface runoff and TP export.*

5.3.7. Relationship between the monthly sub surface runoff and TP export

A significant relationship (($r^2 = 0.72$, $p < 0.05$)) has been derived between monthly sub surface runoff and TP export from the scatter plot diagram shown in Figure 5.12. The positive exponential relationship is shown by the given expression:

$$Y_{TP\_Export} = 0.072 * \exp\left(0.014 * X_{Subsur\_Runoff}\right) \quad \textbf{(5.6)}$$

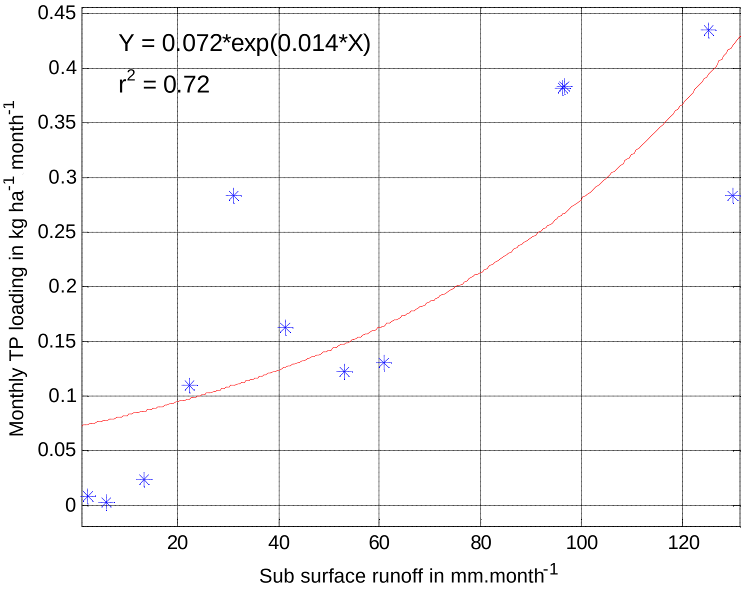

Figure 5.12 *Relationship between the monthly subsurface runoff and TP export.*

Where X_{Subsur_runoff} is the monthly sub surface runoff in mm month^{-1}.

It was previously assumed by researchers that subsurface runoff has no significant influence in phosphorus loss from the catchment (Sharpley and Rekolainen, 1997). But Scanlon et al. (2003) suggests that phosphorous loss, particularly dissolved phosphorous and soluble reactive phosphorous is transported to streams by sub surface runoff.

5.4. The model results

The P uptake by grass and evapotranspiration were high during the summer months with a very low amount of precipitation. The high evapotranspiration leads to a soil moisture deficit compared to winter months. Therefore when the liquid slurry is applied during this time it was rapidly absorbed by the soil and the grass. On the other hand the chemical fertilizer was applied in solid granulate form and due to the high evapotranspiration during summer months the fertilizer integrated with the soil and grass roots in the soil surface. Since there was a very small amount of surface and sub surface runoff (Figures 5.2 and 5.3) during that time the residuals of fertilizer applied remained close to the surface layer of the soil. Later on in the winter months a significant amount of TP was exported by surface and sub surface runoff from this pool of phosphorous even if there was no fertilizer applied during this time.

From the above discussions of TP export we can decide which parameters to keep in this model. It is revealed that grass P uptake, evapotranspiration, surface runoff and sub surface runoff are significant and fertilizer and slurry application rate appears to be less significant No relationship has been found between TP export and the monthly P surplus. In our study we assume that TP loss is caused by the simultaneous effects of the parameters which are significantly correlated with the TP export. So finally we develop the model using six parameters to predict monthly phosphorous export based on non linear regression analysis. We assume an equal weight to each of the six parameters. The expression of the model is given below:

$$\begin{aligned}Y_{TP\_Export} &= 0.166\{0.378*\exp(-0.342*X_{P\_Grass}) + 0.152 + 0.118*X_{P\_Slurry} \\ &+ 0.402*\exp(-0.038*X_{Evap}) + 0.046*\exp(0.418*P_{Fert}) + \\ &0.071*\exp(0.027*X_{Surface\_Runoff}) + 0.072*\exp(0.014*X_{Subsur\_Runoff})\}\end{aligned} \quad \mathbf{(5.7)}$$

The predicted monthly TP export is estimated using (5.7). Comparison of the predicted and monthly TP export for site 3 is shown in Figure 5.13. The results show that the predicted monthly TP export is similar to the observed.

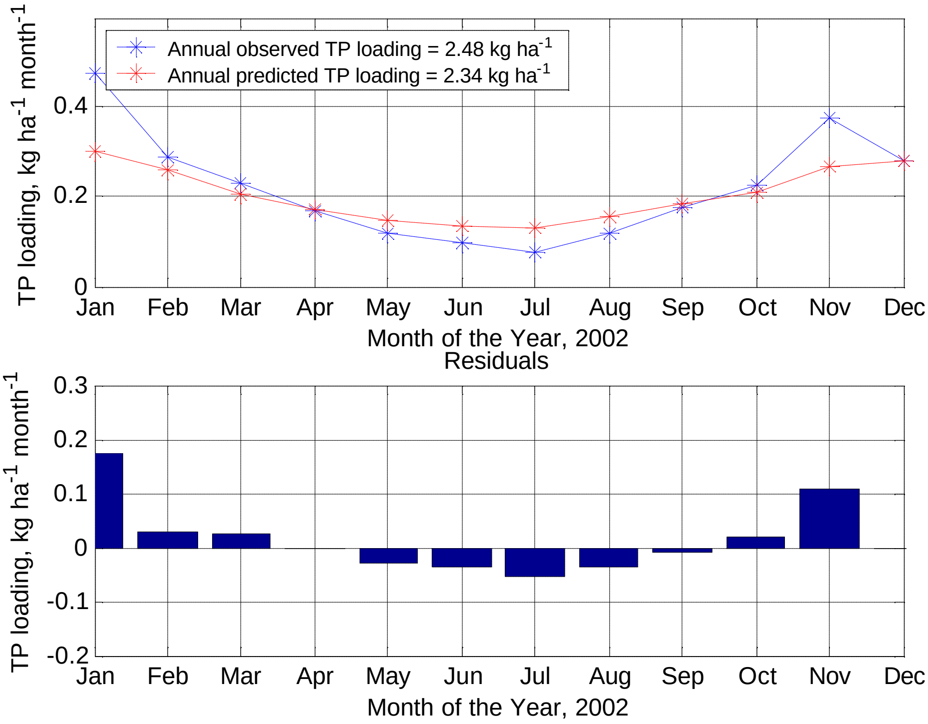

***Figure 5.13** Comparison between the observed and predicted monthly TP export of site 3. The residuals are also shown.*

The observed cumulative annual TP export for site 3 was 2.48 kg ha^{-1} where the model estimated is 2.37 kg ha^{-1}.However in site 3 maximum differences were observed for the months of January and November with under prediction of 36% and 23%, respectively. On the other hand the predicted monthly TP exports in the spring and summer months are slightly higher than the observed values.

5.5. Verification of the model

To verify the phosphorous export coefficient model we applied the model (5.7) to the farm scale catchment, site 1 (area 17 ha). The results are shown in Figure 5.14. The observed cumulative annual TP export for site 1 in 2002 was 2.68 kg ha^{-1} where the model estimated is 2.34 kg ha^{-1}. Figure 5.14 shows that the model gives accurate estimation of TP export for January to April and August. On the other hand the model over estimated the TP exports for June and July; and under estimated for the months of September to December. We consider this monthly model simple at this stage. We expect to reform it and improve the time step in the future.

