

Nutrients in Sullivan's Creek

Fiona Dyer

CSIRO Land and Water, Canberra Technical Report 2/00, January 2000

A study undertaken with support and assistance from:



Centre for Resource and Environmental Science



ANU Department of Geology



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CSIRO LAND and WATER



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Summary

Background

Sullivan's Creek is a small creek which drains both urban and rural land in the north of the Australian Capital Territory (ACT) before discharging into Lake Burley Griffin. The last 2 km of the creek passes through the Australian National University (ANU) where it is a focus of the landscaping of the university grounds. Water within the creek was known to be dirtier, of lower dissolved oxygen levels and higher phosphorus levels than other streams in the ACT. However little was known about the forms or sources of the nutrients.

As part of considering a series of options to improve the appeal and use of the creek within University grounds the Facilities and Services Division of the ANU commissioned this study to provide an understanding of the forms and sources of nutrients in Sullivan's Creek. The results of this study are to be used in the development of strategies aimed at improving the quality of water in the portion of Sullivan's Creek that flows through ANU grounds.

Aims

Three aims were developed to provide the understanding required. These were to investigate:

- 1) the partitioning of phosphorus and nitrogen between inorganic¹ and organic, particulate and dissolved² forms in Sullivan's Creek water.
- 2) the source of the organic matter, and organic phosphorus and nitrogen in transport in Sullivan's Creek
- 3) the release of phosphorus and nitrogen from the bottom sediments of Sullivan's Creek

Methodology

These aims were addressed through a sampling program project undertaken in Sullivan's Creek between November 1998 and November 1999 and experiments conducted using benthic chambers in sections of the creek. Sampling of low flows within the Australian National University (ANU) was undertaken at fortnightly intervals and upstream of the University at monthly intervals. Two rain events were sampled at locations within the University grounds The samples were analysed for the organic and inorganic forms of nitrogen (N) and phosphorus (P) in both dissolved and particulate form. Analysis of this data provides a picture of the spatial and temporal variations in N and P forms within Sullivan's Creek, and also a picture of the N and P transported during storm events.

¹ refers to a measure of orthophosphate, condensed phosphates and lightly bound mineral phosphorus

see section 5 for definition

 $^{^2}$ defined as that which passes through 0.22 μm filters – see section 5 for definition

Findings

Total P concentrations were consistently higher in Sullivan's Creek than in other ACT streams and they exceeded guideline levels for aquatic ecosystems. More than 70% of the phosphorus transported in Sullivan's Creek was in inorganic forms and typically 40-80% of the phosphorus was dissolved. This amount of dissolved phosphorus is unusually high compared with most inland Australian streams. Concentrations of nitrogen in the creek were similar to those measured in other ACT streams but they also exceed the guideline levels for aquatic ecosystems. More than 70% of the N transported in Sullivan's Creek was dissolved and generally 30-60% was in organic form.

The concentration of total P within Sullivan's Creek was observed to have a seasonal correlation and was highest during the warmer months. The forms of P within the creek also appeared to be influenced by temperature with an increase in the proportion dissolved inorganic P in winter months. N concentrations in Sullivan's creek showed no significant seasonal variation.

The Dickson channel consistently delivered high concentrations of both dissolved and particulate P to the main channel of Sullivan's Creek which almost doubled the concentrations of P between Southwell Park and Macarthur Avenue. This channel was not contributing high concentrations of nitrogen.

High flow events (which occurred on less than 20% of the days during the study period) dominated the movement of nitrogen and phosphorus through Sullivan's Creek to Lake Burley Griffin.

Under low flow conditions the Barry Drive GPT was a major contributor of all forms of P to the ANU reach of Sullivan's Creek with total P concentrations doubling across the GPT. Toad Pond increases total P in Sullivan's Creek by 10%. On average total N concentration increased by approximately 30% across the GPT and a smaller increase was observed across Toad Pond. This was predominantly due to an increase in particulate nitrogen. Thus for the majority of the time (greater than 80%) the nutrient concentrations in the ANU section of the creek are being elevated by these two features at the upper end of the University.

Bottom sediments in the GPT and Toad Pond are likely to be the main source of the increased concentrations of dissolved P. Experiments using benthic chambers showed that high rates of degradation of organic carbon occur in Toad Pond and oxygen demand of the sediment exceeds the rate at which oxygen can be supplied from the water column. As a result reducing conditions exist in relatively shallow water causing the production of ammonia and the release of dissolved P from the bottom sediments. Measured production of ammonia and dissolved P were considered to be high in Toad Pond although this only made a small contribution to the overall concentrations in the creek compared with the GPT. Observations indicate that it is reasonable to assume that similar processes are driving the production of dissolved nutrients in the GPT.

The increase in particulate P and N concentrations in the water column at the GPT and Toad Pond is most likely due to the resuspension of organic and inorganic sediments as a result of benthic biological activity or the presence of a significant number of ducks. Although unlikely, the possibility that an urban drain or sewer leak were contributing significant amounts of P and N to the GPT could not be discounted.

The increased nutrient concentrations did not appear to coincide with the major leaf fall period suggesting that it is unlikely that deciduous leaves are making a significant contribution to nutrients in the creek. The higher concentrations of P in the creek in warmer months may be the result of greater biological activity (due to both longer and warmer days) in the creek releasing P to the water column, the use of fertilizers on lawns and ovals near the creeks, or an increase of the amount of lawn clippings on the flood plain.

Under low flow conditions the nutrient concentrations along Sullivan's Creek at least to Ward Bridge and possibly further to the Stepping Stones were dominated by water from Lake Burley Griffin.

During high flows particulate inorganic forms of both P and N dominated the nutrient forms in Sullivan's Creek. This is consistent with higher concentrations of suspended sediment during high flows where the concentrations of nutrients are dominated by those associated with the suspended sediment. A change in sediment and nutrient source from urban to rural was observed during the recession of the main peak flow of a large storm event. At this point of change the concentration of organic P dropped significantly while the concentration of inorganic P remained high and there was a change in the colour and chemistry of the suspended sediment.

Management Implications

Management options aimed at reducing the concentrations of nutrients in the ANU reach of Sullivan's Creek need to target the sections from the GPT to the Stepping Stones separately from the section from the Stepping Stones to Lake Burley Griffin. Nutrient reduction strategies for the section from the GPT to the Stepping Stones should initially focus on curbing the nutrient delivery from the GPT. These strategies should also recognise that Toad Pond contributes P and ammonia to the water column. Management of the nutrients in the section of Sullivan's Creek from the Stepping Stones to Lake Burley Griffin requires that the concentrations of nutrients in the lake be managed.

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1 Introduction

Sullivan's Creek is a 13 km long creek which drains 53 km^2 of both urban and rural land in the Australian Capital Territory before discharging into Lake Burley Griffin. The last 2 km of the creek passes through the Australian National University (ANU) where it is a focus of the landscaping of the university grounds. The Facilities and Services Division of the ANU is concerned about the apparent poor quality of the water in the creek and a series of options to improve the appeal and use of the creek within University grounds are currently being considered.

Previous water quality monitoring programs and field observations suggested that the quality of the water in the creek is dirtier, has lower dissolved oxygen and carries more phosphorus than other monitored streams in the ACT (*Wasson, 1997*). However, the understanding of water quality in the Creek was too poor to design ameliorative catchment strategies. This research project was established to provide the information and understanding that would allow the development of strategies aimed at improving the quality of water in the portion of Sullivan's Creek that flows through ANU grounds.

2 Background

2.1 Sullivan's Creek and Catchment

Sullivan's Creek is located in the northern part of the Australian Capital Territory (Map 1) and is a major tributary to Lake Burley Griffin, the major artificial lake in the centre of Canberra. The creek drains approximately 53 km² of which 11% is conservation reserves, 40% is urbanised and the remaining 49% is rural land with a small area of light industry. The estimated population of the catchment is 31,412 (*June 1996, ABS*) and housing is primarily low density single family. Grazing is the dominant rural activity.

The upper (rural) reaches of the creek (approximately 5 km in length) are extensively gullied with the current creek confined to a small channel within a much larger older gully system (*Middelmann, 1998*). The urban section of the creek (approximately 8.3 km in length) is concrete lined and acts primarily as a stormwater channel. The last 2 km of the creek before it reaches Lake Burley Griffin pass through the grounds of the Australian National University as a series of small pond and short channel sections. Being at the downstream end of the system, the quality of the water in the ANU reach of Sullivan's Creek is largely controlled by upstream activities.

Sullivan's Creek catchment is bounded by steep slopes to the east (the Mt Ainslie and Mt Majura ridges) and the west (Black Mountain and O'Connor Ridges) and these ridges comprise the conservation reserves. The remainder of the catchment is predominantly on a level plain with the headwaters rising in an area of gently rolling hills. The geology of the catchment is moderately complex with areas of sandstone (Black Mountain), shale, limestone and siltstone (O'Connor Ridge and much of the valley floor), Volcanics (Mt Ainslie, Mt Majura and the northern hills of the catchment) and quaternary alluvium (the area adjacent Sullivan's Creek and tributaries - 1:50,000 scale geology map. BMR, 1980).



Map 1. Location of Sullivan's Creek

The climate is classified as temperate with hot summers and cold winters (with an average of 100 frost days per year). Mean annual rainfall varies across the catchment from 640 mm to 740 mm and is evenly distributed throughout the year. Native dry sclerophyll forest and savannah woodland species dominate the reserves, exotic deciduous trees dominate the urban areas of the catchment and the farmed areas of the catchment are largely planted with exotic grasses (*Frawley 1991 and Moore, 1954 quoted in Middelmann, 1998*). The fauna of the catchment has been significantly modified by settlement and comprises a diverse range of both native and introduced birds and mammals. Both introduced vegetation and house pets have been suggested as significant sources of nutrients for the creek.

2.2 Water Quality

The term water quality is used to describe the physical, chemical, biological and aesthetic properties of water that determine its fitness for a variety of uses. These properties (e.g. temperature, pH, salinity, dissolved oxygen concentration, nutrient concentration) are generally controlled by the nature of both the creek and the catchment from which the creek receives its water. Sullivan'sCreek drains both urban and rural land and therefore the quality of water in the creek is the result of both these land use practices as well as the water and waste water management practices within the catchment.

2.2.1 The Influence of Nutrients on Water Quality

Nutrients are a natural component of all water bodies and are generally not toxic. The two most important plant nutrients are nitrogen (N) and phosphorus (P) and increases in the concentration of N and P can result in abnormally high levels of (nuisance) algal and aquatic weed growth. Aside from the risks associated with toxic algal growth, excessive levels of plant growth in water bodies tends to reduce the quality of the water by depleting oxygen levels, diminishing light availability, changing the pH and producing unpleasant odours and an unsightly appearance. Thus while low to moderate concentrations of nutrients do not present a direct health problem for humans and ecosystems, there is an indirect effect on water quality because of their influence on algal production in aquatic ecosystems.

Water Quality Guidelines

Guideline values for nutrients and dissolved oxygen levels from the Australian Drinking Water Guidelines (*NH&MRC*, 1996) and the Draft Australian Water Quality Guidelines for Fresh and Marine Waters (*ANZECC*, 1999) are given in Table 1. It is important to realise that the guideline levels for nutrients in aquatic ecosystems provide trigger levels at which there is some risk of problem aquatic growth occurring. At this point further investigation of the particular ecosystem is recommended to determine the potential for undesirable aquatic plant growth.

Water Quality Parameter		Drinking Water ²		
	Freshwater ¹	Upland Rivers ¹	Lakes and Reservoirs ¹	
Total Nitrogen		340 μg/L	440 μg/L	
NOx-N	120 μg/L			50,000 μg/L
NH4-N	32 μg/L			500 μg/L
Total Phos phorus		35 μg/L	50 μg/L	
¹ AN E CC. 1999	9		² NHMRC, 1996	

Table 1. Summary of guideline levels for nutrients in waters

¹ANZECC, 1999

²NHMRC, 1996

2.2.2 The Quality of Water in Sullivan's Creek

Several different water quality monitoring programs have been undertaken within Sullivan's Creek and the surrounding catchment. Sampling has been performed at a range of locations, the sampling period has varied and a range of physical and chemical properties have been measured. (*Brangwin, 1997*). Analysis of the data from the different water quality monitoring programs indicated that the creek is more turbid, transports more phosphorus (P), and on occasions has lower dissolved oxygen (DO) than most monitored ACT streams (*Wasson 1997*). Wasson's (*1997*) analysis also indicated that the creek carries sufficient P to support algal blooms.

Based on this data and observations that the creek appears to carry a high organic load it was postulated that much of the P in the creek may be in organic form and derived from the deciduous trees of the catchment. It had also been noted that concentrations of radon in a pond section of the creek (below the 'stepping stones' in the ANU grounds – refer Map 2 for location) indicated some input of groundwater (*G. Hancock, CSIRO Land and Water, pers. comm. 1998*) and it was suggested that P may be delivered to the creek in association with groundwater.

Sullivan's Creek is a feature of the landscaping within the ANU and this section of the creek at times supports nuisance algal growth, has an unpleasant smell and is often dark in colour. Based on data from previous water quality monitoring programs which indicated that Sullivan's Creek carries elevated levels of P, the ANU Facilities and Services Division, who are responsible for managing the creek and its environs through the University, were looking to reduce nutrient levels in the creek. The data from previous water quality monitoring programs does not provide the information about the forms or the potential sources of P which would allow management strategies to be developed. As a result, the Facilities and Services Division commissioned this study to provide an understanding of the forms and sources of phosphorus and nitrogen in Sullivan's Creek.

It should be noted that other water quality parameters (eg faecal coliforms, heavy metals or suspended sediment) have not been assessed in detail for the creek and may be significant contributors to poor water quality in the creek. Past studies have found that both bacteria and coliform levels are high in the creek (reported in *Brangwin, 1997*).

3 Project Objectives and Aims

The objective of this study was to provide an understanding of the forms and sources of nutrients in Sullivan's Creek. Three aims were developed to provide the understanding required. These were to investigate:

- 1) the partitioning of phosphorus and nitrogen between inorganic and organic, particulate and dissolved forms in Sullivan's Creek water.
- 2) the source of the organic matter, and organic phosphorus and nitrogen in transport in Sullivan's Creek
- 3) the release of phosphorus and nitrogen from the bottom sediments of Sullivan's Creek

This report uses the terms dissolved, particulate, organic and inorganic in reference to nutrient forms. While not strictly scientifically accurate terms, they are most easily understood by the managers and planners for whom the report is written. The terms used and their definition as applies to this study are given in section 5.

These aims were addressed through a sampling program and experiments conducted using benthic chambers in sections of the creek. This report outlines the findings of the study. The partitioning of phosphorus and nitrogen between inorganic and organic, particulate and dissolved forms in Sullivan's Creek water and the release of phosphorus from the bottom sediments of the creek were well investigated. However, due to analytical difficulties experienced throughout the study, the analysis of a large number of samples for low levels of nutrients and the need to set up and validate an analytical method for the analysis of Total N (something which had not previously been done in the laboratory used), the source(s) of the organic nutrients was not fully explored.

The aims outlined above also test the following three hypotheses, proposed from the conjecture regarding possible sources of P (refer section 2.2.2).

- 1. Most of the phosphorus and nitrogen in Sullivan's Creek is in organic form.
- 2. Most of the phosphorus and nitrogen in Sullivan's Creek is derived from the deciduous trees of the catchment.
- 3. A significant amount of phosphorus is being delivered to the creek in association with groundwater in South Pond.

4 Sampling Program

The sampling program was designed to provide:

- 1) a seasonal and spatial picture of the forms of P and N being transported in Sullivan's Creek;
- 2) a picture of the forms of P and N being transported by 'flood' events; and
- 3) an indication of the contribution of nutrients and organic material by different sections of the catchment.

Sampling was carried out at fortnightly intervals within the University grounds; at monthly intervals upstream of the University; and at half hourly or hourly intervals during two rain events. The ability to process the samples collected proved to be the limiting factor for sampling frequency and density.

4.1 Fortnightly Sampling

Sullivan's Creek within the ANU can be divided into a series of pond and channel sections. Sampling locations were chosen with the aim of developing an understanding of the processes (in terms of nutrient transport) occurring within these different sections of the creek. Initially six locations (four within the University grounds, one just upstream of the University and one at the confluence with Lake Burley Griffin) were chosen for regular fortnightly sampling. A seventh sampling location (D1) was added at the end of April after assessment of the initial data (*Dyer*, 1999). The sampling locations are shown in Map 2 and are described in Table 2.

Identifier	Description	Distance from Lake Burley Griffin (m) [*]
A1	Upstream of Parkes Way (effectively Lake Burley Griffin)	90
А	Downstream of Ward Bridge	590
В	Upstream of the 'stepping stones'	840
С	Upstream of Canberry Bridge	1020
D	Downstream end of Toad Pond	1540
D1	Upstream of Toad Pond	1760
E	Upstream of the Barry Drive GPT, downstream of two piped inputs	1860

Table 2 Fortnightly sampling locations (refer also Map 2)

* distance measured along creek



Map 2. Fortnightly sampling locations

4.1.1 Monthly Sampling

Monthly sampling locations were chosen with the aim of developing an understanding of the nutrient inputs from different parts of the urban catchment. Initially five locations upstream of ANU were chosen for monthly sampling. A further 2 sampling locations (K & L) were added at the start of April to develop an understanding of the inputs from the rural and light industrial section of the catchment. These sampling locations are shown on Map 3 and are described in Table 3.

Identifier	Description	Distance from Lake Burley Griffin (m) [*]
F	Upstream of the Barry Drive GPT, above two piped inputs	1860
G	Upstream of the Masson St bridge	2460
Н	Upstream of David St – above the open drain input from O'Connor	3210
I	Upstream of Macarthur Ave	3710
J	The Dickson Channel, upstream of the Wattle St bridge.	4030
K	Southwell Park, upstream of Mouat St	5230
L	Upstream of Barton Highway	6730

Table 3. Monthly sampling locations (refer also Map 3)

Sample locations E and F were virtually at the same point and initial analyses indicated they were consistent in nutrient form and concentrations. Therefore sampling at location F was discontinued after 1 April 1999.

4.2 Sampling Dates

The sampling dates and locations sampled are listed in Table 4. The initial sampling was limited (as can be seen by the sampling dates and locations from December 1998 to the end of February 1999) and evolved to the sampling regime described above. The rainfall and flow conditions on the day of sampling as well as the rainfall in the week prior to sampling are given in Table 5.



Map 3. Monthly sampling locations

	Locations Sampled													
Date	A1	А	В	С	D	D1	Е	F	G	Н	I	J	K	L
7-Dec-98		Х	Х	Х	Х			Х						
7-Jan-99		Х	Х	Х	Х		Х	Х	Х	Х	Х	Х		
18-Feb-99		Х	Х	Х	Х		Х							
4-Mar-99	Х	Х	Х	Х	Х		Х	Х	Х	Х	Х	Х		
18-Mar-99	Х	Х	Х	Х	Х		Х							
1-Apr-99	Х	Х	Х	Х	Х		Х	Х	Х	Х	Х	Х	Х	Х
15-Apr-99	Х	Х	Х	Х	Х									
8-Jul-99	Х	Х	Х	Х	Х	Х								
26-Jul-99	Х	Х	Х	Х	Х	Х	Х		Х	Х	Х	Х	Х	Х
10-Aug-99	Х	Х	Х	Х	Х	Х								
6-Sep-99	Х	Х	Х	Х	Х	Х								
16-Sep-99	Х	Х	Х	Х	Х	Х	Х		Х	Х	Х	Х	Х	Х
30-Sep-99	Х	Х	Х	Х	Х	Х	Х							
14-Oct-99	Х	Х	Х	Х	Х	Х	Х		Х	Х	Х	Х	Х	Х
28-0ct-99	Х	Х	Х	Х	Х	Х	Х							
11-Nov-99	Х	Х	Х	Х	Х	Х	Х		Х	Х	Х	Х	Х	Х

Table 4. Sampling dates and locations

Table 5. Sampling and antecedent conditions.

