The Influence of High-Flow Events on Phosphorus Delivery to Loch Leven, Scotland, UK.

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Submitted for the degree of Doctor of Philosophy
School of GeoSciences
The University of Edinburgh
August 2008
I certify that the work in this thesis is my own, except where otherwise stated, and that it has not been previously submitted for a degree at this or any other university.
Acknowledgements

Many thanks go to my supervisors at the Centre for Ecology and Hydrology (Dr. Linda May) and the University of Edinburgh (Dr. Kate Heal). Their guidance and most of all, their patience, has been invaluable. I must also acknowledge Dr. Bryan Spears, Dr. Bernard Dudley and Dr. Laurence Carvalho for their helpful conversations, ideas and support during this project. Special thanks go to Julie Carty at the Scottish Environment Protection Agency. Her efficiency and reliability in sending abundant amounts of stream flow and rainfall data was remarkable. Also, thanks are extended to Dr. Brian D’Arcy and Dr. Jeanette MacDonald of the Diffuse Pollution Initiative for financially supporting the work and providing guidance in the early stages. There are not enough words to express my gratitude to my family and close friends who have been there for me during the past 4 years. It has been a long, dark and demanding journey but at last I see the light and I promise I will try and smile and laugh a lot more from now on. And finally to Simon, for reminding me that you can only ever truly rely on one person and that is yourself.

“You are never too old to set another goal or to dream a new dream”

C. S. Lewis

This studentship was funded by the Natural Environmental Research Council (Studentship Number NER/S/A/2004/12081) and the Scottish Environment Protection Agency Diffuse Pollution Initiative.
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Abstract

Loch Leven is the largest eutrophic loch in Scotland and has historically suffered from eutrophication problems due to large inputs of phosphorus (P) from point and diffuse sources. Reducing the transfer of P, especially diffuse source P, to standing water bodies is a key objective for improving water quality and complying with the objectives of the EU Water Framework Directive and the Water Environment (Diffuse Pollution) (Scotland) Regulations. A P loading survey in the Loch Leven catchment showed that 7.69 tonnes total P (TP), 2.68 tonnes soluble reactive P (SRP) and 4.11 tonnes particulate P (PP) was estimated to have been delivered to the loch between January 2005 and January 2006. On an annual basis, PP was found to contribute a greater proportion (57%) of the loch’s TP load compared with a decade ago (38%) due to a reduction of point source P inputs. Per unit of catchment area, the sub-catchment of the Pow Burn contributed approximately 3 times more PP (1.25 kg ha⁻¹ yr⁻¹) to the loch compared to other sub-catchments due to the intense agricultural land use in this area. High-frequency (2-hourly) P monitoring in the Pow Burn between October and December 2006 showed very large temporal variations in P concentrations caused by high stream flow events. These temporal changes were significantly correlated with increasing stream flow ($r$, 0.458 to 0.938, $p = 0.005$ to <0.001) and total suspended sediment (TSS) concentrations ($r$, 0.664 to 0.967, $p < 0.001$). P loads delivered to the loch from the Pow Burn during the 10 week high-flow monitoring period were 459 kg TP, 78 kg SRP and 351 kg PP. Ten high-flow events contributed 363 kg (79%) TP, 49 kg (63%) SRP and 295 kg (84%) PP. The largest event alone contributed 157 kg (34%) TP, 13 kg (16%) SRP and 136 kg (39%) PP. The results presented in this thesis provide new evidence of the magnitude and importance of diffuse PP losses at the catchment scale and the influence of high-flow events on P transport to Loch Leven. This research recommends that knowledge is gained regarding an individual catchment’s high-flow event characteristics and P transport patterns. Such catchment-scale research will help to provide essential results that inform the development of appropriate catchment management measures aimed at reducing diffuse source P pollution and ultimately improve the water quality of freshwaters.
1 Phosphorus and Water Quality

Water is fundamental to human life and as a population we are highly dependent on such resources for drinking water, food, crop growth, industry and recreation. Currently, many freshwater environments are experiencing accelerated rates of water quality degradation due to pollutant inputs from anthropogenic activities such as industry, agriculture, forestry, land clearing, animal husbandry and urbanisation. In particular, the excessive contribution of phosphorus (P) to freshwaters has been responsible for causing major water quality problems on a global scale, primarily due to the process and impacts of eutrophication (Smith et al., 1999). Rapid human population growth and increasing industrial activities has also led to accelerated rates of climate change through higher levels of greenhouse gas emissions (Bates et al., 2008). In turn, warmer atmospheric temperatures have altered the global hydrological cycle resulting in changes in precipitation patterns on a regional and global scale (Trenberth, 2003). In the UK, substantial evidence supports the fact that the frequency of heavy rainfall events has increased (Osborn et al., 2000; Osborn et al., 2002). Phosphorus has been found to be particularly sensitive to precipitation intensity and volume because large quantities of sediment-associated and diffuse source P are mobilised, transported and deposited into freshwaters by high-flow events. (Hergert et al., 1981; Ulen, 1995; Klein, 1984; Fraser et al., 1999; Quinton et al., 2001; Davidson et al., 2005). Therefore, climate change, changing precipitation patterns and subsequent high-flow events have been important contributing factors in the rise in the number of poor quality freshwater bodies in the UK. The aim of this research was to investigate the effect of high-flow events on the transport and delivery of P to Loch Leven, which is the largest artificially eutrophic loch in Scotland (Carvalho and Kirika, 2003) and this chapter outlines the wider context of the research presented in this thesis.

1.1 Eutrophication in freshwaters

Phosphorus is one of the many elements known to be essential for the growth of all plants, including algae and the addition of excess P to freshwater environments
may eventually result in eutrophication (Hecky and Kilman, 1988; Isermann, 1990; Mainstone and Parr, 2002). Eutrophication is currently the most widespread water quality problem in the UK and many other areas of the world (Sharpley et al., 2008). The most common symptoms and impacts of eutrophication are (Wetzel, 2001):

1. An increase in the production and biomass of phytoplankton, epiphytic algae and macrophytes.
2. A shift in a habitat’s characteristics due to a change in the assemblage of aquatic plants.
3. A change in the composition of fish species, with less desirable species dominating.
4. Production of poisonous toxins by some algae can inhibit the use of water for drinking, bathing, animal watering and recreation. Toxins also increase the operating cost of public water supplies, as a result of taste and odour problems. This is a particular problem during periods of algal blooms.
5. Deoxygenation of water, especially after an algal bloom collapses and starts to decay. This can cause fish kills which can result in an economic loss.
6. Impaired recreational use of water due to slime, weed infestation, and noxious odour from decaying algae.
7. Impediments to navigation due to dense weed growth.

Although eutrophication has many known consequences, little data exists on the environmental and health costs associated with the impacts. Pretty et al. (2003) estimated the damage costs of freshwater eutrophication in England and Wales to be £75 – £114.3 million, whilst costs to address the problem were estimated at £54.8 million. These costs were attributed to the reduced value of waterfront dwellings, drinking water treatment costs for nitrogen removal, reduced recreational and amenity value of recreational waters, removal of algal toxins from drinking waters, reduced value of non-polluted atmosphere, ecological impacts on freshwater biota and net economic losses from tourism. An ecological interest in P stems primarily from it limited availability and its major constraint on the production of large crops of planktonic algae (Reynolds, 1984). Because freshwater environments are often phosphorus-limited, the control of P is of prime importance in reducing
eutrophication of fresh waters. Therefore, there would be both great economic and ecological advantages if the causes of eutrophication could be prevented at the source.

1.2 Sources of phosphorus to the aquatic environment

Whilst eutrophication can occur naturally, it is in many instances associated with anthropogenic sources of P. These sources are usually defined as ‘point’ or ‘diffuse’ in origin and are described in the following sections.

1.2.1 Point Sources

A point source pollutant enters a water body at a specific site and is generally readily identified. Point sources are often continuous and can be monitored and managed quite easily because it is possible to identify where a point source enters a water body. Point sources of P into water bodies primarily arise from:

1. Municipal wastewater effluent (sewage treatment works (STW) and rural septic tanks);
2. Industrial wastewater effluent (e.g. power stations and factories);
3. Runoff and leachate from waste disposal, animal feed, construction and industrial sites;
4. Storm sewer outfalls and overflows of combined storm and sanitary sewers.

Point source P inputs to water bodies are typically highly bioavailable as the majority of P in effluent is in the dissolved orthophosphate form (Mainstone and Parr, 2002). Since they are relatively easy to control and regulate, many point source pollutant inputs to freshwaters have been greatly reduced in recent years, mostly through improved sewage treatment such as P stripping and treatment of industrial effluents prior to disposal.

1.2.2 Diffuse sources

A diffuse source is one from spatially widespread activities with no one discrete source. In contrast to point sources, diffuse pollutants are hard to measure and regulate because they enter a water course at many different places and are under
the control of many different environmental factors. In urban areas, diffuse P sources are often associated with road runoff, construction or building activities or other ‘on-street’ activities such as car washing. Recreational areas may also contribute to P sources, for example, the over fertilisation of golf courses. In rural areas, diffuse P sources often have a greater impact on water quality and commonly play a major role in eutrophication problems of rural surface waters (Ekholm et al., 1997). Many researchers have estimated the loss of P from a range of different rural catchments and it is clear that annual P losses are dependent on many different factors. For example, primary land use, fertiliser application practices, soil types, soil characteristics and local climate and hydrology (Jennings et al., 2000). However, agriculture has been recognised for many years as the most prominent diffuse P source in rural areas (Dillon and Kirchner, 1975; Duda, 1993; Hanarahan et al., 2001). DEFRA (2007) estimated that approximately 25% of P emissions to water in the UK are the result of agricultural activities, whilst Morse et al. (1993) and Withers (1994) suggest that agriculture contributes approximately 40% of the total external P loading to UK surface waters.

In catchments dominated by livestock farming, intensive animal production results in the accumulation of large amounts of poorly managed waste products (Carpenter et al., 1998). Although the disposal problems of animal waste are analogous with those associated with the disposal of raw human waste, regulatory standards are not as rigorous and excess manure is often recycled through use as a fertiliser on the land. Over-fertilisation of soil with inorganic fertilisers also intensifies the effects of agricultural P losses in catchments dominated by crop farming. Sharpley et al. (2000) found that fertilised soils were by far the most important source of the diffuse P load to water bodies in the USA because over-fertilisation has lead to many soils becoming P saturated. In the UK, approximately 50% of agricultural soils have a soil P Index of level 3 or higher, which is greater than is needed for maximum crop growth (DEFRA, 2007). This means that most soils require little or no further phosphate fertilisation in order to achieve maximum crop yields (Hooda et al., 2000; Jennings et al., 2000; Sharpley et al., 2003). Nevertheless, fertilisers are still excessively applied to farm land resulting in significant increases in P inputs to water courses (Sharpley et al., 1994; Foy et al.,
1995; Moss et al., 1996; Tunney et al., 1998; Lucey et al., 1999; Frossard et al., 2000; Jennings et al., 2000; Reynolds and Davies, 2001).

Soil erosion and leaching of P through the soil are the main processes which allow P from the land to enter water bodies (Figure 1.1). Ulen et al. (1991) estimated that P losses from arable land can be as high as 1-2 kg P ha\(^{-1}\) yr\(^{-1}\) in the northern temperate zone, especially where soil erosion is widespread. In areas where P leaching and soil erosion is high, it is common to find water bodies of poor water quality because the input of even a small amount of P from surface runoff can result in P concentrations in the water that are of limnological significance (Carpenter et al., 1998; Hooda et al., 2000; Jennings et al., 2000; Ekholm et al., 2000; Klatt et al., 2003).

![Diagram](image)

**Figure 1.1:** Phosphorus can be released from soil and plant material to surface and subsurface runoff water or lost by erosion. Phosphorus concentration in surface runoff is linked to the P concentration in the soil (adapted from Sharpley et al., 2003).

### 1.2.3 Factors controlling diffuse phosphorus transport

Many factors have been identified in controlling P export from agricultural land to surface waters (Gburek et al., 2000; Sharpley and Tunney, 2000). In rural and agricultural areas, periods of heavy rainfall and surface runoff are the primary
factors determining the amount of diffuse P transported to a water body (Ongley, 1996; Sharpley et al., 1997; Carpenter et al., 1998; McDowell et al., 2001). The rate (or intensity) of rainfall in a catchment is also a determinant factor as heavy rainfall that exceeds the soil infiltration capacity often leads to major soil erosion (Davidson et al., 2005). This is because smaller, less dense particles (e.g. clays and organic matter) are preferentially transported into water courses by surface runoff, where they may remain suspended or later settle to form part of the sediment. In turn, intense heavy rainfall provides the greater amount of energy which is often needed to erode, mobilise and transport larger soil particles in surface runoff (Davidson et al., 2005). Edwards and Owens (1991) suggested that >75% of a catchments annual surface runoff can occur during just one or two severe high-flow events. In agreement, Smith et al. (1991) and Littlewood (1993) found that that intense heavy precipitation events can be responsible for up to 80% of total pollutant inputs to surface waters. Similarly, Edwards and Owens (1991) reported that heavy rainfall events could be responsible for over 90% of the annual TP load to a receiving water body.

1.3 Climate change

Large inputs of diffuse source P transported during heavy rainfall events can prevent complete restoration and recovery of artificially eutrophic water bodies (Jeppesen et al., 1999; Gacher et al., 2004). Reducing sources and transfer of diffuse P during storm events is, therefore, a key objective for achieving improved water quality. This presents a major management challenge, as it is expected that the size, intensity, duration and frequency of heavy rainfall events is increasing as a consequence of global climate change and an intensification of the hydrological cycle (Arnell, 1992; Karl et al., 1995; Arnell and Reynard, 1996; Hennessy et al., 1997; Hulme et al., 1998; McGuffie et al., 1999; Osborn et al., 2000; Jones and Reid, 2001). This hydrological intensification has been caused by increasing levels atmospheric water vapour as a result of higher temperatures and a greater degree of land-surface drying. The overall consequence of more water vapour in the atmosphere is expected to be an increase in the risk of heavy precipitation or
'extreme' events occurring on a global scale (Osborn and Hulme, 2002; Trenberth et al., 2003). In Scotland, Jones and Lister (2004) reported that between 1861 and 2000, the Scottish mainland and the Scottish Isles have warmed by 0.69°C and 0.64°C, respectively. Similarly, Barnett et al. (2006) concluded that, since 1914, Scotland's average temperature has increased by 0.5°C and since 1961 average spring, summer and winter temperatures have risen by more than 1°C.

Many studies have already provided evidence to show that rainfall patterns are changing throughout the world (Hennessy et al., 1997; McGuffie et al., 1999; Hulme et al., 2002; Huntingford et al., 2003; Fowler et al., 2005 and Ekström et al., 2005). Osborn et al. (2000) and Osborn and Hulme (2002) showed there have been dramatic changes in precipitation patterns over the whole of the UK since 1961. They reported that many weather stations have seen a shift from light/medium intensity rainfall to a predominantly heavy intensity. In comparison, Fowler and Kilsby (2003) estimated that the magnitude of worldwide extreme rainfall events has already increased two-fold since the 1960s; rainfall intensities previously experienced every 25 years are now seemingly occurring at approximately 6 year intervals. Huntingford et al. (2003) also demonstrated that total monthly rainfalls, which on average previously occurred every 20 years, are now predicted to occur once in every 3 to 5 years. Arnell et al. (1996) and Arnell et al. (1997) estimated that annual runoff would increase between 8.9-11.6 % by 2050 based on predicted changes in rainfall patterns. Similarly, Pilling and Jones (1999) showed that winter surface runoff was expected to increase between 15-30% in many areas of the UK in response to changing precipitation patterns. Barnett et al. (2006) have shown that in Scotland, heavy rainfall events have increased significantly in winter, particularly in northern and western regions (Mayes, 1996; Smith, 1995 and Barnett et al., 2006). With positive evidence of an increasing incidences of extreme rainfall events, regulating and reducing rainfall driven P inputs to water bodies presents an important future management challenge. Until recently, there was no legally binding legislation that required environmental regulatory authorities in the UK to monitor and control diffuse source pollutant inputs to water bodies. However, the introduction of the EU Water Framework Directive (WFD) has for the first time placed a legal requirement on member countries to tackle diffuse pollution. A
general background to the WFD is provided in the following section and its importance in initiating this research is highlighted.

1.4 The Water Framework Directive (2000/60/EC)

Over the past decade or so, there have been large improvements in the quality of lakes, rivers, estuaries and coastal waters in European countries. This has mainly been through an increase in the quality of discharges due to improvements of sewerage and industrial infrastructure and treatment processes (DEFRA, 2007). This has all been brought about by legislation which placed legally controlled limits and environmental quality standards on point source discharges. However, despite the relative success of these directives (Urban Wastewater Treatment Directive, Bathing Waters Directive, Nitrates Directive and Dangerous Substances Directive), the major problem was that, separately, they did not directly protect aquatic ecosystems as a whole. As a result, the European Commission identified a need to design a new encompassing legislation that would bring about a higher level of protection for the water environment by controlling all pollution at the source. This resulted in the formulation of the Water Framework Directive (2000/60/EC), which was transposed into UK law in December 2003. The principal objective of the Directive is for member states to aim to achieve at least good ecological status for all water bodies (surface and groundwater), and to comply with protected area standards and objectives, by 2015. Morris et al. (2006) have suggested that up to 45% of all Scottish water bodies are at risk of failing the WFD requirements. The Scottish Environment Protection Agency (SEPA) has estimated that 913 rivers, 167 lochs, 23 transitional waters, 128 coastal waters and 25 ground waters in Scotland are currently ‘at risk’ from a variety of environmental pressures (such as point and diffuse source pollution, water abstraction and flow regulation, morphology changes or alien species). It also estimates that 25% of rivers, 17% of lochs, 31% of transitional waters, 28% of coastal waters and 43% of ground waters are ‘at risk’ due to diffuse pollution (SEPA, 2005). It is not just inland waters that are at risk from diffuse pollution; many coastal waters are also at risk of failing to comply with the Bathing Water Directive due to unidentified diffuse pollutant sources.
With respect to eutrophication, part of the directive specifically states that ‘member states shall collect and maintain information on the type and magnitude of the significant anthropogenic pressures to which the surface water bodies in each river basin district are liable to be subject, in particular the following: The estimation and identification of significant diffuse source pollution, in particular, substances listed in Annex VIII, from urban industrial, agricultural and other installations and activities’ (OJEC, 2000). Annex VIII further specifies that ‘substances which contribute to eutrophication, in particular nitrates and phosphates’ are a priority pollutant group that requires targeting (OJEC, 2000). As such, the WFD brings about a statutory obligation for the control of P inputs to European waters. It also provides an impetus for the more general control of P, particularly focusing on priority areas such as Special Areas of Conservation (SACs) under the EC Habitats Directive, Special Sites of Scientific Interest (SSSIs) under the Wildlife and Countryside Act 1981, and ‘sensitive areas’ under the EC Urban Wastewater Treatment (UWW T) Directive (Mainstone and Parr, 2002). The research presented in this thesis is a direct consequence of the introduction of the WFD into Scottish law as the Water Environment and Water Services (Scotland) Act 2003. More recently, the introduction of the Water Environment (Diffuse Pollution) (Scotland) Regulations 2008 has further supported the importance of the research carried out and presented in this thesis.

1.5 The Water Environment (Diffuse Pollution) (Scotland) Regulations 2008

To control the impacts of diffuse pollution on the water environment from rural land use activities, the Scottish Government (2008) introduced general binding rules (GBRs) under The Water and Environment (Controlled Activities) (Scotland) Regulations (2005). Controls over diffuse pollution are essential to achieving good water quality and the overall aim is to ensure that water bodies are not at risk from failing WFD targets due to diffuse pollution from rural land use. The GBRs specifically target the use of fertilisers, keeping of livestock, land cultivation, drainage, construction of roads and tracks and the application of pesticides and sheep dip.
1.6 Research requirements and aims

This research was initiated as part of the Scottish Environment Protection Agency’s (SEPA) Diffuse Pollution Initiative (DPI) scheme, which began in 2001. The DPI was set up in response to the increasing awareness of the threat of diffuse pollution to water quality. First, one of the major research gaps identified by the DPI was the need to quantify and characterise diffuse pollution in Scotland, in order to influence new legislation and policy. However, quantification of diffuse P presents a major challenge as most is transported by surface runoff during heavy rainfall events (Sharpley et al., 1995). On an individual catchment basis, there is currently little understanding of the physical and chemical processes controlling P mobilisation, transport and delivery to receiving water bodies. However, this information will be critical in the process of improving environmental management programmes, adhering to the objectives of the Water Framework Directive and achieving ‘good ecological status’ in freshwater bodies. Secondly, Greig (2004a) predicted that up to 93% of the TP load delivered from diffuse sources is missed by current routine monitoring programmes performed by regulatory authorities. The current monitoring regime for freshwaters is designed to assess the impact of point source discharges and is not sensitive to measuring the occurrences of diffuse P inputs and the effect on water quality. This is because intermittent sampling regimes don’t allow an examination of the effects of high-flow events and surface runoff on pollutant transport. Therefore, research is needed to highlight the significance of high-flow events on P transport and delivery to water bodies. It is also required in order to suggest possible ways of increasing the reliability of P load estimates by changing current monitoring programmes. In response to the above requirements, the aims of this research were to:

- Quantify diffuse source P inputs to Loch Leven, a large shallow loch in Scotland that has historically suffered from poor water quality and eutrophication (Chapter 4).
- Examine the influence of high-flow events on P concentrations in an agriculturally influenced stream in the Loch Leven catchment (Chapter 5).
• Investigate the role of high-flow events on P loads to Loch Leven and investigate the error and variability associated with different P sampling strategies and load calculation methods (Chapter 6).