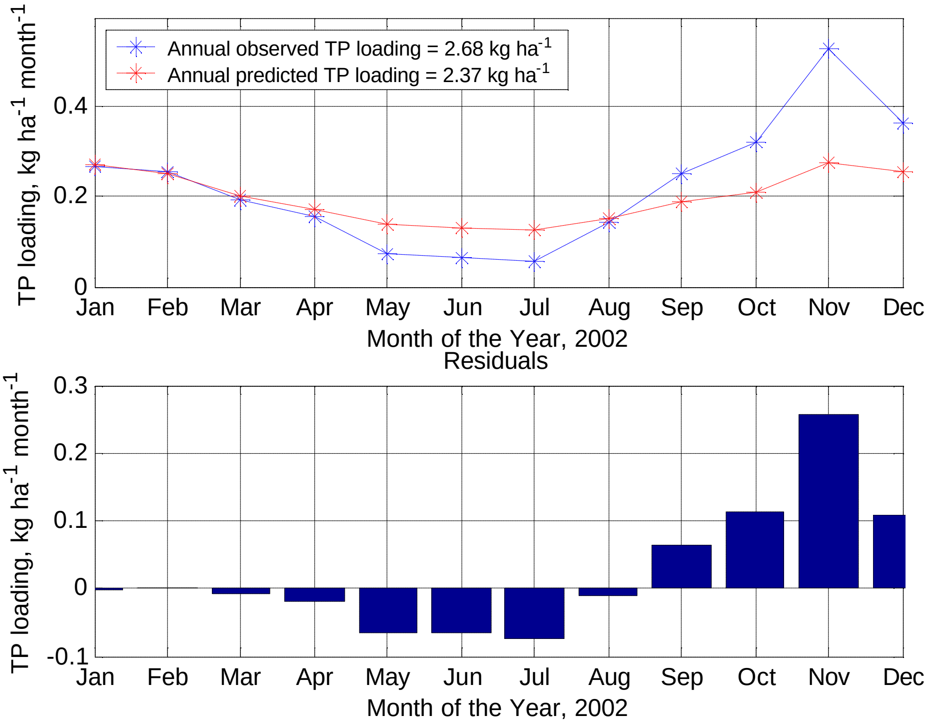

Figure 5.14 *Comparison between the observed and predicted monthly TP export at site 1.*

5.6. Some modelling scenarios

The model is applied for the following scenarios to predict the behaviour of TP-export at site 1 and site 3.

5.6.1. Scenario 1: If no slurry was applied in 2002

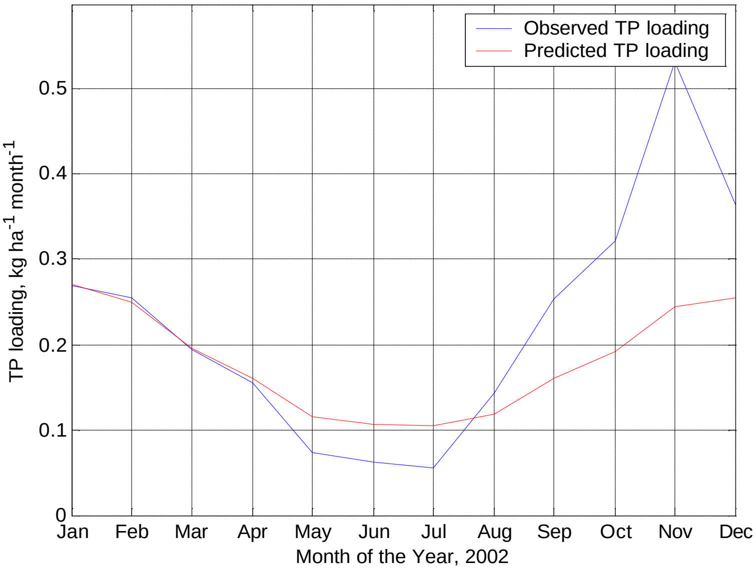

Figure 5.15 *Scenario 1, if no slurry was applied in 2002 at site 1.*

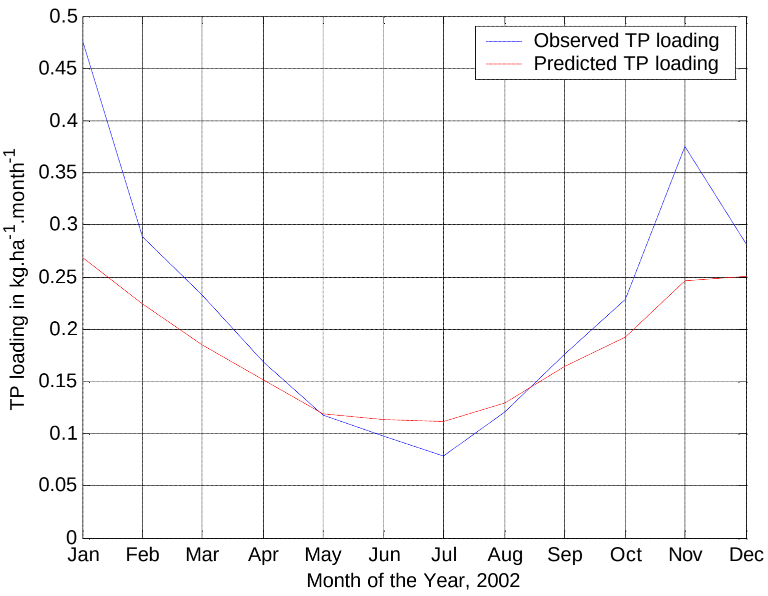

Figure 5.16 *Scenario 1, if no slurry was applied in 2002 at site 3.*

Without any slurry application in 2002 at site 1 and 3 the predicted annual TP exports are 2.14 and 2.1 kg ha^{-1} respectively. These values are 9% and 11% lower respectively than the predicted values with slurry application for the sites (Figures 5.15 and 5.16). This indicates that around 9% and 11% of the total annual TP export in site 1 and 3 respectively were caused by the slurry application.

5.6.2. Scenario 2: If no chemical fertilizer was applied in 2002

The predicted annual TP exports in 2002 at site 1 and 3 without any fertilizer application are 2.23 and 2.2 kg ha^{-1} which are 5% and 7% respectively lower than the

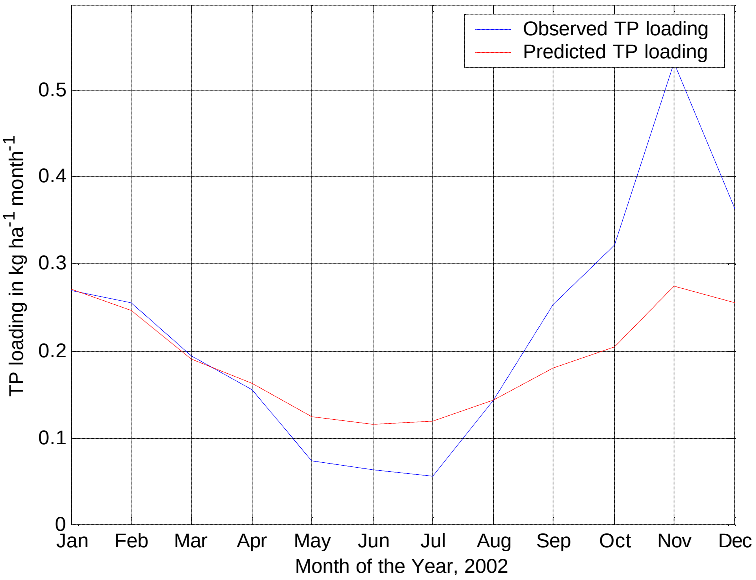

Figure 5.17 *Scenario 2, if no fertilizer was applied in 2002 at site 1.*

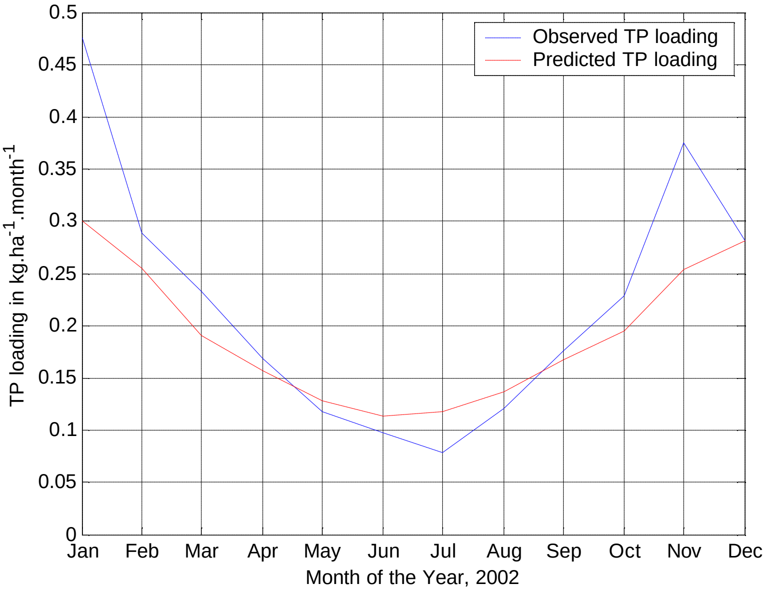

Figure 5.18 *Scenario 2, if no fertilizer was applied in 2002 at site 3.*

predicted values with fertilizer application (Figures 5.17 and 5.18). This indicates that around 5% and 7% of the total annual export were caused by the fertilizer application in site 1 and 3 respectively. It should be noted that, while the annual fertilizer application rate was twice the slurry application rate, the annual TP export caused by the fertilizer application rate is lower than by the slurry application.