Date	Flow ¹		Rainfall ¹	Prior Rainfall (mm) ¹			
(ML/day)		m³/s	(mm)	24 hours	48 hours	7 days	
7-Dec-98	1.31	0.014	0	0	0	0	
7-Jan-99	1.53	0.017	0	0	0	0	
18-Feb-99	0.78	0.008	0	0	7.1	7.1	
4-Mar-99	0.57	0.006	0	3	3	3	
18-Mar-99	0.92	0.010	0	0	0	1.8	
19-Mar-99*	8.95	0.098	4.8	0	0	1.8	
1-Apr-99	0.89	0.010	0	0	0	18	
15-Apr-99	0.39	0.004	0	0	0	0.4	
8-Jul-99	0.71	0.008	0	0	0	0.8	
26-Jul-99	0.76	0.008	0	0	0.2	2.0	
10-Aug-99	1.09	0.012	0	5.2	23.8	23.8	
6-Sep-99	4.37	0.048	0	18.6	20.2	20.4	
16-Sep-99*	233.31	2.57	39.2	0	0	0	
30-Sep-99	8.35	0.091	2.9	0.2	0.4	14.7	
14-Oct-99	6.44	0.070	2.5	0	0	1.9	
28-Oct-99	0.07	< 0.001	0	0.4	0.4	13	
11-Nov-99	6.39	0.070	0.2	0	5.4	14.2	

* High flow events

¹ Data from Environment ACT

4.2.1 Storm Sampling

Two rain events were sampled during the course of the project. One small rain event was sampled on the 19th of March. Approximately 5 mm fell over a 6 hour period. Sampling at 30 minute intervals commenced at 13:10 and stopped at 19:15. Two locations within the University were chosen for sampling this storm event. These were downstream of Ward Bridge and upstream of Canberry Bridge (refer Map 1) and were chosen to provide information about the behaviour of one reach of the creek during a rain event with the reach selected for ease and safety of sampling.

A larger rain event was sampled on the 16/17th of September. Approximately 40 mm of rain fell between 10 am on the 16th and 2 am on the 17th. Sampling at hourly intervals commenced at 11:00 am on the 16th and stopped at 14:50 on the 17th (no sampling occurred between 16/9/99 23:00 and 17/9/99 06:00). Given the results of sampling the first storm event and the time constraints involved in sample processing (the samples require immediate filtration after collection) only one location was sampled (upstream of Canberry Bridge) during this event. The hydrographs and rainfall data for the two storm events are given in Figure 1 and Figure 2.



Figure 1. Rainfall and flow for Sullivan's Creek at Barry Drive 19-20 March 1999. Sampling times are noted on the hydrograph.



Figure 2. Rainfall and flow for Sullivan's Creek at Barry Drive 16-18 September 1999. Sampling times are noted on the hydrograph.

5 Standard Procedures and Methods

5.1 Sample Collection

Clean disposable 2.0 L polyethylene sample bottles were washed with deionised water prior to use^3 . Surface water samples (1.5-2.0 L) were collected by pointing the bottles upstream in the centre of the creek. The sample bottles were initially rinsed with a portion of the creek water before being filled and capped. The samples were placed on ice immediately after collection and returned to the laboratory for processing. Where possible, samples for oxidised nitrogen species and ammonia analyses were filtered in the field using sterile Durapore syringe filters (0.22 μ m) and placed in 15 ml disposable polyethylene auto-analyzer tubes (acid washed with 8% HCl).

5.2 Processing and Laboratory Analysis

All samples were returned to the laboratory, initial sample preparation conducted and the samples were placed in a freezer within 4 hours of collection. Samples were analysed within 30 days of collection for total phosphorus (TP), total dissolved P (TDP), dissolved inorganic phosphorus (DIP), total inorganic phosphorus (TIP), total nitrogen (TN), total dissolved nitrogen (TDN) ammonium nitrogen (NH₄-N) and total oxidisable nitrogen (NOx-N - includes nitrate and nitrite) and according to the procedures outlined in the *APHA*, *1998*.

5.2.1 Definition of terms

Dissolved

The dissolved fraction was considered to be that which passes through 0.22 μ m filters. The more accurate scientific terms is filtrable as this fraction still contains colloids and is therefore not truly dissolved. However, it provides a more accurate representation of the dissolved fraction than that which passes through the more commonly used 0.45 μ m filters (*Gary Hancock, CSIRO Land and Water, pers. comm. 1998*) although it also means that the concentrations of dissolved P and N obtained in this study are not directly comparable with previous work.

Particulate

This is the fraction greater than 0.22 μm and in all cases was determined as the difference between the total and the dissolved fraction.

³ Analysis of a sample blank (deionised water) stored in bottles washed in this manner indicated this was sufficient cleaning to prevent sample contamination.

Inorganic phosphorus	A measure of the orthophosphate, condensed phosphates and lightly bound mineral phosphate (such as are held in surface coatings) in the sample. It is determined after the samples have been acid hydrolyzed at boiling water temperature and thus the more accurate term is acid hydrolyzable phosphorus. The acid hydrolysis procedure may release some organically bound phosphorus (resulting in an overestimate of the inorganic P) and it will not release tightly bound mineral P (resulting in an underestimate of the inorganic P). It provides a good approximation of the inorganic P in the sample.				
Total phosphorus Measured after oxidative digestion of the sample and is a measure amount of P present in the sample.					
Organic phosphorus	Determined as the difference between the total P and the inorganic P.				
Inorganic nitrogen	Defined as the sum of ammonia, nitrate and nitrite present in the sample.				
Total nitrogen	Measured after alkaline persulphate digestion and is a measure of the total amount of N present in the sample.				
Organic nitrogen	Determined as the difference between the total N and the inorganic N				

5.2.2 Initial sample preparation:

On return to the laboratory each sample was thoroughly mixed to resuspend any settled material and the following steps followed:

- 1. 500ml was passed through 0.22µm Durapore membrane filters held in acid washed (8% HCl) filter housings. The filtrate was split into 2 equal samples, placed in sterile 'whirl-paks' and frozen.
- 2. Two 300 ml portions of the unfiltered sample were placed in sterile 'whirl-paks' and frozen.

5.2.3 Sample Analysis

Samples were defrosted at room temperature prior to analysis. The principles of the analytical procedures is given below.

Phosphorus (APHA method 4500 – P)

Samples were combined with ammonium molybdate, potassium antimonyl tartrate and ascorbic acid in acid medium. The absorbance of the resultant molybdenum blue compound (which is proportional to the orthophosphate concentration in the sample) was measured at 690 nm on a Varian Cary 1E UV-Vis spectrometer.

To determine the different forms of phosphorus the samples were first subject to digestion or acid hydrolysis procedures⁴. Dissolved and total inorganic phosphorus (DIP and TIP) was

⁴ Dissolved and total reactive phosphorus (DRP and TRP: phosphates that respond to the above colorimetric test without preliminary hydrolysis or oxidative digestion) were also measured in this study but the results are not presented in this report. This data is available on request.

measured following mild acid hydrolysis at boiling water temperature. Total dissolved phosphorus and total phosphorus (TDP and TP) was measured as phosphate in solution after digestion in nitric acid and hydrochloric acid.

Five standards and a blank were run with each batch of samples and these were processed in the same way as the samples. The limit of detection was $3-4 \,\mu g/L$ and the lowest standard used was 12.5 $\mu g/L$. Calibration checks were run at the end of each batch of samples.

One in five samples was run in duplicate and occasionally samples were run in triplicate. The replicate measurements were used to calculate the standard deviation and coefficient of variation (the standard deviation given as a percentage of the mean) for the measurements. As the variance was non-stationary (i.e. the standard deviation was dependent on the magnitude of the measurement) the uncertainty was taken as the average coefficient of variation for the replicate samples. Therefore the uncertainty in the concentration of reactive phosphorus was 3%, for concentrations of acid hydrolyzable phosphorus it was 11% and for total phosphorus forms, 10%.

These measurements were used to determine the different forms of phosphorus according to:

Total organic $P(TOP) = TP - TIP$	(uncertainty:	15%)
Dissolved organic P (DOP) = $TDP - DIP$	(uncertainty:	15%)
Total particulate P (TPP) = $TP - TDP$	(uncertainty:	14%)
Particulate inorganic P (PIP) = TIP – DIP	(uncertainty:	16%)
Particulate organic $P(POP) = TPP - PIP$	(uncertainty:	20%)

Nitrogen (APHA method 4500-N)

Samples for nitrogen species were measured using an Alpkem segmented flow analyser set up for low level nutrient analyses. The method for ammonium nitrogen (NH₄-N) analysis involved the reaction of ammonia with alkaline phenol and hypochlorite in the presence of sodium nitroferricyanide and an EDTA complexing reagent. The absorbance of indophenol blue produced from this reaction in an amount that is proportional to the ammonia concentration was measured at 660 nm.

The analysis of oxidised forms of nitrogen (NOx-N nitrate and nitrite) involved passing the sample through a packed bed cadmium column to reduce nitrate to nitrite. The nitrite formed plus any additional present in the sample was reacted with sulfanilamide and N-1-naphthylethylenediamine dihydrochloride to form and azo dye, the absorbance of which was measured at 540 nm.

Samples were typically run in duplicate and instrumental reproducibility checked by repeat measurements of every 5th sample. Calibration checks were conducted after every 10th sample. Nine standards and a blank were measured with each batch of samples and the practical detection limit for ammonia (NH₄-N) and the oxidised forms of nitrogen (NOx-N) was 2 μ g/L (due to poor calibration below 2 μ g/L) although the lowest standard was 2 μ g/L. The replicate measurements were used to calculate the standard deviation and coefficient of variation for the

measurements. The variance in ammonia measurements was stationary (i.e. the standard deviation did not vary with the magnitude of the concentration) therefore the uncertainty was taken as the average standard deviation for the replicate samples (1 μ g/L). The variance in NOx-N measurements was non-stationary. Therefore the uncertainty was taken as the average of the coefficient of variation (8%).

Total dissolved and total nitrogen (TFN and TN) concentrations were determined following an alkaline persulphate digestion procedure (APHA method 4500- N_{org} D proposed). Samples were combined with alkaline persulphate and heated under pressure to oxidise all nitrogenous compounds to nitrate. The nitrate produced was analysed using the cadmium reduction procedure given above. A glutamic acid digestion check was used and recoveries were typically 90-100%.

Five standards and several blanks were run with every batch of samples and were processed in the same way as the samples. The practical detection limit was the same as for NOx-N (2 μ g/L) and the lowest standard was 100 μ g/L. A nutrient standard, from 'Analytical Products Group' (traceable to international standard reference materials SRM84J) was diluted to a concentration appropriate to the calibration and run as a blind standard with each batch of samples. The results of this were typically within 10% of the certified value. Samples were run in duplicate and almost half the samples were run in quadruplicate. Instrumental reproducibility was checked by repeat measurements of every 5th sample and calibrations checks were run after every 10 samples. The variance in the measurements was non-stationary therefore the average coefficient of variation was taken as the uncertainty (10%).

Dissolved organic nitrogen was determined as:

Dissolved organic N (DON) = $TDN - (NOx-N + NH_4-N)$ (uncertainty 13%)

6 Reading this report

Much of the data from the regular sampling program is presented as 'box and whisker plots' in which the data is graphed as a box representing statistical values (Figure 3). These were produced using SigmaPlot 4.0 (*SPSS Chicago, 1997*). The boundary of the box closest to zero indicates the 25th percentile, a thin line within the box marks the median, a thicker line within the box marks the mean, and the boundary of the box farthest from zero indicates the 75th percentile. Whiskers above and below the box indicate the 90th and 10th percentiles and outlying data are plotted as points. Not every category will display the 10th and 90th percentiles or outlying points as this is dependent on the number of data points per category.



Figure 3. Box and whisker plots

The spatial data is presented with respect to the distance along the creek from Lake Burley Griffin – the following graph (Figure 4) folds out and allows easy comparison of most plots with the exact location along the creek. In the discussion of the data, locations will be referred by the labels given in Figure 4.

A large amount of data is presented in this report which reduces the ease of reading. Consequently at the end of each section a synthesis is included which summarises and discusses the major findings. The data collected in this study is included as Appendix A.



Figure 4. Graph showing locations along Sullivan's Creek

7 Results

Concentrations of both P and N are given as $\mu g/L$ which is equivalent to parts per billion (ppb). To convert to mg/L (or parts per million, ppm) divide the concentration by 1000. The data collected in this report is included as Appendix A.

7.1 Regular Sampling

The data from the regular sampling has been analysed to determine if there are trends along the creek (spatial trends) and also if there are trends throughout the year (temporal trends).

Spatial trends were identified by collating the data for each site and plotting it as distance from Lake Burley Griffin. In order to identify temporal trends, the data collected along the full length of the creek for each sampling day has been collated in a box and whisker plot. Due to some logistical problems, samples were not collected during May and June. Where possible limited data from Ecowise Environmental⁵ has been used to fill this gap – however only TP, TN and NOx-N data collected by Ecowise was suitable for use. Thus in many cases a significant gap exists in the data set, making identifying trends difficult.

7.1.1 Phosphorus – Spatial Data

Three unusually high concentrations of P were measured during the sampling program: one at Masson St (2460 m, 7-1-99, 321 μ g/L); Barton Highway (6730 m, 1-4-99, 1165 μ g/L); and upstream of the GPT (1860 m, 10-8-99, 725 μ g/L). The high concentration of P (of which 85% was in particulate form) at Masson St on 7-1-99 coincided with what appeared to be a slug of clay moving down the creek. It wasn't possible to determine where this had originated, although works were being undertaken on the bike path beside the creek upstream of this sampling point. It wasn't possible to determine the cause of the high P concentration at either Barton Highway (1-4-99 - all of which was dissolved) or upstream of the GPT (10-8-99 – 80% of which was dissolved). Due to the undue bias these three samples create, they have been removed from the following data analysis.

The average concentrations of the different forms of phosphorus measured at each of the sites sampled are given in Table 6. Average Total Phosphorus (TP) concentrations range from 37 μ g/L at Southwell Park to 123 μ g/L downstream of Toad Pond. Generally TP concentrations in Sullivan's Creek exceed the guideline levels for aquatic ecosystems (Refer Table 1) at most sites. To place the observed concentrations in context, a selection of P and N concentrations measured in a range of other waterways are given in Table 7 and Table 8. The TP concentrations observed in Sullivan's Creek are higher than those measured in other ACT waterways but are similar to the concentrations measured in the Murrumbidgee River. TP

⁵ 16A Lithgow Street, Fyshwick ACT 2609 The Ecowise Environmental laboratory is NATA accredited for the analysis of nutrients in natural waters.

concentrations in Sullivan's Creek are also similar to those measured in Darebin Creek, one of Melbourne's urban creeks.

			Distance from Lake Burley Griffin (m)											
		90	590	840	1020	1540	1760	1860	2460	3210	3710	4030	5230	6730
		A1	Α	В	С	D	D1	E/F	G	Н	Ι	J	K	L
		Parkes	s Way (Lake B	urley G	Griffin)	G	PT		I		Ba	rton H	ighway
TP	Avge	46	75	113	105	123	113	61	45	70	73	113	37	48
	Median	43	75	103	97	124	115	51	49	61	66	118	38	36
	Min	15	23	58	43	78	62	36	29	32	38	50	30	28
	Max	82	153	246	179	216	147	124	54	146	139	150	44	81
	N	12	15	15	14	15	7	15	5	6	6	6	4	3
TDP	Avge	22	38	65	67	69	66	40	28	55	54	74	15	30
	Median	15	36	53	57	67	66	42	35	51	62	91	12	16
	Min	5	11	34	38	16	12	4	7	25	14	16	7	10
	Max	77	80	143	108	129	115	105	42	110	98	115	31	64
	Ν	11	14	14	13	14	7	14	5	6	6	6	4	3
TPP	Avge	26	39	53	42	59	57	24	17	15	19	39	22	19
	Median	21	27	38	41	52	55	25	11	8	16	30	20	18
	Min	2	0	0	4	9	0	0	9	1	0	11	13	12
	Max	58	106	173	82	147	142	65	43	36	41	78	35	26
	Ν	12	15	15	14	15	7	15	5	6	6	6	4	3
DOP	Avge	9	18	16	22	21	9	11	5	8	21	21	5	8
	Median	6	13	9	8	15	2	4	1	8	6	7	3	12
	Min	0	0	0	0	0	0	0	0	0	0	0	0	0
	Max	30	61	53	96	65	34	51	15	19	98	87	16	12
	Ν	12	13	13	12	14	5	14	5	6	6	5	4	3
POP	Avge	9	17	23	16	18	15	5	6	2	5	14	8	4
	Median	9	12	17	13	7	14	0	5	0	4	15	6	5
	Min	0	0	0	0	0	0	0	0	0	0	8	0	0
	Max	37	52	74	39	61	33	19	17	12	13	19	20	7
	Ν	12	10	13	10	14	6	13	5	6	5	4	4	3
PIP	Avge	17	31	36	33	36	41	19	11	14	12	10	14	15
	Median	12	38	29	33	30	31	18	9	8	13	11	10	18
	Min	0	0	0	0	0	0	0	4	0	0	0	5	5
	Max	49	106	101	73	86	142	65	26	36	31	18	30	22
	N	12	10	13	10	14	6	12	5	6	5	4	4	3
DIP	Avge	11	15	42	44	47	28	28	23	47	33	62	10	22
	Median	6	14	42	44	49	10	25	26	39	34	89	7	10
	Min	0	0	0	0	0	0	0	7	6	0	0	0	4
	Max	57	31	90	88	95	115	105	42	103	69	115	27	52
	Ν	12	13	13	12	14	5	14	5	6	6	5	4	3

Table 6. Average concentrations (μ g/L) of the different forms of phosphorus at each of the sampling locations for Sullivan's Creek

Location: Environment ACT monitoring site	TP (μg/L)	TN (μg/L)	
Ginninderra Creek	50	1100	
Lake Ginninderra West	20	1000	
Lake Ginninderra East	40	1000	
Uriara Crossing	20	300	
Sturt Island	50	6500	
Coppins Crossing	40	600	
Gunghalin Pond	40	1400	
Paddy's River	20	400	
Kambah Pool	20	400	
Kambah Wetland	60	1400	
Point Hut Pond	40	1800	
Gudgenby River	30	400	
Dairy Flat	40	900	
Angle Crossing	20	300	
Yass Rd – Molongolo R	30 400		

Table 7. Median total phosphorus and nitrogen concentrations in ACT waterways (Environment ACT 1999)

Table 8. Phosphorus and nitrogen concentrations (μ g/L) in other waterways

		Location		
		Murrumbidgee River ^a	River Murray at Lake Hume ^a	Darebin Creek (Melbourne, Victoria) ^b
TP	Avge	70	20	110*
	Range	<10-760	<10-150	40-460
	n	787	663	86
FRP	Avge	20	<10	
	Range	10-260	<10-100	
	n	673	643	
TN	Avge	630	410	1350*
	Range	50-4300	60-3600	350-8600
	n	709	554	86
NOx-N	Avge	130	80	560*
	Range	<10-1600	<10-710	10-3000
	n	742	563	86
NH ₄ -N	Avge		1050	20*
	Range		19-3960	1-1100
	n		4	86

^a – data from Martin Shafron, Murray Darling Basin Commission;

^b – data from *Coleman, 1998* *median

Total Phosphorus

Total P (TP) concentrations for each site and sampling date are summarised in Figure 5. Concentrations of TP are generally lower from Barton Highway to the GPT than in the reach downstream of the GPT. TP concentrations measured at Wattle St are usually two to three times higher than those measured in the main stream at Southwell Park. As a result, average concentrations at Macarthur Ave are approximately twice those measured at Southwell Park. This indicates that the Dickson branch is a source of phosphorus for the main channel of Sullivan's Creek.

Average TP concentrations increase markedly (almost doubling) downstream of the GPT and a smaller increase is observed below Toad Pond. These concentrations remain high downstream of the GPT to Ward Bridge where a significant drop in TP concentrations is noted. The TP concentrations at Parkes Way (Lake Burley Griffin) are again lower and are similar to the concentrations observed in the reach of Sullivan's Creek above the GPT. This data indicates that there is some input of phosphorus to Sullivan's Creek at the GPT and Toad Pond. The lower TP concentrations at Ward Bridge suggest that the nutrient concentrations at this point are significantly influenced by water from Lake Burley Griffin.



Figure 5. Total phosphorus concentrations along Sullivan's Creek.

Phosphorus Forms

Concentrations of dissolved (TDP) and particulate (TPP) phosphorus are given in Figure 6 and Figure 7. TDP concentrations range consistently between 20 and 120 μ g/L at each of the sampling sites along the creek and are lowest at Parkes Way (Lake Burley Griffin) and Southwell Park. TPP concentrations are generally lower than the TDP concentrations ranging between 10 and 80 μ g/L.