• Identify important sediment sources during high-flow events and investigate their potential P buffering capacity (Chapter 7)

• Investigate the potential bioavailability of sediments transported into Loch Leven during high flow events (Chapter 8).
2 The Research Site

The research area for this project was the catchment of Loch Leven in Perthshire, Scotland. An introduction to the loch and its catchment are detailed in this chapter. Information regarding the history of P inputs to the loch, and management actions that have been previously initiated to improve poor water quality are summarised.

2.1 Loch Leven

Loch Leven is a shallow lake which lies about 35 km north of Edinburgh in the region of Perth and Kinross. The loch is important for migratory, breeding and over-wintering waterfowl (Carvalho and Kirika, 2003) and is an internationally recognised nature reserve, a Special Site of Scientific Interest (SSSI) and a Ramsar site. It is rich in habitat variety and plant species diversity, and is the only area in Britain to accommodate the carrion beetle (Thanatophilis dispar). The island of St. Serfs, located in the middle of the loch, also holds the highest concentration of breeding ducks in Western Europe (LLCMP, 1999). The loch lies at a latitude of 56°10’N, a longitude of 3°30’W and an altitude of 107 m above sea level. It receives water from a drainage catchment with an area approximately 145 km$^2$ (Figure 2.1). The loch itself covers an area of approximately 13.3 km$^2$ and has a mean depth of 3.9 m. The maximum depth is approximately 25.5 m due to the presence of two deep troughs (Figure 2.2). Average annual rainfall in the catchment over the past 14 years has ranged between 702 mm (1996) and 1204 mm yr$^{-1}$ (2006). Water from the catchment is drained by four main rivers: the North Queich, South Queich, Gairney Water and the Pow Burn, along with many minor tributaries. The River Leven constitutes the outlet for the loch. Water draining into the loch originates from a variety of sources; the two most important in terms of pollution control, are effluent from the local sewage treatment works and agricultural runoff. Both activities are significant contributors of P to the loch.
Figure 2.1: Location of Loch Leven in the United Kingdom, and the catchment drainage area (from Spears et al., 2006).

Figure 2.2: Depth profile of Loch Leven indicating the two deep troughs located within a generally shallow water body (from Spears et al., 2007).
2.2 Catchment characteristics

A detailed assessment of the loch’s catchment characteristics is contained in Smith (1974). In summary, the geology of the catchment varies and can be divided into three zones (Figure 2.3). The western hills rise to a height of approximately 500 m above sea level and are formed of volcanic lava and debris of Old Red Sandstone. The detailed structure is complicated by faults and igneous intrusions. The lower hills covering a smaller area in the south of the catchment have a complex form with igneous sills intruding into Carboniferous strata. A narrow band of similar geology also occurs along the north-eastern watershed. The Old Red Sandstone is masked by glacial deposits, which dominate the plain in which the loch is situated. The loch itself occupies a shallow depression in sand and gravel deposits, which overlie boulder clay. The catchment geology is unlikely to adversely affect the river water entering the loch (Smith, 1974).

Figure 2.3: Loch Leven catchment geology (from Smith, 1974).
2.3 Historical poor water quality in Loch Leven

Throughout much of the past century, the impacts of human settlement on the loch have become increasingly evident, being manifested by an increased occurrence of algal blooms and reduced diversity of flora and fauna. The increase in the use and disposal of products containing P, increasing population and changing land use have all been responsible for the degradation of water quality, due to an increase in the amount of P entering the loch. Although Loch Leven is considered to be a naturally nutrient-rich water body, high additional nutrient loadings from anthropogenic sources mean that it is now the largest eutrophic freshwater loch in Scotland (Bailey-Watts and Kirika, 2000). This has also been promoted by its physical characteristics. As a general rule, per unit mass of nutrients supplied, shallow lakes tend to be more productive waters than deeper lakes. This is a consequence of more favourable light conditions, which promote algal growth (Bailey-Watts and Kirika, 1987). The likelihood of light limitation of algal growth is reduced due to the shallow nature of the loch and its large surface area. These features result in the algae maximising the use of available nutrients. Shallow lakes are also generally well mixed water bodies. This is true in Loch Leven, and because of such favourable conditions and historically large nutrient inputs, the loch has suffered from periodic cyanobacterial blooms for many years (Figure 2.4) (Carvalho and Kirika, 2003).

Figure 2.4: Algal bloom in the waters of Loch Leven, August 2004.
2.4 **The importance of Loch Leven to the local economy**

The loch generates important economic income for the area, mostly through tourism. In 1987, Loch Leven was estimated to be worth £1.5 million per year to the local economy (LLCMP, 1996). More recent figures have been difficult to obtain, but inferences can be drawn from the following information: The Loch's historic castle and nature reserve attracts approximately 60,000 visitors per year to the area alone (LLCMP, 1999). These two sites are estimated to generate annual revenues between £690,000 and £2 million. In addition, the use of the loch's water resource as a fishery and the use of water from the River Leven, generates employment opportunities and business revenue. The economic value of the loch is adversely affected when poor water quality causes algal blooms. In 1992, the summer algal bloom was estimated to have cost up to £673,000 to the local shops, hotels and B&Bs and approximately £110,000 to the fishery, in terms of lost business (LLCMP, 1996).

2.5 **Catchment land use**

Loch Leven has an unusually intensively farmed catchment area, compared with other inland lochs of its size in Scotland. Around 80% of the catchment area is utilised for agricultural production (LLCMP, 1996). Mixed farmland predominates, but on the best land, specialist arable areas produce high-value potato and vegetable crops, as well as cereal and oilseed rape. In more upland areas, livestock are primarily farmed. These agricultural areas are a key source of diffuse P to the loch (LLCMP, 1999). The remaining catchment area comprises woodland (predominantly coniferous) (~11%) and major settlements (~2%) of Kinross and Milnathort. Rural houses, roads, water and recreational areas account for the remaining land area (LLCMP, 1999). Within the last two years there has been much expansion of the town of Kinross to accommodate new housing schemes. Such expansion will increase pressure on the sewage treatment works and the number of septic tanks within the catchment.
2.6 Previous assessments of phosphorus inputs to the loch

In 1985, the annual amount of P entering the loch was estimated to be approximately 21 tonnes of total P (TP), with approximately 11.8 tonnes in the highly bioavailable, soluble reactive P (SRP) form. Point sources were by far the largest contributors to the P load, with approximately 12.0 tonnes being contributed from sewage treatment works and the effluent of a local woollen mill (Bailey-Watts and Kirika, 1987). Other P sources at this time also included catchment runoff, rainfall and roosting waterfowl (Bailey-Watts and Kirika, 1987). Improving the water quality, by reducing the P available to the algae in the loch has long been known to be crucial to reducing the frequency, duration and impact of the algal blooms. Reducing the external P inputs to the loch was identified as the only method to achieve this. There had been an action plan to reduce P loads to the loch since the 1970’s, which initially focused on point sources. The impact of this management was clearly evident between 1985 and 1995, when another P loading survey indicated a significant decline in P loadings (Bailey-Watts and Kirika, 1999). It was estimated that both TP and SRP inputs had been significantly reduced due to improved management and regulation of point sources. In 1995, an estimated 8.0 t of TP entered the loch, of which only 5.3 t was in the SRP form (Bailey-Watts and Kirika, 1999). This was primarily the result of the woollen mill ceasing to use P compounds in their manufacturing process and the installation of P-stripping facilities at the Kinross and Milnathort sewage treatment works. However, despite the reduction of point source P loadings the loch has continued to manifest phytoplankton blooms.

In 1995, an algal bloom occurred which was dominated by the cyanobacteria, *Anabaena spiroides*, and had an algal biomass higher than had ever been recorded in the 30 year history of biological monitoring of the loch (Bailey-Watts and Kirika, 1996). A further assessment of the loch’s chlorophyll$_a$ levels in 2000 reported concentrations in excess of the Scottish Environment Protection Agency (SEPA) target value of 15 $\mu$g l$^{-1}$. The mean chlorophyll$_a$ concentration in 2000 was 33.1 $\mu$g l$^{-1}$, with a recorded high of 97.4 $\mu$g l$^{-1}$ (Bailey-Watts and Kirika, 2000). The
reduction of external point source P loads had clearly not had the desired effect on water quality that was originally hoped. An assessment of internal P loading was recently performed by Spears *et al.* (2006), which demonstrated that between April 2004 and April 2005, 92.09 t P was released from the loch's sediments, whilst 68.65 t was adsorbed. Therefore, the internal load to the loch from the sediments was 23.44 t of P (net total), in addition to the external P load from the catchment. During this study the largest recorded sediment P release occurred in the summer months (June / July) and the largest P gain occurred in winter months (December and February). This pattern of P release implies that the loch’s sediments are currently releasing P when algae are most likely to be productive. This process is probably promoting the continuation of high algal populations in summer months.

2.7 The current water quality status Loch Leven

Under the WFD, water quality targets for Loch Leven are now being implemented with an emphasis on the ecology of the lake rather than the chemistry. However, water quality standards for TP under the WFD are also being implemented and are more stringent than those set under the last Loch Leven Area Management Advisory Group (LLAMAG). Under the WFD definition of good/moderate status, the TP target for a shallow, high alkalinity loch in Scotland, such as Loch Leven, is 32 µg l⁻¹, whilst the moderate/poor boundary is 46 µg l⁻¹. Carvalho *et al.* (2007) report that Loch Leven would classify as being of poor status, with 2007 being the only year it was classified as moderate status. Similarly, the good/moderate boundary for chlorophyll for a shallow, high alkalinity lake, such as Loch Leven, is 7.5 µg l⁻¹. However, a site-specific chlorophyll target for Loch Leven has been agreed at 11 µg l⁻¹ for the good/moderate boundary and 22 µg l⁻¹ for the moderate/poor boundary. On the basis of 2007 chlorophyll concentrations, Carvalho *et al.* (2007) reported that the loch is now approaching a moderate status class as annual mean chlorophyll concentration was 24 µg l⁻¹. Comparison of the annual mean TP and chlorophyll concentrations with those recorded over the past forty years suggest that the recovery trend which appeared to stall in recent years (Carvalho *et al.*, 2003; Ferguson *et al.*, 2008) has started to progress again.
However, cyanobacterial blooms still occur in the lake in summer months and there remains a clear requirement for lake and catchment management to continue in order to try to meet WFD targets for chlorophyll and to sustain and enhance the ecological recovery.

### 2.8 Previous catchment management actions

A number of management initiatives designed to reduce diffuse pollution from Scottish catchments have been initiated and implemented in many rural areas. For example:

- Catchment sensitive farming,
- Nitrate vulnerable zones,
- Best practice guidelines for fertiliser application rates and storage,
- Codes of good agricultural practice and
- Farm waste management planning, including the four-point plan which provides guidance on how to reduce dirty water around the farm, improve nutrient use, carry out a land risk assessment for slurry and manure and manage water margins (Scottish Agricultural College, 2008).

In the Loch Leven catchment, there has been a great deal of focus on the reduction of point source P inputs to the loch since the 1970's. However, like in many rural catchments, the current management challenge is to reduce external sources of diffuse P (LLCMP, 1999). A Catchment Management Plan for Loch Leven (LLCMP) was seen as a way to successfully address diffuse pollution in an integrated manner because the plan would involve all responsible stakeholders. The most recent plan for Loch Leven was constructed in 1999 and six key issues were identified. These were:

- Losses of P associated with soil erosion by rainfall and run-off.
- Stream bank erosion due to lack of vegetation, livestock access and natural erosional processes e.g. high river flows.
- Inappropriate river management by land owners to reduce soil erosion.
- Field flooding and lack of flood plains.
- Soil P levels associated with past fertiliser over-use,
• Loss of P associated with other agricultural activities, e.g. fertiliser spillages and poor fertiliser application techniques. Although Good Codes of Practice have been implemented in the catchment, agricultural practices not covered by legislation have exacerbated the natural process of soil erosion. Because P is principally lost in particulate form in association with soil particles, soil erosion is a major P transfer method (Ekholm et al., 2000; Klatt et al., 2003). The risk of soil erosion from fields in the Loch Leven catchment has been predominantly classified as low to moderate, with only a few fields being at high risk (Figure 2.5).

Figure 2.5: Status of soil erosion risk in the Loch Leven catchment. (Data provided by the Scottish Agricultural College and Perth & Kinross Council).

However, the high sensitivity of the loch to P inputs means that losses of soils from the catchment still present a substantial risk to the loch’s water quality. This risk is further increased due to the common farming practice of overuse of soil fertilisers, which commonly results in catchment soils becoming very high in P (Withers et al., 2002). There are no data available referring to fertiliser application rates in the catchment, however, in the late 1990’s most fields in the Loch Leven
catchment were assessed to be of low to moderate P status (categories 0-3, 10-45 mg P l\(^{-1}\) soil) with only a few showing high P levels (category 4, 46-70 mg P l\(^{-1}\) soil) (after the ADAS Soil P Index) (Figure 2.6). The high P soil levels were found to coincide with intensive vegetable farming or cereal production (LLCMP, 1999).

Controlling diffuse P sources has presented a major management challenge in the catchment because they are technically more difficult to address compared to point source pollution. The LLCMP (1999) made the following management recommendations to tackle this problem:

- Prevent soil erosion associated with grazing and poaching by livestock by providing alternative watering facilities where possible.
- Reduce soil loss from flood-plains and establish flood-plains that would not be cultivated.

Figure 2.6: Soil phosphorus status in the Loch Leven catchment. Note: figures in brackets refer to the number of fields in the corresponding category. Categories 0-3 = 10-45 mg P l\(^{-1}\) soil and category 4 = 46-70 mg P l\(^{-1}\) soil. Blank areas = no data. (Data provided by the Scottish Agricultural College and Perth & Kinross Council).
• Assist farmers to minimise soil erosion and losses, especially in fields identified as high risk areas and/or that have high P status.
• Encourage the implementation of buffer strips and better management of riparian land.
• Promote better use of fertilisers and perform regular soil P analysis.
• Encourage the use and implementation of Waste Management Plans.
• Assist farmers in reducing the direct loss of nutrients to water courses, by encouraging land owners and farmers to carry out their own river management.
• Reduce the risk and loss of P from commercial woodland and encourage land owners to establish new riparian woodlands.

However, much of the management progress continues to target point sources and only a handful of strategies to control diffuse pollution (e.g. buffer strips in the Pow Burn catchment, advice leaflets on erosion control and the Four Point Plan) have been performed. Furthermore, the actual impact of these strategies in terms of reduced P inputs remains unknown due to the simple lack of information and data regarding the inputs of diffuse source P to the loch. This information will be needed in order to successfully tackle diffuse source P inputs in the future. To fill this knowledge gap, the research presented in this thesis provides new information regarding the transport of diffuse source P to Loch Leven during high-flow events.
3 Analysis Methods of Water Samples for Different Phosphorus Forms

This project has assessed P inputs to Loch Leven from a variety of sources. Therefore, the measurement of P fractions from water and sediment samples has been a major requirement throughout this project. To avoid repetition between chapters, a description of the methods performed in this research is given separately in the following section.

3.1 Introduction

Phosphorus is present in water samples either in the dissolved (soluble) form or associated with particulate matter. These fractions are present in either inorganic or organic forms. Inorganic 'soluble' P usually refers to orthophosphate species, such as the \( \text{PO}_4^{3-} \) ions in the \( \text{H}_2\text{PO}_4 \) and \( \text{HPO}_4^{2-} \) forms. These are the primary forms of soluble P present within the pH range found in natural waters. Soluble P is bioavailable once it enters surface waters and can be readily utilised by microorganisms and aquatic plants. Particulate P (PP) consists mostly of fine, light soil particles (e.g. silts, clays, fine sands and organic matter). In rural catchments, PP is mainly organic or sediment-bound, entering the aquatic environment mostly as litter fall or eroded soils during sediment transport processes. Particulate P fractions are not considered immediately bioavailable, but may over time become available for biological utilisation due to solubilisation processes (Sonzogni et al., 1984). They can therefore provide a long-term source of bioavailable P. Table 3.1 summarises the bioavailability of different fractions of P.

3.2 Phosphorus analysis of water samples

The separation of P into its various forms is defined analytically, with the analytical differentiations being selected so that they may be used for interpretive purposes (APHA, 1998). Phosphorus analyses generally embody two procedural steps; the conversion of the P form of interest to dissolved orthophosphate (\( \text{PO}_4^{3-} \)) and subsequent colorimetric determination. Total P (TP) measures all of the P
fractions in a sample, both soluble and particulate (Figure 3.1). Particulate P (PP) is an estimation of the P associated with particulate matter only. Total soluble P (TSP) and soluble reactive P (SRP) constitute the soluble fractions within a sample.

**Table 3.1:** *Summary of phosphorus fractions and their biological availabilities (adapted from Sonzogni et al., 1984)*.

<table>
<thead>
<tr>
<th>Phosphorus Fraction</th>
<th>Biological Availability</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dissolved Inorganic P (DIP/SRP)</strong></td>
<td>Directly available</td>
</tr>
<tr>
<td>(in the form of $\text{H}_2\text{PO}_4^-$ and $\text{HPO}_4^{2-}$)</td>
<td></td>
</tr>
<tr>
<td><strong>Condensed dissolved P</strong></td>
<td>Converted to dissolved inorganic P through fairly rapid hydrolysis. Mostly relevant in waste waters rather than natural waters.</td>
</tr>
<tr>
<td>(present in natural compounds and phosphate detergents)</td>
<td></td>
</tr>
<tr>
<td><strong>Dissolved Organic P (DOP)</strong></td>
<td>DOP from plant tissues and animal wastes are converted quickly into dissolved inorganic P through biological mineralization, the speed of which will vary depending on the complexity of the molecule. DOP from soils is more stable. Mostly relevant in waste waters rather than natural waters.</td>
</tr>
<tr>
<td>(released from plant tissues and animal wastes, and soils in runoff)</td>
<td></td>
</tr>
<tr>
<td><strong>Particulate Inorganic P (PIP)</strong></td>
<td>A high proportion of NAIP is potentially available to algae, whilst AlP is essentially unavailable.</td>
</tr>
<tr>
<td>(This fraction can be subdivided into the non-apatite inorganic P (NAIP) and the apatite inorganic P (AlP) fractions.</td>
<td></td>
</tr>
<tr>
<td>The NAIP fraction comprises mainly of inorganic P adsorbed to Fe and Al hydrous oxides but may also include Fe and Al minerals.</td>
<td></td>
</tr>
<tr>
<td>The AlP fraction consists of inorganic P in apatite minerals (mineral family containing most of the P from the Earth's crust)</td>
<td></td>
</tr>
<tr>
<td><strong>Particulate Organic P (POP)</strong></td>
<td>Converted to dissolved inorganic P through biological mineralization; may be rapid for substantial fraction of fresh plant tissues or animal wastes; slow for soil and sediment organic P which are small sources in natural waters.</td>
</tr>
<tr>
<td>(nucleic acids, phospholipids, inositol phosphates)</td>
<td></td>
</tr>
<tr>
<td><strong>Condensed particulate P (CPP)</strong></td>
<td>Released from plant tissue at senescence and hydrolysed to dissolved inorganic P; this is a small fraction compared to organic P.</td>
</tr>
</tbody>
</table>

26
To separate the dissolved from the particulate form, the samples are filtered through a 0.45 μm pore diameter membrane filter. In this research, Whatman® 0.45 μm glass fibre (GFC) filters were used to perform this step. Filtration through this pore size does not definitely separate the dissolved from the particulate fraction (APHA, 1998), as fine colloidal material may pass through a membrane of this pore size and be hydrolysed by the strong acid medium of the colorimetric method (Rigler, 1966; Sharpley, 1997). However, the method proposed is merely a replicable and convenient analytical technique designed to make a gross separation. This membrane size is, nevertheless, widely used in the determination of P fractions and is generally considered to be the standard method for separation of the dissolved and particulate forms.

Total P and TSP were analysed during this research after the methods of Eisenreich et al. (1975). For the determination of TP, an unfiltered water sample was first subjected to an acid hydrolysis reaction prior to colorimetric analysis. This was achieved by mixing the water sample with a solution of sulphuric acid (H₂SO₄) and potassium persulfate (K₂S₂O₈). The sample was then autoclaved for 30 minutes at 121°C. This process converts all of the soluble and particulate phosphates into dissolved orthophosphate. The same digestion technique was performed on a filtered water sample, which allowed the determination of the TSP fraction. In this instance, the procedure converts the dissolved P fractions that would not otherwise respond to colorimetric determination. The PP content of a sample can then determined as the difference between the TP and TSP fractions.

