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***Phosphorus, Nitrogen and Suspended Sediment  
loss from Soil to Water from  
Agricultural Grassland***

By

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### Statement

The water chemistry samples were collected and analysed in the laboratory of the aquatic services unit, Zoology dept. U.C.C. by Mr. Gerard Morgan and his colleagues.

## Terms used

TP	<i>Total Phosphorus</i> . Phosphorus occurs in natural water almost solely as phosphates. These are classified as orthophosphates, condensed phosphates (pyro-, meta-, and other polyphosphates), and organically bound phosphorus (ANON, 1985).
TDP	<i>Total Dissolved Phosphorus</i> . TDP is a measure of TP after filtration through a 0.45- $\mu$ m-pore-diam membrane (ANON, 1985).
PP	<i>Particulate Phosphorus</i> is the difference between TP and TDP (ANON, 1985).
SRP	<i>Soluble Reactive Phosphorus</i> . This is a measure of orthophosphate. This is the component of phosphorus immediately available for algal growth and hence the promotion of eutrophication.
NO <sub>3</sub>	Nitrate
NO <sub>2</sub>	Nitrite
NH <sub>4</sub>	Ammonium
TON	<i>Total Oxidised Nitrogen</i> . This is the sum of nitrate and nitrite
SS	Suspended Sediment
S1	Site 1. Catchment area 17 ha. The most upstream of the nested catchments in Dripsey.
S3	Site 3. Catchment area 211 ha. The most central of the nested catchments in Dripsey.
S4	Site 4. Catchment area 1524 ha. The most downstream of the nested catchments in Dripsey.

## ***Abstract***

The concentration of phosphorus, nitrogen and suspended sediment in rivers and streams fed by runoff from grassland catchments is dependent on the catchment characteristics, weather and land management within the catchment. In order to identify remedial measures (e.g. improved farm management), baseline data on hydrology, water chemistry and farm management practices are required on a catchment scale. A study of three nested grassland catchments in the south of Ireland (areas 17ha, 211ha and 1524ha) was carried out for the year 2002. In an effort to understand the controls on the release of nutrients and suspended sediment to water bodies, the specific objectives of this study were: (1) to determine the cumulative export loads of total phosphorus (TP), total dissolved phosphorus (TDP), soluble reactive phosphorus (SRP), total oxidised nitrogen (TON), ammonium (NH<sub>4</sub>) and suspended sediment over one year; (2) to examine the seasonal relationships between TP, TDP, SRP, TON NH<sub>4</sub> and SS; and (3) to examine the relative contribution of chemical fertiliser and slurry to the phosphorus, nitrogen and suspended sediment export.

We monitored the chemical fertiliser applied to the 17 and 211 ha catchments from February to September 2002 which amounted to 16.4 and 23.7 kg P ha<sup>-1</sup> and 186 and 214 kg N ha<sup>-1</sup> respectively. Slurry was applied randomly through the year and the 17 and 211 ha catchments received 10.7 and 14.0 kg P ha<sup>-1</sup> and 68.8 and 90 kg N ha<sup>-1</sup>. For the year 2002, we estimated the annual TP export to water as 2.61, 2.48 and 1.61 kg from the 17, 211 and 1524ha catchment areas respectively. This represents 12.1% and 7.2% of applied phosphorus from the 17 and 211ha catchments respectively. The annual export of nitrogen for the year 2002 as NH<sub>4</sub> was 0.76, 0.9 and 0.56 kg N ha<sup>-1</sup> from the 17, 211 and 1524 ha catchments, respectively. The export of TON was 48.5, 38.5 and 46.7 kg N ha<sup>-1</sup> year<sup>-1</sup> from catchments 1, 3 and 4 respectively. Most of the nutrients and SS were exported during the winter months and in the case of TP, NH<sub>4</sub>, and SS during the months of heavy rainfall (i.e. October to February).

This study provides a baseline data that may be used to identify remedial measures for the reduction of nutrients especially for phosphorus loss from agricultural grassland. These measures could firstly focus on a reduction of slurry applications in the five most vulnerable months of October to February, when effective rainfall is highest, and secondly to address excess of chemical fertiliser.

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# Chapter 1

## Introduction

## **1.1 Background**

The Irish Environmental Protection Agency (EPA) has pointed to declining water quality “as the primary environmental challenge facing Ireland today” (Regan, 2000). In Ireland there has been an increasing trend of slight and moderate pollution in the river systems since the late 1970s (EPA, Ireland, 2000). Despite some recent improvements, over 30% of Irish rivers are still classified as polluted to some extent. Groundwaters in many areas show an unacceptably high level of bacteriological contamination and in some areas are polluted or at risk from nitrates. Thirteen sections of tidal waters are classified as eutrophic (over-enriched) and a further four as potentially eutrophic (Lehane, 2002).

The decrease in water quality is due in part to the increasing levels of phosphorus and nitrogen entering freshwater streams from agricultural land (Heathwaite, 1997 and Strebel et al., 1989). An increase in nutrients in rivers, lakes and estuaries increases the risk of eutrophication in the summer months, which is highly undesirable. High nitrate levels have been observed in groundwater due in part to poor control of animal wastes. (McGarrigle et al., 2002). This is a cause for concern because of the human health risk resulting from high levels of nitrate in drinking water (Page et al., 2002) and the increased cost in treating water for human consumption. Phosphorus is considered to be the limiting nutrient in freshwaters (Tunney, 2000), whereas nitrogen is considered limiting in coastal areas (Powlson, 2000). The build-up of sediment in reservoirs and estuaries is undesirable due to the reduction of storage and cost of dredging. This is relevant in the Lee catchment in Cork as there is a reservoir on the river. High amounts of suspended sediment (SS) in rivers also deplete oxygen levels, which can result in fish kills. Sediment deposition in low-lying areas may cause blockages and increase the risk of flooding.

The concentration of phosphorus, nitrogen and suspended sediment in streams and rivers, fed by runoff from grassland catchments is dependent primarily on the catchment characteristics, weather and land management (Hack-ten Broeke et al., 1999 and Goulding, 2000). Catchments with sandy soils are more prone to nutrient leaching than areas with heavy clay soils (Breen and Mullen, 1992). Nutrient losses also depend

on the application rates, timing and the availability of the nutrient content of slurry and chemical fertiliser applications. The presence of livestock (Mignolet et al., 1999), the choice of crops (Jaynes, 2001), and cropping patterns may also influence losses of nutrients and suspended sediment. River sediment fluxes are sensitive to many influences especially any change in land use or land clearance, reservoir construction or soil and water conservation measures (Walling and Fang, 2003).

Weather also influences phosphorus, nitrogen and suspended sediment concentrations in streams and rivers. The rainfall amount and intensity, the antecedent soil moisture conditions, the extent of overland and sub-surface flows, the soil moisture status particularly in the near stream fields and the potential for erosion of the hill-slopes and the duration of high water flows, all influence erosion and leaching.

## **1.2 Literature review**

Annual total phosphorus (TP) losses from agricultural soils generally amount to 0.5 - 2.0 kg P ha<sup>-1</sup>, which is about 1 - 5% of the input from fertiliser and slurry (Sherwood, 1990). On frozen grounds the annual losses of up to 13% of manure input have been reported (Young and Mutchler, 1976). Lennox et al., (1997) estimated the dissolved reactive phosphorus (DRP) export in flow from a 430-km<sup>2</sup> grassland catchment in Northern Ireland to be 0.36 kg P ha<sup>-1</sup> year<sup>-1</sup>. Chapman et al (2001) estimated that 1.57 kg ha<sup>-1</sup> of particulate phosphorus (PP) was lost from a 5.9 grassland ha site in the UK. Artola et al (1995) estimated the total phosphorus feeding three eutrophic reservoirs near Madrid (catchment areas 240, 244 and 91 km<sup>2</sup>), to be 0.18, 0.3 and 8.1 kg ha<sup>-1</sup>. From small catchments in Finland, Rekolainen et al., (1995) estimated TP losses to be 0.9 - 1.8 kg P ha<sup>-1</sup> year<sup>-1</sup>. Kronvang et al., (1995) reported TP losses of 0.23 - 0.34 kg P ha<sup>-1</sup> year<sup>-1</sup> from small catchments in Denmark. McKergow et al., (2003) reported TP loads of 0.2-0.6 kg ha<sup>-1</sup> over a ten-year period from a 590 ha catchment with a Mediterranean climate in Western Australia. In this latter catchment, after riparian management practices (setting trees along the riparian zone) were introduced, there was no change in TP export loads but a major improvement in suspended solids loading. Ulen et al., (2001), reported TP export loads of 0.03-0.5 kg ha<sup>-1</sup> year<sup>-1</sup> from a small catchment with fifteen fields over a period of 20 years. McDowell and Trudgill (2000), found a mean annual TP loss over eight years of 0.62 kg ha<sup>-1</sup> to be equivalent to about 7.5% of the P fertiliser applied to a 94 ha catchment.

The limited results available in Ireland indicated that phosphorus loss from low fertility and low intensity grassland is low, of the order of  $0.2 \text{ kg P ha}^{-1} \text{ year}^{-1}$  of water-soluble phosphorus (Tunney et al., 1998). The mean annual TP concentration considered to lead to deterioration in water quality is  $0.035 \text{ mg/l}$  (Tunney, 2000). This suggests that we should be aiming at an annual export of TP not to exceed  $0.35 \text{ kg ha}^{-1}$  (based on a stream runoff of  $1000 \text{ mm/year}$ ). If we assume  $\text{TP} \approx 1.55 \text{ SRP}$ , then the annual export of SRP with a rainfall of  $1000 \text{ mm/year}$  should not exceed  $0.22 \text{ kg P ha}^{-1}$ .

In Denmark the average nitrate ( $\text{NO}_3$ ) leaching from sandy catchments during 1989-1996 amounted to  $123 \text{ kg N ha}^{-1} \text{ year}^{-1}$  and from loamy catchments it was  $72 \text{ kg N ha}^{-1} \text{ year}^{-1}$  (Grant et al., 1997). Watson et al., (2000) reported the annual losses of  $\text{NO}_3$  in drain flow for plots in Northern Ireland receiving  $300 \text{ kg N}$  in fertiliser ranged from  $16$  to  $52 \text{ kg N ha}^{-1}$  and were highest after a dry summer. These nitrogen losses represented 5 to 23% of the added nitrogen. The average loss of TON from arable land in 1985 in Sweden was estimated to be  $29 \text{ kg N ha}^{-1} \text{ year}^{-1}$  (Arheimer and Brandt, 2000). Cuttle et al., (1995) showed that low stocking rates with an application of  $200 \text{ kg N ha}^{-1} \text{ year}^{-1}$  on undrained soils had a nitrogen loss of  $18 \text{ kg N ha}^{-1} \text{ year}^{-1}$ . However with a larger stocking rate in drained soil with a fertiliser application rate of  $400 \text{ kg N ha}^{-1} \text{ year}^{-1}$  the loss increased to  $194 \text{ kg N ha}^{-1} \text{ year}^{-1}$ . Modelled nitrogen leaching from the organic systems varied from  $19$  to  $30 \text{ kg N ha}^{-1} \text{ year}^{-1}$  on loam soils and  $36$  to  $65 \text{ kg N ha}^{-1} \text{ year}^{-1}$  on sandy soils (Hansen et al., 2000). It has been shown that the very best environmentally conscious arable farmers can reduce losses below  $20 \text{ kg N ha}^{-1} \text{ year}^{-1}$  (Goulding, 2000). In the United States the monthly average of concentrations of nitrate in tile drainage system ranged from  $6$  to  $28 \text{ mg N/l}$  (Jaynes et al., 2001).

Annual losses of ammonium ( $\text{NH}_4$ ) and nitrite ( $\text{NO}_2$ ) in the same plot were not related to fertiliser rate and ranged from  $0.2$  to  $4 \text{ kg N ha}^{-1}$  and  $8$  to  $540 \text{ g N ha}^{-1}$ , respectively (Watson et al., 2000).

Walling et al., (2002) estimated that the annual export of suspended sediment from two small lowland, agricultural catchments in the UK was  $90 \text{ t/km}^2$  ( $900 \text{ kg ha}^{-1}$ ). These values were considered high by UK standards. Erosion from channel banks contributed about 10 and 6% from the two catchments. Concentrations of suspended

sediment in the UK range from 2 to 400 mg/l in upland streams but may go as high as 2000 mg/l in lowland rivers (Hudson, 2003).

The nitrate directive of the European commission states that the  $\text{NO}_3$  concentration in groundwater that is intended to be used for drinking water may not exceed 50 mg/l (11.3 mg/l N), (91/676/EEC). A new phosphate regulation was introduced in Ireland in 1998 with the aim of setting a target to reduce the phosphorus content of freshwater to 0.035 mg P/l. (Tunney, 2000). The EU Freshwater Fish Directive (79/659/EEC) stipulates that, in order to protect game fish, SS concentrations should not exceed an annual average of 25 mg/l.

### **1.3 Objectives**

There are still many unanswered questions relating to nutrient losses for grasslands. Do nutrient losses and concentrations increase with flow?; Does the loss of nutrients attenuate with increasing catchment size?; What are the relative contributions of fertiliser and slurry to the phosphorus and nitrogen export and to the different fractions of phosphorus and nitrogen?; how do the environmental parameters (rainfall, soil moisture, soil P etc.) contribute to nutrient and SS export?

In an effort to understand the underlying processes of nutrient and suspended solids loss from soil to water bodies, a one-year study (2002) of three nested grassland catchments with known fertilisation regimes was carried out. The specific objectives were: (1) to determine the cumulative export loads of total phosphorus (TP), total dissolved phosphorus (TDP) and soluble reactive phosphorus (SRP), ammonium ( $\text{NH}_4$ ), total oxidised nitrogen (TON) and suspended sediment (SS) over one year; (2) to examine the contribution of fertiliser and slurry to the export of phosphorus, nitrogen and suspended solids; and (3) to examine the hydrologic controls on nutrient export.

## 1.4 Previous work, on the Dripsey catchment

A program of research carried out in the Cork Lee catchment in 1993-1994 (Tunney et al., 1995), is summarised in Tables 1.1 and 1.2.

**Table 1.1** LU\*, fertiliser and slurry P estimates for 1993-1994. (Tunney et al., 2000)

Name	Area ha	LU ha <sup>-1</sup>	Fertiliser P kg P ha <sup>-1</sup>	Slurry P kg P ha <sup>-1</sup>
S3	211	2.04	21.45	19.25
S4	1524	1.5	17.1	15.3
S5	5578	1.59	-----	-----

\*LU: Live stock unit.

**Table 1.2** Export loads from the 1993-1994 study (Tunney et al., 2000)

Name	Area ha	TP kg (kg ha <sup>-1</sup> )	SRP kg (kg ha <sup>-1</sup> )	TON kg (kg ha <sup>-1</sup> )	NH <sub>4</sub> kg (kg ha <sup>-1</sup> )	SS kg (kg ha <sup>-1</sup> )
S3	211	744 (3.52)	428 (2.02)	15000 (71)	478 (2.27)	58000 (275)
S4	1524	2996 (1.97)	1347 (0.9)	82000 (53.8)	1666 (1.09)	355000 (232)
S5	5578	10574 (1.89)	4764 (0.85)	303000 (54.3)	7167 (1.28)	2055000 (368)

Some of the annual export loads of Tables 1.1 and 1.2 are particularly high. The SRP values of 2.02, 0.9 and 0.85 kg P ha<sup>-1</sup> correspond to annual mean values P concentrations of 0.17, 0.10 and 0.06 mg P/l for S3, S4 and S5. The threshold value of total phosphorus considered to cause eutrophication of freshwaters is 0.35 kg P ha<sup>-1</sup> (0.22 kg P ha<sup>-1</sup> SRP). Table 1.2 shows that both the TP and SRP export loads in the 1993-1994 study exceed these levels at all three sites.

## 1.5 Methods

The study was carried out on grazed grassland in the Dripsey catchment in the south of Ireland. Three nested catchments were used (17, 211 and 1524 ha) with known fertiliser and slurry applications for the two smaller catchments. Data on applications (amount and timing) was supplied on a monthly basis by the eight landowners in the

211 ha catchment. Composite water samples were taken at regular intervals from control sites in the three catchments over the one-year period of 2002 and analysed for phosphorus, nitrogen and suspended solids. The different fractions of phosphorus monitored in the streams were: total dissolved phosphorus (TDP), soluble reactive phosphorus (SRP) and total phosphorus (TP). Particulate phosphorus (PP) was calculated to be the difference between TP and TDP. The two different components of nitrogen analysed are: ammonium ( $\text{NH}_4$ ) and total oxidised nitrogen (TON) consisting mainly of nitrate ( $\text{NO}_3$ ) with some nitrite ( $\text{NO}_2$ ). Suspended sediment (SS) was also recorded. Rainfall (at 30 minute intervals) and continuous flow (at 15 minute intervals) were also measured for the year 2002. A meteorological station at catchment 1 provided 30-minute data for a range of meteorological parameters.

## 1.6 **Layout of Thesis**

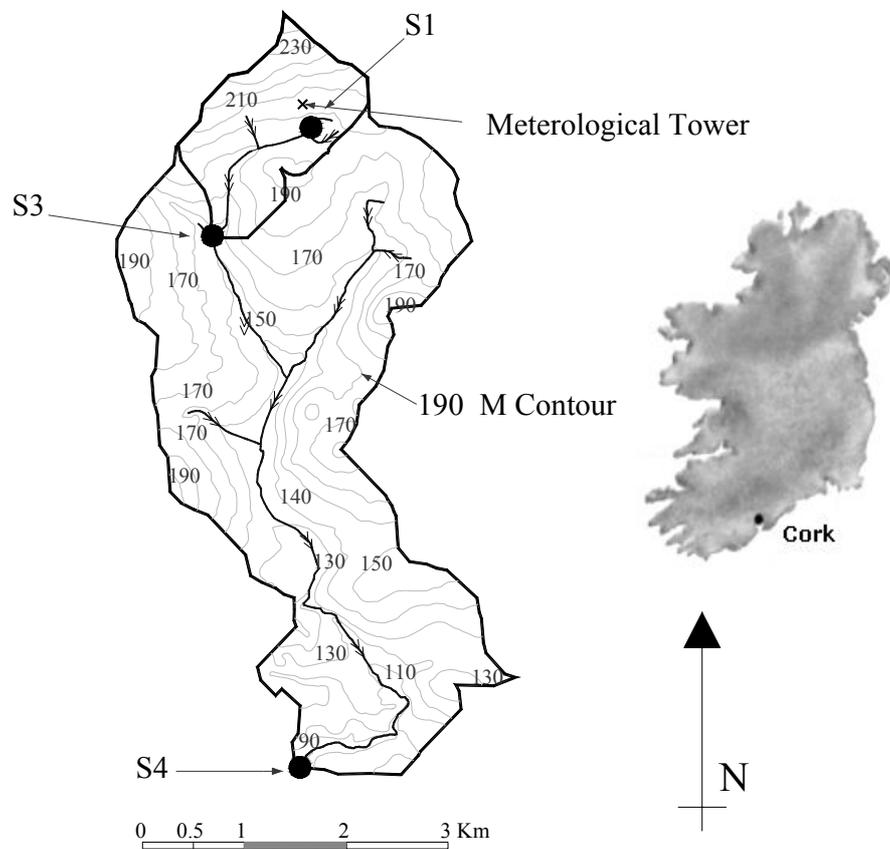
Chapter 2 describes the catchments studied and the methods used to estimate the flow, nutrient and suspended sediment concentrations. Chapter 3 presents all the data observed on site principally as time series. Chapter 4 describes the gap filling methods used to estimate the nutrient concentrations when no water chemistry samples were taken on site. Chapter 5 estimates the annual and seasonal export of phosphorus, nitrogen and suspended sediment. Chapter 6 contains a discussion and analysis of the results from the three sites for the year 2002. Chapter 7 presents the conclusions and recommendations and makes suggestions for continuing research. The Appendices include a copy of a journal of hydrology paper (submitted), a poster presentation at the EGS conference, Nice, France in April 2003. Appendix D contains some of the information received from the farmers in catchment 3. Appendix E describes the data set used and a CD of same. All analysis was done using MATLAB®.

# Chapter 2

## Site Description & Land Management

## 2.1 Site location

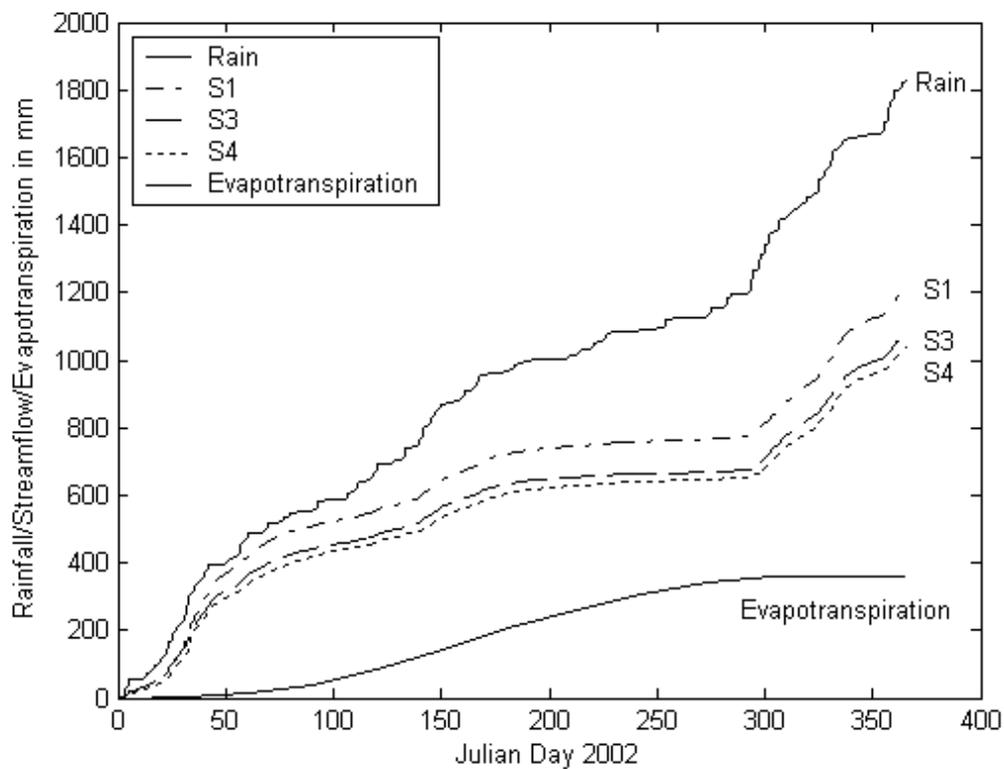
The study area is the upland Dripsey catchment, a sub catchment of the river Lee in Cork, Ireland. Three nested catchments named as catchment 1, catchment 3 and catchment 4 have areas of 17, 211, and 1524 ha respectively. The experimental sites are located approximately 25 km northwest of Cork city (52°N, 08°44'W). Figure 2.1 shows the location of the three in-stream control points S1, S3 and S4 used for data collection (streamflow and water chemistry). The elevations of the three control points are 210, 160, 80 meters above sea level (masl) respectively. A gauged catchment 2 exists but no water chemistry analysis was carried out for the year 2002.



**Figure 2.1** Contour map of catchment 4 also showing the location of the three weirs in Catchment 1 (S1), Catchment 3 (S3) and Catchment 4 (S4).

## 2.2 Site description

The overall catchment is considered homogenous with respect to geology, hydrology, meteorology, vegetation and land use. The geology is old red sandstone with rock depth ranging from 2 to 5 m. The topsoils at the higher elevations are peaty podzols with brown podzols over most of the catchment. The profile of the soil is characterised by a dark organic loam to a depth of 15 to 25 cm overlying a yellowish-red, iron enriched b-horizon of loam texture. This grades to a reddish-brown sandy loam material at about 75 cm (Gardiner, 1980). The topsoil is rich in organic matter to a depth of about 15 cm (about 12% organic content, Daly, 1999).



**Figure 2.2** For the year 2002, the cumulative rainfall (mm) recorded near S1 and stream flow (mm) at the outfall of the three catchments, normalised per unit area.

## 2.3 Climate

The rainfall for the year 2002 was 1812 mm (see Figure 2.2), compared to the 1472 mm average for the period 1997-2002. The stream flow normalised with catchment area was measured as 1206 mm at S1, 1080 mm at S3 and 1035 mm at S4.

The reduced runoff at catchment 3 and catchment 4 is likely due to the increasing catchment area and the decreasing elevation as we move down slope from S1 to S3 to S4. The single rainfall measurement location is at an elevation of 190masl near S1 (see Figure 2.1). Evapotranspiration was estimated as 362 mm (Jaskic et al., 2003) from the eddy covariance system near S1. The monthly rainfall ranges from under 50 mm in the summer months to over 250 mm in the winter. The mean monthly temperature is 5°C in the winter and 15°C in the summer (Jaksic, 2003).

## **2.4 Data collection**

Stream discharge and water chemistry samples were collected at the control points S1, S3 and S4 for the calendar year 2002. Stream discharge was measured continuously (at 15 minute intervals) using an OTT Thalimedes water level recorder at the control points. These points are in the form of a v-notch, a rectangular weir and a crump weir for S1, S3 and S4, respectively.

Composite, flow-weighted water samples for the three sites were collected in flow-actuation mode by ISCO 6712 auto-samplers at the control points. The intakes for the autosamplers were positioned approximately 0.25 m above the streambed, 2m upstream from the weirs at S1 and S3 and 5 m upstream from the weir at S4. The composite samples are made up of a number of smaller samples. These are collected more often during periods of high flow and less frequently in periods of low flow. The duration of composite samples range from about two hours at high flow to 2 days at low flow (see Figure 3.10).

### **2.4.1 Laboratory analysis**

The water chemistry samples were returned to the laboratory, from the auto-samplers within 1-2 days of collection. Weekly grab samples were taken to supplement the composite sampling strategy. Laboratory analysis was carried for total phosphorus (TP), soluble reactive phosphorus (SRP), total dissolved phosphorus (TDP), total oxidised nitrogen (TON) consisting mainly of nitrate, ammonium (NH<sub>4</sub>) and suspended sediment (SS) within four hours of arrival in the laboratory.

### **2.4.2 Phosphorus**

Phosphorus analyses for the stream-water were performed manually by spectrophotometer after standard methods, based on a molybdate/ascorbic acid method. For TDP, the samples were membrane filtered using 0.45 µm filters and then digested using sulphuric acid/ammonium persulphate in an autoclave. No filtering was performed for the TP measurements, (Scanlon et al.,2003).

### **2.4.3 Nitrogen**

TON (nitrate and nitrite combined) was analysed following cadmium reduction to nitrite (ANON, 1985). The latter was the only parameter analysed using an automated method on a Tecator Flow Injectin Analyser. Ammonium was analysed on unfiltered samples using the phenol/alkaline hypochloride colourimetric method (ANON, 1985).

### **2.4.4 Suspended sediment**

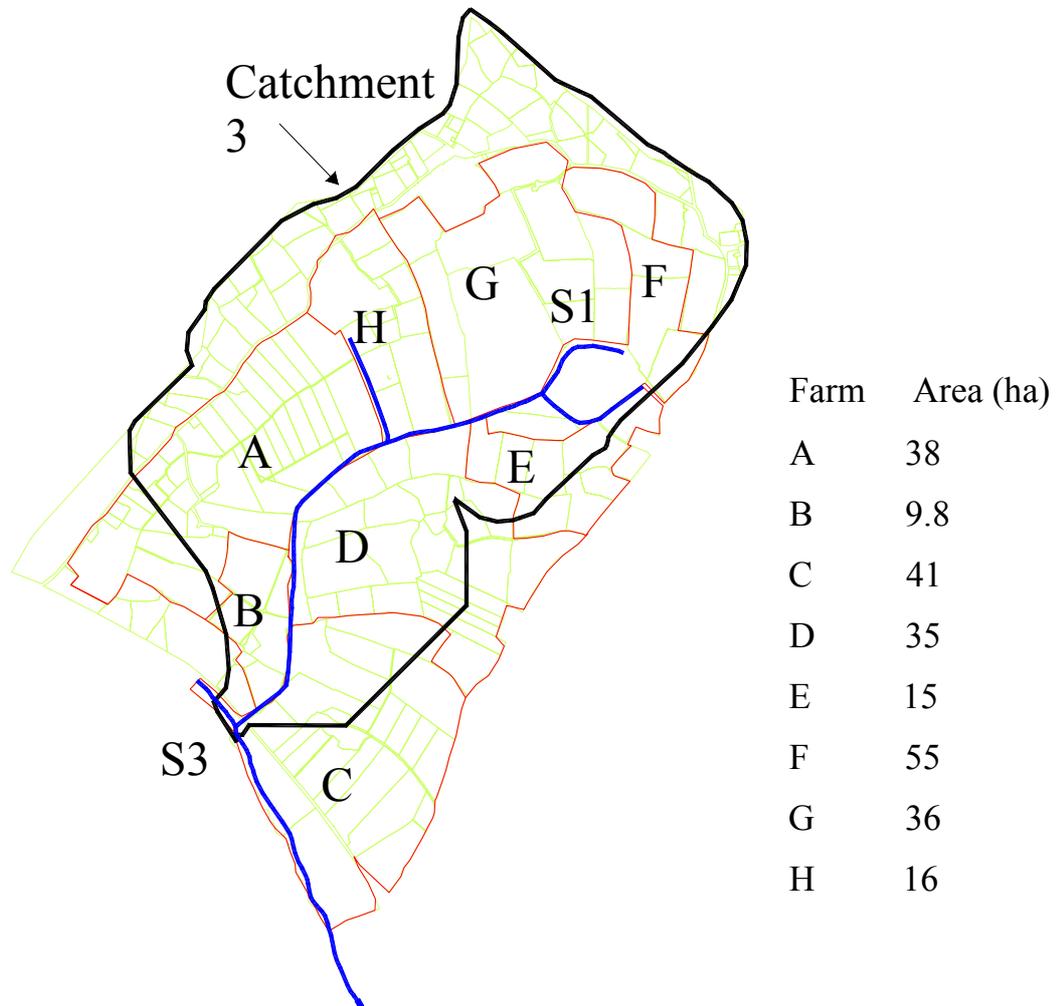
Suspended sediment were filtered on whatman GF/C and determined gravimetrically after drying over night at 103-105°C (ANON, 1985).

## **2.5 Farming practices**

Approximately 45% of the total area of Ireland is under grassland, comprised of dairy and beef farms (Coulter et al., 2002). Farming layout and farming practices in this area of county Cork are typical of Irish farming. Farm sizes range from 10 to 55 ha. Land cover is dominated by agricultural grassland of high quality pasture and meadows consisting of perennial rye-grass with a presence of clover. One farmer owns 80% of the area of catchment 1. Catchment 3 consists of eight farms (see Figure 2.3), five are primarily dairy (with some beef production), two are silage production for export (to outside the catchment) and one farm is sheep only. Catchment 4 consists of 47 farms.

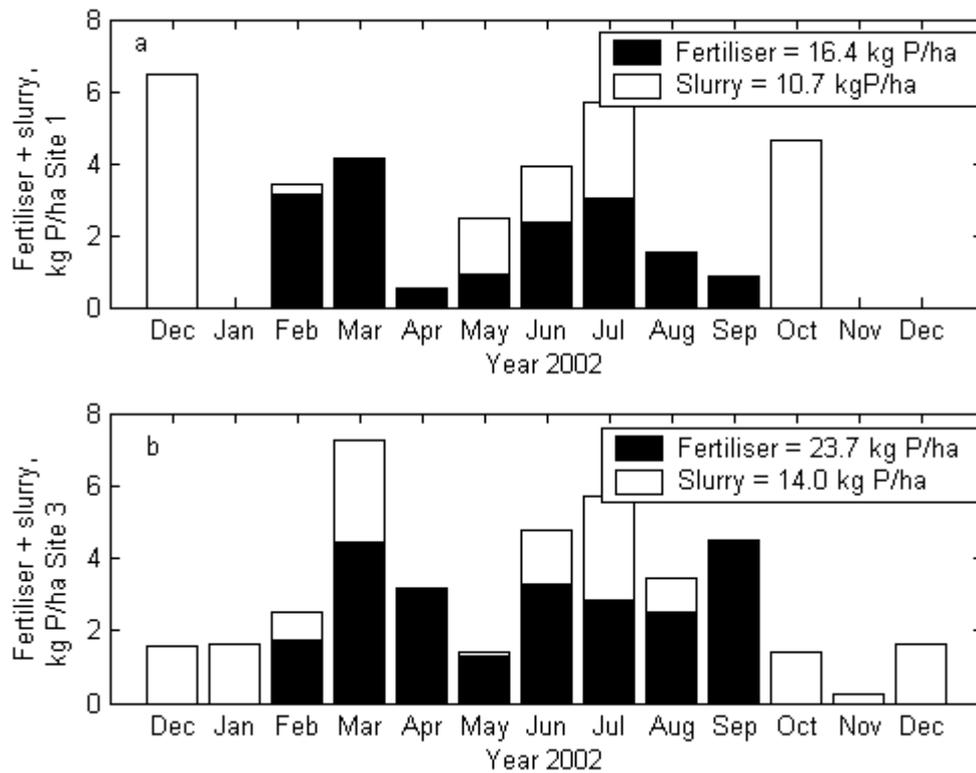
Soils samples were taken in January 2002 and analysed for Morgans P (Morgan 1941) in each of 117 fields covering 188 ha of the 211 ha catchment. This is representative of the land use and vegetation in this part of the county. The growing season in Ireland is weather dependant but generally starts in early March and ends in October. 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 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.



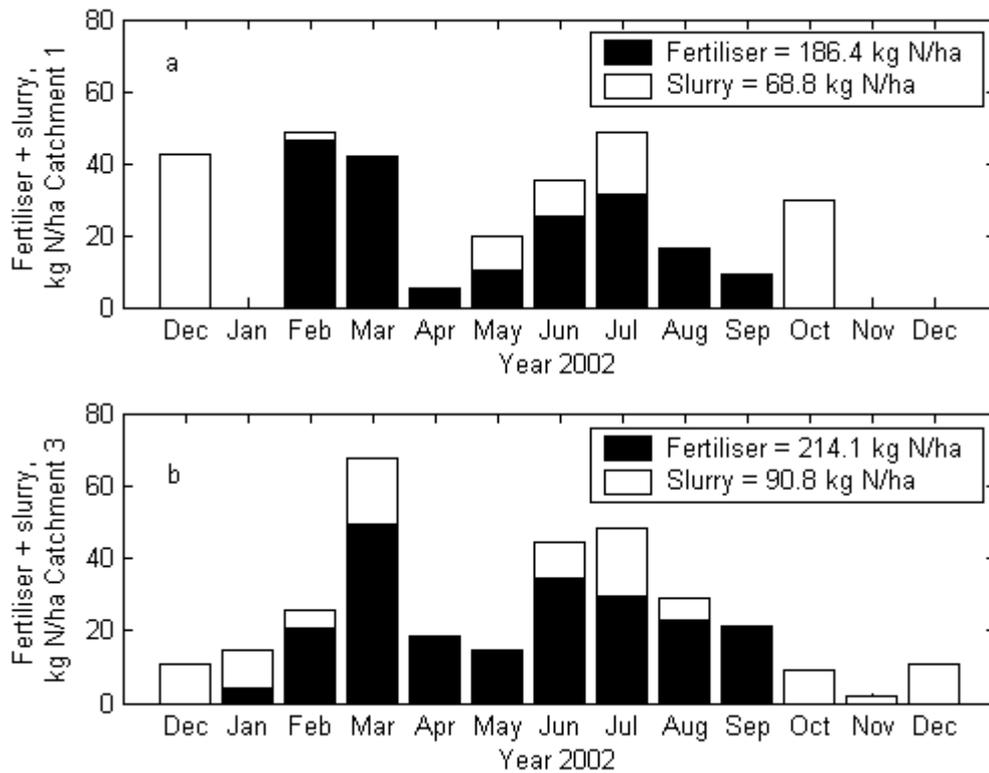
**Figure 2.3** The layout of the eight farms in catchment 3 and the outline of catchment 3

Fertiliser and slurry applications were recorded by all farmers in the 211 ha catchment for the year 2002. We have no fertiliser/slurry data, downstream of S3 (i.e. for the largest catchment) Chemical fertiliser is applied on all farms except the sheep farm; farm H (16 ha). The fertiliser applications began in February and continue at about four to six week intervals until September. Slurry is applied irregularly, its amount and timing dependent on what had accrued from winter housing of the cattle. We show in Figures 2.4 (a) and 2.4 (b) the monthly applications of fertiliser and slurry phosphorus in catchment 1.



**Figure 2.4** The monthly applications of phosphorus ( $\text{kg P ha}^{-1}$ ) of chemical fertiliser and slurry in Catchment 1 (17ha) and Catchment 3 (211ha).

The monthly applications of slurry and fertiliser in catchment 3 are shown in Figures 2.5 (a) and 2.5 (b) respectively. The make up of the chemical fertiliser applied during the year 2002 was  $214 \text{ kg N ha}^{-1}$  and  $24 \text{ kg P ha}^{-1}$  in catchment 3 and the make up of the animal slurry applied for 2002 was  $90 \text{ kg N ha}^{-1}$  and  $14 \text{ kg P ha}^{-1}$ . In Figure 2.4 it is relevant to note that in catchment 1, there was a significant application of slurry in December 2001 and in October 2002. However in the larger catchment, catchment 3, the applications of slurry were not so significant in the winter months. The catchment wide average of phosphorus in fertiliser and slurry was  $35 \text{ kg P ha}^{-1}$ . The range of phosphorus applied to each of the 117 fields was 0 to  $58 \text{ kg P ha}^{-1}$ . The catchment wide average of nitrogen in fertiliser and slurry was  $303 \text{ kg N ha}^{-1}$  with the range of nitrogen applied to the fields ranging from 0 to  $800 \text{ kg N ha}^{-1}$ .



**Figure 2.5** The monthly applications of nitrogen ( $\text{kg N ha}^{-1}$ ) of chemical fertiliser and slurry in Catchment 1 (17ha) and Catchment 3 (211ha).

## 2.6 Livestock unit

A dairy cow is taken as the basic grazing livestock unit (LU). All other stocks are given equivalents based on this (Coulter et al., 2002). The data received from the eight farmers in catchment 3 is presented in appendix D. This data enabled us to calculate the LU/ha for each of the farms and the average for catchments 1 and 3. Catchment 3 is intensively grazed grassland with an average of 2.2 livestock units per hectare (LU/ha). This is a slight increase from the LU/ha for 1993 estimated by Tunney et al., (2000). The LU/ha in catchment 211 in 1993 was 2.04 LU/ha.

The average nationwide is approximately 1.4 LU/ha (Breen and Mullen, 1992). Hence the farms in the Dripsey catchment would be considered as intensively grazed grassland.

# Chapter 3

## Raw Data Presentation

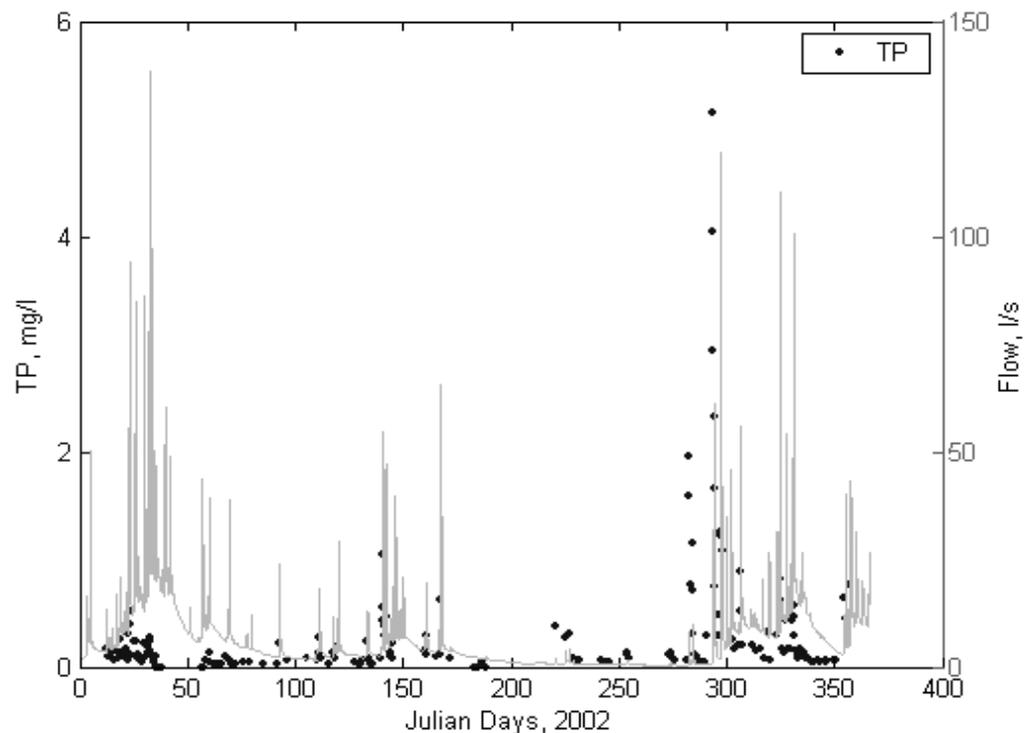
### 3.1 Introduction

After analysis of the water samples in the laboratory we examined the time series of the concentration of nutrients and suspended sediment with flow for the year 2002 at the three sites. Figures 3.1, 3.2 and 3.3 show the concentrations of TP and observed flow for the year 2002 at sites 1, 3 and 4 respectively. The concentrations of TDP, SRP, TON, NH<sub>4</sub>, SS and observed flow at site 1 are shown in Figures 3.4, 3.5, 3.6, 3.7 and 3.8, respectively. Similar observations are presented for the two larger catchments.

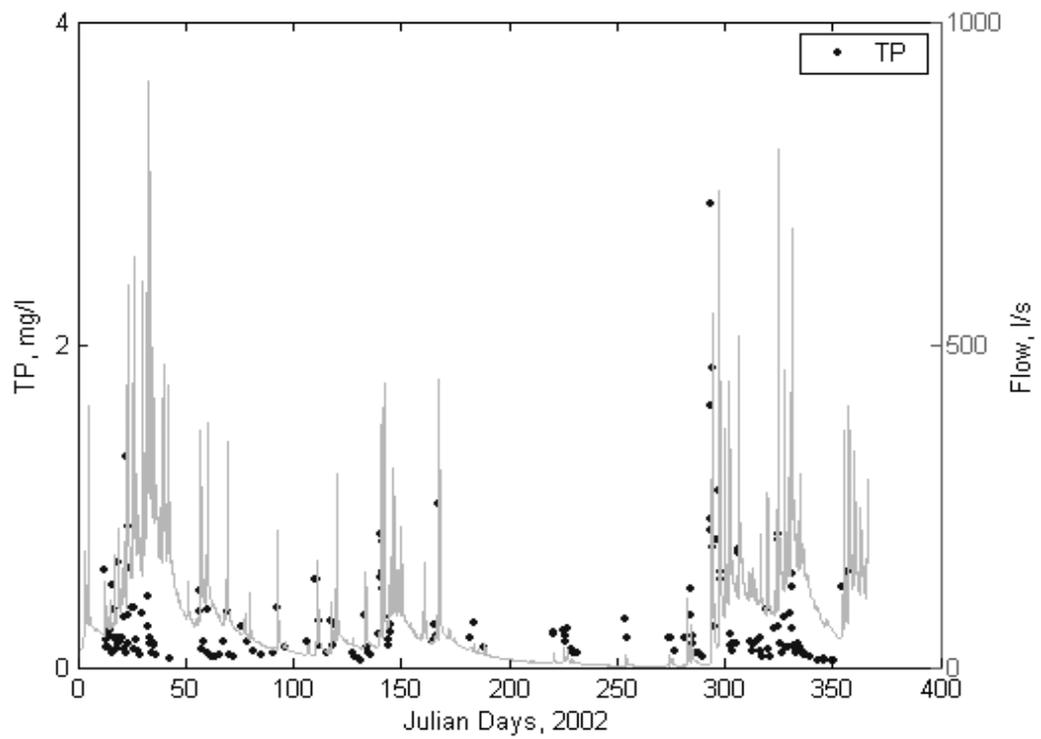
### 3.2 Phosphorus

#### 3.2.1 Total phosphorus (TP)

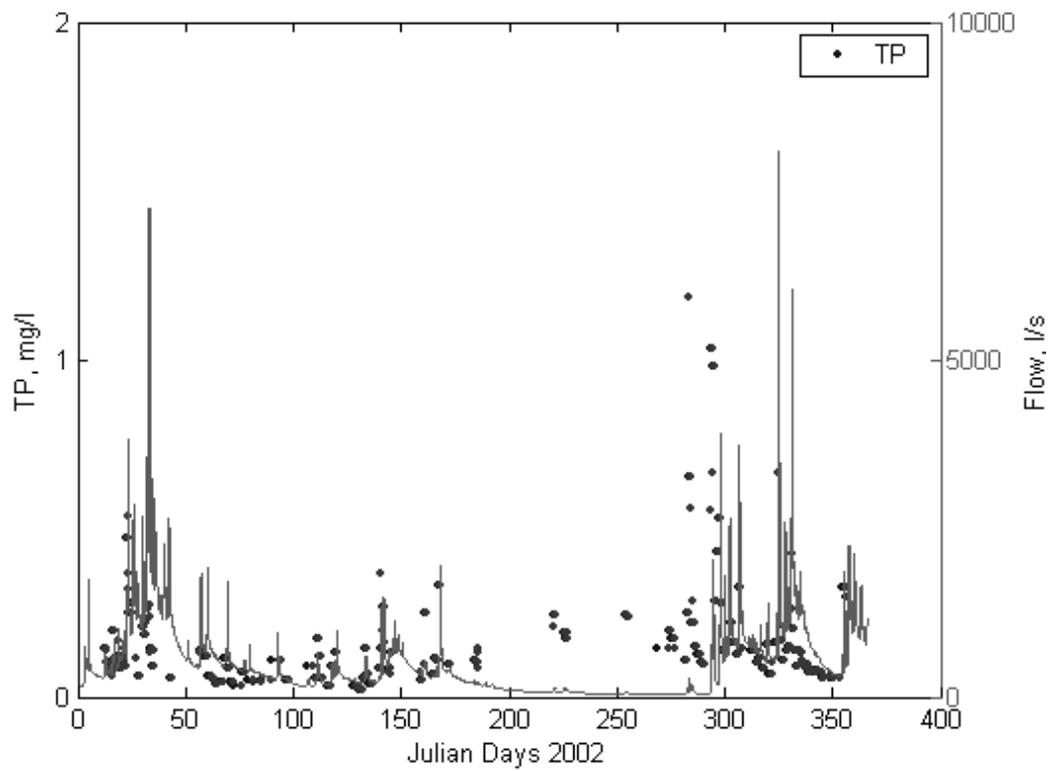
At site 1 the highest TP concentration of 5.1 mg/l was measured on October 20<sup>th</sup> (see Figure 3.1). The peak concentrations at S1, S3 and S4 on October 20<sup>th</sup> were 5.1, 2.8 and 0.55 mg/l, respectively (see Table 3.1). This suggests that the high concentration measured at S1 was partially diluted on reaching S3 (1.5 Km downstream) and significantly diluted on reaching S4, (9 Km downstream). The lowest measured concentrations were 0.02 mg/l at S1 and 0.04 mg/l at S3 and S4



**Figure 3.1** The time series over the year 2002 of total phosphorus (TP) in mg/l and discharge (Q) in l/s at site 1 (17 ha).