Figure 6. Total dissolved and particulate phosphorus concentrations along Sullivan's Creek



Figure 7. Total organic and inorganic phosphorus concentrations along Sullivan's Creek

Both TDP and TPP concentrations increase (TDP by 60% and TPP by 130%) at the sampling sites downstream of the GPT and a smaller increase is noticeable downstream of Toad Pond (Figure 6). The concentrations remain high to the stepping stones and are then lower at Ward Bridge and Parkes Way (Lake Burley Griffin). This pattern is similar to that observed in TP concentrations (Figure 5) and indicates that there is an input of both dissolved and particulate P to the water column in the GPT and Toad Pond. This is matched by the total organic and inorganic P concentrations with increase across the GPT and Toad Pond (Figure 7).

The contribution from the Dickson branch is comprised of both dissolved and particulate P as concentrations of both these forms are higher at Wattle St than in the main channel. Interestingly, the contribution of dissolved P by the Dickson channel makes the largest change downstream with TPD increasing almost three fold from Southwell Park to Macarthur Ave.

The relative proportion of P transported in dissolved form during low flows is given in Figure 8. There is a considerable range in the proportion of dissolved P from 20 to 100%, but typically 40-80%, of the total load. Observations made in other river systems also indicate considerable variation in the relative proportions of dissolved and particulate P but, in contrast to the results of this study, the other studies generally show that the greatest proportion of P is particulate (refer for example Oliver, 1993; Cullen, 1995; Erskine and Saynor, 1995: Heathwaite and

Nutrients in Sullivan's Creek

Johnes, 1996; and Russell et al., 1998). The direct comparison is not entirely valid as the other studies mentioned have been in rural areas, where the channel is unlined and the suspended sediment concentrations much higher. Sullivan's Creek on the other hand is mostly concrete lined. It has not been possible to find comparable studies as most urban nutrient work has been performed on storm events where the concentrations of nutrients in the stormwater are an order of magnitude higher than measured here (e.g. *Allison et al, 1998*).

The proportion of dissolved P is relatively constant downstream of Masson St although a slight decrease in the proportion of dissolved P is noticeable from Canberry Bridge to Parkes Way (Lake Burley Griffin). The sampling site at David St consistently shows a high proportion of dissolved P and the Southwell Park and Barton Highway sites are generally lower in proportion of dissolved P.



Figure 8. The relative proportion of dissolved phosphorus along Sullivan's Creek.

Most of the P in Sullivan's Creek is inorganic (Figure 9), with typically 70% or more of the P transported in inorganic form. The proportion of inorganic P is relatively consistent along the creek, although the sites from Wattle St to David St sites generally have the highest proportion (>80%) of inorganic P. There is a slight drop in the proportion of inorganic P at the GPT and the subsequent downstream sampling sites show a higher variation in the proportion of inorganic P than the upstream sites.



Figure 9. The relative proportion of inorganic phosphorus along Sullivan's Creek

Dissolved organic P (DOP) is the smallest component of the total P load with generally less than 20% of the P in the creek transported in the dissolved organic form. This is consistent with the findings of Russell et al. (1998). In their study of two river basins in the UK that the dissolved organic component was the smallest contributor of P. However, in the rural English setting analysed by Russell et al (1998), DOP accounted for less than 10% of the P load in the rivers which is half the observed contribution in the current urban Australian setting. There is a trend of decreasing proportion of DIP and increasing proportion of PIP from Wattle St to Parkes Way (Lake Burley Griffin) which indicates a change in form of the inorganic fraction from dissolved to particulate moving downstream.

7.1.2 Phosphorus - Temporal Data

Total Phosphorus

Total P concentrations in Sullivan's Creek for each sampling date between November 1998 and November 1999 are summarised in Figure 10. There appears to be a pattern of high P concentrations in January to March with concentrations then decreasing to a low in June to August and then increasing again slightly in September to November. This pattern, although not statistically significant due to the high variability in concentration for each date, is similar to that of the mean monthly temperature for Canberra for the corresponding sampling period (Figure 11). This suggests that there may be some seasonal or temperature effect on the concentrations of P in Sullivan's Creek.



Figure 10. Total phosphorus concentrations in Sullivan's creek between November 1998 and November 1999.



Figure 11. Average maximum monthly temperatures in Canberra for the period November 1998 to November 1999

Phosphorus Forms

The absence of data for May and June makes it difficult to determine if similar trends exist in the concentrations of dissolved and particulate P (Figure 12) but it appear unlikely especially for dissolved P. There is possibly a matching trend (of high concentrations in warmer months) in the concentrations of organic P and a less distinct trend in inorganic P concentrations (Figure 13).



Figure 12. Concentrations of dissolved and particulate phosphorus in Sullivan's Creek between November 1998 and November 1999.



Figure 13. Concentrations of organic and inorganic phosphorus in Sullivan's Creek between November 1998 and November 1999

The relative proportions of dissolved and inorganic P shows a distinct increase over the months of December to April (Figure 14 and Figure 15 respectively). The proportion is high in July and August and decreases from August to November. This in an inverse correlation with temperature (refer Figure 11) and shows that the proportion of dissolved inorganic P is lowest over the colder months.


Figure 14. The relative proportion of dissolved phosphorus in Sullivan's Creek between November 1998 and November 1999.



Figure 15. Relative proportion of inorganic phosphorus in Sullivan's Creek between November 1998 and November 1999.

7.1.3 Synthesis - Phosphorus Data

The measurement of P forms along Sullivan's Creek at regular intervals has shown that total P concentrations in the creek are consistently higher than in other ACT streams and exceed the guideline levels for aquatic ecosystems. Total P concentrations are similar to those measured in the Murrumbidgee River and in one of Melbourne's urban creeks (Darebin Creek).

More than 70% of the phosphorus transported under low flow conditions in Sullivan's Creek is in inorganic forms and therefore one of the hypotheses proposed in section 2.2.2 "*Most of the phosphorus and nitrogen in Sullivan's Creek is in organic form*" is rejected for phosphorus during low flow conditions. Typically 40-80% of the phosphorus in Sullivan's Creek is in forms less than 0.22 μ m which is unusually high compared to the proportion observed in other inland Australian streams although this comparison is not entirely valid as most published data is for rural environments. However, information regarding phosphorus forms for other urban streams under low flow conditions was not available for comparison.

The Dickson channel, which drains part of the Mt Ainslie-Mt Majura reserve, sections of the suburbs of Ainslie, Hacket and most of the suburb of Dickson, appears to deliver higher concentrations of both dissolved and particulate P to the main channel of Sullivan's Creek during low flows. This results in a doubling in average total phosphorus concentrations between Southwell Park and Macarthur Ave indicating that the Dickson channel is a significant source of P to Sullivan's Creek. Sampling was not undertaken further upstream along the Dickson channel which means that it was not possible to determine the cause of these high P concentrations. However, one possible explanation is that it may be, at least in part, the result of slightly higher P concentrations in both the top-soils and the sub-soils of the Mt Ainslie – Mt Majura region compared with the rest of the catchment (*Middelmann, 1998*).

The concentration of total P in Sullivan's Creek almost doubles across the GPT and there is a smaller increase across Toad Pond. This increase occurs for all forms of P and indicates that the GPT contributes approximately half of the P in the ANU reach of Sullivan's Creek under low flow conditions. Toad Pond is comparatively smaller contributor of P adding 10% to the total P concentrations. A slight decrease in the proportion of inorganic P at the GPT was noted which suggests that the GPT may be contributing proportionally more organic phosphorus than inorganic phosphorus but the differences are small due to the relatively small concentrations of TOP.

There are several possible causes of the increased phosphorus concentrations at the GPT and Toad Pond:

 Organic rich material transported during flood events and trapped in the GPT and Toad Pond is being broken down by bacteria – a process which consumes oxygen from the overlying water. The subsequent depletion of oxygen produces reducing conditions which facilitate the release of phosphorus from the sediments and deposited material thus increasing the concentration of dissolved P. While some of the P released to the water column is organic and is therefore derived from the deposited organic matter, most is inorganic. Unfortunately it is not possible to conclusively say that the inorganic P released to the water column is derived solely from inorganic sediments as the complete breakdown of organic P produces dissolved inorganic P.

- 2) The increase in particulate P may be due to resuspension of material in the GPT and Toad Pond. Both sites show high levels of biological activity which may be causing resuspension. At Toad Pond in particular there is a large amount of methane production evident as bubbles of gas regularly rising to the surface. This bubbling may result in the resuspension of particulate P and it may also assist the movement of dissolved P released from the sediments into the surface waters.
- 3) The increase in particulate P may also be due to the use of the GPT and Toad Pond by a large number of ducks. These ponds are the first of the Creek to be used by a significant number of ducks (as many as 40 ducks have been noted on Toad Pond during sampling) and their normal activities may result in resuspension of sediments from shallow waters and also some contribution of particulate P to the creek water
- 4) It is not possible to entirely discount that one of the drains directly entering the GPT is contributing high levels of phosphorus to the creek or that there is a direct delivery of sewerage to the creek. It is unlikely that one of the urban drains is making a significant contribution given the amount of phosphorus required to double the concentration of P in the GPT and the drains at this point appear to be only contributing small amounts of water. Main trunk sewers follow the creek for most of its length and although unlikely, a leak is possible.

The measurement of P forms in Sullivan's Creek over a 12 month period have indicated a possible seasonal variation in total P concentration with average TP concentrations 50-100% higher in September to March than in April to August. This additional contribution is not obviously from any one particular form of P. There is a temporal change in the proportion of dissolved inorganic P in the creek with most of the P transported in winter months in dissolved inorganic form. The proportion of organic P is relatively constant throughout the year indicating no seasonal change in the relative proportion of organic P that might be expected if deciduous leaves were a significant source of P.

Like the spatial variation there are several possible explanations for the higher concentrations of P in the creek during warmer months:

- 1) Periods of both longer and warmer days result in increased biological activity in the creek and this may result in the release of more P to the water column.
- 2) The warmer months are the 'growing season' in Canberra and during this time there is a substantial increase in the use of fertilizers on lawns, gardens and ovals near the creeks, as well as an increase in watering. These combined processes may increase the levels of P in the ground and drain water and therefore the creek water.
- 3) More frequent lawn mowing occurs during warmer months. When the grassed reserve areas adjacent the creek are mown, the clipping are left on the ground. The breakdown of the cut grass clippings has the potential to deliver P to the creek water.

7.1.4 Nitrogen – Spatial Data

The average concentrations of the different forms of nitrogen measured at each of the sites sampled along Sullivan's Creek are given in Table 9. Average TN concentrations range from 615 μ g/L at Barton Highway to 1370 μ g/L downstream of the GPT. Total N concentrations in Sullivan's Creek are similar to those observed in other ACT streams and one of Melbourne's urban streams (Table 7 and Table 8) These concentrations are slightly higher than the average TN concentrations in the Murrumbidgee River (Table 8) and they exceed the guideline levels for aquatic ecosystems (refer Table 1).

			Distance from Lake Burley Griffin (m) A1 A B C D D1 E/F G H I J K L													
		A1	A1 A B C D D1 E/F G H I J K 0 590 840 1020 1540 1760 1860 2460 3210 3710 4030 5230 0													
		90	590	840	1020	1540	1760	1860	2460	3210	3710	4030	5230	6730		
		Parkes	s Way (Lake			GPT					Ba	rton H	ighway		
		Burley	Griffin)												
TN	Avge	810	850	990	900	1190	1370	830	980	770	760	790	810	620		
	Median	790	690	890	940	1210	1350	820	930	770	680	650	620	630		
	Min	380	370	420	480	750	750	380	340	450	380	380	440	200		
	Max	1240	1480	1700	1330	1740	2020	1900	2300	1050	1200	1620	1380	1020		
	n	8	10	10	10	10	4	11	5	5	5	5	3	3		
TDN	Avge	640	520	730	730	770	930	680	580	610	550	660	630	450		
	Median	630	560	630	720	800	760	610	570	640	540	650	460	560		
	Min	290	270	300	480	470	560	260	300	290	240	250	400	200		
	Max	970	910	1100	1010	1090	1630	1800	900	880	880	1090	1030	590		
	n	8	9	9	9	9	4	9	4	4	4	4	3	3		
TPN	Avge	170	290	280	190	450	440	160	70	120	100	160	180	160		
	Median	130	250	150	190	430	430	140	60	120	110	65	160	40		
	Min	10	90	60	0	180	140	10	0	60	30	0	40	0		
	Max	400	920	730	470	890	760	400	140	170	170	530	360	450		
	n	8	9	9	9	9	4	9	4	4	4	4	3	3		
DON	Avge	400	380	480	440	460	540	400	300	340	300	350	230	380		
	Median	440	420	540	480	530	530	460	340	340	300	360	250	450		
	Min	140	0	7	100	140	310	70	70	150	100	160	50	190		
	Max	540	560	1090	630	880	800	680	440	500	490	520	380	480		
	n	7	8	9	9	9	4	9	4	4	4	4	3	3		
NOx-N	Avge	190	100	110	180	170	330	150	490	280	230	270	290	32		
	Median	140	80	80	90	130	320	90	400	210	170	190	200	30		
	Min	36	0	0	4	3	65	6	41	0	0	0	120	5		
	Max	470	250	300	460	430	640	480	1420	870	660	640	630	65		
	n	12	14	14	14	14	8	14	6	6	6	6	4	4		
NH ₄ -N	Avge	100	85	160	190	210	190	63	64	65	61	62	87	55		
	Median	75	44	110	190	240	190	18	38	20	22	23	59	44		
	Min	10	1	11	25	5	3	6	10	6	6	4	2	0		
	Max	300	270	510	400	470	500	230	200	250	220	230	230	130		
	n	12	14	14	14	14	8	14	6	6	6	6	4	4		

Table 9. Average concentrations (μ g/L) of the different forms of nitrogen in Sullivan's Creek.

Average NOx-N concentrations measured in Sullivan's Creek range from 32 μ g/L at Barton Highway to 490 μ g/L at the Masson St and are generally slightly higher than the average concentrations measured in the Murrumbidgee River but are lower than concentrations measured in Darebin Creek. Average NH₄-N concentrations measured in Sullivan's Creek range between 55 μ g/L at Barton Highway to 211 μ g/L just below Toad Pond. These NH₄-N concentrations are higher than those measured in the Murray River or in Darebin Creek. Both NOx-N and NH₄-N concentrations in Sullivan's Creek exceed the guideline levels for aquatic ecosystems (Table 1).

Total Nitrogen

Total nitrogen (TN) concentrations along Sullivan's Creek are given in Figure 16. A wide range of TN concentrations were observed at each site but a general spatial trend exists in the data. TN concentrations are relatively constant upstream of the GPT, except for some consistently low concentrations at David St. TN concentrations increase by 30% (for average concentrations) downstream of the GPT and then decrease again over the following two sampling sites. The concentrations of TN in the reach from Canberry Bridge to Parkes Way (Lake Burley Griffin) are similar to those measured upstream of the GPT. This data indicates that there is an input of nitrogen at the GPT. The low TN concentrations at Ward Bridge support the P evidence which suggests that the nutrient concentrations at this point are influenced by water from Lake Burley Griffin.

Unlike the phosphorus concentrations, TN concentrations at Wattle St are consistent with those at Southwell Park indicating that the Dickson drain is not contributing higher amounts of nitrogen to the creek.



Figure 16. Total nitrogen concentrations along Sullivan's Creek.

Nitrogen Forms

Concentrations of dissolved N (TDN) and particulate N (TPN) are given in Figure 17. Concentrations of TDN are relatively constant along Sullivan's Creek with most ranging from 500 to 1000 μ g/L. TPN concentrations are significantly lower than the TDN concentrations, (most less than 400 μ g/L) but the spatial trend in TPN concentrations matches that of the TN concentrations showing a marked increase downstream of the GPT. These elevated concentrations are held to the downstream end of Toad Pond and over subsequent downstream sampling points the TPN concentrations return to the levels observed upstream of the GPT. This indicates that the increase in TN concentration observed at the downstream ends of the GPT are a result of an increase in particulate N in the water.



Figure 17. Total dissolved nitrogen (TDN) and total particulate nitrogen (TPN) concentrations along Sullivan's Creek.

Typically more than 70% of the TN is transported in dissolved form and 50-90% of this is organic. This is consistent with other studies (cf. Russell et al., 1998) which show the dominance of the dissolved fraction in the TN load.

Dissolved NH₄-N shows a much greater range of concentrations within the University grounds than in the upstream reaches of the creek (Figure 18). Upstream of the ANU NH₄-N concentrations are generally <100 μ g/L (approximate mean 60 μ g/L), concentrations then increase downstream of the GPT and again downstream of Toad Pond (to around 200 μ g/L). NH₄-N concentrations then decrease at subsequent downstream sampling points and mean values at the lake end of Sullivan's Creek are approximately 50% higher than upstream of the GPT. Although a significant increase is observed in the concentration of NH₄-N in the creek between the GPT and Toad Pond, the TDN concentrations do not rise significantly (refer Figure 17). This is because NH₄-N makes up only a small percentage of the TDN concentration. Although the increase in NH₄-N concentrations are not important in terms of the total N concentration, the observed increase in concentration is indicative of reducing conditions in the GPT and Toad Pond.



Figure 18. Concentrations of NH₄-N along Sullivan's Creek.

Concentrations of NOx-N display almost the opposite trend along Sullivan's Creek to the Ammonia concentrations (Figure 19). Concentrations are highest upstream of the GPT with the highest concentrations measured at Masson St. The NOx-N concentrations remain high across the GPT but then drop noticeably across Toad Pond and remain low at subsequent sampling sites to Parkes Way (Lake Burley Griffin).



Figure 19. Concentrations of NOx-N along Sullivan's Creek

7.1.5 Nitrogen - Temporal Data

Due to the break in sampling over May and June and difficulties in analysing samples collected in July and August for total N there is insufficient data to assess TDN and TPN concentrations for temporal trends. This analysis will therefore focuss on TN, NOx-N and NH₄-N data.

Total Nitrogen

Total N concentrations in Sullivan's Creek between November 1998 and November 1999 are given in Figure 20. Considerable variation in concentrations were measured on each sampling date and no temporal trends are evident indicating no significant seasonal controls.



Figure 20. Total nitrogen concentrations in Sullivan's Creek between November 1998 and November 1999.

Nitrogen forms

Concentrations of NOx-N in Sullivan's Creek between November 1998 and November 1999 are given in Figure 21. Although there is significant variation in concentration this data shows higher (almost double) NOx-N concentrations from June to September than in the rest of the year. The lack of a similar trend in TN is because NOx-N only makes up a small proportion of TN but it also indicates that there may be some seasonal effect on the form of N transported in Sullivan's Creek rather than the total. Interestingly the temporal trend in NOx-N concentrations does not match that of the trend in P concentrations.



Figure 21. NOx-N concentrations in Sullivan's Creek between November 1998 and November 1999.

Ammonia (NH₄-N) concentrations in Sullivan's Creek also show a seasonal trend (Figure 22). Concentrations of NH₄-N are almost three times higher in the months of April and July than concentrations measured in the rest of the year. Like the phosphorus data, this suggests a temperature or seasonal effect effect on NH₄-N concentrations however the lack of data for May and June means this is not conclusive.



Figure 22. NH₄-N concentrations in Sullivan's Creek between November 1998 and November 1999.

7.1.6 Synthesis - Nitrogen data

The measurement of N forms along Sullivan's Creek at regular intervals has shown that concentrations of nitrogen in the creek are similar to those measured in other ACT streams and the Murrumbidgee River and Darebin Creek, one of Melbourne's urban streams. NOx-N concentrations in the creek are similar to those measured in the Murrumbidgee River and NH₄-N concentrations are higher than those measured in Darebin Creek. TN, NOx-N and NH4-N concentrations in Sullivan's Creek exceed their guideline levels for aquatic ecosystems. More than 70% of the N transported in Sullivan's Creek is dissolved and generally 30-60% is in organic form.

There is a 30% increase in TN concentration across the GPT which is predominantly due to an increase in particulate nitrogen. This has resulted in a decrease in the proportion of N transported in dissolved form below the GPT. The increased concentrations of particulate N are probably caused by the same mechanisms proposed for increasing the particulate P concentrations (resuspension by benthic biological activity, ducks or drain and sewer inputs).

There is also an increase in NH₄-N and a decrease in NOx-N concentrations below the GPT and Toad Pond which do not impact on the TN concentrations but give some indication of the processes occurring in the ponds. The increase in NH₄-N concentration and corresponding decrease in NOx-N is indicative of organic matter degradation under low oxygen conditions resulting in nitrate reduction and the production of NH₄-N (equation 1). Therefore both the N and P data indicate that there are reducing conditions in the GPT and Toad Pond which are resulting in the release of nutrients to Sullivan's Creek contribute significantly to the nutrients in the ANU section of the creek.