Soluble reactive P reacts with colorimetric tests without any form of hydrolysis or oxidative digestion of the sample and is therefore analysed immediately after filtration after the methods of Murphy and Riley (1962). The general principle behind the colorimetric determination of orthophosphate in a water sample is that ammonium molybdate ([(NH₄)₆Mo₇O₂₄.4H₂O) and potassium antimonyl tartrate (PAT) (C₈H₄K₂O₁₂Sb₂) react in an acid medium (H₂SO₄) with orthophosphate (PO₄³⁻). This reaction is catalysed by potassium PAT. A yellow heteropoly acid – phosphomolybdic acid complex is formed, which is reduced to a more stable complex by ascorbic acid (C₆H₈O₆) in the presence of orthophosphate ions. This reduction results in an intensely coloured molybdenum blue solution. The intensity
of colour formation is quantified by measuring the absorbance of the samples in a Phillips PU8620 Series UV/VIS/NIR single beam spectrophotometer, using a 4 cm flow cell and a wavelength of 882 nm. The concentrations of P within a sample were subsequently determined using a linear regression calibration equation generated from the measured absorbance values of known P standards. The P detection limit of water samples was 2.0 µg l⁻¹. All water samples analysed for P forms were performed in triplicate to ensure accuracy and quality of results. Figure 3.1 details the exact laboratory procedure followed during P analysis.
Figure 3.1: Standard laboratory procedure for the determination of phosphorus fractions in water samples, after the methods of Eisenreich et al. (1975) and Murphy and Riley (1962). Details of the preparation of analytical solutions / reagents are provided in Chapter 11, Appendix A.1.
4 Estimating an Annual Phosphorus Load to Loch Leven

4.1 Introduction

Chapter 2 introduced Loch Leven and some history surrounding P loadings, water quality problems and associated catchment management initiatives over the past 20 years. Although there has been considerable improvement in the management of the catchment, the overall water quality of the loch has yet to fully recover from eutrophication (Carvalho et al., 2007). To further improve water quality and to comply with the Water Framework Directive, reducing diffuse P sources now requires urgent attention and investigation. In order to assess the external P load to the loch and the potential contribution of diffuse P to Loch Leven, a loading study was instigated as part of this research. Due to the size of study required to investigate individual diffuse P sources, this study has made the assumption that the majority of PP entering the loch from external sources has originated from the surrounding land. This assumption has been made on the grounds that the Loch Leven catchment is dominated by agriculture and that the greatest proportion of PP will be suggestive of soil-associated P losses. The primary aims of the study were to:

- Estimate the annual P load to Loch Leven in 2005 and compare this with historical loading estimates.
- Identify areas of the Loch Leven catchment where diffuse P losses were high.
- Identify important periods of the year when diffuse P losses from the catchment were greatest.

4.2 Methods

4.2.1 Sample site selection

Flow gauging and nutrient analyses on 12 major inflows to Loch Leven and one outflow were conducted at 8-day intervals from 18th January 2005 to 17th January 2006 (Figure 4.1). The 8-day interval ensured that P monitoring included measurements from every day of the week over the sampling period. This was
required as point source P inputs vary on a daily basis. Field methodology was adapted from Bailey-Watts and Kirika (1987, 1999) who performed previous loading surveys during 1985 and 1995. Sample sites were located at easily accessible points and ensured P analysis was performed on all major inflows. Three small inlet streams and a number of small drainage channels were not sampled due to time and cost constraints. The smaller streams often ran dry throughout much of the year due to their small size and were difficult to sample due to in-channel vegetation. Inspection of the drainage channels revealed that these had been modified by a nearby turf company. The company had installed a number of large drainage pumps to irrigate nearby land and had re-directed most channels away from the loch in order to retain the water. Reliable estimates of the amount of water entering the loch from these channels would have been difficult and inaccurate.

Figure 4.1: Location and nomenclature of sampling points during the 2005 phosphorus loading survey (modified from Bailey-Watts and Kirika, 1999).
4.2.2 Sample collection

For the collection of water samples, 250 ml plastic sample bottles were washed in Decon 90® and rinsed twice with distilled water in the laboratory prior to use. In the field, the bottles were rinsed twice with stream water prior to sample collection. Stream water was collected by holding the bottle approximately 20 cm below the water surface with the mouth of the bottle facing upstream. All samples were taken from the bank using an extendable pole in order to avoid contamination of samples through sediment disturbance. Duplicate water samples were collected at each sample site and were stored in a dark, chilled cool box until analysis in the laboratory. All collected water samples were analysed for total P (TP), total soluble P (TSP) and soluble reactive P (SRP). Particulate P was the sum of TP minus TSP. A detailed description of the methods has been provided in Chapter 3.

4.2.3 Catchment rainfall

Daily rainfall was measured by a 0.2 mm tipping-bucket gauge located on the North Queich (Site Ne, Figure 4.1). This device was maintained by the Scottish Environment Protection Agency (SEPA), who kindly provided data for the period of the survey.

4.2.4 Stream flows

Flow gauging stations were equipped with a continuous flow recording device and/or a stage board. Continuous gauges and stage boards were located at the Pow Burn (Pb), South Queich (Sc) and North Queich (Ne). Stream flow (m³ sec⁻¹) was recorded every 15 minutes at these sites. These stations were operated and maintained by SEPA, who provided stream flow data at these three sites for the period of the survey. Stage board measurements were also recorded on each sample day at Camel Burn (Cc), Gairney Water (Gb) and the Hatton Burn (Nh) as well as the other three sites (Pb, Ne, Sc) and stream flow was estimated using a rating curve.
Ratings curves were constructed from a number of direct measures of stream flow at known gauge heights.

4.2.5 Measuring stream flows to construct ratings curves

A model 1205 price type "mini" current meter with a top setting wading rod and CMD 9000 digimeter (Scientific Instruments, Inc., WI, USA) was used to measure water velocity at the Gariney Water, Hatton Burn and Camel Burn. Stream flow was determined using the velocity ($V$), area ($A$) method. Firstly, the cross sectional area (CSA) of the river reach was divided into 3 to 5 segments (depending on width of the river). The mean velocity at 0.6 of the water depth and the CSA of the stream channel was measured (Equation 4.1). The stream flow at each segment was calculated as the product of $V$ and $A$ (Equation 4.2). Total flow was the sum of the flows in each segment. A ratings curve was then constructed using measures of stream flow regressed against gauge height at the time of measurement (presented in Section 4.3.2, Figure 4.4).

$$\text{CSA} = \frac{\sum D}{2} \times d$$  \hspace{1cm} (Equation 4.1)

Where:

CSA = cross sectional area of channel, m$^2$.

$D$ = water depths bounding segment, m. (e.g. D1+D2, D2+D3 etc).

$d$ = distance between depth measurements, m.

$$Q = V \times A$$  \hspace{1cm} (Equation 4.2)

Where:

$Q$ = stream flow, m$^3$ sec$^{-1}$.

$V$ = average water velocity in channel, m sec$^{-1}$.

$A$ = cross sectional area of channel, m$^2$.
4.2.6  Phosphorus concentrations and estimates of stream flow at sites that were not monitored

Two small streams flowing into the loch were not included in the survey. These were the Ury Burn and the Kinnesswood Burn. Phosphorus concentrations at these sites were assumed to be the same as the nearest measured catchment. This was the North Queich (Ne) and the Pow Burn, respectively. Stream flow at the un-gauged sites was also presumed to be in direct proportion to the measured stream flows at the North Queich (Ne) and the Pow Burn (Equation 4.3). This method was employed because Bailey-Watts and Kirika (1987) previously found strong correlations \((r = 0.97, p < 0.05)\) between mean discharge and drainage area. This method was also used to account for additional stream flow downstream of sample sites and for water draining directly into the loch from the catchment area out-with the sampled catchments.

\[
Q_{ug} = \left( \frac{Q_g}{CA_g} \right) \times CA_{ug}
\]

(Equation 4.3)

Where:

- \(Q_{ug}\) = stream flow of un-gauged catchment, m\(^3\)sec\(^{-1}\).
- \(Q_g\) = stream flow of gauged catchment, m\(^3\)sec\(^{-1}\).
- \(CA_{ug}\) = catchment area of un-gauged catchment, km\(^2\).
- \(CA_g\) = catchment area of gauged catchment, km\(^2\).

4.2.7  Estimating an annual phosphorus load

An estimate of the annual load of P to the loch was calculated after the methods of Stevens and Smith (1978) and Ferguson (1986). This was the applied methodology during the 1995 Loch Leven annual P loading survey (Bailey-Watts and Kirika, 1999). This method provides a means of estimating ‘continuous’ P concentrations and loads in response to continually changing stream flows. The
primary advantage of this method is the assumption that continuous values of P may provide a better, more accurate estimate of P loading (Bailey-Watts and Kirika, 1999). This is because 8-day sampling of stream flow and P are likely to miss important short-lived episodes of high flow events or spells of low flows that can lead to both under or over-estimations of P load (Figure 4.2) (Webb et al., 1997).

![Figure 4.2: An illustration of how estimating phosphorus loads from intermittent sampling regimes, rather than continuous ones, can cause considerable inherent estimation errors (modified from Bailey-Watts and Kirika, 1999).](image)

**4.2.8 Sequence of analysis to estimate phosphorus loads**

An annual P load to Loch Leven was calculated in the following steps:

1. Phosphorus concentrations and stream flow measurements were sampled as previously described.

2. Continuous stream flow data was available on the Pow Burn, South Queich and North Queich catchments. In the absence of continuous flow data at the remaining three stage gauged sites (Gairney Water, Hatton Burn and Camel Burn), correlation analysis was used to assess the strength of relationships between instantaneous measures of stream flows at all sites.
3. Regression analysis was then performed between the most highly correlated sites and continuous stream flows generated using the regression equations.

4. Continuous stream flows from remaining inflows not flow gauged were estimated using a flow / catchment area relationship as described in Equation 4.3.

5. Through regression analysis, the relationship between the 8-day, instantaneous P concentrations and stream flows was assessed using log10-log10 regression analysis after Stevens and Smith (1978). The regression equations were used to estimate continuous P concentrations using continuous stream flow data.

6. The annual P load to the loch (from each inflow) was then calculated using:

\[
\text{Stream Load} = \sum_{i=1}^{n} (\log C_i \cdot \log Q_i) \\
\text{Total Load} = K \left( \sum_{i=1}^{n} (C_i Q_i) \right) \\
\text{(Equation 4.4)}
\]

Where:
- \( K \) = conversion factor to take account of time period of record.
- \( n \) = number of samples.
- \( C_c \) = estimate of P concentration from continuous stream flow value.
- \( Q_c \) = direct measurement or estimate of continuous flow, m\(^3\) sec\(^{-1}\).

7. Finally, a statistical correction factor (CF) was applied to estimated P loadings as proposed by Ferguson (1986). The CF compensated for the inherent under-estimation of stream loads using regression relationships and was calculated as follows:

\[
\frac{s^2}{(n-2)} = \sum_{i=1}^{n} \left( \log C_i - \log C_p \right)^2 \\
\text{(Equation 4.5)}
\]

\[
CF = \exp (2.65s^2) \\
\text{(Equation 4.6)}
\]
Where:

\[ s^2 = \text{variance (measured scatter) of data points about regression line.} \]

\[ C_I = \text{direct measurement of P concentration, } \mu g \ l^{-1}. \]

\[ C_P = \text{estimate of P conc. from log-log regression equation, } \mu g \ l^{-1}. \]

4.3 Results – part one

4.3.1 Phosphorus concentrations

An example of temporal changes of P concentrations measured over the course of the survey period are shown for the Pow Burn (Figure 4.3). Remaining figures are located in Chapter 12, Appendix A.2. Table 4.1(a-d) summarises the P concentrations measured over the survey period at all sample site locations. Total P concentrations ranged between \(<10 \ \mu g \ l^{-1}\) to \(c. \ 600 \ \mu g \ l^{-1}\), mean TP values ranged from \(34 \ \mu g \ l^{-1}\) to \(129 \ \mu g \ l^{-1}\) and median values ranged from \(27 \ \mu g \ l^{-1}\) to \(102 \ \mu g \ l^{-1}\). Soluble reactive P concentrations ranged between \(<2 \ \mu g \ l^{-1}\) to \(c. \ 195 \ \mu g \ l^{-1}\). Mean SRP concentrations ranged between \(13 \ \mu g \ l^{-1}\) to \(49 \ \mu g \ l^{-1}\), whilst median values ranged between \(9 \ \mu g \ l^{-1}\) and \(39 \ \mu g \ l^{-1}\). Particulate P concentrations ranged between \(<2 \ \mu g \ l^{-1}\) to \(c. \ 470 \ \mu g \ l^{-1}\). Mean PP concentrations ranged between \(12 \ \mu g \ l^{-1}\) to \(81 \ \mu g \ l^{-1}\), whilst median values ranged between \(7 \ \mu g \ l^{-1}\) and \(54 \ \mu g \ l^{-1}\).
Figure 4.3: Phosphorus concentrations measured every 8 days at the Poy Burn.

Day due to lab closure.

Note: Data gap was a missed sampling between January 2005 and January 2006.
Table 4.1a: Summary statistics for total phosphorus measured ‘intermittently’ (every 8 days) between January 2005 and January 2006 in the inflows and outflow of Loch Leven.

<table>
<thead>
<tr>
<th>Catchment</th>
<th>Site</th>
<th>Mean TP Conc. (μg l⁻¹)</th>
<th>Median TP Conc. (μg l⁻¹)</th>
<th>TP Conc. Range (μg l⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pow Burn</td>
<td>Pb</td>
<td>93.5</td>
<td>65.1</td>
<td>33.6 – 415</td>
</tr>
<tr>
<td>North Queich</td>
<td>Na</td>
<td>57.6</td>
<td>43.0</td>
<td>22.5 – 237</td>
</tr>
<tr>
<td></td>
<td>Ne</td>
<td>33.5</td>
<td>27.3</td>
<td>6.0 – 117</td>
</tr>
<tr>
<td>Hatton Burn</td>
<td>Nh</td>
<td>87.0</td>
<td>65.3</td>
<td>37.6 – 355</td>
</tr>
<tr>
<td>Foccy Burn</td>
<td>Nf</td>
<td>53.6</td>
<td>48.9</td>
<td>24.1 – 132</td>
</tr>
<tr>
<td>South Queich</td>
<td>Sc</td>
<td>42.7</td>
<td>28.3</td>
<td>13.8 – 319</td>
</tr>
<tr>
<td></td>
<td>Sa</td>
<td>44.3</td>
<td>32.0</td>
<td>11.5 – 310</td>
</tr>
<tr>
<td>Gairney Water</td>
<td>Gb</td>
<td>40.9</td>
<td>31.6</td>
<td>12.7 – 171</td>
</tr>
<tr>
<td></td>
<td>Gc</td>
<td>37.3</td>
<td>27.1</td>
<td>8.2 – 205</td>
</tr>
<tr>
<td></td>
<td>Gu</td>
<td>73.0</td>
<td>48.1</td>
<td>21.85 – 252</td>
</tr>
<tr>
<td>Camel Burn</td>
<td>Cc</td>
<td>57.4</td>
<td>34.9</td>
<td>14.1 – 414</td>
</tr>
<tr>
<td>Fish Farm</td>
<td>Ca</td>
<td>129.0</td>
<td>102.5</td>
<td>52.4 – 608</td>
</tr>
<tr>
<td>Loch Outflow</td>
<td>L</td>
<td>75.4</td>
<td>62.5</td>
<td>30.2 – 164</td>
</tr>
</tbody>
</table>

Table 4.1b: Summary statistics for total soluble phosphorus measured ‘intermittently’ (every 8 days) between January 2005 and January 2006 in the inflows and outflow of Loch Leven.

<table>
<thead>
<tr>
<th>Catchment</th>
<th>Site</th>
<th>Mean TSP Conc. (μg l⁻¹)</th>
<th>Median TSP Conc. (μg l⁻¹)</th>
<th>TSP Conc. Range (μg l⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pow Burn</td>
<td>Pb</td>
<td>58.7</td>
<td>48.3</td>
<td>16.3 – 256</td>
</tr>
<tr>
<td>North Queich</td>
<td>Na</td>
<td>35.1</td>
<td>29.9</td>
<td>16.6 – 90</td>
</tr>
<tr>
<td></td>
<td>Ne</td>
<td>20.9</td>
<td>19.3</td>
<td>4.6 – 51</td>
</tr>
<tr>
<td>Hatton Burn</td>
<td>Nh</td>
<td>61.5</td>
<td>48.5</td>
<td>23.4 – 205</td>
</tr>
<tr>
<td>Foccy Burn</td>
<td>Nf</td>
<td>29.5</td>
<td>26.2</td>
<td>15.2 – 56.2</td>
</tr>
<tr>
<td>South Queich</td>
<td>Sc</td>
<td>22.9</td>
<td>17.8</td>
<td>7.3 – 88.4</td>
</tr>
<tr>
<td></td>
<td>Sa</td>
<td>23.2</td>
<td>20.6</td>
<td>6.8 – 87.6</td>
</tr>
<tr>
<td>Gairney Water</td>
<td>Gb</td>
<td>23.9</td>
<td>21.5</td>
<td>10.1 – 53.3</td>
</tr>
<tr>
<td></td>
<td>Gc</td>
<td>23.2</td>
<td>20.5</td>
<td>5.8 – 70.1</td>
</tr>
<tr>
<td></td>
<td>Gu</td>
<td>51.2</td>
<td>36.5</td>
<td>15.2 – 150</td>
</tr>
<tr>
<td>Camel Burn</td>
<td>Cc</td>
<td>32.9</td>
<td>23.4</td>
<td>11.2 – 129</td>
</tr>
<tr>
<td>Fish Farm</td>
<td>Ca</td>
<td>47.3</td>
<td>47.5</td>
<td>9.5 – 136</td>
</tr>
<tr>
<td>Loch Outflow</td>
<td>L</td>
<td>27.5</td>
<td>23.2</td>
<td>12.1 – 62.9</td>
</tr>
</tbody>
</table>
Table 4.1c: Summary statistics for soluble reactive phosphorus measured ‘intermittently’ (every 8 days) between January 2005 and January 2006 in the inflows and outflow of Loch Leven.

<table>
<thead>
<tr>
<th>Catchment</th>
<th>Site</th>
<th>Mean SRP Conc. ((\mu g \text{ l}^{-1}))</th>
<th>Median SRP Conc. ((\mu g \text{ l}^{-1}))</th>
<th>SRP Conc. Range ((\mu g \text{ l}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pow Burn</td>
<td>Pb</td>
<td>45.6</td>
<td>38.7</td>
<td>10.3 – 196</td>
</tr>
<tr>
<td>North Queich</td>
<td>Na</td>
<td>25.1</td>
<td>20.5</td>
<td>5.5 – 61.9</td>
</tr>
<tr>
<td></td>
<td>Ne</td>
<td>13.9</td>
<td>12.1</td>
<td>3.2 – 37.4</td>
</tr>
<tr>
<td>Hatton Burn</td>
<td>Nh</td>
<td>49.2</td>
<td>44.9</td>
<td>14.4 – 159</td>
</tr>
<tr>
<td>Foccy Burn</td>
<td>Nf</td>
<td>20.8</td>
<td>21.7</td>
<td>&lt;2 – 43.3</td>
</tr>
<tr>
<td>South Queich</td>
<td>Sc</td>
<td>14.2</td>
<td>11.5</td>
<td>&lt;2 – 55.3</td>
</tr>
<tr>
<td></td>
<td>Sa</td>
<td>13.3</td>
<td>9.5</td>
<td>&lt;2 – 52.6</td>
</tr>
<tr>
<td>Gairney Water</td>
<td>Gb</td>
<td>15.1</td>
<td>14.8</td>
<td>5.1 – 34.3</td>
</tr>
<tr>
<td></td>
<td>Gc</td>
<td>16.6</td>
<td>14.3</td>
<td>4.5 – 49.9</td>
</tr>
<tr>
<td></td>
<td>Gu</td>
<td>38.9</td>
<td>25.0</td>
<td>8.0 – 124</td>
</tr>
<tr>
<td>Camel Burn</td>
<td>Cc</td>
<td>23.4</td>
<td>15.9</td>
<td>4.3 – 105</td>
</tr>
<tr>
<td>Fish Farm</td>
<td>Ca</td>
<td>30.1</td>
<td>27.1</td>
<td>&lt;2 – 103</td>
</tr>
<tr>
<td>Loch Outflow</td>
<td>L</td>
<td>13.6</td>
<td>11.6</td>
<td>&lt;2 – 42.4</td>
</tr>
</tbody>
</table>

Table 4.1d: Summary statistics for particulate phosphorus measured ‘intermittently’ (every 8 days) between January 2005 and January 2006 in the inflows and outflow of Loch Leven.