5.6.3. Scenario 3: If fertilizer application rate was reduced by 25% in each month in 2002

For a reduction of fertilizer application by 25% in each month of the year 2002 the

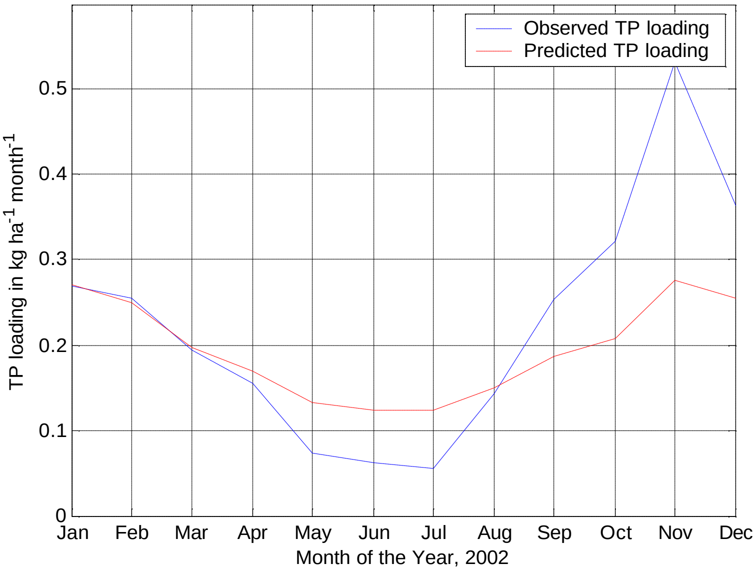

Figure 5.19 *Scenario 3, if fertilizer application was reduced by 25% in each month in 2002 at site 1.*

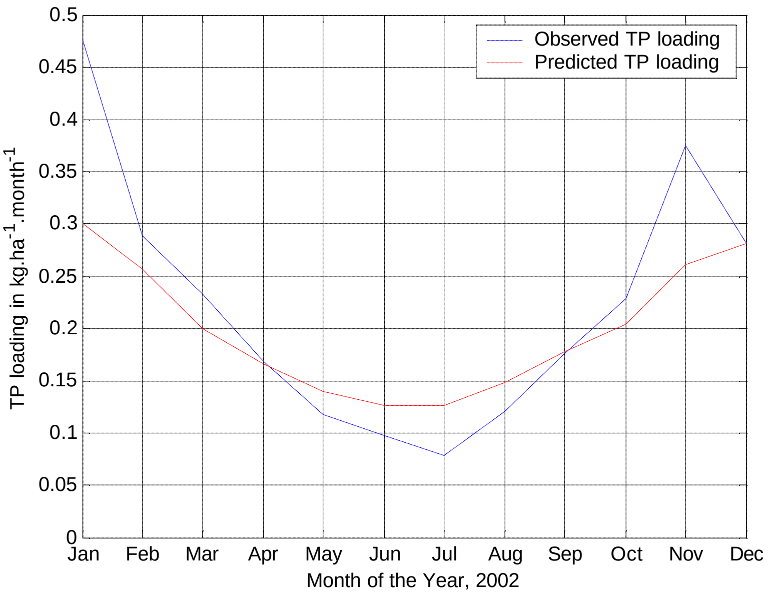

Figure 5.20 *Scenario 3, if fertilizer application was reduced by 25% in each month of the year 2002 at site 3.*

predicted annual TP export for site 1 and 3 are respectively 2.3 and 2.29 kg ha^{-1} (Figures 5.19 and 5.20). This illustrates that a reduction in fertilizer application in each month results a slight decrease in annual TP export.

5.6.4. Scenario 4: If fertilizer application rate was reduced by 50% in each month of the year 2002

For a reduction of fertilizer application by 50% in each month of the year 2002 the

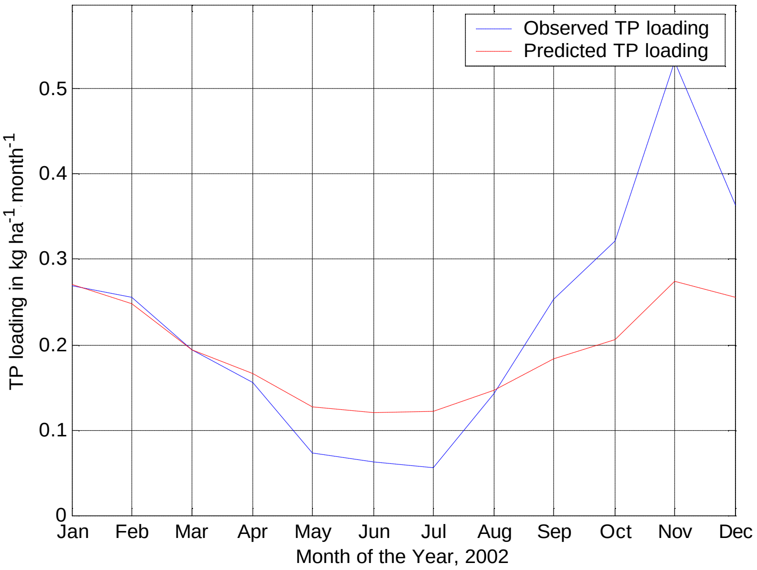

Figure 5.21 *Scenario 4, if fertilizer application rate was reduced by 50% in each month of the year 2002 at site 1.*

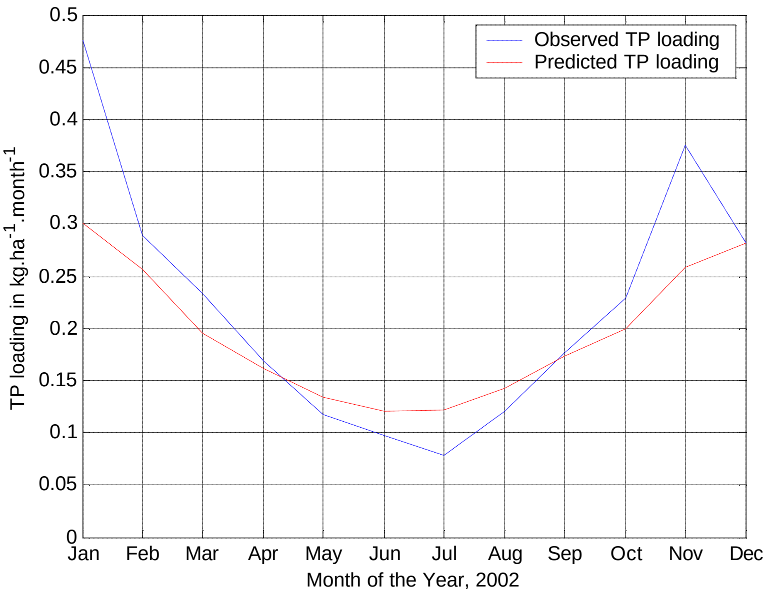

Figure 5.22 *Scenario 4, if fertilizer application rate was reduced by 50% in each month of the year 2002 at site 3.*

predicted annual TP export for site 1 and 3 are respectively 2.28 and 2.25 kg ha^{-1} (Figures 5.21 and 5.22). This illustrates that even if a significant reduction in fertilizer application does not reduce the annual TP export that much.

5.6.5. Scenario 5: If subsurface flow was reduced by 25% in each month in 2002

For a reduction of sub surface runoff by 25% in each month of the year 2002 the

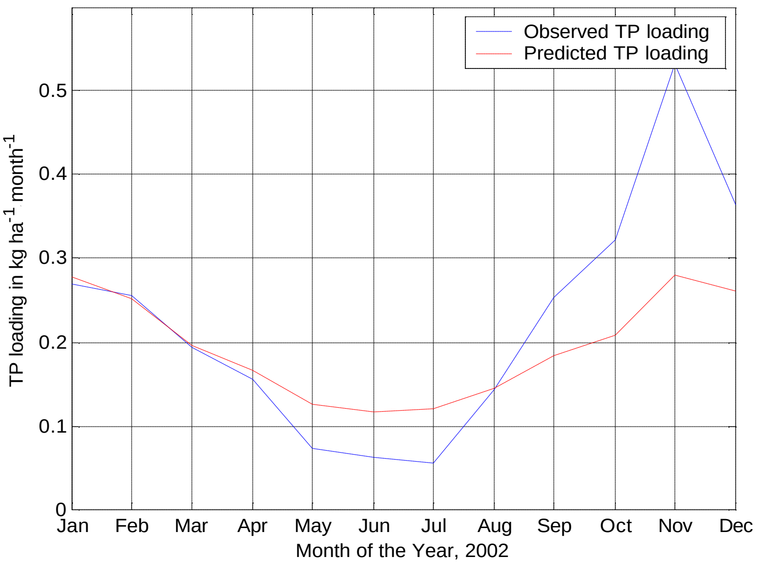

Figure 5.23 *Scenario 5, if sub-surface flow was reduced by 25% in each month over the year 2002 at site 1.*