Equation 1. $2(CH_2O) + NO_3^- + 2H^+ \implies 2CO_2 + NH_4^+ + H_2O$

In spite of gaps in the data sets the measurement of N forms over a 12 month period has shown TN concentrations in the creek are not seasonally influenced. However, both NH₄-N and NOx-N show small temporal trends with increased NH₄-N concentrations from April to July and increased NOx-N concentrations from June to September. There are two possible explanations for increased NH₄-N concentrations over April to July.

1) Low dissolved oxygen concentrations (caused by low temperatures) result in more utilisation of the oxidisable forms of N in the breakdown organic matter with the subsequent production of NH₄-N.

2) Increased delivery of deciduous leaves to the creek (this coincides with the main leaf fall time) and the subsequent breakdown is causing the available dissolved oxygen to be used rapidly. Consequently the oxidisable forms of N are used and NH₄-N is produced.

Both of these explanations would result in a decrease of NOx-N corresponding with the increase in NH₄-N which was not observed. The breakdown of organic matter under low dissolved oxygen concentrations would also be expected to increase the release of P to the water column during these months but the opposite was observed (lower P concentrations in winter). The increased delivery of deciduous leaves might also be expected to increase the TN concentrations which was also not observed.

7.2 Rain Events

7.2.1 Small Rain Event: 19/3/99

Phosphorus

Concentrations of TP measured at Canberry Bridge and Ward Bridge for the small rain event of 19/3/99 are given in Figure 23 along with the flow at Barry Drive. TP concentrations were initially higher at Canberry Bridge than at Ward Bridge. The TP concentration at Canberry Bridge increased during the first 2.5 hours to a fairly constant concentration. TP concentrations at Ward Bridge increased over the course of the rain event to reach the same concentrations at Canberry Bridge. This indicates that it took the full event for the water from the Canberry Bridge sampling site to become mixed with that at Ward Bridge. This data supports the earlier observation that the nutrient concentration of the water at Ward Bridge is dominated by Lake Burley Griffin rather than water flowing along Sullivan's Creek. Concentrations of total P increased during the event and were still high once the water receded (after 8 hours of sampling).



Figure 23. Concentrations of total P at Ward and Canberry Bridges during the rain event 19/3/99.

The proportion of dissolved P increased dramatically during the sampling period at Ward Bridge, but didn't show the same distinct trend at Canberry Bridge (Figure 24). This may be because the proportion of dissolved P was already relatively high at Canberry Bridge at the start of the event compared with Ward Bridge.



Figure 24. Proportions of dissolved P at Ward Bridge and Canberry Bridge during the rain event of 19/3/99.

While the proportion of organic P at Ward Bridge remained relatively constant over the entire event (apart from one sampling point Figure 25), at Canberry Bridge it tended to increase toward the middle of the event and then decrease at the end. This may be associated with the washing of organic material from the streets and paths into the stream.



Figure 25. The proportion of organic P at Ward Bridge (left) and Canberry Bridge (right) during the rain event of 19/3/99.

Nitrogen

Concentrations of TN at the two locations follow those of TP concentrations (Figure 26 and compare with Figure 23). Canberry Bridge shows the highest initial TN concentrations (interestingly these are significantly higher than the average TN values from fortnightly sampling –Table 9), these increase slightly over the first few hours of the event and then become relatively constant. Ward Bridge samples show the lowest initial concentrations of TN, but these increase steadily over the rain event to be the same as the concentrations at Canberry Bridge . This again shows that it takes almost the whole event for the water from Canberry

Bridge to reach Ward Bridge and confirms that the nutrient concentrations at Ward Bridge are strongly influenced by Lake Burley Griffin.



Figure 26. Total N concentrations at Ward and Canberry Bridges during the rain event of 19/3/99

As observed during low flows, the majority of the N transported in the creek was dissolved (Figure 27).



Figure 27. Proportions of dissolved and particulate N at Ward Bridge and Canberry Bridge during the rain event of 19/3/99.

NH₄-N concentrations decreased over the course of the event at Canberry Bridge, and increased at Ward Bridge (Figure 28). This indicates that the storm water produced in this event was low in NH4-N and as the fresh stormwater reaches Canberry Bridge, the concentrations of NH4-N

are diluted. The flush of water along the creek is initially high in NH4-N and as this mixes with water at Ward Bridge, the concentrations decrease.



Figure 28. NH₄-N concentrations at Ward and Canberry Bridges during the rain event of 19/3/99.



Figure 29. NOx-N concentrations at Ward and Canberry Bridges during the rain event 19/3/99.

Concentrations of NOx-N remain low at Ward Bridge until late in the event when they increase dramatically (400%, Figure 29). At Canberry Bridge, initial NOx-N concentrations are low but they rise dramatically about 2.5 hours after sampling began. This may correspond to the arrival of well oxygenated water from the catchment.

7.2.2 Large Rain Event: 16/9/99

Phosphorus

Concentrations of phosphorus measured at Canberry Bridge during the larger rain event on 16/9/99 are given in Figure 30 along with the flow measured at Barry Drive. TP concentrations tend to follow the pattern of the hydrograph but the concentration peaks ahead of the flow peak which is typical behaviour for pollutants in storm flows. Peak concentrations of TP were 400 μ g/L which is four times the average concentration at Canberry Bridge (Table 6).



Figure 30. Concentrations of total P at Canberry Bridges during the rain event 16/9/99.

The TP concentration shows a disproportionately high peak during the first 6 hours of sampling compared with the flow peaks. This is explained by the dissolved and particulate P concentrations for the event (Figure 31). Concentrations of dissolved and particulate P are virtually the same during the first 6-8 hours of the storm combining to produce the disproportionately large peak in TP. The dissolved P then remains constant for the remainder of the event with only the particulate P concentration following the pattern of the flow. Thus the proportion of dissolved P drops significantly during the main peak of the flow.



Figure 31. Dissolved and particulate P concentrations at Canberry Bridge during the rain event of 16/9/99.

As is the case during low flows, most of the P transported during the storm was inorganic (Figure 32). The concentrations of both the organic and inorganic forms of P tend to follow the hydrograph and there was little change in the proportional contribution until approximately 10 pm on the 16th. After this the concentration of organic P was very low and yet the concentration of inorganic P remained high. This corresponded to a major change in colour of the sediment being transported in the creek and a significant change in the chemistry of the samples (Figure 33) indicating a change in the source of the sediment at this point. The most likely explanation for the change is that at this point in the event, runoff from the rural part of the catchment (upstream of Mitchell) carrying suspended sediment (most likely derived from the channel banks) has reached Canberry Bridge. This is supported by anecdotal evidence that the rural section of the catchment is disconnected from the urban part of the catchment except during large events.

The major element chemistry data (see also Appendix A) from the suspended sediments collected early in this event is virtually the same as the chemistry of the samples that Middelmann (1998) classed as 'purely urban'. The chemistry of the samples later in the event does not fit with an increase in inorganic sediment. Due to the small mass of sample available, there are significant errors in the major element concentrations which means that a great deal of caution should be used in interpreting the major element data.



Figure 32. The concentrations of organic and inorganic phosphorus at Canberry Bridge during the rain event of 16/9/99.



Figure 33. The major element chemistry of suspended sediments during the rain event of 16/9/99

Nitrogen

Concentrations of total nitrogen during the rain event (16/9/99) follows the pattern of the total phosphorus concentrations (Figure 34 and compare with Figure 30) with the concentrations peaks occurring ahead of the flow peaks but the TN concentrations remain high following the event instead of dropping to pre-event concentrations. The initial TN concentration peak is of greater disproportion than the initial TP peak and is the result of high dissolved N concentrations during the initial stages of the event (Figure 35). The TN concentrations following the event are almost as high as the peak TN concentration and is all dissolved nitrogen.



Figure 34. Total N concentrations at Ward and Canberry Bridges during the rain event of 16/9/99



Figure 35. Concentrations of dissolved and particulate N at Canberry Bridge during the rain event of 16/9/99.

Most of the N transported during the event was dissolved with the exception being the main peak flows where particulate N dominated (Figure 36). This indicates a change in the nature of the material being transported in the event.



Figure 36. Proportions of dissolved N at Canberry Bridge during the rain event of 16/9/99.

Concentrations of NOx-N and NH₄-N during the event are given in Figure 37. Both show a peak in concentration with the early peak of the hydrograph and not with the main peak. This is because these forms of N are dissolved and most of the N transported in the peak flow is particulate. Both NOx-N and NH₄-N concentrations remain high after the flow has receded.



Figure 37. NOx-N and ammonia concentrations at Canberry Bridge during the rain event of 16/9/99.

7.2.3 Synthesis – Storm data

Two very different rain events were sampled during this study. The first, a small event of only 5 mm, provided little information about the behaviour of nutrients during rain events. However, it did show that it took almost all of the rain and subsequent runoff for the nutrient concentrations at Ward Bridge to be affected, yet the nutrient concentrations at Canberry Bridge were affected almost immediately. This indicates that under low flow conditions Lake Burley Griffin influences the nutrient concentrations along Sullivan's Creek at least to Ward Bridge and possibly further to the Stepping Stones.

The second, much larger, event of 40 mm showed the typical pattern of pollutant concentrations for storm events with the concentrations peaks just in advance of the flow peaks. During the main peak flow, particulate inorganic forms of both P and N dominated the nutrient concentrations. This is consistent with higher concentrations of suspended sediment during high flows – and thus the concentrations of P and N are dominated by those associated with the suspended sediment. During the early smaller peaks of this event the proportions of the different forms of P and N more closely resembled that under low flows.

There was also evidence of a change in sediment and nutrient source from urban to rural during the recession of the main peak flows. At this point, the concentration of inorganic P remained high and the concentration of organic P dropped significantly. It also corresponded with a major change in colour and chemistry of the suspended sediment.

The major difference in total N and P behaviour during the large event was that once the flow had receded, concentrations of P dropped yet the concentration of N (as dissolved N) remained high.

8 Discussion

8.1 Loads

Nutrient concentration data (as provided in the above sections) provide some insight into the spatial and temporal processes occurring within the creek and facilitates comparisons with concentrations in other streams and guideline values. In terms of the quality of water in the receiving body, (e.g. Lake Burley Griffin) it is more useful to look at the total mass of nutrients (nutrient load) delivered by the creek. The nutrient load of the creek for a specific time period is given by multiplying the nutrient concentrations by the flow for that time period.

Calculations of load are problematic because, although continuous records of flow are commonly available, concentration data are usually only from samples taken at specific time intervals. There are various procedures employed to estimate loads on the basis of intermittent concentration data and all of these have problems associated with them (Walling and Webb, 1985). Bearing the limitations in mind, with prudent use of data it is possible to make some estimates of load.

The concentration of most substances transported by rivers is flow dependent and this dependence is frequently incorporated in load estimation techniques. The TN and TP concentrations measured as part of this study did not show significant flow dependence at low flows to be used to estimate loads for Sullivan's Creek. The relationship between concentration and flow for high flows is complex due to variability within and between events. Consequently, the estimation of loads for the creek has been divided into two sections with high and low flows treated separately.

8.1.1 Low flows

Daily flow for Sullivan's Creek was recorded at the Barry Drive GPT. Data from this guaging station provide a reasonable estimate of flows through the ANU as there are no major inputs between Barry Drive and Lake Burley Griffin. Low flows were defined as less than 5 ML/day, because rainfall of 1 mm or less results in flows of up to 4 ML/day. Flows of less than 5 ML/day account for more than 80% of the days between the 1st December 1998 and 30th November 1999.

Loads were calculated for the sites upstream of the GPT, downstream of Toad Pond and Canberry Bridge. The sites upstream of the GPT and downstream of Toad Pond were chosen to provide information on the nutrient load being delivered to the creek under low flow conditions from the combination of these two features⁶. Canberry bridge was chosen as it is possible to

⁶ Although the concentration data indicates the GPT is the more significant contributor of nutrients to the creek, concentration data between the GPT and Toad Pond had only been collected for part of the year. To calculate low flow loads for the full study period, it was more appropriate to use the complete data set from the site downstream of Toad Pond.

determine high flow loads at this site thereby allowing comparison of high and low flow loads. It was not possible to determine loads further upstream in the catchment as suitable flow data is not available.

The loads of phosphorus and nitrogen entering and leaving the GPT and Toad Pond and passing Canberry Bridge during low flows were calculated by multiplying the average daily flow and average concentration for the period from December 1998 through to the end of November 1999. The daily loads were summed to give an approximate annual load for the period of this study. The temporal variability in phosphorus concentration (refer section 7.1.2) was accounted for by using separate average concentrations for the period of January to March, April to August and August to September (see Table 10). The average nitrogen concentration used is also given in Table 10.

Table 10. Average concentrations of phosphorus and nitrogen (μ g/L) used in the calculation of load. Numbers in parentheses are coefficients of variation.

Period	Concentration (µg/L)												
	Upstream of the GPT	Downstream of the GPT and Toad Pond	Canberry Bridge										
Phosphorus													
January – March	77 (34%)	150 (30%)	140 (30%)										
April – July	47 (30%)	97 (30%)	81 (30%)										
August – December	52 (56%)	114 (17%)	103 (17%)										
Nitrogen													
January – December	829 (50%)	1191 (30%)	896 (34%)										

Table 11. Phosphorus and nitrogen loads (kg) in Sullivan's Creek during flows of less than 5 ML/day between 1-Dec-98 and 30-Nov-99

Location	Canberry Bridge	Upstream of the GPT	Downstream of the GPT and Toad Pond	Contribution from the GPT and Toad Pond
Phosphorus Load (kg)	33 ± 7	18 ± 8	37 ± 7	19 ± 5
Nitrogen Load (kg)	280 ± 95	260 ± 130	370 ± 110	90 ± 52

Table 11 shows the loads of phosphorus and nitrogen under low flow conditions for the study period. The key points to note from this are that the masses transported under low flows are small and that the GPT and Toad Pond are contributing significant amounts of phosphorus (approximately 50%) and nitrogen (approximately 30%) to the ANU section of the creek under low flow conditions.

8.1.2 High flows

High flows were defined as greater than 5 ML/day and this accounts for less than 20% of the days between the 1st December 1998 and 30th November 1999. Loads transported during high flows are more difficult to estimate than low flow loads due to the large variation in nutrient concentration within a rainfall event and, in this case, because only two storm events were sampled during the study period.

An estimation of the loads transported past Canberry Bridge in the two high flow sampled was obtained by multiplying concentration by the total flow for hourly periods and summing this for the entire event. The results of this are given in Table 12. This shows that more phosphorus and nitrogen was transported past Canberry bridge during the September rain event than for the entire low flow conditions in the rest of the sampling period.

 Table 12. Phosphorus and nitrogen loads transported past Canberry Bridge in the events of 19/3/99 and 16/9/99.

Event	Phosphorus Load (kg)	Nitrogen Load (kg)
19 March 1999 (9 hours)	1.5 ± 0.2	14 ± 2
16 September 1999 (36 hours)	70 ± 10	440 ± 50

These results were used to provide an estimate of the loads transported during other high flow events. Each event was analysed to give a total load for a 24 hour period. These 2 points were then used to determine a linear relationship between flows greater than 5 ML/day and load. This was applied to all high flows during the period December 1998 to November 1999 to give the total load transported during high flow events for the study period.

Table 13. Total Loads passing Canberry bridge during the period December 1998 to November 1999. The errors provided for high flows are a 'best guess' of the uncertainties in the calculations.

	Phosphorus load (kg)	Nitrogen load (kg)
High flows	800 ± 250	4800 ± 1500
Low flows	33 ± 7	280 ± 95
Total annual	840 ± 260	5000 ± 1600
% high flows	95%	80%

What these results clearly indicate is that the movement of nitrogen and phosphorus through Sullivan's Creek is dominated by the high flow events with 95% of the P and 80% of the N transported during less than 20% of the days. This is important in terms of managing total loads, as nutrient concentrations in high flow events are not easily controlled through works such as artificial wetlands.

8.2 Sources of Nutrients

The sources of nutrients for Sullivan's Creek can be classed as either in-stream or catchment sources. The increase in concentrations across the GPT and Toad Pond suggested in stream sources whereas the higher than usual concentrations of P observed upstream of the GPT indicate catchment sources. Benthic chamber experiments were used to investigate in-stream sources and the sampling data used to investigate catchment sources.

8.2.1 In stream sources

At the end of April, assessment of the data collected indicated that either the GPT or Toad Pond were contributing significant amounts of both N and P to Sullivan's Creek. Previous studies had also resulted in the suggestion that the pond between the Stepping Stones and Ward Bridge (hereafter known as 'South Pond') was also supplying P to the water column (although the initial monitoring data did not appear to support this). Based on these observations collaboration was undertaken with scientists at AGSO to measure the flux of nutrients from the sediments in both Toad and South Ponds and determine if they were significant sources of nutrients in the creek. This involved the deployment of benthic chambers in Toad Pond (2nd November 1999) and South Pond (4th of November 1999) to measure the nutrient flux.

A benthic chamber is effectively a large capped tube which is sealed onto the bottom of the creek by pushing it into the creek bed. Tubes coming out of the chamber allows water to be sampled at specific time intervals and from this it is possible to measure the nutrients released from the sediments. It was not practical to deploy the benthic chambers in the GPT as it would be unlikely that a good seal would be achieved between the bottom of the chamber and the concrete base of the GPT. The report provided by AGSO outlining the results of these experiments is included as Appendix B.

This work found that there were very high rates of degradation of organic carbon in Toad Pond and to a lesser extent in South Pond. In both cases oxygen demand of the sediment exceeded the rate at which oxygen could be supplied from the water column. Consequently, the water column was depleted in oxygen and denitrification, FeOOH, MnO_2 and sulphate reduction were occurring. Such low oxygen conditions are ideal conditions for the production of hydrogen sulphide (also known as rotton egg gas) methane and ammonia.

Ammonia production in Toad Pond was very high ($36 \text{ mM/m}^2/\text{day}$ the highest ever measured by the team at AGSO) as was the production of dissolved P ($2 \text{ mM/m}^2/\text{day}$). The production of both ammonia and dissolved P was quite low in South Pond (0.4 and 0.5 mM/m²/day respectively). This supports the sampling evidence that Toad Pond makes a contribution to the nutrient concentrations in Sullivan's Creek but South Pond does not. The low dissolved oxygen concentrations at both sites indicated respiration was greater than photosynthesis. The dominance of respiration suggests bottom sediments in Toad Pond are likely to have been a significant source of N and P at the time of the survey. This evidence means that the third hypothesis: "A significant amount of phosphorus is being delivered to the creek associated with groundwater in South Pond" is rejected.

The sampling program has indicated that the GPT contributes more nutrients to the water column than Toad Pond and it is assumed that similar processes are driving the production of dissolved N and P in the GPT. In terms of the nutrients within the ANU reach of Sullivan's Creek under low flow conditions, the GPT contributes (on average) over half of the phosphorus and about one third of the nitrogen.

8.3 Catchment Sources

Phosphorus concentrations between Barton Highway and the GPT are higher than in most other ACT streams and this is due in part to the high concentrations delivered by the Dickson channel. The cause of the high concentrations in the Dickson channel is unknown – but it is delivered as both particulate and dissolved P. Most of the P in the reach between Barton Highway and the GPT is inorganic and a high proportion is dissolved. The consistency of N concentrations upstream of the GPT indicates that there are no significant point sources of N from Barton Highway to the GPT. Nitrogen concentrations within this reach of Sullivan's Creek are consistent with those measured in other ACT streams and most of the N is dissolved and fairly evenly divided between organic and inorganic forms.

8.3.1 The contribution from deciduous tree leaves

In this study it has not been possible to fully test the hypothesis that "*Most of the phosphorus and nitrogen in Sullivan's Creek is derived from the deciduous trees of the catchment*". However, based on the data collected and the (limited) literature available some comments can be made.

McCann and Michael (1995) showed that under low oxygen conditions in distilled water most of the leachable nitrogen and phosphorus in oak leaves was released to the water column in 48 hours. Therefore if deciduous trees were a significant contributor of nutrients it is expected that there would be an increase in nutrient concentrations close to the time of major leaf fall - late Autumn or early winter. This was not observed in the data collected, suggesting that nitrogen and phosphorus concentrations from deciduous leaf fall is not making a significant contribution to the nutrients in the creek. McCann and Michael (1995) also showed that the majority of the phosphorus released from the oak leaves was as dissolved inorganic P (Ortho-P). Although this was solely from leaching and not bacterial breakdown (which may result in the release of some organic forms of P), it indicates that it will not be possible to determine where the dissolved inorganic P in the water column has originated (i.e. both leaching from organic matter and release from mineral sediments produces dissolved inorganic P).