<table>
<thead>
<tr>
<th>Catchment</th>
<th>Site</th>
<th>Mean PP Conc. ((\mu g \text{ l}^{-1}))</th>
<th>Median PP Conc. ((\mu g \text{ l}^{-1}))</th>
<th>PP Conc. Range ((\mu g \text{ l}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pow Burn</td>
<td>Pb</td>
<td>34.8</td>
<td>19.5</td>
<td>&lt;2 – 270</td>
</tr>
<tr>
<td>North Queich</td>
<td>Na</td>
<td>22.7</td>
<td>12.5</td>
<td>&lt;2 – 146</td>
</tr>
<tr>
<td></td>
<td>Ne</td>
<td>12.4</td>
<td>2.3</td>
<td>&lt;2 – 65.8</td>
</tr>
<tr>
<td>Hatton Burn</td>
<td>Nh</td>
<td>25.8</td>
<td>9.9</td>
<td>&lt;2 – 201</td>
</tr>
<tr>
<td>Foccy Burn</td>
<td>Nf</td>
<td>24.2</td>
<td>17.8</td>
<td>&lt;2 – 108</td>
</tr>
<tr>
<td>South Queich</td>
<td>Sc</td>
<td>19.7</td>
<td>10.9</td>
<td>&lt;2 – 230</td>
</tr>
<tr>
<td></td>
<td>Sa</td>
<td>21.5</td>
<td>11.6</td>
<td>&lt;2 – 223</td>
</tr>
<tr>
<td>Gairney Water</td>
<td>Gb</td>
<td>16.7</td>
<td>8.6</td>
<td>&lt;2 – 131</td>
</tr>
<tr>
<td></td>
<td>Gc</td>
<td>13.9</td>
<td>7.3</td>
<td>&lt;2 – 135</td>
</tr>
<tr>
<td></td>
<td>Gu</td>
<td>20.5</td>
<td>11.9</td>
<td>&lt;2 – 149</td>
</tr>
<tr>
<td>Camel Burn</td>
<td>Cc</td>
<td>24.2</td>
<td>9.8</td>
<td>&lt;2 – 288</td>
</tr>
<tr>
<td>Fish Farm</td>
<td>Ca</td>
<td>81.4</td>
<td>54.3</td>
<td>9.1 – 471</td>
</tr>
<tr>
<td>Loch Outflow</td>
<td>L</td>
<td>47.0</td>
<td>38.1</td>
<td>&lt;2 – 149</td>
</tr>
</tbody>
</table>
4.3.2 Constructing rating curves to estimate 8-day stream flows

Stream flow within the catchment was measured by either continuous monitoring gauges or from stage gauge measurements and the application of ratings curves. Stream flow at gauged sample sites was estimated using linear regressions between measured stream flow and staff gauge height (Figure 4.4). Data were log$_{10}$ transformed if necessary. The percentage of residual variance ($r^2$) accounted for by these regressions was > 90 %, except at the Camel Burn (78.7 %) and regressions were significant in all cases (p < 0.05).

![Graphs showing the relationship between stream flow and gauge height for various sites in the Loch Leven catchment.](image)

**Figure 4.4:** Ratings relationships and equations for determination of stream flow from stage gauge heights at water chemistry sampling sites in the Loch Leven catchment. Sites Pb, Ne and Sc were continuously gauged. Ratings curves were created to allow calculation of missing continuous flow data. Sites at Gb, Nh and Cc were measured manually.
Stream flow at the Camel Burn (Cc) was particularly hard to accurately estimate. This was due to aquatic vegetation growing within the channel through out much of the survey year, which impeded the flow of water through the stream. This almost certainly affected the estimation of low stream flows from measured staff gauge heights. However, water entering the loch from the Camel Burn was mostly controlled by the demands and operations of the fish farm, through diversion to fish ponds and receipt of waste water. All the sites with stage gauges ranged between 0.02 \( \text{m}^3 \text{sec}^{-1} \) and 10.01 \( \text{m}^3 \text{sec}^{-1} \). The largest high-flow event was measured at the South Queich (Sc), and the smallest high-flow event was recorded at the Camel Burn (Cc). This reflected the size of the varying sizes of sub-catchment drainage areas (Table 4.2).

**Table 4.2: Summary statistics for stream flows measured intermittently (every 8 days) between January 2005 and January 2006.**

<table>
<thead>
<tr>
<th>Site</th>
<th>Catchment Area (km(^2))</th>
<th>Mean Flow (m(^3) sec(^{-1}))</th>
<th>Median Flow (m(^3) sec(^{-1}))</th>
<th>Flow Range (m(^3) sec(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>11.40</td>
<td>0.176</td>
<td>0.154</td>
<td>0.02 – 0.92</td>
</tr>
<tr>
<td>Sc</td>
<td>32.22</td>
<td>0.910</td>
<td>0.370</td>
<td>0.09 – 10.01</td>
</tr>
<tr>
<td>Ne</td>
<td>24.96</td>
<td>0.750</td>
<td>0.457</td>
<td>0.08 – 5.66</td>
</tr>
<tr>
<td>Gb</td>
<td>28.79</td>
<td>0.590</td>
<td>0.520</td>
<td>0.07 – 2.37</td>
</tr>
<tr>
<td>Cc</td>
<td>2.02</td>
<td>0.053</td>
<td>0.052</td>
<td>0.03 – 0.114</td>
</tr>
<tr>
<td>Nh</td>
<td>6.97</td>
<td>0.176</td>
<td>0.118</td>
<td>0.05 – 1.53</td>
</tr>
</tbody>
</table>

Figure 4.5 summarises the time trends of intermittently measured stream flow that occurred at each gauged sample site on the Pow Burn, North Queich, South Queich, Gairney Water, Camel Burn and Hatton Burn, over the course of the survey. This shows that a full range of stream flows were sampled for P at each sampling location throughout the year, including 4 high-flow events. Each site was characterised by a period of low flow in the summer months.
Figure 4.5: Intermittent 8-day stream flows at the Pow Burn (Pb), South Queich (Sc), North Queich (Ne), Gairney Water (Gb), Camel Burn (Cc) and Hatton Burn (Nh), between January 2005 and January 2006.
4.3.3 Continuous flow time series at gauged and un-gauged sites

Stream flows at the Pow Burn, South Queich and North Queich were continuously measured by automatic flow gauges over the sampling year. At other sites, such equipment was not in place and so continuous flows were estimated using regression relationships between highly correlated sites (Steps 3 and 4 of Section 4.2.8). Table 4.3 summarises the results of Spearman’s rank correlation analysis. Stream flow between all sites was strongly and significantly correlated with each other ($r_s \geq 0.857, p < 0.001$). The purpose of generating continuous flows at each sampling site was to allow the calculation of P loads based on continuous measures of stream flow. Regression analysis was performed between the most highly correlated continuously gauged and intermittently gauged sites. Stream flows in the Camel Burn and the Hatton Burn were most strongly correlated with continuous flow measured at the Pow Burn (Figure 4.6a and Figure 4.6b). Stream flow at the Gairney Water was most strongly correlated with continuous stream flow at the South Queich (Figure 4.6c). Regressions were very highly significant and explained a large amount of residual variation ($r^2 \geq 86.0\%, p < 0.001$). Graphs showing continuous flows over the survey period are shown in Figure 4.7.

**Table 4.3:** Correlation coefficients ($r_s$ value and significance) indicating the relationships between measurements of flow at different inflows to Loch Leven.

<table>
<thead>
<tr>
<th>Catchment (Site)</th>
<th>Pow Burn (Pb)</th>
<th>Sth Queich (Sc)</th>
<th>Nth Queich (Ne)</th>
<th>Gairney Water (Gb)</th>
<th>Camel Burn (Cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sth Queich (Sc)</td>
<td>0.917</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>p &lt; 0.001</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nth Queich (Ne)</td>
<td>0.922</td>
<td>0.984</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>p &lt; 0.001</td>
<td>p &lt; 0.001</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gairney Water (Gb)</td>
<td>0.917</td>
<td>0.973</td>
<td>0.953</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>p &lt; 0.001</td>
<td>p &lt; 0.001</td>
<td>p &lt; 0.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Camel Burn (Cc)</td>
<td>0.935</td>
<td>0.868</td>
<td>0.857</td>
<td>0.900</td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>p &lt; 0.001</td>
<td>p &lt; 0.001</td>
<td>p &lt; 0.001</td>
<td>p &lt; 0.001</td>
<td></td>
</tr>
<tr>
<td>Hatton Burn (Nh)</td>
<td>0.941</td>
<td>0.922</td>
<td>0.930</td>
<td>0.927</td>
<td>0.907</td>
</tr>
<tr>
<td></td>
<td>p &lt; 0.001</td>
<td>p &lt; 0.001</td>
<td>p &lt; 0.001</td>
<td>p &lt; 0.001</td>
<td>p &lt; 0.001</td>
</tr>
</tbody>
</table>
Figure 4.6: Linear regressions between 8-day measured values of stream flow between sites where continuous stream flow data was available.
Figure 4.7: Continuous stream flow at gauged sites between January 2005 and January 2006.
Maximum stream flows measured at the Pow Burn, South Queich and North Queich were 3.95 m³ sec⁻¹, 24.59 m³ sec⁻¹ and 12.83 m³ sec⁻¹, respectively (Table 4.4). These results show that the highest stream flows were not sampled for P concentrations during the 8-day survey monitoring programme.

Table 4.4: Summary statistics for continuously (every 15 minutes) measured and modelled (italics) stream flows between January 2005 and January 2006.

<table>
<thead>
<tr>
<th>Site</th>
<th>Mean Flow (m³ sec⁻¹)</th>
<th>Median Flow (m³ sec⁻¹)</th>
<th>Flow Range (m³ sec⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>0.169</td>
<td>0.154</td>
<td>0.02 - 3.9</td>
</tr>
<tr>
<td>Sc</td>
<td>0.675</td>
<td>0.393</td>
<td>0.002 - 24.6</td>
</tr>
<tr>
<td>Ne</td>
<td>0.634</td>
<td>0.435</td>
<td>0.07 - 12.8</td>
</tr>
<tr>
<td>Gb</td>
<td>0.522</td>
<td>0.387</td>
<td>0.007 - 8.80</td>
</tr>
<tr>
<td>Cc</td>
<td>0.053</td>
<td>0.054</td>
<td>0.02 - 0.195</td>
</tr>
<tr>
<td>Nh</td>
<td>0.148</td>
<td>0.118</td>
<td>0.06 - 3.99</td>
</tr>
</tbody>
</table>

4.3.4 Catchment rainfall

Heavy rainfall generates high river flows especially when a large amount of rain falls in a short space of time. Such conditions also cause significant amounts of surface runoff which provides a transport mechanism for P from the land to water courses. As such, periods of heavy rainfall and high stream flow are likely to significantly increase the amount of diffuse source P being delivered to Loch Leven. Average annual rainfall in the catchment between 1992 and 2006 was 1061 mm (Figure 4.8). Between 18th January 2005 and 17th January 2006 a total of 780 mm of rain fell in the catchment, therefore, 2005 could be considered a relatively dry year. 2005 daily rainfall amounts ranged from 0 mm to 35 mm (Figure 4.9). October was the wettest month with a total of 125.8 mm of rain which accounted for approximately 16% of the annual rainfall amount. October also had the highest average daily rainfall amount and the highest amount of rain to fall on one day. November was the second wettest month with a total of 89.6 mm of rainfall, which accounted for approximately 11% of the total annual rainfall.
Figure 4.8: Total annual rainfall in the Loch Leven catchment between 1992 and 2006 (dashed line shows the annual average rainfall over this period).

Figure 4.9: Hourly rainfall amounts in the North Queich catchment during 2005.
Table 4.5: Summary of annual rainfall that fell in the North Queich catchment over the sampling period of the phosphorus loading survey (Data supplied by SEPA).

<table>
<thead>
<tr>
<th>Month (2005)</th>
<th>Total Rainfall (mm)</th>
<th>% of Annual Rainfall</th>
<th>Average Daily Rainfall (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>January 18th – 31st</td>
<td>1.0</td>
<td>0.13</td>
<td>0.08</td>
</tr>
<tr>
<td>February</td>
<td>52.6</td>
<td>6.74</td>
<td>1.88</td>
</tr>
<tr>
<td>March</td>
<td>77.2</td>
<td>9.89</td>
<td>2.49</td>
</tr>
<tr>
<td>April</td>
<td>76.8</td>
<td>9.84</td>
<td>2.56</td>
</tr>
<tr>
<td>May</td>
<td>84.2</td>
<td>10.79</td>
<td>2.72</td>
</tr>
<tr>
<td>June</td>
<td>69.6</td>
<td>8.92</td>
<td>2.33</td>
</tr>
<tr>
<td>July</td>
<td>19.2</td>
<td>2.46</td>
<td>0.62</td>
</tr>
<tr>
<td>August</td>
<td>55.2</td>
<td>7.07</td>
<td>1.78</td>
</tr>
<tr>
<td>September</td>
<td>49.2</td>
<td>6.30</td>
<td>1.64</td>
</tr>
<tr>
<td>October</td>
<td>125.8</td>
<td>16.12</td>
<td>4.06</td>
</tr>
<tr>
<td>November</td>
<td>89.6</td>
<td>11.48</td>
<td>2.99</td>
</tr>
<tr>
<td>December</td>
<td>52.4</td>
<td>6.71</td>
<td>1.69</td>
</tr>
<tr>
<td>Jan 1st – 17th 2006</td>
<td>27.6</td>
<td>3.54</td>
<td>1.62</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>780.4</strong></td>
<td><strong>100</strong></td>
<td></td>
</tr>
</tbody>
</table>

4.3.5 Log-log linear regression analysis

To complete step 5 of the loading calculation process (refer to Section 4.2.8), regression analysis was performed to assess the relationship between stream flow and P concentrations at each flow gauged site. A visual examination of scatter plots of the data revealed that there were P outliers in some data sets. Townsend (2006) recommended that, if outliers are present among a data set, it should be carefully considered whether the anomaly could be due to some ‘freak’ condition or event during sample collection or analysis. An investigation into the identified outlying points indicated that a small number of points had been caused by either:

1. A point-source contamination event, characterised by a low flow with unusually high soluble phosphorus concentration or,
2. A catchment contamination event, characterised by a large increase in particulate P concentration that was not associated with a high stream flow.

It was considered appropriate to remove these data points, as regression analysis is very sensitive to such outlying values (Townsend, 2006). Anderson Darling normality tests revealed that the stream flow and water chemistry data were not
normally distributed and showed positive skewness. Logarithmic transformation was applied in order to achieve normality of data distribution, but this was not successful on all occasions. Data skewness was caused by the small number of high flows sampled for water chemistry over the period of the survey. Log-log linear regression equations for each sample site are provided in Figure 4.10 to Figure 4.13. All linear regressions were significant \( p < 0.005 \) and coefficients of determination \( (r^2) \) ranged from 27% to 69%.

### 4.3.6 Error propagation

Error in the estimated annual P load value can be attributed to a number of factors. First, there is error associated with the determination of P concentrations in water samples. On average, the standard error associated with measuring TP concentrations in water samples was 1.8 \( \mu g \) l\(^{-1}\) or approximately 4% of the final estimated concentration. The largest amount of error associated with the log-log regression method is associated with the estimation of flows in streams. All flows were estimated using regressions between measured stream flow and gauge heights. In an ideal situation, structural weirs and continuous flow devices would be located on all inflows as this would appreciably minimise the error associated with estimating stream flows. However, this is generally not possible due to resource constraints and stream flows must be estimated using the best available methodology. However, although unquantifiable, it is acknowledged that with every estimate of stream flow the error associated with the final estimate of annual P load increases. Finally, there was a large amount of scatter of the data points about the regression lines presented in Figures 4.10 to 4.13. This was particularly evident at sample sites (e.g. Gairney Water and Hatton Burn) where the relationships between stream flow and P were not strongly correlated (Table 4.6). This indicates that stream flow is not the principal factor determining P concentrations and the streams were likely to be influenced by rural point sources, e.g. septic tanks. Therefore, other factors are also likely to explain P concentrations in streams and to use only one i.e. stream flow, to estimate P concentrations has its limits.
Table 4.6: Results of Spearman’s rank correlation analysis between measures of stream flow and phosphorus at inflows in the Loch Leven catchment.

<table>
<thead>
<tr>
<th>Catchment</th>
<th>Site</th>
<th>TP</th>
<th>P value</th>
<th>TSP</th>
<th>P value</th>
<th>SRP</th>
<th>P value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pow Burn</td>
<td>Pb</td>
<td>0.595</td>
<td>0.001</td>
<td>0.698</td>
<td>0.001</td>
<td>0.711</td>
<td>0.001</td>
</tr>
<tr>
<td>South Queich</td>
<td>Sc</td>
<td>0.562</td>
<td>0.01</td>
<td>0.768</td>
<td>0.001</td>
<td>0.823</td>
<td>0.001</td>
</tr>
<tr>
<td>North Queich</td>
<td>Ne</td>
<td>0.606</td>
<td>0.001</td>
<td>0.726</td>
<td>0.001</td>
<td>0.733</td>
<td>0.001</td>
</tr>
<tr>
<td>Gairney Water</td>
<td>Gb</td>
<td>0.517</td>
<td>0.001</td>
<td>0.448</td>
<td>0.003</td>
<td>0.540</td>
<td>0.001</td>
</tr>
<tr>
<td>Hatton Burn</td>
<td>Nh</td>
<td>0.437</td>
<td>0.003</td>
<td>0.385</td>
<td>0.01</td>
<td>0.369</td>
<td>0.05</td>
</tr>
<tr>
<td>Camel Burn</td>
<td>Cc</td>
<td>0.656</td>
<td>0.001</td>
<td>0.614</td>
<td>0.001</td>
<td>0.566</td>
<td>0.001</td>
</tr>
</tbody>
</table>

However, despite the propagation of error associated with using the log-log regression method to estimate an annual P load to Loch Leven, the method is still considered to be the most appropriate and least inaccurate on the basis of the available data and the frequency at which the data was collected during this study. A further discussion of the errors associated with this method is provided in Section 4.6.3. The regression equations presented in Figures 4.10 to 4.13 were used to estimate continuous P concentrations from which the annual P load to Loch Leven was calculated (refer to steps 6 and 7 of Section 4.2.8). These results are presented in the following section.
Figure 4.10: Log-log linear regressions on stream flow and phosphorus concentrations at the Pow Burn and North Queich.
Figure 4.11: Log-log linear regressions on stream flow and phosphorus concentrations at the South Quiech and Gairney Water.
Figure 4.12: Log-log linear regressions on stream flow and phosphorus concentrations at the Hatton Burn and Camel Burn.
Figure 4.13: Log-log linear regressions on stream flow and phosphorus concentrations at the Ury Burn and Kinesswood Burn.
4.4 Results – part two

4.4.1 Annual phosphorus loads to Loch Leven (2005)

The first aim of this study was to estimate the annual P load to Loch Leven in 2005. It was calculated that a total of 7.69 t TP, 3.57 t TSP, 2.68 t SRP and 4.11 t PP was delivered to Loch Leven from the catchment in 2005. The sub-catchments that contributed the most P to the loch were the North Queich, Pow Burn, South Queich and the Gairney Water, which corresponded to the four largest sub-catchments (Figure 4.14). The South Queich, North Queich, Gairney Water, Camel Burn, Ury Burn and Kinesswood Burn were dominated by the SRP fraction (41-58%). In contrast, the annual P load from the Pow Burn and the fish farm was dominated by the PP fraction (74.8% and 60%, respectively) (Figure 4.15). Phosphorus losses per unit area of catchment ranged between 0.32 to 1.25 kg TP ha\(^{-1}\) yr\(^{-1}\), 0.1 to 2.4 kg SRP ha\(^{-1}\) yr\(^{-1}\) and 0.09 to 0.93 kg PP ha\(^{-1}\) yr\(^{-1}\). Per unit of catchment area, the Pow Burn contributed notably more P, especially in the particulate form, compared to other sub-catchments (Figure 4.16).

Figure 4.14: Annual phosphorus loadings to Loch Leven from sub-catchments in 2005.
Figure 4.15: Percentage contribution of soluble and particulate phosphorus to the annual TP (=SRP+PP+SURP) load from catchment inflows to Loch Leven in 2005.

Figure 4.16: Phosphorus losses (per hectare) from the catchment to Loch Leven in 2005.
4.4.2 Comparison of 20 years of phosphorus loads to Loch Leven

The second aim of the study was to compare the annual P load in 2005 to previous historical loading estimates. In order to determine if management actions in the catchment have led to a reduction in P loads, a comparison has been made to load estimates from previous surveys in 1985 and 1995 (Bailey-Watts and Kirika, 1987, 1999) (Figure 4.17). A large reduction in P loads of approximately 12.1 t TP and 6.8 t SRP occurred between 1985 and 1995. It is noted that these two estimates were calculated using different methods. In 1985, the annual P load was estimated on the basis of an interpolation method after Rodda and Jones (1981) whilst in 1995 annual P load was estimated using the log10-log10 extrapolation method presented in this chapter. The difference is that the interpolation method applied a discharge weighting to measured P concentration values and did not account for changing stream flow conditions between sampling days. This method can lead to underestimations of P loads because high stream flow events were probably not sampled (Johnes, 2007). Therefore, despite the differences in estimation method, the reduction in P load between 1985 and 1995 is realistic given that 1985 loads were probably underestimated. Between 1995 and 2005 TP did not notably decrease as there was only a 0.3 t reduction. In contrast, SRP loads continued to fall between 1995 and 2005, decreasing by 2.31 t whilst PP loads increased by 1.35 tonnes.