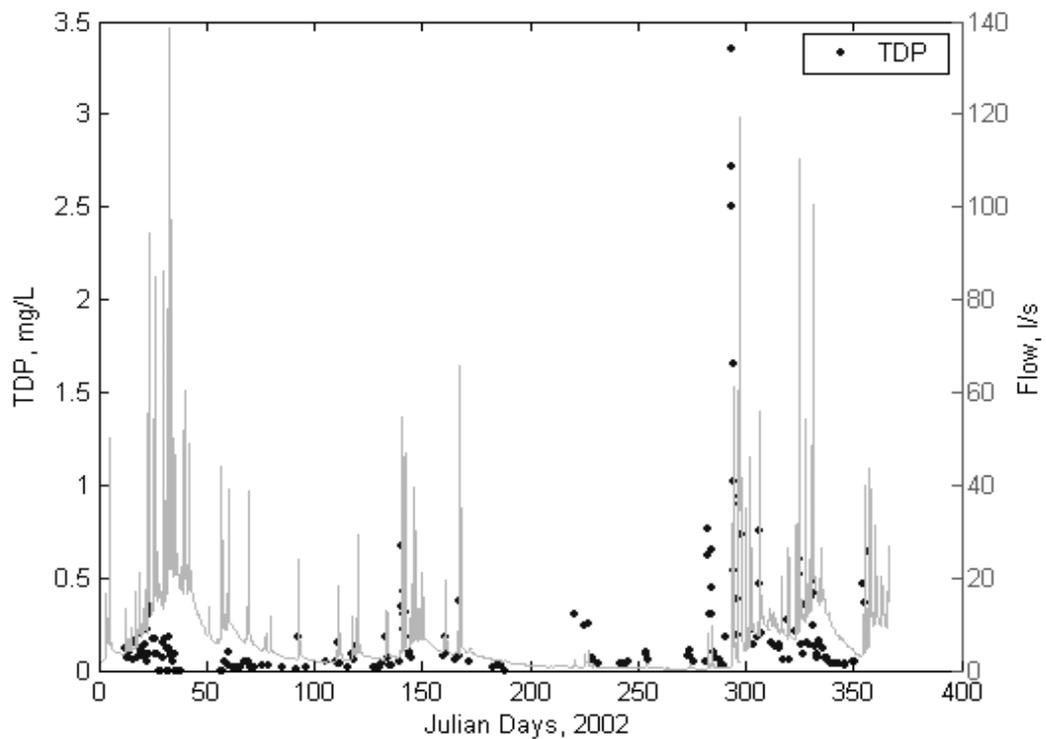
**Figure 3.2** The time series over the year 2002 of total phosphorus (TP) in mg/l and discharge (Q) in l/s at site 3 (211 ha).



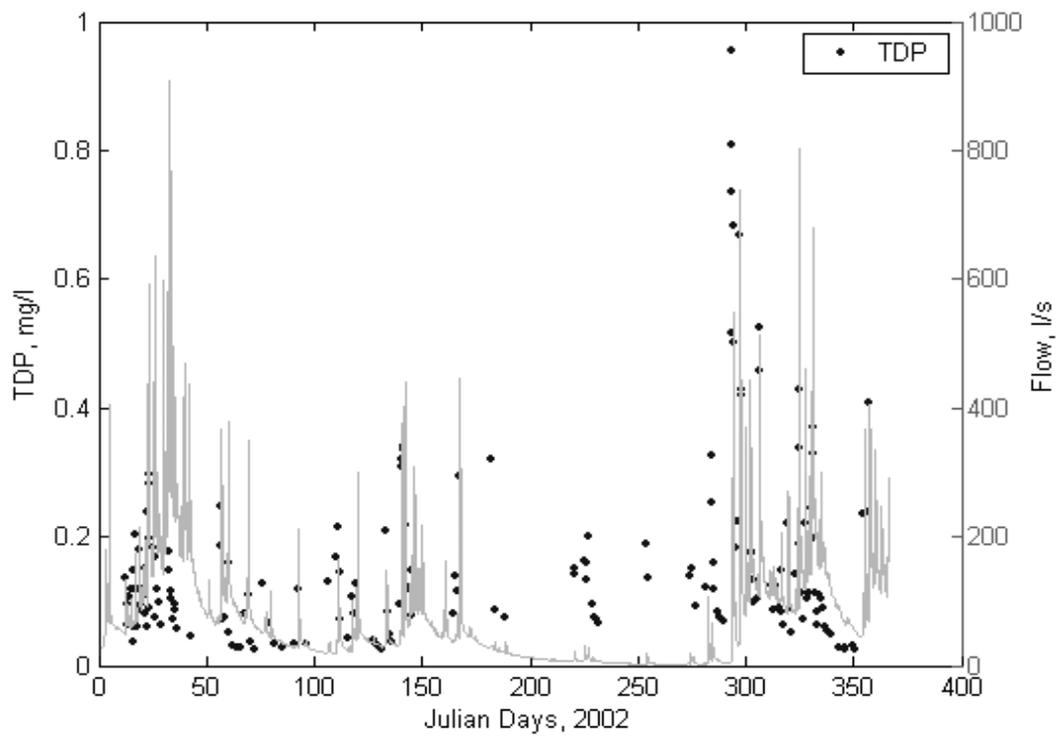
**Figure 3.3** The time series over the year 2002 of total phosphorus (TP) in mg/l and discharge (Q) in l/s at site 4 (1524 ha).

### 3.2.2 Total dissolved phosphorus (TDP)

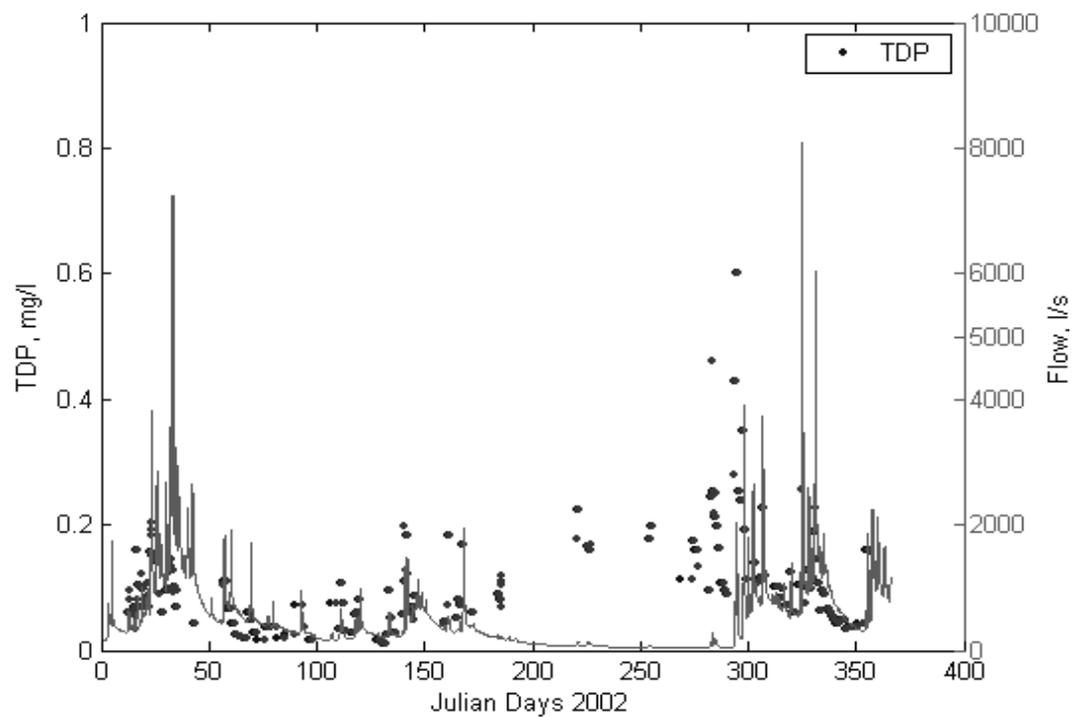
The total dissolved phosphorus concentrations and flow observed at S1, S3 and S4 are shown in Figures 3.4, 3.5 and 3.6. At site 1 the highest TDP concentration of 3.34 mg/l was measured on October 20<sup>th</sup> (see Figure 3.4). As with TP the peak concentrations at S1, S3 and S4 all occurred during the flood caused by the rain on October 20<sup>th</sup>. The peak concentrations were 3.34, 0.95 and 0.6 mg/l, respectively (see Table 3.2). The lowest TDP values for the three sites occurred in different seasons, April 2<sup>nd</sup>, December 16<sup>th</sup> and May 9<sup>th</sup> for S1, S3 and S4 respectively. The lowest measured concentrations were 0.01 mg/l recorded at S4.



**Figure 3.4** The time series over the year 2002 of total dissolved phosphorus (TDP) in mg/l and discharge (Q) in l/s at site 1 (17 ha).



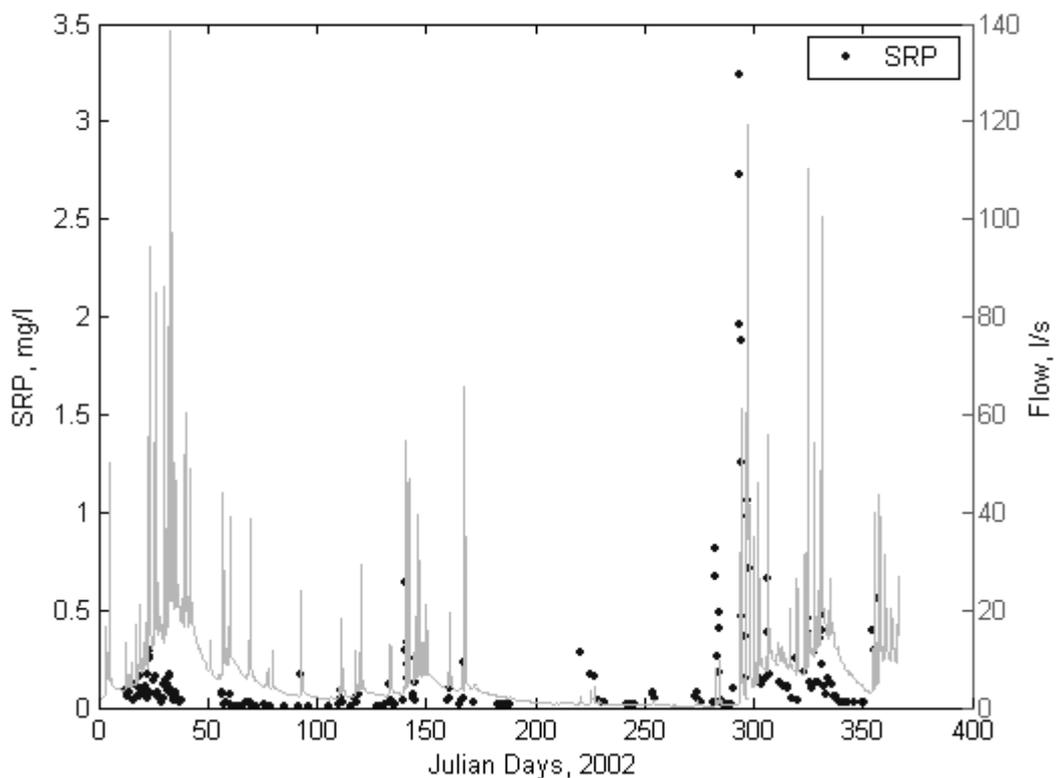
**Figure 3.5** The time series over the year 2002 of total dissolved phosphorus (TDP) in mg/l and discharge (Q) in l/s at site 3 (211 ha).



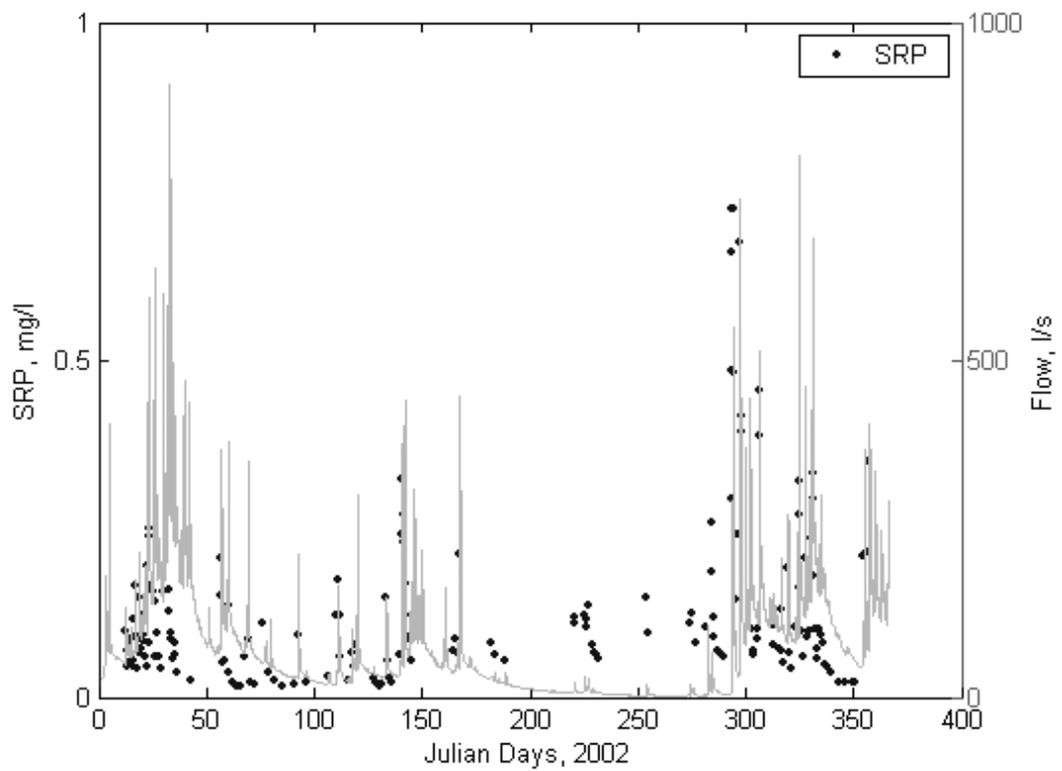
**Figure 3.6** The time series over the year 2002 of total dissolved phosphorus (TDP) in mg/l and discharge (Q) in l/s at site 4 (1524 ha).

### 3.2.3 Soluble reactive phosphorus (SRP)

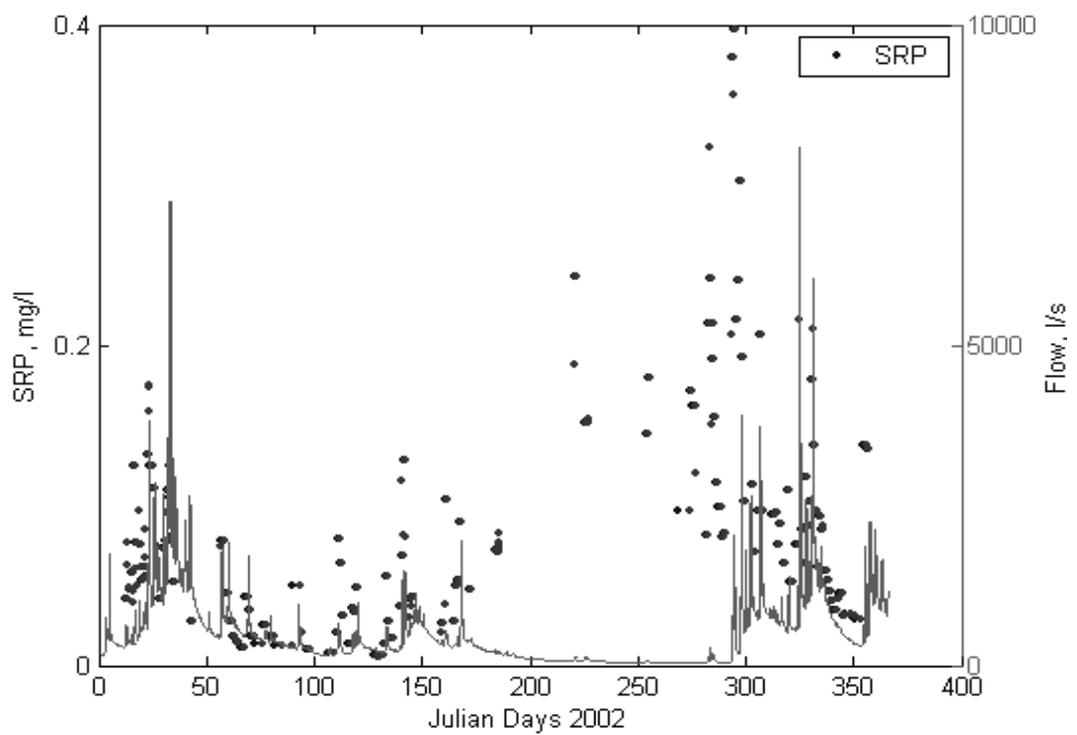
The soluble reactive phosphorus concentrations and flow observed at S1, S3 and S4 are shown in Figures 3.7, 3.8 and 3.9. Like TP and TDP the highest concentrations all occurred in the flood on the 20<sup>th</sup> of October. At site 1 the highest SRP concentration observed was 3.25 mg/l (see Figure 3.7). The peak concentrations were 3.25, 0.72 and 0.38 mg/l at S1, S3 and S4 respectively (see Table 3.3). The lowest SRP values for the three sites were in spring and early summer. The lowest measured concentrations were 0.001 mg/l recorded at S1. The concentrations of SRP are important as it is considered to be readily available for algal growth (Lennox et al., 1997).



**Figure 3.7** The time series over the year 2002 of soluble reactive phosphorus (SRP) in mg/l and discharge (Q) in l/s at site 1 (17ha).



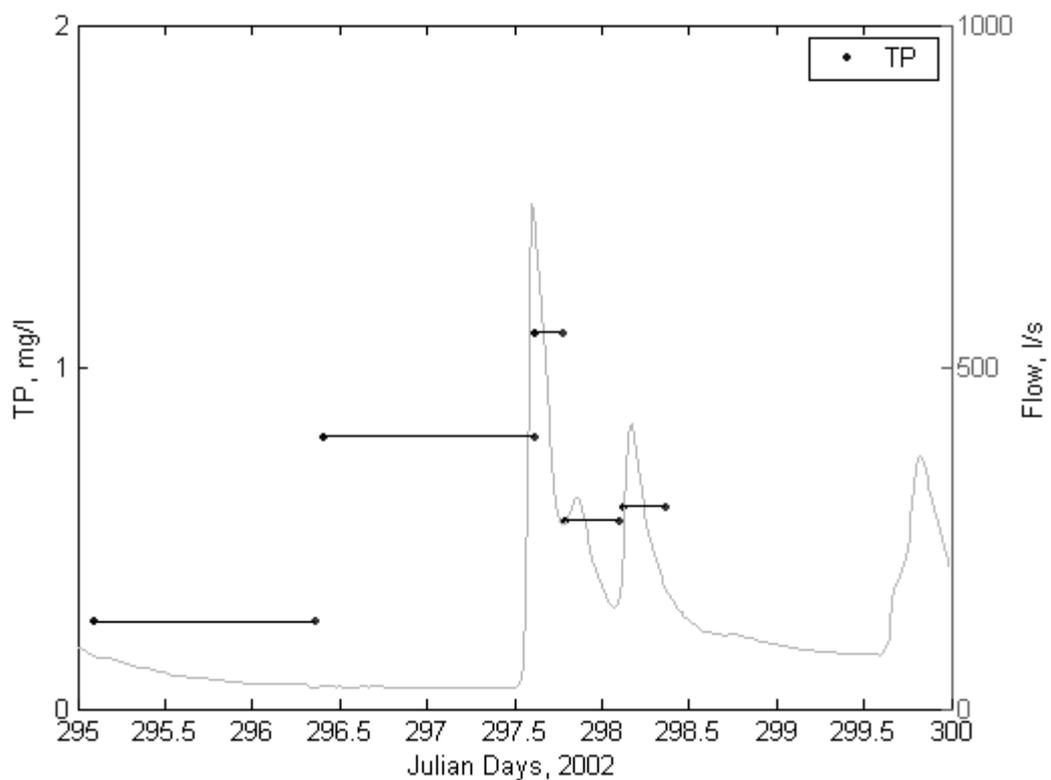
**Figure 3.8** The time series over the year 2002 of soluble reactive phosphorus (SRP) in mg/l and discharge (Q) in l/s at site 3 (211 ha).



**Figure 3.9** The time series over the year 2002 of soluble reactive phosphorus (SRP) in mg/l and discharge (Q) in l/s at site 4 (1524 ha).

### 3.2.4 Phosphorus variation with flow

It is clear from Figures 3.1 3.2 and 3.3 that as flow increases so does TP, suggesting that autumn and winter produce high exports of TP. Figure 3.10 shows the variation of TP concentrations with flow during one rain event on the 25<sup>th</sup> of October. The concentrations of TP increase with flow. These low flows could be considered to be base flow as the weeks previous to this were very dry and the higher flows probably originated from overland flow. Figure 3.10 also shows that TP concentrations are higher on the rising limb of a hydrograph than on the falling limb for the same flows.

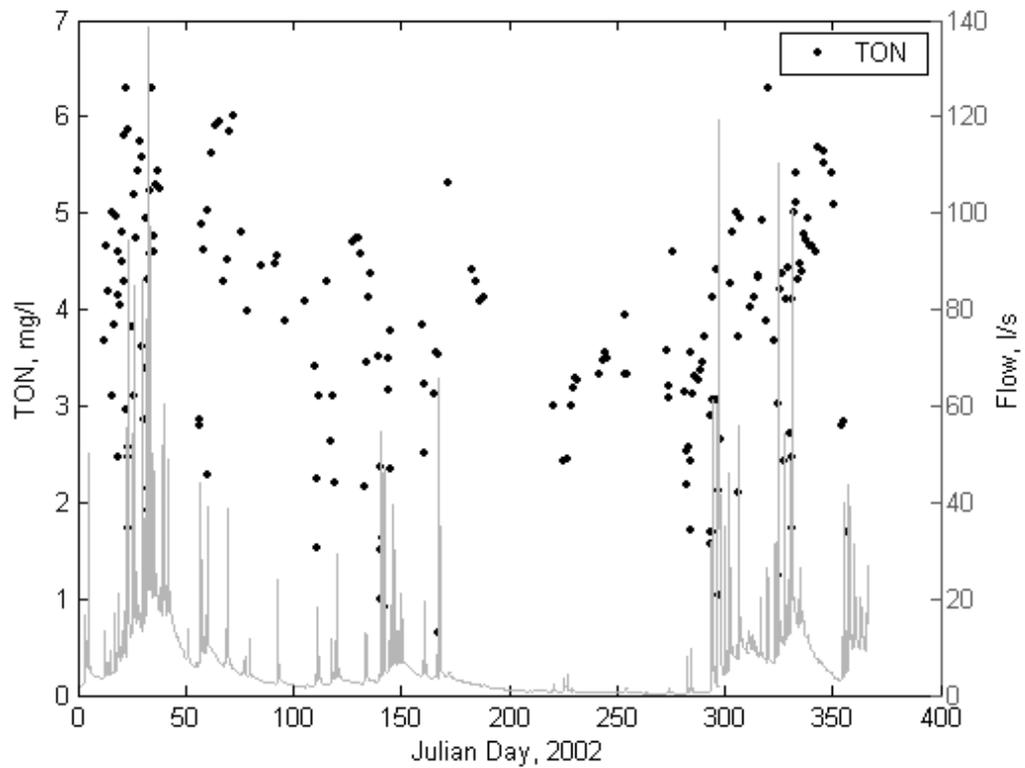


**Figure 3.10** The time series over 5 days of total phosphorus (TP) in mg/l of the composite samples and discharge (Q) in l/s at site 3 (211 ha). Note that at low flows the concentrations are low and the duration of the composite sample is long. At higher flows, the concentrations are higher and the duration of the composite sample is shorter.

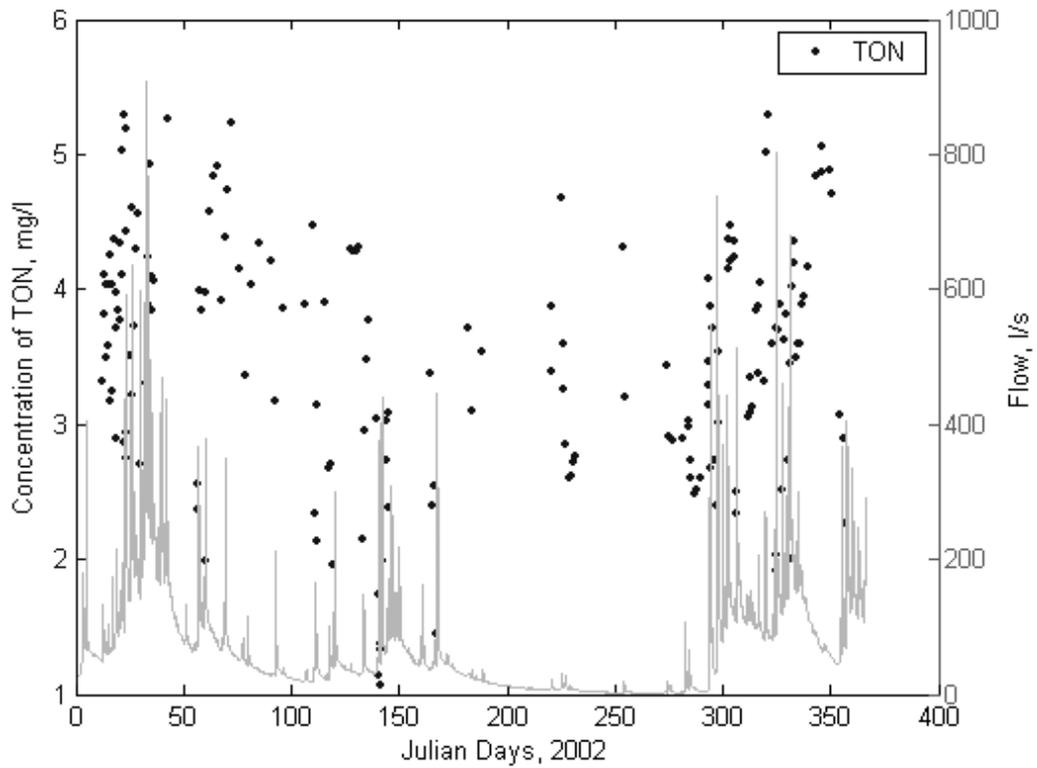
### 3.3 Nitrogen

#### 3.3.1 Total oxidised nitrogen (TON)

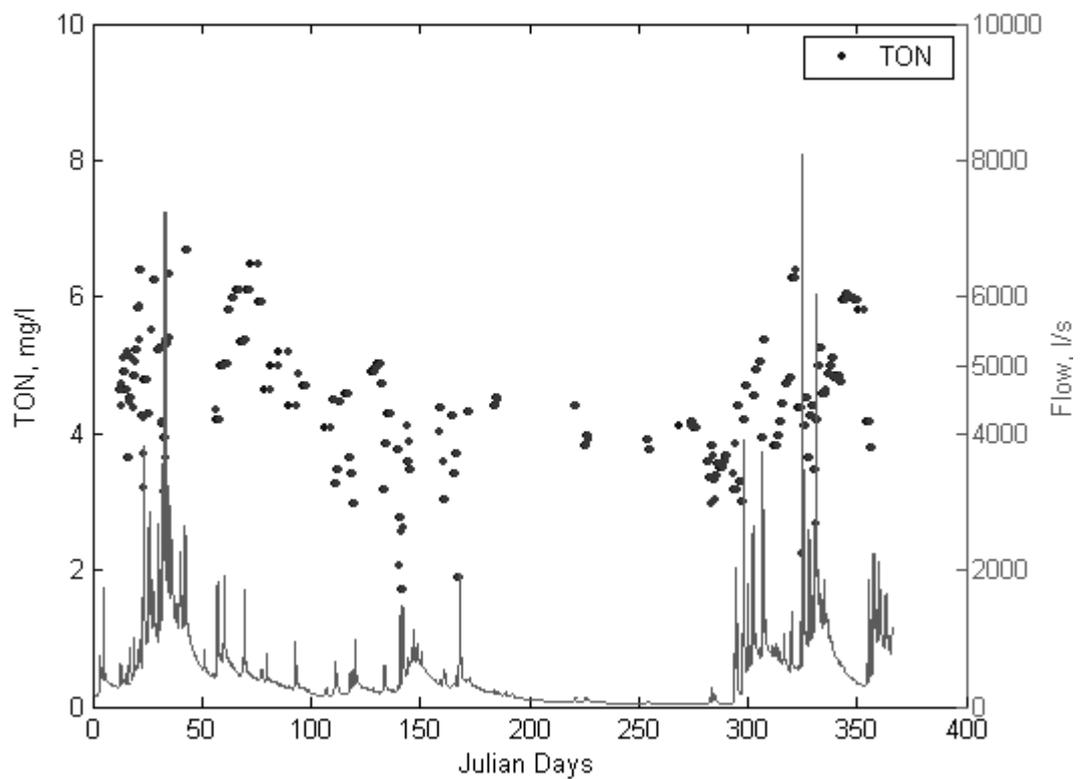
Figures 3.11, 3.12 and 3.13 show the discharge  $Q$  (l/s) and the TON concentrations (mg/l) in the composite samples taken at S1, S3 and S4. The lowest concentrations of TON occurred in early to mid summer for the three catchments. The highest concentrations occur in winter (see Table 3.4). The concentrations of TON range from 0.5 to 6.5 mg/l at all three sites with little variation from site to site.



**Figure 3.11** The time series over the year 2002 of total oxidised nitrogen (TON) in mg/l and discharge ( $Q$ ) in l/s at site 1 (17 ha).



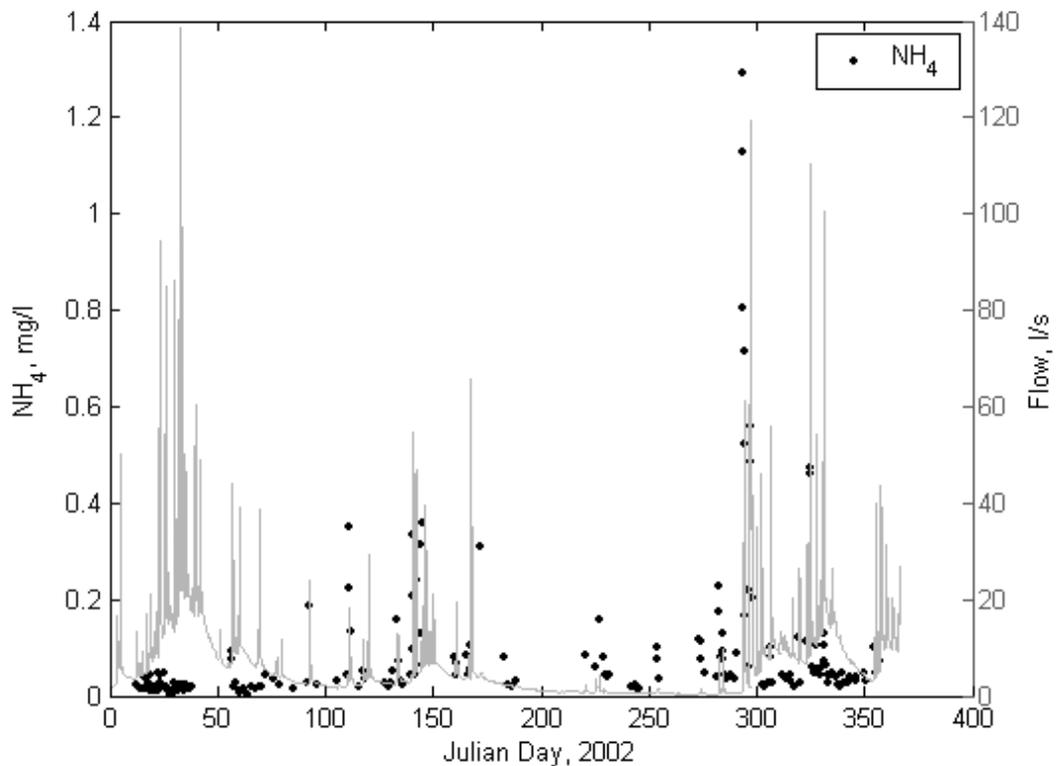
**Figure 3.12** The time series over the year 2002 of total oxidised nitrogen (TON) in mg/l and discharge (Q) in l/s at site 3 (211 ha).



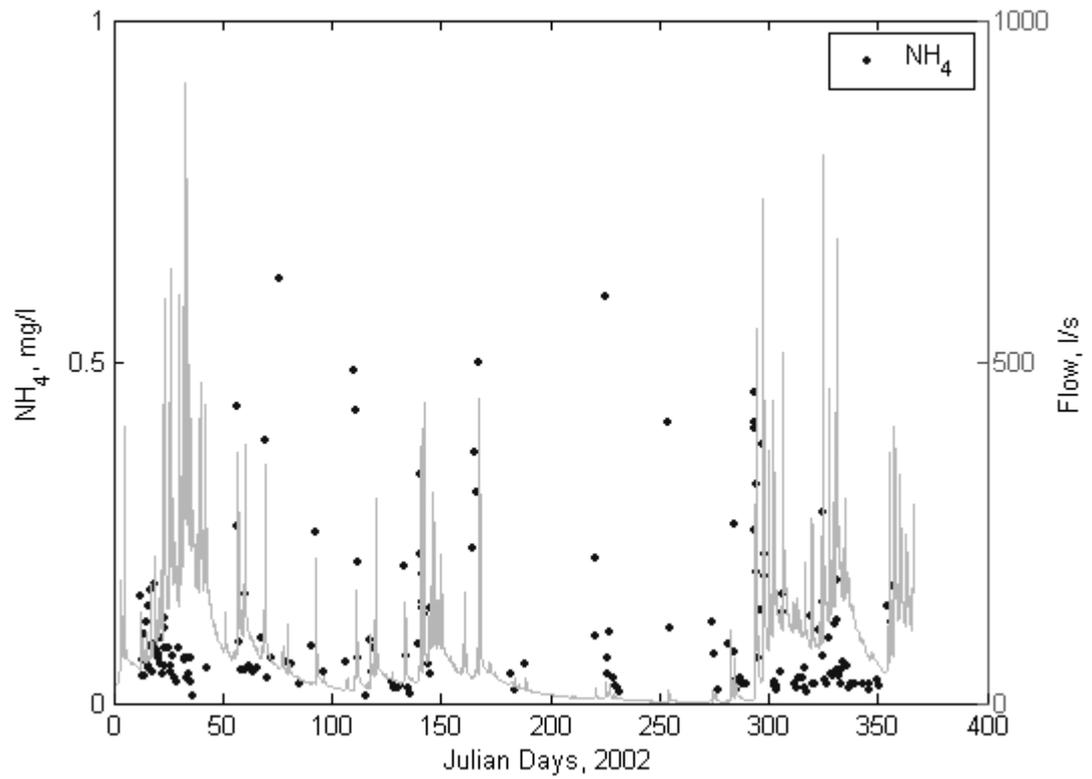
**Figure 3.13** The time series over the year 2002 of total oxidised nitrogen (TON) in mg/l and discharge (Q) in l/s at site 4 (1524 ha).

### 3.3.2 Ammonium (NH<sub>4</sub>)

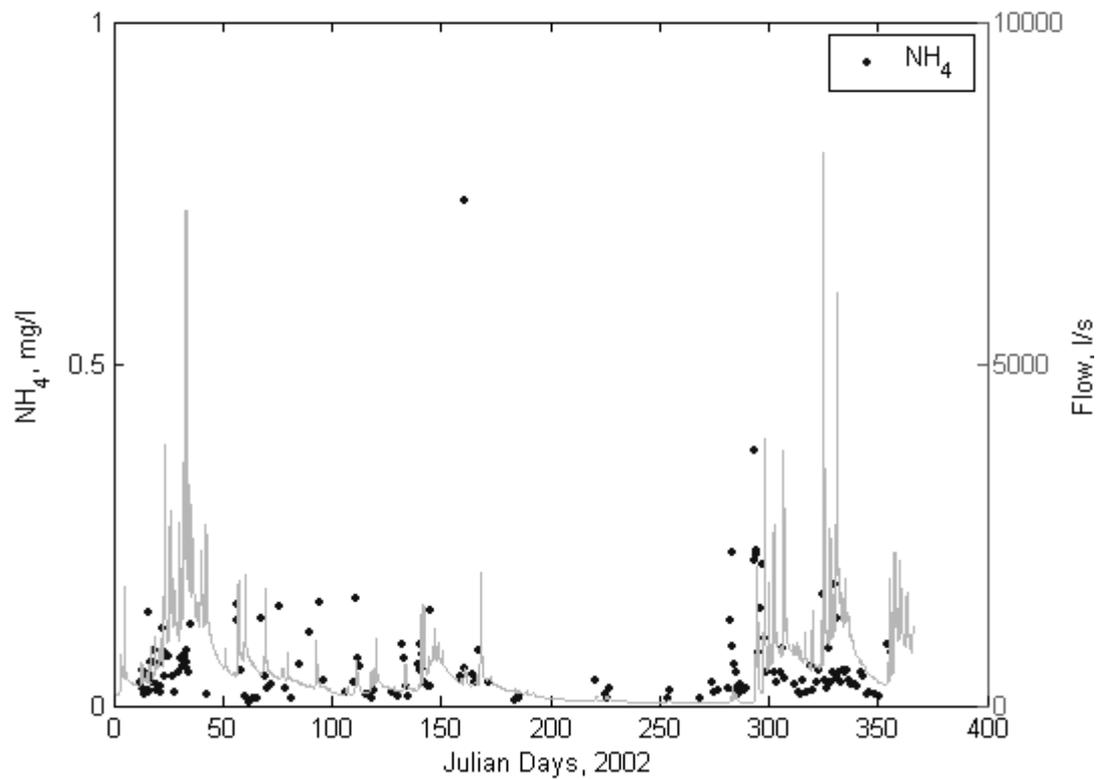
The ammonium concentrations and flow observed at S1, S3 and S4 are shown in Figures 3.14, 3.15 and 3.16. The highest concentrations of NH<sub>4</sub> all occurred in different seasons (Table 3.5) for the three sites. Similar to TP, high concentrations of NH<sub>4</sub> corresponding to applications of slurry were observed throughout the year. The lowest concentrations occurred in early Spring. Values of NH<sub>4</sub> were low for most of the year (under 1 mg/l). Several larger values were observed throughout the year. These were likely due to slurry applications and rainfall. The relatively high concentrations of NH<sub>4</sub> at S3 during periods of low flow may be due to the presence of farmyards in catchment 3. There are no farmyards or any known sources of point pollution in catchment 1.



**Figure 3.14** The time series over the year 2002 of ammonium concentration (NH<sub>4</sub>) in mg/l and discharge (Q) in l/s at site 1 (17ha).



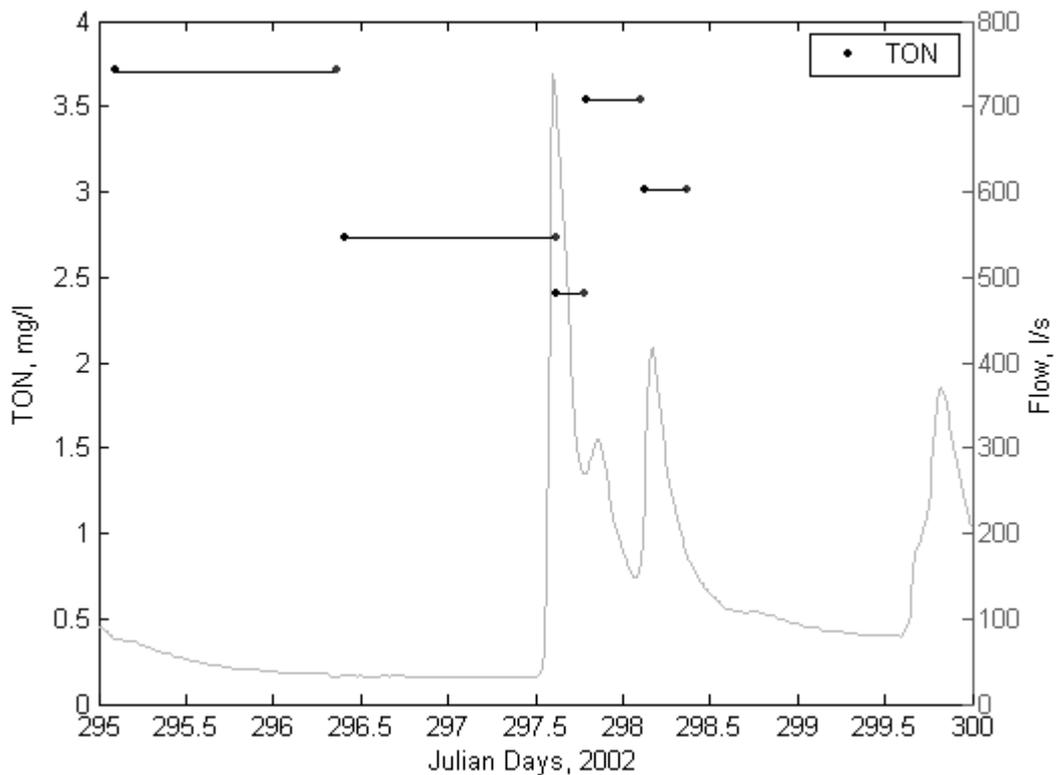
**Figure 3.15** The time series over the year 2002 of ammonium concentration ( $\text{NH}_4$ ) in mg/l and discharge ( $Q$ ) in l/s at site 3 (211 ha).



**Figure 3.16** The time series over the year 2002 of ammonium concentration ( $\text{NH}_4$ ) in mg/l and discharge ( $Q$ ) in l/s at site 4 (1524 ha).

### 3.3.3 Total oxidised nitrogen variation with flow

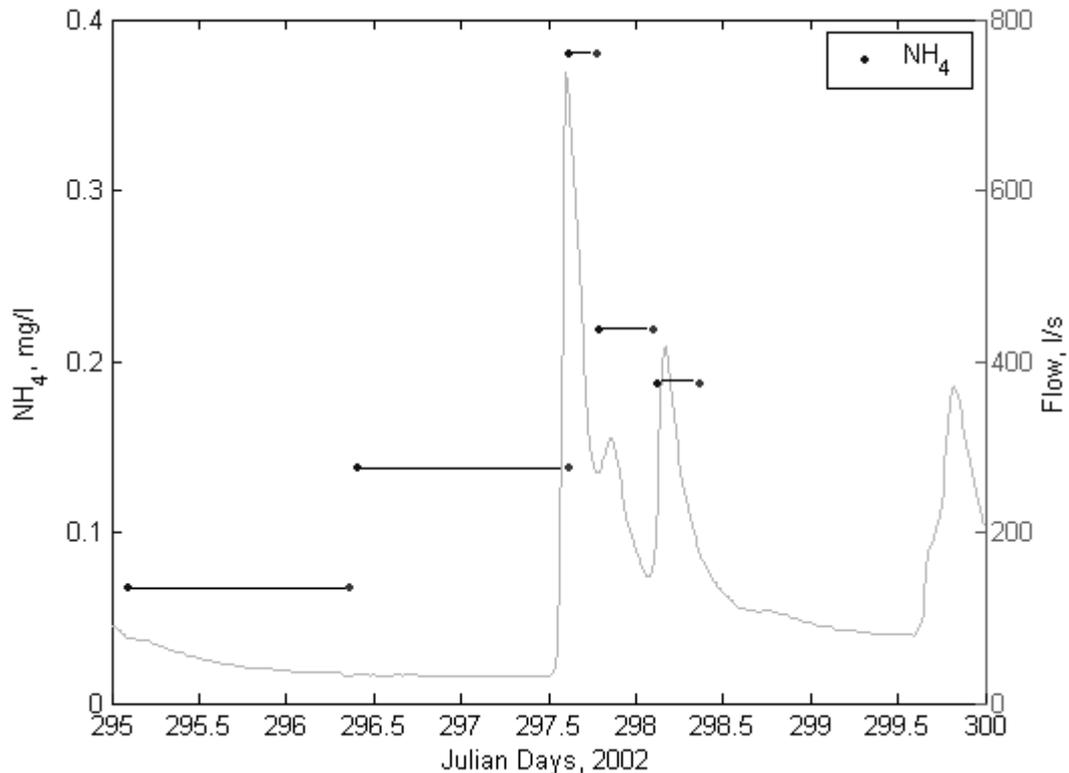
The concentrations of the two forms of nitrogen exhibit a different response to flow. Figure 3.17 shows the variation of TON concentration with flow following one rain event on October 25<sup>th</sup>. TON decreases in concentration with increasing flow. The concentration in the base flow before the increase in flow was higher than the concentration of TON during the flood event. High flow dilutes TON, reducing its concentration.



**Figure 3.17** The time series over 5 days of total oxidised nitrogen (TON) in mg/l and discharge (Q) in l/s at site 3 (211 ha).

### 3.3.4 Ammonium Variation with flow

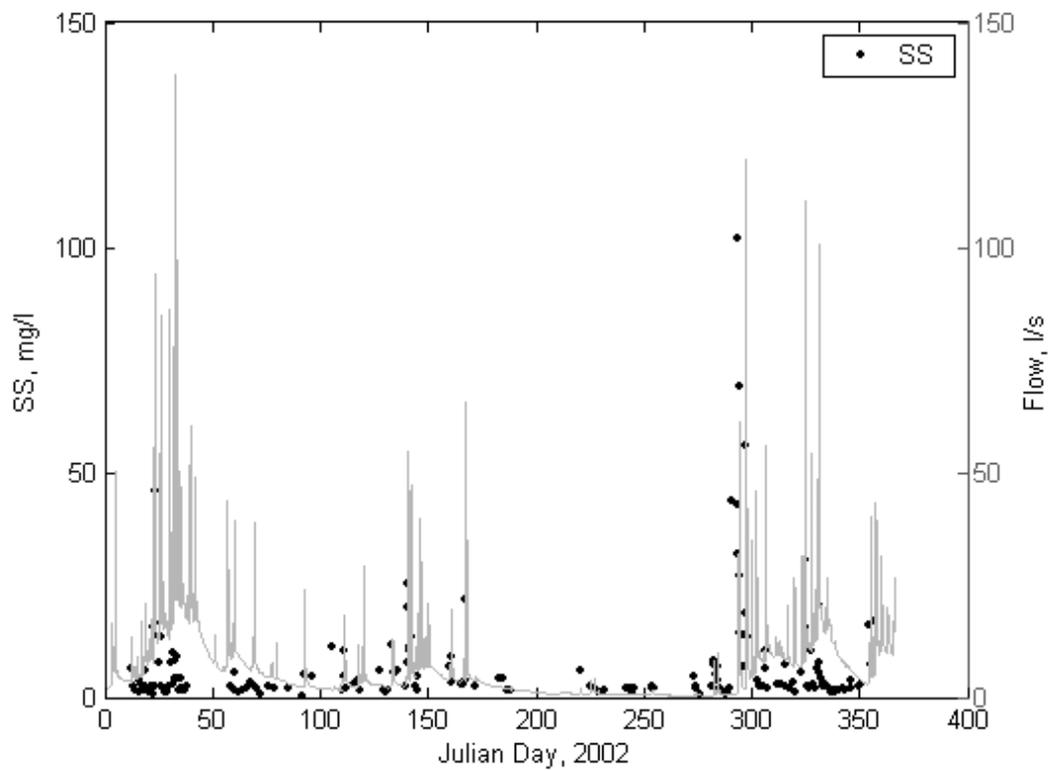
As flow increases so does the concentration of  $\text{NH}_4$ . Figure 3.18 shows the change of  $\text{NH}_4$  with a change of flow. This is the same rain event that saw an increase in TP but a decrease in TON. In just under 12 hours the concentration of  $\text{NH}_4$  increases from 0.13 to 0.38 mg/l.