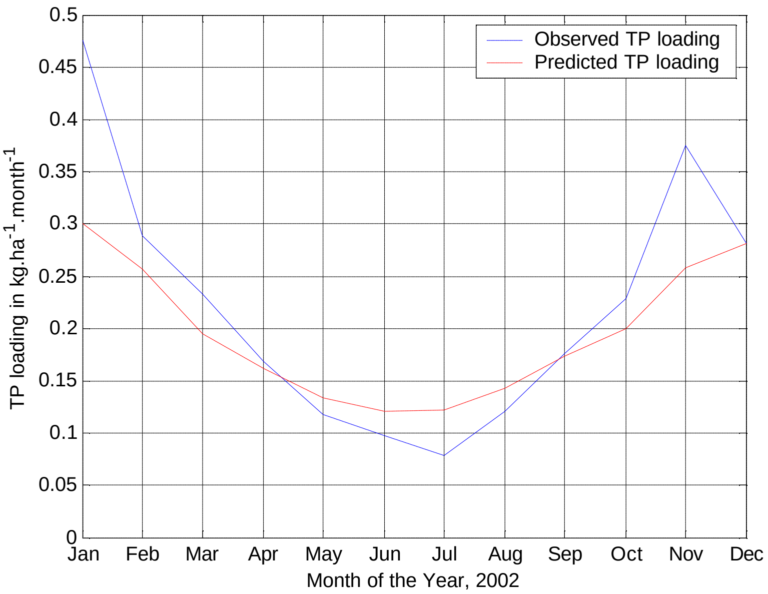

Figure 5.24 *Scenario 5, if subsurface flow was reduced by 25% in each month in 2002 at site 3.*

predicted annual TP export for site 1 and 3 are respectively 2.28 and 2.28 kg ha^{-1} (Figures 5.23 and 5.24).

5.6.6. Scenario 6: If surface and sub-surface flow were reduced by 50% in January, February and October to December in 2002

For a 50% reduction in the surface and subsurface runoff in January, February and October to December in 2002 the annual predicted TP export for site 1 and 3 are 1.97

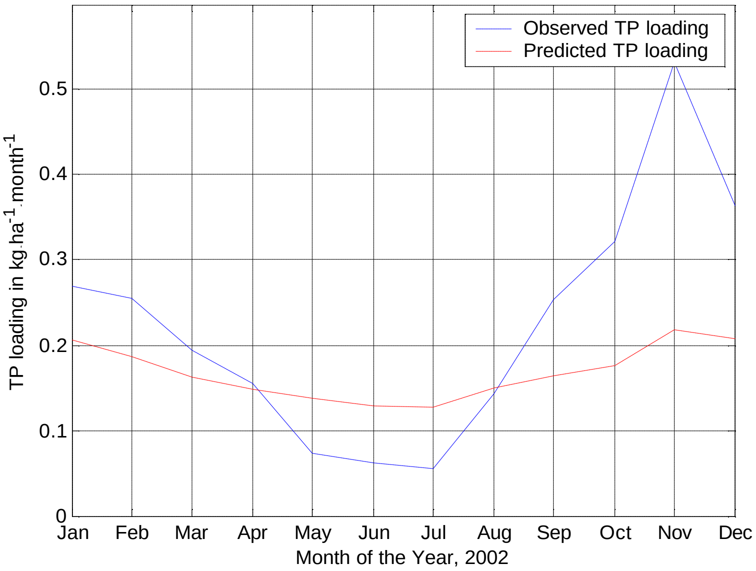

Figure 5.25 *Scenario 6, if surface and sub-surface flow were reduced by 50% in January, February and October to December in 2002 in site 1.*

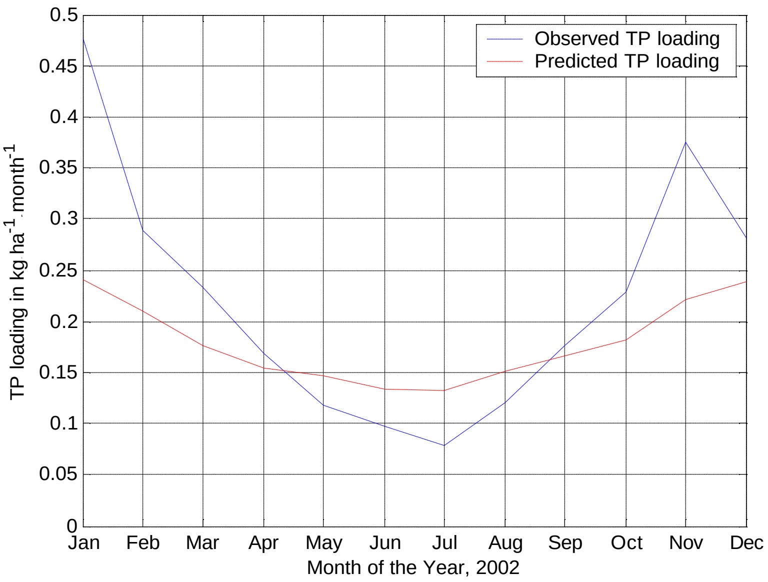

Figure 5.26 *Scenario 6, if surface and sub-surface flow were reduced by 50% in January, February and October to December in 2002 in site 3.*

and 2.08 kg ha^{-1} respectively (Figures 5.25 and 5.26). These values are 16% and 12% lower than the predicted values with the existing surface and subsurface runoff.

5.7. Limitations of the model

The limitations of this model are:

1. This model is applicable for only the monthly time step.
2. From this study we found that the residual P from the previous applications may remain in the soil for a certain time and cause P export to the stream. This suggests that there was a time lag after the fertilizer application before its effects was noticeable in the stream. Since in this model the relationship between the monthly TP export and fertilizer application rate is less significantly correlated ($r^2 = 0.10$, $p < 0.5$), the time lag between fertilizer application and its associated export to the stream as P is not yet clear. The P from the fertiliser may enter the stream sometime after the application and this time may be from approximately one month to possibly years.

5.8. Model summary

The phosphorous export coefficient model is developed based on a simplistic approach using non linear regression analysis. The key parameters of the model are grass P uptake; slurry and fertilizer application rate; evapotranspiration; and surface and subsurface runoff. Grass P uptake and evapotranspiration are negatively correlated with phosphorous export. Slurry and fertilizer application rate are positively correlated with phosphorous export. Surface and subsurface runoff are positively correlated with the TP export. Here it was assumed that the amounts of phosphorous transported from the catchment are a function of catchment hydrology, in terms of surface and subsurface runoff and the amount of P added as fertilizer and slurry. The model was calibrated using the results of site 3 (catchment area 211 ha) and verified by applying to site 1 (catchment area 17 ha). The model is in a monthly time step and showed similar results as the observed data.

5.9. Scenarios summary

The results of the scenarios can be summarised as:

1. No slurry application over the year 2002 reduces the annual TP export by 11% in site 3.
2. No chemical fertilizer application over the year 2002 reduces the annual TP export by approximately 7% in site 3.
3. A reduction in fertilizer application by 25% in each month in 2002 reduces the annual TP export by 3%.
4. A reduction in fertilizer application by 50% in each month in 2002 reduces the annual TP export by 5%
5. A reduction in subsurface flow by 25% in each month of the year 2002 reduces the TP export by approximately 4%.
6. Finally a reduction in surface and subsurface runoff by 50% in January, February and October to December reduces the annual TP export by 12%.

The above scenarios are assumed linear (the model assumes equal weight to each parameter). If we stop slurry spreading, stop fertilizer application and reduce the runoff by 25% (to simulate an average year) the model predicts a reduction in phosphorus export of 22%. For the year 2002, the annual TP export would reduce from 2.48 kg P ha^{-1} to 1.9 kg P ha^{-1}. This improvement is not enough to attain the recommended water quality standard of approximately 0.5 kg P ha^{-1}. This suggests that any remedial measures will be required to be long term (may be one or two decades). The above analyses also suggest that the high reservoir P in the soil is central to the problem of P loss from soil to water.