The % contribution of SRP and PP to TP loads was investigated. In 1995, SRP and PP loads contributed 63% and 37% of the annual TP load, whilst in 2005 SRP and PP loads contributed 37% and 56% (Figure 4.18). Continued management of point sources in the catchment have also continued to reduce SRP loadings and PP loads has increased resulting in PP now contributing the greater proportion of the annual TP load to Loch Leven. This study also concludes that PP specifically from diffuse sources is now the dominant P source to the loch. This assumption has been made on the grounds that the majority (~80%) of the Loch Leven catchment is dominated by agricultural land and that PP inputs are suggestive of soil-associated P losses which are eroded during periods of heavy rainfall and surface runoff (Figure 4.19).
Figure 4.17: Estimated annual total phosphorus and soluble reactive phosphorus loadings to Loch Leven and annual catchment rainfall in 1985, 1995 and 2005.

Figure 4.18: The contributions of soluble and particulate phosphorus to the annual total phosphorus load in 1985, 1995 and 2005.
Sources of P from the Loch Leven catchment

Diffuse sources
- Agricultural sources, e.g. inorganic and organic fertilisers.
- Eroded catchment soils and associated P
- Re-suspended stream sediments
- Desorbed P from soils and sediments

Point sources
- Sewage treatment effluent
- Septic tanks
- Source areas from farmyards and farm animals
- Storm overflow or land drainage pipes

Figure 4.19: Conceptual model of primary sources of soluble and particulate phosphorus from the Loch Leven catchment. (Note: Size of arrows indicates contribution from diffuse and point sources).

4.4.3 Comparison of monthly phosphorus loads to Loch Leven

As mentioned, diffuse P is in many cases, predominantly driven by periods of high rainfall and runoff that leads to increasing PP transport from the catchment (Johnes and Hodgkinson, 1998; Heathwaite and Dils, 2000). Therefore, comparisons between monthly loads and P proportions and rainfall amounts have been made in order to investigate the times of the year when PP inputs to the loch were highest (Figure 4.20). Results showed that summer months (July, August, and September) contributed least to the annual P load, with TP, SRP and PP contributing only 7%,
6% and 7%, respectively. In contrast, P loads greatly increased during winter. October and November were the wettest months and contributed just over a third of the annual loads of TP, SRP and PP (33%, 36% and 34%, respectively). Accordingly, October and November contributed the greatest amounts of TP, PP and SRP to the loch compared to other months. Monthly TP, SRP and PP loads were significantly correlated with monthly rainfall (Pearson’s Product Moment Correlation $r = 0.716, 0.715$ and $0.708$, $p < 0.01$), despite increasing rainfall in August and September not leading to notable increasing loads.

Figure 4.20: Monthly phosphorus loads to Loch Leven during 2005 (TP is the sum of SRP, PP and SURP).

4.5 Results summary

In summary, the results of the research presented so far have shown that:

1. According to the applied methodology and calculations, the annual P load to Loch Leven has not notably decreased over the past ten years. However, the contribution of SRP and PP sources has changed. Compared to SRP, PP now contributes a greater proportion of the annual TP load to Loch Leven because
catchment management has reduced point source P loads from sewage treatment works and PP loads have also increased.

2. The catchment of the Pow Burn contributed most of its annual TP load in the PP form. This is most likely due to the intense agricultural land use in this catchment, maybe making it an important source of diffuse PP.

3. Loss rates between sub-catchments ranged from 0.32 to 1.25 kg TP ha$^{-1}$ yr$^{-1}$, with the average loss rate being 0.58 kg TP ha$^{-1}$ yr$^{-1}$, which is considered to be low compared to other catchments of similar character. The Pow Burn had the highest TP loss rates compared to other sub-catchments, most notably in the PP form.

4. 33% of the annual TP and PP loads were delivered to Loch Leven during the winter months (Oct, Nov and Dec).

4.6 Discussion

4.6.1 Phosphorus concentrations in Loch Leven

Total phosphorus (TP) concentrations provide a simple index of the trophic status of the loch. In 2005, the annual mean TP concentration at the loch outflow was 75 µg l$^{-1}$ with maximum TP concentrations reaching 164 µg l$^{-1}$ in late September and early October. This value was much higher than the target mean annual TP concentration of 40 µg l$^{-1}$ set by the Loch Leven Area management Group in 1993 and approved in the Loch Leven Management Plan (LLCMP, 1999). However, in this research measurements were performed at one location on the loch; at the outflow. Water quality monitoring data collected by the Centre for Ecology and Hydrology showed that the average TP concentration in the loch in 2005 was 73.5 µg l$^{-1}$, ranging from 34 µg l$^{-1}$ to 140 µg l$^{-1}$ in 2005 ($n = 48$). This average was based on samples from three different areas of the loch, two of which were in open water. Chlorophyll$\text{a}$ concentrations in the loch in 2005 showed fairly typical patterns of change for a mesotrophic shallow loch (Reynolds, 1984; Carvalho and Kirika, 2001). As the day length increases in February and March and when nutrient levels were fairly high, an increase in chlorophyll$\text{a}$ concentrations was observed. Throughout
April and May concentrations declined. This was followed by two large pulses in mid August and early November, when chlorophyll$_a$ concentrations peaked at 56 µg Chl$_a$ l$^{-1}$ and 100 µg Chl$_a$ l$^{-1}$, respectively. The annual mean concentration was 32 µg Chl$_a$ l$^{-1}$, which still exceeds the target value of 15 µg l$^{-1}$ set by SEPA. This data suggests that the loch still has some way to go in terms of recovery from eutrophication.

4.6.2 Phosphorus concentrations in streams and rivers

Phosphorus concentrations in all rivers and streams draining the Loch Leven catchment were also of limnological significance, given that a eutrophic water body is classified as having mean annual TP concentrations between 35 and 100 µg l$^{-1}$ (OECD, 1982). Annual mean TP concentrations from the sampling sites fell into three main groups. The first group comprised the Pow Burn (Pb), the Hatton Burn (Nh) and a small tributary of the Gairney Water (Gu). These sites had a mean annual TP concentration greater than 70 µg l$^{-1}$, reflecting reasonably intensively managed agricultural catchments and areas of point source inputs. The effluent discharged from the fish farm into the Camel Burn also had a mean annual TP concentration above 70 µg l$^{-1}$. The second group comprised the North Queich at sample site Ne, the South Queich (Sc and Sa) and the Gairney Water (Gc and Gb). These sites had a mean annual TP concentration between 30 µg l$^{-1}$ and 45 µg l$^{-1}$. These sites received runoff from less intensive agricultural areas and experienced little point source pollution from sewage treatment works or industrial effluents. The remaining sample sites on the North Queich (Na and Nf) and the Camel Burn (Cc) above the fish farm, had intermediate mean annual TP concentrations in the region of 50 µg l$^{-1}$ to 57 µg l$^{-1}$. Site Na on the North Queich receives treated effluent from a local sewage treatment works, which is subsequently diluted by the joining of the North Queich’s tributaries. The Foccy Burn (Nf) runs through the small town of Milnathort and is likely to receive additional runoff from urban land and possible septic tank inputs from rural housing. Similar groupings of sites were evident for TSP and SRP, with mean annual concentrations between 20 to 61 µg l$^{-1}$ and 13 to 49 µg l$^{-1}$, respectively. Mean PP concentrations, however, showed little variation between
sample sites (12 μg l\(^{-1}\) to 25 μg l\(^{-1}\)). The exceptions were the sample sites at the fish farm on the Camel Burn (Ca) and the Pow Burn (Pb). These sites had higher mean annual PP concentrations (81.4 μg l\(^{-1}\) and 34.8 μg l\(^{-1}\)) compared to all other sites, reflecting the higher proportion of agricultural land use in the Pow Burn catchment, and the activities associated with fish rearing.

Point source contamination is sometimes characterised by large increases in soluble P concentrations when stream flow is low, and small soluble P concentrations when stream flow is high (Evans and Johnes, 2004; Wood et al., 2005). Evidence of point source P pollution was observed in two small tributaries of the Gairney Water and the North Queich. SRP concentrations were seen to increase with decreasing stream flow in summer months demonstrating a concentrating effect characteristic of point source P contamination. These small streams were most likely impacted by septic tanks from a large number of nearby rural houses. In most rural catchments, septic tanks are the primary method of waste disposal, with the effluent draining away to a soakaway to allow nutrients to be dissipated, bound and degraded by surrounding soils (Harper, 1992). Carvalho et al. (2003) commented that seepage of P from these systems in the UK is higher than expected due to poor maintenance and mismanagement. Frost (1996) reported that P export from septic tanks systems in the Loch Leven catchment could be as high as 0.33 kg P capita\(^{-1}\) yr\(^{-1}\). Elevated summer SRP concentrations in these tributaries were diluted as they joined with larger inflows before discharging into the loch. Better management of septic tanks in the catchment could further reduce the delivery of high SRP concentrations and loads to the loch via small tributaries. High summer SRP concentrations in the Camel Burn were also observed due to the influence of fish farm effluent. Such sources can have a significant effect on P concentrations in receiving waters (Wood et al., 2005) as well as on local benthic communities (Kendra, 1991). Since the time of this study, the fish farm has ceased to operate, so a further point source of P has been removed.

Considering the proportions of soluble and particulate P being delivered to the loch was important because SRP is often considered to be the most bioavailable fraction. However, some fraction of the PP reaching the loch may eventually be utilised by algae (Boström et al., 1988). Therefore, the delivery of all forms of P to the loch is important (Johnes and Hodgkinson, 1998). The dominance of soluble and
particulate fractions changed between low and high flows. Soluble reactive P was most frequently the dominant P fraction during base flow conditions, whilst PP dominated the TP fraction during elevated flows. This is a characteristic response when streams are principally influenced by diffuse source, rather than point source P. Accordingly, P concentrations were positively correlated with stream flow in most of the inflows, except those already identified as having significant point source influences. Both SRP and PP concentrations increased as stream flows increased, but at different magnitudes. Particulate P increased by a larger amount compared to SRP, most likely as a result of greater erosion and transport during periods of high catchment runoff (Russell et al., 1998; Caruso, 2000). Higher SRP concentrations during higher flows indicated that diffuse sources of P in the catchment were, along with point sources, an important source of SRP. However, these two sources could not be distinguished by this study as individual point sources were not identified and assessed separately.

4.6.3 Estimating nutrient loads using intermittent data and log-log regressions

The assessments of P concentrations and stream flows were performed in order to calculate P loads to Loch Leven during the survey year. The next part of the discussion considers the method by which P loads were calculated, as it is well documented that there are many assumptions and errors associated with different load estimation methods (Walling and Webb, 1981). As a number of important conclusions have been made on the basis of the P loads calculated in this study, it is appropriate to address and justify the method applied.

The problems associated with reliably estimating nutrient loads transported by rivers have been clearly recognised over the years (Ongley, 1973; Verhoff et al., 1980, Walling and Webb, 1981; Rodda and Jones, 1983; Rekolainen et al., 1991) and the debate surrounding the most error-free method still continues today (Walling and Webb, 1997; Phillips et al., 1999; Johnes, 2007). The most commonly applied methods are either based on either interpolation or extrapolation calculations. Interpolation methods use values of instantaneous stream flows ($Q_i$) and pollutant concentrations ($C_i$). In contrast, extrapolation methods use relationships between
measured values of $Q_i$ and $C_i$ to provide a method of predicting high-frequency concentrations on the basis of continuously measured values of $Q$. However, much of the literature that has investigated the reliability of load estimation methods has concluded that the accuracy of both methods is questionable (Walling et al., 1997; Johnes, 2007). This study has presented P loading results based on the use of an extrapolation procedure commonly used to generate high frequency estimates of $C$ on the basis of $Q$ measurements (Stevens and Smith, 1978; Ferguson, 1986). Therefore, it is appropriate to evaluate the accuracy of this technique used for estimating the P loads presented so far. Undoubtedly the most commonly recognised issue is that the inaccuracy of load estimates is, in most instances, the result of infrequent sampling. This is because intermittent sampling significantly reduces the chance of incorporating short-term, extreme flow conditions within a data set leading to an under-estimation of load (Dolan et al., 1981; Phillips et al., 1999; Horowitz, 2003 and Johnes, 2007). To compensate for this, the use of extrapolation techniques is, more often than not, the favoured method to account for the influence of high flow events on pollutant transport.

The most commonly used extrapolation technique is the one applied in this study, which creates log-log linear regressions between measured values of $Q_i$ and $C_i$. The use of this method results in known concentrations of P being replaced by an estimated concentration based on an empirical relationship between $C_i$ and $Q_i$. It was soon recognised on that such a technique could under-estimate river loadings by up to 50%, as a result of scatter about the regression line, as well as the effect of converting log values to arithmetic-values (Walling and Webb, 1988; Horowitz, 2003). This was originally addressed by Ferguson (1986) who suggested the application of a statistical correction factor. However, Johnes (2007) provided evidence that using the log-log regressions with correction factors still underestimated P loads, even when ratings curves were based on daily observations of $C_i$ and $Q_i$. This was also reported in earlier studies by Webb and Walling (1992), Kronvang and Bruhn (1996) and Webb et al. (1997). Although the use of a correction factor can help to counteract the inherent underestimation of log-log regression equations, it cannot alter the scatter of data points about the regression line. As such, the use of linear regression analysis for the purpose of predicting a
dependant variable from an independent variable is often abused because the statistic has a number of assumptions that must be met in order to be statistically robust.

Firstly, linear regression analysis implies that one of the variables is actually dependent on another, and that the relationship is described by a straight line. Therefore, in terms of P loadings, the accuracy will be determined by the strength of the correlation between $Q_i$ and $C_i$ and the goodness of fit (or the scatter) of the regression line through the data points. Generally, TP and PP concentrations are highly dependent on stream flow and can be estimated with much greater certainty than soluble P fractions (Johnes, 2007). This is because the PP fraction is usually highly correlated with stream flow due to its close relationship with SS concentrations (Kronvang et al., 1997). SRP, however, is often observed to be flow-independent in streams or rivers which are dominated by point source P contamination. SRP may also be leached from diffuse sources, such as bed sediments, so a strong a relationship between $Q_i$ and $C_i$ may not always be evident. The strength of these relationships varied greatly in the current study ($r^2 = 0.27$ to $0.68$). Therefore, in some instances, it may not have been appropriate to use log-log linear regressions to fill in the gaps between data points using continuous values of stream flow as the predictor variable. At some sampling sites, for example, P concentrations at Gairney Water (Gb) and the Hatton Burn (Nh) did not show strong relationships with stream flow. Therefore, it is likely that the accuracy of P load estimates varied in this study. Other authors have highlighted the complex relationships that exist between P concentrations and flow rate. Kronvang (1992) found that the relationship between SRP and flow rate varied depending on the degree to which flow rate was changing at the time of sampling - the highest concentrations were measured when flow rates were increasing rapidly. Bailey-Watts and Kirika (1987) showed that point P sources significantly reduced the correlation between log $Q_i$ and log $C_i$.

A number of suggestions to improve P load estimates have been postulated in the literature. Dolan et al. (1981) suggested using seasonal log-log regressions, rather than annual regressions, whilst Johnes (2007) suggested applying a stratified sampling programme. This method would use data from daily sampling on the 35 highest flows of the year, combined with weekly sampling during the remainder of
the year. Horowitz (2002) also supported this notion, suggesting that if sampling was hydrologically distributed to encompass 80-85% of the typical range of stream discharges, the associated estimation errors would probably be less. This is often considered to be a reasonable option in terms of resource constraints, whilst taking into account the impacts of extreme events on P loads. In practical terms however, it is not always possible to ensure that sampling on the 35 highest flows takes place. Johnes (2007) also reported that it was common to find that the inclusion of just one extreme high flow event in a data set lead to a significant over-estimate of nutrient loads in some systems. This was explained by the strong relationship between suspended sediments and stream discharge, which tend to be more biased towards larger flow events (Webb et al., 1996). Because TP is often highly correlated with suspended sediment concentrations (Kronvang et al., 1997), loads may be overestimated where a few high flow events have been sampled during an intermittent sampling programme. In this study, sampling took place on four occasions of high flow, which may have compensated for the under-estimation associated with the log-log regressions. However, the contribution that high flow events make to an annual load will be more reliably estimated by sampling individual high-flow events at a much higher frequency.

Sampling frequency is not the only reason for inaccuracy and variability of load estimates. Johnes (2007) demonstrated that it was also a function of catchment related factors, such as population density, point source influences and catchment hydrological characteristics. Catchments with a high base flow index had strongly buffered flow and P concentrations, so were observed to be relatively insensitive to the load estimation method chosen. In contrast, for catchments with low base flow index, a high human population density or were impacted by point source P inputs, returned a relatively high degree of imprecision in load estimates, even when these were based on daily sampling measures. Furthermore, Jordan et al. (2007b) commented that single daily measures of P and discharge can lead to significantly large errors in load estimates. This demonstrates that choosing a reliable method to calculate an accurate load from a catchment is not easy. In this study, applying the log-log extrapolation procedure was the most practical and cost effective method of accounting for the influence of high flow events and continuously changing values of
Q and C. In addition, by applying the same method as previous P loading surveys, it was possible to make comparisons and conclusions regarding historical changes in P loads in the Loch Leven catchment.

4.6.4 Twenty years of phosphorus loading in the Loch Leven catchment

Annual P loads to Loch Leven have now been estimated for 1985, 1995 and 2005. Between 1985 and 1995, there was a substantial reduction in P loads to the loch. There were three main explanations for this reduction. First, point sources of SRP in the catchment were reduced significantly due to the closure of a local woollen mill in 1989. The mill ceased to pump SRP-rich effluent into the South Queich and this action alone was estimated to have reduced the annual SRP load by approximately 6.29 t (LLCMP, 1999). Secondly, there were significant improvements to sewage treatment facilities in the catchment between 1993 and 1997. A new treatment works was constructed at a cost of approximately £2.9 M in order to perform secondary waste water treatment. The new system discharged 1.0 kg TP and 0.3 kg SRP day\(^{-1}\), compared to the daily outputs of 2.8 kg TP and 2.2 kg SRP day\(^{-1}\) from the old treatment works (Bailey-Watts and Kirika, 1999). The sewage effluent from the village of Kinnesswood was also diverted out of the catchment. Lastly, diffuse P inputs to the loch might have been substantially lower in 1995 due to the lower annual rainfall (Bailey Watts and Kirika, 1999). A total of 1250 mm rainfall fell in the catchment in 1985; 189 mm above the annual average (between 1994 and 2006). This probably resulted in higher amounts of PP entering the loch as a result of increased catchment runoff.

Between 1995 and 2005, the reduction of P load to the loch was not as dramatic as the previous decade. However, the TP and SRP load to the loch decreased by 0.3 t and 2.31 t respectively, suggesting that catchment management continues to reduce point P inputs more effectively than diffuse sources. As such, a reduction in the percentage contribution of SRP to the annual TP load was also evident. Reductions in SRP loads have been greatly influenced and driven by the introduction of European legislation, most recently the Water Framework Directive (2000/60/EC), which was implemented into Scottish law in December 2003. More
locally however, the publication of the Loch Leven Catchment Management Plan (1999) also encouraged the involvement of many of the catchment’s stakeholders in achieving reduced P inputs to the loch. Chapter 2 has already expanded on some of the Plan’s initiatives proposed to tackle P pollution in the catchment.

Nevertheless, results of the current P loading survey suggest that whilst SRP loads continue to fall PP now contributes a greater percentage of the annual TP load. Further improvement in water quality will require significant reductions in P loadings from diffuse P sources (Carpenter et al., 1998). Management initiatives primarily targeting agriculture will be critical to achieve further reductions of P loads (Johnes and Hodgkinson, 1998). In order to achieve successful reductions, there is a requirement to obtain catchment specific information relating to diffuse P sources. Examining P loadings between sub-catchments and analysing monthly P loadings identified important areas of the catchment that contributed a large amount of diffuse source PP. Critical periods when a significant amount of diffuse source PP entered the loch were also identified. These key points are discussed in further detail in the following sections.