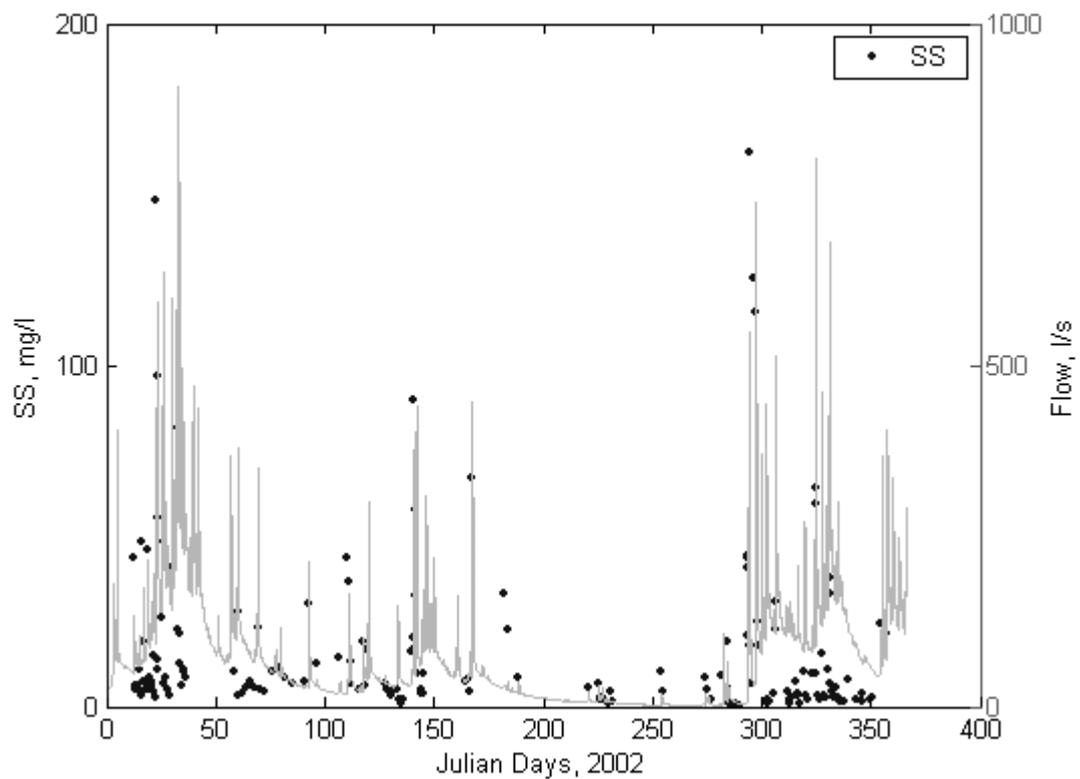
**Figure 3.18** The time series over 5 days of Ammonium ( $\text{NH}_4$ ) in mg/l and discharge (Q) in l/s at site 3 (211 ha).

### 3.4 Suspended sediment

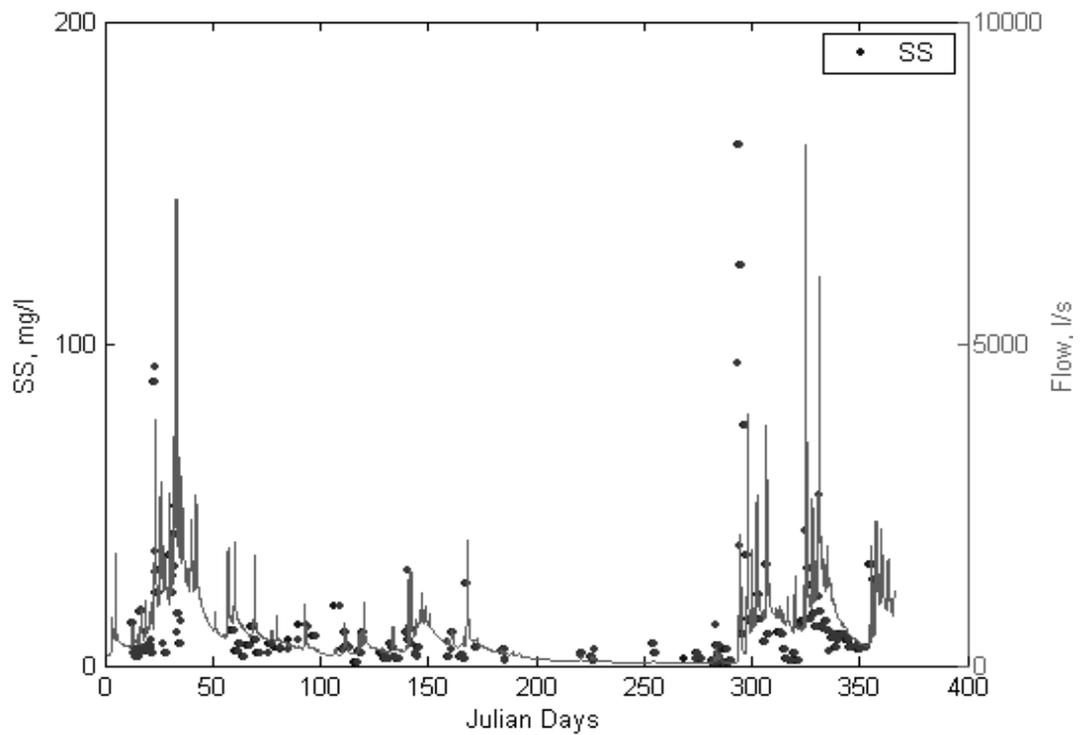
The suspended sediment concentrations and flow observed at S1, S3 and S4 are shown in Figures 3.19, 3.20 and 3.21. High concentrations of SS occurred in flood events. The highest concentrations of suspended sediment occurred during the rain event on October 20<sup>th</sup> coinciding with the peak concentrations of phosphorus and ammonium. The highest concentration of 162 mg/l (see Table 3.6) was observed at S3. The corresponding SS concentrations at S1 were 102 mg/l and at S4 was 161 mg/l. The lowest concentrations at S3 and S4 occurred one to two weeks before the highest concentrations were recorded.



**Figure 3.18** The time series over the year 2002 of Suspended solids concentration (SS) in mg/l and discharge (Q) in l/s at site 1 (17ha).



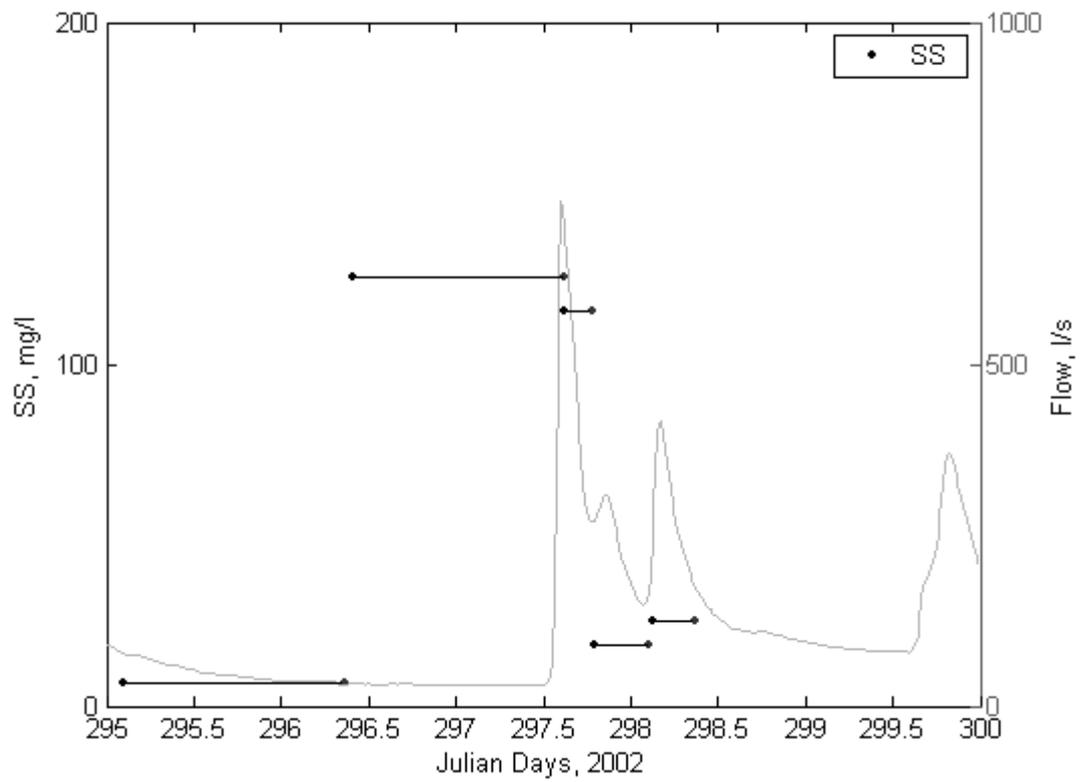
**Figure 3.19** The time series over the year 2002 of Suspended solids concentration (SS) in mg/l and discharge (Q) in l/s at site 3 (211 ha).



**Figure 3.20** The time series over the year 2002 of suspended sediment (SS) concentration in mg/l and discharge (Q) in l/s at site 4 (1524 ha).

### 3.4.1 Variation of suspended sediment with flow

Figure 3.20 shows the change of suspended sediment (SS) concentrations in a single flood. SS concentrations increase with increasing flow. Background concentrations of SS are approximately 1mg/l while flood flow SS concentrations are of order 10 mg/l. In exceptional flows the SS concentrations increase to approximately 100 mg/l.



**Figure 3.22** The time series over 5 days of suspended sediment (SS) in mg/l and discharge (Q) in l/s at site 3 (211 ha).

**Table 3.1.** Summary results of total phosphorus concentrations at the three sites.

Site	Range of TP in samples (mg/l)	Annual average concentration (mg/l)	Percentage of year covered	Lowest TP date	Highest TP date
S1	0.02 – 5.1	0.21	42%	Apr 13 <sup>th</sup>	Oct 20 <sup>th</sup>
S3	0.04 – 2.8	0.22	40%	Dec 16 <sup>th</sup>	Oct 20 <sup>th</sup>
S4	0.02 – 1.2	0.155	43 %	May 10 <sup>th</sup>	Oct 10 <sup>th</sup>

**Table 3.2** Summary results of total dissolved phosphorus concentration at the three sites.

Site	Range of TDP in samples (mg/l)	Annual average concentration (mg/l)	Percentage of year covered	Lowest TDP date	Highest TDP date
S1	0.01 – 3.3	0.14	42%	Apr 2 <sup>nd</sup>	Oct 20 <sup>th</sup>
S3	0.02– 0.96	0.13	40%	Dec 16 <sup>th</sup>	Oct 20 <sup>th</sup>
S4	0.01 – 0.6	0.1	43 %	May 9 <sup>th</sup>	Oct 21 <sup>st</sup>

**Table 3.3** Summary results of soluble reactive phosphorus concentration at the three sites.

Site	Range of SRP in samples (mg/l)	Annual average concentration (mg/l)	Percentage of year covered	Lowest NH <sub>4</sub> date	Highest NH <sub>4</sub> date
S1	0.001 – 3.2	0.12	42%	Mar 6 <sup>th</sup>	Oct 20 <sup>th</sup>
S3	0.015– 0.72	0.11	40%	Mar 4 <sup>th</sup>	Oct 20 <sup>th</sup>
S4	0.005 – 0.38	0.08	43 %	May 9 <sup>th</sup>	Oct 21 <sup>st</sup>

**Table 3.4** Summary results of total oxidised nitrogen concentration at the three catchments

Site	Range of TON in samples (mg/l)	Annual average concentration (mg/l)	Percentage of year covered	Lowest TON date	Highest TON date
S1	0.6 – 6.3	4.12	42%	Jun 16 <sup>th</sup>	Jan 22 <sup>nd</sup>
S3	1.1 – 5.3	3.56	40%	May 22 <sup>nd</sup>	Nov 18 <sup>th</sup>
S4	1.7 – 6.7	4.5	43 %	Jun 22 <sup>nd</sup>	Feb 12 <sup>th</sup>

**Table 3.5** Summary results of ammonium concentration at the three-catchments.

Site	Range of NH <sub>4</sub> in samples (mg/l)	Annual average concentration (mg/l)	Percentage of year covered	Lowest NH <sub>4</sub> date	Highest NH <sub>4</sub> date
S1	0.001 – 1.3	0.017	42%	Jan 29 <sup>th</sup>	Oct 20 <sup>th</sup>
S3	0.01– 0.62	0.013	40%	Feb 5 <sup>th</sup>	Mar 19 <sup>th</sup>
S4	0.005 – 0.73	0.02	43 %	Mar 4 <sup>th</sup>	Jun 10 <sup>th</sup>

**Table 3.6** Summary results of suspended sediment concentration at the three-catchments.

Site	Range of SS in samples (mg/l)	Annual Average concentration (mg/l)	Percentage of year covered	Lowest SS date	Highest SS date
Site 1	102.0 – 0.2	4.9	42%	Apr 2 <sup>nd</sup>	Oct 20 <sup>th</sup>
Site 3	162.0– 0.4	13.1	40%	Oct 16 <sup>th</sup>	Oct 21 <sup>st</sup>
Site 4	161.7 – 0.5	13.1	43 %	Oct 9 <sup>th</sup>	Oct 21 <sup>st</sup>

# Chapter 4

## Gap filling

### 4.1 Introduction

We have a detailed record of the river flow at 15-minute intervals for the full year at S1, S3 and S4. The composite water samples cover approximately half the year for the three sites. Covering 100% of the year for water chemistry was not possible due to cost. There are gaps in the data - most frequently at low flows but not exclusively so. The following section explains the methodology of how the gaps in the data were infilled. At sites 1, 3, 4 the sampling strategy covered 42%, 40% and 43% of the year, respectively. Therefore we require a robust gap filling technique for the remainder of the year.

The instantaneous total phosphorus,  $e$ , for a given stream location is calculated as the product of the river instantaneous discharge  $Q_i$  and the concentration of phosphorus  $C_i$ , (Webb et al., 1997).

$$e = Q_i * C_i \quad (4.1)$$

The cumulative flow in the stream for the year is computed from the observed 15-minute flow data. The phosphorus export load ( $L$ ) for any period is calculated from

$$L = (Q_{i+1} - Q_i) * \bar{C} \quad (4.2)$$

where  $Q_i$  is cumulative flow at the start of a period in question,  $Q_{i+1}$  is cumulative flow at the end of a period and  $\bar{C}$  is the mean concentration of the phosphorus during the period. The annual export of P is then

$$AE = \sum_{i=1}^{i=n} L_i \quad (4.3)$$

where  $n$  is the number of composite sampling periods over the year. The total export for the year is then normalized (per unit area) for comparison within the nested catchments.

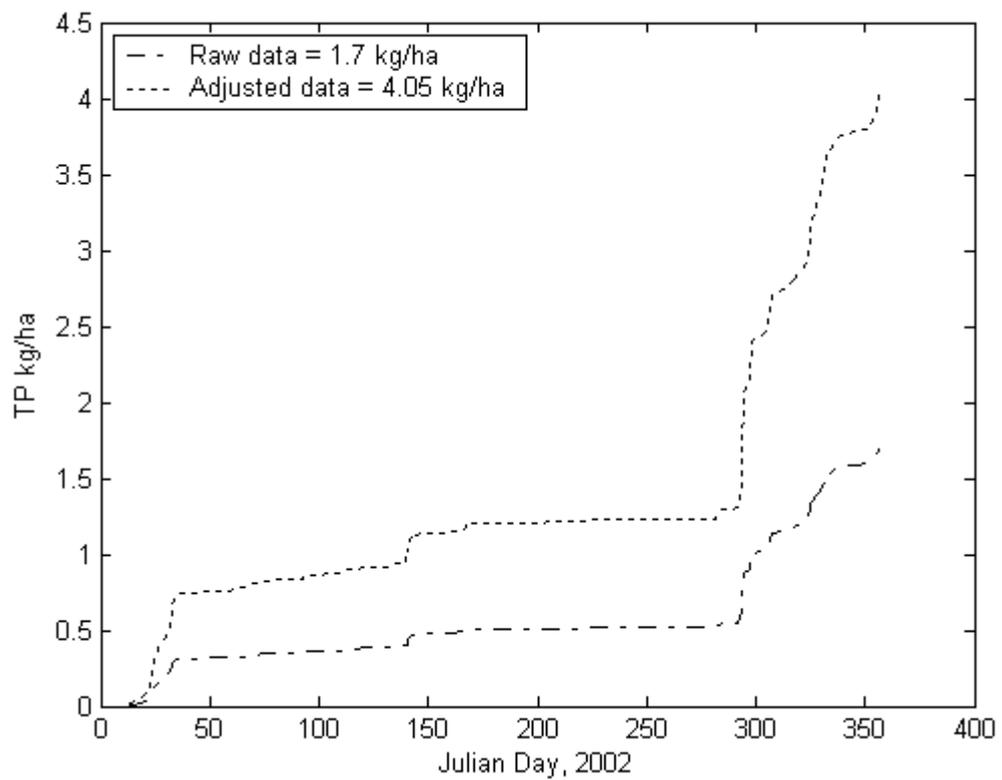
$$NAE = \frac{AE}{Area} \quad (4.4)$$

where  $Area$  is the area of the catchment in hectares.

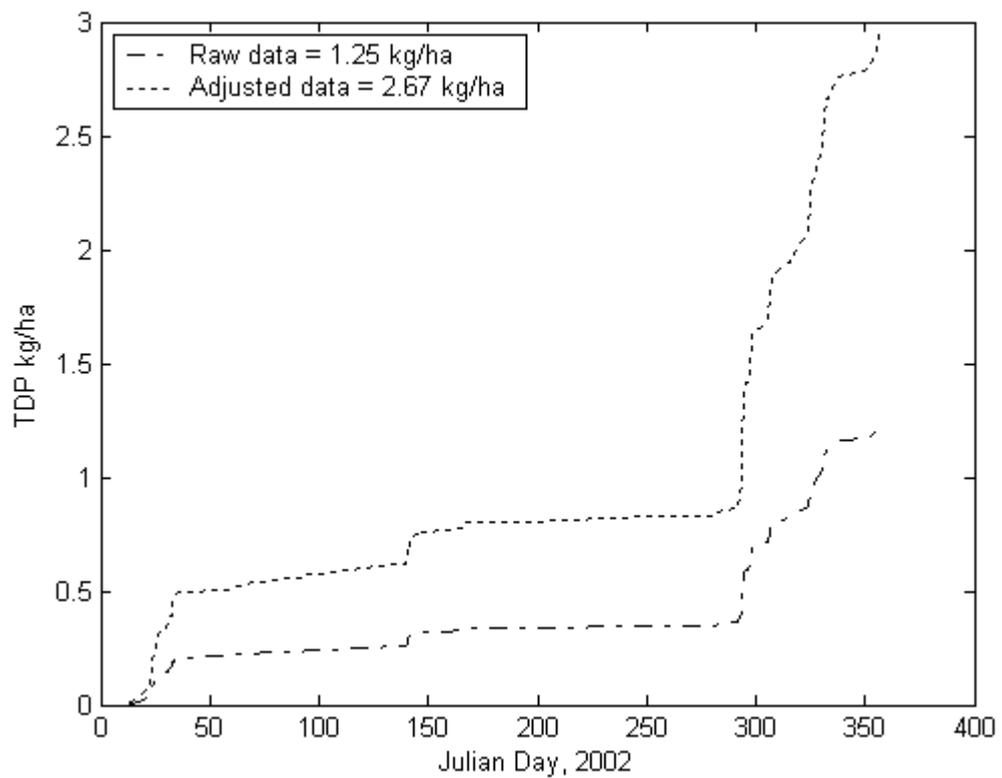
## 4.2 Raw data

Following the procedure described in section 4.1, the export of TP was estimated from the raw data from catchment 1. The raw data consisted of samples that covered 42% of the year and the TP exported in this time period was estimated at  $1.7 \text{ kg ha}^{-1}$ . This figure is considered to be the lower bound of the TP export. If  $1.7 \text{ kg ha}^{-1}$  was exported during 42% of the year then assuming that this loss rate was uniform,  $4.05 \text{ kg ha}^{-1}$  would have been lost if the samples covered 100% of the year (see Figure 4.1). This value is an upper bound as more water chemistry samples were taken in periods of high flow where most of the nutrient loss occurred. The true value should lie between  $1.7$  and  $4.05 \text{ kg ha}^{-1}$ . The upper bounds and lower bounds for TDP are  $1.25$  and  $1.67 \text{ kg P ha}^{-1}$  (see Figure 4.2). For SRP  $1.12$  and  $2.68 \text{ kg ha}^{-1}$  were estimated to be the lower and upper bounds (see Figure 4.3).

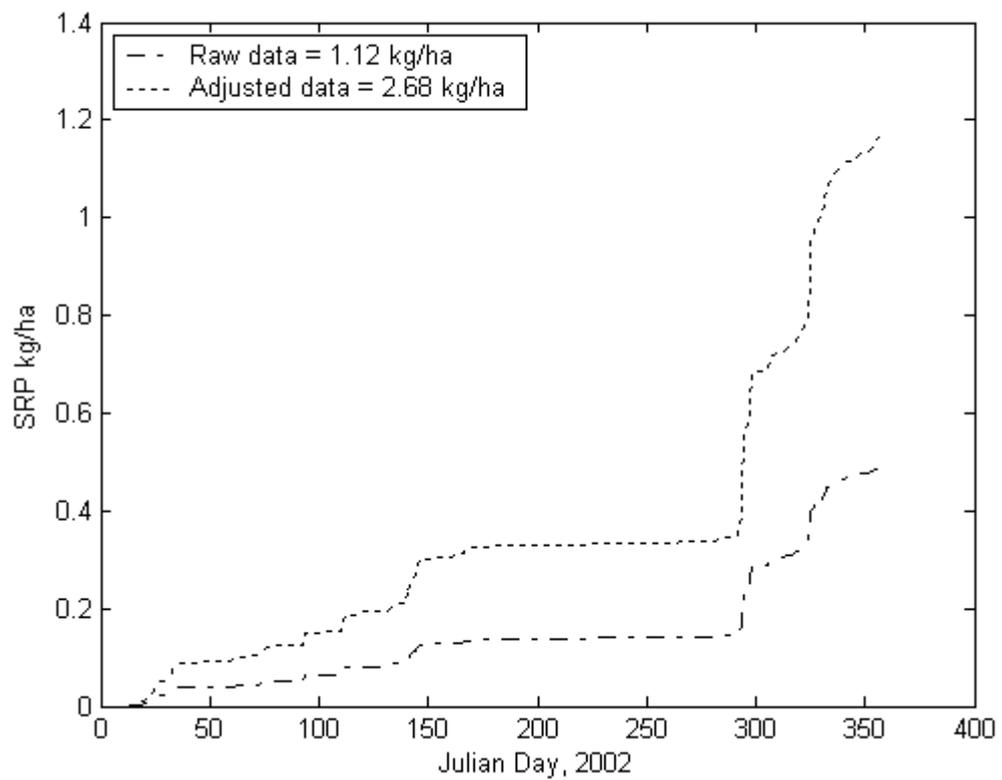
This process was repeated for the nitrogen export. The lower bound TON export estimated for the raw data was  $29 \text{ kg N ha}^{-1}$  and the upper bound was estimated at  $69 \text{ kg N ha}^{-1}$  at S1 (see Figure 4.4). The lower and upper exports (Figure 4.5) of  $\text{NH}_4$  are  $0.49$  and  $1.17 \text{ kg N ha}^{-1}$  at S1. Figure 4.6 shows the suspended sediment lower and upper bounds ( $46$  and  $109 \text{ kg ha}^{-1}$ , respectively) at S1.



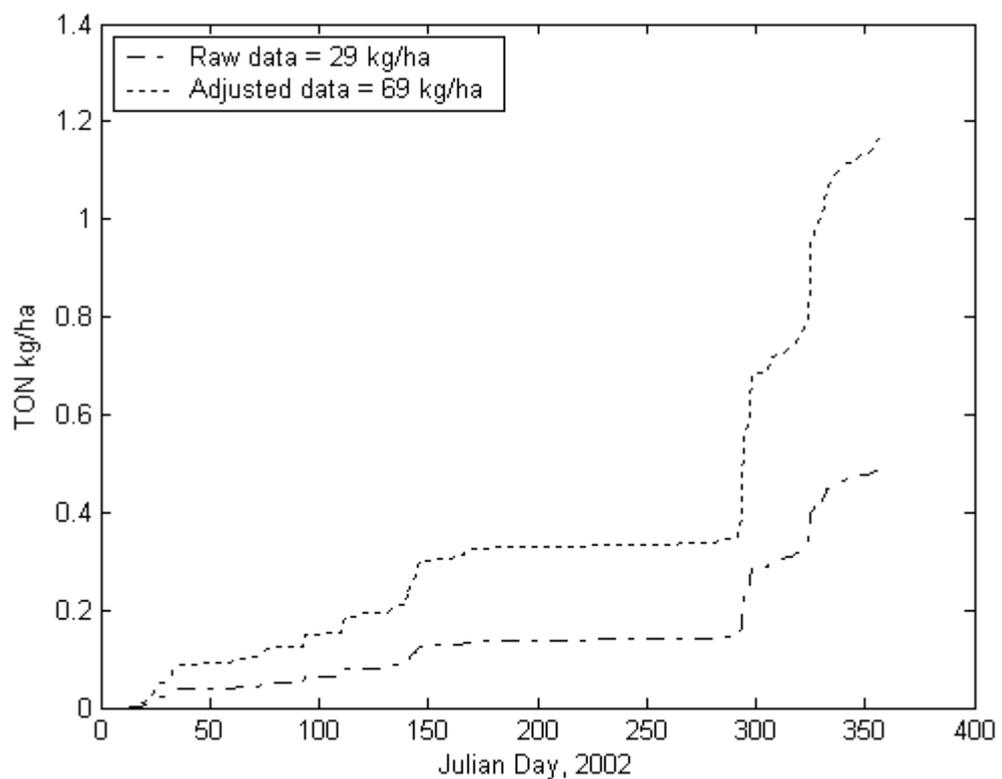
**Figure 4.1** Upper and lower bound estimates of TP export at S1.



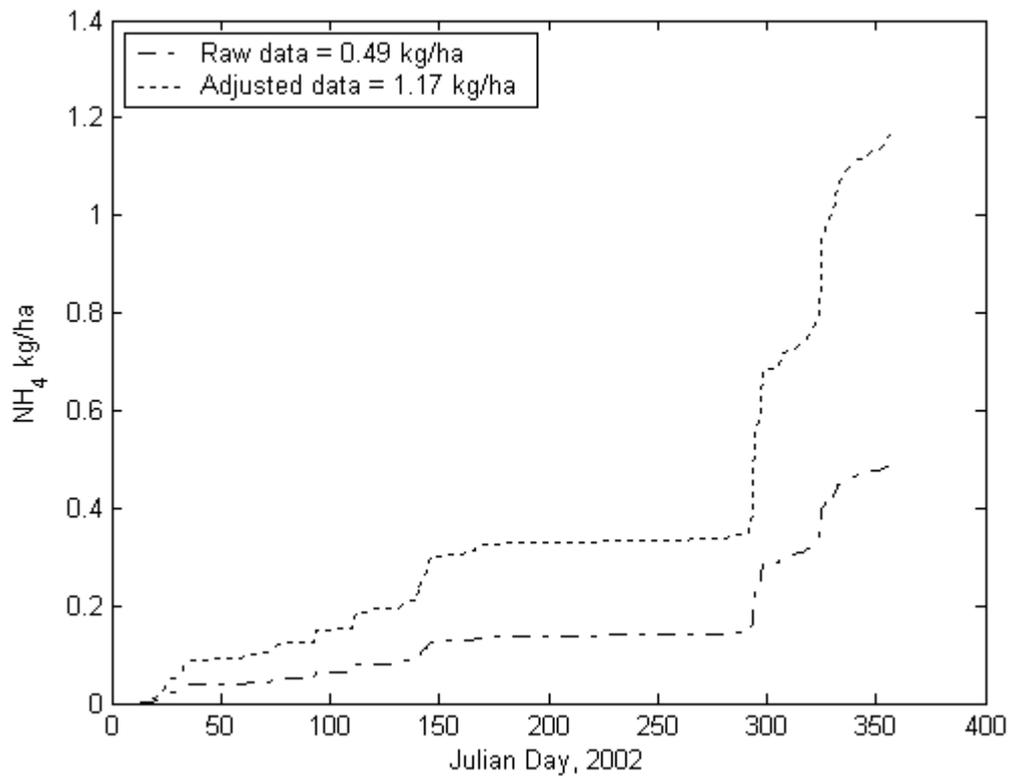
**Figure 4.2** Upper and lower bound estimates of TDP export at S1.



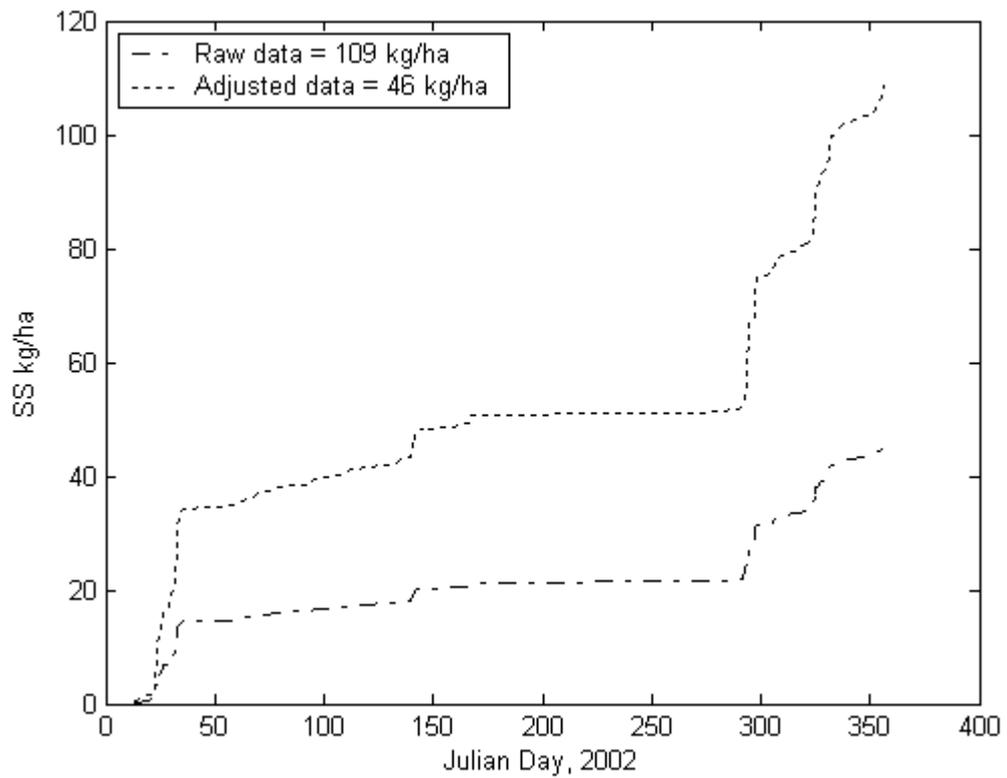
**Figure 4.3** Upper and lower bound estimates of SRP export at S1.



**Figure 4.4** Upper and lower bound estimates of TON export at S1.



**Figure 4.5** Upper and lower bound estimates of NH<sub>4</sub> export at S1.



**Figure 4.6** Upper and lower bound estimates of SS export at S1.

### 4.3 Gap filling Method A

Method A is a simple manual technique of gap filling. Most of the gaps in the data occurred in the summer or during periods of low flow (when the contribution to phosphorus export is least). Due to the fact that fluctuations in total phosphorus concentrations in the stream are largely due to rainfall events it was assumed that there would be little change in total phosphorus concentrations in periods of low flow. Following a visual examination of flow and concentration, interpolation or extrapolation of concentrations of composite and grab sample data were used to estimate the concentration value in the gap.

This method is approximate but it was considered a useful starting point and gave a first estimate of the annual export which fell between the upper and lower bound estimates of section 4.2. This value was used as a reference value for method B.

### 4.4 Gap filling Method B

In order to estimate more scientifically the concentration in the gaps a relationship was developed between known flows  $Q$ , and concentrations  $C$ . An empirical power law relationship was used between  $C$  and  $Q$

$$C = mQ^n \quad (4.5)$$

where  $C$  is the concentration (mg/l),  $Q$  is the flow in (l/s) and  $m$  and  $n$  are catchment (and/or seasonal) specific constants. This technique is to plot  $C$  vs.  $Q$  for known data for all the year and determine a single annual relationship as in (4.5). Figures 4.7 shows the total phosphorus, CQ relationships at S3. Similar relationships for TP at S1 and S4 were also derived.

This procedure was repeated for TDP, SRP, TON, NH<sub>4</sub> and SS at all three sites. In a catchment with seasonal variation of flows and seasonal variation of application of fertiliser (and slurry) it may be more appropriate to plot the known data for each of the four seasons. This gives four empirical relationships for the year (for each of the three sites) rather than one relationship for the full year. We applied both sets (the single annual and the four seasonal curves) to estimate the annual export load. However the

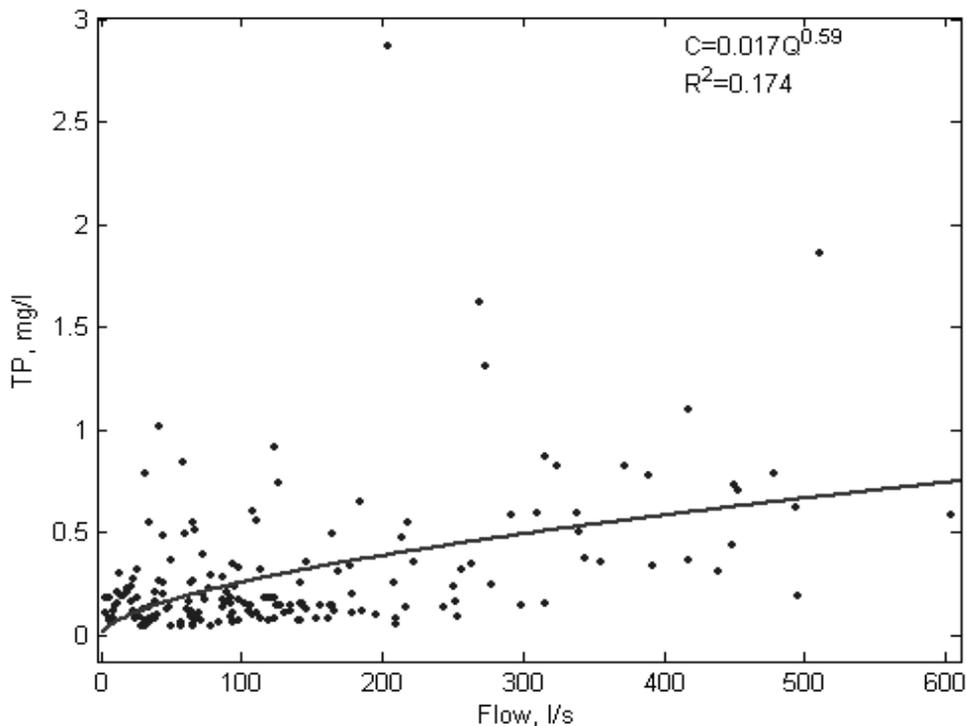
results were very similar and so it was decided to use one single relationship in order to reduce the number of calculations.

The total phosphorus,  $CQ$  relationships for site 3 was estimated as:

$$C = 0.017Q^{0.59} \quad (4.6)$$

The  $R^2$  for S3 was 0.174. It was found for all the gap filled estimates that the annual export value was between the upper and lower bound estimates (of section 4.2) and close to the manual estimate of section 4.3.

$R^2$  is a measure of how successful the fit is in explaining the variation of the data. A  $R^2$  value of 1 is a perfect fit and a value of 0 indicates that there is no relationship between the data.  $R^2$  is defined as the ratio of the sum of the squares of the regression and the total sum of squares. The confidence interval used in all analysis is 95%.



**Figure 4.4** Total phosphorus concentration and streamflow for catchment area 3 (211 ha).

# Chapter 5

## Exports of Phosphorus, Nitrogen & Suspended Sediment

## 5.1 Introduction

After completing the ‘gap filling’ exercise described in chapter 4 the exports from the catchments for the entire year were estimated for: total phosphorus (TP); particulate phosphorus (PP); total dissolved phosphorus (TDP); soluble reactive phosphorus (SRP); total oxidised nitrogen (TON); ammonium (NH<sub>4</sub>) and suspended sediment (SS).

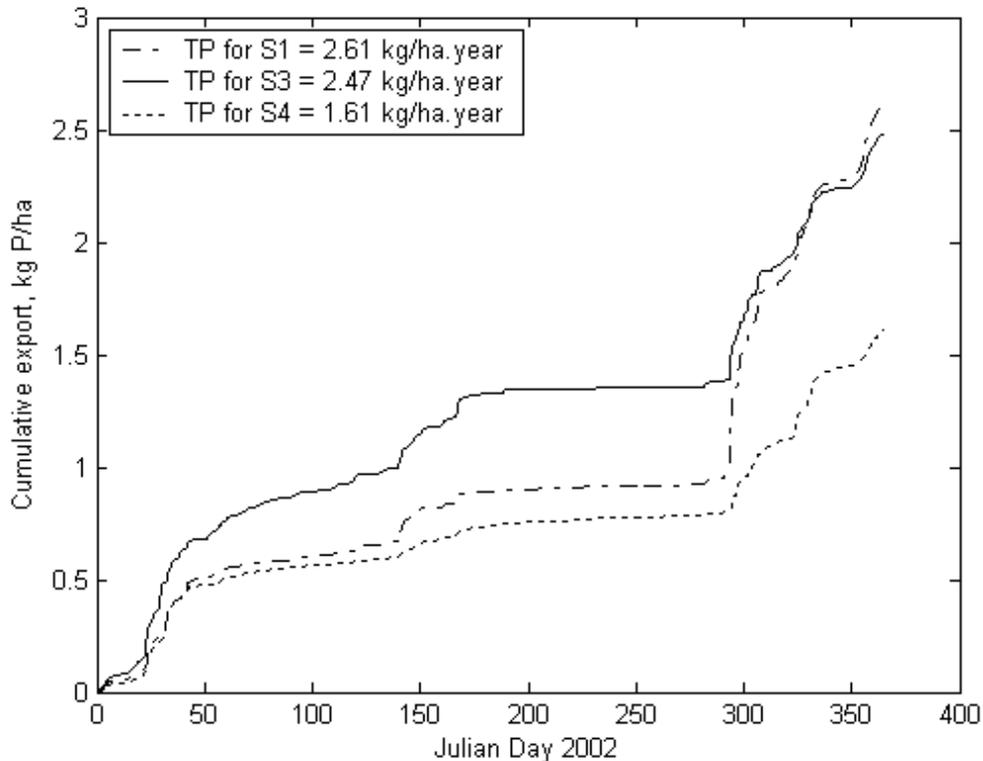
## 5.2 Exports of phosphorus

The total phosphorus exports from the three catchments in 2002 were estimated at 2.61, 2.47 and 1.61 kg P ha<sup>-1</sup> for the 17, 211 and 1524 ha catchments respectively (see Figure 5.1). S1 had the highest export of TP at 2.61 kg P ha<sup>-1</sup> with 45% of the annual export occurring in the last three months of the year. This is due to a combination of slurry application and heavy monthly rainfalls after October. The annual exports of total phosphorus from catchments 3 and site 4 were lower at 2.5 and 1.61 kg P ha<sup>-1</sup> respectively. For the 17 and 211 ha catchments, the export rates represent 12.1% and 7.2%, respectively, of the combined chemical fertiliser and slurry application.

From January to mid October 0.8 and 0.9 kg P ha<sup>-1</sup> (TP), respectively, were exported from catchments 3 and 4. On the 15<sup>th</sup> of October there was a significant slurry application in three fields in catchment 1 (consisting of 35% of area). In combination with heavy rainfall on October 20, this resulted in a significant increase in the export of TP from catchment 1 but the same increase was not observed at site 4, (9.5km downstream see Figure 5.1). In catchment 1, the export rose from 0.9 at October 15 to 2.61kg P ha<sup>-1</sup> on December 31, while during the same time period the export increased from 0.8 to 1.61 kg P ha<sup>-1</sup> at site 4. There are no farmyards contributing to S1. There are two farmyards contributing to S3. If we examine the TP export up to October (Julian day 280), we note that the TP export from S3 exceeds TP export from S1 by 0.44 P kg ha<sup>-1</sup>. For the same period the TP exports for S1 and S4 are similar. This suggests that the two farmyards may be contributing an amount equal to 0.44 kg P ha<sup>-1</sup> up to October for which the TP export for site 1 was 0.91 kg ha<sup>-1</sup>. As there are no differences in land use and management practices between S1 and S3 this suggests that the two farmyards may be contributing approximately 30% of the export from S3.

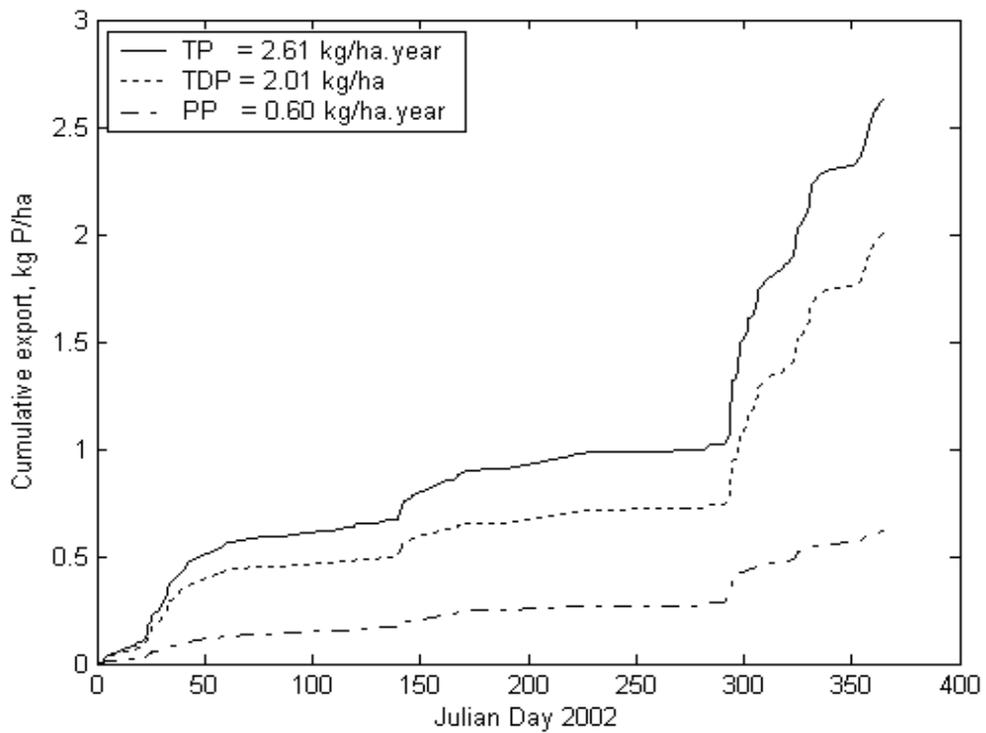
In section 1.2 we noted that to comply with regulations the threshold annual export of TP should not exceed 0.5 kg ha<sup>-1</sup>. The export of TP exceeded 0.5 kg P ha<sup>-1</sup> at

the three sites in less than 50 days (see Figure 5.1) i.e. before the end of February. This has implications for water quality.

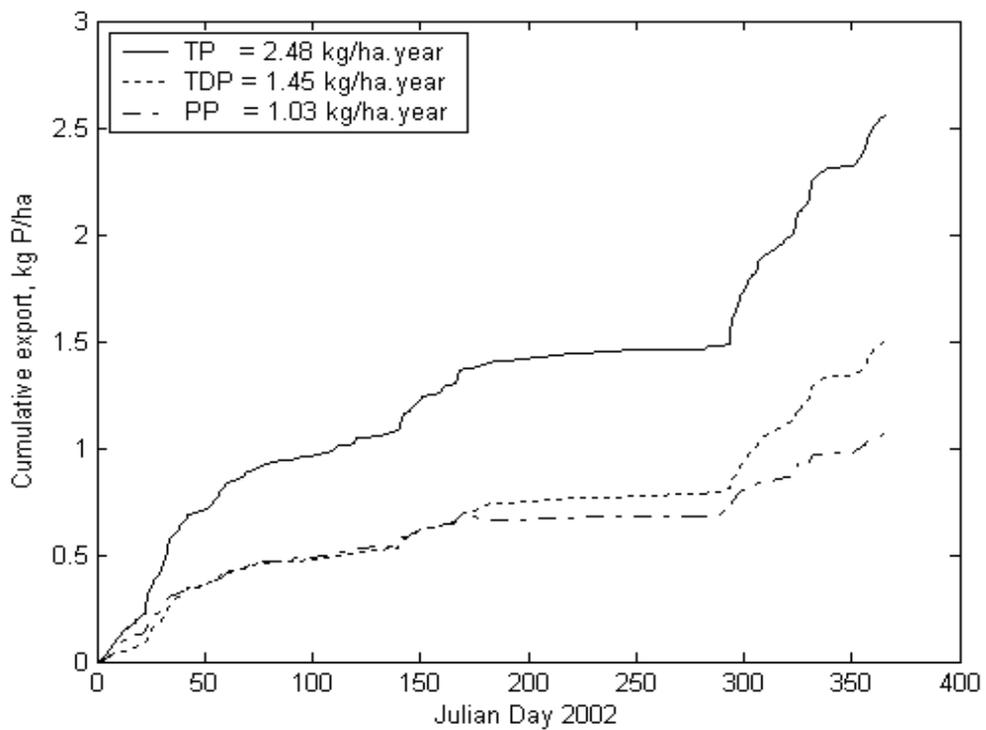


**Figure 5.1** The normalised cumulative total phosphorus export ( $\text{kg ha}^{-1}$ ) from the three catchments 1, 3 and 4.