Chapter 6: Conclusions and Recommendations

6.1. Summary of the soil phosphorous test and degree of soil phosphorous saturation

To understand the spatial variability of the soil phosphorous concentration in the catchment, the *STP* level of the 117 fields for two was examined. Two separate methods (P_index and *DSSP*) were developed based on the Morgan's soil P level to better understand the soil P level. The use of the soil P index provides a crude means of identifying the fields that have a low or moderate potential for P loss to surface water, as well as fields that have a high risk of P loss which require limiting the manure and fertilizer application. In our study except for a slight decrease in the percentage of fields with P_index 4, no significant change was found between the soil P_index level of 1993 and 2002. In 2002 almost half of the fields (42%) have a P index of 4 which is above the agronomic requirements and has potential to cause P loss from soil to water. The highest soil test P results are in fields closest to the stream. The existence of high soil P in the fields near the stream is likely to be one of the contributing causes of high P loss from soil to water. A pedotransfer function based on Morgan's P was developed to measure the phosphorous saturation level relative to the 25% P saturation capacity of the fields. The degree of P soil saturation describes the potential of soil to DP loss in runoff and also helps to predict how much of the P added in fertilizers and slurries will be retained by the soil in a form that is resistant to loss in surface runoff.

6.2. Summary of the phosphorous budget modelling

The annual phosphorous budgets for each of the farms were estimated for the year 2002. The phosphorous budgets of the pasture and silage farms were estimated using two different conceptual models based on the existing management practices and the phosphorous cycle. The annual inputs (fertilizer, slurry, excreta, food concentrates) and outputs (P uptake by grass and P export to the stream) of the phosphorous for each farm was estimated based on the available data. For four of the eight farms, the annual soil P surplus was greater than 18 kg P ha^{-1} $year^{-1}$. The mean annual P surplus is 17 kg P ha^{-1} $year^{-1}$.This indicates an intensive practice of fertilizer within the catchment in excess of grass growth requirement. Furthermore based on the existing soil P level and annual phosphorous application to each field the critical P source areas within the catchment were identified. The area average soil P level and P surplus for each farm was compared but no significant relationship has been found between the soil P level and P surplus.

6.3. Summary of the phosphorous export modelling

A phosphorus export coefficient model was developed based on the management and hydrological parameters that significantly influence the phosphorous export process. The parameters of the model are phosphorous uptake by grass, fertilizer application rate, slurry application rate, evapotranspiration, surface runoff, and sub surface runoff. Where phosphorous uptake by grass and evapotranspiration are negatively and slurry and fertilizer application rate, surface and sub surface runoff are positively correlated with the TP export from the soil. The model was calibrated using the results of site 3 (catchment area 211 ha) and verified by applying to site 1 (catchment area 17 ha). The model shows similar results as the observed data. Scenarios of remedial measures were modelled and the results of the model are presented in section 5.6.

6.4. Conclusions

3. For 2002, about 42% of the fields had a Morgan's P level of greater than 10 mg l^{-1}. In 1993, the percentage was 48%.
4. The fields with a higher soil P level are located close to the stream.
5. The soil texture in Dripsey is a stony gravel loam which has a propensity for its soil moisture to drain more rapidly than the peaty soil texture.
6. The national annual average of P in fertilizer application is 12 kg P ha^{-1} for pasture fields. The corresponding application (mean annual catchment average) in Dripsey for 2002 was 25 kg P ha^{-1}.
7. In this study, we did not measure any farmyard runoff. Therefore, the relative phosphorous contribution of the yards and the fields were not taken into account in this study.
8. In the soil P budget analysis for the farms, four of the eight farms have a P surplus in excess of 18 kg P ha^{-1} and are deemed as risk of P loss.
9. A simple phosphorous export coefficient model was developed which reasonably predicts the phosphorous exports for site 1 and 3.
10. We use the export coefficient model to evaluate remedial scenarios. This suggests that if no fertilizer and slurry was applied and the subsurface runoff was reduced by 25% (in each month over the year 2002) the annual phosphorous export would only be reduced by 22%. This indicates that a significant amount of phosphorous is exported from the existing high soil phosphorous reservoir.
11. To reduce the annual export from 2.48 kg P ha^{-1} to 0.5 kg P ha^{-1} the reduction in the soil P level is required. The process of P build up in soil to

its current levels of 10 mg l^{-1} Morgan’s P has taken approximately two decades. The reduction to sustainable level of, 8 mg l^{-1} will likely take a decade of fertilizer applications well below current rates.

6.5. Recommendations

High soil P is not only a long term source of P export but also accelerates the P export from current fertilizer application. The focus to control phosphorous export should be farm management strategies for fertilizer and slurry applications so as to reduce the immediate loss of phosphorous as well as the decrease the soil P concentration level. It is recommended that:

1. No slurry to be spread is recommended during the winter months (February to October).
2. The fertilizer application should be based on the existing soil P level in each field.

6.6. Suggestions for further research

Suggestions for further research include:

1. To develop a P_index with multiple parameters, e.g. Morgan’s P, rainfall, fertilizer and slurry application rate, distance from the stream and LU ha^{-1}.
2. Extend the research of this thesis to the 1524 ha catchment (47 farms).
3. Improve the phosphorous export coefficient model.

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Appendix

Appendix A: Glossary of Terms

Base discharge (for peak discharge)

-Is a discharge value, determined for selected stations, above which peak discharge data are published. The base discharge at each station is selected so that an average of about three peak flows per year will be published. See also *Peak flow.*

Base flow

-Streamflow which results from precipitation that infiltrates into the soil and eventually moves through the soil to the stream channel. This is also referred to as ground water flow, or dry-weather flow.

Base width

-The time duration of a unit hydrograph.

Catchment

-An area of land, bounded by a *divide*, in which water flowing across the surface will drain into a stream or river and flow out of the area through a specified point on that stream or river.

Catchment area

-An area having a common outlet for its surface runoff. Also see *Drainage Area or Basin*, *Watershed.*

Direct Runoff

-The runoff entering stream channels promptly after rainfall or snowmelt. Superposed on base runoff, it forms the bulk of the hydrograph of a flood.

Discharge

-Or flow, is the rate that matter passes through a cross section of a stream channel or other water body per unit of time. The term commonly refers to the volume of water (including, unless otherwise stated, any sediment or other constituents suspended or dissolved in the water) that passes a cross section in a stream channel, canal, pipeline, etc., within a given period of time (cubic feet per second). Discharge also can apply to the rate at which constituents, such as suspended sediment, bedload, and dissolved or suspended chemicals, pass through a cross section, in which cases the quantity is expressed as the mass of constituent that passes the cross section in a given period of time (tons per day).

Discharge curve

-A curve that expresses the relation between the discharge of a stream or open conduit at a given location and the stage or elevation of the liquid surface at or near that location. Also called Rating Curve and Discharge Rating Curve.

Discharge table

-A table showing the relation between two mutually dependant quantities or variable over a given range of magnitude.

Total Dissolved Phosphorus (TDP)

-Phosphorus form present in water that had been filtered through 0.45 µm membrane then subjected to oxidative digestion process (APHA, 1989). Includes both dissolved organic and inorganic P.

Distribution (hydro) graph

-A unit hydrograph of direct runoff modified to show the proportions of the volume of runoff that occur during successive equal units of time.

Evaporation

-Process by which liquid water is converted into water vapor.

Evapotranspiration

-Combination of evaporation from free water surfaces and transpiration of water from plant surfaces to the atmosphere.

Ground water flow

-Streamflow which results from precipitation that infiltrates into the soil and eventually moves through the soil to the stream channel. This is also referred to as baseflow, or dry-weather flow.

Hydrograph

-A graph showing the water level (stage), discharge, or other property of a river volume with respect to time.

Hydrograph separation

-The process where the storm hydrograph is separated into baseflow components and surface runoff components.

Hydrologic cycle

-The natural pathway water follows as it changes between liquid, solid, and gaseous states.

Hydrologic unit

-Is a geographic area representing part or all of a surface drainage basin or distinct hydrologic feature as defined by the former Office of Water Data Coordination and delineated on the State Hydrologic Unit Maps by the USGS. Each hydrologic unit is identified by an 8-digit number.

Infiltration

-Movement of water through the soil surface into the soil.

Infiltration capacity

-The maximum rate at which water can enter the soil at a particular point under a given set of conditions.

Interception

-The process by which precipitation is caught and held by foliage, twigs, and branches of trees, shrubs, and other vegetation, and lost by evaporation, never reaching the surface of the ground. Interception equals the precipitation on the vegetation minus streamflow and through fall.

Nonpoint-source water pollution

-Water contamination that originates from a broad area (such as leaching of agricultural chemicals from crop land) and enters the water resource diffusely over a large area.

Nutrient

-Any inorganic or organic compound needed to sustain plant life.