4.6.5 Critical source areas in the Loch Leven catchment for diffuse source phosphorus

The average P loss rate from the catchment to the loch was estimated to be approximately 0.58 kg TP ha\(^{-1}\) yr\(^{-1}\). Loss rates between sub-catchments ranged from 0.32 kg TP ha\(^{-1}\) yr\(^{-1}\) up to 1.25 kg TP ha\(^{-1}\) yr\(^{-1}\). Kronvang and Bruhn (1996) reported P loss rates between 0.24 kg TP ha\(^{-1}\) yr\(^{-1}\) to 2.0 kg TP ha\(^{-1}\) yr\(^{-1}\) from agricultural catchments in Denmark. Vuorenmaa et al. (2002) estimated the mean annual loss specific for agricultural land in Finland to be c. 1.1 kg TP ha\(^{-1}\) yr\(^{-1}\) whilst the average P loss in a small catchment was c. 1.4 kg TP ha\(^{-1}\) yr\(^{-1}\). Johnes and Hodgkinson (1998) reported P losses of 0.71 kg TP ha\(^{-1}\) yr\(^{-1}\) in upland grass catchments with low density animal and human populations and up to 4.15 kg TP ha\(^{-1}\) yr\(^{-1}\) in lowland dairy catchments. In comparison to these figures, P loss rates from the Loch Leven catchment can be considered fairly low in the majority of the catchment. This compares with previous assessments by the Scottish Agricultural College that most of the catchment is at low to moderate risk of erosion and that soil P levels are also
fairly low (Chapter 2, Section 2.7). The Pow Burn, however, had the highest P loss rates reflecting the intense agricultural land use, moderate risk of erosion and limited point source influences. The majority of P was lost as PP indicating that P losses were primarily caused by surface runoff. This is because PP losses are characteristic of this transfer method (Ginting et al., 1998; Gillingham and Thorrold, 2000; Gburek et al., 2005). Kronvang et al. (2003) also showed that the export of TP increased dramatically with increases in runoff due to increasing PP inputs (Gburek et al., 2005). However, exact pathways of P transfer resulting from hydrological processes are hard to describe as they incorporate a broad range of spatial scales of flow and variations in flow directions, as well as different time scales (Gburek et al., 2005). The relatively small catchment size may also be a factor influencing high P losses in the Pow Burn catchment. Kronvang et al. (2003) showed that P export per unit area increased dramatically as catchment size decreased. This was explained by a greater connectivity in the catchment, i.e. by the closer link and shorter travelling distances between fields from which P is exported and the streams into which runoff enters. However, P losses are also reported to be strongly controlled by a number of other regional factors, such as history of P application to agricultural land, crop types, soil type, drainage, tillage, livestock densities and erosion. This demonstrates that there are many physical and chemical processes that influence P losses between catchments.

4.6.6 Critical periods of particulate-associated phosphorus delivery

The winter months (October, November and December) were identified as the largest contributors to the annual P load to Loch Leven. 46%, 17% and 24% of the annual TP, SRP and PP loads to the loch was delivered in these 3 months. Winter months were, therefore, much more important in the delivery of particulate associated P than soluble P. It was concluded that high TP and PP loads were due to higher rainfall, higher river flows and elevated concentrations. Higher stream flows and P concentrations occur in the winter months due to significantly higher quantities of surface runoff (Smith et al., 1999). Surface runoff is the product of catchment soils becoming saturated after frequent periods of heavy rainfall. As winter
progressed and heavy rainfall continued, the catchment no longer had the potential to absorb precipitation. Thereby, direct runoff was promoted as overland flow into adjacent stream and river systems in the Loch Leven catchment. This high energy runoff was observed to be frequently rich in particulate material (most commonly soils and fine sediment) due to high energy levels eroding loose soil particles from both the surrounding land and from within the river channels. The steep hills in the upper part of the Pow Burn catchment may also have encouraged greater soil erosion and P loss rates compared to other sub-catchments. The intense agricultural land use in this catchment would also mean that sources of diffuse PP were widespread. Eroded fertilised soils were undoubtedly a significant source of P entering streams during periods of heavy rainfall. Although monthly rainfall was relatively constant from March to June, P loads steadily decreased during this time. Interestingly, monthly rainfall in August and September was much higher than in July but P loads did not respond and remained low. This indicated that rainfall during August and September did not result in higher stream flows and/or P concentrations which was probably due to antecedent conditions. For example, as summer rainfall decreased and temperatures became warmer the catchment dried out due to greater rates of evapo-transpiration. The drying out of catchment soils can have two contrasting effects on catchment runoff response. Firstly, dry soils that have become hydrophillic and impermeable to water may promote surface runoff during rainfall periods in the summer. In addition, dry soil particles less resistant to erosion by surface runoff can promote higher PP losses (Ide et al., 2008). Alternatively, the majority of summer rainfall may be absorbed by dry soils resulting in less water reaching streams via surface runoff but maintains groundwater reserves and stream base flow. Rainfall during summer months would not, therefore, induce the increasing stream flows and P loads that are seen during winter months when catchment soils become water saturated. The results of the 2005 survey suggest that summer rainfall was absorbed and retained in the catchment resulting in minimal transfer of diffuse PP. Therefore, winter months were responsible for the major proportion of P delivery to the loch.
4.7 Conclusion

Although there is potential for point sources to be further reduced in the Loch Leven catchment, attention must now focus on reducing diffuse sources of P pollution. Diffuse P sources are difficult to regulate and address, as they are primarily transported in runoff from a varied and widespread catchment area (D'Arcy et al., 2000). This study has shown that diffuse sources of PP now account for a significantly higher proportion of the annual TP load than in the past and that winter months contribute a largest proportion of the annual load. This period is often characterised by high flows and occasional storm events. Before any further catchment management can take place, there is an urgent need to gather detailed information relating to specific diffuse P sources (Greig, 2004b). This information is required to enable more successful restoration and management measures to be put in place to address the loss of P from diffuse sources across the catchment. Therefore, there is a need to investigate, in detail, the role of winter high-flow events in transporting P to the loch and the impact these events have on P concentrations and loadings. There is also a need to investigate the reliability of calculation methods and sampling programmes used to estimate annual P loads (Johnes, 2007). This is important as the success of P reduction initiatives are often assessed on the basis of reduced P loads. Although load estimation methodologies have been developed to account for the temporal variation in values between sampling occasions, large amounts of error still result in the final values (Walling and Webb, 1985). Chapter 5 and Chapter 6 present the results of these research requirements.
5 The Influence of High-Flow Events on Phosphorus Transport

5.1 Introduction

It has long been recognised that phosphorus (P) in freshwater bodies has resulted in water quality problems and eutrophication in many parts of the world. Increasing inputs of point and diffuse source P to freshwaters have resulted in a significant rise in the number of poor quality water bodies (Haygarth and Jarvis, 1999). Such environments have seen changes in species composition, biomass and diversity. In particularly bad instances of eutrophication, low oxygen levels cause fish kills and a loss of desirable fish species (Wetzel, 2001). As well as causing negative environmental impacts, nutrient enrichment and eutrophication also affect the domestic, industrial and recreational use of water. In Europe, the Water Framework Directive (WFD) (2000/60/EC) now places a legal requirement on environmental regulatory authorities to restore all ‘poor’ quality water bodies and to prevent deterioration of ‘good’ quality water bodies. Its primary aim being to reach ‘good ecological status’ in all water bodies by 2015. To achieve this, more stringent controls on the inputs of P to watercourses from both point and diffuse sources are necessary. The WFD has been particularly important in initiating research that investigates aspects of diffuse pollution as it has identified the need to improve the understanding of the temporal and spatial nature of diffuse P transport within individual catchments.

The nature of a catchment’s rainfall and hydrology is particularly important (Haygarth and Jarvis, 1996) with respect to diffuse P sources, as the rate and intensity of rainfall often determines the nature of PP export. Many researchers (e.g. Verhoff et al., 1982; Sharpley et al., 1995; Doritz, 1996; Kronvang and Bruhn, 1996; Poinke et al., 1999; Heathwaite and Dils, 2000; May et al., 2001; Old et al. 2003; Evans and Johnes, 2004; Haygarth et al., 2005; Bowes et al., 2005) report that the highest P loads to a water bodies in rural catchments are associated with high rainfall and surface runoff. Furthermore, it is common that >80% of a water bodies annual P load is transported by just two or three large high-flow events (Smith et al., 1991;
Osborn et al. (2000), Osborn and Hulme (2002), Fowler et al. (2005) and Ekström et al., (2005) have provided evidence that high-flow events in the UK have been increasing in frequency due to climate change. This is expected to be having a direct impact on the transport of diffuse source P to water bodies. Greig et al. (2004) and Stutter et al. (2008) comment that an improved understanding of P behaviour is necessary in order to relate water quality problems to specific P sources. Furthermore, qualitative and quantitative information concerning P transport during high-flow events will also provide a useful basis on which regulatory authorities can mitigate and manage diffuse P losses (Poinke et al., 1999).

One freshwater body that has historically suffered from poor water quality and eutrophication due to P inputs is Loch Leven in Scotland (refer to Chapter 2 for a detailed description of the loch and the catchment). In rural catchments dominated by agriculture, diffuse source P is often the greatest contributor of P being transported through streams and rivers (McDowell and Sharpley, 2002). The sub-catchment of the Pow Burn in the Loch Leven catchment was identified as being a significant source of diffuse P to the loch as it is under intense agricultural land use (refer to Chapter 4). The aim of this study, therefore, was to assess the temporal variability of P concentrations during high-flow events to provide detailed information regarding the importance of high-flow events on P transport in this catchment.

5.2 Site selection and description

The site identified as suitable for high-flow event monitoring was selected on the basis of the following considerations. First, the site should not be located in close proximity to point source inputs. Secondly, high quality hydrological data, i.e. continuous measures of stream flow and rainfall, should be available within the catchment as pollutant inputs and fluxes from diffuse sources are frequently linked to changes in hydrological conditions. Thirdly, the site should represent a range of landscape characteristics and land cover types and should be in a zone affected by
surface runoff (Greig, 2004a). The catchment of the Pow Burn was identified as an ideal location for high-flow event monitoring data in the Loch Leven catchment. It is a 2nd order tributary of Loch Leven (Figure 5.1) and the main stem of this stream and its primary tributaries are 12.9 km in length and the stream drains a catchment of 10.9 km².

![Map showing the Loch Leven catchment and location of the high-flow event monitoring station on the Pow Burn.](image)

**Figure 5.1:** Map showing the Loch Leven catchment and location of the high-flow event monitoring station on the Pow Burn.

It receives no inputs of P from regulated point sources as there are no discharges from sewage treatment works or industrial effluents. The sub-catchment is primarily under agricultural land use with both arable farming and livestock grazing being well established (Figure 5.2). It also contains areas of rural housing and the stream is known to receive runoff from surrounding land during periods of heavy rainfall. Results of the 2005 P loading survey (Chapter 4) showed that there were strong, significant positive correlations between stream flow and P concentrations at this site ($r_s = 0.842 - 0.687$, $p < 0.001$) indicating that much of the P being transported through the Pow Burn was from flow driven, diffuse sources. Phosphorus content of the soils in the Loch Leven catchment were measured by the Scottish Agriculture College in the late 1990's and found that the P content of the
majority of fields in the steep, upper part of the Pow Burn catchment were low in P content (0-25 mg P / L soil), whilst fields in the lower part of the catchment were found contain moderate levels of P (26-70 mg P / L soil) (refer to Figure 2.6 in Chapter 2). Unfortunately, there is no data documenting more recent measures of soil P levels in the Pow Burn catchment. An automatic, continuous stream flow gauge was already being operated by SEPA on the Pow Burn and recorded stream flow every 15 minutes (Figure 5.3). Rainfall intensity was measured by a Casella CEL tipping bucket rain gauge that recorded tips of 0.2 mm depth, which were aggregated into 15 min time series data for analysis. This was located in the nearby North Queich sub-catchment (refer to Figure 5.1).
Figure 5.2: Catchment relief and land cover map of the Pow Burn sub-catchment

(from Greig, 2003)
Figure 5.3: Schematic diagram of the stream flow gauging station and picture of the weir at the Pow Burn.
5.3 **Methods**

5.3.1 **Sample collection**

Water samples were collected at the Pow Burn site over the hydrograph of high-flow events using two Hach Lange® EPIC automatic water samplers. The samplers were located approximately 0.5 km above the mouth of Pow Burn, which ultimately flows into Loch Leven. Care was taken to ensure that the monitoring set-up allowed the collection of reliable chemistry data sets, with special attention given to the positioning of the sample nozzles within the water column. Nozzles were elevated off the river bed by securely attaching them to large concrete building blocks, therefore potential interference from suspended river bed sediments was minimised. Figure 5.4 details the monitoring set up.

![Diagram showing the setup of Hach Lange EPIC® water samplers on the Pow Burn.]

**Figure 5.4:** Set up of Hach Lange EPIC® water samplers on the Pow Burn.

The pipes and water collection chamber were rinsed by pre-purging before each sample was collected. Each sampler was programmed to collect 500 ml water...
samples every 2 hours, running in parallel to each other for 48 hours to give
duplicate water samples. Following sample collection, the pipes were cleared of
water by post-purging for 30 seconds. This reduced both the contamination between
samples and the likelihood of blockages developing due to sediment deposition. The
samplers ran continuously from 10th October to 5th December 2006. Using this
continuous sampling regime it was possible to collect water samples over a large
range of river flows. This was thought to be the most effective and reliable method
of sampling P concentration temporal variability over periods of high-flow. All
samples were analysed for total P (TP), total soluble P (TSP), soluble reactive P
(SRP) and particulate P (PP = TP-TSP) within 48 hours of collection. Total
suspended sediments (TSS) were also selectively measured over periods of high-flow
(APHA methods, 1996).

5.3.2 Water sample stability trials

Some studies have reported losses of SRP from environmental water samples
during storage may be rapid and unpredictable (Burton, 1973; Haygarth et al., 1995)
due to the unstable and interactive nature of orthophosphate ions (Ryden et al., 1973;
Lambert et al., 1992; Ferguson, 1994; Kotlash and Chessman, 1998; Burke et al.,
2002). The storage of samples prior to SRP analysis is, therefore, not always
desirable (Maher & Woo, 1998). In a study that involves high frequency, high-flow
event sampling, the ideal situation would be to have field-based instrumentation,
which would have eliminated the need for sample collection and storage. However,
such equipment was not available and an alternative method was applied by
employing the use of automatic samplers. These types of water sampler are
increasingly being used for water quality monitoring of rivers and stream because
they are cheaper and easier to maintain than automatic nutrient samplers. Therefore,
changes in SRP concentrations in stored water samples should be investigated to
determine if any significant changes in sample composition occurs prior to sample
analysis (APHA, 1998; Burke et al., 2002). Therefore, the effect of storage time on
measured concentrations of SRP in water samples collected at the Pow Burn was
investigated before high-flow event monitoring began. In summary, results showed
that, for water samples with both high and low initial SRP concentrations (approximately 50 μg L⁻¹ and 250 μg L⁻¹), there was no significant difference between SRP concentrations measured at 0 hours and after 24 and 48 hours storage in EPIC® polyethylene water bottles (paired t-tests, p = 0.056 to 0.822). However, concentrations were significantly lower after 96 hours storage (paired t-test, p = 0.01 to 0.037). Therefore, storage of water samples for up to 48 hours before SRP analysis was considered acceptable and was unlikely to have any noticeable effect on measured SRP concentrations. (Refer to Chapter 13, Appendix A.3 for more in depth results and discussion).

5.4 Hydrological conditions prior to and during the study period

Hydrological conditions for the Pow Burn during 2006 exhibited the usual seasonality for Scotland, i.e. dry summer months and wet winter months (Figure 5.5). High-flow events occurred in the catchment from January to March and August to December. Wet conditions were also experienced during spring (April and May) but high-flow events did not occur lending towards a dry summer with consistent base flows. Periods of rainfall resulting in 4 small high-flow events between mid August and late September re-wetted the catchment prior to the onset of high-flow event sampling in October. In total, 10 high-flow events were monitored between 10th October and 5th December 2006 (Figure 5.6). The duration of the events ranged from 32 to 92 hours (Figure 5.7). Increasingly wet conditions in October and November caused high-flow hydrograph peaks and gradually increasing base flows. Events in October were characterised by hydrographs with one clear discharge peak, whilst events in November were more complex showing multimodal peaks. High-flow events in the Pow Burn were the result of substantial precipitation falling over the catchment (Figure 5.8). Daily rainfall ranged between 0 and 26.8 mm. Intense hourly rainfall resulted in high-flow events that ranged in magnitude. On the 24th and 25th October rainfall intensity reached a peak at 9.6 mm hr⁻¹. This resulted in the largest high-flow event in the catchment with discharge peaking at 3.82 m³ sec⁻¹.

Figure 5.9 shows that large high-flow events (> 3.0 m³ sec⁻¹) in the Pow Burn may be occurring more frequently. Unfortunately, stream flow data were only
available from 1994 onwards so it was only possible to observe a likely pattern of change regarding high-flow event frequency in the catchment. Between 1994 and 1997, the largest events recorded in the catchment ranged from 2.0 m$^3$ sec$^{-1}$ to 3.0 m$^3$ sec$^{-1}$ occurring approximately twice a year. From 1997 onwards there is a visible pattern of increasingly larger events occurring. Maximum discharges reached between 3.0 m$^3$ sec$^{-1}$ and 4.0 m$^3$ sec$^{-1}$. Events of this size have been recorded in the catchment approximately once or twice a year in the winter season. One particularly large high-flow event occurred in 2002, reaching approximately 7.0 m$^3$ sec$^{-1}$. Hence, high-flow events in the Pow Burn are potentially becoming both larger and more frequent.

5.5 Phosphorus concentrations measured during high-flow events

Figure 5.7 summarises the P and total suspended sediments concentrations measured during high-flow events in the Pow Burn. Mean SRP concentrations during high flow events ranged from 52 to 85 µg l$^{-1}$ with maximum observed values ranging between 81 and 375 µg l$^{-1}$. Mean TP concentrations ranged between 207 and 478 µg l$^{-1}$ with maximum observed values measured between 881 and 2156 µg l$^{-1}$. Mean PP concentrations ranged between 116 to 426 µg l$^{-1}$ with maximum observed values between 719 and 2021 µg l$^{-1}$ (Figure 5.7). Particulate P was clearly the dominant P fraction during high-flow events due to large increases in TSS.
Figure 5.5: Maximum daily stream flow in the Pow burn and rainfall in the North

Maximum Daily Stream Flow
at Pow Burn (m³ sec⁻¹)

Daily Rainfall (mm)
Stream Flow at Pow Burn (m$^3$ sec$^{-1}$)

- A: 10th Oct 2006
- B: 20th Oct 2006
- C: 24th Oct 2006
- D: 11th Nov 2006
- E: 1st Dec 2006
- F: 5th Dec 2006

Event indicators:
- Event: major hydrological event in the catchment.
Figure 5.7: Median measures (with maximum and minimum values as error bars) of stream flow, rainfall intensity, and duration, phosphorus and total suspended sediment concentrations during high-flow events in the Pyc Burn.
Figure 5.8: Hourly rainfall measured in the Loch Laven catchment and stream flow

Stream Flow at Pow Burn (m$^3$ sec$^{-1}$)

Hourly Rainfall in Catchment (mm)
Weekly Max Stream Flow (m$^3$ sec$^{-1}$) at Pow Burn

Between 1994 and 2006, a hydrograph showing weekly maximum stream flows in the Pow Burn.
5.6 **Types of high-flow events in the Pow Burn**

Figure 5.10 and Figure 5.11 show the temporal variability of TP, PP, SRP and stream flow in the Pow Burn during the monitoring period. Jordan et al. (2005) categorised high-flow events into 3 event types. These were:

1. **Type 1 events** are characterised by increasing P concentrations during base flow conditions that are often caused by a) large TP increases due to small amounts of rainfall in the catchment or b) due to the discharge of one or more high P concentration point sources, particularly sewage treatment works or industrial effluents.

2. **Type 2 events** are distinguished when P concentrations are positively correlated with increasing discharge, normally due to agricultural diffuse runoff.

3. **Type 3 events** are described as discrete, short-lived events that show high magnitude P transfers that are unrelated to rainfall or changes in stream discharge.

Examples of all event types of event occurred in the Pow Burn between October and December 2006 and are highlighted in Figure 5.10. Type 2 events are discussed in more detail in Section 5.4 and Types 1 and 3 events are discussed further in Section 5.5.

All high-flow events in the results section are referred to by letter, as indicated previously in Figure 5.5.
Types of high-flow events as described by Jordan et al. (2007) are shown. Phosphorus (µg l⁻¹) and particulate phosphorus and stream flow at the Pow Burn between October 10th and December 5th 2006. Type 1 Event: Increasing P-caused by increasing stream flow. Type 2 Event: TP increases with increasing stream flow. Type 3 Event: TP increases independent of rainfall and discharge.
Figure 5.11: Time series of soluble reactive phosphorus and stream flow at the Pow Burn between October 10th and December 31st 2006.

Soluble Reactive Phosphorus (µg l⁻¹)

Stream Flow at Pow Burn (m³ sec⁻¹)
5.7 Results

5.7.1 Type 2 Events

In summary, detailed examination of type 2 events in the Pow Burn revealed that:

1. Phosphorus concentrations were higher during high-flow events than during base flow conditions.
2. Total P, PP and TSS responded positively to increases in stream flow but the response of SRP varied.
3. Phosphorus transport was dominated by the particulate fraction due to high TSS concentrations.
4. The magnitude of P response was not proportional to the size of the high-flow event.
5. Clockwise hysteresis (peak P concentrations before peak discharge) inferred that sources of soluble and particulate P were not infinite, often being depleted before the end of a high-flow event. Sediments stored within the stream channel and fast erosion of stream banks provided a rapidly responding P source early in the event season that was quickly exhausted. Furthermore, a change towards anti-clockwise hysteresis (peak P concentrations after peak discharge) during later high-flow events suggested that the timing of P export varied between events due to changing P source areas.

Evidence supporting these statements is provided and discussed in more detail in the following sections.