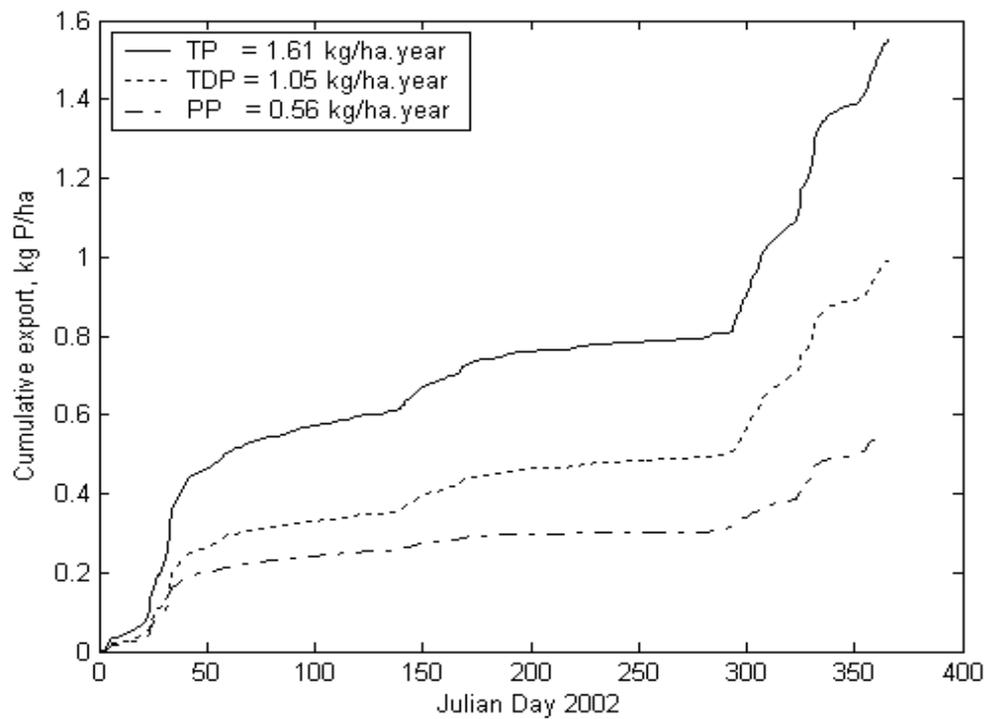
The different fractions of phosphorus (dissolved and particulate) were also analysed for the full year. Particulate phosphorus (PP) is defined as  $\text{TP} - \text{TDP}$ . At site 1 (see Figure 5.2) the PP remained relatively constant for the year at approximately 25% of TP. Catchment 3 (Figure 5.3) has a different pattern. At S3 the PP was approximately 50% of the total phosphorus for the first 100 days of the year. There is less PP in the second half of the year. At the end of the year, 43% of the exported phosphorus was in particulate form. Catchment 4 (see Figure 5.4) has a similar pattern to catchment 1. At the end of the year the particulate fraction was 37% of TP. The particulate fraction exported from catchment 4 varied more throughout the year than at catchment 1 but less than at catchment 3. The PP export is examined in more detail when the export of SS is discussed. SRP is considered important because it is readily available for algal uptake (Lennox et al., 1997). Soluble reactive phosphorus loss from all three catchments was also estimated. The export of SRP was 1.7, 1.18 and 0.82  $\text{kg P ha}^{-1} \text{ year}^{-1}$  from catchments 1, 3 and 4, respectively (see Figure 5.5).



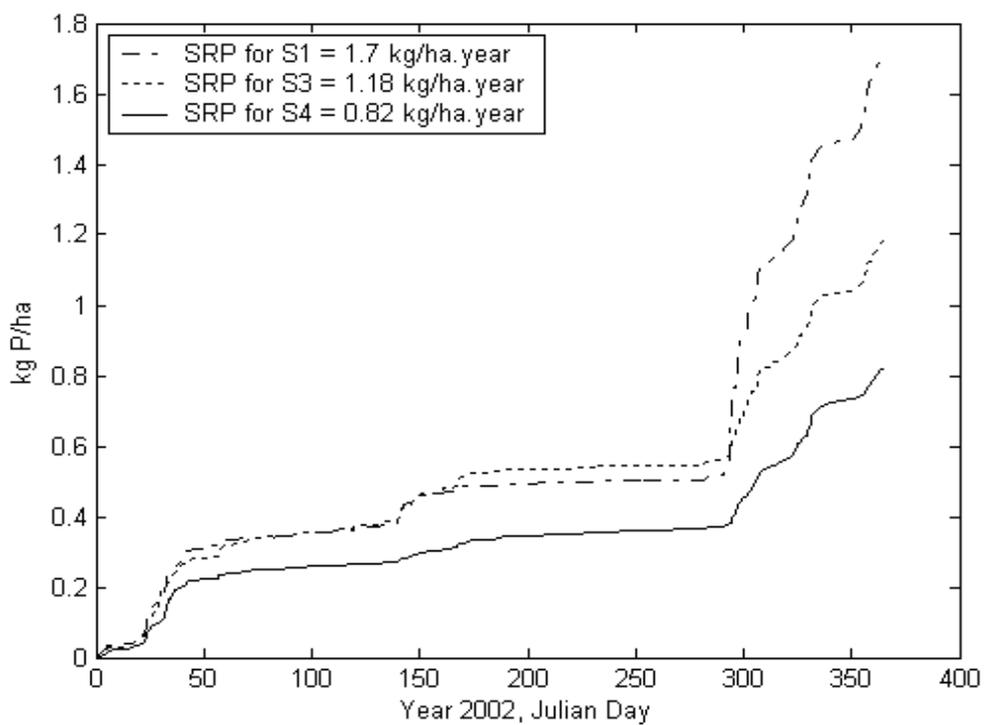
**Figure 5.2** The normalised export ( $\text{kg ha}^{-1}$ ) of total phosphorus (TP), total dissolved phosphorus (TDP) and particulate phosphorus (PP) at site 1 (17 ha catchment).



**Figure 5.3** The normalised export ( $\text{kg ha}^{-1}$ ) of total phosphorus (TP), total dissolved phosphorus (TDP) and particulate phosphorus (PP) at site 3 (211 ha catchment).

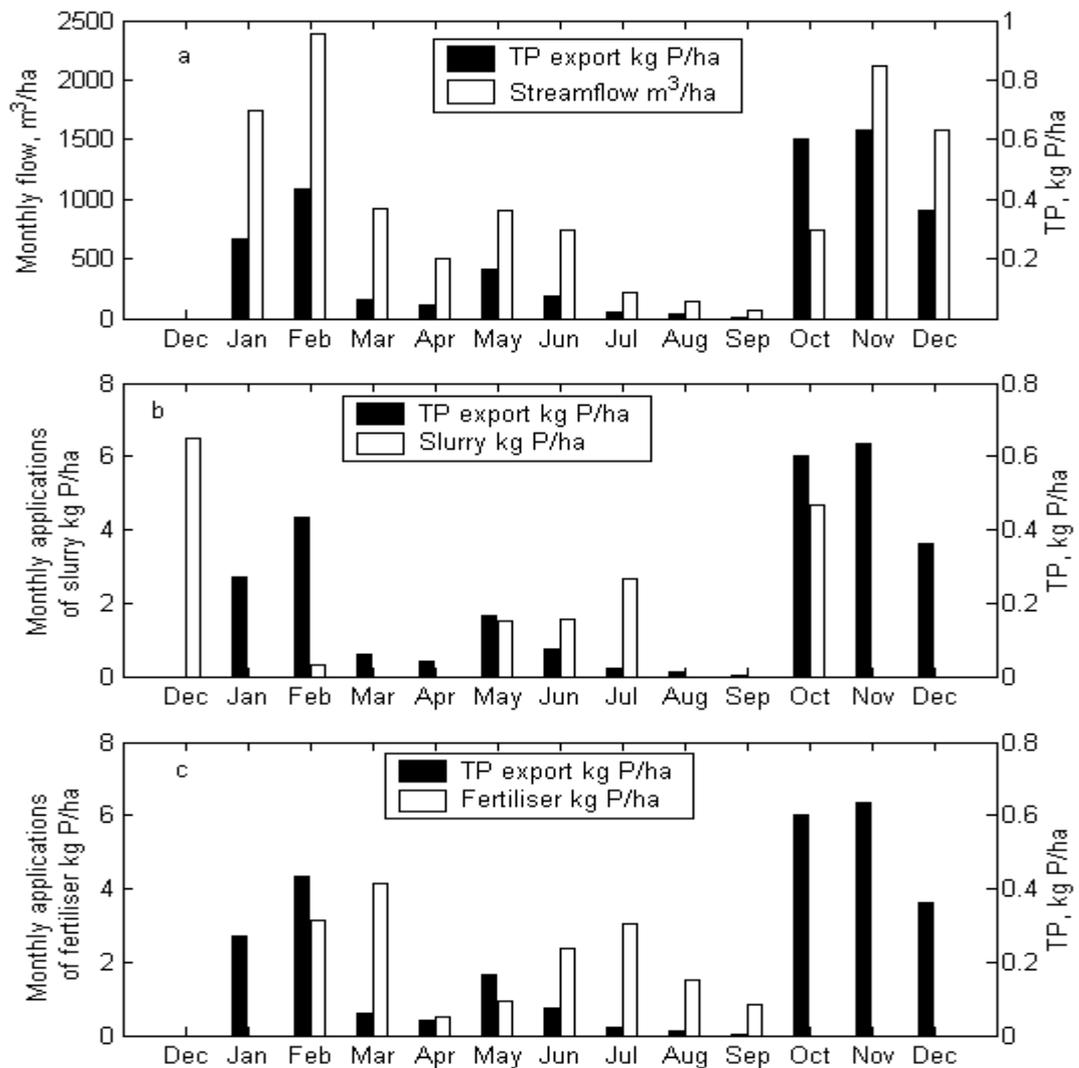


**Figure 5.4** The normalised export ( $\text{kg ha}^{-1}$ ) of total phosphorus (TP), total dissolved phosphorus (TDP) and particulate phosphorus (PP) at site 4 (1524 ha catchment).



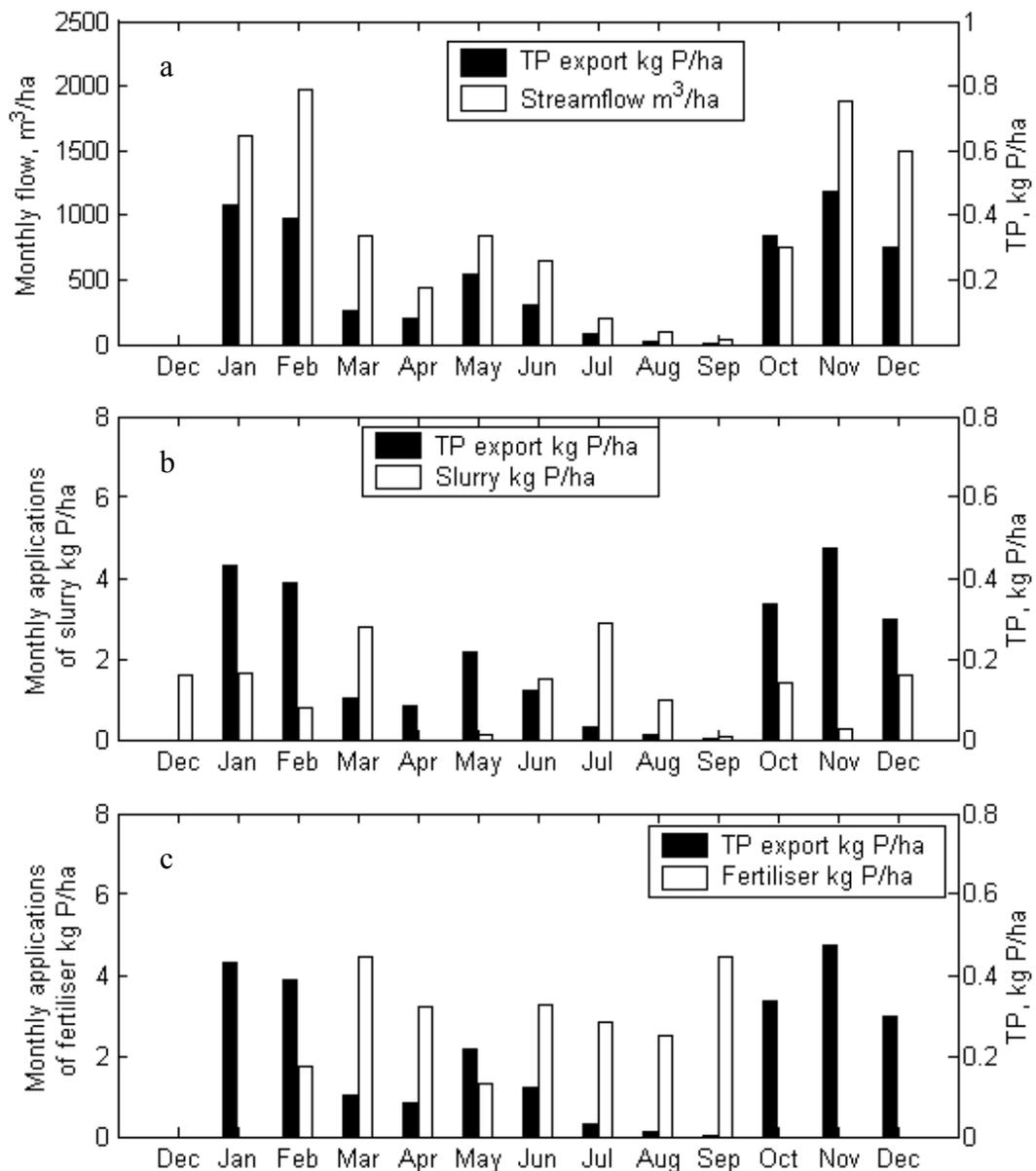
**Figure 5.5** The normalised cumulative soluble reactive phosphorus (SRP) export ( $\text{kg ha}^{-1}$ ) from the three catchments, 1, 3 and 4.

Figure 5.6 (a) shows the monthly exports of TP with monthly stream flows, with fertiliser and with slurry applications from catchment 1. It can be seen that months with high stream flows also have high export of TP. Figure 5.6 (b) shows the monthly chemical fertiliser applications and the monthly export rates of TP. As the fertiliser is spread from February to September, the large exports of TP do not coincide with the months of fertiliser application. The monthly slurry application and the monthly exports of TP are shown in Figure 5.6 (c). This shows that months with high exports of TP coincide or lag the months of high slurry applications. Figures 5.6 (a), 5.6 (b) and 5.6 (c) suggest that exports of TP are dependent on high flows and slurry applications. The chemical fertiliser applications appear to have less of an impact on exports of phosphorus than slurry or rather the random applications of slurry.



**Figure 5.6** (a). Monthly TP export and monthly streamflow at S1;  
 (b). Monthly TP export and monthly slurry applications at S1;  
 (c). Monthly TP export and monthly fertiliser applications S1;

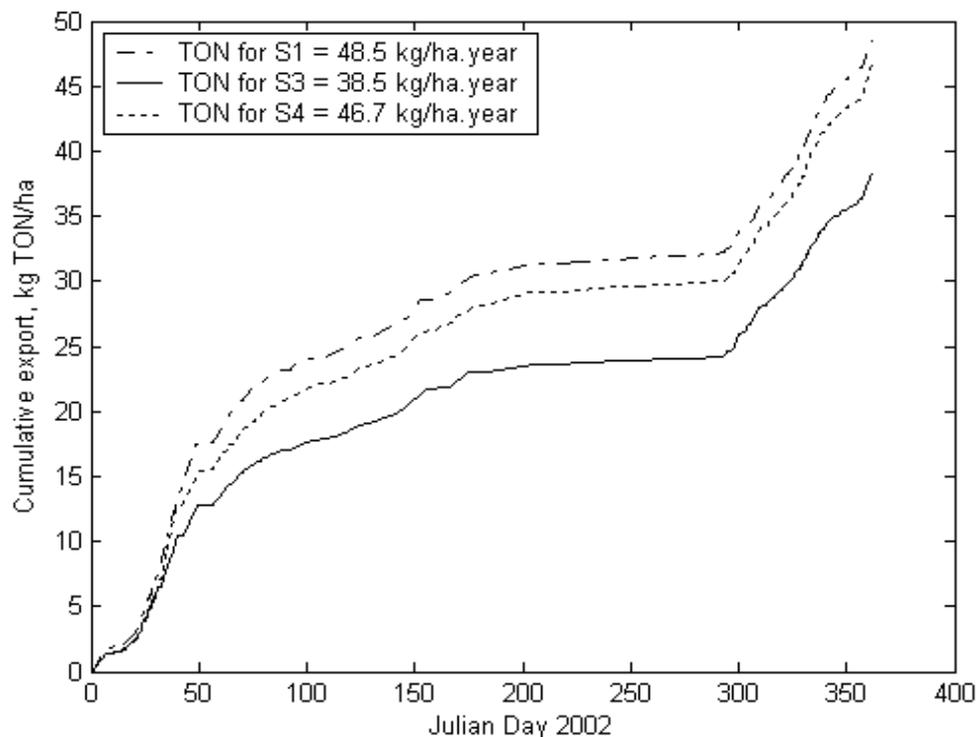
The monthly exports of TP with monthly stream flows, with fertiliser and with slurry applications from catchment 3 are shown in Figure 5.7 (a), 5.7 (b) and 5.7 (c). Like catchment 1, Figure 5.7 (a) shows that months with higher rainfall tend to have higher TP losses. The months of December 2001, January 2002 had significant applications of slurry. The two months of January and February had some of the highest TP exports in the year 2002. Fertiliser applications during the dry months appear to have an immediate effect on TP export.



**Figure 5.7** (a). Monthly TP export and monthly streamflow at S3;  
 (b). Monthly TP export and monthly slurry applications in S3;  
 (c). Monthly TP export and monthly fertiliser applications at S3.

## 5.2 Exports of nitrogen

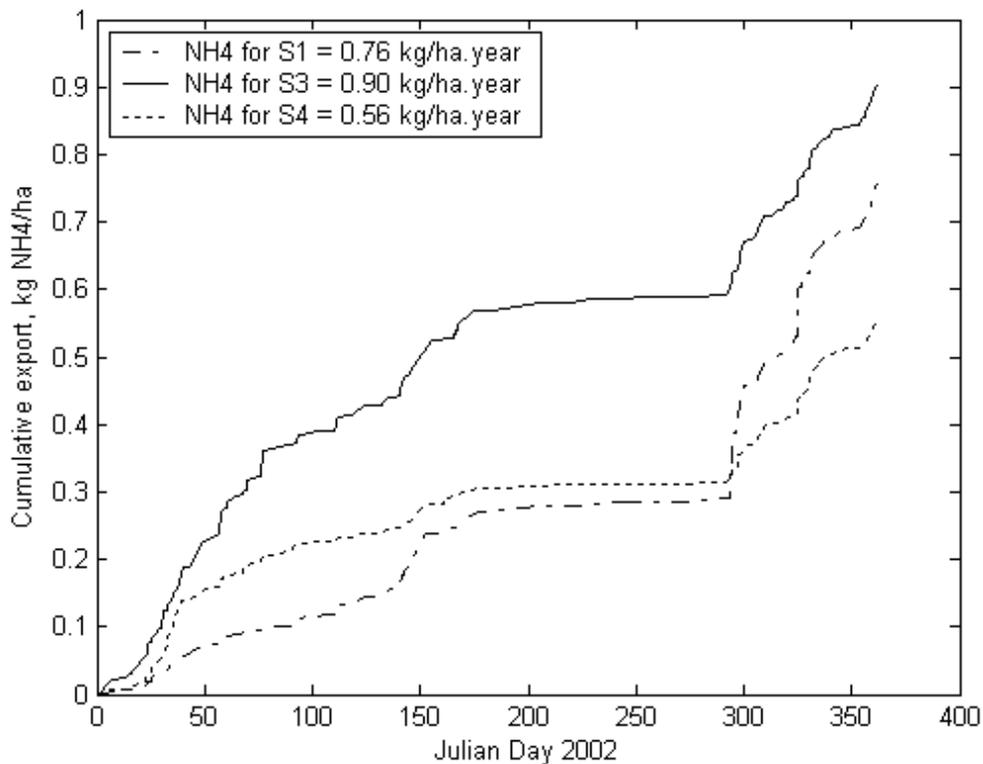
Figure 5.8 shows the cumulative export of total oxidised nitrate (TON) from the 3 sites. Catchment 1 had the highest export of TON at  $48.5 \text{ kg N ha}^{-1}$ , catchment 4 was slightly lower at  $46.7 \text{ kg N ha}^{-1}$  and catchment 3 had the lowest export of TON at  $38.5 \text{ kg N ha}^{-1} \text{ year}^{-1}$ . Unlike the export of  $\text{NH}_4$  there was no sudden increase in export at any time of the year. The pattern of TON export had a similar shape to the cumulative flow from the catchments (Figure 2.2) with much of the export in spring and winter and much lower exports in summer.



**Figure 5.8** The normalised cumulative TON export ( $\text{kg N ha}^{-1}$ ) from the three catchments 1, 3 and 4.

The exports of nitrogen for the year 2002 as ammonium ( $\text{NH}_4$ ) was  $0.76$ ,  $0.9$  and  $0.56 \text{ kg N ha}^{-1} \text{ year}^{-1}$  from catchments 1, 3 and 4 (see Figure 5.9). Catchment 3 has the highest export of  $\text{NH}_4$  at  $0.9 \text{ kg N ha}^{-1} \text{ year}^{-1}$ . The exports from catchments 1 and 4 were  $0.76$  and  $0.56 \text{ kg N ha}^{-1} \text{ year}^{-1}$ , respectively. These were considerably lower than catchment 3. In the first 5 months of the year 56% of the total load of  $\text{NH}_4$  had been exported in catchment 3 compared to 29% for the same period at catchment 1. This is likely due to land management practices as catchment 3 received over 2.5 times as

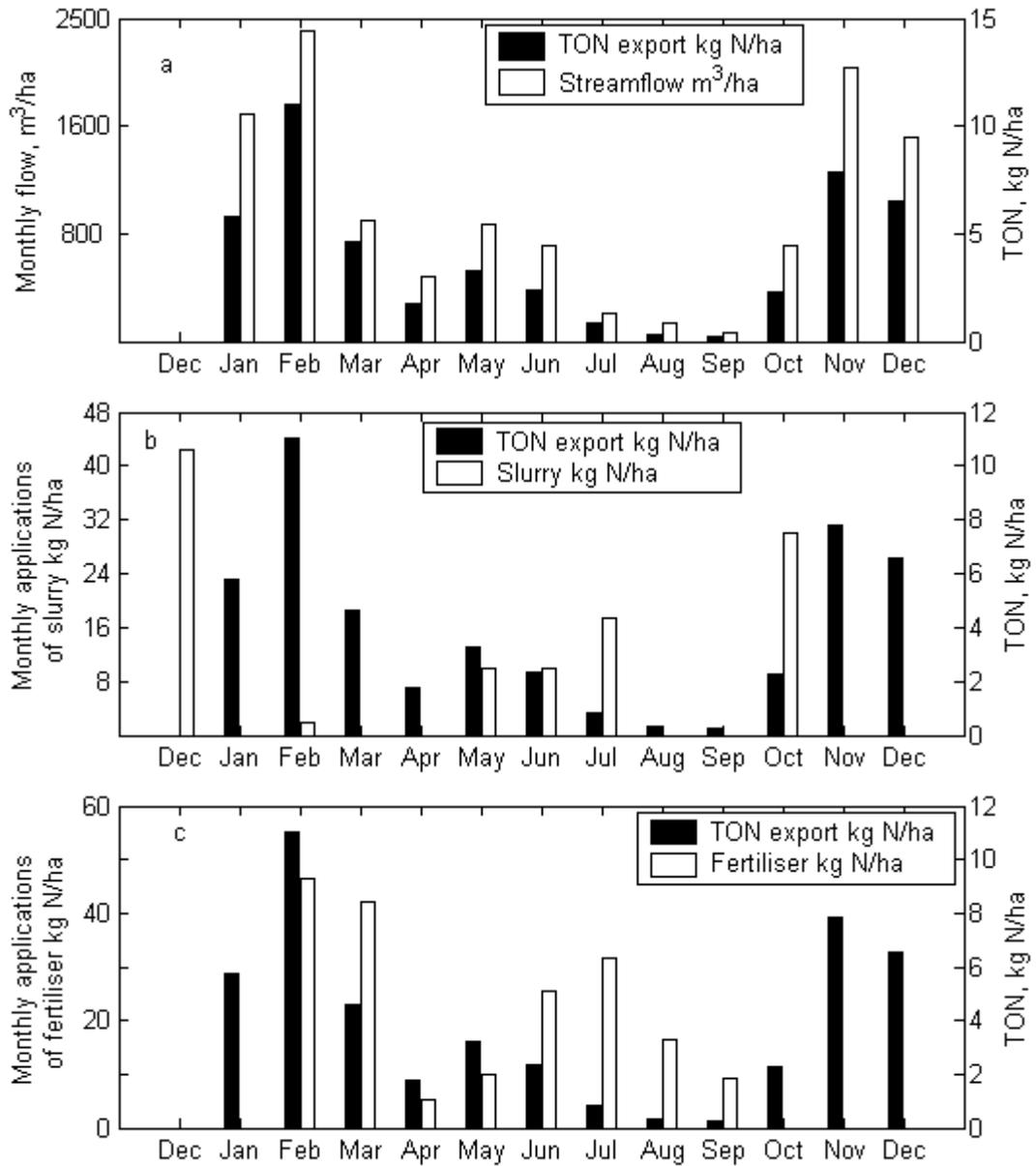
much slurry (per ha) as catchment 1 in the first 5 months of the year. Catchment 1 had the lowest export of  $\text{NH}_4$  until October when there was a large slurry application at catchment 1. This slurry application caused a significant increase in export from catchment 1 following a significant rainfall event and this large export was also observed at S3. The export from catchment 1 represented 27% of the export from catchment 3 during this event though catchment 1 represents only 8% of the area of catchment 3.



**Figure 5.9** The normalised cumulative  $\text{NH}_4$  export ( $\text{kg N ha}^{-1}$ ) from the three catchments 1, 3 and 4.

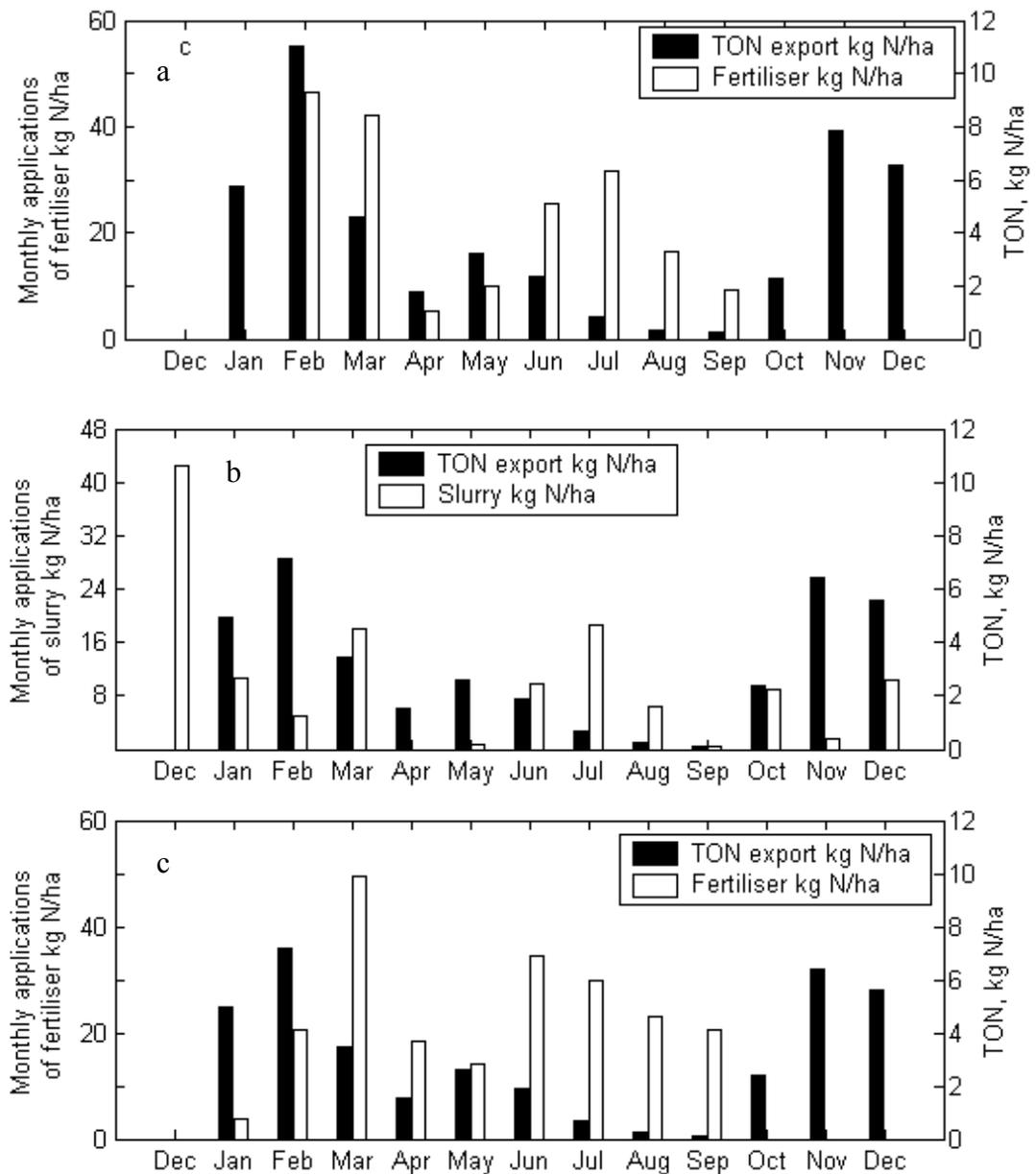
The monthly flows, slurry applications and fertiliser applications and monthly export of TON from catchment 1 can be seen in Figure 5.10 (a), 5.10 (b) and 5.10 (c). It can be clearly seen from Figure 5.10 that the export of TON is related to flow. The export falls in the summer months when the flow is low and increases with the larger flows in autumn and winter. Figures 5.10 (b) and 5.10 (c) show the export of TON and applications of fertiliser and slurry respectively. Unlike flow, the larger monthly

exports of TON do not coincide with large monthly inputs of nitrogen fertiliser. A similar pattern was observed for catchment 3.



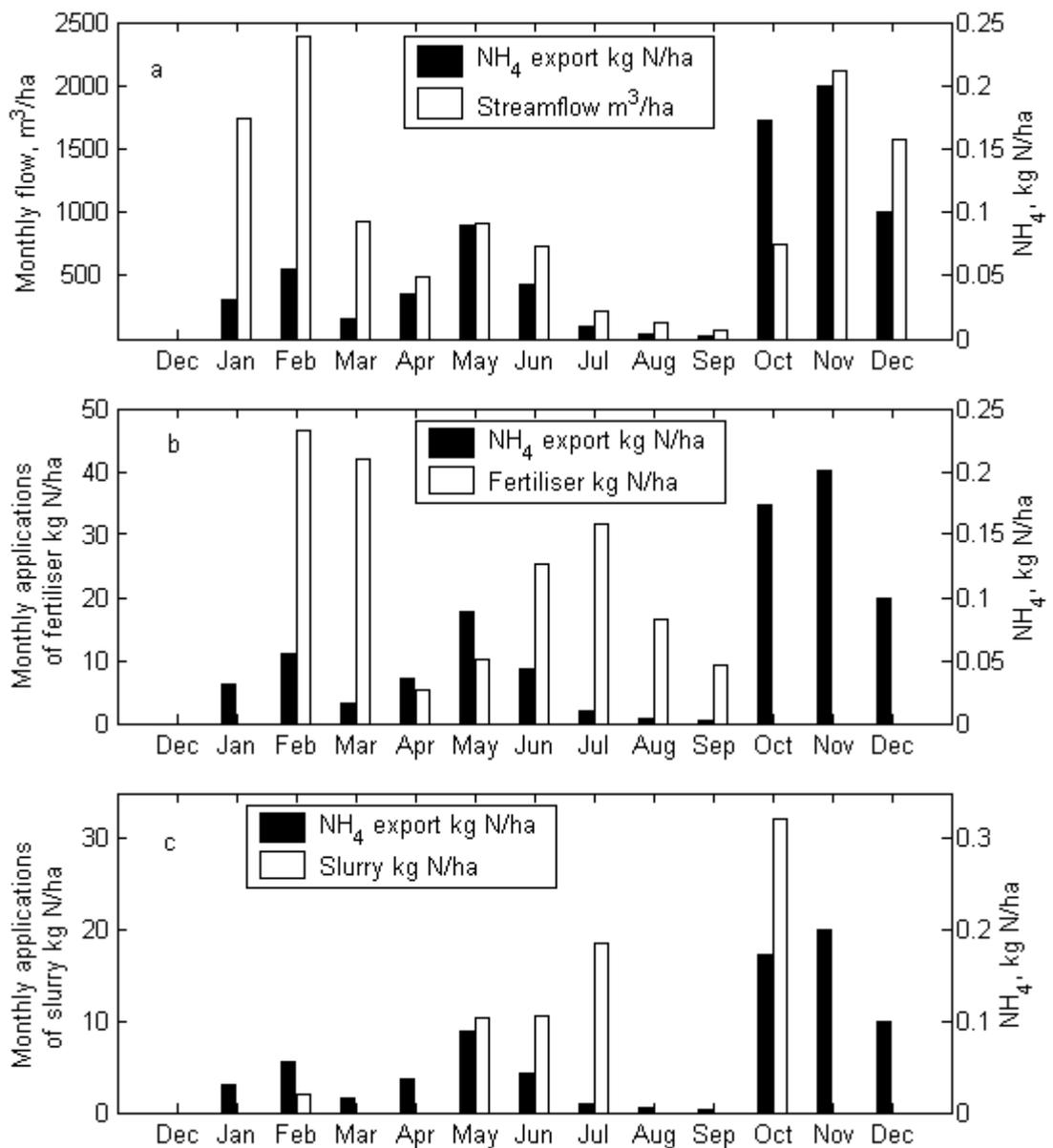
**Figure 5.10** (a). Monthly TON export and monthly streamflow at S1;  
 (b). Monthly TON export and monthly slurry applications at S1;  
 (c). Monthly TON export and monthly fertiliser applications at S1.

Figures 5.11 (a), 5.11 (b) and 5.11 (c) show monthly flows, slurry applications and fertiliser applications and monthly export of TON from catchment 3. The TON export pattern from catchment 3 is similar to catchment 1. TON is correlated with flow (see Figure 5.10). Slurry and fertiliser applications appear to have no immediate effect on TON monthly exports. Mulqueen et al., (1999) found that cattle and pig slurry spread at normal rates of 30 to 33 m<sup>3</sup>/ha did not give rise to leaching of TON. Slurries spread at excessively heavy rates (200 to 250<sup>3</sup>/ha) did give rise to leaching of TON particularly in winter. The application rate in October was estimated at 22 m<sup>3</sup>/ha.



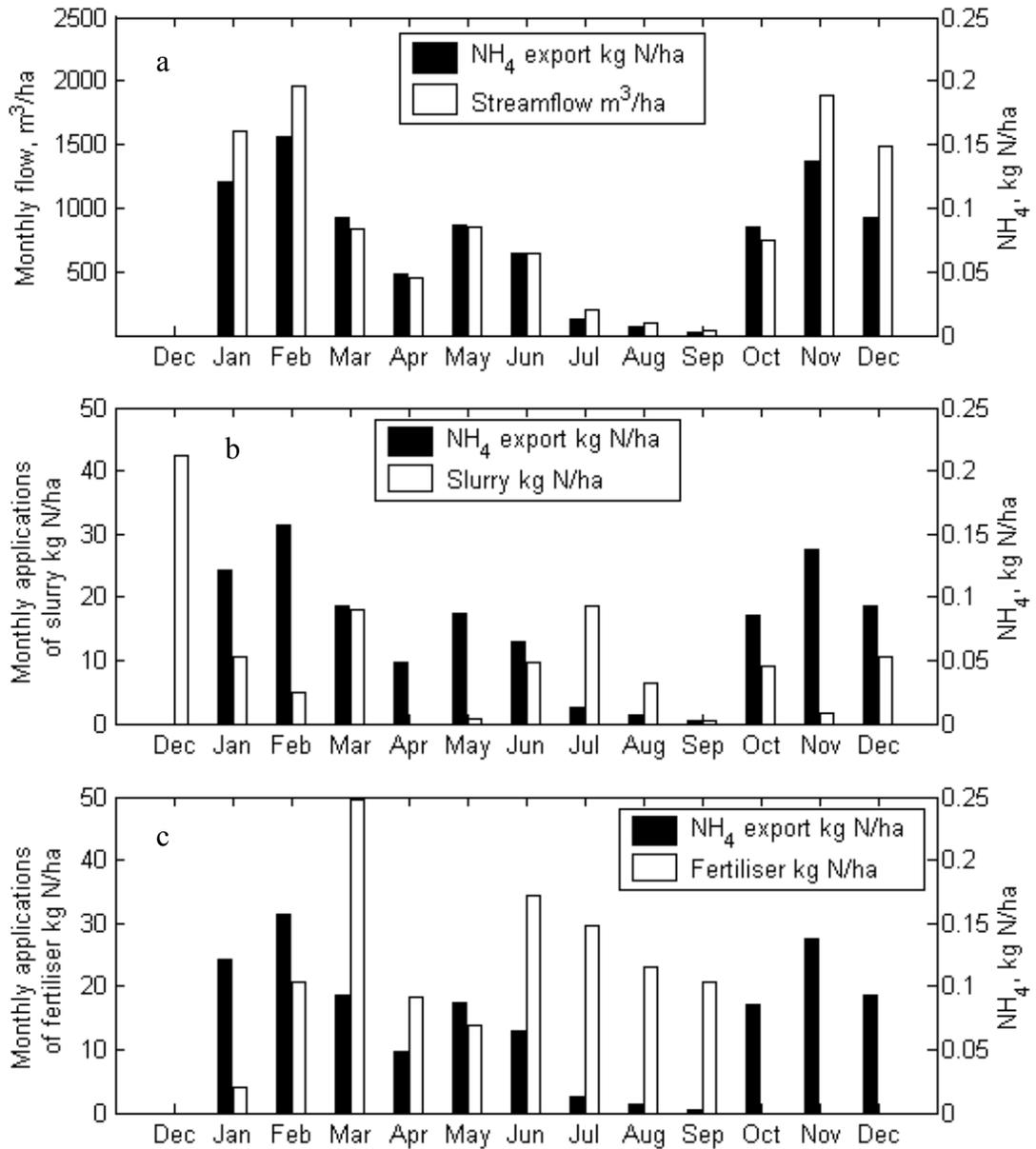
**Figure 5.11** (a). Monthly TON export and monthly streamflow at S3;  
 (b). Monthly TON export and monthly slurry applications at S3;  
 (c). Monthly TON export and monthly fertiliser applications at S3.

Figure 5.12 (a), 5.12 (b) and 5.12 (c) shows the monthly export of  $\text{NH}_4$  with flow, fertiliser application and slurry application, respectively, in catchment 1. Similar to TON,  $\text{NH}_4$  export is possibly related to flow.  $\text{NH}_4$  loss appears independent of fertiliser applications. This was also observed by Watson et al.,(2000) in Northern Ireland. Export of  $\text{NH}_4$  correlate with slurry applications (Figure 5.12 c), as the monthly  $\text{NH}_4$  exports following a large slurry application are much higher. A similar pattern was observed at S3 where the export was dependant on stream flow and slurry applications but again appeared independent of fertiliser applications.



**Figure 5.12** (a). Monthly  $\text{NH}_4$  export and monthly streamflow at S1; (b). Monthly  $\text{NH}_4$  export and monthly slurry applications at S1; (c). Monthly  $\text{NH}_4$  export and monthly fertiliser applications at S1.

Figure 5.13 (a), 5.13 (b) and 5.13 (c) shows the monthly export of  $\text{NH}_4$  with flow, fertiliser application and slurry application, respectively, in catchment 3. The export of  $\text{NH}_4$  is closely related to flow at S3.  $\text{NH}_4$  export appears unrelated to fertiliser applications but related to slurry applications.

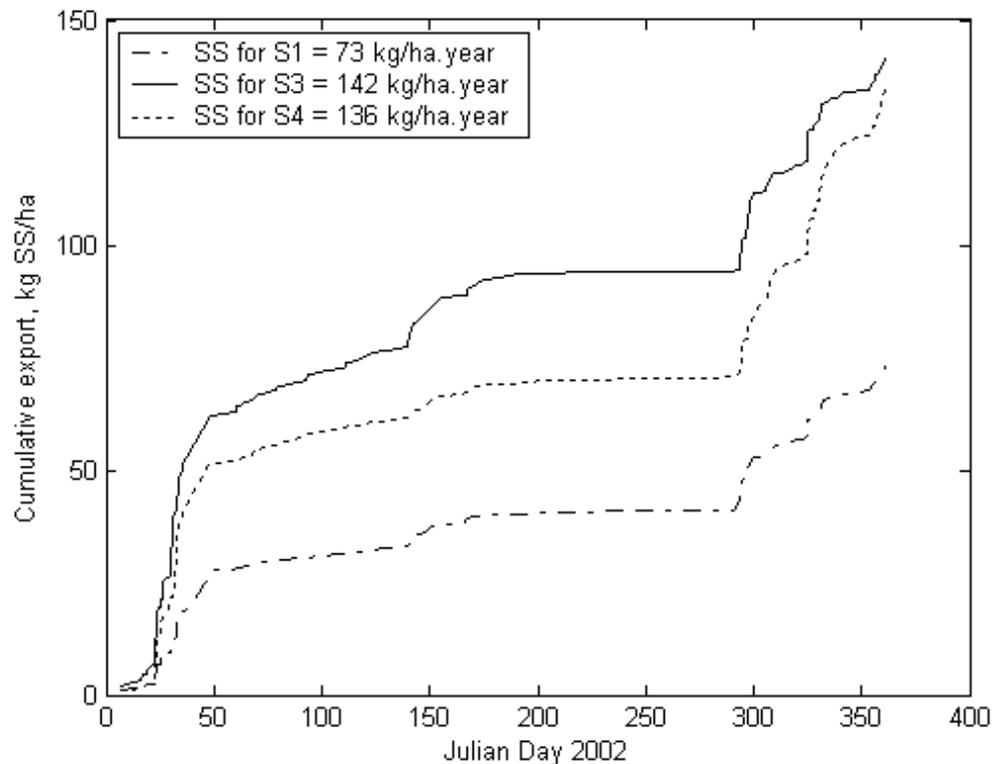


**Figure 5.13** (a). Monthly  $\text{NH}_4$  export and monthly streamflow at S1; (b). Monthly  $\text{NH}_4$  export and monthly slurry applications in S3; (c). Monthly  $\text{NH}_4$  export and monthly fertiliser applications in S4.

### 5.3 Export of suspended sediment

The annual export of SS from catchments 1, 3 and 4 was 73, 142 and 136 kg ha<sup>-1</sup> for the year 2002 (see Figure 5.14). The intermediate catchment (S3) has the highest export of suspended sediment. This catchment also had the highest export of particulate phosphorus (see Figure 5.3). This would suggest that there is more erosion in the land at this scale due in part to areas of steeper gradient. We examine the relationship between SS and PP in chapter 6. Catchment 1 had the lowest export of SS. This may be due to the influence of farmyards. There are no farmyards in catchment 1 whereas both catchment 3 and 4 have houses and farmyards.

The annual average concentration of SS in the stream was under the recommended level of 25 mg/l at all sites. The highest measured concentration was under 147 mg/l (see Table 3.6). Little is known about the long term average rates of soil loss from agricultural land and even less about how much of this reaches watercourses. Average rates are thought to be low, less than 5000 kg ha<sup>-1</sup> year<sup>-1</sup> in the UK. (D'Arcy et al., 2001). The export loads in the Dripsey could be considered low in comparison to these values.



**Figure 5.14** The normalised cumulative SS export (kg ha<sup>-1</sup>) from the three catchments 1, 3 and 4.

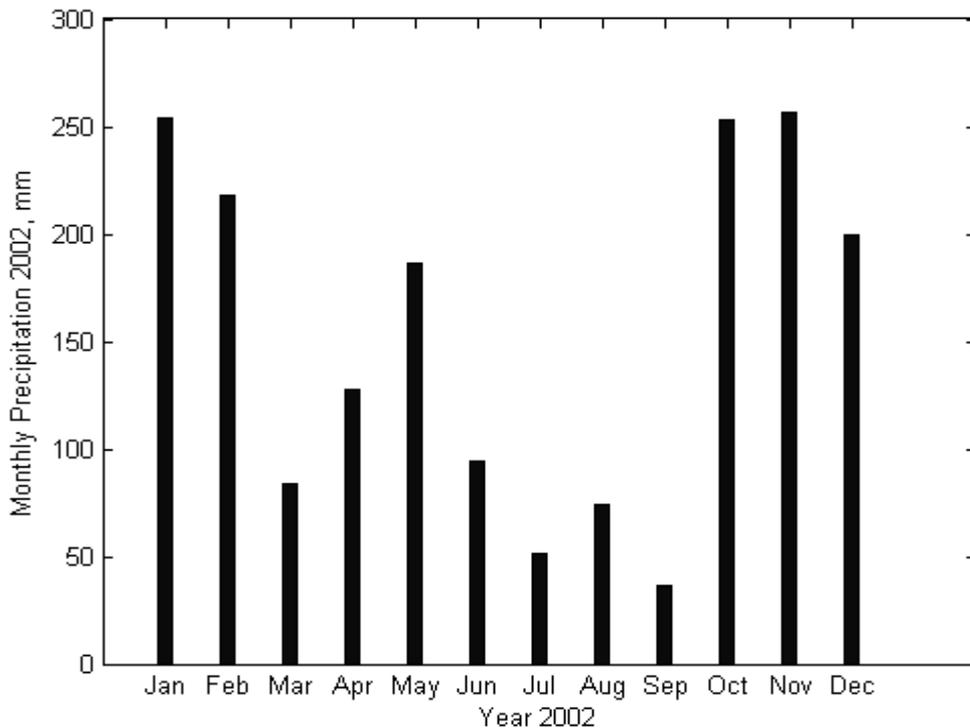
# Chapter 6

## Analysis of Results

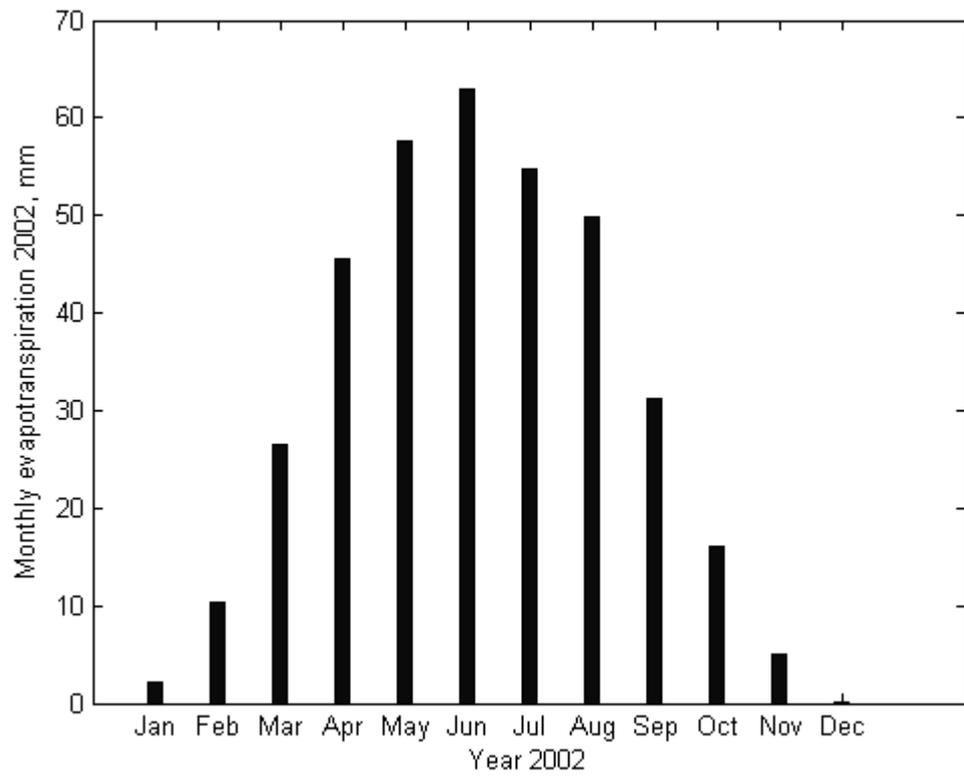
## 6.1 Hydrological controls

This section examines the hydrological controls on the export of TP. Figures 6.1a and 6.1b show the monthly precipitation and monthly evapotranspiration, respectively. Figure 6.2 shows monthly effective precipitation. Effective precipitation = actual precipitation – evapotranspiration. Months with a relatively high effective precipitation also have a large export of TP. Months with low effective precipitation have low exports. The vulnerable months for slurry spreading are October to February as these months have the highest effective precipitation. The other seven months have a lower risk of pollution from slurry applied. All the catchments exhibit a similar response to effective precipitation (see Figures 6.3a, 6.3b, and 6.3c).