Particulate Phosphorus

-Phosphorus fraction that is adsorbed or absorbed on soil or sediment particles, and may be comprised of both organic and mineral forms. This fraction is usually quantified by subtracting total dissolved phosphorous (TDP) from TP.

Percolation

-The movement of water, under hydrostatic pressure, through the interstices of a rock or soil, except the movement through large openings such as caves.

Precipitation

-As used in hydrology, precipitation is the discharge of water, in a liquid or solid state, out of the atmosphere, generally onto a land or water surface. It is the common process by which atmospheric water becomes surface, or subsurface water. The term "precipitation" is also commonly used to designate the quantity of water that is precipitated. Precipitation includes rainfall, snow, hail, and sleet, and is therefore a more general term than rainfall.

Precipitation intensity

-[$L\ T^{-1}$], a measure of the rate of precipitation, commonly computed for a specified duration.

Runoff

-Is the quantity of water that is discharged ("runs off") from a drainage basin during a given time period. Runoff data may be presented as volumes in acre-feet, as mean discharges per unit of drainage area in cubic feet per second per square mile, or as depths of water on the drainage basin in inches. See also *Annual runoff*.

Saturated zone

-A subsurface zone in which all the interstices or voids are filled with water under pressure greater than that of the atmosphere. See also *Water table*.

Skew ness

-Numerical measure of the lack of symmetry of an asymmetrical frequency distribution.

Soil moisture

-Water contained in the upper regions near the earth’s surface.

Soil-water content

-Is the water lost from the soil upon drying to constant mass at 105 °C; expressed either as mass of water per unit mass of dry soil or as the volume of water per unit bulk volume of soil.

Soluble reactive Phosphate (SRP)

-Phosphorus form that responds to colorimetric test without preliminary hydrolysis or digestion. Although reactive phosphate is comprised largely of orthophosphates, it may include easily hydrolysable inorganic and organic forms of P (APHA, 1989, Baldwin, (1998).

Stream/channel inflow

-Water, which at any instant, is flowing into the channel system form surface flow, subsurface flow, base flow, and rainfall that has directly fallen onto the channel.

Streamflow

-Is the discharge that occurs in a natural channel. Although the term "discharge" can be applied to the flow of a canal, the word "streamflow" uniquely describes the discharge in a surface stream course. The term "streamflow" is more general than "runoff" as streamflow may be applied to discharge whether or not it is affected by diversion or regulation.

Surface runoff

-The runoff that travels overland to the stream channel. Rain that falls on the stream channel is often lumped with this quantity.

Tipping-bucket rain gauge

-A precipitation gage where collected water is funneled into a two compartment bucket; 0.01, 0.1 mm, or some other designed quantity of rain will fill one compartment and overbalance the bucket so that it tips, emptying into a reservoir and moving the second compartment into place beneath the funnel. As the bucket is tipped, it actuates an electric circuit.

Topography

-The general configuration of a land surface or any part of the Earth's surface, including its relief and the position of its natural and man-made features.

Total phosphorous (TP)

- The amount of total phosphorous detected in the sample. The forms of phosphorous: dissolved phosphorous, particulate phosphorous, soluble reactive phosphorous etc.

Appendix B: Matlab program for base flow separation

```
% BFI 18 Hour Site 03.m
% DESCRIPTION:
% Empirical method used in our study to separate
% baseflow from stream hydrograph

clear all

%
% Site 3 flow data for '02.
%

s3=load('S1234_flow_1_365_02.csv')
jd=s3(:,1);                   %0.0104 Julian Days
ave15min02=s3(:,4);           %Flow 2002
min_15(1:35041) = 1:35041;

%
%Load all Rainfall Files for Site 1
%
s1_02=load('ra30_02.csv');

%Year 2002
ra_02       = s1_02(:,5)
cum02       = cumsum(ra_02);
jd1         = s1_02(:,3)
Time        = s1_02(:,4)
hr          = round(Time/100)
min1        = Time - hr*100
dhrmin      = jd1 + hr/24 + min1/60/24
for k       = 1:730
    min24_hour02(k)     = min(ave15min02(48*(k-1)+1:(48*k)));
    hour(k)             =k;
end

counter = 1;
for k=1:728
      if(min24_hour02(k+1)*0.9<min24_hour02(k))&
      (min24_hour02(k+1)*0.9 < min24_hour02(k+2));
            QB(counter) = min24_hour02(k+1);
            for j=(((k*48)+1):((k*48)+48))
                  if (QB(counter)==ave15min02(j))
```

```
                        lowflow_15min(counter) = j;
                  end
            end
                  counter = counter+1;
      end
end

counter                 = length(lowflow_15min);

first_lowflow_15min     = lowflow_15min(1);
last_lowflow_15min      = lowflow_15min(counter);

for i=1:counter-1
      inter(i) = lowflow_15min(i+1)-lowflow_15min(i);
end

for a=2:counter
      avgQB(a-1)  = ((QB(a-1) + QB(a))/2);
      prod(a-1)   = avgQB(a-1)*inter(a-1);
end

Baseflow_Volume   = sum(prod);
Total_volume=
sum(ave15min02(first_lowflow_15min:1:last_lowflow_15min))

bf(1)= sum(prod(1:43))/211;
bf(2) = sum(prod(44:84))/211;
bf(3) = sum(prod(85:140))/211;
bf(4)= sum(prod(141:187))/211;
bf(5) = sum(prod(188:237))/211;
bf(6)= sum(prod(238:290))/211;
bf(7) = sum(prod(291:349))/211;
bf(8) = sum(prod(350:395))/211;
bf(9) = sum(prod(396:446))/211;
bf(10) = sum(prod(447:484))/211;
bf(11) = sum(prod(485:529))/211;
bf(12) = sum(prod(530:577))/211;

%csvwrite('MeanResults.csv',QB);
%csvwrite('MeanResults.csv',                              inter);
```

```
min_15            = min_15/96;
lowflow_15min     = lowflow_15min/96;

figure(1);
plot(min_15,ave15min02,'k');
hold on;
plot(lowflow_15min,QB,'k');
hold on;
area(lowflow_15min,QB,'FaceColor','b');
title('Total Stream Flow and Base Flow for Site 3, 2002')
xlabel('Julian Days of Year 2002');
ylabel('Flow Rate in Liter.Sce^-^1');
grid on;

month       = 1:1:12
figure(2)
bar(month, bf)
xlabel('Months of the Year 2002');
ylabel('Base flow in m^3.ha^-^1.month^-^1');
set(gca,'XTick',[1 2 3 4 5 6 7 8 9 10 11 12])
set(gca,'XTickLabel','Jan|Feb|Mar|Apr|May|Jun|Jul|Aug|Sep|Oct|Nov
|Dec')
title('Monthly base flow for 2002')
grid on;

%*****************************************************************
% Part two
% Estimate daily runoff from the value
% of stream flow and baseflow
%*****************************************************************

xi1   = 1:365;
yi1   = interp1(min_15, ave15min02, xi1);

%
% Estimate julianday baseflow data
%

xi2   = 1:365;
```

```
yi2   = interp1(lowflow_15min, QB, xi2);

%
% Determine runoff data from the difference
% of julian day streamflow and
% baseflow data

for i = 1:365
runoff(i) = yi1(i) - yi2(i)
end

%************************************************************
figure(3);
subplot(2, 1, 1),plot(min_15,ave15min02,'b');
hold on;
plot(xi2,yi2,'k');
xlabel('Julian Days of Year 2002');
ylabel('Flow Rate in Liter.Sce^-^1');
legend('Stream Flow','Baseflow');
title('Total Stream Flow and Base Flow for Site 3, 2002')
hold on;
grid on

subplot(2, 1, 2),plot(min_15,ave15min02,'b');
hold on
plot(xi2,runoff,'r');
xlabel('Julian Days of Year 2002');
ylabel('Flow Rate in Liter.Sce^-^1');
axis([0 400 0 800])
grid on;
legend('Stream Flow','Runoff');
title('Total Stream Flow and Runoff for Site 3, 2002')
```

Appendix C: Fertilizer application

Month of year, 2002	**Fertilizer type**
January	_
February	N:P:k (0:7:30)
March	N:P:k (27:2.5:5), N:P:k (24:5:5), N:P:k (24:2.5:10)
April	N:P:k (27:2.5:5), N:P:k (24:2.5:10), N:P:k (0:7:30)
May	N:P:k (27:2.5:5)
June	N:P:k (27:2.5:5), N:P:k (24:2.5:10)
July	N:P:k (27:2.5:5), N:P :k (24:5:5), N:P:k (24:2.5:10), N:P:k (23:2.5:5),
August	N:P:k (27:2.5:5), N:P:k (24:5:5)
September	N:P:k (27:2.5:5),
October	_
November	_
December	_