Grass clippings as a major source of P and N for urban stormwater has been flagged by Strynchuck et al (1998) who showed that under anoxic conditions organic matter (grass clippings and leaf litter) breaks down rapidly with the majority of the phosphorus and nitrogen leached into the water column within 1-22 days. This rapid breakdown means that there should be increased levels of both N and P close to times when there are large amounts of grass clippings around. In Sullivan's Creek elevated P concentrations were noted during months (December to April) when there are more grass clippings on ovals, reserves and gardens near the creek suggesting that grass clippings may be a significant source of P. This suggestion has to be discounted as a corresponding increase in N was not observed.

The contribution that organic matter (deciduous leaves and grass clippings) may make to the nutrients in Sullivan's Creek is to increase the organic loads in the GPT and Toad Pond, thus causing reducing conditions which facilitates the release of P from inorganic sediments.

9 Conclusions

Total P concentrations were consistently higher in Sullivan's Creek than in other ACT streams and they exceeded guideline levels for aquatic ecosystems. More than 70% of the phosphorus transported in Sullivan's Creek was in inorganic forms and typically 40-80% of the phosphorus was dissolved. This amount of dissolved phosphorus is unusually high compared with most inland Australian streams. Concentrations of nitrogen in the creek were similar to those measured in other ACT streams but they also exceed the guideline levels for aquatic ecosystems. More than 70% of the N transported in Sullivan's Creek was dissolved and generally 30-60% was in organic form.

The concentration of total P within Sullivan's Creek was observed to have a possible seasonal correlation and was highest during the warmer months. The forms of P within the creek also had a seasonal variation with an increase in the proportion dissolved inorganic P in winter months. N concentrations in Sullivan's creek showed no significant seasonal variation.

The Dickson channel delivered high concentrations of both dissolved and particulate P to the main channel of Sullivan's Creek during the study period. This almost doubled the concentrations of P between Southwell Park and Macarthur Avenue. This channel was not contributing high concentrations of nitrogen.

High flow events, which occur less than 20% of the time, dominate the movement of nitrogen and phosphorus through Sullivan's Creek to Lake Burley Griffin.

The Barry Drive GPT was a major contributor of all forms of P to the ANU reach of Sullivan's Creek during low flow conditions with total P concentrations doubling across the GPT. Toad Pond increases total P in Sullivan's Creek by 10%. On average total N concentration increased by approximately 30% across the GPT and a smaller increase was observed across Toad Pond. This was predominantly due to an increase in particulate nitrogen. Thus for the majority of the time (greater than 80%) the nutrient concentrations in the ANU section of the creek are being elevated by these two features at the upper end of the university.

Bottom sediments in the GPT and Toad Pond are likely to be the main source of the increased concentrations of dissolved P. Experiments using benthic chambers showed that high rates of degradation of organic carbon occur in Toad Pond and oxygen demand of the sediment exceeds the rate at which oxygen can be supplied from the water column. As a result reducing conditions exist in relatively shallow water causing the production of ammonia and the release of dissolved P from the bottom sediments. Measured production of ammonia and dissolved P were considered to be high in Toad Pond although this only made a small contribution to the overall concentrations in the creek compared with the GPT. Observations indicate that it is reasonable to assume that similar processes are driving the production of dissolved nutrients in the GPT.

The increase in particulate P and N concentrations in the water column at the GPT and Toad Pond is most likely due to the resuspension of organic and inorganic sediments as a result of benthic biological activity or the presence of a significant number of ducks. Although unlikely, the possibility that an urban drain or sewer leak were contributing significant amounts of P and N to the GPT could not be discounted.

The increased nutrient concentrations did not appear to coincide with the major leaf fall period suggesting that it is unlikely that deciduous leaves are making a significant contribution to nutrients in the creek. The higher concentrations of P in the creek in warmer months may be the result of greater biological activity (due to both longer and warmer days) in the creek releasing P to the water column, the use of fertilizers on lawns and ovals near the creeks, or an increase of the amount of lawn clippings on the flood plain.

Under low flow conditions (greater than 80% of the time) Lake Burley Griffin dominated the nutrient concentrations along Sullivan's Creek at least to Ward Bridge and possibly further to the Stepping Stones.

During high flows particulate inorganic forms of both P and N dominated the nutrient forms in Sullivan's Creek. This is consistent with higher concentrations of suspended sediment during high flows where the concentrations of nutrients are dominated by those associated with the suspended sediment. A change in sediment and nutrient source from urban to rural was observed during the recession of the main peak flow of a large storm event. At this point of change the concentration of organic P dropped significantly while the concentration of inorganic P remained high and there was a change in the colour and chemistry of the suspended sediment.

10 Management Implications and Options

Problems with the quality of the water in the ANU reach of Sullivan's Creek (e.g. unpleasant smell and dark color) are most evident during low flow conditions. Therefore to obtain maximum improvement in the appeal of the creek, the causes of the poor water quality under low flow conditions (which exist more than 80% of the time) need to be targeted.

The Barry Drive GPT contributes on average over half of the P and one third of the N in the reach of Sullivan's Creek from Barry Drive to the Stepping Stones under low flow conditions. This is a result of the combination of sediment resuspension and anoxic conditions facilitating the release of P to the water column. Toad Pond is a further source of nitrogen and phosphorus for similar reasons, but is less dominant than the GPT. Therefore any attempts to reduce the levels of nutrients in this section of Sullivan's Creek under low flow conditions need to primarily address the nutrient delivery from the GPT but Toad Pond should also be considered in any management plan.

Medium to high flows carry the majority of the sediment and organic matter delivered to the GPT and the ponds within the university grounds. The breakdown of the organic matter delivered during these events results in the release of nutrients to the water column and also facilitates the release of nutrients from the sediments. Therefore nutrient reduction strategies must address sediment and organic matter delivered to the GPT and Toad Pond during such flow events.

As nutrient concentrations in the section of Sullivan's Creek from the Stepping Stones to Lake Burley Griffin are dominated by lake water, attempts to reduce the levels of nutrients in this section of the creek can only be undertaken by reducing nutrients levels in the lake. Obviously Sullivan's Creek contributes nitrogen and phosphorus to Lake Burley Griffin and the majority of these nutrients are delivered during high flows. Therefore, controlling the nutrients delivered by the creek during high flows may contribute to a reduction in nutrient levels in the lake (depending, of course, on the magnitude of other nutrient sources to the lake) and consequently, the lower end of Sullivan's Creek.

Possible options to curb nutrient delivery are:

- more frequent cleaning of the GPT, especially after storms in late autumn to remove organic matter which may be contributing to the high oxygen demand and subsequent reducing conditions;
- occasional cleaning of Toad Pond;
- installation of sediment traps upstream of the GPT to prevent sediment from reaching the GPT and being subject to reducing conditions where it will release P to the water column. Care needs to be taken in the design of such traps to prevent the problem simply being moved upstream;
- installation of high flow sediment traps along main channel of the creek and along the tributaries;
- more regular street cleaning in autumn and summer to minimise the delivery of leaves and grass clippings;

- installation of an aerator in the GPT to increase the levels of oxygen and therefore reduce the release of P to the water column;
- redesign the GPT to be drained under low flows
- pumping water from Lake Burley Griffin during low flow periods to just upstream of the GPT. This would act to 'flush' the system and probably prevent anoxic conditions in the GPT and Toad Pond; and
- discourage the ducks on the ponds within the creek

Although the Dickson drain was identified as delivering larger amounts of P to the main channel of the creek, it makes only a small contribution to the ANU reach of the creek compared with the GPT and is therefore of much lower priority for nutrient reduction activities.

This report has focussed on the sources and forms of nutrients within Sullivan's Creek. There may be other parameters present in the creek, such as bacteria, faecal coliforms and heavy metals, that have a detrimental effect on the quality of the water. It is recommended that the effect of these parameters be investigated as part of any management plan for the creek.

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Appendix A

Sample Code	Date	Location	TRP	DRP	ΤР	TDP	TPP	%DP	%PP	ТОР	TIP	%TOP	%TIP	DOP	POP	PIP	DIP	%DOP	%POP	%PIP	%DIP
SK98001	7-Dec-98	F		7.9	36.7	7.3	29.43	20%	80%						0.00	29.43					
SK98004	7-Dec-98	В		20.7	75.6	35.8	39.73	47%	53%	75.56	0	100%	0%	35.8	39.73	0.00	0.0	47%	53%	0%	0%
SK98005	7-Dec-98	А		3.9	52.0	11.6	40.38	22%	78%	51.98	0	100%	0%	0.0	51.98	0.00	11.6	0%	100%	0%	22%
SK99001	5-Jan-99	D	31.8	6.8	100.8	16.2	84.55	16%	84%	4.92	96	5%	95%		4.92	79.62		0%	5%	79%	0%
SK99003	7-Jan-99	Α	49.3	3.2	116.0	10.5	105.50	9%	91%	0.00	116	0%	100%	0.0	0.00	105.50	10.5	0%	0%	91%	9%
SK99004	7-Jan-99	В	64.3	42.1	111.5	77.5	33.97	70%	30%					0.0	0.00	33.97	77.5	0%	0%	30%	70%
SK99005	7-Jan-99	С	79.6	62.9	108.0	83.4	24.62	77%	23%					0.0	0.00	24.62	83.4	0%	0%	23%	77%
SK99006	7-Jan-99	D	51.4	23.2	131.2	54.1	77.09	41%	59%	0.00	131	0%	100%	0.9	0.00	77.09	53.2	1%	0%	59%	41%
SK99007	7-Jan-99	E	73.6	53.2	124.1	59.3	64.80	48%	52%	0.00	124	0%	100%	0.0	0.00	64.80	59.3	0%	0%	52%	48%
SK99008	7-Jan-99	F	60.7	48.2	88.0	51.0	37.00	58%	42%					51.0			0.0				
SK99009	7-Jan-99	G	217.5	35.7	320.6	54.0	266.64	17%	83%	0.00	321	0%	100%	1.1	0.00	266.64	52.9	0%	0%	83%	16%
SK99010	7-Jan-99	Ι	113.2	92.9	138.8	98.1	40.70	71%	29%					98.1			0.0				
SK99011	7-Jan-99	J	98.9	74.3	150.0	87.1	62.89	58%	42%	0.00	150	0%	100%	87.1			0.0				
SK99012	7-Jan-99	Н	90.4	88.9	145.6	109.5	36.05	75%	25%	0.00	146	0%	100%	6.8	0.00	36.05	102.8	5%	0%	25%	71%
SK99013	18-Feb-99	Α	45.0	23.2	75.1	14.2	60.91	19%	81%	20.81	54	28%	72%	0.0	20.81	40.11	14.2	0%	28%	53%	19%
SK99014	18-Feb-99	В	127.5	60.0	207.5	54.0	153.54	26%	74%	74.60	133	36%	64%	0.4	74.22	79.32	53.6	0%	36%	38%	26%
SK99015	18-Feb-99	С	76.8	36.4	99.9	43.2	56.66	43%	57%	49.29	51	49%	51%	10.2	39.13	17.53	33.0	10%	39%	18%	33%
SK99016	18-Feb-99	D	78.2	45.0	132.5	60.5	71.99	46%	54%	77.12	55	58%	42%	16.0	61.09	10.91	44.5	12%	46%	8%	34%
SK99017	18-Feb-99	Е	70.0	51.4	72.1	42.6	29.50	59%	41%	9.97	62	14%	86%	24.9	0.00	29.50	17.7	35%	0%	41%	24%
SK99018	4-Mar-99	J	108.6	96.8	138.7	114.8	23.92	83%	17%	8.33	130	6%	94%	0.0	8.33	15.59	114.8	0%	6%	11%	83%
SK99019	4-Mar-99	Ι	58.0	50.0	80.5	67.4	13.06	84%	16%	5.52	75	7%	93%	12.9	0.00	13.06	54.5	16%	0%	16%	68%
SK99020	4-Mar-99	Н	62.5	35.4	85.4	53.6	31.85	63%	37%	12.07	73	14%	86%	13.5	0.00	31.85	40.1	16%	0%	37%	47%
SK99021	4-Mar-99	G	33.6	21.8	50.3	41.0	9.37	81%	19%	12.30	38	24%	76%	14.9	0.00	9.37	26.0	30%	0%	19%	52%
SK99022	4-Mar-99	F	30.2	21.4	51.4	42.0	9.35	82%	18%	11.81	40	23%	77%	15.8	0.00	9.35	26.2	31%	0%	18%	51%
SK99023	4-Mar-99	Е	29.6	20.0	60.6	35.4	25.22	58%	42%	9.67	51	16%	84%	12.4	0.00	25.22	23.0	20%	0%	42%	38%
SK99024	4-Mar-99	A1	22.9	7.5	37.1	19.0	18.18	51%	49%	1.46	36	4%	96%	8.6	0.00	18.18	10.3	23%	0%	49%	28%
SK99025	4-Mar-99	А	26.1	2.9	67.5	67.0	0.49	99%	1%	31.29	36	46%	54%	61.2			5.8				
SK99026	4-Mar-99	В	90.0	69.3	169.2	143.2	26.09	85%	15%	42.67	127	25%	75%	52.8	0.00	26.09	90.4	31%	0%	15%	53%

Phosphorus Forms. Concentrations are in $\mu g/L$

Sample Code	Date	Location	TRP	DRP	ТР	TDP	TPP	%DP	%PP	TOP	TIP	%TOP	%TIP	DOP	POP	PIP	DIP	%DOP	%POP	%PIP	%DIP
SK99027	4-Mar-99	С	106.1	71.1	175.7	107.9	67.87	61%	39%	35.31	140	20%	80%	21.6	13.69	54.18	86.3	12%	8%	31%	49%
SK99028	4-Mar-99	D	105.0	79.6	169.4	128.9	40.50	76%	24%	80.47	89	48%	52%	33.6	46.84	-6.34	95.2	20%	28%	-4%	56%
SK99029	18-Mar-99	A1	16.8	3.1	36.7	13.8	22.93	38%	62%	27.56	9	75%	25%	13.8	13.80	9.13	0.0	38%	38%	25%	0%
SK99030	18-Mar-99	Α	31.2	5.6	95.9	21.5	74.36	22%	78%	47.28	49	49%	51%	21.5	25.78	48.58	0.0	22%	27%	51%	0%
SK99031	18-Mar-99	В	143.8	58.3	245.9	72.6	173.32	30%	70%	72.58	173	30%	70%	0.0	72.58	100.74	72.6	0%	30%	41%	30%
SK99032	18-Mar-99	С	120.5	87.5	179.1	96.8	82.25	54%	46%	43.39	136	24%	76%	8.6	34.83	47.42	88.3	5%	19%	26%	49%
SK99033	18-Mar-99	D	90.3	39.9	215.5	68.7	146.85	32%	68%	97.74	118	45%	55%	37.3	60.42	86.43	31.4	17%	28%	40%	15%
SK99034	18-Mar-99	Е	51.4	35.1	68.2	50.6	17.56	74%	26%					23.0			27.6				
SK99059	1-Apr-99	L	1165.4	1165	1165.4	1165.0	0.40	100%	0%	0.00	1165	0%	100%	0.0	0.00	0.40	1165.0	0%	0%	0%	100%
SK99060	1-Apr-99	K	16.3	12.4	30.2	15.6	14.61	52%	48%	13.66	17	45%	55%	15.6	0.00	14.61	0.0	52%	0%	48%	0%
SK99061	1-Apr-99	J	85.1	79.7	106.3	95.7	10.66	90%	10%	19.63	87	18%	82%	6.9	12.76	0.00	88.8	6%	12%	0%	84%
SK99062	1-Apr-99	I	41.0	37.7	63.9	56.9	7.03	89%	11%	2.28	62	4%	96%	0.0	2.28	4.76	56.9	0%	4%	7%	89%
SK99063	1-Apr-99	Н	52.8	48.6	73.9	69.9	3.95	95%	5%	12.83	61	17%	83%	0.8	12.03	0.00	69.1	1%	16%	0%	94%
SK99064	1-Apr-99	G	37.1	16.3	54.0	41.9	12.10	78%	22%	0.00	54	0%	100%	0.0	0.00	12.10	41.9	0%	0%	22%	78%
SK99065	1-Apr-99	Е	37.4	36.6	46.1	46.1	0.05	100%	0%	1.30	45	3%	97%	1.8	0.00	0.05	44.2	4%	0%	0%	96%
SK99066	1-Apr-99	D	89.8	47.0	126.4	74.6	51.77	59%	41%	20.05	106	16%	84%	0.0	20.05	31.72	74.6	0%	16%	25%	59%
SK99067	1-Apr-99	С	70.0	38.9	92.7	56.6	36.11	61%	39%	10.99	82	12%	88%	0.0	10.99	25.12	56.6	0%	12%	27%	61%
SK99068	1-Apr-99	В	81.3	33.1	103.1	51.9	51.21	50%	50%	23.76	79	23%	77%	0.0	23.76	27.45	51.9	0%	23%	27%	50%
SK99069	1-Apr-99	Α	40.4	18.9	58.8	35.6	23.21	61%	39%					12.5			23.1				
SK99070	1-Apr-99	A1	23.9	6.9	50.5	15.2	35.26	30%	70%	36.52	14	72%	28%	0.0	36.52	0.00	15.2	0%	72%	0%	30%
SK99071	15-Apr-99	A1	32.7	19.5	33.6	20.0	13.60	60%	40%	0.01	34	0%	100%	0.0	0.01	13.59	20.0	0%	0%	40%	60%
SK99072	15-Apr-99	Α	30.9	16.2	40.9	18.2	22.68	45%	55%	5.71	35	14%	86%	0.0	5.71	16.97	18.2	0%	14%	42%	45%
SK99073	15-Apr-99	В	59.2	15.1	67.5	38.6	28.94	57%	43%	9.92	58	15%	85%	17.0	0.00	28.94	21.6	25%	0%	43%	32%
SK99074	15-Apr-99	С	60.3	30.1	73.8	62.4	11.35	85%	15%	12.14	62	16%	84%	0.0	12.14	0.00	62.4	0%	16%	0%	85%
SK99075	15-Apr-99	D	82.7	72.4	107.4	98.1	9.34	91%	9%	21.34	86	20%	80%	25.4	0.00	9.34	72.7	24%	0%	9%	68%
SK99076	15-Apr-99	Е	55.3	35.3	66.9	58.7	8.15	88%	12%	4.30	63	6%	94%	7.0	0.00	8.15	51.7	10%	0%	12%	77%
SK99077	8/07/99	A1	7.8		14.8		14.83			5.20	10	35%	65%	0.0	5.20	9.63	0.0	0%	35%	65%	0%
SK99078	8/07/99	Α	6.8		22.5		22.51			5.22	17	23%	77%	0.0	5.22	17.29	0.0	0%	23%	77%	0%
SK99079	8/07/99	В	59.4		58.9		58.94			3.23	56	5%	95%	0.0	3.23	55.71	0.0	0%	5%	95%	0%