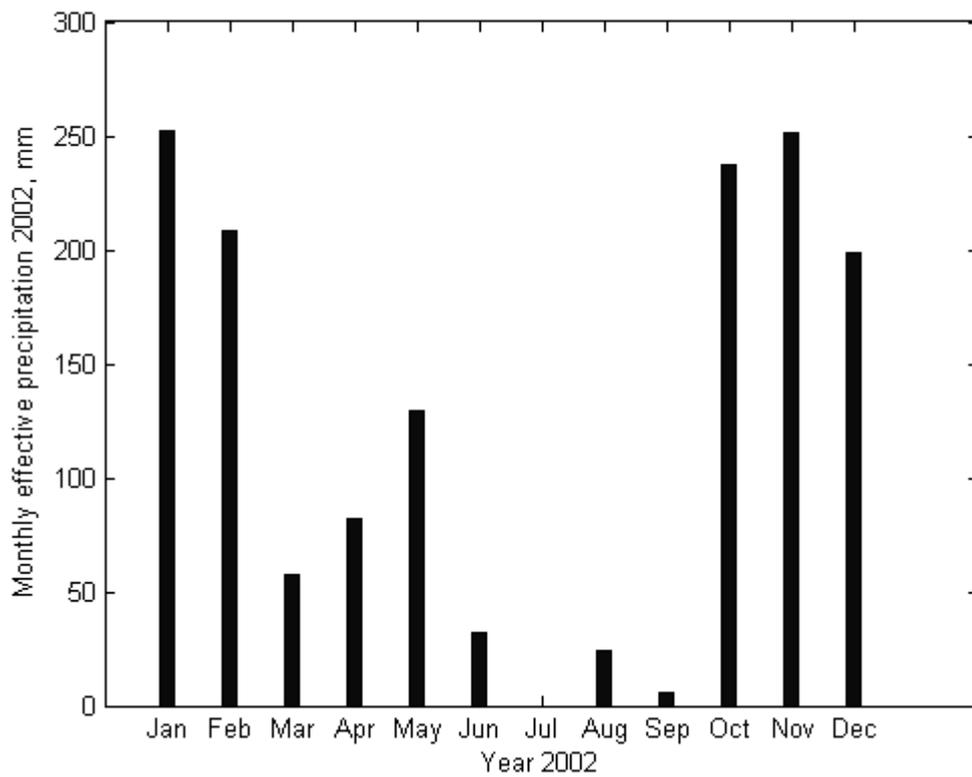
During wet months the soils become saturated. As a result of this most of the rain falling on the catchment will find its way to the streams. The overland flow will increase the erosion in the top 5 cm of the soil where most of the phosphorus in the soil is located (Daly, 1999). Any “unbonded” phosphorus in the top 5 cm of the soil will then be vulnerable to erosion in heavy rainfall events that result in overland flow. The higher the soil P (Morgans P) in the fields of the catchment, the greater the risk to high concentrations of stream phosphorus in wet months.



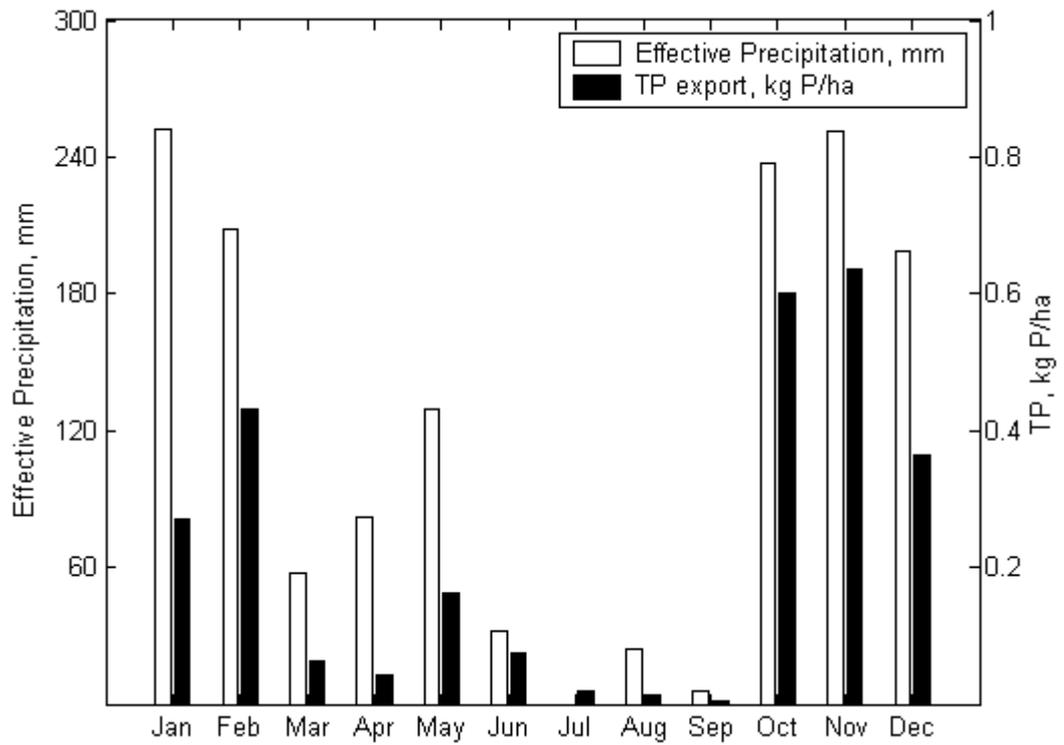
**Figure 6.1a** Monthly precipitation 2002 at S1.



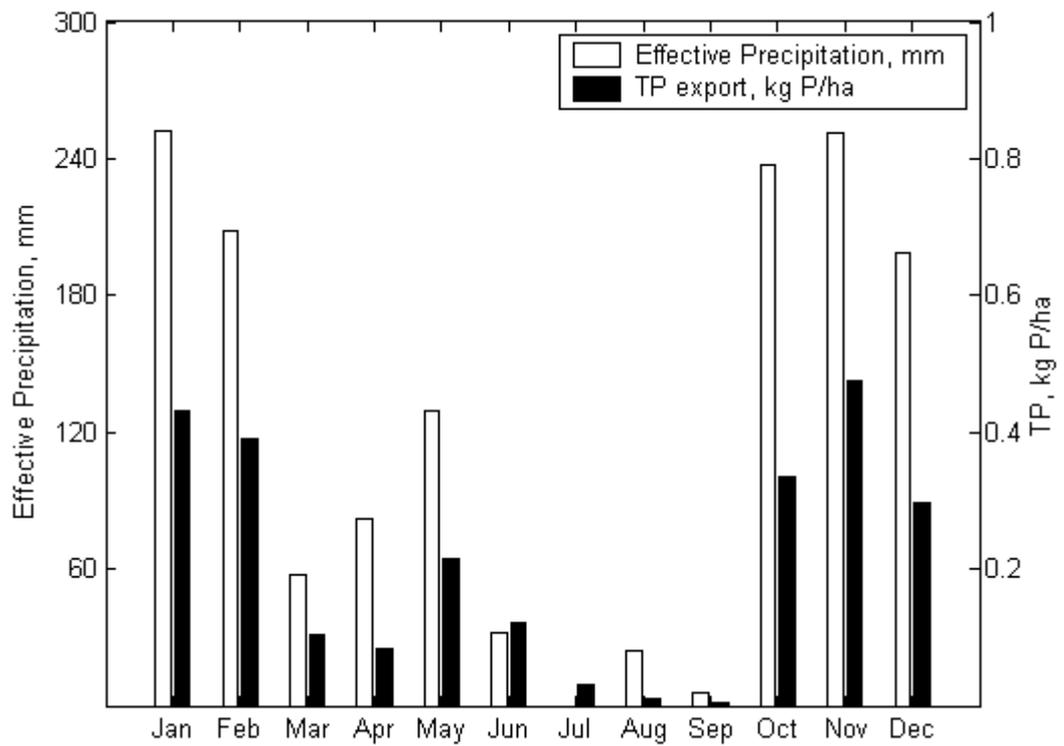
**Figure 6.1b** Monthly evapotranspiration at S1.



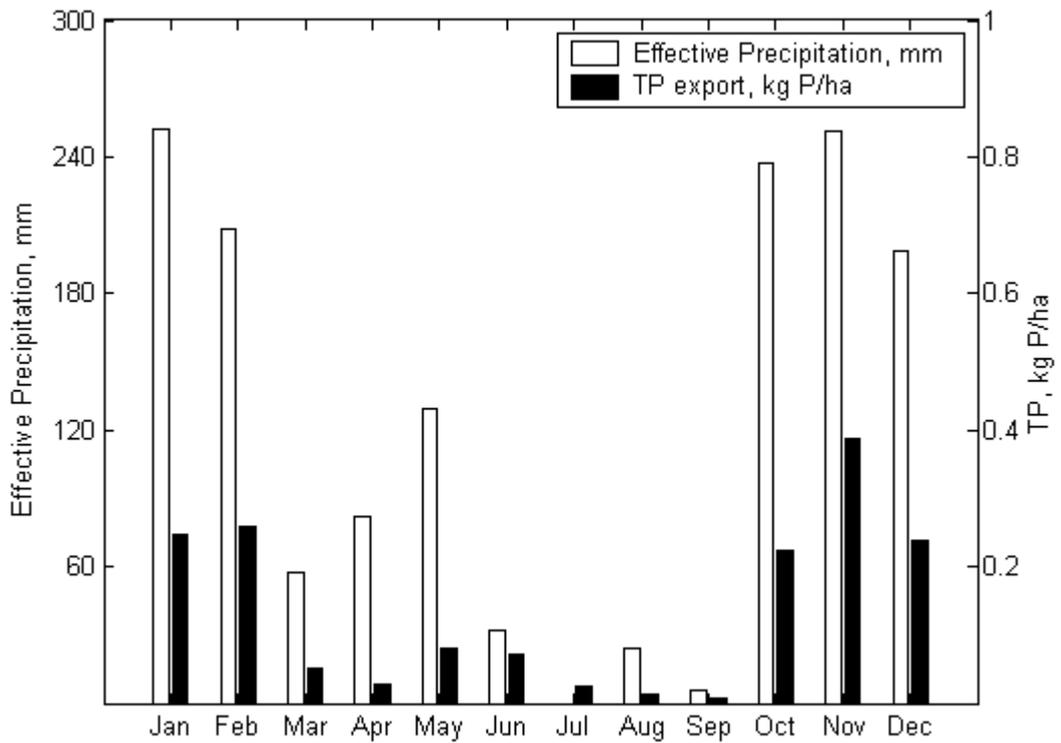
**Figure 6.2** Effective precipitation at S1.



**Figure 6.3a** TP export and effective precipitation at S1

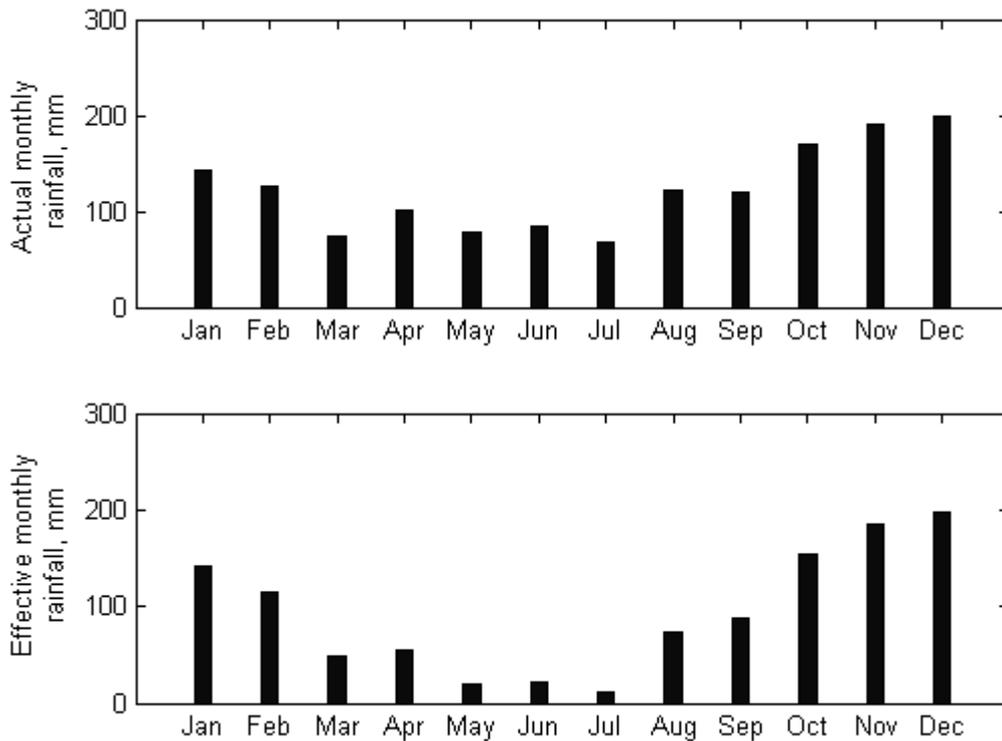


**Figure 6.3b** TP export and effective precipitation at S3



**Figure 6.3b** TP export and effective precipitation at S4

The average monthly rainfall at S1 for the period 1997-2002 is shown in Figure 6.4 (a). If we assume that the average evapotranspiration for the years 1997 to 2002 is similar to the evapotranspiration measured for the year 2002 then we can show in Figure 6.4 (b) the estimated effective monthly rainfall for the years 1997 to 2002. We can infer from Figure 6.4 (b) that the high effective rainfall which is likely to correspond with high streamflow months are the times of greatest concern for nutrient and SS export. These months are clearly October to February.

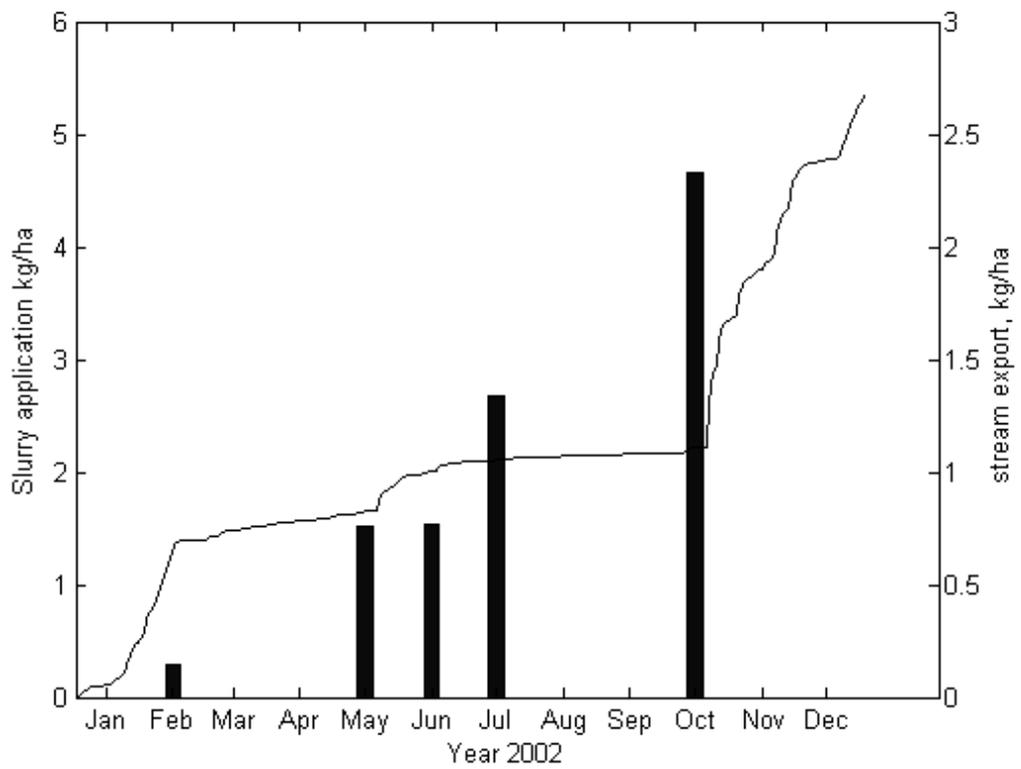


**Figure 6.4** (a) Average monthly rainfall for the period 1997-2002.  
 (b) Estimated effective monthly rainfall for the period 1997-2002.

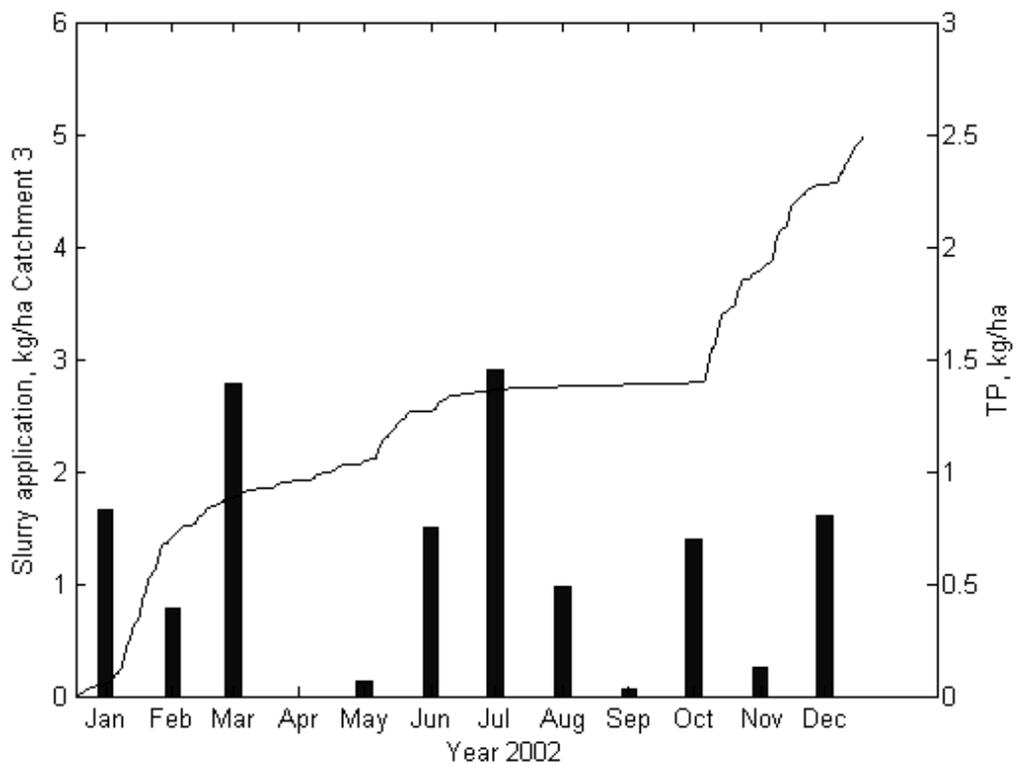
## 6.2 The influence of slurry applications

Figures 6.5 and 6.6 show the monthly applications of slurry with the cumulative TP export from catchments 1 and 3. In Figure 6.5 it can be seen that following a heavy application of slurry at catchment 1 (in October 2002) there was a dramatic increase of TP export. Slurry was applied in three fields (comprising of 35 % of catchment 1) adjacent to the stream at S1. There is a similar increase of export in October from catchment 3 (see Figure 6.6). Catchment 3 received more slurry in the first six months of 2002 and also had a higher export of TP in this period than in catchment 1. At site 1 the Slurry applications in December 2001 allied with high flows in January and February caused the high export of TP in the first two months of the year 2002.

In Figure 6.6 is it noticeable that slurry applications in summer months appears to have little immediate effect on phosphorus export.



**Figure 6.5** Slurry applications and TP export, catchment 1



**Figure 6.6** Slurry applications and TP export, catchment 3.

## 6.4 Comparison of export loads between 1993-94 and 2002

Tables 6.1 and 6.2 show the phosphorus inputs as fertiliser and slurry in 1993 and the exports of TP, SRP, TON, NH<sub>4</sub> and SS at sites 3, 4 and 5. The inputs and exports from the same catchments are presented in Tables 6.3 and 6.4 for the year 2002. Note catchment 1 was not studied in 1993-94 and catchment 5 was not studied in 2002. The water chemistry samples taken in the 1993 to 94 period only covered approximately 20% of the year. This may contribute to some of the differences in exports between the two studies.

**Table 6.1** LU, fertiliser and slurry P estimates for 1993-1994. (Tunney et al., 1995)

Name	Area ha	LU/ha	Fertiliser P kg P ha <sup>-1</sup>	Slurry P kg P ha <sup>-1</sup>
S3	211	2.04	21.45	19.25
S4	1524	1.5	17.1	15.3
S5	5578	1.59	-----	-----

**Table 6.2** Export loads from the 1993-1994 study (Tunney et al., 1995)

Name	Area Ha	TP kg (kg ha <sup>-1</sup> )	SRP kg (kg ha <sup>-1</sup> )	TON kg (kg ha <sup>-1</sup> )	NH <sub>4</sub> kg (kg ha <sup>-1</sup> )	SS kg (kg ha <sup>-1</sup> )
S3	211	744 (3.52)	428 (2.02)	15000 (71)	478 (2.27)	58000 (275)
S4	1524	2996 (1.97)	1347 (0.9)	82000 (53.8)	1666 (1.09)	355000 (232)
S5	5578	10574 (1.89)	4764 (0.85)	303000 (54.3)	7167 (1.28)	2055000 (368)

**Table 6.3** LU, fertiliser and slurry P estimates 2002

Name	Area ha	LU/ha	Fertiliser P kg P ha <sup>-1</sup>	Slurry P kg P ha <sup>-1</sup>
S1	17	2.17	16.4	10.7
S3	211	2.2	23.7	14.0
S4	1524	-----	-----	-----

**Table 6.4** Export load estimates 2002.

Name	Area Ha	TP kg (kg ha <sup>-1</sup> )	SRP kg (kg ha <sup>-1</sup> )	TON kg (kg ha <sup>-1</sup> )	NH4 kg (kg ha <sup>-1</sup> )	SS kg (kg ha <sup>-1</sup> )
S1	17	44.3 (2.61)	28.9 (1.7)	827 (48.5)	13 (0.76)	1241 (73)
S3	211	521 (2.47)	249 (1.18)	8123.5 (38.5)	189 (0.90)	29962 (142)
S4	1524	2438 (1.61)	853 (0.56)	71171 (46.7)	854 (0.56)	207264 (136)

From these tables we note that:

1. Fertiliser rates are similar for 1993 and 2002.
2. Slurry rates are less in 2002 (by about 25%).
3. Export rates of phosphorus are down by approximately 30% on the 1993 levels.
4. Export rates of nitrogen are down by approximately 50% on the 1993 levels.
5. Export rates of SS are down by approximately 50% on the 1993 levels

## **6.4 Relationships between nutrients**

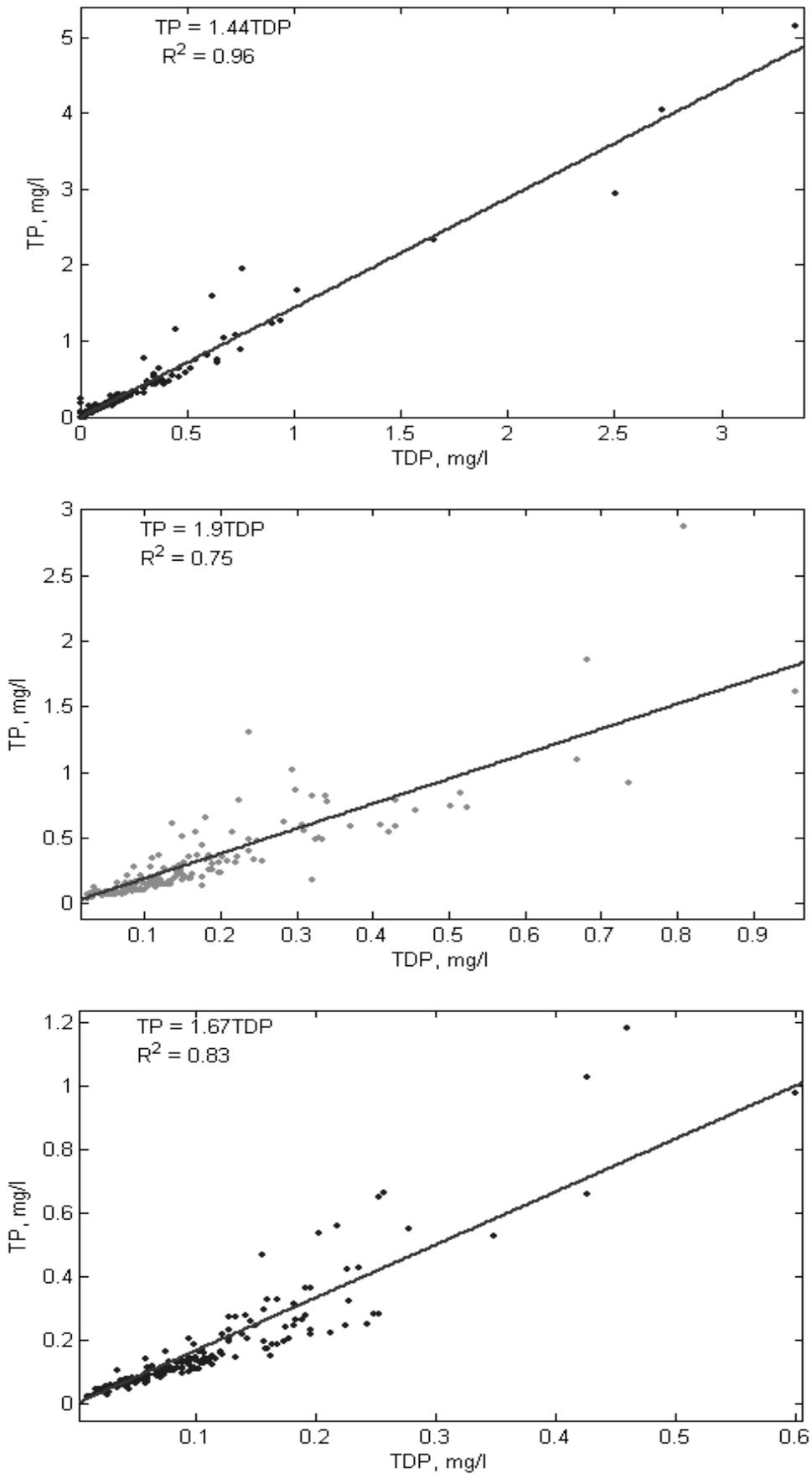
### **6.4.1 Phosphorus**

Figures 6.7, 6.8 and 6.9 show that there is a strong linear relationship between TP and all the other forms of phosphorus, TDP, SRP and PP. TDP represents 69%, 52% and 60% of the TP export. The greatest variation of the TDP fraction in TP is at S3 where the  $R^2$  value is 0.75 with S1 varying the least ( $R^2 = 0.96$ ). This suggests that futures work at these sites could be limited to measuring one phosphorus parameter.

SRP represents 66%, 43% and 50% of the TP load at S1, S3 and S4, respectively as shown in Figure 6.8. Like TDP there is a strong linear relationship particularly at S1 between TP and SRP. Figure 6.9 shows that there is also a linear relationship between TP and PP. Approximately 37%, 61% and 51% of the TP export is in particulate form at sites 1, 3 and 4 respectively.

As Figure 6.10 shows most of the dissolved phosphorus in the streams is SRP. The TDP exported from catchment 1 contains 96% SRP with catchments 3 and 4 slightly lower at 84%. The fraction of SRP in TDP varies little through the year with very high  $R^2$  values of 0.94 and 0.97. This suggests that most of the dissolved phosphorus in the streams in the Dripsey catchment is readily available for algal growth.

The relationship between TDP and PP is not as strong with lower  $R^2$  values (see Figure 6.11), especially at S3 and S4. There is also a poor relationship between SRP and PP (see Figure 6.12).



**Figure 6.7** a b and c, TP vs. TDP at sites 1 3 and 4 respectively

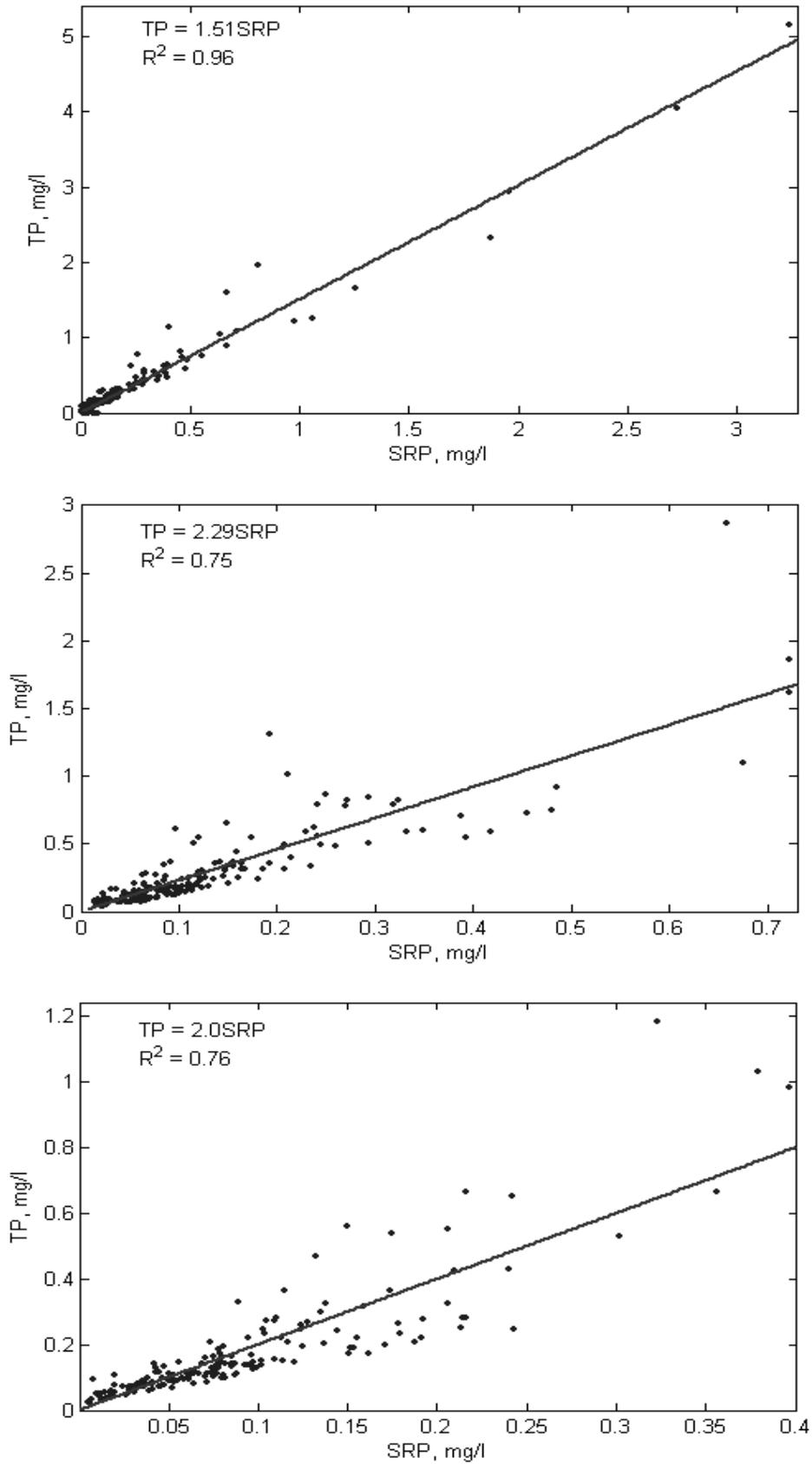
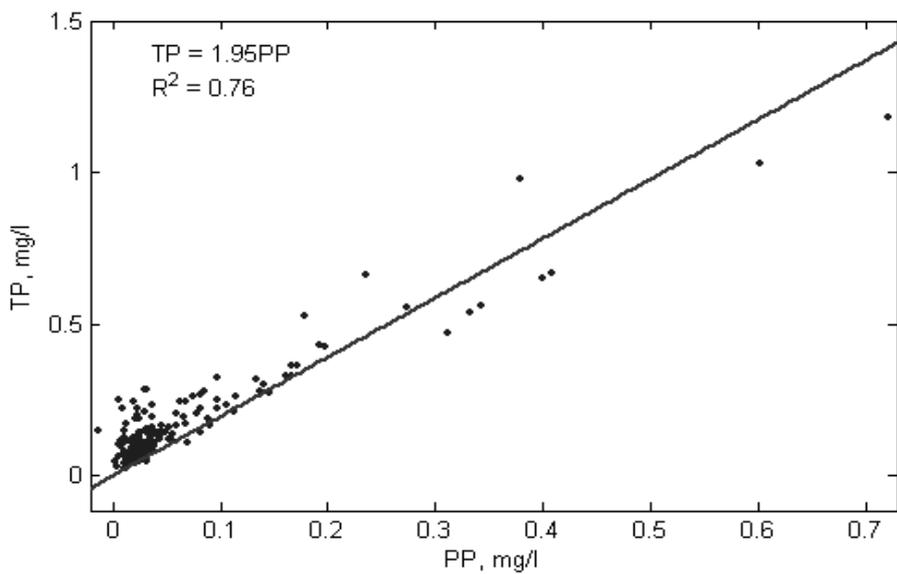
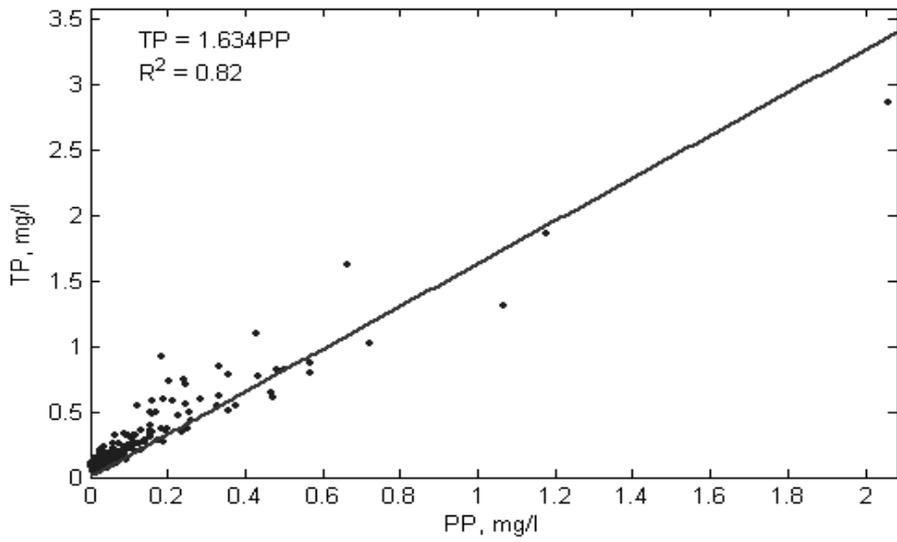
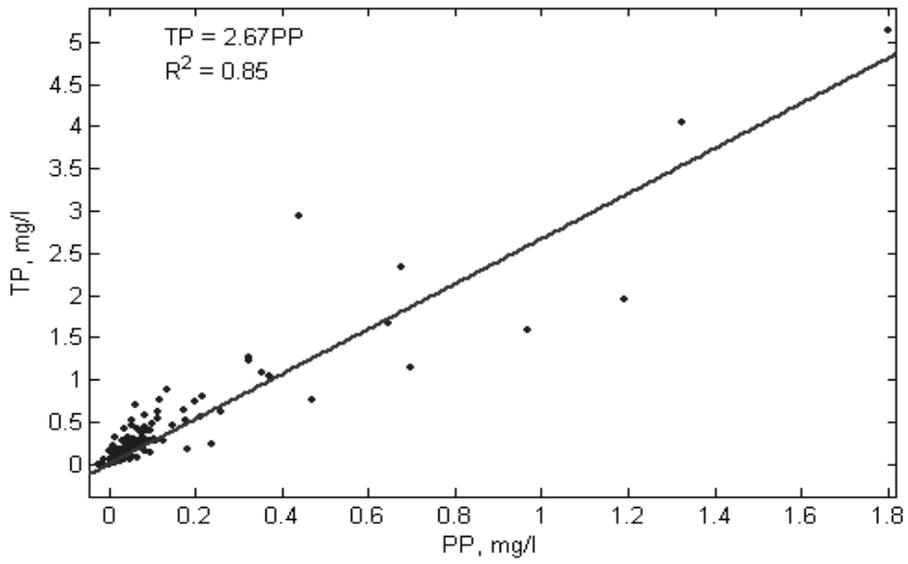


Figure 6.8 a b and c, TP vs. SRP at sites 1 3 and 4 respectively.



**Figure 6.9** a b and c, TP vs. PP at sites 1 3 and 4 respectively.

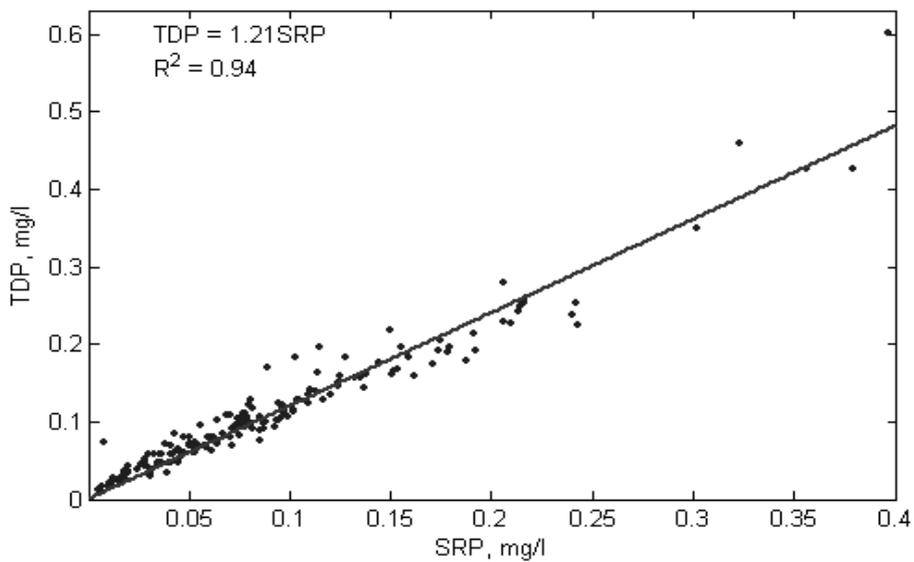
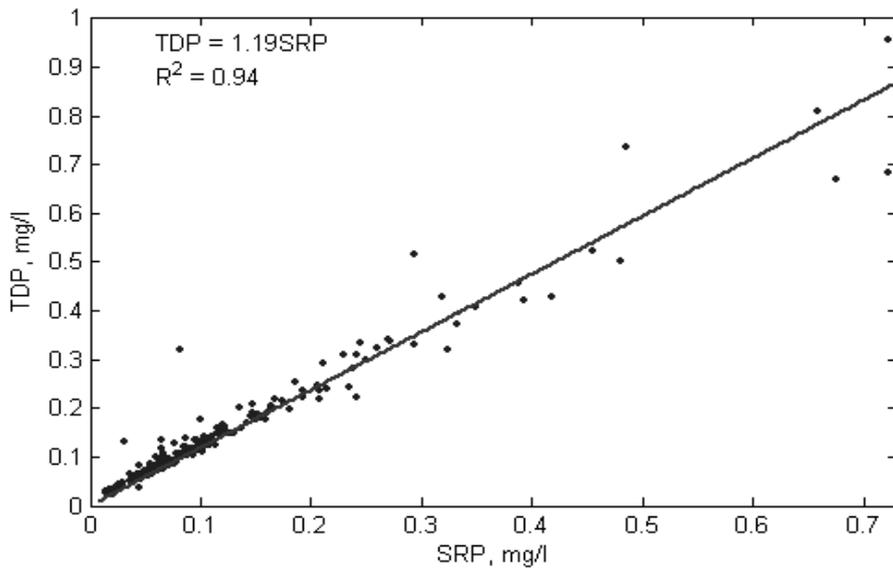
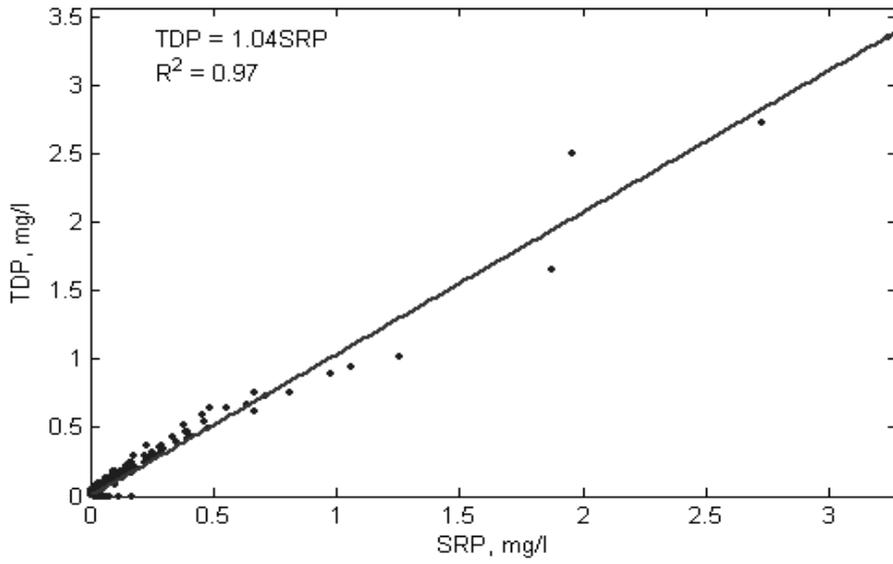


Figure 6.10 a, b and c, TDP vs. SRP at sites 1, 3 and 4 respectively.