5.7.2 Correlations between TP, PP and stream flow

Figure 5.12 provides an example of the temporal changes in TP, PP and TSS during two high-flow events in November. During all high-flow events, P concentrations were greater than under base flow conditions. Figure 5.12 shows the close relationships between P, TSS and stream flow. It also shows the close relationships between TP, PP and TSS. Spearman’s rank correlation coefficients ($r_s$) were calculated to determine the strength of relationships between stream flow and P
concentrations, as well as between stream flow and TSS. Results are provided in Table 5.1 and show that TP and PP were highly significant and positively correlated with stream flow during all events. TSS was highly significant and positively correlated with stream flow during 9 out of 10 events. Therefore, the vast majority of high flow events in the Pow Burn can be classified as type 2 events, as defined by Jordan et al. (2005). Total P and PP were significantly and highly correlated with TSS during all monitored high-flow events. These results suggest that TP and PP will respond positively to increases in stream flow when a high-flow event occurs in the Pow Burn due to increasing concentrations of suspended sediments being transported through the fluvial system.

Figure 5.12: An example showing the close relationship between a) stream flow, total phosphorus and particulate phosphorus and b) stream flow and total suspended sediments, measured during two high-flow events in the Pow Burn catchment in November 2006. (Note differences between graphs scales between figures).
Table 5.1: Spearman's rank correlation coefficients ($r_s$) showing the strength of correlation between stream flow, total suspended sediments and phosphorus measured during periods of high-flow flow in the Pow Burn.

<table>
<thead>
<tr>
<th>Event</th>
<th>TP</th>
<th>PP</th>
<th>SRP</th>
<th>TSS</th>
<th>TP</th>
<th>PP</th>
<th>SRP</th>
</tr>
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<td>A</td>
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<td>0.727</td>
<td>0.901</td>
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<td>$p &lt; 0.001$</td>
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<td>$p &lt; 0.001$</td>
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<tr>
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<td>C</td>
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<td>D</td>
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<td>$p &lt; 0.001$</td>
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<tr>
<td>E</td>
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<td>0.944</td>
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</tr>
<tr>
<td>G</td>
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<td>0.781</td>
<td>0.847</td>
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<tr>
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<tr>
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<tr>
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<td>0.963</td>
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<td>$p &lt; 0.001$</td>
<td>$p &lt; 0.001$</td>
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</tr>
</tbody>
</table>

**5.7.3 Correlations between SRP and stream flow**

SRP was strongly correlated ($r_s > 0.6$) with stream flow during 7 out of 10 high-flow events. However, correlations were not as strong as those between TP/PP and stream flow (Table 5.1). SRP was also strongly ($r_s > 0.6$) correlated with TSS during 9 high-flow events, compared to 10 events for TP/PP. Figure 5.13 provides an example of how SRP responded to increasing stream flows during 4 different high-flow events (A, C, F and J). Peak SRP concentrations occurred at different times during early and later high-flow events. Early autumn events were characterised by maximum SRP concentrations occurring on the rising limb of the hydrograph and a few hours before peak stream flow, whilst peak SRP concentrations were reached on or after peak discharge during later autumn high-flow events.
5.7.4 The contribution of PP during high-flow events

Under base flow conditions (i.e. before the start of the rising limb of the hydrograph), SRP contributed the largest proportion of TP except when events quickly succeeded each other. PP contributed most to TP concentrations during conditions of increasing and peak stream flow. Figure 5.14 shows stream flow and percentage contribution of PP and SRP during 9 of the high-flow events monitored in the Pow Burn. Minimum % PP ranged from 23% to 53% prior to the onset of increasing stream flows. It was clear that PP becomes the primary contributor to TP under high-flow flow conditions as during peak flows the % PP increased to 82% to 95% of TP. It also shows that the contribution of PP to TP concentrations was non-specific to the size of the high-flow event as small events initiated the same PP response as larger ones.

Figure 5.13: Examples of the close relationship between stream flow and soluble reactive phosphorus concentrations measured during four high-flow events in the Pow Burn between October and December 2006. (Note different vertical scales on graphs).
5.7.5 **Magnitude of P response during high-flow events**

Larger high-flow events did not generate proportionally larger concentrations of P or TSS. Figure 5.15 illustrates this point by showing that the largest TP, PP and TSS concentrations were measured during a relatively small high-flow event (Event H). Figure 5.16 compares the temporal variation in P concentrations during 4 events of differing magnitude in the Pow Burn catchment. It also highlights the rainfall intensities in the catchment prior to the onset of high-flow events. The largest high-flow event in the catchment was event D (peak $Q = 3.82 \text{ m}^3 \text{ sec}^{-1}$). This was considerably higher than other events as the second highest peak flow was <1.0 m$^3$ sec$^{-1}$. The intensity of rainfall during event D reached 5.6 mm hr$^{-1}$ and the duration of rainfall was over a short time period (10 hours) (Figure 5.16). However, despite being the largest event, it did not generate higher P concentrations compared to some of the smaller events e.g. event C and event H (Figure 5.15 and Figure 5.16). The highest concentrations of TP, PP and TSS were measured during event H (2156 µg l$^{-1}$, 2021 µg l$^{-1}$ and 740 mg l$^{-1}$, respectively) when flow peaked at 0.719 m$^3$ sec$^{-1}$. Visual inspection of the water samples during this event indicated that TSS was dominated by very fine silt and clay particles, which have a particularly high capacity for associated PP (Heathwaite, 1997). However, although maximum rainfall intensity was the same as event D (5.6 mm hr$^{-1}$) rainfall duration was longer (36 hours). In comparison to TP and PP, the largest SRP concentration was measured during event C (375 µg l$^{-1}$) when stream flow peaked at just 0.416 m$^3$ sec$^{-1}$. However, maximum rainfall intensity prior to this event reached 9.4 mm hr$^{-1}$, the highest rainfall intensity measured during the monitoring period. These results clearly show that larger stream flows did not automatically translate into recording the highest P concentrations. It appeared that rainfall intensity and duration were also factors determining the temporal changes in P and TSS concentrations during high-flow events (refer to Figure 5.16).
Figure 5.14: The contribution of soluble and particulate phosphorus to total phosphorus concentrations during high-flow events in the Cow Burn. (Note the different scales on the y-axes of each graph.)
Figure 5.15: A comparison between the response of phosphorus, total suspended sediments and streamflow during three events of varying size in the Pow Burn.
Event C and D - 24th October to 27th October 2006

Event G and H - 15th November to 21st November 2006

Figure 5.16: Comparison between rainfall intensity and magnitude of phosphorus response during successive high-flow events in the Pow Burn catchment. (Note different scales on the y-axis between graphs).
5.7.6  Phosphorus hysteresis during consecutive high-flow events

Results indicated that there appeared to be a ‘flushing’ or ‘wash-out’ effect of SRP, meaning that sources of P were depleted by consecutive high-flow events. This was shown by concentrations peaking and receding before peak stream flow and there being no apparent increase in SRP concentrations during quickly successive high-flow events. Figure 5.17 highlights these observations by showing hysteresis plots of SRP against stream flow during events C & D and G & H.

Figure 5.17: Soluble reactive phosphorus concentrations plotted against stream flow during two succeeding high-flow events, demonstrating the ‘wash-out’ effect of the earlier high-flow event.
Events C and G both showed increasing SRP concentrations but the events that quickly followed (D and H) did not. Peak SRP concentrations during event C reached 375 µg l\(^{-1}\), however SRP concentration during event D increased from 56 µg l\(^{-1}\) to just 91 µg l\(^{-1}\). This was despite peak stream flow during event D being about 10 times greater than the preceding event. Similarly, SRP concentrations increased from 42 µg l\(^{-1}\) to 85 µg l\(^{-1}\) during event H having peaked at 250 µg l\(^{-1}\) during event G. These results suggest that after large peak flow-triggered increases in SRP, further increases are of a lesser magnitude if another high-flow event quickly followed. This suggests that catchment SRP sources require a regeneration time between events and that high-flow event SRP concentration is dependent on catchment antecedent, as well as hydrological, conditions.

Figure 5.18 shows an example of how maximum TP, PP and TSS concentrations can peak and recede a few hours before peak discharge. This pattern is indicative of P and sediment source depletion. The rapid transfer of P during the start of high-flow events is characteristic of overland surface runoff (Irvine et al., 2002; Jordan et al., 2005). It is also associated with re-suspended streambed sediment containing fine particulate matter with adsorbed P (McDowell and Sharpley, 2001). This conclusion was further supported by a pattern of P and sediment transport which was evident during the two earliest high-flow events (A and B) (Figure 5.18). During these events there were large increases in TSS and TP/PP concentrations prior to the onset of the rising limb of the hydrograph. This pre-peak of TSS was responsible for the corresponding high TP and PP concentrations. Significant, positive correlations between TSS and PP during high-flow events indicated that there was no evidence to suggest that the P content of sediments decreased at higher discharges, which has been reported by other studies e.g. House and Warwick (1998). The ‘pre-peak’ pattern was not evident during later events (C to J) suggesting that this particular sediment source was exhausted quickly and early on in the event season. These results indicate that catchment sources of sediment and P were not infinite, often being depleted quickly during periods of heavy rainfall and runoff. Jordan et al. (2007) also reported finding evidence of transfer-limited P transport in the Lough Neagh catchment, Northern Ireland.
particulate phosphorus during high-flow events in the flow burn. Examples of wash-out effects of total suspended sediments and
5.7.7 Phosphorus export patterns

Hysteresis was observed for all P fractions during most monitored high-flow events. The pattern of hysteresis was influenced by the number of peak discharges that occurred during an event. Events with one peak discharge showed simple clockwise hysteresis patterns, whilst events with more than one discharge peak showed much more complex P export patterns. Later, more complex high-flow events often displayed both clockwise and anticlockwise hysteresis patterns. Table 5.2 summarises the observed P export patterns of the 10 high-flow events monitored in the Pow Burn catchment. A clockwise hysteresis pattern occurred when P and TSS concentrations were higher on the rising limb and lower on the falling limb of the hydrograph. Figure 5.19 shows an example of hysteresis patterns of P and TSS during two high-flow events (A and G) that were characterised with one discharge peak. In both instances TP, PP, SRP and TSS concentrations peaked before maximum discharge and further demonstrate the incident of P ‘wash-out’ effects. During later high-flow events hysteresis loops became more complex due to multiple discharge peaks (Figure 5.20).

Table 5.2: Hysteresis patterns of phosphorus and total suspended sediments during ten high-flow events in the Pow Burn between October and December 2006 (C/c = strongly/weakly clockwise, A/a = strongly/weakly anticlockwise) (* events with multiple discharge peaks showed complex hysteresis patterns, therefore, results characterise the predominant pattern observed).

<table>
<thead>
<tr>
<th>High-flow Event</th>
<th>No. of Peak Discharges</th>
<th>TSS</th>
<th>Hysteresis Pattern</th>
<th>Pre-Peak of P &amp; TSS?</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1</td>
<td>C</td>
<td>C</td>
<td>C</td>
</tr>
<tr>
<td>B</td>
<td>1</td>
<td>C</td>
<td>C</td>
<td>C</td>
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<tr>
<td>C</td>
<td>1</td>
<td>C</td>
<td>C</td>
<td>C</td>
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<tr>
<td>D</td>
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<td>C</td>
</tr>
<tr>
<td>E</td>
<td>2</td>
<td>C</td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>F*</td>
<td>2</td>
<td>a</td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>G</td>
<td>1</td>
<td>C</td>
<td>C</td>
<td>C</td>
</tr>
<tr>
<td>H*</td>
<td>2</td>
<td>C</td>
<td>C</td>
<td>C</td>
</tr>
<tr>
<td>J*</td>
<td>5</td>
<td>c</td>
<td>c</td>
<td>c</td>
</tr>
<tr>
<td>J*</td>
<td>3</td>
<td>c</td>
<td>c</td>
<td>c</td>
</tr>
</tbody>
</table>
These high-flow events were characterized by one discharge peak concentration during an early (October 2006) high-flow event in the Round Barn. 

Figure 5: Hysteresis patterns of phosphorus and total suspended sediment.
These events were characterised by numerous discharge peaks.
Anti-clockwise hysteresis loops were the result of a delay between maximum discharge and peak concentrations. TP and PP showed anti-clockwise hysteresis patterns during event E, whilst TP, PP, SRP and TSS showed anti-clockwise behaviour during event F. These two events followed the largest high-flow event in the catchment (event D). The dominance of anti-clockwise patterns of export during the two successive events suggests that P sources were further away from the river channel, as nearby P and sediment sources may have been diminished by event D. These results suggest that there were multiple P and sediment sources exported from within the catchment during high-flow event periods and that exact source dominance was a factor of antecedent and hydrological conditions.

5.8 Type 1 and type 3 events

A closer inspection of the time series concentration data indicated there were occasions when P transfer and transport in the Pow Burn were independent of stream flow increases (Figure 5.21).

**Figure 5.21:** Two-hourly time series discharge and phosphorus concentration data highlighting the incidences of hydrologically independent TP and PP transfers and transport in the Pow Burn.
Jordan *et al.* (2007) classified such events as ‘type 3’ events, i.e. discrete, high magnitude P transfers unrelated to rainfall or changes in stream discharge, probably caused by single pollutant incidences. Evidence of this was provided during one incident of flow-independent P transfer which was the result of elevated P concentrations due to the mobilisation of farmyard waste (concluded by visual examination of samples). TP and SRP concentrations increased from 120 µg l\(^{-1}\) to 765 µg l\(^{-1}\) and 50 µg l\(^{-1}\) to 192 µg l\(^{-1}\), respectively. P transfer was primarily in the PP form, as might be expected from raw wastewater sources. However, there was no rainfall in the catchment at the time of P transport (1am). Similar to the above findings, Jordan *et al.* (2007) also found that these short duration events occurred mostly at night. The exact origin of the source from within the catchment was not traceable but these results draw attention to the fact that discrete pollution incidences are occurring in the catchment. Other rapid increases in P concentrations were the result of small amounts of rainfall in the catchment that did not increase stream discharge to any noticeable degree, i.e. ‘type 1’ events (refer back to Figures 5.8 and 5.10). Jordan *et al.* (2007) recorded similar results during periods of summer base flow and commented that these base flow periods were susceptible to rapid increases in TP concentrations due to small amounts of rainfall. In the first week of December, two large TP peaks (1000 µg l\(^{-1}\) and 680 µg l\(^{-1}\)) occurred. Phosphorus peaks were again primarily in the PP form (952 µg l\(^{-1}\)and 626µg l\(^{-1}\)). These quick events corresponded to low intensity rainfall in the catchment (2.2 mm hr\(^{-1}\) and 1.8 mm hr\(^{-1}\)) but with no associated increase in stream flow.

### 5.9 Discussion

This study presents results from ten different high-flow events that occurred in the Pow Burn, in the Loch Leven catchment between October and December 2006. Results of this research have shown that different types of P transport occur in the catchment which is primarily influenced by a combination of rainfall and increasing stream flows. One discrete pollution incident within the catchment also occurred. Phosphorus export from diffuse PP sources was generally low during base flow conditions, with the majority of P export in the Pow Burn being triggered by
high-flow events. These events activated a number of hydrological pathways for P transport and mobilised P from a variety of diffuse sources in the Loch Leven catchment. There are relatively few studies in the literature that have investigated the influence of high-flow events on P transport, mostly due to the inherent difficulty of collecting the required high frequency data. However, it was evident that there were both similarities and differences when the results of the current research presented in this chapter were compared to similar studies.

5.9.1 High-flow event phosphorus concentrations

To put P concentrations during high-flow events into context, values are compared to water quality standards for P in rivers. For a river to be classified as having high/good ecological status under the WFD, annual mean SRP concentrations must be between 20 and 50 \( \mu g l^{-1} \) (depending on typology classification) (Duncan et al., 2006). Measured TP concentrations during all high-flow events were considerably greater than 50 \( \mu g l^{-1} \), which is the environmental threshold in flowing water at above which surface water eutrophication may be accelerated (Gibson et al., 2000; Sharpley et al., 2008). P delivered to Loch Leven by high-flow events is, therefore, almost certainly having an impact on the water quality of the loch through P enrichment of the water column.

5.9.2 High-flow event variation of phosphorus fractions

SRP and PP export from land can occur in surface runoff, sub-surface runoff or through ground water flow (Ryden et al., 1973). The exact form of P in runoff depends on the original source, the hydrological pathway from land to water, and any biological, chemical and physical changes that may take place during transport (Heathwaite, 1993). Total P, PP and TSS were consistently correlated with stream flow during all monitored high-flow events in the Pow Burn. These results were attributed to large amounts of sediment entering the stream as a result of increased soil erosion from the catchment. This was expected to have been caused by rainfall and subsequent surface runoff, as reported by other studies, e.g. Heathwaite (1997), Russell et al. (1998), Fraser et al. (1999), Davidson et al. (2005) and Sharpely et al.
Most of the TP transported during high-flow events in the Pow Burn comprised PP as a result of high TSS concentrations. Evans and Johnes (2004), Poinke et al. (1999), Fraser et al. (1999), Petry et al. (2002) and Caruso (2000) documented similar findings, showing TP and PP concentrations were also highly correlated with increasing stream flow and suspended sediments. Bowes et al. (2003) recorded that the proportion of PP rose from 40% of TP before and after the high-flow event, to 95% at the hydrograph peak in the River Swale (Northern England), whilst Olsen et al. (1975) reported high-flow event PP export in the range 67% to 97%. These are similar percentages reported in this study, where %PP increased from c. 30% up to 80% to 95% during peak discharges.

SRP was strongly correlated with increasing stream flows during 7 out of 10 events. Results have been documented by Kronvang (1992), Dils and Heathwaite (1996), Haygarth et al. (1998) and Poinke et al. (1999) also showing that SRP concentrations during high-flow events were positively correlated with stream flow. In contrast, Kronvang (1992), Evans and Johnes (2004), House and Denison (1998), Robson and Neal (1997), House and Warwick (1998) and Edwards et al. (2000) have reported finding a negative, diluting relationship of SRP concentration with increasing stream flow. In these studies, this was due to the strong influence of point sources at respective sites dominating base flows. In the Pow Burn, there was no evidence to suggest a diluting effect under base flow conditions, reflecting the absence of continual inputs from regulated point source inputs (i.e. sewage treatment works or industrial effluents). However, Evans and Johnes (2004) commented that stream flow does not always fully account for the variation in SRP concentrations and that in-stream processes are also important. This is probably due to the fact that SRP concentrations at a given discharge reflect the combined inputs from a number of different P sources from different parts of the catchment. Significantly higher concentrations of SRP during high-flow events possibly indicate the importance of SRP release from catchment soils, surface applied fertilisers and manure (Kronvang, 1992; Sharpley et al., 2008). Suspended river-bed sediments can also contribute to elevated stream and water body SRP concentrations, as P-rich particles can release orthophosphate ions when subjected to alterations in environmental conditions (e.g. pH, redox and temperature changes) that promote SRP desorption or dissolution.
SRP in surface runoff can also be derived from stores of mineralised P that have accumulated in the upper soil profile during dry periods (Heathwaite, 1997). The low strength of correlations between SRP and stream flow in some instances was probably due, in part, to SRP showing little or no response when high-flow events quickly succeeded one another. In any catchment, soils can only give up a finite quantity of nutrients to percolating water and surface runoff (Morgan, 1997). The results presented in this study suggested that dissolution and desorption processes in the surface soils (and river-bed sediments) did not have time to replenish levels of soluble P in interstitial waters.

5.9.3 Rainfall intensity and magnitude of phosphorus response

Jordan et al. (2007) and Dils and Heathwaite (1996) reported that the size of TP peaks progressively decreased following each high-flow event in their study catchments. This was due to readily available catchment PP sources gradually diminishing. This was not found to be the case in the Pow Burn. Results showed that the size of P peaks varied between different sized events and did not show a reducing magnitude as time progressed. Small high-flow events late in the season showed comparable or higher TP concentrations compared to early or large high-flow events. Results also showed that maximum TP, PP and TSS concentrations were recorded during a small high-flow event (max $Q < 1.0 \, m^3 \, s^{-1}$), generated by a short, intense period of rainfall. This suggested that rainfall intensity was just as important in determining P response as the overall size of the high-flow event hydrograph.

The influence of P transport factors, such as surface runoff and erosion, on the movement of P is well documented (Sharpley, 1985; Gbruek et al., 2000; Sharpley et al., 2001; McDowell et al., 2004; Shigaki et al., 2007). The transport of sediment and P to waters by surface runoff is driven by the ability of rainfall to erode and detach a soil particle (Renard et al., 1997; Havlin, 2004). This is generally estimated to be a function of the kinetic energy of each drop of rainfall (Van Dijk et al., 2002) and of a raindrop’s mass and the velocity at which it falls (Davidson et al., 2005). The relationship between kinetic energy and rainfall quantity varies between
rainfall events. Therefore, although a high-flow event may be relatively small or short lived in nature, it is likely to possess more erosional energy than a prolonged period of less intense rainfall that generates, overall, larger high-flow events. Evans (1992) suggested rainfall ≥ 7.5 mm hr⁻¹ can cause incidences of soil erosion in temporal regions, whilst rainfall of 5 mm hr⁻¹ is representative of high intensity rainfall in temperate regions.