Sample Code	Date	Location	TRP	DRP	TP	TDP	TPP	%DP	%PP	ТОР	TIP	%TOP	%TIP	DOP	POP	PIP	DIP	%DOP	%POP	%PIP	%DIP
SK99080	8/07/99	С	66.7		73.4		73.37			0.52	73	1%	99%	0.0	0.52	72.85	0.0	0%	1%	99%	0%
SK99081	8/07/99	D	96.9		124.0		123.97							0.0			0.0				
SK99082	8/07/99	D1	137.0		141.6		141.60			0.00	142	0%	100%	0.0	0.00	141.60	0.0	0%	0%	100%	0%
SK99083	8/07/99	Е	26.4		40.1		40.11			7.71	32	19%	81%	0.0	7.71	32.40	0.0	0%	19%	81%	0%
SK99084	26/07/99	A1	14.9	5.9	19.8	12.5	7.25	63%	37%	1.55	18	8%	92%	5.1	0.00	7.25	7.4	26%	0%	37%	38%
SK99085	26/07/99	Α	24.3	26.0	38.7	35.5	3.19	92%	8%	9.38	29	24%	76%	5.1	4.24	0.00	30.4	13%	11%	0%	78%
SK99086	26/07/99	В	47.0	40.3	73.2	43.0	30.19	59%	41%	39.77	33	54%	46%	1.0	38.75	0.00	42.0	1%	53%	0%	57%
SK99087	26/07/99	С	72.9	63.5	43.3	39.5	3.84	91%	9%	8.73	35	20%	80%								
SK99088	26/07/99	D	60.1	48.3	78.0	61.9	16.01	79%	21%	8.87	69	11%	89%	7.2	1.64	14.37	54.7	9%	2%	18%	70%
SK99089	26/07/99	D1	127.8	105.9	114.7	114.7	0.00	100%	0%	0.00	115	0%	100%	0.0	0.00	0.00	114.7	0%	0%	0%	100%
SK99090	26/07/99	Е	21.2	24.0	36.0	30.6	5.37	85%	15%	8.05	28	22%	78%	1.8	6.28	0.00	28.8	5%	17%	0%	80%
SK99091	26/07/99	G	33.0	31.9	43.8	35.1	8.66	80%	20%	6.08	38	14%	86%	1.0	5.11	3.55	34.1	2%	12%	8%	78%
SK99092	26/07/99	Н	36.5	34.7	48.6	47.5	1.13	98%	2%	8.38	40	17%	83%	9.3	0.00	1.13	38.2	19%	0%	2%	79%
SK99093	26/07/99	I	82.6	64.2	68.9	68.9	0.00	100%	0%	12.96	56	19%	81%	0.0	12.96	0.00	68.9	0%	19%	0%	100%
SK99094	26/07/99	J	107.5	109.7	129.9	105.5	24.38	81%	19%	22.71	107	17%	83%	3.8	18.86	5.51	101.7	3%	15%	4%	78%
SK99095	26/07/99	K	29.2	22.6	43.7	31.2	12.55	71%	29%	10.99	33	25%	75%	3.7	7.25	5.30	27.5	9%	17%	12%	63%
SK99096	26/07/99	L	72.0	51.0	81.5	63.8	17.73	78%	22%	8.38	73	10%	90%	12.2	0.00	17.73	51.6	15%	0%	22%	63%
SK99097	10/08/99	A1	25.0	16.2	41.6	29.8	11.77	72%	28%	41.62	0	100%	0%	29.8	11.77	0.00	0.0	72%	28%	0%	0%
SK99098	10/08/99	Α	39.5	26.7	56.3	37.2	19.11	66%	34%	56.34	0	100%	0%	37.2	19.11	0.00	0.0	66%	34%	0%	0%
SK99099	10/08/99	В	41.2	31.1	57.5	49.4	8.16	86%	14%	57.54	0	100%	0%	49.4	8.16	0.00	0.0	86%	14%	0%	0%
SK99100	10/08/99	С	90.2	66.6	123.3	95.5	27.73	78%	22%	123.3	0	100%	0%	95.5	27.73	0.00	0.0	78%	22%	0%	0%
SK99101	10/08/99	D	59.1	45.9	86.4	65.1	21.32	75%	25%	86.42	0	100%	0%	65.1	21.32	0.00	0.0	75%	25%	0%	0%
SK99102	10/08/99	D1	96.6	66.9	147.0	92.4	54.64	63%	37%	0.00	147	0%	100%								
SK99103	10/08/99	Е	500.3	501.4	724.8	572.8	152.00	79%	21%	0.00	725	0%	100%	0.0	0.00	152.00	572.8	0%	0%	21%	79%
SK99111	6/09/99	A1	34.6	39.5	78.9	77.3	1.55	98%	2%	16.88	62	21%	79%	19.9	0.00	1.55	57.4	25%	0%	2%	73%
SK99112	6/09/99	Α	30.5	24.9	90.0	64.4	25.55	72%	28%	0.25	90	0%	100%								
SK99113	6/09/99	В	41.4	65.9	107.0	107.0	0.00	100%	0%	17.02	90	16%	84%								
SK99114	6/09/99	С	60.0	42.2	82.9	49.2	33.72	59%	41%					49.2			0.0	59%	0%	0%	0%
SK99115	6/09/99	D	59.7	53.5	112.3	95.8	16.48	85%	15%	0.00	112	0%	100%	9.5	0.00	16.48	86.3	8%	0%	15%	77%

Sample Code	Date	Location	TRP	DRP	ТР	TDP	TPP	%DP	%PP	TOP	TIP	%TOP	%TIP	DOP	POP	PIP	DIP	%DOP	%POP	%PIP	%DIP
SK99116	6/09/99	D1	67.6	77.6	114.8	114.8	0.00	100%	0%	51.40	63	45%	55%								
SK99117	6/09/99	Е	61.6	55.4	104.7	104.7	0.00	100%	0%	9.29	95	9%	91%	0.0	9.29	-9.29	104.7	0%	9%	-9%	100%
SK99118	16/09/99	A1	9.2	7.6	10.6	10.0	0.60	94%	6%	0.00	11	0%	100%	0.0	0.00	0.60	10.0	0%	0%	6%	94%
SK99119	16/09/99	Α	16.2	6.7	42.4	15.8	26.54	37%	63%	15.71	27	37%	63%	0.6	15.15	11.39	15.3	1%	36%	27%	36%
SK99120	16/09/99	В	17.6	6.7	38.0	10.9	27.06	29%	71%	9.90	28	26%	74%	0.0	9.90	17.16	10.9	0%	26%	45%	29%
SK99121	16/09/99	С	26.7	15.3	50.5	31.7	18.75	63%	37%	13.40	37	27%	73%	4.8	8.61	10.14	26.9	9%	17%	20%	53%
SK99122	16/09/99	D	35.9	12.0	59.4	19.0	40.41	32%	68%	5.20	54	9%	91%	0.0	5.20	35.21	19.0	0%	9%	59%	32%
SK99123	16/09/99	D1	28.4	17.3	71.3	38.9	32.41	55%	45%	21.60	50	30%	70%	2.8	18.79	13.61	36.1	4%	26%	19%	51%
SK99125	16/09/99	E	161.5	117.0	265.2	158.5	106.71	60%	40%	234.1	31	88%	12%	2.7	231.44		155.8	1%	87%	0%	59%
SK99126	16/09/99	G	177.8	149.2	360.2	263.0	97.20	73%	27%	0.00	360	0%	100%	0.0	0.00	97.20	263.0	0%	0%	27%	73%
SK99127	16/09/99	Н	107.8	77.3	182.0	110.8	71.20	61%	39%	0.00	182	0%	100%	0.0	0.00	71.20	110.8	0%	0%	39%	61%
SK99129	16/09/99	I	173.7	130.1	264.6	183.0	81.60	69%	31%	0.00	265	0%	100%	0.0	0.00	81.60	183.0	0%	0%	31%	69%
SK99130	16/09/99	J	85.1	71.0	130.2	84.3	45.86	65%	35%	0.00	130	0%	100%	6.8	0.00	45.86	77.5	5%	0%	35%	60%
SK99131	16/09/99	K	98.4	64.8	189.0	80.1	108.90	42%	58%	16.22	173	9%	91%								
SK99132	16/09/99	L	112.6	56.2	147.1	69.1	78.06	47%	53%	15.75	131	11%	89%								
SK99149	30/09/99	E	11.11	3.47	41.17	4.33	36.85	11%	89%	19.42	22	47%	53%	0.5	18.91	17.94	3.8	1%	46%	44%	9%
SK99150	30/09/99	D1	26.04	10.42	84.54	11.87	72.67	14%	86%	34.61	50	41%	59%	1.7	32.95	39.73	10.2	2%	39%	47%	12%
SK99151	30/09/99	D	62.85	37.50	105.07	29.40	75.67	28%	72%	22.02	83	21%	79%	0.0	22.02	53.66	29.4	0%	21%	51%	28%
SK99152	30/09/99	С	59.03	40.63	93.62	38.05	55.57	41%	59%	15.50	78	17%	83%	1.3	14.20	41.37	36.8	1%	15%	44%	39%
SK99153	30/09/99	В	52.43	27.78	84.57	33.55	51.03	40%	60%	27.96	57	33%	67%	10.3	17.66	33.37	23.2	12%	21%	39%	27%
SK99154	30/09/99	Α	56.60	30.90	76.67	36.11	40.57	47%	53%	7.02	70	9%	91%	18.9	0.00	40.57	17.2	25%	0%	53%	22%
SK99155	30/09/99	A1	42.71	7.29	55.43	9.78	45.66	18%	82%	15.28	40	28%	72%	4.9	10.39	35.26	4.9	9%	19%	64%	9%
SK99156	14/10/99	A1	31.3	7.3	44.4	5.0	39.45	11%	89%	13.05	31	29%	71%	0.0	13.05	26.40	5.0	0%	29%	59%	11%
SK99157	14/10/99	Α	70.5	41.8	79.9	52.9	27.04	66%	34%	7.73	72	10%	90%								
SK99158	14/10/99	В	68.8	45.8	80.8	43.0	37.73	53%	47%	7.95	73	10%	90%								
SK99159	14/10/99	С	62.5	42.0	85.5	38.9	46.62	45%	55%	15.17	70	18%	82%								
SK99160	14/10/99	D	51.4	37.8	90.4	24.7	65.73	27%	73%	23.30	67	26%	74%	24.7	0.00	65.73	0.0	27%	0%	73%	0%
SK99161	14/10/99	D1	79.9	64.2		66.2									0.00	0.00					
SK99162	14/10/99	Е	20.7	5.2	39.7	5.5	34.21	14%	86%	8.73	31	22%	78%	0.0	8.73	25.48	5.5	0%	22%	64%	14%

Sample Code	Date	Location	TRP	DRP	TP	TDP	TPP	%DP	%PP	TOP	TIP	%TOP	%TIP	DOP	POP	PIP	DIP	%DOP	%POP	%PIP	%DIP
SK99163	14/10/99	G	23.3	5.6	49.4	6.5	42.88	13%	87%	17.00	32	34%	66%	0.0	17.00	25.88	6.5	0%	34%	52%	13%
SK99164	14/10/99	Н	29.5	15.6	34.6	26.3	8.31	76%	24%	-0.01	35	0%	100%	0.0	n/a	8.31	26.3	0%		24%	76%
SK99165	14/10/99	I	35.4	11.8	48.7	13.6	35.06	28%	72%	3.89	45	8%	92%	0.0	3.89	31.17	13.6	0%	8%	64%	28%
SK99166	14/10/99	J	150.3	35.8	103.1	25.3	77.85	25%	75%	3.04	100	3%	97%								
SK99167	14/10/99	K	30.0	5.2	43.3	8.2	35.07	19%	81%	5.21	38	12%	88%	0.0	5.21	29.85	8.2	0%	12%	69%	19%
SK99168	14/10/99	L	25.3	5.9	36.3	10.0	26.34	28%	72%	4.67	32	13%	87%	0.0	4.67	21.67	10.0	0%	13%	60%	28%
SK99170	28/10/99	D1	87.2	46.2	126.8	50.1	76.73	39%	61%	65.17	62	51%	49%	33.5	31.65	45.07	16.6	26%	25%	36%	13%
SK99171	28/10/99	D	99.3	76.4	127.6	93.7	33.95	73%	27%	20.56	107	16%	84%	14.9	5.65	28.30	78.8	12%	4%	22%	62%
SK99172	28/10/99	С	94.4	55.4	116.0	55.6	60.47	48%	52%	16.42	100	14%	86%	6.8	9.66	50.81	48.8	6%	8%	44%	42%
SK99173	28/10/99	В	94.4	51.0	112.6	90.8	21.79	81%	19%	6.70	106	6%	94%	9.0	0.00	21.79	81.9	8%	0%	19%	73%
SK99174	28/10/99	Α	98.6	42.7	97.5	51.6	45.87	53%	47%	0.00	98	0%	100%	23.5			28.2				
SK99175	28/10/99	A1	90.4	12.2	82.2	24.4	57.77	30%	70%	29.01	53	35%	65%	20.6	8.45	49.31	3.8	25%	10%	60%	5%
SK99207	11/11/99	A1	58.7	7.3	61.59	14.85	46.74	24%	76%	16.06	46	26%	74%	6.1	9.99	36.75	8.8	10%	16%	60%	14%
SK99208	11/11/99	Α	66.3	14.6	153.42	79.54	73.88	52%	48%	83.73	70	55%	45%	48.4	35.36	38.52	31.2	32%	23%	25%	20%
SK99209	11/11/99	В	111.6	29.9	141.78	64.56	77.22	46%	54%	49.53	92	35%	65%	32.1	17.41	59.81	32.4	23%	12%	42%	23%
SK99210	11/11/99	С	88.2	38.5	116.81	105.62	11.19	90%	10%	41.91	75	36%	64%	67.4			38.2				
SK99211	11/11/99	D	87.2	36.3	132.25	89.05	43.20	67%	33%	60.08	72	45%	55%	52.6	7.51	35.69	36.5	40%	6%	27%	28%
SK99212	11/11/99	D1	19.8	0.3	62.17	12.17	50.00	20%	80%	39.26	23	63%	37%	11.7	27.56	22.44	0.5	19%	44%	36%	1%
SK99213	11/11/99	Е	10.4	4.2	38.30	16.98	21.33	44%	56%	24.60	14	64%	36%	10.8	13.78	7.55	6.2	28%	36%	20%	16%
SK99214	11/11/99	G	12.5	5.9	29.06	17.97	11.09	62%	38%	14.87	14	51%	49%	9.4	5.48	5.61	8.6	32%	19%	19%	30%
SK99215	11/11/99	Н	12.0	4.9	32.00	24.98	7.02	78%	22%	16.44	16	51%	49%	19.1	0.00	7.02	5.9	60%	0%	22%	18%
SK99216	11/11/99	I	11.1	3.5	38.06	18.68	19.37	49%	51%	20.00	18	53%	47%	13.2	6.82	12.56	5.5	35%	18%	33%	14%
SK99217	11/11/99	J	24.0	4.9	50.41	15.63	34.77	31%	69%	26.13	24	52%	48%	9.5	16.59	18.18	6.1	19%	33%	36%	12%
SK99218	11/11/99	K	7.3	2.8	32.21	6.85	25.36	21%	79%	21.57	11	67%	33%	1.9	19.68	5.68	5.0	6%	61%	18%	15%
SK99219	11/11/99	L	6.3	1.4	27.60	16.04	11.56	58%	42%	19.13	8	69%	31%	12.3	6.88	4.69	3.8	44%	25%	17%	14%
[-																			
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Sample Code	Sample Date	Location	TDN	TN	TPN	NOx-N	NH_4 -N	DON	DIN	%DON	%DIN	%TPN	%organic								
SK99001	5-Jan-99	F	680	950	270			680		72%	0%	28%	100%								
SK99003	7-Jan-99	Α		1100		0	10		11												
SK99004	7-Jan-99	В		800		0	54		54												
SK99005	7-Jan-99	С		700		6	226		231												
SK99006	7-Jan-99	D		870		5	5		10												
SK99007	7-Jan-99	E		870		28	11		40												
SK99008	7-Jan-99	F				6	13		20												
SK99009	7-Jan-99	G		2300		1425	61		1486												
SK99010	7-Jan-99	I		1200		0	29		29												
SK99011	7-Jan-99	J		660		0	27		27												
SK99012	7-Jan-99	Н		920		0	25		25												
SK99013	18-Feb-99	Α	380	550	170	10	14	356	24	65%	4%	31%	94%								
SK99014	18-Feb-99	В	450	810	360	0	77	373	77	46%	10%	44%	83%								
SK99015	18-Feb-99	С	530	570	40	7	167	356	174	62%	31%	7%	67%								
SK99016	18-Feb-99	D	470	810	340	52	102	316	154	39%	19%	42%	67%								
SK99017	18-Feb-99	E	1800	1900	100	1391	21	388	1412	20%	74%	5%	22%								
SK99018	4-Mar-99	J	650	650	0	127	13	510	140	78%	22%	0%	78%								
SK99019	4-Mar-99	I	600	680	80	195	16	390	210	57%	31%	12%	65%								
SK99020	4-Mar-99	Н	710	770	60	265	16	429	281	56%	36%	8%	60%								
SK99021	4-Mar-99	G	900	940	40	457	13	430	470	46%	50%	4%	48%								
SK99022	4-Mar-99	F	790	820	30	272	14	504	286	61%	35%	4%	64%								
SK99023	4-Mar-99	E	690	830	140	200	12	478	212	58%	25%	17%	69%								
SK99024	4-Mar-99	A1	570	580	10	36	17	517	53	89%	9%	2%	91%								
SK99025	4-Mar-99	Α	570	660	90	3	11	556	14	84%	2%	14%	98%								
SK99026	4-Mar-99	В	1100	1200	100	0	11	1089	11	91%	1%	8%	99%								
SK99027	4-Mar-99	С	660	1000	340	4	25	631	29	63%	3%	34%	96%								
SK99028	4-Mar-99	D	900	1200	300	3	15	883	17	74%	1%	25%	98%								
SK99029	18-Mar-99	A1	440	510	70	79	10	351	89	69%	17%	14%	80%								
SK99030	18-Mar-99	Α	330	660	330	31	1	298	32	45%	5%	50%	90%								
SK99031	18-Mar-99	В	570	1300	730	13	45	512	58	39%	4%	56%	90%								

Nitrogen forms. Concentrations are in μ g/L

Sample Code	Sample Date	Location	TDN	TN	TPN	NOx-N	NH ₄ -N	DON	DIN	%DON	%DIN	%TPN	%organic
SK99032	18-Mar-99	С	820	1100	280	44	293	482	338	44%	31%	25%	59%
SK99033	18-Mar-99	D	710	1600	890	18	164	527	183	33%	11%	56%	74%
SK99034	18-Mar-99	E	570	600	30	37	39	493	77	82%	13%	5%	87%
SK99059	1-Apr-99	L	590	630	40	5	134	452	138	72%	22%	6%	77%
SK99060	1-Apr-99	K	400	440	40	123	227	50	350	11%	79%	9%	13%
SK99061	1-Apr-99	J	650	650	0	257	231	162	488	25%	75%	0%	25%
SK99062	1-Apr-99	I	470	500	30	145	225	99	371	20%	74%	6%	21%
SK99063	1-Apr-99	Н	565	656	91	163	254	149	416	23%	63%	14%	26%
SK99064	1-Apr-99	G	345	345	0	68	205	71	274	21%	79%	0%	21%
SK99065	1-Apr-99	E	370	380	10	69	227	74	296	20%	78%	3%	20%
SK99066	1-Apr-99	D	570	750	180	34	398	137	433	18%	58%	24%	24%
SK99067	1-Apr-99	С	560	560	0	67	397	96	464	17%	83%	0%	17%
SK99068	1-Apr-99	В	590	740	150	27	514	49	541	7%	73%	20%	8%
SK99069	1-Apr-99	Α	270	370	100	47	234	0	281	0%	76%	27%	0%
SK99070	1-Apr-99	A1	440	520	80	77	228	135	305	26%	59%	15%	31%
SK99071	15-Apr-99	A1	287	385	97	80	303		383			25%	0%
SK99072	15-Apr-99	Α	280	644	364	57	270		327			57%	0%
SK99073	15-Apr-99	В	304	421	117	39	258	7	298	2%	71%	28%	2%
SK99074	15-Apr-99	С	478	478	0	80	230	168	310	35%	65%	0%	35%
SK99075	15-Apr-99	D	614	1047	433	23	324	267	347	26%	33%	41%	44%
SK99076	15-Apr-99	E		716		22	156		177				
SK99077	8-Jul-99	A1				120	53		173				
SK99078	8-Jul-99	Α				25	38		63				
SK99079	8-Jul-99	В				261	273		534				
SK99080	8-Jul-99	С				459	322		781				
SK99081	8-Jul-99	D				431	473		904				
SK99082	8-Jul-99	D1				455	341		797				
SK99083	8-Jul-99	E				104	62		166				
SK99084	26-Jul-99	A1				181	108		289				
SK99085	26-Jul-99	Α				138	103		241				