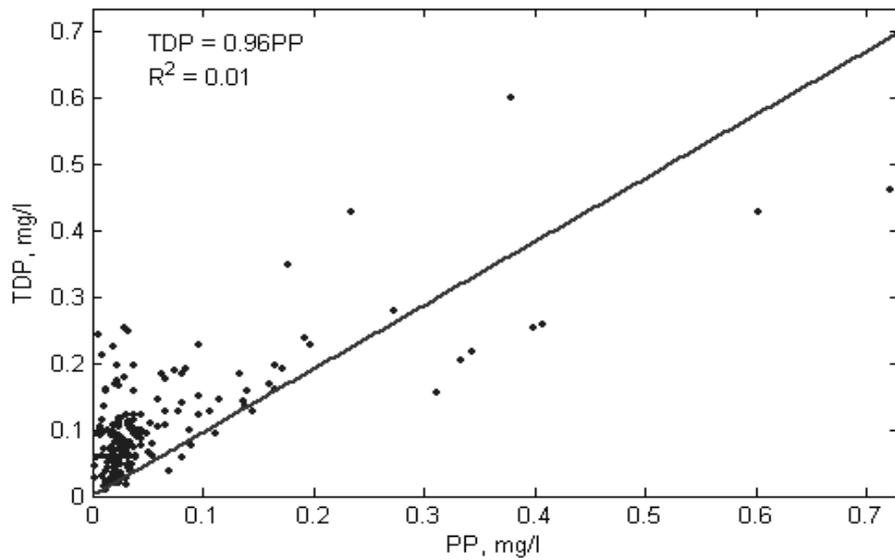
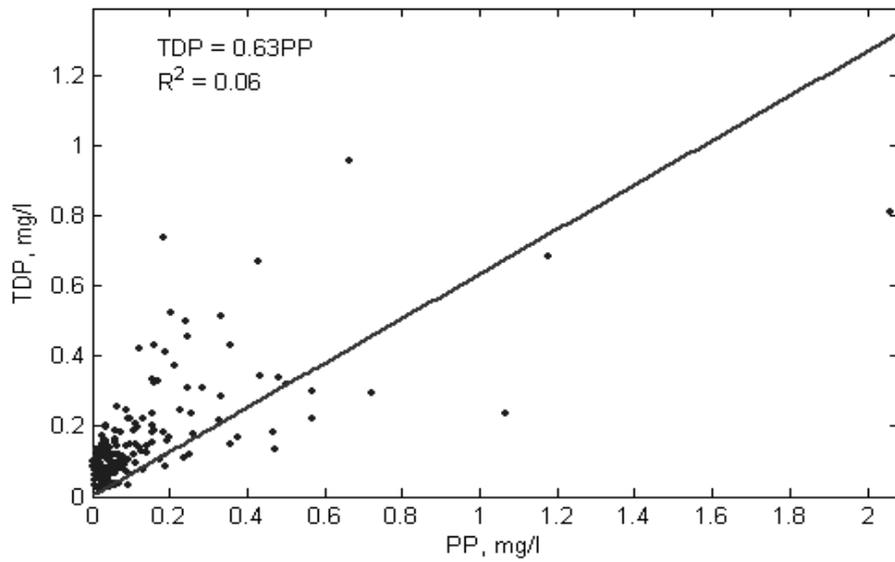
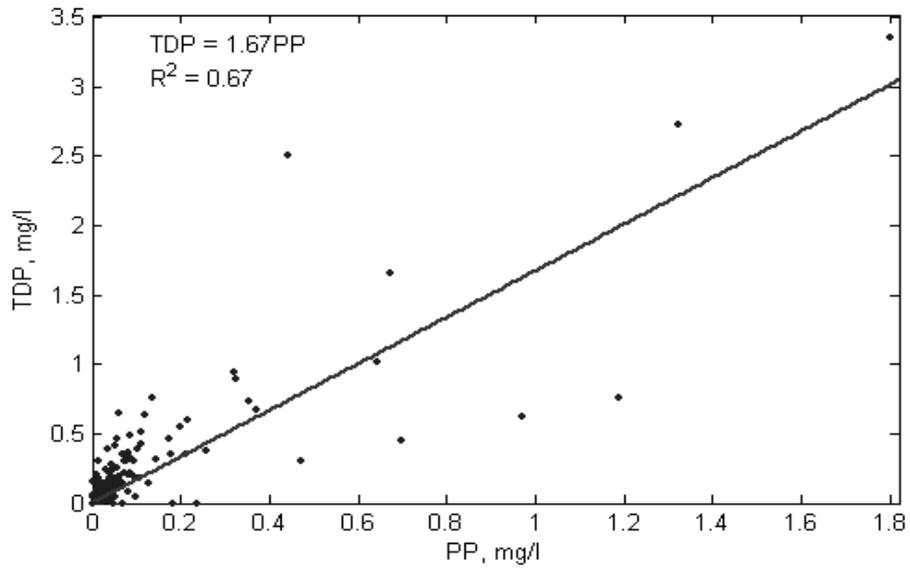
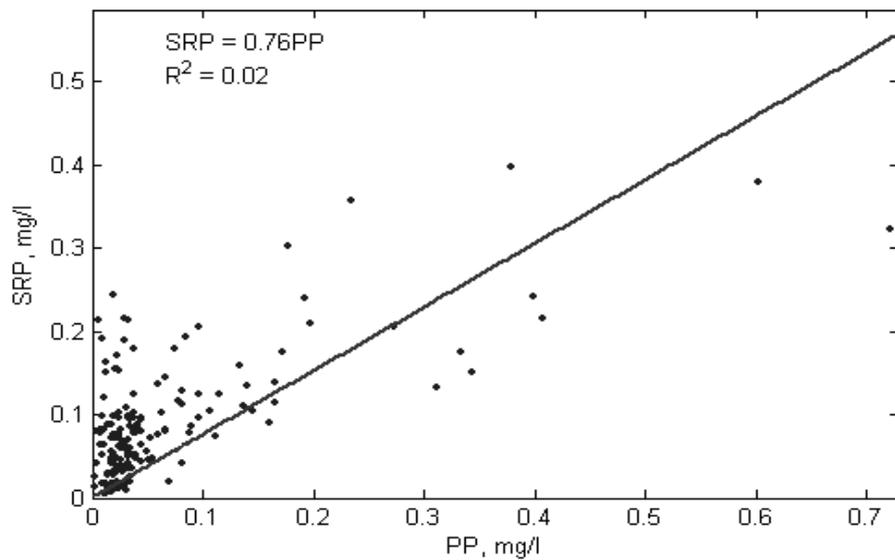
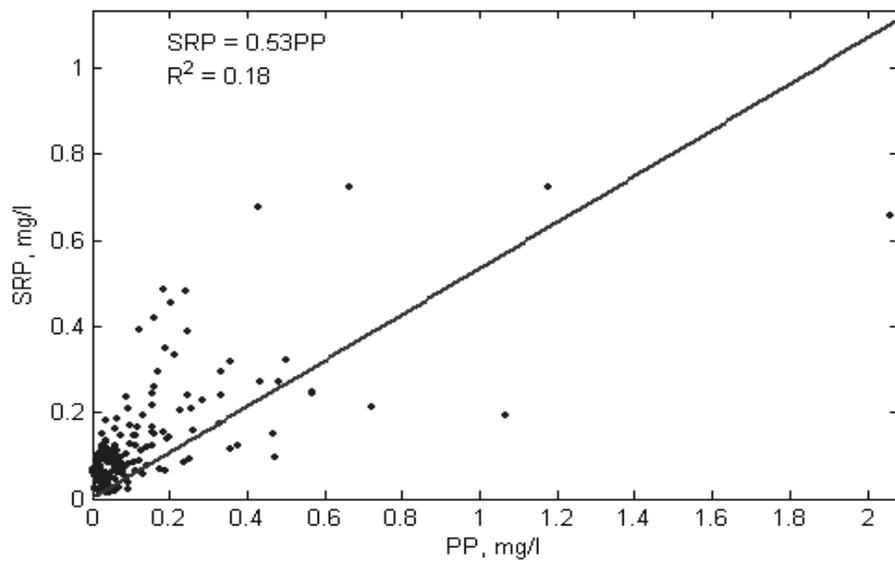
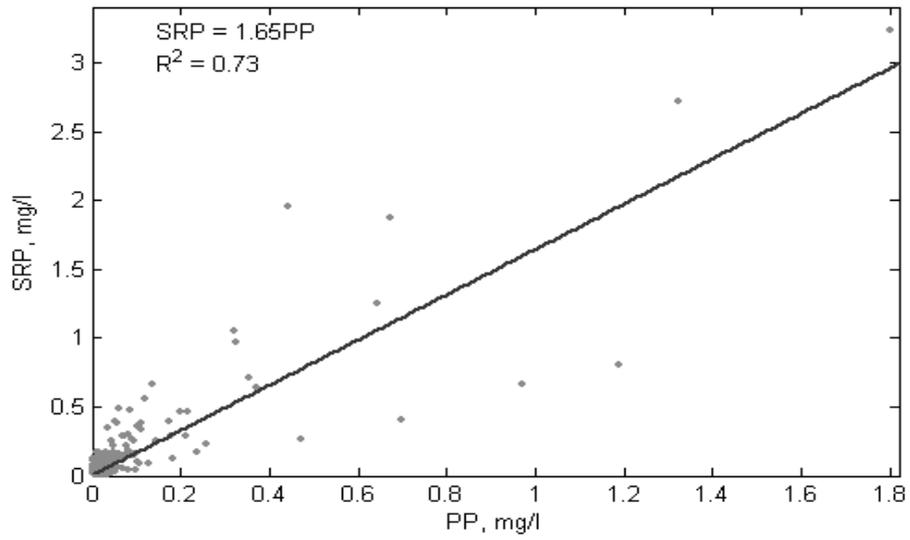


Figure 6.11 a, b and c, TDP vs. PP at sites 1, 3 and 4 respectively.



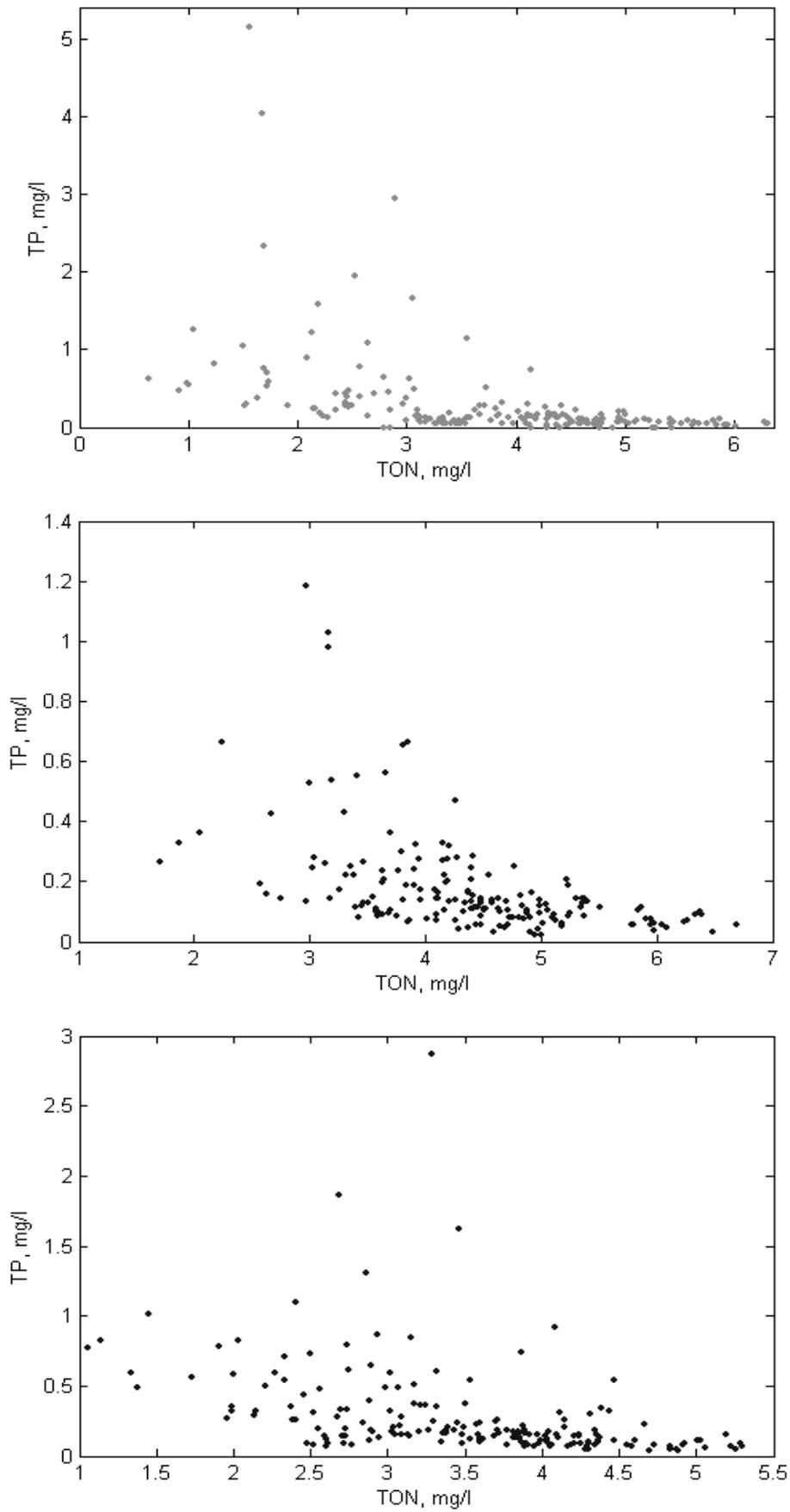
**Figure 6.12** a, b and c SRP vs. PP at sites 1, 3 and 4 respectively.

## 6.4.2 Nitrogen

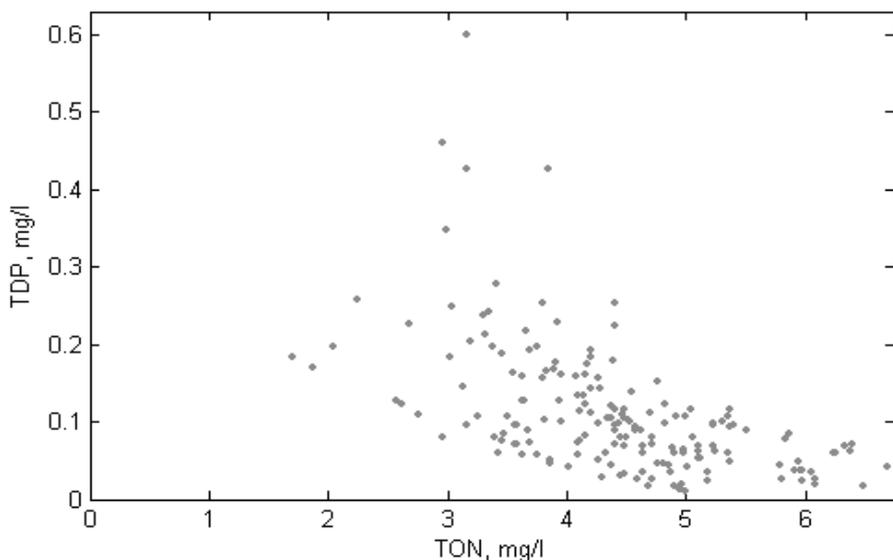
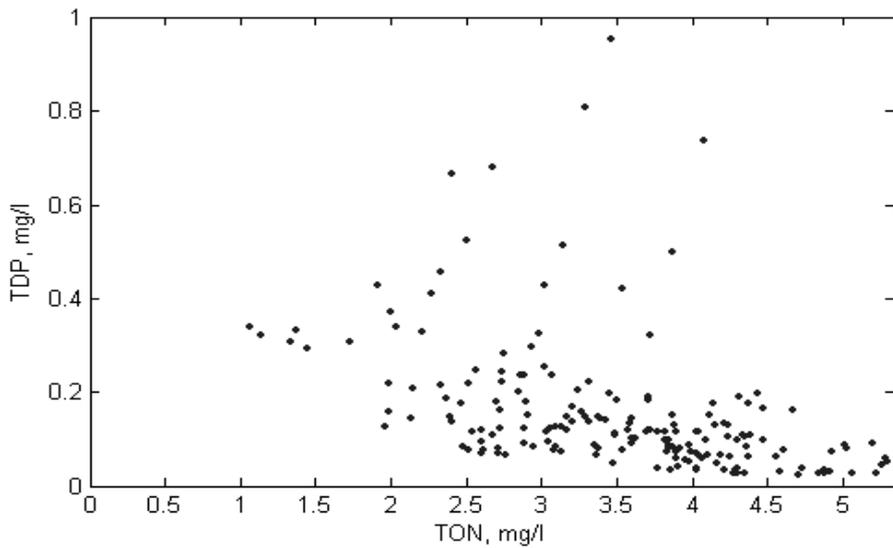
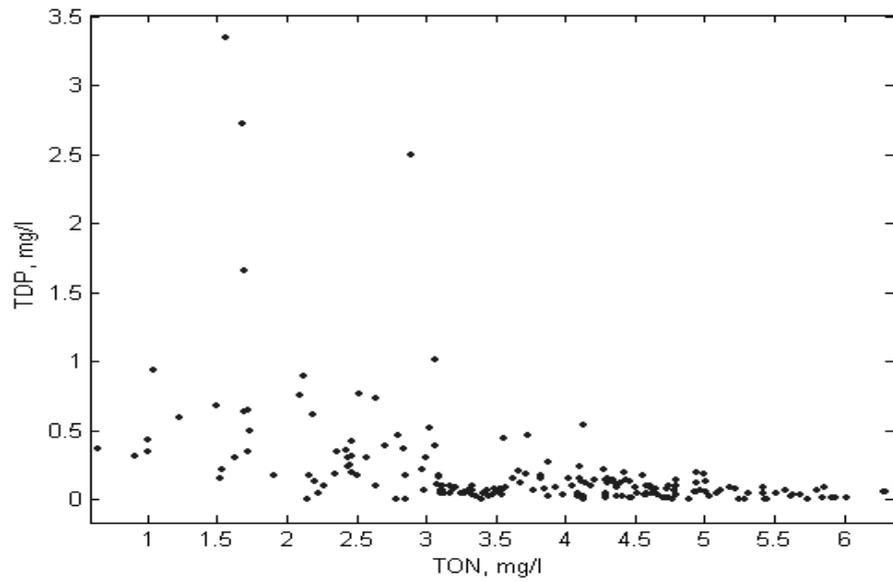
Figures 6.13, 6.14, 6.15 and 6.16 show that there is no simple relationship between TON and any of the forms of phosphorus (TP, TDP, SRP and PP). The independence of TON from any of the other nutrients suggests that it is transported under different conditions to phosphorus. It was noted in section 3.3.3 that TON concentrations decreases with increasing flow whereas concentrations of TP increased with increasing flow. It is more likely that TON is lost from deeper in the soil profile as the concentrations of TON are higher in low flow than during rain events. Scanlon et al.,(2003) concluded that most of the TP is leached in shallow subsurface flow and not from deeper in the soil profile.

There is a relationship between  $\text{NH}_4$  and phosphorus (see Figure 6.17). SRP, TDP and PP show similar trends to  $\text{NH}_4$  (see Figures 6.18, 6.19 and 6.20). The close relationship between phosphorus and  $\text{NH}_4$  especially the high concentrations suggest that both are lost from the same location in the soil profile. During the winter much of the nitrogen excreted by the cattle and stored as slurry is converted from its organic form to ammonium ( $\text{NH}_4$ ) (Whitehead, 2000). Two weeks before the high measured concentrations of  $\text{NH}_4$  and TP at S1, part of catchment 1 received a heavy slurry application. These concentrations also coincided with the first significant rainfall event after the slurry application. This suggests that  $\text{NH}_4$  is a chemical signature of slurry applications, so we should be able to retrace the  $\text{NH}_4$  time series measurements and identify when (but not the amount of) slurry was applied.

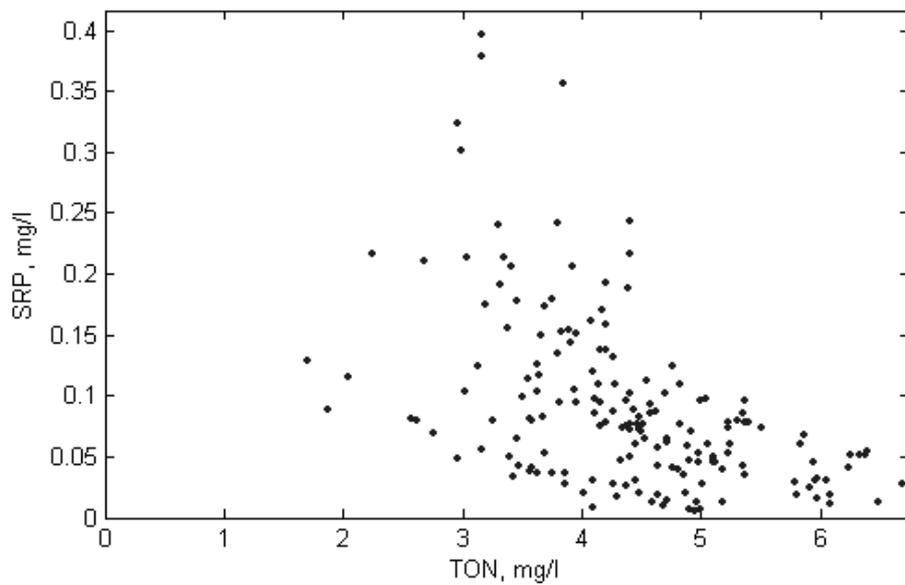
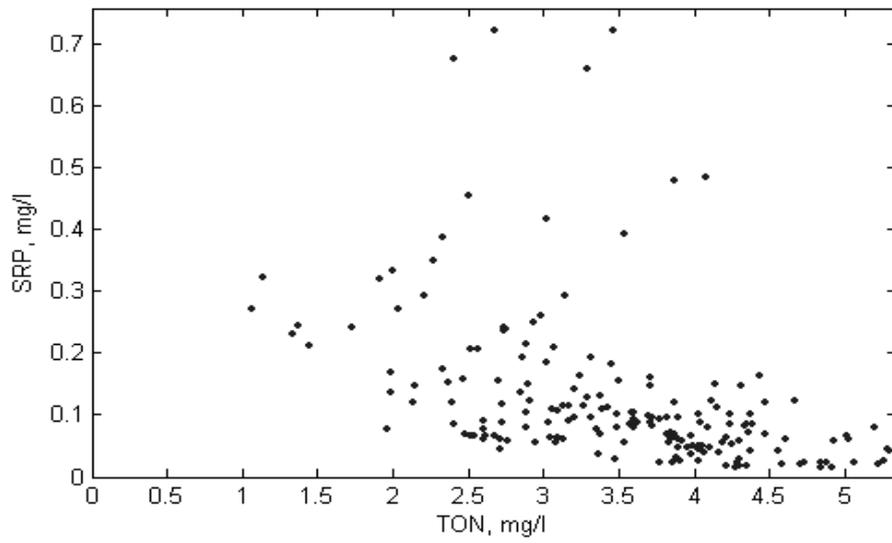
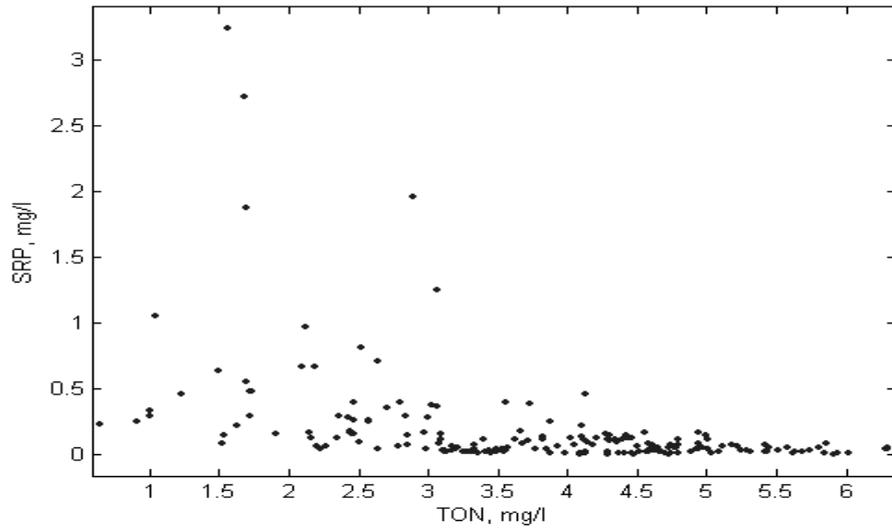
The above also suggests that one or other of the phosphorus components may be used as a surrogate for  $\text{NH}_4$ .



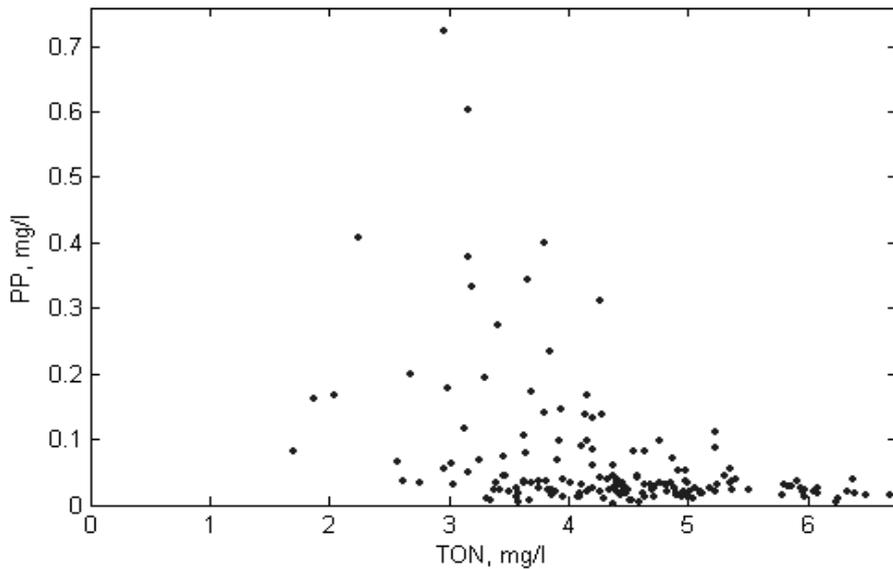
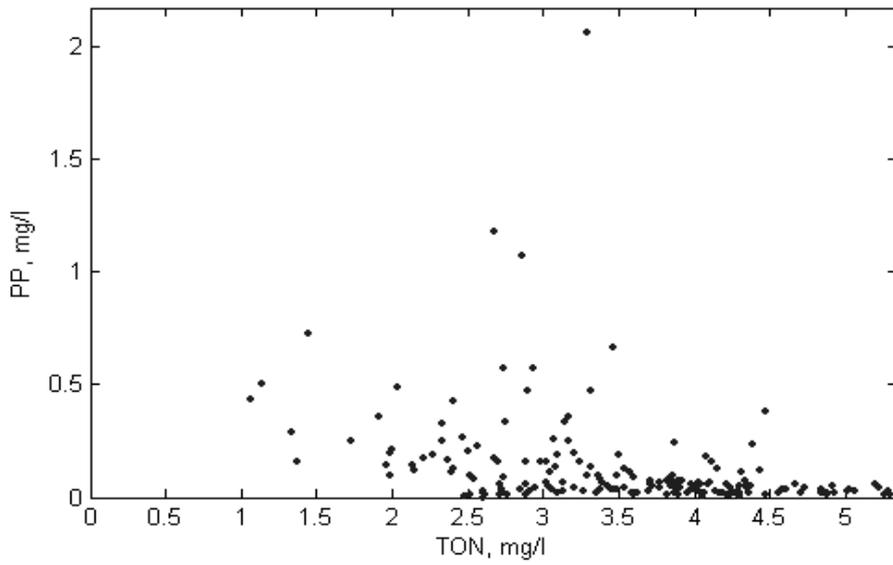
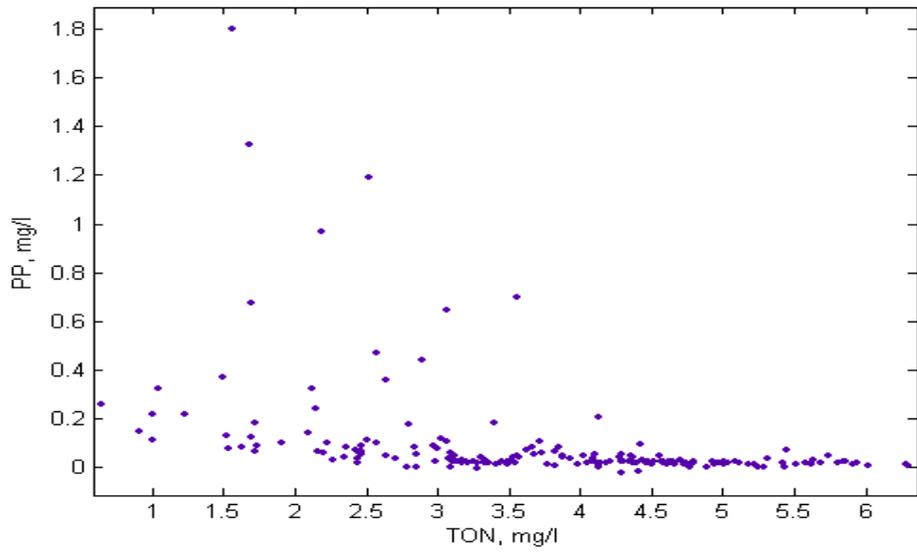
**Figure 6.13** a, b and c, TP vs. TON at sites 1, 3 and 4 respectively.



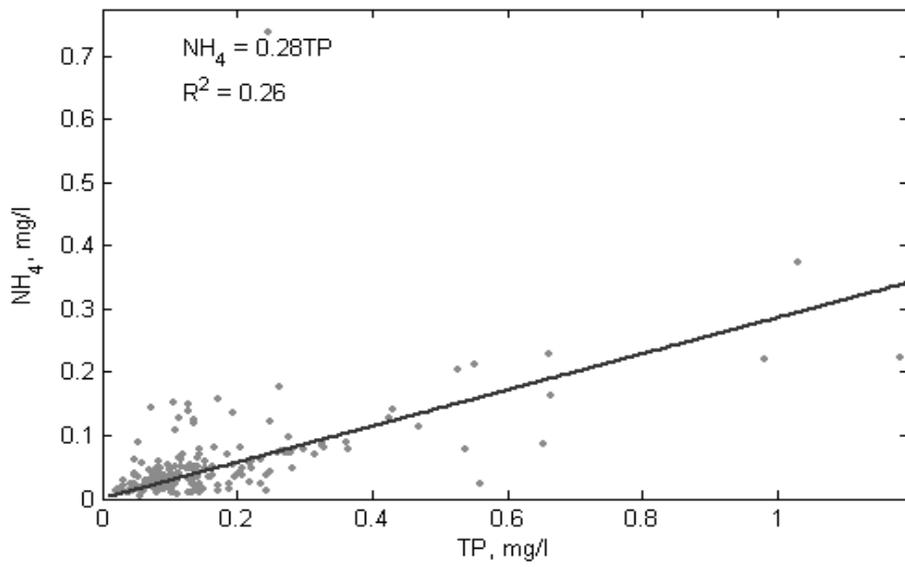
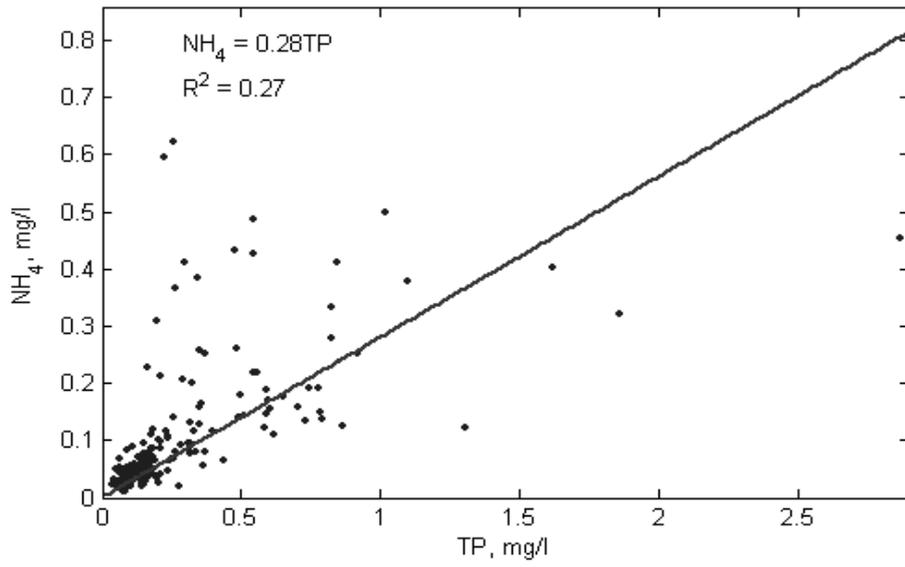
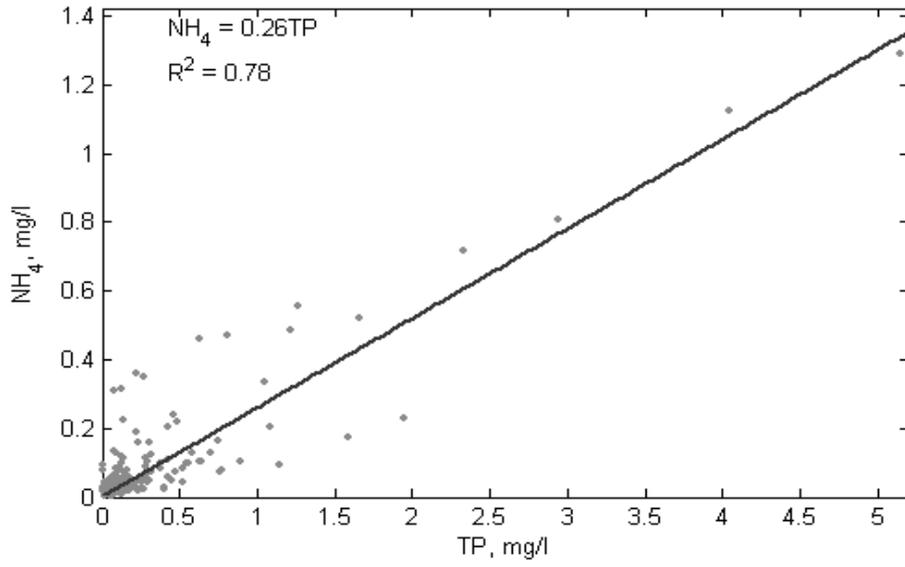
**Figure 6.14** a, b and c, TDP vs. TON at sites 1, 3 and 4 respectively.



**Figure 6.15** a, b and c, SRP vs. TON at sites 1, 3 and 4 respectively.



**Figure 6.16** a, b and c, PP vs. TON at sites 1, 3 and 4 respectively.



**Figure 6.17** a, b and c,  $NH_4$  vs. TP at sites 1, 3 and 4 respectively.

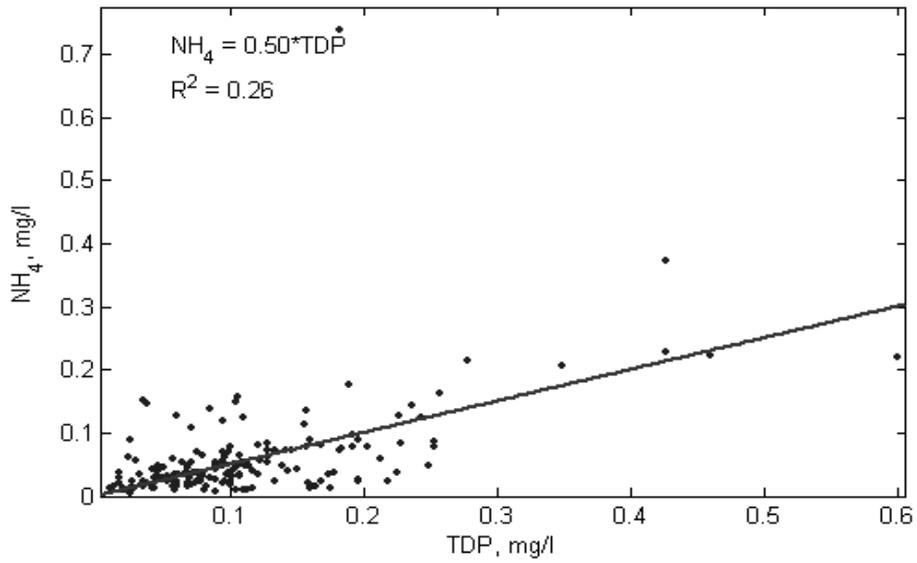
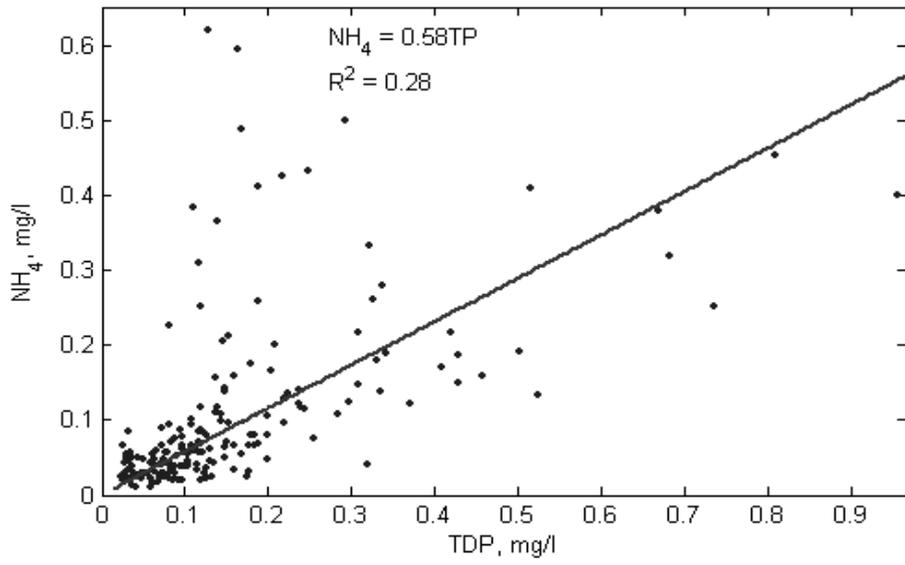
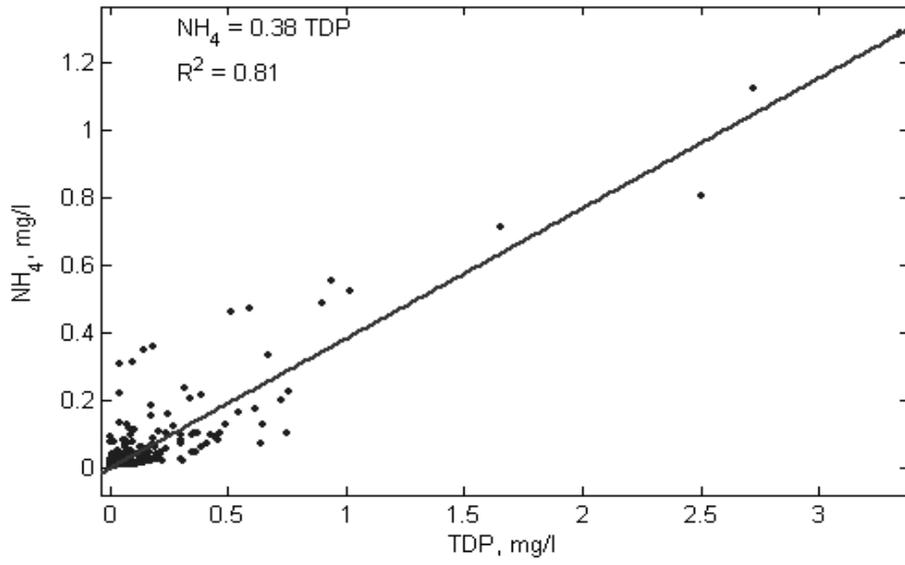
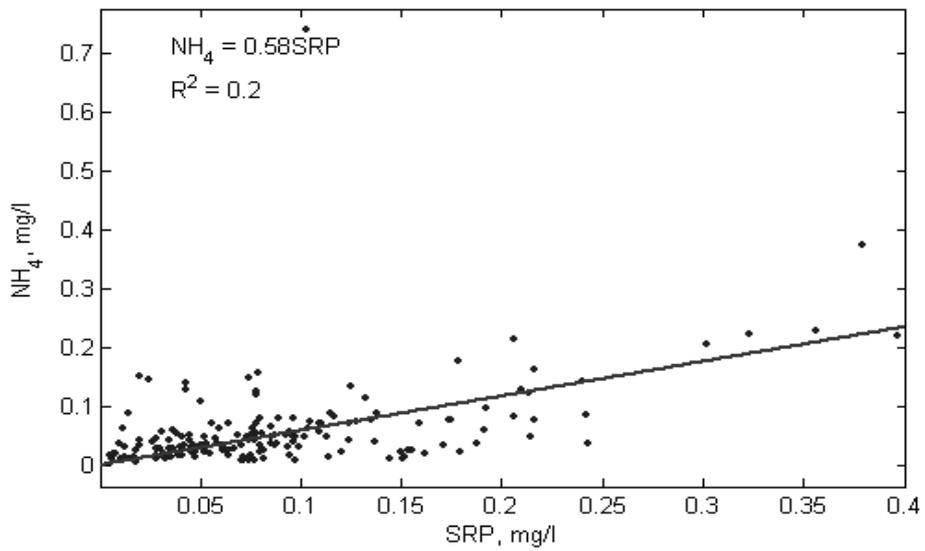
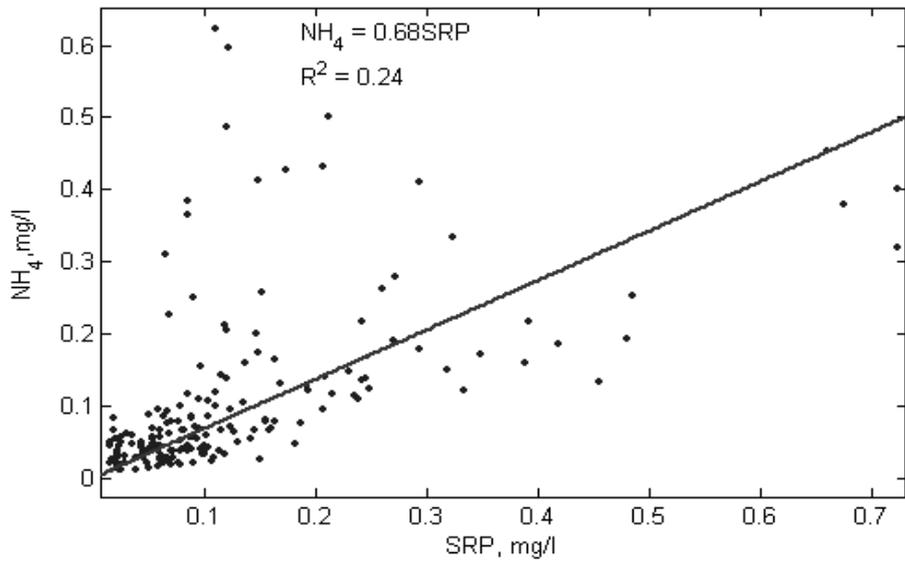
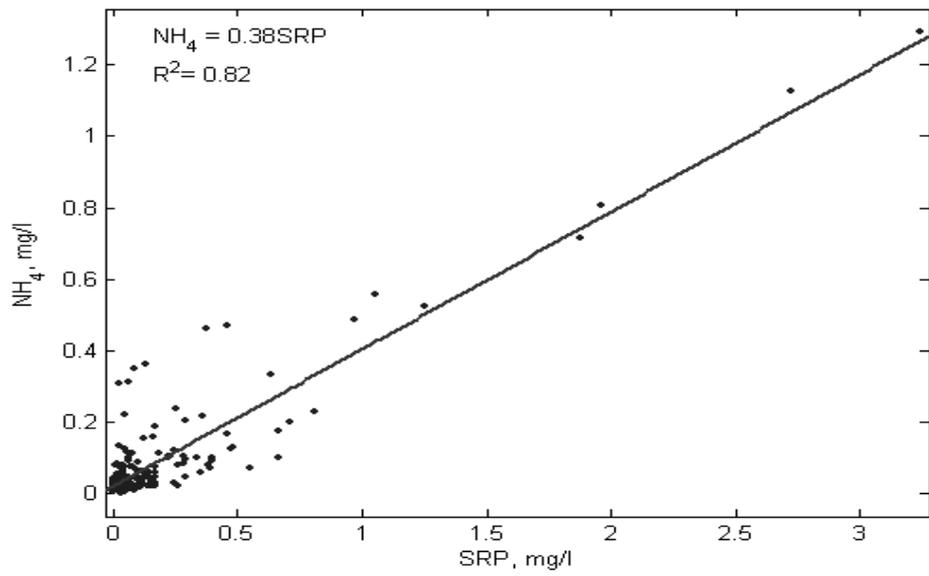


Figure 6.18 a, b and c,  $NH_4$  vs. TDP at sites 1, 3 and 4 respectively.



**Figure 6.19** a, b and c,  $\text{NH}_4$  vs. SPP at sites 1, 3 and 4 respectively.

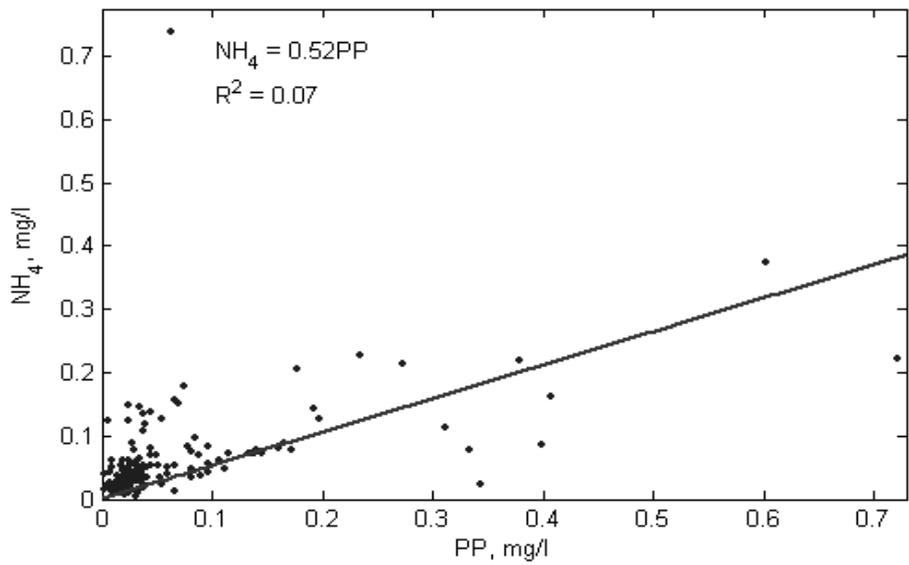
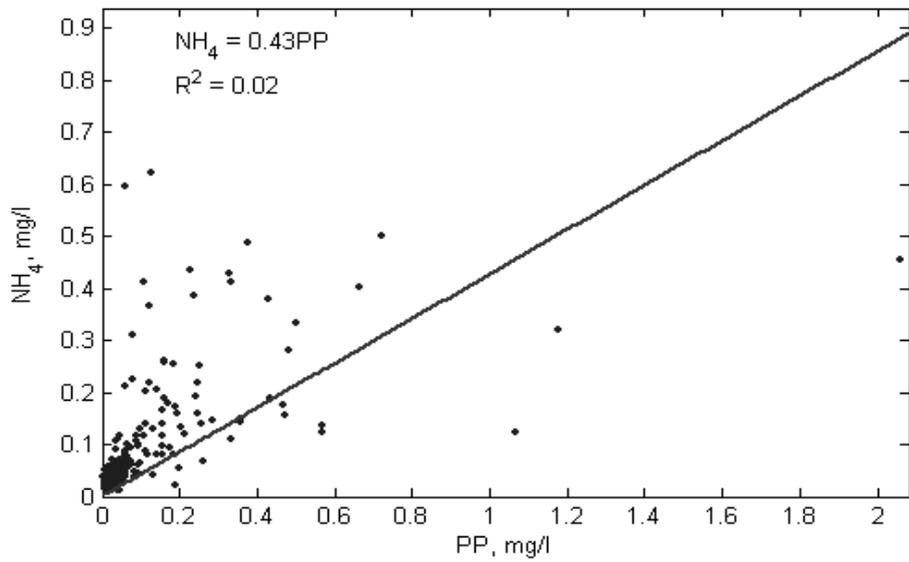
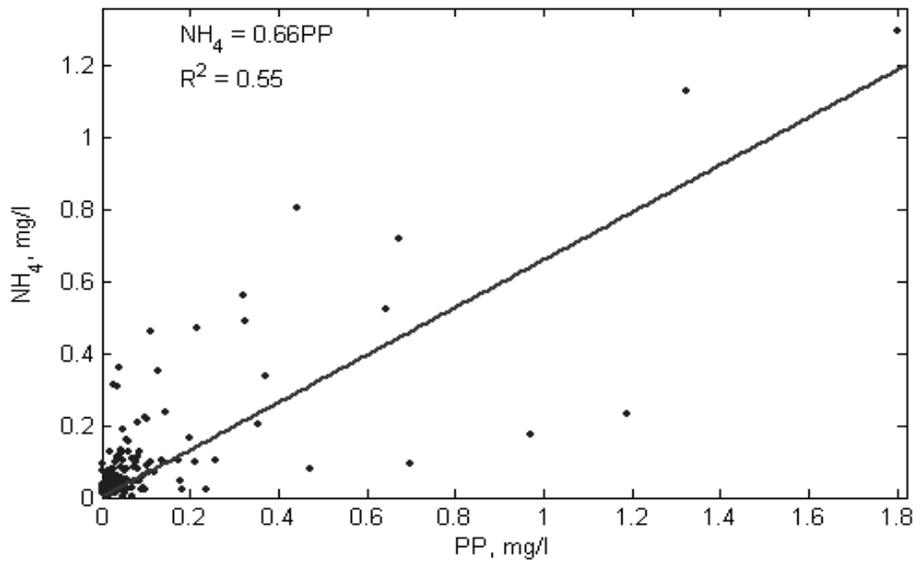


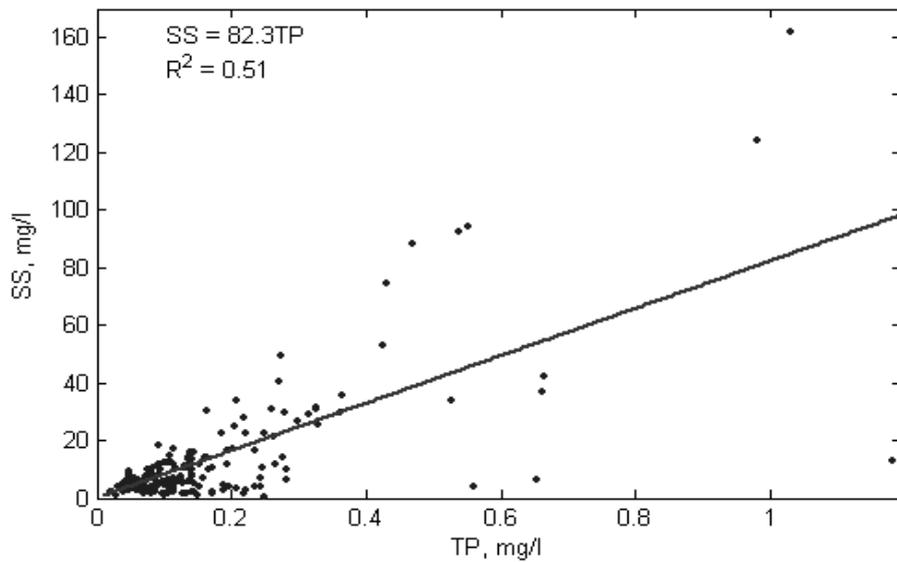
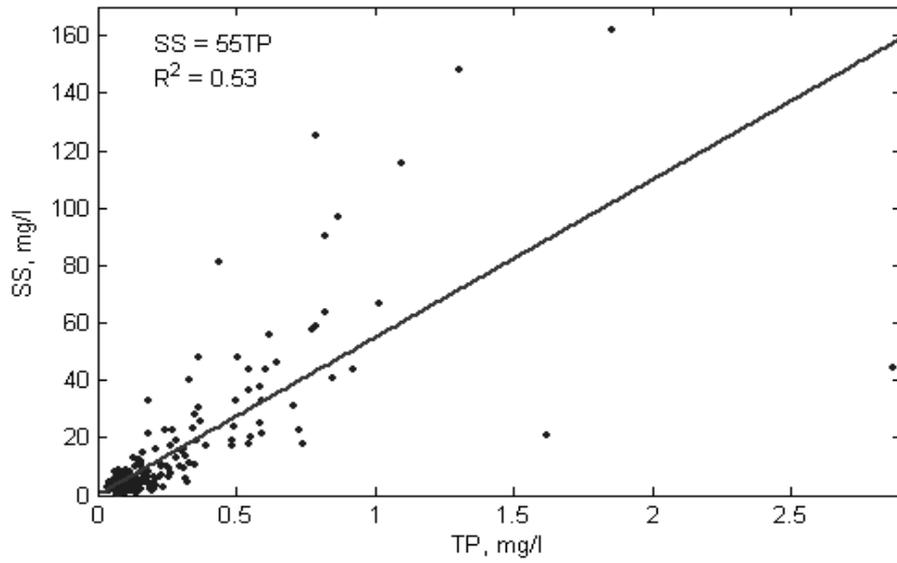
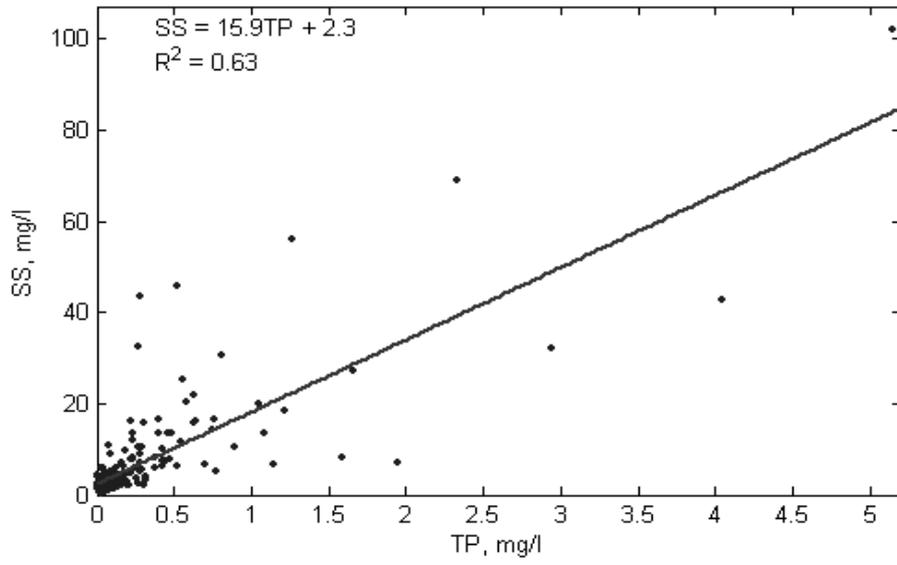
Figure 6.20 a, b and c,  $NH_4$  vs. PP at sites 1, 3 and 4 respectively.