Appendix D: Complimentary Presentation

Phosphorus balance of a grassland subject to chemical and manure fertilizer

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Introduction

In areas of intensive agricultural production, manure applications together with P-fertilizer lead to excess P additions, and a consequent surplus of P in the soil (Hooda et al, 2001). Such land management systems can result in an increased loss of P from soil to water that may contribute to eutrophication of freshwaters (Sharpley et al, 1994). Long term P surpluses lead to P accumulation in soil, elevating the soil P test level (STP, e.g. Morgan's P). The effects of long-term P surpluses are: a reduction in the soil P-sorption capacit and an increase in the degree of soil P saturation (DSSP) Hooda et al (2001). The national P budget for Ireland shows a surplus of P of around 30,000 tonnes per year with a continued upward trend of STP (Tunney, 2002). As part of a project to understand the processes of P loss from soil to water, this study examines, in an intensive grassland catchment (2.1 km2), the P loading from chemical and manure fertilization for one year, the STP levels in 127 fields and the Phosphorus load in the stream. The soil P index based on Morgan's P is used to predict the potential for P loss to surface and ground waters. A pedotransfer function based on Morgan's soil P and the degree of soil P saturation is derived to measure the soil's remaining capacity to bind soluble P additions.
Our specific objectives are: (1) to quantify the soil phosphorous budget of eight farms consisting of 127 fields and (2) to examine the impact of the soil P level and the degree of phosphorous saturation on the stream water quality.

Study Area

The study area is located 25 km north-west of Cork, Ireland (Latitude: 52.14ºN, Longitude: 8.66ºW). The catchment 211 ha (consists of eight farms) is part of the Dripsey upland tributary of the river Lee which flows through Cork city. Five of the farms are mixed dairy and beef, two are silage production for export and one farm is sheep only. The hill slopes to the stream with gradients ranging from 1% to 7%. Elevation ranges from about 250 m (metres above sea level) in the upstream end to 160 m in the downstream end (See Figure 1a). The topography of the Dripsey catchment as 3D-surface is shown in Fig. 1b. The mean annual precipitation in the catchment is approximately 1470 mm. The range of monthly temperature is 5ºC in December and January to 15ºC in July and August. The soil is broadly classified as brown-grey podzols. The grassland type is moderately high quality pasture and meadow, with perennial ryegrass being the dominant plant species. This is representative of the land use and vegetation in this part of the county.

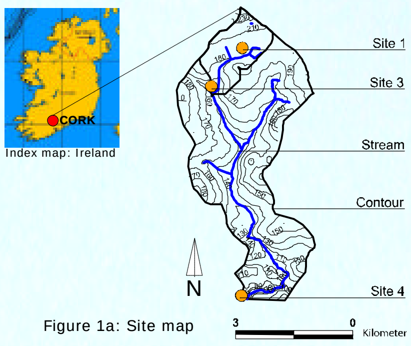

Figure 1a: Site map

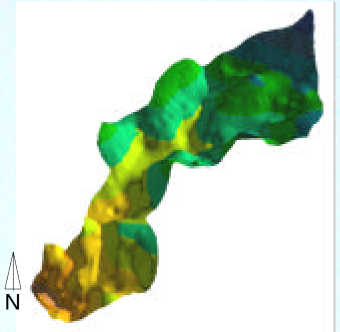

Figure 1B: 3D surface map

Methods

Data on chemical fertilizer and manure application rates of the seven farms were collected over the year 2002. Stream discharge, water chemistry samples (composite flow weighted and grab samples) at the outlets of the Catchment and soil samples from the 117 fields were collected for the study year.
Total phosphorous and Morgan's soil P were determined from the collected water and soil samples respectively. Composite water samples were taken throughout the year and covered 43% of full year. Phosphorous concentrations in the stream for the remaining time period of year (57%) were estimated from the concentration-discharge (C-Q) relationships:

$$C = aQ^b \qquad (1)$$

Where, C = TP loadings, Q = discharge (mm hr^{-1}), b and a are constants which were used to describe the observed variations in stream water phosphorous concentrations as a function of discharge. Total Phosphorous concentration was derived from the log-transformed data.
The P sorption capacity (PSC) and DSSP (Psat$_{ox}$) are calculated as

$$PSC = a*(Fe_{ox} + Al_{ox})/100 \qquad (\%) \qquad (2)$$

$$Psat_{ox} = P_{ox}/PSC \qquad (\%) \qquad (3)$$

Where, PSC = P sorption capacity, Fe$_{ox}$ = Oxalate extractable Fe, Al$_{ox}$ = Oxalate extractable Al, P$_{ox}$ = Oxalate extractable P and Psat$_{ox}$ = percentage Pox accounting for the quantity of P in the soil. The coefficient estimates the fraction of Fe$_{ox}$ and Al$_{ox}$, a = 0.5.

The conceptual phosphorous budgets model of the pasture and silage farms are shown in Fig. 2a and Fig. 2b.

Phosphorous Flow Chart

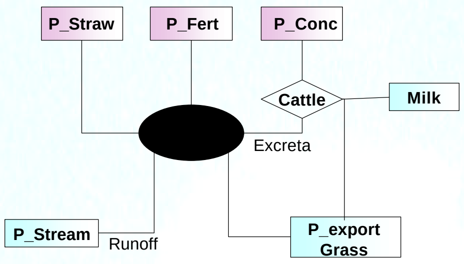

Figure 2a: P flow diagram of pasture farms.

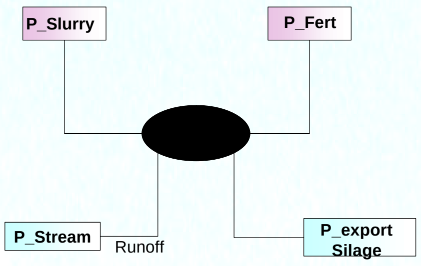

Figure 2b: P flow diagram of silage farms.

Phosphorous budgets for pasture farms and silage farms are estimated based on the equation (4a) and (4b) respectively.

$$\text{Pasture: } SPBp = (F + E) - (St + G) \qquad (\text{kg P ha}^{-1}) \qquad (4a)$$

$$\text{Silage: } SPBp = (F + Sl) - (St + Si) \qquad (\text{kg P ha}^{-1}) \qquad (4b)$$

Where, SPBp = annual soil phosphorous surplus or deficiency, F = chemical fertilizer, E = excreta, Sl = slurry application, St = P loss to stream, G = P uptake by grass and Si = P uptake by silage.

Results and Discussion

Soil P Index for 1993 and 2002

The soil P index of the individual fields within the catchment (for 1993) is shown in Fig. 3a. and those for the year 2002 are shown in figure 3b. It is notable that the soil P Index in 2002 (Fig. 3b), has a similar distribution to that of 1993. The soil P level at index 4 has fallen by 5% (47.6% to 42.3%) suggesting a minor improvement of P application over the past nine years (Table.1). Comparing Fig. 3a and 3b it is seen that that the decrease in percentage soils in index 4 (from 1993 to 2002) is replaced by the rise in percentage in index 3 (46%).

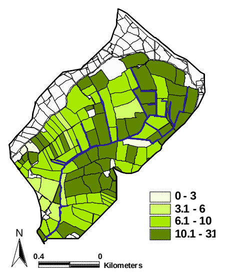

Figure 3a:Soil P_Index in 1993

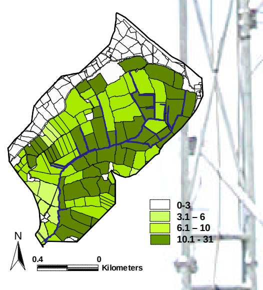

Figure 3b:Soil P_Index in 2002

There is no substantial change in soil P index between the years 1993 and 2002. This indicates that there has been no phosphorous deficiency or surplus over the nine years within the catchment. The evident feature in our study is the trend of high soil P index fields close to the stream. These fields are rich in organic matter and have relatively high P sorption capacity. Despite having a high P sorption capacity, the soils of these fields are weekly bonded with P. In addition, as binding energy is negatively correlated with P desorption, these fields have a high level of P desorption to solution (Daly, 2003). As a result a high amount of P loss occurs from these fields.

Table 1: Areas of the catchment under different categories of P Index for 1993 and 2001.