Sample Code	Sample Date	Location	TDN	TN	TPN	NOx-N	NH ₄ -N	DON	DIN	%DON	%DIN	%TPN	%organic
SK99086	26-Jul-99	В				205	138		343				
SK99087	26-Jul-99	С				323	140		463				
SK99088	26-Jul-99	D				258	251		510				
SK99089	26-Jul-99	D1				112	177		289				
SK99090	26-Jul-99	E				476	74		550				
SK99091	26-Jul-99	G				612	83		695				
SK99092	26-Jul-99	Н				868	80		948				
SK99093	26-Jul-99	I				656	76		732				
SK99094	26-Jul-99	J				637	76		712				
SK99095	26-Jul-99	K				193	104		297				
SK99096	26-Jul-99	L				54	71		126				
SK99097	10-Aug-99	A1				233	51		284				
SK99098	10-Aug-99	Α				253	38		291				
SK99099	10-Aug-99	В				301	43		345				
SK99100	10-Aug-99	С				465	88		553				
SK99101	10-Aug-99	D				425	99		524				
SK99102	10-Aug-99	D1				639	96		735				
SK99103	10-Aug-99	E				422	1796		2218				
SK99111	6-Sep-99	A1				264	40		304				
SK99112	6-Sep-99	Α				243	64		307				
SK99113	6-Sep-99	В				287	84		371				
SK99114	6-Sep-99	С				393	121		514				
SK99115	6-Sep-99	D				314	238		553				
SK99116	6-Sep-99	D1				333	500		832				
SK99117	6-Sep-99	E				297	227		524				
SK99149	30-Sep-99	E	331	564	233	18	7	307	25	54%	4%	41%	92%
SK99150	30-Sep-99	D1	560	1041	481	65	15	479	81	46%	8%	46%	86%
SK99151	30-Sep-99	D	805	1231	426	95	79	630	175	51%	14%	35%	78%
SK99152	30-Sep-99	С	722	886	164	60	33	629	93	71%	11%	18%	87%
SK99153	30-Sep-99	В	633	788	156	47	24	562	71	71%	9%	20%	89%

Sample Code	Sample Date	Location	TDN	ΤN	TPN	NOx-N	NH ₄ -N	DON	DIN	%DON	%DIN	%TPN	%organic
SK99154	30-Sep-99	Α	618	726	109	117	49	452	166	62%	23%	15%	73%
SK99155	30-Sep-99	A1	687	999	312	148	99	440	247	44%	25%	31%	64%
SK99156	14-0ct-99	A1	834	1235	400	140	152	543	292	44%	24%	32%	65%
SK99157	14-0ct-99	Α	787	1040	254	109	175	503	284	48%	27%	24%	64%
SK99158	14-0ct-99	В	1007	1145	138	117	307	583	424	51%	37%	12%	58%
SK99159	14-0ct-99	С	1010	1211	201	286	226	497	513	41%	42%	17%	49%
SK99160	14-0ct-99	D	1086	1336	250	239	284	564	523	42%	39%	19%	52%
SK99161	14-0ct-99	D1	1634	2018	384	631	206	796	838	39%	42%	19%	49%
SK99162	14-0ct-99	E	613	1008	395	141	12	459	153	46%	15%	39%	75%
SK99163	14-0ct-99	G	787	926	139	334	14	439	348	47%	38%	15%	56%
SK99164	14-0ct-99	Н	880	1054	173	366	12	503	378	48%	36%	16%	57%
SK99165	14-0ct-99	I	884	1056	172	380	14	489	394	46%	37%	16%	55%
SK99166	14-0ct-99	J	1092	1619	527	551	19	522	570	32%	35%	33%	48%
SK99167	14-0ct-99	K	1027	1382	355	628	14	385	642	28%	46%	26%	37%
SK99168	14-0ct-99	L	563	1016	453	65	16	481	82	47%	8%	45%	85%
SK99170	28-0ct-99	D1	901	1664	763	121	197	583	318	35%	19%	46%	65%
SK99171	28-0ct-99	D	970	1735	765	171	239	560	410	32%	24%	44%	58%
SK99172	28-0ct-99	С	859	1328	469	106	145	607	252	46%	19%	35%	71%
SK99173	28-0ct-99	В	984	1697	713	159	175	650	334	38%	20%	42%	66%
SK99174	28-0ct-99	Α	910	1212	302	230	164	516	394	43%	32%	25%	57%
SK99175	28-0ct-99	A1	902	1113	211	400	174	328	574	29%	52%	19%	36%
SK99207	11-Nov-99	A1	969	1135	166	474	30	465	504	41%	44%	15%	48%
SK99208	11-Nov-99	Α	566	1484	918	163	11	392	174	26%	12%	62%	69%
SK99209	11-Nov-99	В	923	979	56	126	256	541	382	55%	39%	6%	59%
SK99210	11-Nov-99	С	941	1129	188	252	220	469	472	42%	42%	17%	50%
SK99211	11-Nov-99	D	830	1328	498	313	288	229	601	17%	45%	38%	28%
SK99212	11-Nov-99	D1	617	753	136	300	3	313	304	42%	40%	18%	51%
SK99213	11-Nov-99	E	264	476	211	23	6	235	30	49%	6%	44%	89%
SK99214	11-Nov-99	G	296	379	83	41	10	245	50	65%	13%	22%	83%
SK99215	11-Nov-99	Н	288	446	158	22	6	260	28	58%	6%	35%	90%

Sample Code	Sample Date	Location	TDN	ΤN	TPN	NOx-N	NH ₄ -N	DON	DIN	%DON	%DIN	%TPN	%organic
SK99216	11-Nov-99	I	241	384	143	22	6	214	27	56%	7%	37%	89%
SK99217	11-Nov-99	J	251	380	130	30	4	217	34	57%	9%	34%	86%
SK99218	11-Nov-99	K	462	620	158	213	2	247	215	40%	35%	25%	54%
SK99219	11-Nov-99	L	198	198	0	5	0	193	5	98%	2%	0%	98%

Sample Code	Date	Time	Location	TP	TDP	TPP	DOP	POP	PIP	DIP	% DP	% PP	%DOP	% POP	% PIP	% DIP
SK99035	19-Mar-99	13:10	А	68	14	54	5	13	41	9	20%	80%	8%	19%	61%	13%
SK99037	19-Mar-99	13:40	А	82	28	54	0	22	32	28	34%	66%	0%	27%	39%	34%
SK99039	19-Mar-99	14:10	А	90	18	72	0	0	72	18	20%	80%	0%	0%	80%	20%
SK99041	19-Mar-99	14:40	Α	91	14	77	0	33	44	14	15%	85%	0%	36%	48%	15%
SK99043	19-Mar-99	15:10	А	87	22	65	12	17	48	10	25%	75%	14%	19%	55%	12%
SK99045	19-Mar-99	15:40	Α	128	68	60	0	46	14	68	53%	47%	0%	36%	11%	53%
SK99047	19-Mar-99	16:10	А	126	97	29	40	0	29	57	77%	23%	32%	0%	23%	45%
SK99049	19-Mar-99	16:40	Α	112	61	51					55%	45%	0%	0%	0%	0%
SK99051	19-Mar-99	17:10	А	128	118	10	48	0	9	71	92%	8%	37%	0%	7%	55%
SK99053	19-Mar-99	18:10	А	156	156	0					100%	0%	0%	0%	0%	0%
SK99055	19-Mar-99	19:10	А	170	124	46					73%	27%	0%	0%	0%	0%
SK99036	19-Mar-99	13:15	С	147	86	60	6	1	59	80	59%	41%	4%	1%	40%	55%
SK99038	19-Mar-99	13:45	С	157	88	69	3	32	36	85	56%	44%	2%	20%	23%	54%
SK99040	19-Mar-99	14:15	С	177	72	105	9	0	105	63	40%	60%	5%	0%	59%	36%
SK99042	19-Mar-99	14:45	С	215	137	78	40	54	24	97	64%	36%	19%	25%	11%	45%
SK99044	19-Mar-99	15:15	С	179	58	122	1	78	44	56	32%	68%	1%	43%	24%	31%
SK99046	19-Mar-99	15:45	С	192	81	111	0	58	53	81	42%	58%	0%	30%	28%	42%
SK99048	19-Mar-99	16:15	С	176	135	41	0	33	8	135	77%	23%	0%	19%	5%	77%
SK99050	19-Mar-99	16:45	С	218	102	116	0	87	29	102	47%	53%	0%	40%	13%	47%
SK99052	19-Mar-99	17:15	С	172	43	129					25%	75%	0%	0%	0%	0%
SK99054	19-Mar-99	18:15	С	199	120	79	0	61	18	120	60%	40%	0%	30%	9%	60%
SK99056	19-Mar-99	19:15	С	169	82	87					49%	51%	0%	0%	0%	0%

Phosphorus forms during the rain event 19/3/99. Concentrations are in $\mu\text{g/L}$

Sample Code	Location	Date and Time	TRP	DRP	TP	TDP	TPP	%TDP	%TPP	TOP	TIP	DOP	POP	PIP	DIP	%TOP	%TIP	%DOP	%POP	%PIP	%DIP
SK99121	С	16/09/99 11:00	27	15	50	32	19	63%	37%	13	37	5	9	10	27	27%	73%	9%	17%	20%	53%
SK99124	С	16/09/99 12:50	76	40	150	62	89	41%	59%	46	104	6	40	49	55	31%	69%	4%	26%	33%	37%
SK99128	С	16/09/99 13:50	104	64	187	93	94	50%	50%	10	177	0	10	84	93	5%	95%	0%	5%	45%	50%
SK99133	С	16/09/99 15:04	125	93	232	115	117	50%	50%	18	214	0	18	99	115	8%	92%	0%	8%	43%	50%
SK99134	C	16/09/99 15:53	119	100	202	103	99	51%	49%	52	149	0	52	46	103	26%	74%	0%	26%	23%	51%
SK99135	С	16/09/99 16:50	93	69	108	60	49	55%	45%	0	108	0	0	49	60	0%	100%	0%	0%	45%	55%
SK99136	С	16/09/99 17:50	95	63	103	50	53	48%	52%	7	96	7	0	53	43	7%	93%	7%	0%	52%	42%
SK99137	С	16/09/99 18:50	113	62	127	63	64	50%	50%	8	119	6	2	62	58	6%	94%	4%	2%	49%	45%
SK99138	С	16/09/99 19:50	139	57	149	48	101	32%	68%	63	86	15	48	53	33	42%	58%	10%	32%	35%	22%
SK99139	С	16/09/99 20:50	365	60	365	77	288	21%	79%	0	365	0	0	288	77	0%	100%	0%	0%	79%	21%
SK99140	С	16/09/99 21:50	209	66	411	74	337	18%	82%	130	281	0	130	207	74	32%	68%	0%	32%	50%	18%
SK99141	С	16/09/99 22:50	184	75	199	85	114	43%	57%	0	199	0	0	114	85	0%	100%	0%	0%	57%	43%
SK99142	С	17/09/99 6:50	131	65	146	76	70	52%	48%	0	146	0	0	70	76	0%	100%	0%	0%	48%	52%
SK99143	С	17/09/99 7:50	128	77	128	82	46	64%	36%	0	128	0	0	46	82	0%	100%	0%	0%	36%	64%
SK99144	С	17/09/99 8:50	120	60	131	63	68	48%	52%	22	109	18	4	64	45	17%	83%	14%	3%	48%	35%
SK99145	С	17/09/99 9:50	114	103	112	82	30	73%	27%	2	110	2	0	30	80	2%	98%	2%	0%	27%	71%
SK99146	С	17/09/99 10:55	115	56	132	49	84	37%	63%	22	110	20	3	81	29	17%	83%	15%	2%	61%	22%
SK99147	С	17/09/99 11:50	114	55	130	64	66	49%	51%	0	130	0	0	66	64	0%	100%	0%	0%	51%	49%
SK99148	С	17/09/99 14:50	113	49	111	53	58	48%	52%	0	111	0	0	58	53	0%	100%	0%	0%	52%	48%

Phosphorus forms during the rain event 16/9/99. Concentrations are in $\mu\text{g/L}$

Sample Code	Location	Date:	Time	TDN	ΤN	TPN	%TDN	%TPN	NH ₄ -N	NOx-N	DON	%DON	%DIN
SK99035F	А	19-Mar-99	13:10	380	680	300	56%	44%	0	48	331	49%	7%
SK99037F	А	19-Mar-99	13:40	350	730	380	48%	52%	0	43	307	42%	6%
SK99039F	А	19-Mar-99	14:10	380	760	380	50%	50%	1	40	340	45%	5%
SK99041F	А	19-Mar-99	14:40	360	680	320	53%	47%	0	27	333	49%	4%
SK99043F	А	19-Mar-99	15:10	360	550	190	65%	35%	0	29	331	60%	5%
SK99045F	А	19-Mar-99	15:40	400	880	480	45%	55%	0	42	358	41%	5%
SK99047F	А	19-Mar-99	16:10	420	760	340	55%	45%	17	51	353	46%	9%
SK99049F	А	19-Mar-99	16:40	400	780	380	51%	49%	19	32	349	45%	7%
SK99051F	А	19-Mar-99	17:10	460	820	360	56%	44%	27	385	48	6%	50%
SK99053F	А	19-Mar-99	18:10	670	1200	530	56%	44%	117	160	393	33%	23%
SK99055F	А	19-Mar-99	19:10	1000	1300	300	77%	23%	138	312	550	42%	35%
SK99036F	С	19-Mar-99	13:15	1100	1600	500	69%	31%	325	161	614	38%	30%
SK99038F	С	19-Mar-99	13:45	980	1400	420	70%	30%	331	104	545	39%	31%
SK99040F	С	19-Mar-99	14:15	950	1500	550	63%	37%	259	180	511	34%	29%
SK99042F	С	19-Mar-99	14:45	1200	1400	200	86%	14%	226	56	917	66%	20%
SK99044F	С	19-Mar-99	15:15	1000	1700	700	59%	41%	231	335	434	26%	33%
SK99046F	С	19-Mar-99	15:45	1800	2200	400	82%	18%	329	843	628	29%	53%
SK99048F	С	19-Mar-99	16:15	1800	2000	200	90%	10%	253	889	659	33%	57%
SK99050F	С	19-Mar-99	16:45	1500	2000	500	75%	25%	210	738	552	28%	47%
SK99052F	С	19-Mar-99	17:15	1300	1500	200	87%	13%	169	623	507	34%	53%
SK99054F	С	19-Mar-99	18:15	1300	1300	0	100%	0%	127	560	612	47%	53%
SK99056F	С	19-Mar-99	19:15	1100	1400	300	79%	21%	68	490	542	39%	40%

Nitrogen Forms during the rain event 19/3/99. Concentrations are in μ g/L

Nitrogen Forms during the rain event 16/9/99. Concentrations are in μ g/L

Description:	Location	Date and Time	TDN	TN	TPN	%TDN	%TPN	NOx	NH4	DON	DIN	%DON	%DIN
SK99121U	С	16/09/99 11:00	499	649	150	77%	23%	46	24	430	70	66%	11%
SK99124U	С	16/09/99 12:50	728	1475	748	49%	51%	163	122	442	285	30%	19%
SK99128U	С	16/09/99 13:50	1380	2229	849	62%	38%	423	311	646	734	29%	33%
SK99133U	С	16/09/99 15:04	1425	2096	671	68%	32%	479	404	543	882	26%	42%
SK99134U	С	16/09/99 15:53	1675	1675	0	100%	0%	362	318	995	680	59%	41%
SK99135U	С	16/09/99 16:50	700	1314	614	53%	47%	392	28	280	420	21%	32%
SK99136U	С	16/09/99 17:50	716	1105	389	65%	35%	421	71	223	493	20%	45%
SK99137U	С	16/09/99 18:50	1195	1346	151	89%	11%	520	119	556	639	41%	47%
SK99138U	С	16/09/99 19:50	736	1086	350	68%	32%	486	48	202	534	19%	49%
SK99139U	С	16/09/99 20:50	730	3116	2385	23%	77%	317	36	377	353	12%	11%
SK99140U	С	16/09/99 21:50	590	2155	1565	27%	73%	230	59	301	290	14%	13%
SK99141U	С	16/09/99 22:50	911	1390	479	66%	34%	420	38	453	458	33%	33%
SK99142U	С	17/09/99 6:50	2600	2600	0	100%	0%	1238	297	1066	1534	41%	59%
SK99143U	С	17/09/99 7:50	2900	2900	0	100%	0%	568	187	2145	755	74%	26%
SK99144U	С	17/09/99 8:50	2700	2700	0	100%	0%	941	300	1459	1241	54%	46%
SK99145U	С	17/09/99 9:50	2700	2700	0	100%	0%	1108	270	1321	1379	49%	51%
SK99146U	С	17/09/99 10:55	2487	2487	0	100%	0%	1380	298	809	1678	33%	67%
SK99147U	С	17/09/99 11:50	2700	2700	0	100%	0%	1194	271	1235	1465	46%	54%
SK99148U	С	17/09/99 14:50	3000	3000	0	100%	0%	1113	265	1622	1378	54%	46%

		Day																														
Month	Data	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
Dec 98	Flow	1.36	1.21	1.64	1.43	2.24	1.41	1.53	59.38	7.64	1.88	1.72	1.37	1.10	0.92	1.02	1.90	0.94	1.02	2.63	0.90	0.80	0.82	107.9	1.60	0.86	0.79	0.81	149.1	15.21	23.46	1.15
	Rainfall	0	0	0	0	0	0	0	17.46	0.37	0	0.19	0	0	0	0	0	0	0	1.67	0	0	0	20.6	0.19	0.19	0	0	13.0	6.32	3.72	0.19
Jan 99	Flow	0.83	0.74	0.73	0.69	0.72	0.73	0.65	0.68	2.01	0.85	0.76	0.77	0.78	0.74	1.09	29.11	0.81	0.78	0.75	0.77	0.74	0.76	0.76	0.74	0.47	0.31	0.16	0.25		1	
	Rainfall	0	0	0	0	0	0	0	0	1.12	0.56	0	0	0	0	0	7.06	0	0	0	0	0	0	0	0	0.19	0.19	0	0			
Feb 99	Flow	0.12	0.10	11.99	0.57	0.28	0.21	0.26	0.21	0.16	0.11	0.27	0.72	5.56	0.95	0.88	0.95	0.98	0.92	8.95	147.9	43.20	25.20	1.14	0.91	0.84	0.75	72.30	3.39	1.01	0.91	0.89
	Rainfall	0	0	2.79	0	0	0	0.56	0	0	0	0	0	1.67	0.19	0	0	0	0	4.831	21.18	10.22	5.016	0	0	0.19	0.419	9 16.75	0.628	0	0	0
Mar 99	Flow	0.90	0.92	0.95	15.24	274.8	2.74	1.13	0.99	0.95	0.85	0.71	0.60	0.53	0.44	0.39	0.38	0.31	0.26	0.23	0.20	0.17	0.13	0.01	0.00	0.00	0.05	0.35	0.19	0.29	0.32	
	Rainfall	0	0	0	14.24	37.05	0	0	0	0	0.42	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.21	0.21	0	
Apr 99	Flow	0.30	0.33	0.38	0.21	0.29	0.13	0.11	0.80	0.28	0.39	0.39	0.39	0.51	0.55	11.24	0.92	0.79	0.72	0.92	0.63	0.64	0.60	0.62	0.91	17.74	1.00	0.93	0.73	0.68	52.10	2.90
	Rainfall	0	0	0	0	0	0	0	1.46	0	0	0	0	0.42	0	4.40	0	0	0	0	0.20	0	0	0	0	6.3	0	0	0	0	13.6	0
May 99	Flow	1.04	0.88	0.83	0.81	0.79	37.15	2.15	0.94	39.66	29.60	1.61	1.04	13.71	2.77	1.06	0.86	0.74	17.38	3.94	0.94	0.85	0.74	0.61	0.56	0.63	0.60	0.59	0.59	0.63	1.86	
	Rainfall	0.203	0	0	0	0	9.75	0.20	0	13.0	4.88	0.61	0.20	4.67	0.203	0	0	0	7.32	0.40	0	0	0	0	0	0	0	0.20	0	0	1.22	
Jun 99	Flow	2.08	0.93	1.01	1.04	1.11	0.75	0.63	0.71	0.95	0.81	0.85	0.86	1.06	0.86	0.78	0.71	0.68	27.35	1.71	2.55	0.91	0.95	0.75	0.72	0.69	0.76	0.79	0.75	0.77	2.45	
	Rainfall	0.813	0	0	0	0	0	0	0	0.4	0	0.2	0	0.6	0	0	0	0	11.4	1	0.2	0.4	0.2	0	0.2	0	0	0	0	0	2	
Jul 99	Flow	0.68	0.70	0.71	0.75	0.75	0.77	0.80	77.04	22.76	1.09	0.85	0.80	23.14	6.92	0.88	0.70	0.68	0.68	0.66	0.60	0.62	0.60	0.62	0.61	0.73	20.29	83.95	5.36	1.56	1.03	1.02
	Rainfall	0	0	0	0	0	0	0	18.6	5.2	0	0	0.4	4.4	2.2	0.2	0	0	0	0	0	0	0	0	0	0	14.2	7.2	1.2	0	0.2	0.1
Aug 99	Flow	1.03	1.07	0.90	2.20	88.52	4.33	1.60	0.93	0.81	0.77	0.89	0.81	0.86	0.88	0.97	233	58.5	4.17	1.81	1.39	1.26	1.07	0.99	1.38	40.27	5.48	1.23	2.48	1.38	8.36	-
	Rainfall	0	0	0	1.6	18.6	0	0	0.4	0	0	0	0	0	0	0	39.22	1.47	0.21	0	0	0	0.21	0.21	0	8.39	5.66	0	0.21	0.21	2.94	
Sep 99	Flow	67.48	5.18	305.5	192.1	74.40	19.50	8.33	5.66	3.42	2.96	5.62	3.48	3.49	6.44	3.29	2.20	2.21	75.07	140.9	14.31	3.61	2.8	18.3	41.8	14.8	5.32	2.94	0.07	0.25	2.48	1.71
	Rainfall	14.3	0.21	49.70	9.437	1.47	0.21	0.42	0	0	0	1.47	0	0	2.52	0	0	0	20.76	17.62												
Oct 99	Flow	1.37	1.35	1.45	1.47	7.41	24.18	1.89	24.14	2.28	1.92	6.39	2.76	1.30	1.25	5.07	2.01	4.91	0.80	0.73	0.74	82.40	9.77	1.32	0.69	0.64	0.62	0.59	0.59	0.57	56.94	
	Rainfall																															-
Nov 99	Flow	1.42	1.53	1.47	1.49	1.48	1.32	1.31	1.00	0.01	0.00	0.26	0.97	2.64	1.23	29.58	1.11	1.05	1.07	1.15	1.07	1.03	1.11	5.59	6.59	6.44	26.07	1.70	1.26	1.34	1.30	1.73
	Rainfall	0	0	0	0	0	0	0	0	0	0	0	0	0	0.74	8.18	0.19	0	0	0	0	0	0	0	0	0	5.57	0	0	0	0	0
-			1	1	1	1	1	1	1	1	1	1	1	1		1	1		1	1	1	1	1		1	1		1	1		_	