### 6.4.3 Suspended sediment

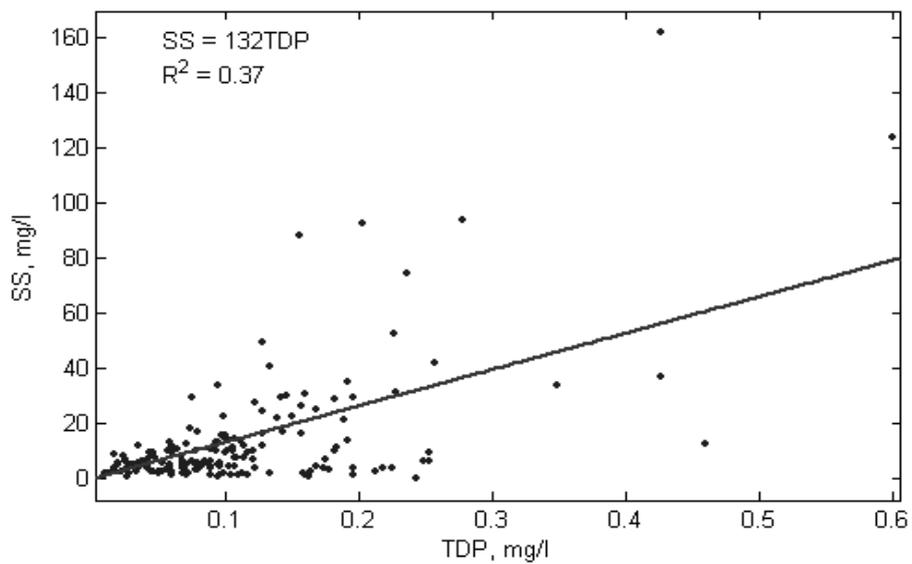
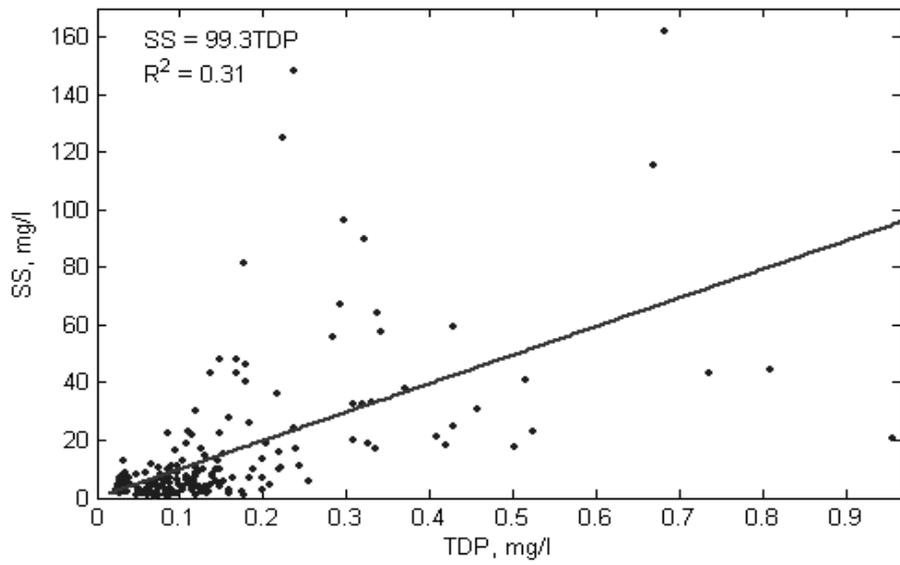
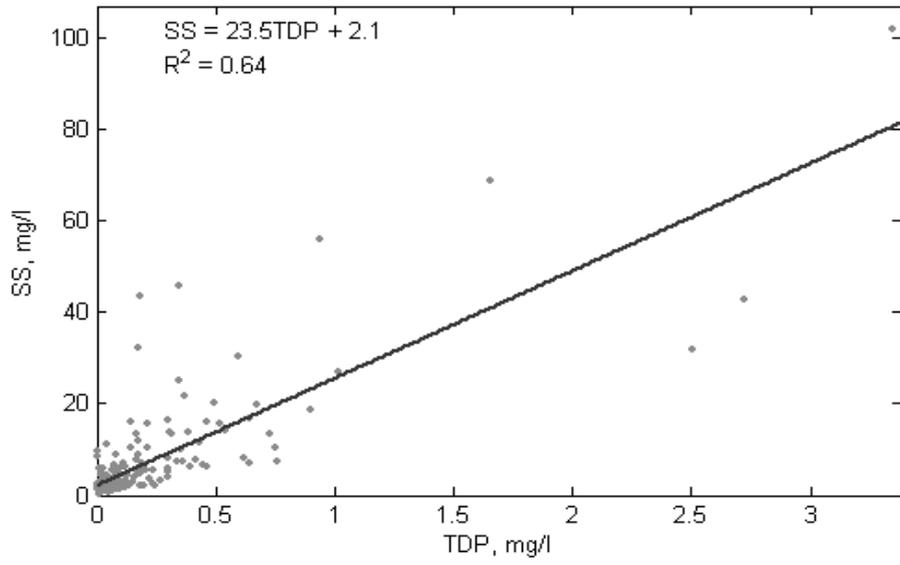
There is a strong relationship between SS and TP. The concentrations of TP are small compared to concentrations of SS. The concentrations of TP relative to SS decrease with increasing catchment area (see Figure 6.21). The TP concentrations are 6%, 1.8% and 1.2% of the SS concentrations. A similar pattern can be seen in Figure 6.22 between SS and TDP and SS and SRP in Figure 6.23.

The relationship between SS and PP is stronger with all three sites having similar  $R^2$  values, unlike any of the previous relationships where S1 usually had a much higher  $R^2$  value. As can be seen from Figure 6.24 the particulate form of phosphorus is only a very small part of the total suspended sediment in the streams and decreases further with increasing catchment size. The PP fraction is 2.8%, 1.2% and 0.6% of SS. It is also interesting to note that there are times when there is no phosphorus content in the suspended sediment.

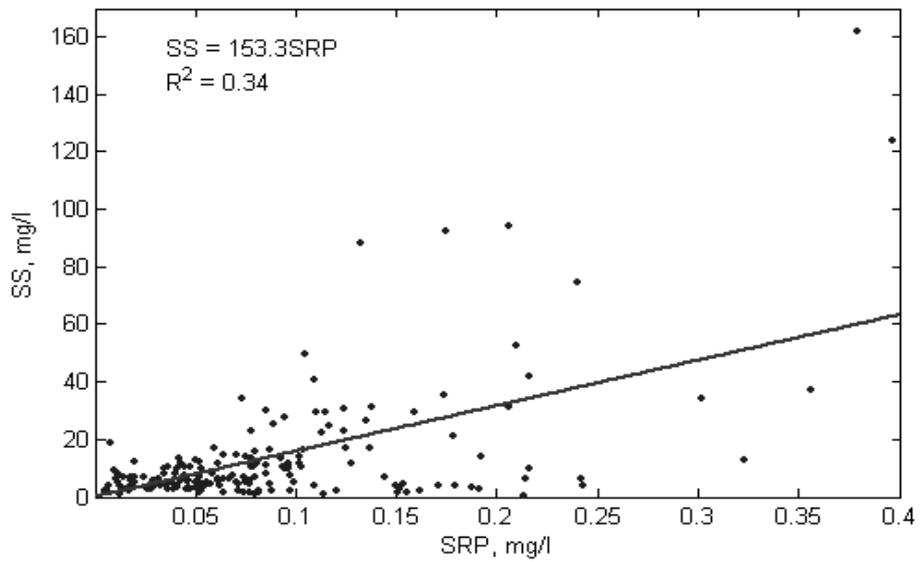
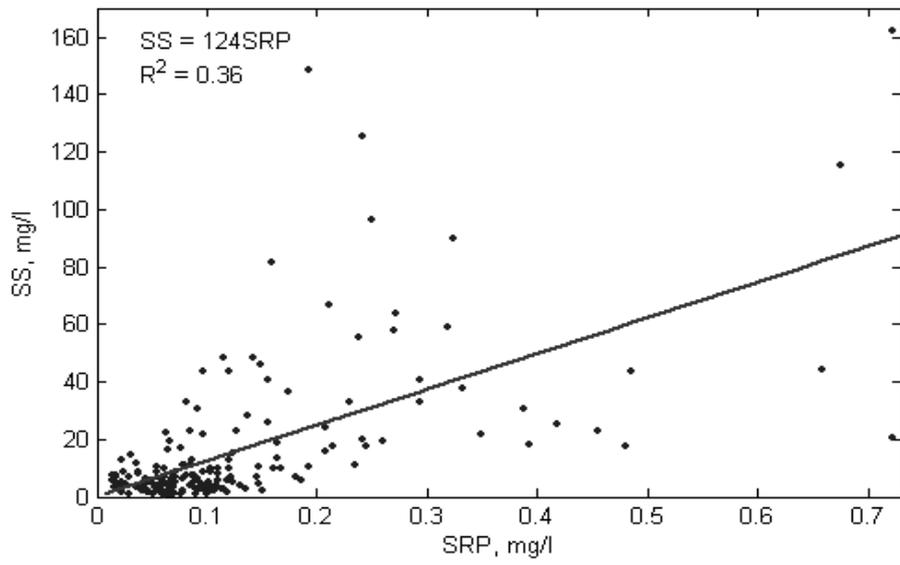
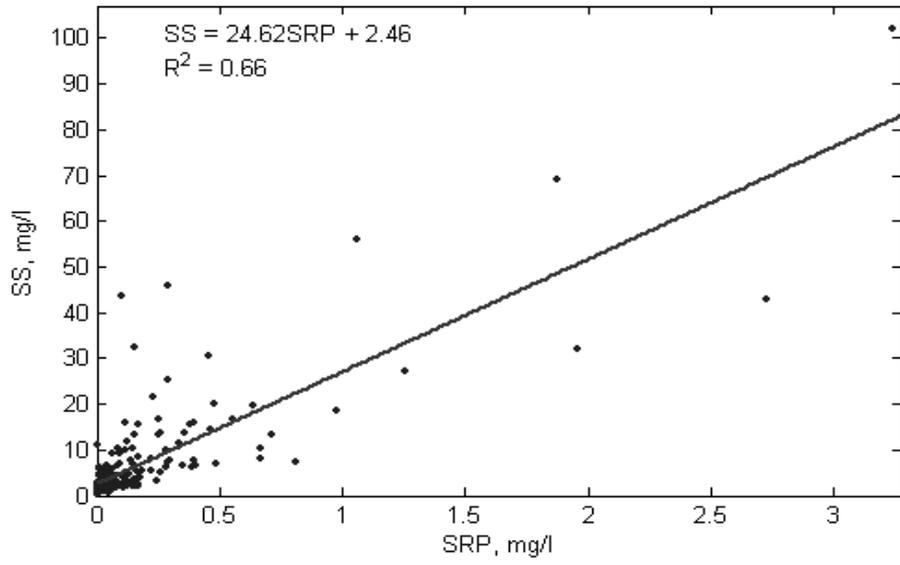
There is a poor power relationship between SS and TON. The power fit (see Figure 6.25) was not very successful suggesting that there is no connection between the concentrations of TON and SS in the streams. There was a linear relationship between  $\text{NH}_4$  and SS with the strongest relationship again at between the nutrients at S1 (see Figure 6.26).



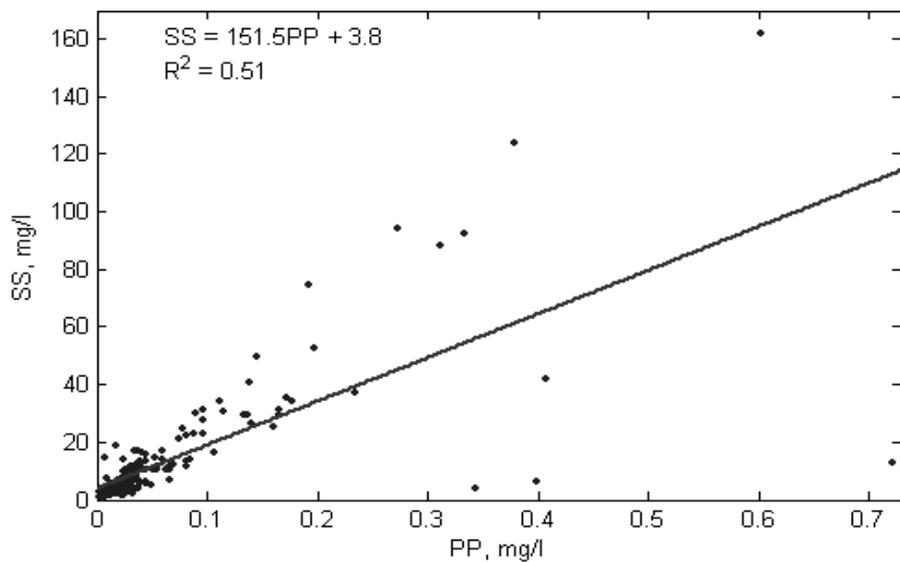
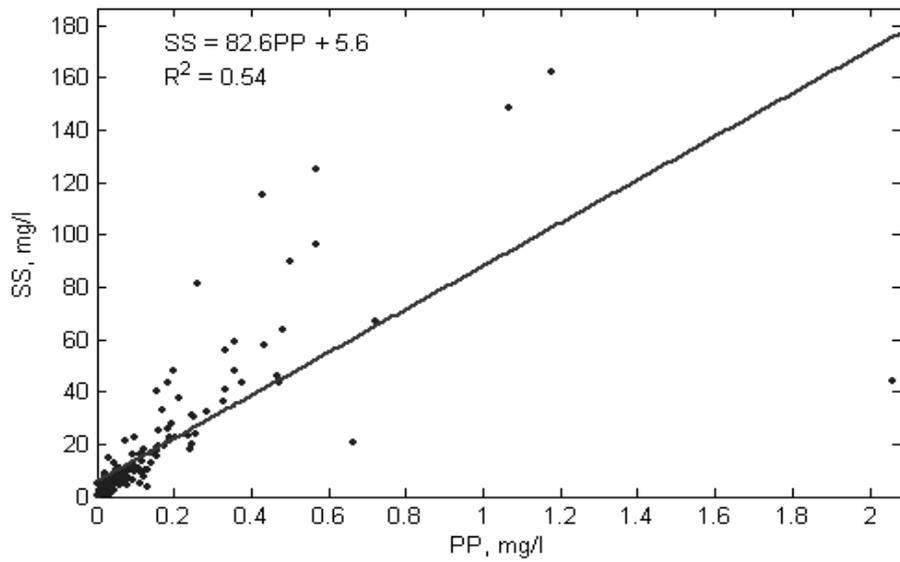
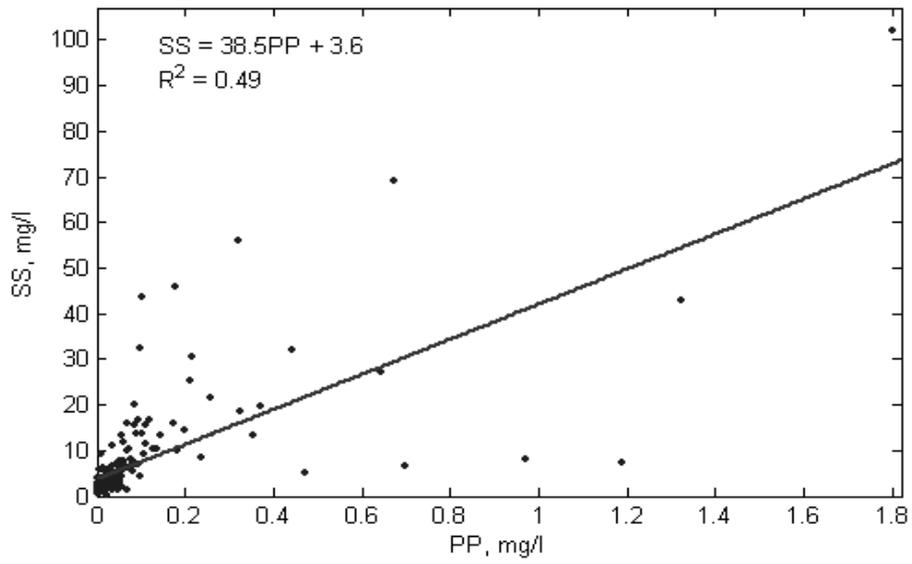
**Figure 6.21** a, b and c, SS vs. TP at sites 1, 3 and 4 respectively.



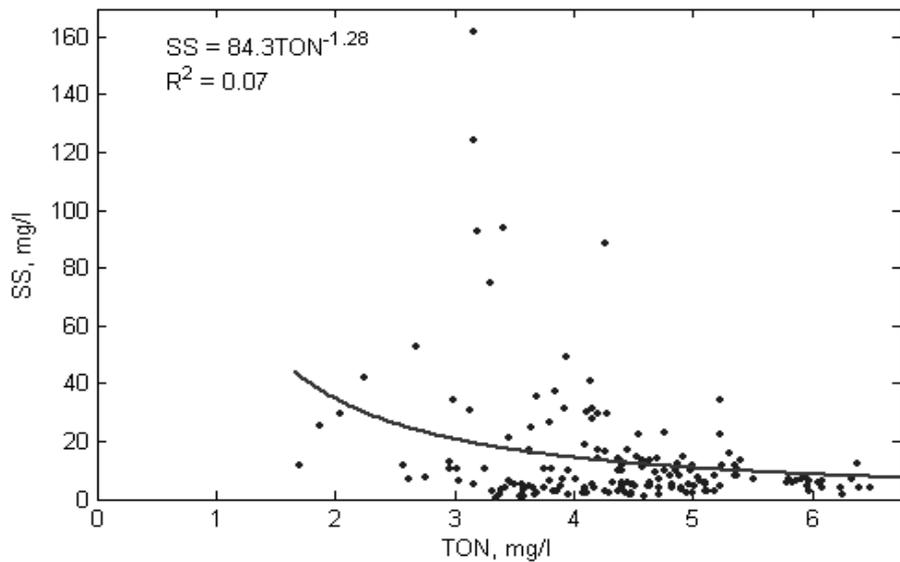
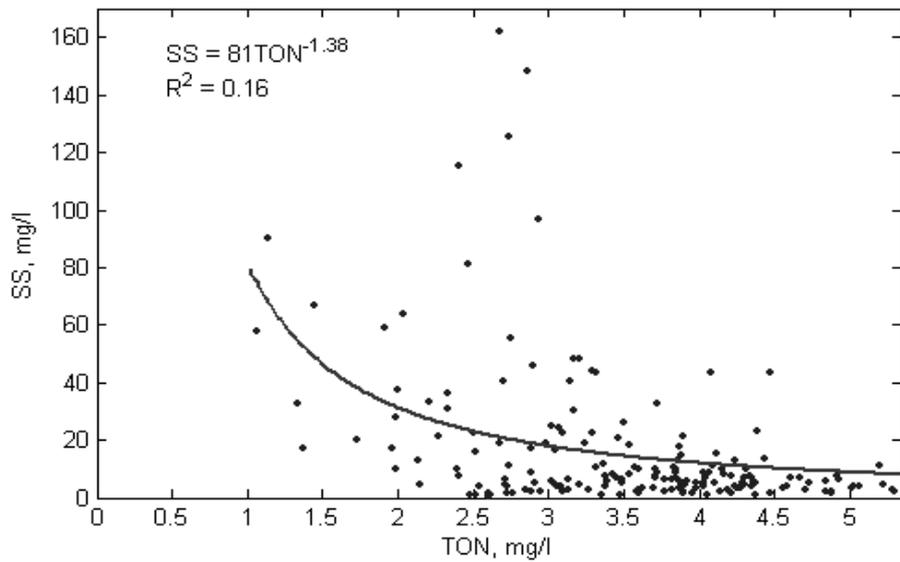
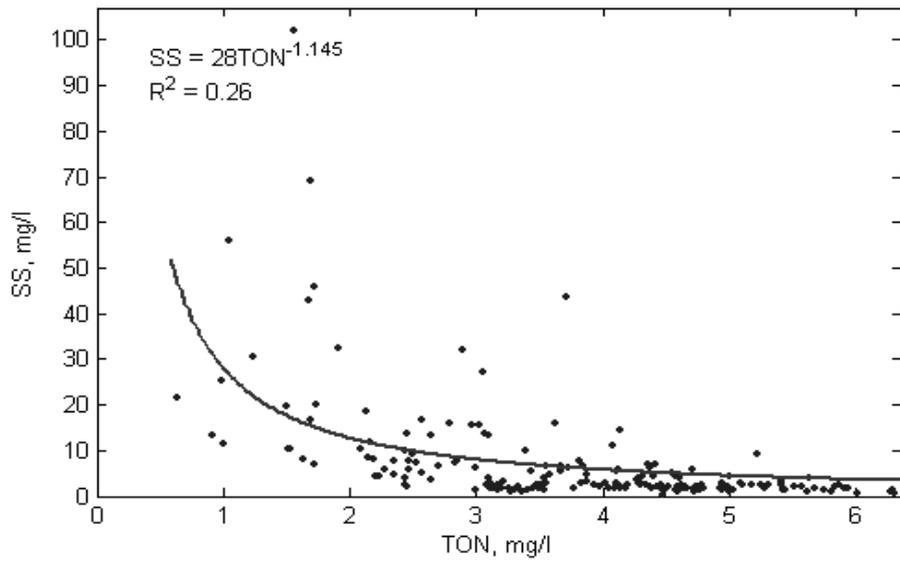
**Figure 6.22** a, b and c, SS vs. TDP at sites 1, 3 and 4 respectively.



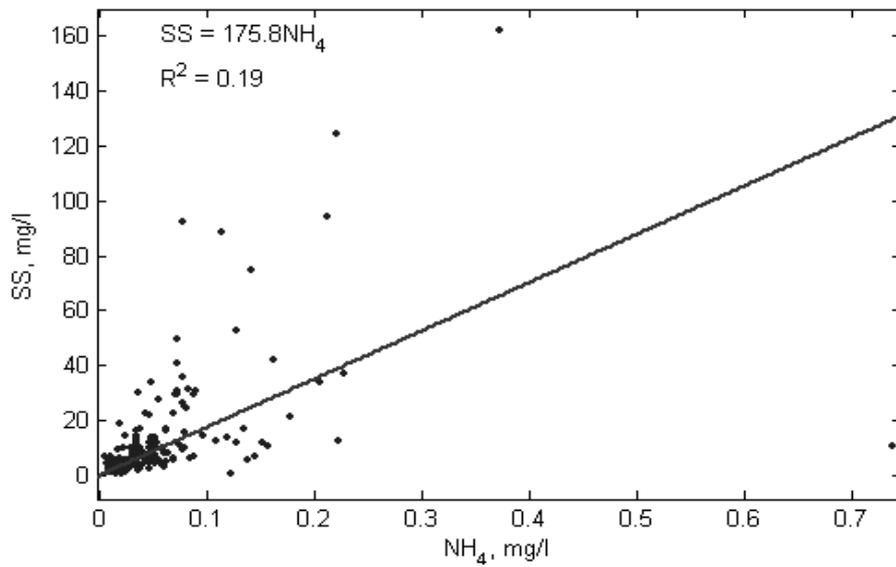
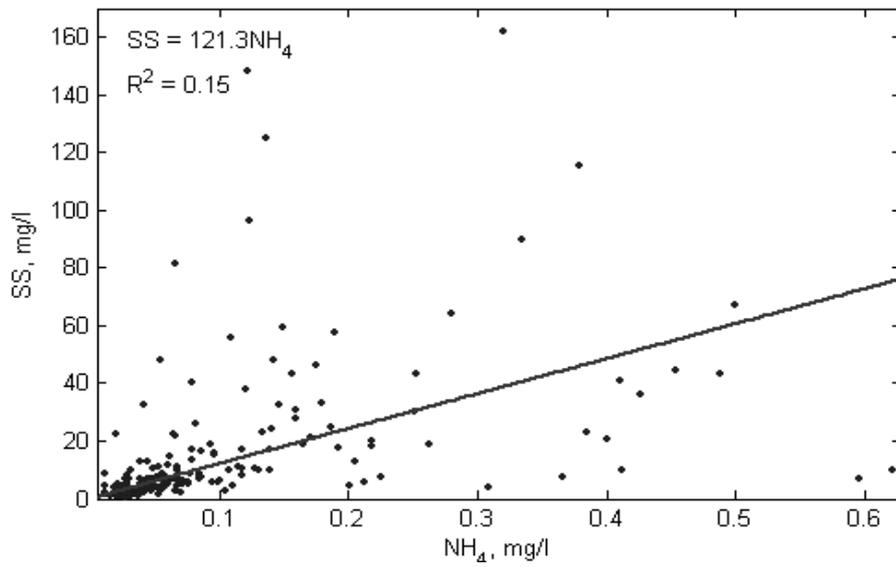
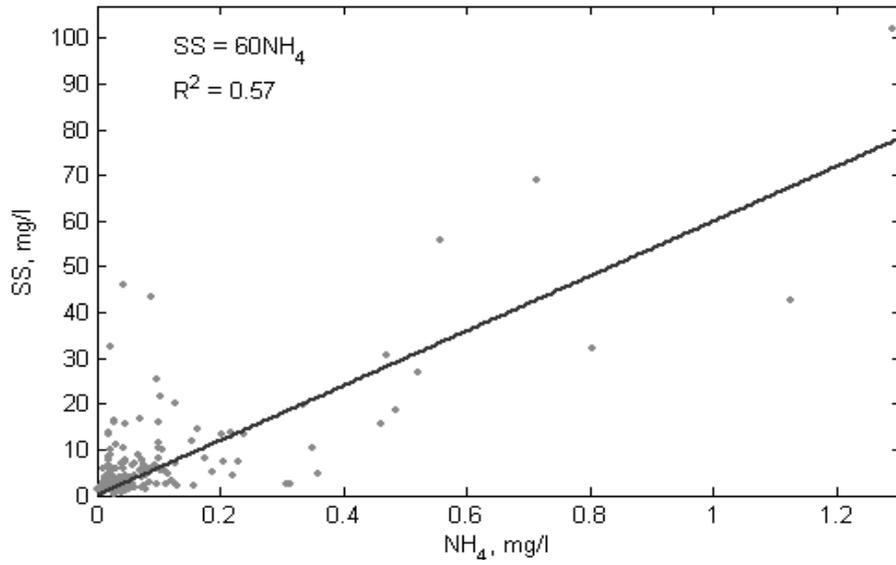
**Figure 6.23** a, b and c, SS vs. SRP at sites 1, 3 and 4 respectively.



**Figure 6.24** a, b and c, SS vs. PP at sites 1, 3 and 4 respectively.



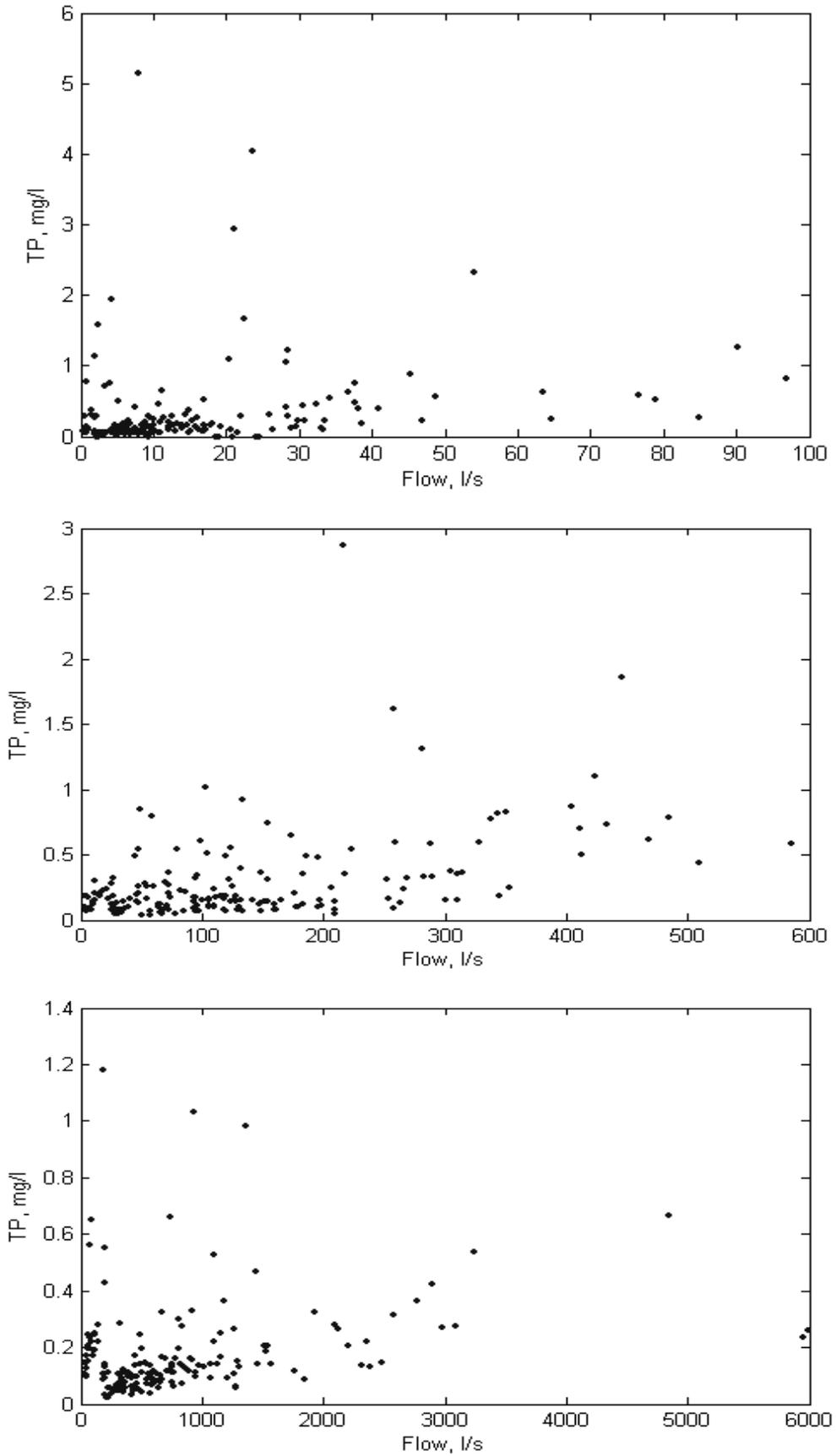
**Figure 6.25** a, b and c, SS vs. TON at sites 1, 3 and 4 respectively.



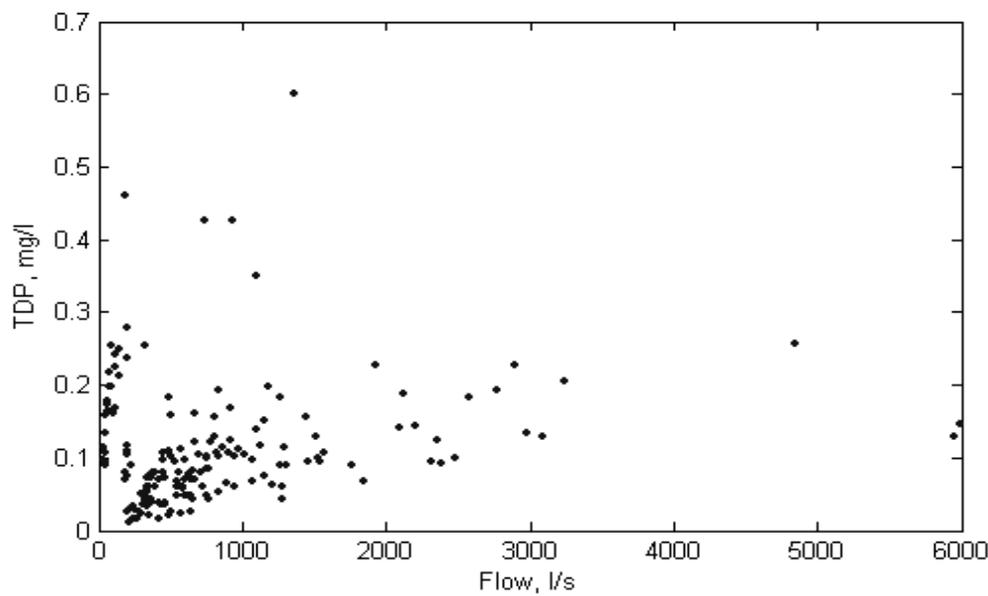
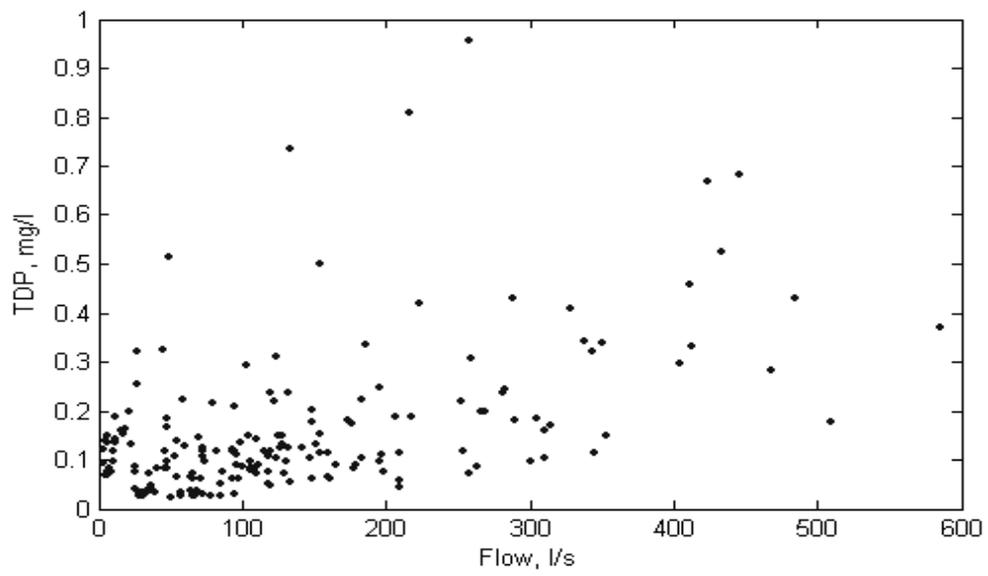
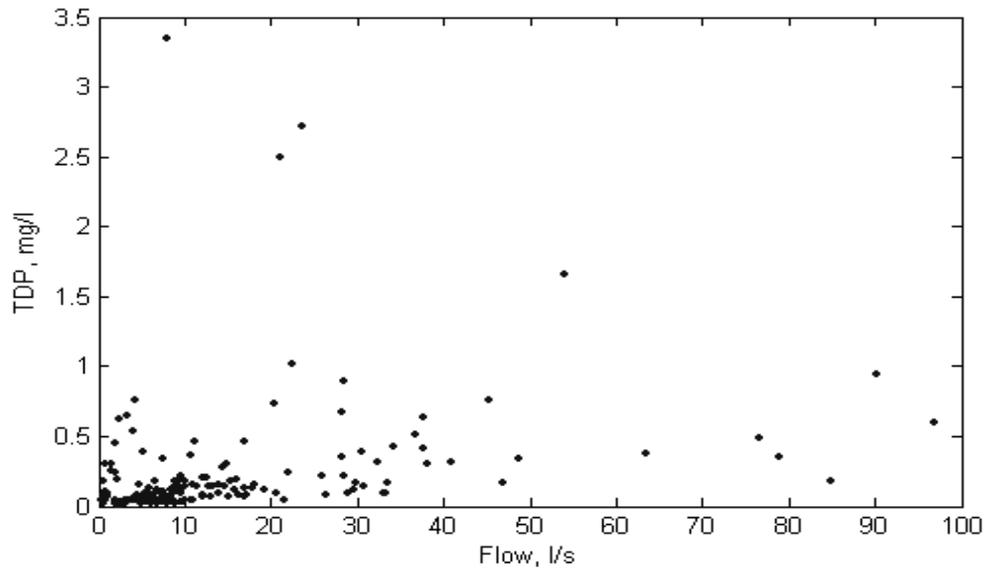
**Figure 6.26** a, b and c, SS vs.  $\text{NH}_4$  at sites 1, 3 and 4 respectively.

## **6.5 Relationships of flow with nutrients and SS**

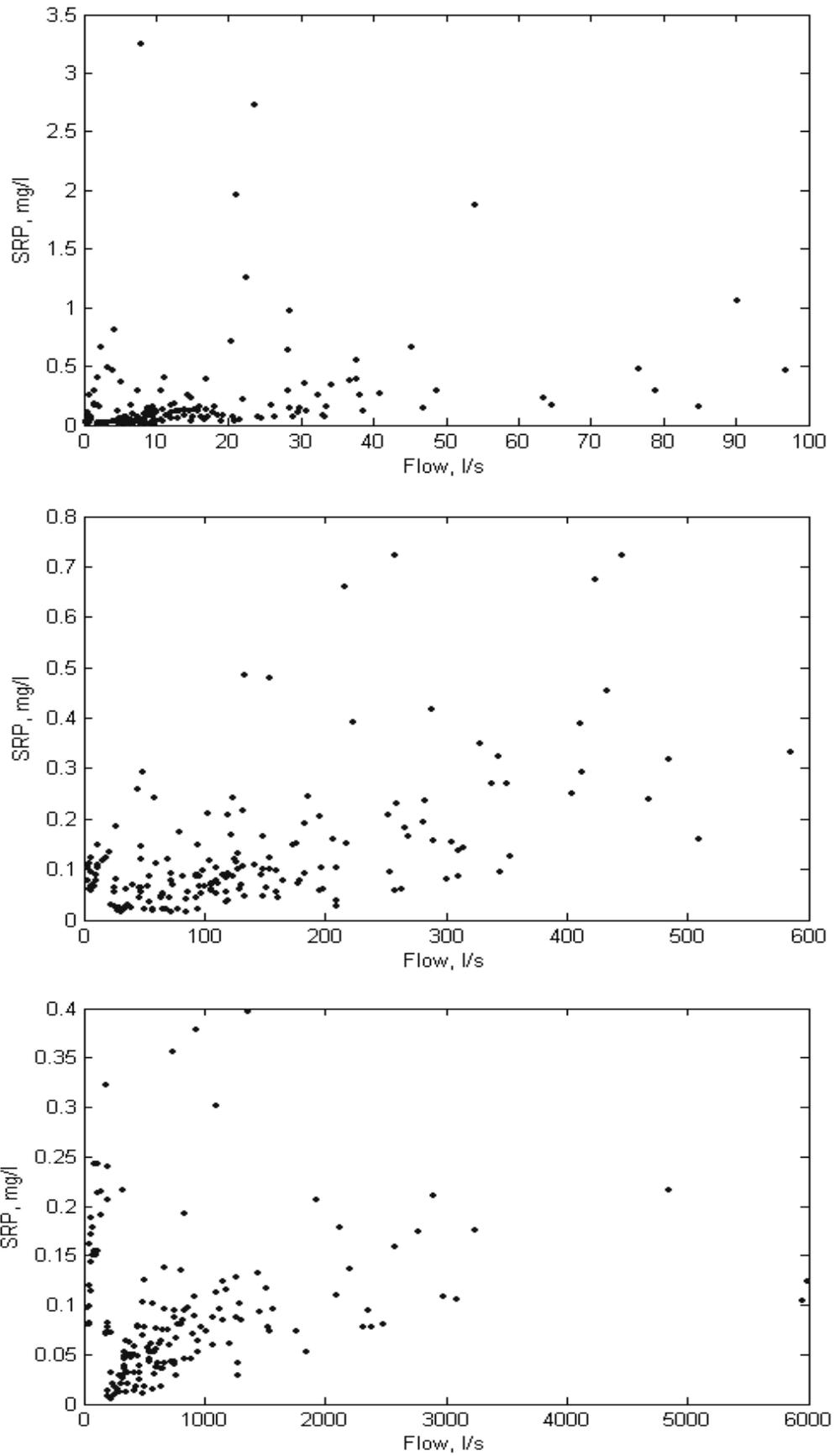
Figures 6.27 and 6.28 show there is a trend for TP and NH<sub>4</sub> to increase with increasing flow. TDP, SRP, PP and NH<sub>4</sub> also increase with increasing flow as shown in Figures 6.28, 6.29 6.30 and 6.32. However, as Figure 6.31 shows TON decreases with increasing flow. This would suggest that TON is transported in higher concentrations in the base flow route than in the overland or subsurface flow. The base flow is diluted during flood events. The converse is true for TP and NH<sub>4</sub>. These both increase significantly with increasing flow suggesting that they are transported in the main by overland or subsurface flow. SS as expected increased with increasing flow due to the increased erosion with higher flows (see Figure 6.33).



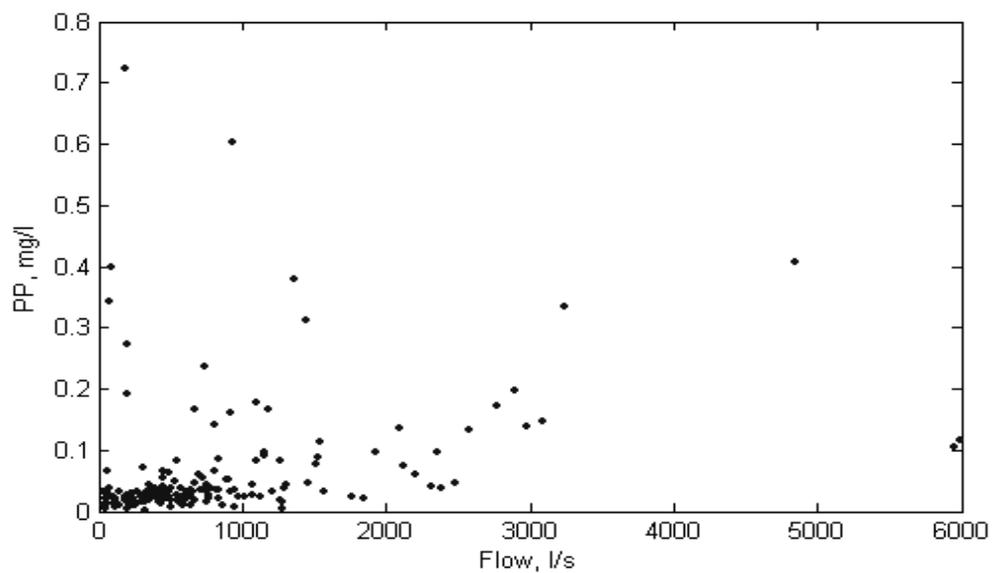
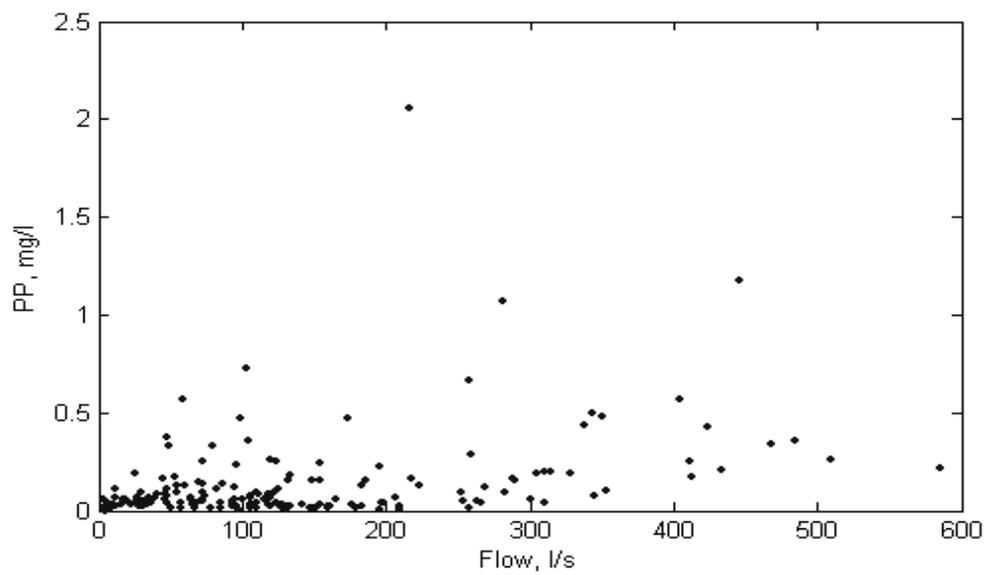
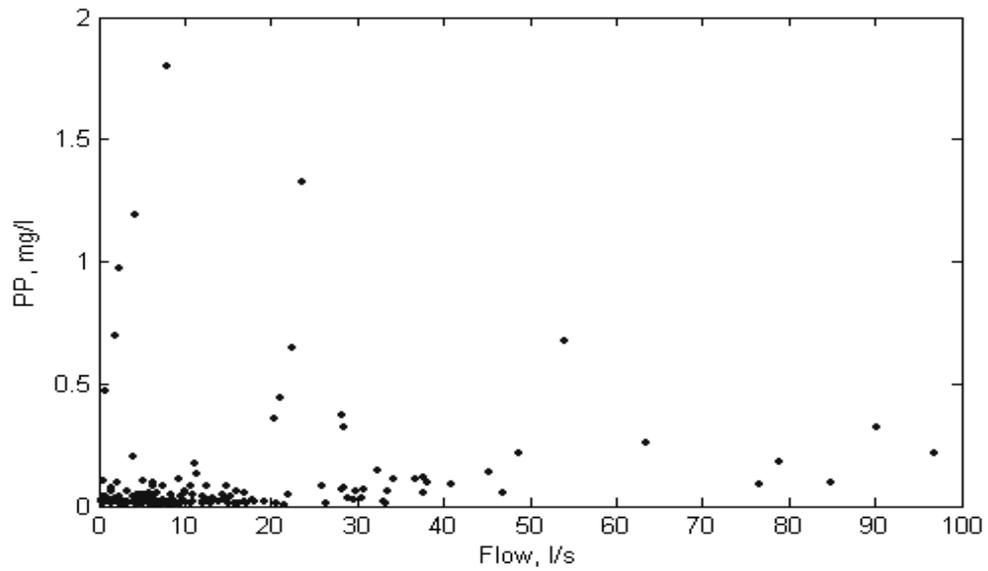
**Figure 6.27** a, b and c. TP vs. Flow, for the year 2002.