P Index	Morgan's P(mg/l)	Area_1993 (ha)	%	Area_2002 (ha)	%
1	0 - 3	0	0	6.3	3.35
2	3.1 - 6	18.6	9.94	15.0	8.04
3	6.1 - 10	79.4	42.46	86.5	46.30
4	10.1 - 31	89.0	47.60	79.1	42.30
		187	*100*	*187*	*100*

Degree of saturation of soil P (DSSP)

In our study, a similar relationship based on 10 samples from the Cork catchment (Daly, 1999) is shown in Fig.4 and takes the form of equation (5)

$$Psat = 6.87 + 1.36\,Pm \qquad (r = 0.90) \qquad (5)$$

The PSC value of 25% corresponds to a Morgan's P value of 13.33 mg/l.

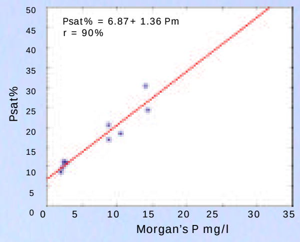

Figure 4: Relationship between Psat and Pm

Chemical fertilizer & slurry application rate

For the year 2002, in our catchment study the chemical fertilizer was applied from February to September with a range of monthly application of 1.3 to 4.4 kg P ha^{-1} (Fig. 5). In addition to chemical fertilizer, slurry has also been applied throughout the year except in April. The estimated monthly slurry rate ranges from 0.1 to 2.8 kg P ha^{-1} (Fig. 5). The annual P loading in chemical fertilizer of the 117 fields ranges from 0 to 55 kg ha^{-1} (Fig. 6a). The annual P loading in slurry ranges from 0 to 25 kg ha^{-1} (Fig. 6b). The total annual P application is 38 kg p ha^{-1} Year^{-1}.

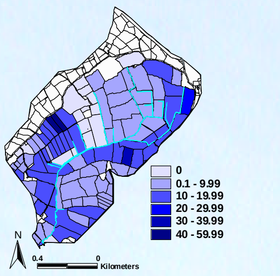

Figure 6a:Monthly chemical fertilizer application rate.

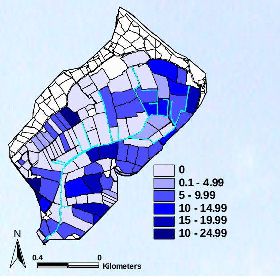

Figure 6b:Monthly slurry application rate.

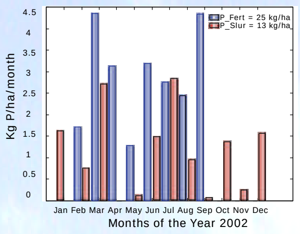

Figure 5: Monthly chemical fertilizer and slurry application rate

Phosphorous uptake by grass

The monthly phosphorous requirement of grass over the year is presented in Fig. 7. These results are based on data from a similar grassland ecological site (Teagasc, Moorepark, Co, Cork) close to the catchment for the year 2002. The data included weekly biomass yields in kg of dry matter per hectare, from February to November (nitrogen application rate of 150kg.N/ha). The monthly P uptake by grass varied from 0 to 7.5 kg ha-1 (depending on the season). The annual average P uptake is estimated at 32kg ha-1.

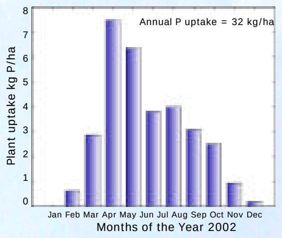

Figure 7: Monthly P uptake by grass

Total Phosphorous loading in the stream

Monthly TP loadings in the stream (Fig. 8a) range from 0 to 0.48 kg ha-1 (with a mean monthly loading of 0.2 kg ha-1). In our study an average monthly TP concentration of 0.22 mg/l is derived which is twice higher than the given threshold limits of 0.1 mg/l (by Irish EPA).

The cumulative flow and cumulative TP export to the stream is shown in Figure 8b. The export of TP of 2.48kg.P/ha is 9.9% of the chemical application rate (25kg.P/ha) or 6.6% of the chemical plus slurry (total = 38kg.P/ha) application rate.

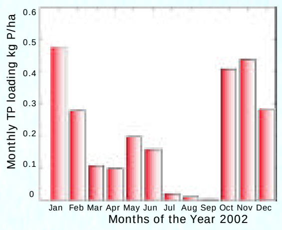

Figure 8a:Monthly TP loading in the stream

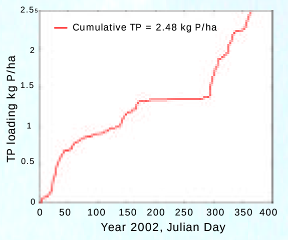

Figure 8b:Cumulative TP loading in 2002

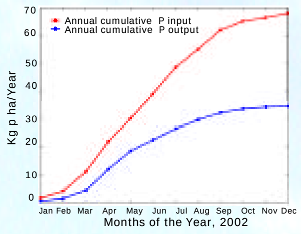

Figure 9: Annual cumulative input and output within the catchment

Soil Phosphorous balance

The annual P balances of the eight farms is shown in Table. 2. Four farms have a net surplus of more than 18 kg p ha-1 yr-1. The annual total P input and output is shown in Fig. This high surplus leads to P accumulation in soils as well as results in progressive saturation of the P-sorption capacity

Table 2: ▪ Annual Phosphorous soil balance (kg/ha) for eight farms

	Input (kg/ha/yr)						Output (kg/ha/yr)			Surplus(kg/ha/ yr)
Farm	P_fert	P_slur	P_conc	P_fodd	P_str	P_exceta	P_grass	P_stream	Tran_si.	
A	26.7	17.0	5.1	0	1.4	26.0	32	2.5	0	22.9
B	25.9	11.1	0.5	0.5	0	12.0	32	2.5	15.9	3.4
C	26.2	9.6	24.5	0.1	0.1	39.6	32	2.5	0	31.4
D	17.6	12.1	17.8	0.1	0.2	34.9	32	2.5	0	18.3
E	40.8	14.2	0	0	0	0	32	2.5	32	6.3
F	32.1	17.4	8.8	1.8	0.6	29.8	32	2.5	0	28.0
G	13.8	7.7	5.3	0	0	26.1	32	2.5	0	5.4
H	0	0	0	0	0	11.2	16	2.5	0	-7.3

* Since slurry includes yard excreta, slurry was not included in the P balance.
* Some amount of silage produced within the farm were transferred to other areas were included under column 11.

Conclusion

Management strategies with a more long-term perspective are now required to reduce this P accumulation in soil. We recommend a one year pilot project where the P fertilizer application might be reduced by say 20% and the effects on its soil P and stream water quality be assessed.

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Appendix E: Raw data files

Table A: The list of raw data files used in this thesis.

File name	**Description**	**Column 1**	**Column 2**	**Column 3**	**Column 4**	**Column 5**	**Column 6**	**Column 7**	**Column 9**
Soildepth_Morgan'sP_Papplication_xls	Morgan's P for different P applications.	Soil depth mm	Morgan's P for 0 $kg.ha^{-1}.yr^{-1}$application	Morgan's P for 15 $kg.ha^{-1}.yr^{-1}$ application	Morgan's P for 30 $kg.ha^{-1}.yr^{-1}$ application				
Stride_report.xls	Monthly TP export & flow in 1993 – 1994.			Monthly TP export $kg.ha^{-1}$			Monthly flow in mm		
ra30_02.csv	Rainfall calculation.			Julian day	Time	Rainfall in mm			
DSSP_03.xls	DSSP, Psat%, PSC calculation.	Sample no	Alox $mg.l^{-1}$	Feox $mg.l^{-1}$	Pox $mg.l^{-1}$	Psatox	Psat%	Morgan's P	DSSP
GKsoilP_fert_slurry_02.xls	Fertilizer and slurry application.	The titles of the columns are given in the file.							
Soil_P_Fert_Slur.xls	Total P application in fields.	Field no		Soil P 2002 $mg.l^{-1}$	P_fertilizer application $kg.ha^{-1}.yr^{-1}$	P_Slurry application $kg.ha^{-1}.yr^{-1}$			
Grass_New.xls	Monthly grass P	Month	Monthly						

	uptake		grass P uptake								
s1234_1_365_02.csv c1fill_02.xls s1234_1_365_02.csv c3fill_1_365_02.xls	TP export flow calculation for Site 1 & 3.										
Fert_Slurry_2may.xls	Monthly P budget calculation.	The titles of the columns are given in the file.									
SoilP_Surplus.xls	Surplus & soil P relationship.	Farm name	Farm Type	Farm soil P mg.l^{-1}	Farm P surplus kg.ha^{-1}						
S1234_flow_1_365 _02.xls	Base flow separation for site 1 and 3.	Julian day	Flow at site 1 in L.sec^{-1}		Flow at site 3 in L.sec^{-1}						
Correlation_Site3.xls	Correlation among parameters.	The titles of the columns are given in the file.									