Daily flow and Rainfall: December 1998 – November 1999. Data provided by Environment ACT

Sample Code	Date and Time	% MgO	% Al ₂ O ₃	% SiO ₂	% P ₂ O ₅	% SO ₃	% K ₂ 0	% CaO	% TiO ₂	% Mn ₃ O ₄	% Fe ₂ O ₃
SK99136	16/09/99 17:50	3.88	17.73	47.30	0.38	3.72	15.18	5.44	1.37	0.43	4.58
SK99137	16/09/99 18:50	2.08	14.91	62.60	0.28	2.36	4.35	5.38	1.36	0.28	6.39
SK99138	16/09/99 19:50	1.23	16.81	63.18	0.30	1.26	4.92	3.20	2.34	0.25	6.51
SK99139	16/09/99 20:50	1.33	15.81	70.09	0.40	0.72	2.43	2.02	1.05	0.16	5.99
SK99141	16/09/99 22:50	0.79	12.59	73.78	0.33	0.75	3.13	2.20	1.19	0.26	4.98
SK99142	17/09/99 6:50	10.95	11.37	27.01	0.23	16.60	6.92	22.87	0.50	0.16	3.38
SK99143	17/09/99 7:50	12.69	8.49	26.07	0.12	20.89	4.70	23.06	0.68	0.25	3.05
SK99144	17/09/99 8:50	11.12	9.14	29.77	0.21	16.41	4.46	24.29	0.92	0.27	3.43
SK99145	17/09/99 9:50	11.93	8.67	24.64	0.15	19.76	6.46	24.76	0.54	0.21	2.88
SK99146	17/09/99 10:55	11.93	9.71	27.08	0.13	18.82	7.79	20.61	0.74	0.25	2.94
SK99147	17/09/99 11:50	12.18	9.10	24.38	0.23	19.33	5.42	25.77	0.42	0.17	3.02

Major element chemistry data for samples from the storm event of 16/9/99

Date and Time	Discharge (MI)	Discharge (m ³ s ⁻¹)	Rainfall (mm)
	Total	Mean	Total
19/03/99 0:00	0.036	0.01	0
19/03/99 1:00	0.036	0.01	0
19/03/99 2:00	0.036	0.01	0
19/03/99 3:00	0.036	0.01	0
19/03/99 4:00	0.036	0.01	0
19/03/99 5:00	0.036	0.01	0
19/03/99 6:00	0.036	0.01	0
19/03/99 7:00	0.036	0.01	0
19/03/99 8:00	0.036	0.01	0
19/03/99 9:00	0.038	0.01	0
19/03/99 10:00	0.05	0.014	0.557
19/03/99 11:00	0.066	0.018	0.929
19/03/99 12:00	0.213	0.059	1.115
19/03/99 13:00	1.639	0.455	1.301
19/03/99 14:00	2.074	0.576	0.557
19/03/99 15:00	1.828	0.508	0.186
19/03/99 16:00	1.29	0.358	0
19/03/99 17:00	0.671	0.186	0.186
19/03/99 18:00	0.336	0.093	0
19/03/99 19:00	0.152	0.042	0
19/03/99 20:00	0.081	0.022	0
19/03/99 21:00	0.068	0.019	0
19/03/99 22:00	0.057	0.016	0
19/03/99 23:00	0.047	0.013	0
20/03/99 0:00	0.039	0.011	0

Hourly discharge and rainfall: 19/3/99 Data provided by Environment ACT

Bata prot				
ae and Time	Discharge (MI)	Discharge (m ³ s ⁻¹)	Rainfall (mm)	
	Total	Mean	Total	
16/09/99 0.00	0.042	0.012	0	
16/09/99 1:00	0.042	0.012	0	
16/09/99 2.00	0.041	0.011	0	
16/09/99 3.00	0.041	0.011	0	
16/09/99 4.00	0.04	0.011	0	
16/09/99 5.00	0.04	0.011	0	
16/09/99 6.00	0.04	0.011	0	
16/09/99 7.00	0.041	0.011	0	
16/09/99 8.00	0.042	0.012	0	
16/09/99 9.00	0.042	0.012	0	
16/09/99 10.00	0.043	0.012	0 629	
16/09/99 11:00	0.032	0.014	1.679	
16/09/99 11:00	2 002	0.000	1.070	
16/09/99 12:00	2.302	0.020	0.410	
16/09/99 13:00	2 107	0.901	2 007	
16/09/99 14:00	5.19/	0.000	2.097	
16/09/99 15:00	0.000	1.37	0.920	
16/09/99 16:00	9.203	2.373	0.639	
16/09/99 17:00	0.125	1.545	2.307	
16/09/99 18:00	9.135	2.338	2.097	
16/09/99 19:00	18.985	5.274	4.194	
16/09/99 20:00	34.898	9.694	11.534	
16/09/99 21:00	64.857	18.016	6.292	
16/09/99 22:00	45.396	12.61	1.88/	
16/09/99 23:00	29.213	8.115	1.049	
17/09/99 0:00	16	4.445	0	
17/09/99 1:00	8.233	2.28/	0	
17/09/99 2:00	5.143	1.429	0	
17/09/99 3:00	3.979	1.105	0	
17/09/99 4:00	3.348	0.93	0	
17/09/99 5:00	2.851	0.792	0	
17/09/99 6:00	2.326	0.646	0	
17/09/99 7:00	1.814	0.504	0	
17/09/99 8:00	1.458	0.405	0	
17/09/99 9:00	1.283	0.356	0	
17/09/99 10:00	1.202	0.334	0.21	
17/09/99 11:00	1.121	0.311	0	
17/09/99 12:00	0.952	0.264	0	
17/09/99 13:00	0.772	0.214	0	
17/09/99 14:00	0.638	0.177	0	
17/09/99 15:00	0.534	0.148	0	
17/09/99 15:00	0.454	0.126	0	
17/09/99 17:00	0.422	0.11/	0 000	
17/09/99 18:00	0.4/	0.131	0.839	
17/09/99 19:00	0.555	0.154	0.21	
17/09/99 20:00	1.665	0.462	0	
17/09/99 21:00	1.587	0.441	0.21	
17/09/99 22:00	0.985	0.2/4	0	
1//09/99 23:00	0.659	0.183	0	
18/09/99 0:00	0.422	0.117	0	

Hourly discharge and rainfall: 16-17/9/99 Data provided by Environment ACT

Appendix B

Sediment-Water Nutrient Fluxes at Two Sites in Sullivan's Creek

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BACKGROUND

Sullivans Creek runs through the northern suburbs of Canberra before flowing into Lake Burley Griffin's West Basin. The creek drains a predominantly urban catchment, with rural contributions in the headwaters. Water quality monitoring undertaken along the Sullivan's Creek drainage system has indicated a significant source of nutrients occurs in the lower reaches. Two potential sources are Toad Pond and South Pond, both of which are located within the Australian National University (Fig. 1.).



Fig. 1. Sullivans Creek, including sample sites.

<u>AIMS</u>

This study aimed to measure the flux of dissolved inorganic nutrients from sediments in Toad and South Ponds and assess whether they were a significant source of nutrients to Sullivan's Creek.

METHODS

Two benthic chambers were deployed at each site. The benthic chambers consisted of simple plexiglass cylinders which captured 7-9 litres of water above the bottom sediments. Oxygen, salinity, pH and temperature were measured every two minutes within the chamber and in ambient bottom waters by YSI 600XLM self-logging probes. The chamber lid was left open for at least two hours following deployment of the chambers to allow the water to equilibrate. Subsequently the lid was closed and a spike of high salinity (100 psu) water injected. The salinity in the chamber was monitored during each deployment to determine both the volume of water captured in the chamber and the rate of tracer loss from the chamber.

Samples were withdrawn from the chamber using 100 ml plastic syringes. The sample extraction was accompanied by an intake of fresh bottom water through an inlet valve. The first sample (SampBW) was drawn prior to the tracer spike in order to determine ambient water conditions. Table 1. Shows the timing of door closure, spike injection and sample withdrawal at each site.

	Toad	Pond	South Pond			
	Time of Day	Time from Injection	Time of Day	Time from Injection		
Door	10:23		11:23			
Spike	10:26		11:24			
BW Sample	10:26	0.00	11:24	0.00		
Sample 1	10:56	0.55	11:32	0.48		
Sample 2	12:11	1.80	12:42	1.32		
Sample 3	13:43	3.33	13:40	2.28		
Sample 4	15:12	4.82	14:36	3.22		
Sample 5	16:25	6.03	15:42	4.32		

Table 1. Sample times (decimal hours).

Chamber volumes (V_{ch}) and heights (H_{ch}) were calculated using the following formula:

$$V_{ch} = V_{sp} \frac{(C_{sp} - C_b)}{(C_{max} - C_b)}$$

$$H_{ch} = \frac{V_{ch}}{A_{ch}}$$

where V_{sp} and C_{sp} are the spike volume and concentration, C_b is the background (ambient) chamber concentration, C_{max} is the maximum concentration of the spike in the chamber and A_{ch} is the area of sediment covered by the chamber (0.066052 m²).

Sub-samples for nutrient analysis were filtered immediately through a 0.22µM filter and stored at 4°C prior to analysis (usually within 48 hours). The pH of unfiltered samples was measured immediately and alkalinity determined by titration on an unfiltered sample by Gran titration within 24 hours.

Benthic fluxes of nutrients and metabolites were calculated from the rate of change of concentration within the chamber (corrected for the intake of ambient water).

$$Flux = \frac{\delta c}{\delta t} * V_{ch}$$

Produced by: Australian Geological Survey Organisation

 $\delta c/\delta t$ was estimated by least squares regression of concentration against time for the initial linear portion of the relationship.

Analysis

Dissolved inorganic nutrients (NOx, NH_4 and PO_4) were measured colorimetrically by F.Dyer of CSIRO.

Alkalinity was determined by Gran titration and carbonate alkalinity (CA) estimated by subtracting the alkalinity contribution of $B(OH)_4^-$. Total CO₂ (TCO₂) was estimated from pH and carbonate alkalinity using:

$$TCO_2 = CA \frac{1 + K_2 / a_H + a_H / K_1}{1 + 2K_2 / a_H}$$

where a_h = activity of the hydrogen ion, and K₁ and K₂ are the first and second ionisation constants of carbonic acid (Mehrbach et al., 1973).

RESULTS

Two chambers were deployed in Toad and South Ponds, however, the rapid loss of tracer in one chamber at each site indicated a significant leak occurred. Bed conditions at each site were poor and not conducive to chamber operations.

Figure 2 shows the time course of oxygen, TCO_2 , alkalinity and nutrient concentrations within the chamber deployed in Toad Pond. The dissolved oxygen concentration at the start of the incubation was only 80 μ M (or 25 % of saturation). The oxygen was consumed rapidly in the water within the chamber and became anoxic with in 2 hours. The alkalinity, TCO_2 and NH_4 concentrations all increased throughout the chamber incubation whereas NOx decreased with time and was completely consumed within 5 hours. The dissolved phosphorus concentration remained constant before increasing after the 3 hour mark, while there was no real trend in the reactive phosphorus.



Fig. 2. Results from Toad Pond chamber deployment 2/11/99.

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Fig. 3. Results from South Pond chamber deployment 4/11/99.

Figure 3 shows the time course of oxygen, TCO₂, alkalinity and nutrient concentrations within the chamber deployed in South Pond. Oxygen was consumed but at a much lower rate than in Toad Pond (Table 2). The concentrations of alkalinity and TCO₂ were higher than those in Toad Pond, however, the production rates were smaller. The last sample was not incorporated (in calculating production rates) as it appears ambiguous. NOx showed a slight consumption while NH_4 and PO_4 production rates were negligible.

Table 2. Production Rates in Sullivans Creek (mM/m²/day)

	O ₂	Alk.	error	TCO ₂	error	NH ₄	error	NOx	error	PO ₄	error
Toad	-166.092	248.345	14.17	485.356	45.46	36.142	8.39	-4.914	0.93	2.105	1.47
South	-18.401	12.983	59.17	210.576	53.57	0.475	1.87	-1.205	0.15	0.511	0.57



Fig. 4. Toad Pond tracer loss.



Fig. 5. South Pond tracer loss.

Figures 4 and 5 show the normalised tracer concentration plotted against time (dark diamonds) and tracer concentration estimated using a simple diffusion model (open squares). The tracer data was normalised using:

$$C = \frac{(C_t - C_b)}{(C_{\max} - C_b)}$$

where C_t is the concentration at time t, C_b is the background (or ambient) concentration and C_{max} is the concentration immediately after the spike injection. In each case tracer loss rates were greater than predicted by diffusion, loss rates were greatest in South Pond. These data indicate advective processes occurred in both chamber deployments.

DISCUSSION

It is generally recognised that organic matter degradation in sediments proceeds using the available oxidant producing the greatest free energy (Reeburgh, 1983). This degradation produces CO_2 , DIN and DIP in a ratio determined by the composition of the organic matter. In the oxic layer, reaction 1 continues as long as sufficient O_2 is available for the oxidation process. The depth of O_2 penetration depends on its downward diffusion and advection from overlying water and the consumption of O_2 by aerobic decomposition of organic matter (Song & Müller, 1999). Freshwater sediments generally have higher organic matter contents than marine sediments, which leads to a rapid consumption of O_2 . As a result, O_2 is depleted below a few millimeters of the sediment-water interface in freshwater sediments (Jørgensen, 1983).

(1)	O_2 Consumption (respiration) CH ₂ O + O ₂	\rightarrow	$CO_2 + H_2O$
(2)	Denitrification $2(CH_2O) + 2(NO_3) + 4H^+$	\rightarrow	$2CO_2 + N_2 + 4H_2O$
(3)	Nitrate Reduction $2(CH_2O) + NO_3^- + 2H^+$	\rightarrow	$2CO_2 + NH_4^+ + H_2O$
(4)	Reduction of $Mn(IV)$ 2(CH ₂ O) + 4(MnO ₂) + 8H ⁺	\rightarrow	$2CO_2 + 4Mn^{2+} + 6H_2O$
(5)	Reduction of Fe(III) CH ₂ O + 4(FeOOH) + $8H^+$	\rightarrow	$CO_2 + 7H_2O + 4Fe^{2+}$
(6)	Sulphate Reduction, Productio 2(CH ₂ O) + SO ₄ ²⁻ + H ⁺	n of H ₂ S →	$2\text{CO}_2 + \text{HS}^2 + 2\text{H}_2\text{O}$
(7)	Methane Fermentation 2(CH ₂ O)	÷	$CH_4 + CO_2$

The rate of TCO₂ production in Toad Pond (485.356 mM/m²/day) is the highest that we have measured. The O₂ production rate (-166.092 mM/m²/day) is insufficient for degradation of all the organic matter (TCO₂), therefore other oxidants must have been utilised. South Pond shows the same trend with a TCO₂ production rate of 210.576 mM/m²/day and an O₂ production rate of -18.401 mM/m^2 /day, this is also insufficient to balance TCO₂ production.

Once oxygen has been consumed nitrate will then take over as the major oxidant (reactions 2 & 3). The NOx production rates at Toad Pond and South Pond (-4.914 and $-1.205 \text{ mM/m}^2/\text{day}$ respectively) show that denitrification of water column nitrate occurred at both sites.

The NH_4^+ production rate at Toad Pond (36.1423 mM/m²/day) is also greater than any other rate that we have measured. However, the rate is lower than would be expected given the large TCO₂ production rate and assuming a Redfield (algal) composition of the organic matter in the sediments. The C:N flux of 13.5:1 measured in Toad Pond is approximately 50% lower than a Redfield ratio of 6.6:1. South Pond has a very low NH₄ production rate (0.475 mM/m²/day) and therefore a C:N ratio of 27.33:1. A different source of the organic matter (mixed algal, aquatic plants and terrestrial) will account for this deviation from Redfield stoichiometry, however coupled nitrification/denitrification may also contribute to the low N flux.

The reduction of Mn(IV) (reaction 4) and Fe(III) (reaction 5) generally do not oxidise large quantities of organic matter in freshwater sediments. Since we did not measure metal or metal oxide concentrations, we can not account for the amount of organic matter they will oxidise.

Sulphate reduction (reaction 6) and methane fermentation (reaction 7) occur in anoxic sediments. Like reactions 4 and 5, sulphate reduction is a more dominant process in marine environments. In freshwater sediments $SO_4^{2^-}$ may be depleted rapidly within the sediments because of the oxidation of organic matter and methane fermentation (reaction 7) becomes the dominating process (Kuivila *et al.*, 1989). Methane was observed bubbling from the sediments, when disturbed, at both sites. We believe that methane fermentation is a significant process at both the sample sites in Sullivans Creek. The proportion of organic carbon oxidised via sulphate reduction and methane fermentation is not known but is likely to be large given the observed rate of methane ebullition and the low O_2/TCO_2 flux ratio.

The background dissolved oxygen concentrations for both sites were also very low. Toad Pond had a DO of 25% while South Pond had a background DO of 40% (both measurements were taken at noon on the day of sampling). These low oxygen measurements add weight to theory that both sites are near anoxic and any oxygen is quickly consumed.

The tracer data (figures 4 and 5) shows that a process other than diffusion is working to move the tracer into the sediment. This advection could be due to bio-irrigation, ground water movement, or some other physical, chemical or biological process.

CONCLUSION

There are very high rates of degradation of organic carbon in Toad Pond and to a lesser extent in South Pond. In both cases oxygen demand of the sediment exceeds the rate at which oxygen can be supplied from the water column.

There is evidence of water column denitrification, FeOOH, MnO_2 and sulphate reduction, and methane fermentation occurring in both ponds. NH_4 flux rates were high (36.142 mM/m²/day).

The low dissolved oxygen concentrations in both sites indicate respiration as greater than photosynthesis. The dominance of respiration at a system level suggests bottom sediments are likely to have been a significant source of nutrients at the time of the survey. These nutrients are derived from the degradation of organic matter. The organic matter may be derived from aquatic plants and algae or from terrestrial sources such as leaves, etc. Rates of nutrient release are likely to be controlled, at least in part, by organic carbon inputs and may well be much greater during autumn when input of leaf litter is highest.

Management option include:

- 1. Controlling the input of nutrients (N and P) which promote growth of algae and aquatic plants within the ponds.
- 2. Controlling the input of terrestrial organic matter from the catchment. Organic matter in the ponds may have accumulated over many years and may not reflect current inputs.
- 3. Removal of sediments, however any dredging must be undertaken to minimise downstream impacts of turbidity and mobilisation of pore waters with high nutrient concentrations.

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