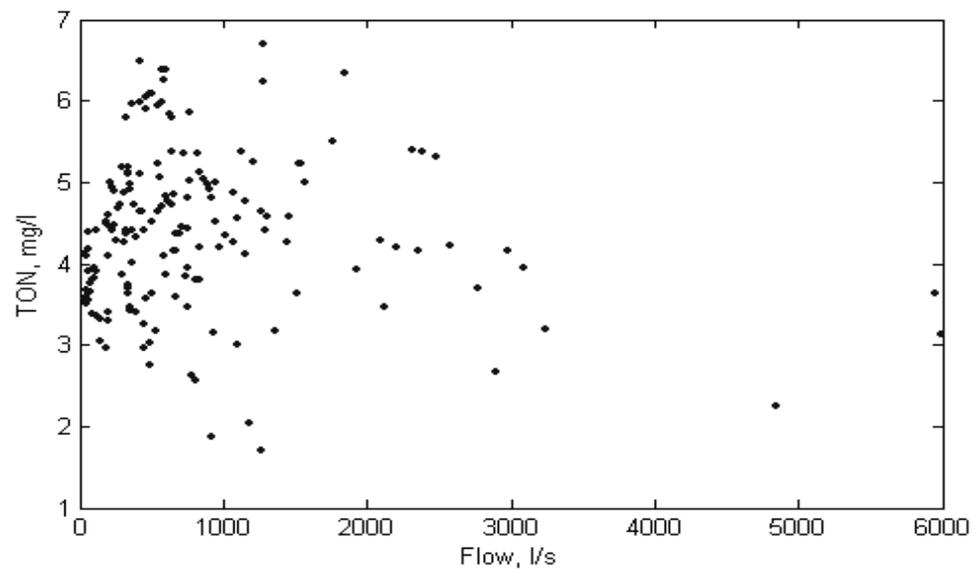
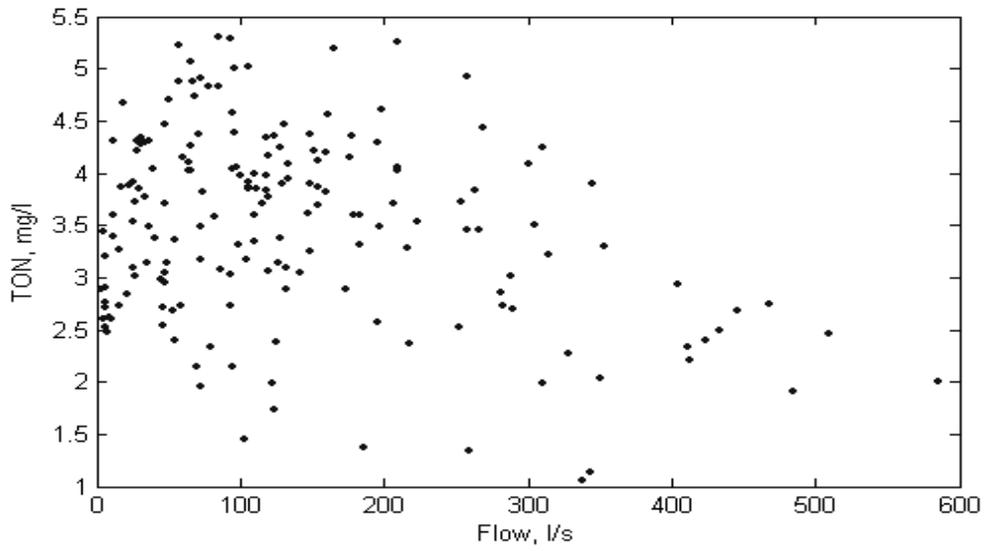
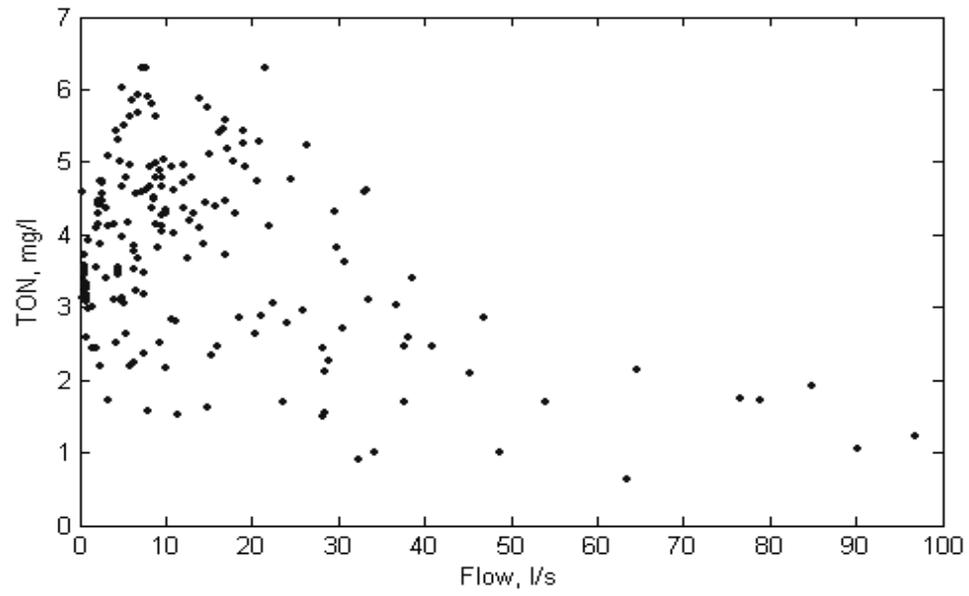
**Figure 6.28** a, b and c. TDP vs. Flow, for the year 2002.



**Figure 6.29** a, b and c. SRP vs. Flow, for the year 2002.



**Figure 6.30** a, b and c. PP vs. Flow, for the year 2002



**Figure 6.31** a, b and c. TON vs. Flow, for the year 2002

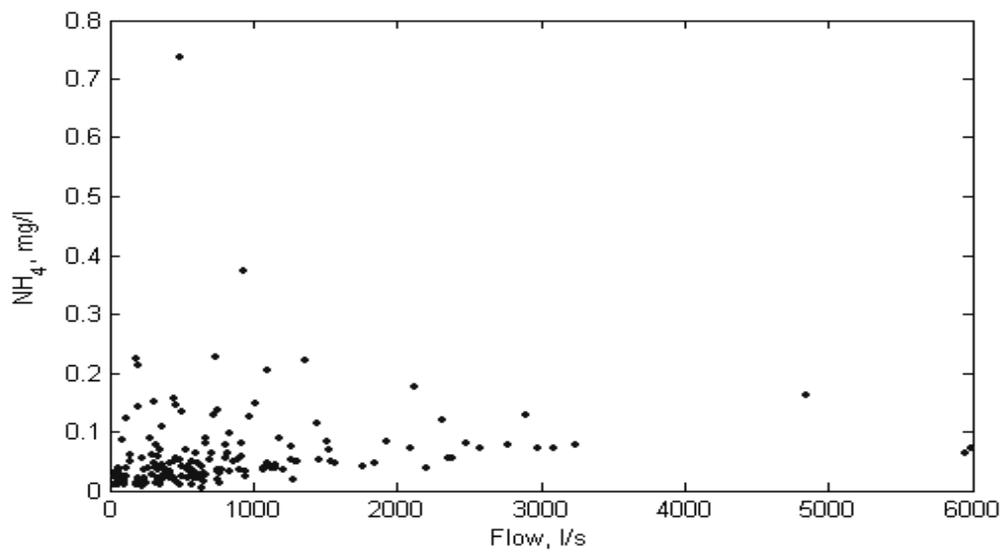
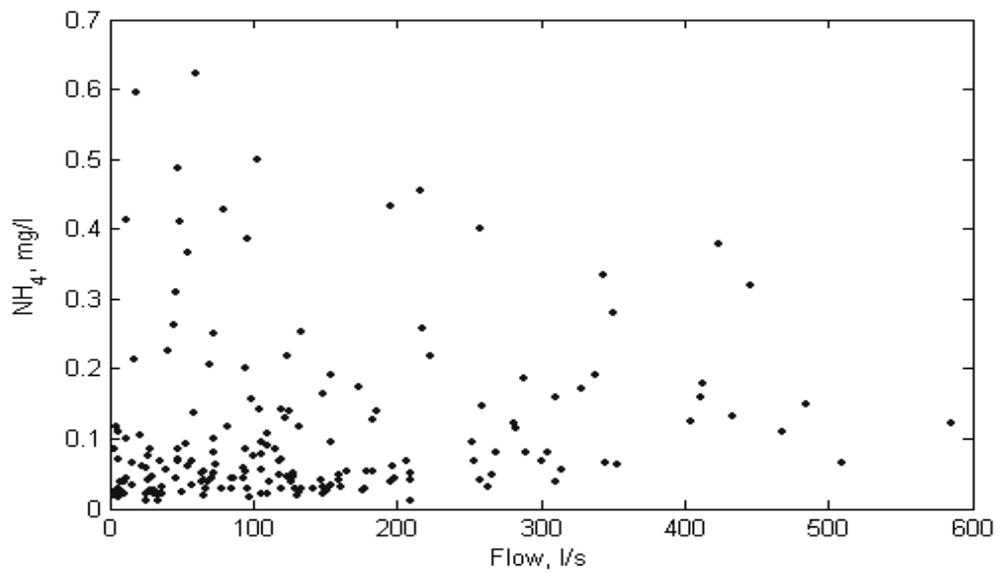
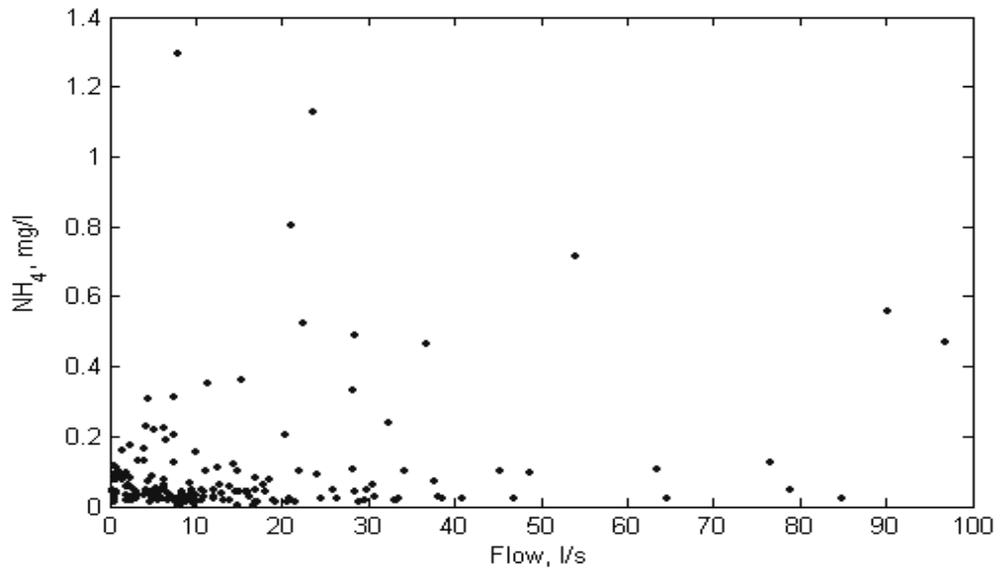
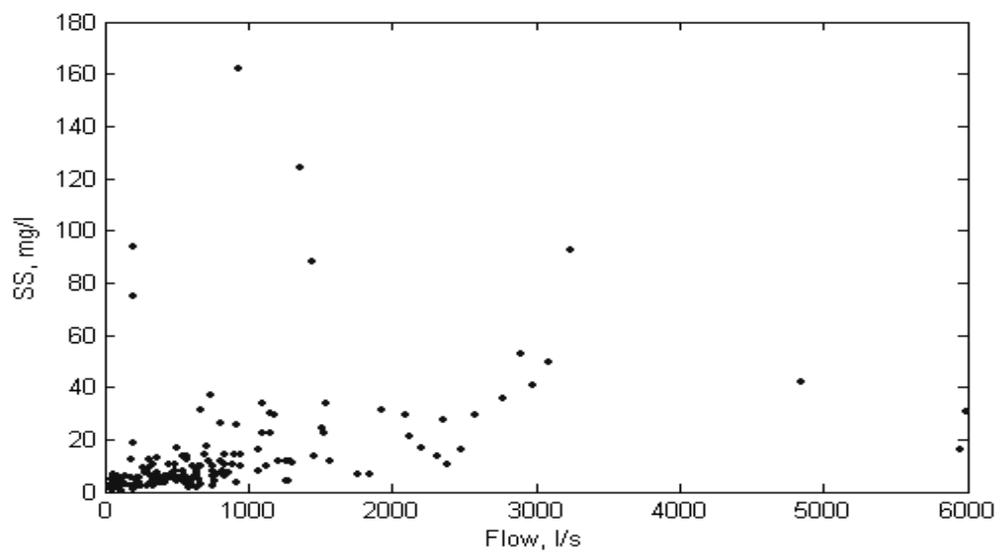
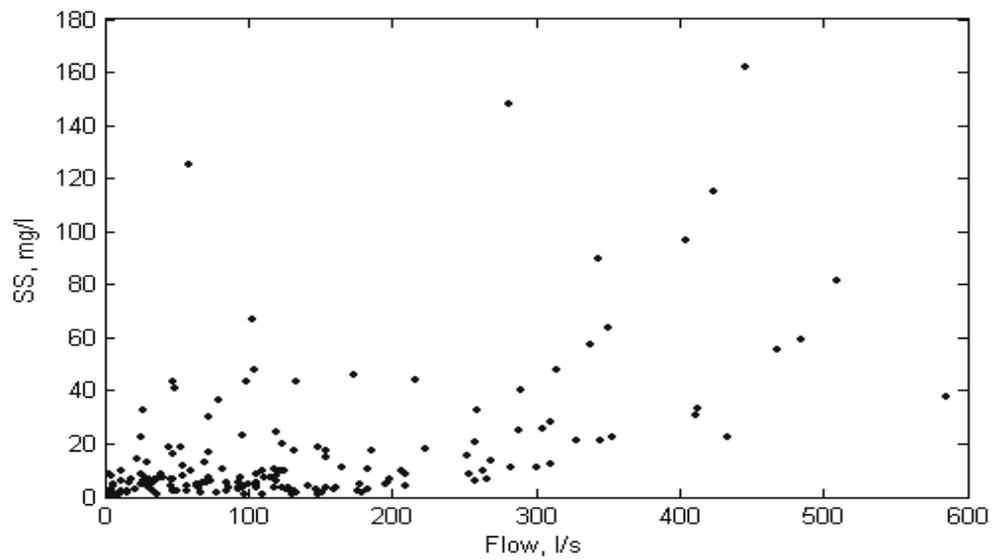
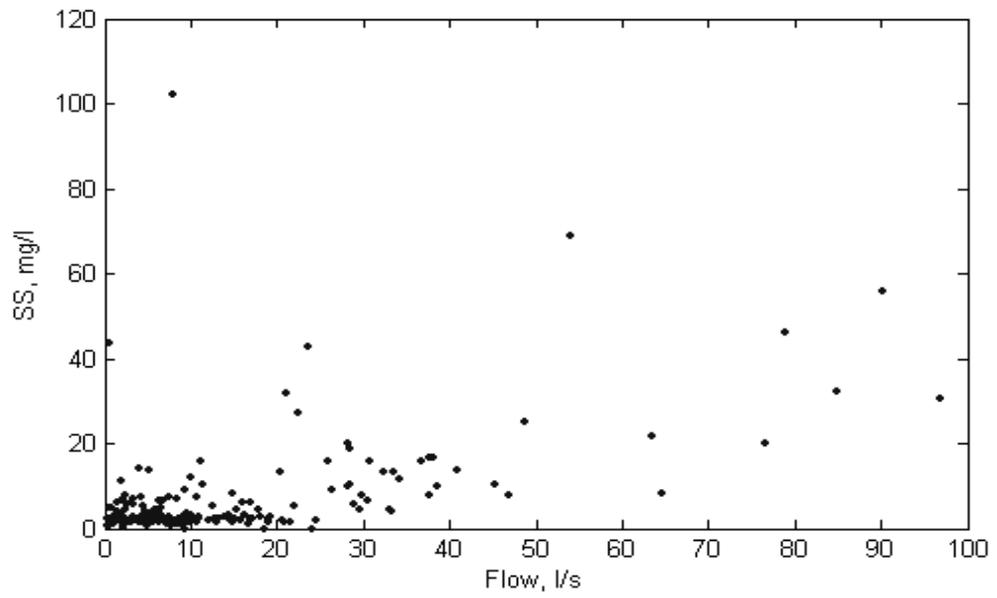


Figure 6.32 a, b and c.  $\text{NH}_4$  vs. Flow, for the year 2002



**Figure 6.33** a, b and c. SS vs. Flow, for the year 2002.

## 6.6 Summary of intra and inter-relationships of nutrients and suspended sediments.

**Table 6.5** Intra-relationships of phosphorus (Figures 6.7-6.9).

Site	TP/TDP	TP/SRP	TP/PP
S1	TP = 1.44TDP $R^2 = 0.96$	TP = 1.5SRP $R^2 = 0.96$	TP = 2.67PP $R^2 = 0.85$
S3	TP = 1.9TDP $R^2 = 0.75$	TP = 2.3SRP $R^2 = 0.75$	TP = 1.6PP $R^2 = 0.82$
S4	TP = 1.97TDP $R^2 = 0.83$	TP = 2.0SRP $R^2 = 0.76$	TP = 1.95PP $R^2 = 0.76$

**Table 6.6** Intra-relationships of phosphorus (Figures 6.10-6.12).

Site	TDP/SRP	TDP/PP	SRP/PP
S1	TDP = 1.04SRP $R^2 = 0.97$	TDP = 1.67PP $R^2 = 0.67$	SRP = 1.65PP $R^2 = 0.73$
S3	TDP = 1.19SRP $R^2 = 0.94$	TDP = 0.63PP $R^2 = 0.06$	SRP = 0.53PP $R^2 = 0.18$
S4	TDP = 1.21SRP $R^2 = 0.94$	TDP = 0.96PP $R^2 = 0.01$	SRP = 0.76PP $R^2 = 0.02$

**Table 6.7** Intra-relationships of nitrogen.

Site	TON/NH <sub>4</sub>
S1	None
S3	None
S4	None

We note that for Tables 6.5 and 6.6 and 6.7 that there are some high  $R^2$  relationships between the different phosphorus components at all sites.

**Table 6.8** Inter-relationships of phosphorus with nitrogen and SS (Figures 6.13, 6.17 and 6.21).

Site	TP/TON	NH <sub>4</sub> /TP	SS/TP
S1	None	NH <sub>4</sub> = 0.26TP R <sup>2</sup> = 0.78	SS = 15.9TP + 2.3 R <sup>2</sup> = 0.63
S3	None	NH <sub>4</sub> = 0.28TP R <sup>2</sup> = 0.27	SS = 55TP R <sup>2</sup> = 0.53
S4	None	NH <sub>4</sub> = 0.28TP R <sup>2</sup> = 0.26	SS = 82.3TP R <sup>2</sup> = 0.51

**Table 6.9** Relationships between phosphorus and flow (Figures 6.27, 6.28, 6.29).

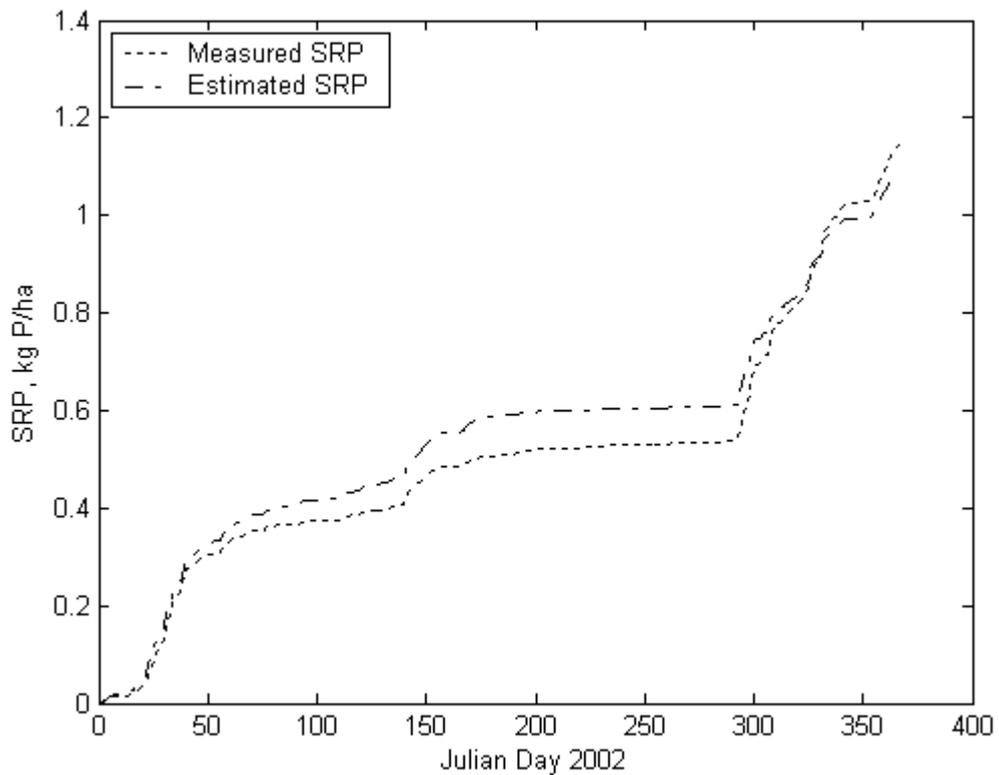
Site	TP	TDP	SRP
S1	TP = 0.11Q <sup>0.44</sup> R <sup>2</sup> = 0.06	TDP = 0.07Q <sup>0.49</sup> R <sup>2</sup> = 0.1	SRP = 0.05Q <sup>0.54</sup> R <sup>2</sup> = 0.06
S3	TP = 0.017Q <sup>0.59</sup> R <sup>2</sup> = 0.174	TDP = 0.01Q <sup>0.57</sup> R <sup>2</sup> = 0.29	SRP = 0.0035Q <sup>0.73</sup> R <sup>2</sup> = 0.12
S4	TP = 0.05Q <sup>0.194</sup> R <sup>2</sup> = 0.027	TDP = 0.09Q <sup>0.02</sup> R <sup>2</sup> = 0.001	SRP = 0.089Q <sup>0.003</sup> R <sup>2</sup> = 0.0004

**Table 6.10** Relationships between nitrogen, suspended sediment and flow (Figures 6.31- 6.33).

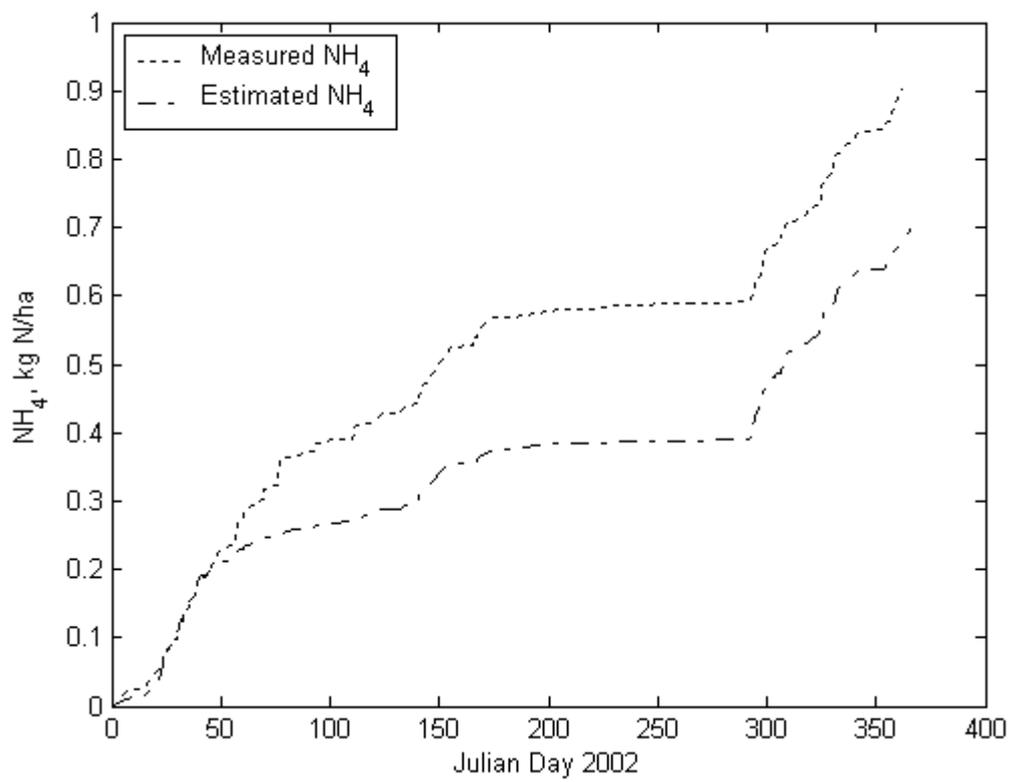
Site	TON	NH <sub>4</sub>	SS
S1	TON = -0.0045Q <sup>1.46</sup> + 4.1 R <sup>2</sup> = 0.21	NH <sub>4</sub> = 0.039Q <sup>0.37</sup> R <sup>2</sup> = 0.05	SS = 0.504Q <sup>0.95</sup> R <sup>2</sup> = 0.06
S3	TON = -0.00003Q <sup>1.73</sup> + 3.7 R <sup>2</sup> = 0.12	NH <sub>4</sub> = 0.06Q <sup>0.13</sup> R <sup>2</sup> = 0.01	SS = 0.038Q <sup>0.12</sup> R <sup>2</sup> = 0.29
S4	TON = -15.36Q <sup>-0.005</sup> + 19.3 R <sup>2</sup> = 0.008	NH <sub>4</sub> = 0.013Q <sup>0.24</sup> R <sup>2</sup> = 0.004	SS = 0.336Q <sup>0.57</sup> R <sup>2</sup> = 0.16

## 6.7 Using measured TP to estimate exports of SRP, NH<sub>4</sub> and SS.

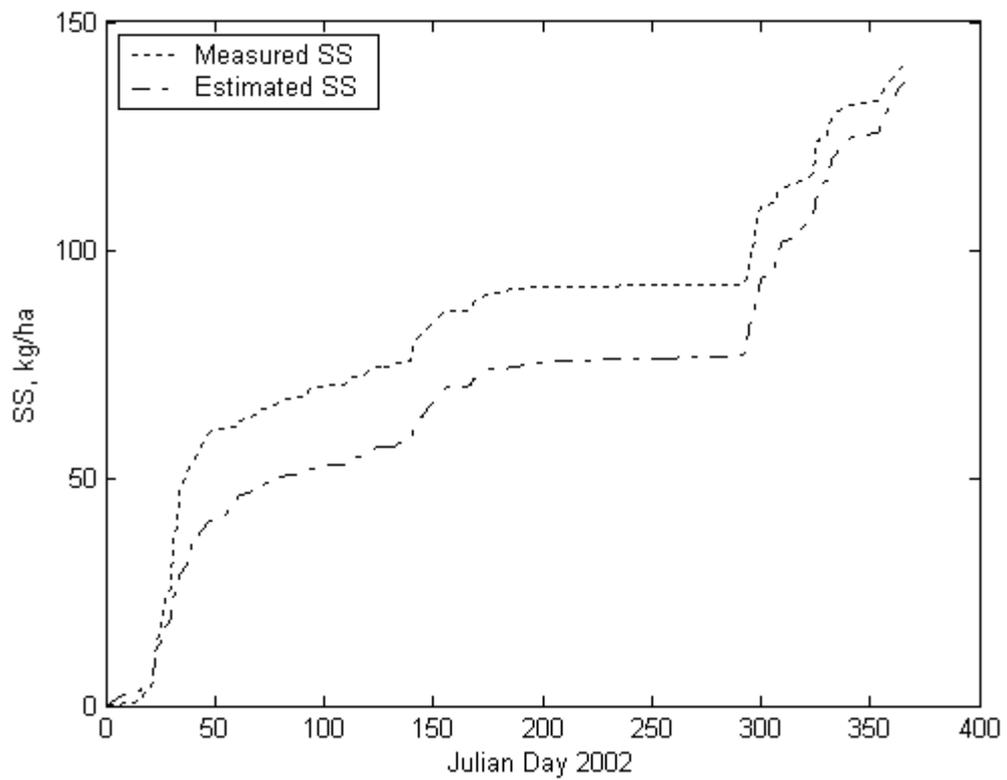
At S3,  $TP = 2.29SRP$  ( $R^2 = 0.75$ ). Figure 6.34 shows the estimated export of SRP using the measured SRP and that estimated from TP. The exports of NH<sub>4</sub> and SS both calculated from TP are shown in Figures 6.35 and 6.36. The estimated SRP and SS exports are very similar to the measured exports loads. This raises the possibility just measuring TP and TON at the three sites and using these to estimate TDP, SRP, PP, NH<sub>4</sub> and SS.



**Figure 6.34** SRP export measured and calculated (Figure 6.8b).



**Figure 6.35** NH<sub>4</sub> export measured and calculated (Figure 6.17b).



**Figure 6.36** SS export measured and calculated (Figure 6.21b).

# Chapter 7

## Conclusion

### 7.1 Conclusion

1. The annual total phosphorus export was estimated at 2.47 and 1.6 kg P ha<sup>-1</sup> for the 211 and 1524 ha catchments respectively. This equates to 0.22 and 0.155 mg/l as the mean annual concentrations of TP for catchments 3 and 4, respectively. This far exceeds the recommended threshold of 0.035 mg/l. To achieve this recommended level, the annual export should not exceed 0.5 kg P ha<sup>-1</sup>.
2. Approximately 30% of the TP export at S3 is from farmyards.
3. The annual total oxidised nitrogen export was estimated at 38.5 kg N ha<sup>-1</sup> and 46.7 kg N ha<sup>-1</sup> for the 211 ha and 1524 ha catchments respectively. This equates to 3.56 and 4.5 mg/l as the mean annual concentrations of TON for catchments 3 and 4, respectively. This does not exceed the allowable nitrate levels for potable water of 11.3 mg/l.
4. For the three catchments, simple linear relationships with good R<sup>2</sup> value, exist between TP and TDP, between TP and SRP, between TP and NH<sub>4</sub> and TP and SS. Future work in these catchments might be complete by measuring TP and TON only.
5. The five months of October to February are the months which contribute more than 80% of each nutrient. Remedial policies need to address measures for these months.
6. Slurry applications in this period of October to February contribute to significant exports of phosphorus.
7. High phosphorus concentrations (exports) occur simultaneously with high streamflows.
8. Significantly high concentrations of phosphorus (leading to high exports) occur in the winter months when no slurry or fertilisers are applied (as with site 3). This suggests that the soil reservoir of phosphorus is high (about half the fields in catchment 3 have a Morgans P of greater than 10 mg/l, (Khandokar et al., 2003). Therefore high winter rainfalls producing high winter streamflow will continue to export high phosphorus loads until the soil pool of phosphorus is significantly reduced below 10 mg/l. This is likely to take a decade of reduced fertiliser applications which should be significantly less than current applications rates.

## **7.2 Recommendations**

1. Policy should consider methods to assure that slurry is not spread between October and February.

*Reason* These five months have high effective rainfall making them vulnerable to significant exports of phosphorus nitrogen and suspended sediment.

2. Monitoring of farmyards is suggested as to quantify their relative contribution to phosphorus export.

*Reason* The farmyards in Catchment 3 appear to contribute approximately 30% of the TP export at S3.

3. Catchment 3 described in this thesis is farmed by eight farmers. If assistance were given to prevent slurry spreading for the months from October to February, it would be desirable to monitor the catchment and determine the impact of this new policy.

*Reason* The monitoring infrastructure is in place. Relatively small sums of money would be required to evaluate the impact of a new slurry policy.

4. The high soil P (greater than 10mg/l) in nearly half the fields of catchment 3 provides a reservoir of phosphorus eligible for export to the streams. This reservoir of phosphorus should be reduced to more realistic soil P levels (< 8mg/l). A pilot scale project of the eight farms of catchment 3 to evaluate the impact of a 20% fertiliser reduction on an ongoing period for three to five years is recommended.

*Reason* If a policy of reduction of fertiliser (or slurry) is considered, the landowners and the EPA should know the effects on (a) water quality and (b) grass yield.

### **7.3 Suggestions for further research**

- Continue the study to evaluate when annual rainfall is less than the exceptionally wet year of 2002.
- Continue the study for 1 year with agreements from farmers that no slurry would be spread from October to February.
- Continue the study by reducing the fertiliser input by say 20% while also monitoring grass (biomass) growth.
- Examine instrumentations to automate the analysis for nutrients in-place.
- Continue the study with farmers' input (slurry and fertiliser monitoring) for the 1524 ha catchment. (47 farms).
- Extend the study to the Dripsey catchment of 90 km<sup>2</sup> area.

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# APPENDICES

## Appendix A

Samples of MATLAB code used to create graphs.

MATLAB is a high-performance language for technical computing. It integrates computation, visualization, and programming in an easy-to-use environment.

```
% A programme to plot the cumulative rain and flow (in mm)
% for each of the three sites and evapotranspiration
clear all

%Rain data
raindata=csvread('ra30_02.csv');
rain=raindata(:,5);                                %Rainfall at 30 min intervals

%Evapotranspirations data
evap_data=csvread('daily_evapotranspiration.csv');
evap_time=evap_data(:,1);
evap=evap_data(:,2);

for i=1:17521
    jday_rain(i)=((i/48)+1-(1/48));                %Create Julian days time series
end                                                %for rain data

%Read in height of water flowing over weirs.
S1=load('s1234_1_365_02.csv');
h1=S1(:,7);                                        %S1
h3=S1(:,9);                                        %S3
h4=S1(:,10);                                       %S4
```

```

% Calculating the flow (l/s) from the height of flow over weir
q1=(1378*(h1.^2.48))*900/170000;
q3=(3011*h3.^1.4)*900/2110000;
q4=(2207*h4.^1.565)*900/15240000;

flow_q1=q1*900; %Convert the flow from
flow_q3=q3*900; %l/s to flow every 15 min.
flow_q4=q4*900;

s1_flow=flow_q1/1000/17; %Converting to flow mm
s3_flow=flow_q1/1000/211;
s4_flow=flow_q1/1000/1524

cu_q1=cumsum(s1_flow); %Calculate cumulative flow and
cu_q3=cumsum(s1_flow); %and rain
cu_q4=cumsum(s1_flow);
cu_rain=cumsum(rain);

for i=1:35041 %time series for flow
    jday_flow(i)=((i/96)+1-(1/96));
end

%Plotting the data.
figure(1)
plot(jday_rain,cu_rain,'k',jday_flow,cu_q1,'--k',evap_time,cumsum(evap),'k'...
jday_flow,cu_q3,'-k',jday_flow,cu_q4,':k')
xlabel('Julian Days')
ylabel('Rainfall/Streamflow/Evapotranspiration in mm')
legend('Rain','S1','S3','S4','Evapotranspiration')

```

## **Appendix B**

Paper submitted to the *Journal of Hydrology*.

See back for paper

## Appendix C

Poster presentation in session HS24 at the EGS/AGU number conference, Nice 2003

Phosphorus loss from soils to water; annual budget from a nested catchment study of a temperate grazed grassland

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Abstract.

We present results and analysis for the one-year budget of phosphorus loss from a grazed grassland in a temperate climate. The nested catchment approach utilises three scales: 17ha; 211ha; and 1524ha. Streamflow was collected continuously at 15-minute intervals at the three sites for the year 2002. Composite water samples were collected which covered over 40% of the year. The gaps in water samples were 'filled' with data from grab samples and some discrete samples. The water samples were analysed for total phosphorus, soluble reactive phosphorus and total dissolved phosphorus. The cumulative total phosphorus loading to the stream was  $2.61 \text{ kg ha}^{-1}$ ,  $2.47 \text{ kg ha}^{-1}$ , and  $1.61 \text{ kg ha}^{-1}$  for the 17, 211 and 1524 ha respectively. For the two smaller catchments the total phosphorus applied in fertiliser over the year was approximately  $20 \text{ kg ha}^{-1}$  and the phosphorus applied in slurry (manure) was similar. The soil phosphorus as measured with Morgan's P varied in the fields from 4 to 23mg/L. The agronomic phosphorus requirement for grass growth was estimated at  $33 \text{ kg ha}^{-1}$ . The annual rainfall at 1790mm was 26% greater than the long-term annual average. Above average rainfall, high initial soil phosphorus and particular land management practices resulted in high losses of phosphorus from soil to water for the year 2002.

Poster see back

## Appendix D

Livestock data for 2002 received from farmers.

### Farm A: Farm Stats for 2002 (January 2003)

1	Number of Cattle	*Cows 60 Calves ?
2	Number of Cattle Sold	5 cows
3	Annual Milk Production in 2002	80400 gals p.a.
4	Livestock dates	Late Feb for a few hours per day until end of March then out full-time until mid-November
5	Amount of concentrated per	500kg /cow (late Jan to early Dec) i.e. 30 tonnes
7	Any fodder imported ?	No
8	Any straw imported	1200-1500 small bales
9	Silage	30 acres; 24 <sup>th</sup> of June 1 <sup>st</sup> cut; 12-15 tons per acre; Dry Matter 16-20%
10	Slurry Storage Vol.s	Main Tank 597 m3 1 <sup>st</sup> small tank 57m3 2 <sup>nd</sup> small tank 108 m3

\* There are in fact 90 cows but because the cattle only remain approximately 66% of their time on this holding and 33% on another one outside the Mini-Catchment, I have treated them as just 60. Thus the milk production and fodder fed ahs been adjusted accordingly.

**Farm B: Farm Stats for 2002 (January 2003)**

1	Number of Cattle	<p>No Cows</p> <p>9 bullocks bought 10Feb (average wgt 370kg)</p> <p>These bullocks were sold on June 10<sup>th</sup> at 500kg average wgt.</p> <p>15 bullocks bought 30March (average wgt 370kg) 9 of these at 550kg/head live wgt were sold around mid- November and the remaining 6 weighing 485kg per head were sold around mid December.</p> <p>1<sup>st</sup> of July 20 heifers of 350kg each were bought and these were sold in mid—December at 450kg/head</p>
3	Annual Milk Production in 2002	None
5	Amount of concentrated per	3.48kg of concentrate fed to each beast per day for 2 months before sale, to fatten them for market, except for 6 of the batch of 15 bullocks which were not fed concentrates (these were sold in mid December).
7	Any fodder imported ?	23 round bales of barley straw for fodder. Not sure of the wgt of these large bales, probably more than 100-120kg per bale.
8	Any straw imported	
9	Silage	21 acres (13 acres on May 20 <sup>th</sup> and the balance on July 20 <sup>th</sup> .) <b>Note that 16 acres of silage was exported.</b> Each load was estimated to be about 15 tons/acre

**Farm C: Farm Stats for 2002 (January 2003)**

1	Number of Cattle	Cows 84 Dry Cattle Calves 27
2	Number of Cattle Sold	None
3	Annual Milk Production in 2002	107,100 gal. p.a
4	Date cattle put out 2002	mid- March all out during the day, end of March all out during the day and night;
5	Date Cattle brought in 2002	all in mid-November
6	Amount of concentrated per year	153.6 tonnes p.a.
7	Types of concentrate fed	Dairy Pride from Dairygold (?) 16% protein
8	Any fodder imported ?	20 round bales of hay imported and fed to calves
9	Any straw imported	20 round bales (barley straw)
10	How was straw disposed	??
11	Silage	1000 tonnes of first-cut 390 tonnes 2 <sup>nd</sup> cut

**Farm D: Farm Stats for 2002 (January 2003)**

1	Number of Cattle	Cows 42 Dry Cattle 30 yearlings x 350kg per head Calves 32
2	Number of Cattle Sold	None
3	Annual Milk Production in 2002	42,000 gal. p.a
4	Date cattle put out 2002	Cows: 15th March for daytime only, 1 <sup>st</sup> of April all day. Yearlings: Out 1 <sup>st</sup> May and back in from mid-May to Mid July and out again until 1 <sup>st</sup> week in November
5	Date Cattle brought in 2002	All in 1 <sup>st</sup> week of November
6	Amount of concentrated per year	96.36 tonnes per yr
7	Types of concentrate fed	Dairy Pride from Dairygold
8	Any fodder imported ?	20 round bales of hay imported and fed to calves
9	Any straw imported	30 round bales (barley straw)
10	How was straw disposed	??
11	Silage	720 tonnes of first-cut 67% DMD (Dry matter digestibility – <i>not dry matter</i> )

**Farm E: Stats for 2002 (January 2003)**

1	Number of Cattle	Cows 20 Under yearlings 100 x 150kg each
2	Number of Cattle Sold	None
3	Annual Milk Production in 2002	1800 (farm used almost exclusively for silage production)
4	Livestock dates	<i>Yearlings</i> grazed freely in the farm for 7 weeks (August to last week in Sept)  20 <i>Cows</i> graze only from September – November (end) (10 left out until Christmas week)
5	Amount of concentrated per head per day While housed	None
6	Amount of concentrated per head per day While housed	None
7	Any fodder imported ?	No
8	Any straw imported	No
9	Silage	961 tonnes (1 <sup>st</sup> cut) 768 tonnes (2 <sup>nd</sup> cut)

**Farm F: Stats for 2002 (January 2003)**

1	Number of Cattle	Cows 40 Dry Cattle 1 Calves 36
2	Number of Cattle Sold	None
3	Annual Milk Production in 2002	56,000 gal. p.a
4	Date cattle put out 2002	1 <sup>st</sup> week of march all out during the day, end of March all out during the day and night; 11 in-calf heifers on the land from May-July (after and before this they were kept on rented land which is not in the mini-catchment); calves out for just 1month after which they were sent to the other holding
5	Date Cattle brought in 2002	Half of the cattle in by November 25 <sup>th</sup> , most of the remainder in by mid-December, few left out until about the 23 <sup>rd</sup> .
6	Amount of concentrated per year	32 tonnes per yr
7	Types of concentrate fed	Dairy Pride from Dairygold
9	Any fodder imported?	10 acres of whole-crop maize, about 50% of which was fed to the cows
10	Any straw imported	3 tonnes

11	How was straw disposed	The dung was only spread on the out-lying farm i.e. not on Farm F
12	Silage	224 tonnes of first-cut ~ 20% DM

**Farm G: Stats for 2002 (January 2003)**

1	Number of Cattle	Cows 40 Dry Cattle 30 Calves 30
2	Number of Cattle Sold	None
3	Annual Milk Production in 2002	44,000 gals
4	Date cattle put out 2002	End March/begin April; all cows back in from mid-May to mid-July (dry cattle remained out)
5	Date Cattle brought in 2002	1 <sup>st</sup> week in December (?)
6	Amount of concentrated per annum	Cows: 30,000kg Dry Cattle none Calves none
7	Types of concentrate fed	Dairy Pride by Dairygold
8	Any fodder imported?	No
9	Any straw imported	No
10	How was straw disposed	Dung Spread (on fields 11 & 12 i.e. 12.18ha)
11	Silage	1 <sup>st</sup> cut 476 tonnes
12	Silage bales	162 tonnes (quite dry)

## **Appendix E**

Raw data files. These files can be found on a compact disc at the back of the thesis.

### **Rain data**

The rain data for the years 1997, 1998, 1999, 2000, 2001 and 2002 are contained in the files *ra20\_97*, *ra20\_98*, *ra20\_99*, *ra20\_00*, *ra30\_01* and *ra30\_01*. The first column contains the julian day for the year, the second column contains the time in hours and the last column contains the rainfall. Note the rainfall was recorded at 20-minute intervals in the years 1997, 1998, 1999 and 2000. The rainfall was recorded at 30-minute intervals in the following two years.

### **Flow data**

*S1234\_1\_365\_02.csv*.

This file contains the height of the flow over the 4 weirs in the Dripsey catchment at 15-minute intervals for the year 2000.

**Table E.1** Data contained in the file *S1234\_1\_365\_02.csv*.

<b>Column</b>	<b>Parameter</b>
1	Day
2	Month
3	Year
4	Hour
5	Minute
6	Site 1 (height in m)
7	Site 2 (height in m)
8	Site 3 (height in m)
9	Site 4 (height in m)

The height of water flowing over the weirs was converted to flow (l/s) for sites 1, 3 and 4 by using equations E.1, E.2 and E.4, respectively.

$$\text{Flow\_S1} = 1.378H^{2.48} \quad \text{E.1}$$

$$\text{Flow\_S3} = 3.011H^{1.4} \quad \text{E.2}$$

$$\text{Flow\_S4} = 2.207H^{1.565} \quad \text{E.3}$$

Where H is the height of water flow over the weir

#### **Flow data**

*C1raw\_14\_365\_02.xls*, *C3raw\_14\_365\_02.xls* and *C4raw\_14\_365\_02.xls* contain the composite sample data for S1, S3 and S4, respectively.

*Grab\_samples.xls*, *Grab samples\_22\_11.xls* and *Grab samples\_25\_11.xls*, contain the grab samples taken on site.

All parameters are explained with in the file.

#### **Flow data**

*NPK slurry Application data.xls*, contains the fertiliser applications in  $\text{kg ha}^{-1}$  for each of the fields in catchment 3.

*NPK slurry Application data.xls* contains the slurry applications in  $\text{kg ha}^{-1}$  for each of the fields in catchment 3.

#### **Flow data**

*Field area.xls*.

This file contains all the fields and their area in hectares in catchment 3