Klein (1984) provided evidence that rainfall intensity and the rate of hydrograph rise were more important than runoff in controlling suspended sediment transfer, especially in small river basins. In contrast, Davidson et al. (2005) found this to be the case in many parts of England and Wales and Quinton et al. (2001) observed increasing erosion and PP transport with greater rainfall intensities. Fraser et al. (1999) monitored surface runoff from fields planted with winter crops and observed that with an increase in rainfall intensity from 1.0 to 10 mm hr⁻¹, there was an increase in soil erosion (14 to 144 kg ha⁻¹ hr⁻¹), soluble P content (15 to 218 g ha⁻¹ hr⁻¹) and PP loss (16 to 319 g ha⁻¹ hr⁻¹). Fraser et al. (1999) also reported that heavy rain high-flows that typically only lasted a few hours were characterised by high losses of PP. Ahuja et al. (1981) and Sharpley (1985) suggested that this would be due to the degree and depth of interaction between runoff and surface soil being larger with heavier rainfall, therefore providing greater P source availability. Similarly, Kleinman et al. (2006) suggested that there would be a greater mass of soil in runoff at higher rainfall intensities and, as such, a larger available pool of P that could be released into runoff water. The relationships between rainfall and erosion capability is most likely why small high-flow events in the Pow Burn showed comparable or sometimes greater TP, PP and TSS concentrations compared to larger events.

5.9.4 Importance of antecedent conditions

House (2003) found that antecedent weather conditions were particularly important in controlling the fine sediment pool and associated PP that was available for re-mobilisation during high-flow events. Similarly, McDowell and Sharpnley (2002) provided evidence that soil moisture fluctuations greatly affected erosion and
P transport. Simulation experiments by McDowell and Sharpley (2002) showed that wetter soils produced surface runoff more quickly than dry soils and that less suspended sediment was transported from wet soils. These differences were attributed to the potential for soil aggregates to breakdown and disperse. Re-wetting of dry soils by rainfall also affected soil surface sealing and crusting. Therefore, soil antecedent moisture conditions and potential for selective erosion during surface runoff affect P transport.

The results of this study suggest that antecedent conditions in the Pow Burn also exerted an influence on P responses. These conditions included a period of dry, summer months that probably resulted in high levels of fine sediment settlement in the river channel, dry soil moisture conditions in the catchment and high soluble P concentrations in soil and sediment pore waters due to dissolution and desorption. In this study, the influence of antecedent conditions was most evident for SRP. Hysteresis patterns showed that concentrations were likely to increase at a much smaller magnitude, or not at all, during a high-flow event that quickly followed another. This was due to catchment soluble P sources being depleted and not having a chance to regenerate through dissolution processes. Also, early high-flow events depleted rapidly mobilised P sources and resulted in a slower delivery of P during successive high-flow events. Bowes et al. (2005) reported a similar result, proposing that when a high-flow event follows immediately after another, much of the marginal P has already been removed by the previous flood. This phenomenon reduced the gradient of hysteresis loops as the number of high-flow events increased. Shigaki et al. (2007) reported that the magnitude of concentration change of SRP and PP in surface runoff was higher during earlier rainfall events and decreased with time and increasing number of rainfall applications. They also found the concentration of SRP in runoff was influenced by the differing rate of P dissolution from different sources.

Kronvang (1992) suggested that another source of SRP during periods of high flow could be contributed by sub-surface losses of soluble P that could be dissolved into interstitial water or desorbed from particulate matter. The transport of P in surface runoff dominates P transport in most agricultural catchments, with most P being transported in the particulate phase (Sharpley and Menzel, 1987, Morgan, 1997). P export by sub-surface runoff is not as well documented compared to
surface runoff. However, most sub-surface runoff is expected to transport SRP rather than PP. Evans and Johnes (2004) suggested that delayed inputs of SRP via through-flow mechanisms were more prevalent during later high-flow events when catchment soils were saturated. It is possible that sub-surface P sources supply a larger percentage of the P transported during later high-flow events in the Pow Burn. However, Sharpley and Menzel (1987) stated the opposing view that sub-surface soluble P losses are generally small compared to surface runoff. This was due to the strong binding capacities of soils which allow most SRP to be bound and retained during periods of sub-surface flow.

5.9.5 Phosphorus hysteresis patterns

Hysteresis patterns for suspended sediments and nutrients during high-flow events have been reported in the literature for some time, e.g. Porter (1975), Walling and Webb (1982, 1995) and more recently Jordan et al. (2007) and Stutter et al. (2008). These patterns describe the changes in nutrient concentrations during high-flow events, being characterised as clockwise or anticlockwise, depending on whether concentrations increase or decrease with stream flow. However, hysteresis is a complex phenomenon that is dependent on many physical, hydrological and chemical factors within catchment soils and the river channels themselves (Zonta et al., 2005) and the extent and degree of hysteresis will reflect these factors (House and Warwick, 1998). These include soil mineralogy (e.g. P content, organic matter content, P buffering capacity, texture, type), soil chemistry (pH, temperature), soil moisture conditions, land use (e.g. types of crop or livestock) and land management (e.g. fertiliser application and timing). Important hydrological factors are characteristics of high-flow events and transported sediment, different flow paths (e.g. overland flow and through-flow), sediment flushing and changing sources (e.g. catchment and within-channel sources). Phosphorus export patterns are also dependent on the history of the source water and the degree of interaction with the soil components (House and Warwick, 1998). McDiffett et al. (1989) proposed that hysteresis effects may be used as a technique for determining the source of chemicals measured in streams. Given the large number of factors that influence hysteresis, it
can be difficult to identify the exact factors governing the patterns of P losses. However, such analysis can help determine the importance of diffuse P sources during high-flow events.

### 5.9.5.1 Clockwise hysteresis

When P concentrations and flows were compared, early autumn high-flow events displayed clear clockwise hysteresis patterns, with TP and PP concentrations increasing on the rising limb of the hydrograph and decreasing just before peak discharge. This pattern of P export and large increases in PP concentrations reflected the importance of diffuse P transfers and the rapid delivery of sediment-associated PP to the stream. Decreasing concentrations before peak discharge indicated that diffuse sources were not infinite and were prone to depletion. This flushing effect has also been witnessed during high-flow events captured by Jordan et al. (2007) and Bowes et al. (2005). Although the majority of P transport seemed to be associated with particulate matter being eroded and transported from the surrounding land, results suggested that in-stream stores of sediment and nearby sediment sources (e.g. river banks) could provide an important P source early in the event season. Klein (1984) and Bowes et al. (2005) suggested that rapid increases in sediment and TP/PP concentrations before the onset of the high-flow hydrograph are caused by an early flush of fine, readily mobilised sediments through the fluvial system. This very easily mobilised and rapidly delivered sediment source was most likely from re-suspended bed sediments (Bowes et al., 2005). Mass balance studies have demonstrated that much of the PP associated with sediment entering a river can be retained and deposited within a river channel during the summer, low flow season (Bowes and House, 2001; Evans and Johnes, 2004). Subsequent rainfall and greater discharges could easily mobilise these settled bed sediments, as well as bank sediment sources, by scouring (Brown et al., 1995; Evans and Johnes, 2004). Bowes et al. (2003) reports that SRP sources are also retained by this fine sediment and subsequent re-mobilisation during high-flows results in significant SRP desorption and export. However, the exact role of channel storage of sediments during low
flows, and subsequent remobilisation of PP during high-flow events still remains uncertain due to limited research (Walling et al., 1996; Evans and Johnes, 2004).

5.9.5.2 *Anticlockwise hysteresis*

As the number of high-flow events increased in the catchment, hysteresis patterns changed dramatically, displaying a variation of clockwise and anticlockwise patterns. Anti-clockwise hysteresis is when concentrations peak after peak discharge and decline during the falling limb of the hydrograph. Changing hysteresis patterns reflected changing P sources and a change in the timing of P and sediment delivery (Bowes et al., 2005). Generally, anticlockwise patterns are not as common as clockwise hysteresis and are normally observed in more mobile chemical parameters (e.g. nitrate) and chemicals not strongly sorbed to particulate material (e.g. phosphorus) (House and Warwick, 1998). However, some studies have reported anticlockwise patterns for both sediment and phosphorus. Klein (1984) suggested that these patterns were a function of increased travelling time and source distance. Similarly, Wood (1977) proposed that they were result of diffuse sources from the catchment being more important than in-channel processes, as a catchment became water saturated. Jordan et al. (2007) agreed suggesting that this pattern of change was indicative of new water interacting with previously flushed soils. It was further believed that anticlockwise hysteresis may be indicative of a ‘true’ diffuse source in comparison with flushing of previously attenuated material at the onset of high-flow runoff. Anti-clockwise patterns may also be due to the exhaustion of fast delivered, nearby sediment sources in early high-flow events. Wood (1977) suggested that anticlockwise hysteresis resulted as mobile P in the river channel, either bound to fine upper bed-sediment or held as soluble P in the pore waters, became depleted by previous high-flow events. Jansson (2002) and Bowes et al. (2005) commented that anticlockwise hysteresis showed that the majority of P is derived from a source that is mobilised slowly or is some distance away from the stream and sampling point. In this instance, the delay in P delivery could also be due to the delivery of sub-surface water, caused as rainfall infiltrates the soil and moves laterally through the upper soils. This water source may be more important during high-flow events later in the
season, as catchment soils become water logged due to continuing rainfall. However, as already mentioned, the strong P binding capacity of soils probably means that sub-surface water sources will be relatively low in soluble P. In addition, sub-surface flow is likely to be fairly small compared to surface runoff volumes. Therefore, the most likely sediment and P sources during later high-flow events arose from soil eroded from higher up in the catchment by surface runoff.

5.9.6 High-flow independent phosphorus transfers

During this research, the high frequency (2-hourly) sampling regime captured a short-lived, rural point source pollution event that might not have been identified by a less intense survey regime. The chronic pollution event in the Pow Burn was caused by the transport of a large amount of slurry through the fluvial system (personal observation). Although this evidence was circumstantial, Neal *et al.* (2005) and Jordan *et al.* (2005) commented that such chronic P transfers are most likely the result of a combination of poorly managed septic tanks and/or farmyard infrastructure. Aitken *et al.* (2001) observed that in many livestock farms in SW Scotland, domestic foul drainage and rainwater drainage systems were often poorly maintained, incorrectly installed and inappropriately used and were considered an importance cause of discrete pollution incidences. High frequency monitoring also identified periods when rainfall caused a short, rapid delivery of P through the stream when discharge did not change to any significant degree. Edwards and Withers (2008) commented that un-consented point sources are generally not considered when predicting the impacts of nutrient inputs to water bodies, due to their strong temporal and spatial variability. However, Jordan *et al.* (2005) and Jordan *et al.* (2007) commented that these events are important in terms of river water quality as these P sources may maintain streams in a eutrophic state between high-flow events. At first glance, we considered the Pow Burn catchment to suffer only from diffuse agricultural P sources as there were no consented point source inputs. However, this research has shown that the catchments watercourses are also being impacted by un-consented point source inputs such as farmyard runoff. Other un-consented inputs are likely to include septic discharge and road and track runoff. Jarvie *et al.* (2003).
reported that the contribution of these sources can often be blamed for localised nutrient impacts in streams, whilst Neal et al. (2005) commented that reduction of these un-consented nutrient transfers may help restore good water quality on an individual tributary basis. Therefore, in addition to high-flow event P transfers, a much better understanding of the contribution of these additional P sources is also required. This will help target and control of nutrient inputs at the local catchment scale more efficiently (Edwards and Withers, 2008).

5.10 Summary

The changes in stream water P concentrations measured during an intensive survey in the Pow Burn catchment are complex as they involve a magnitude of interlinked riverine and catchment processes. In summary, this research has shown that:

1. Average and maximum P concentrations measured in stream water during high-flow events were notably above the recognised eutrophication threshold limits for both SRP and TP. This confirms the importance of reducing P losses from catchment sources in order to meet the 'good ecological status' classification set by the WFD.

2. High-flow events contributed 58% of the total stream flow during the monitored period (10th October to 5th December 2006). During these events, 62% of TP, 45% of SRP and 71% of PP was delivered to Loch Leven. Therefore, notably more PP was exported during high flows than during base flows.

3. Surface runoff from the catchment and subsequent high stream discharges were responsible for the delivery and transport of large amounts of P laden suspended sediments. Transport during high-flows was, therefore, dominated by the PP fraction, which was associated with high TSS concentrations originating from diffuse sources. Reducing the delivery of diffuse PP sources to Loch Leven will require the reduction of sediment erosion from the catchment.
4. Larger high-flow events did not result in the transport of the highest P concentrations through the Pow Burn. Rainfall intensity and duration were also important in determining the magnitude of P response.

5. Hysteresis analysis showed that the largest clockwise loops for P and TSS occurred in two early events in mid October and one event in November. These loops were characteristic of events that occur after a prolonged period of relatively dry antecedent conditions. In such conditions, fine sediment that had settled in the channels and along nearby river margins was more easily and rapidly mobilised, forming readily available P sources.

6. The size of SRP hysteresis loops decreased during successive high-flow events, highlighting the importance of antecedent conditions and the depletion of available SRP sources within the catchment. The fast succession of an event meant that dissolution and desorption processes in catchment soils and river sediments needed time to replenish available SRP sources.

7. Later high-flow events showed more complex hydrographs that tended towards anticlockwise P hysteresis behaviour. This was attributed to the depletion of rapidly mobilised, within-channel and nearby sediment sources being depleted by earlier events. During later events, sediment and P originated from less mobile and more distant sources. Therefore, delivery times and transport distances were longer.

8. The Pow Burn is regarded as receiving no known consented point source P inputs; however, this study has provided evidence to suggest that unregulated point source P inputs did occur. These chronic, low flow P transfers can have a major eutrophic impact on a river system and must be researched in order for catchment management activities to be appropriately targeted. High-frequency nutrient sampling and targeted nutrient audits will be required to achieve the aims of the WFD.

9. 
5.11 Conclusion

First, this study has confirmed that high-flow events in the Pow Burn catchment resulted in significantly elevated concentrations of TSS, TP, PP and SRP being delivered to Loch Leven during winter months. Results also reaffirm the importance of high-flow events in contributing to P loss from rural catchments where surface runoff dominates during periods of heavy rainfall. It is envisaged that the large amounts of P delivered to Loch Leven during winter high-flow events may contribute to poor water quality problems by adding new sources P to loch sediments. Secondly, the importance of high-frequency sampling regimes that allow short-lived high-flow and non-high-flow P transfers to be monitored has also been highlighted. Kronvang and Iverson (2002), Jordan et al. (2005) and Jordan et al. (2007) have also documented the need for more automated, high frequency nutrient monitoring to be performed. This is required to capture the importance of diffuse P transfers efficiently and accurately during high-flow events. This high-frequency sampling study also identified that un-consented point source discharges contributed to P transfers from the catchment. Different P sources require specific and targeted remedial measures, particularly at the small catchment scale. High resolution P monitoring allows both high-flow events and un-consented point source transfers to be assessed, providing critical information that will aid successful and targeted catchment management initiatives. Targeted management will be vital in achieving the full aims of the Water Framework Directive (Jordan et al., 2005; Jordan et al., 2007) especially in eutrophic water body catchments like Loch Leven.
6 Uncertainties Associated with Estimating Phosphorus Loads

6.1 Introduction

When designing a programme to estimate an accurate pollutant load, two key questions are usually addressed (Walling and Webb, 1985; Rekolainen et al., 1991; Johnes et al., 2007). How often should measures of Q and C be taken and second, which load calculation method should be applied. How these questions are addressed are influenced by some common constraints, usually budgets (Johnes, 2007), project goals (concentration versus loads) and desired accuracy with respect to 'true' loads (Tate et al., 1999; King and Harmel, 2003). However, choosing an appropriate approach is difficult because of a lack of information about different sampling strategies and associated errors. Nevertheless, it is imperative that the chosen sampling protocol provides sufficient data to accurately measure P loads because water quality research, nutrient export modelling and efficient catchment management rely on the assumption that sampling programmes provide an accurate estimate of 'true' P loads (Walling and Webb, 1982; King et al., 2005; Johnes, 2007). Accurate information will also allow the effectiveness of management measures which aim to improve water quality to be assessed (Johnes, 2007).

The most common sampling strategy employed by regulatory authorities involves regular time-interval sampling at a very low frequency (i.e. monthly or weekly) (Greig, 2005). Although simple and cost effective, low-frequency sampling was designed to characterise point source pollution which, until recently, has been the dominant source of P causing water quality problems. Since the introduction of the Urban Waste Water Treatment Directive (UWWTD) and the significant reduction of point P sources, P inputs in many rural catchments are now dominated by diffuse P sources. Because diffuse P inputs are primarily driven by storm events (Evans and Johnes, 2004, Jordan et al., 2007; Sharpley, 2008) periodic grab sampling must be supplemented with storm event monitoring (King et al., 2005). Statistical sampling theory suggests that shorter sampling intervals produce more accurate estimates of P loads compared to longer intervals (Haan, 2002; Harmel and King, 2005) because a more frequent sampling strategy captures short-lived storm events.
that may account for the majority of annual P loads (Walling and Webb, 1996; Phillips et al., 1999; Jordan et al., 2007). Therefore, the influence of these events needs to be included in any calculation of the ‘true’ P load. In spite of this, there has been little progress in increasing sampling frequency in national monitoring programmes, even though this will be vital in order to meet the requirements of the Water Framework Directive (Greig, 2005). For the most part, resources and equipment are the main constraints on sampling frequency, the outcome being that many sampling programmes continue to collect insufficient or representative data to accurately estimate P loads (Harmel et al., 2003).

A number of studies have tried to quantify the variability and accuracy of pollutant loads estimated using different calculation methods and sampling strategies (e.g. Walling and Webb, 1981; Walling et al., 2001; Kronvang and Bruhn, 1996; Johnes, 2007). However, there are very few loading studies highlighting the exact importance of storm events on P load estimates (e.g. Zonta et al., 2005). This paper reports on the variability of P load estimates as a result of (a) different sampling strategies (weekly versus daily), (b) different interpolation and extrapolation calculation methods and (c) different sampling times. The accuracy of each load estimate was assessed by comparing the estimated loads to the actual or ‘true’ P loads. This research also aimed to provide evidence of the importance of capturing storm events during regulatory sampling regimes.

6.2 Methods

Water samples were collected at the Pow Burn between 10th October and 5th December 2006. Water samples were collected every 2 hours using two Hach Lange® EPIC automatic water samplers, capturing 10 high-flow events which occurred during this monitoring period. All water samples were analysed for total P (TP), total soluble P (TSP), soluble reactive P (SRP) and particulate P (PP = TP-TSP) within 48 hours of collection following the methods of Eisenreich et al. (1975) and Murphy and Riley (1962). High frequency flow data (every 15 minutes) was recorded by a continuous flow gauge that was located on the Pow Burn (refer back to Chapter 5, Figure 5.3). Flow data for the period of the study was provided by the
6.3 **Data analysis**

6.3.1 *Estimating ‘true’ phosphorus loads*

First, the ‘true’ TP, PP and SRP loads for the study period was determined from measures of \( C_i \) and \( Q_i \) collected at 2-hourly intervals between 10\(^{th}\) October and 5\(^{th}\) December 2006 (Equation 6.1).

\[
L_t = K \left( \sum_{i=1}^{n} C_i Q_i \right)
\]

*(Equation 6.1)*

Where:

- \( L_t \) = estimate of the ‘true’ phosphorus load
- \( K \) = conversion factor to take account of time period of record.
- \( n \) = number of samples.
- \( C_i \) = instantaneous phosphorus concentration (µg l\(^{-1}\)).
- \( Q_i \) = instantaneous discharge at time of chemical sampling (m\(^3\) sec\(^{-1}\)).

6.3.2 *Different calculation methods*

Seven calculation methods were used to estimate P loads (Table 6.1a and Table 6.1b). These methods were selected from the literature and determined as the most commonly applied methods in loading studies.

6.3.3 *Different sampling strategies*

The load estimate inaccuracy associated with sampling frequency was estimated by taking the original 2-hourly data set containing 2-hourly measures of \( C_i \) and \( Q_i \), and artificially constructing the data to create a series of weekly and daily data sets (Table 6.2) consisting of one paired value of \( C_i \) and \( Q_i \). For weekly sampling programmes, the interval between sampling was 8 days as this was the sampling strategy used to determine annual P loads to Loch Leven in 1985, 1995 and 2005.
(refer back to Chapter 4). Weekly sampling intervals are also the most common sampling programmes performed by regulatory authorities.

Table 6.1: Load estimation procedures using intermittent values of stream flow and phosphorus concentration over a fixed time period.

<table>
<thead>
<tr>
<th>Method</th>
<th>Interpolation Procedures</th>
<th>Original Reference Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Total Load = ( K \left( \sum_{i=1}^{n} \frac{C_i}{n} \right) \left( \sum_{i=1}^{n} \frac{Q_i}{n} \right) )</td>
<td>Verhoff et al. (1980)</td>
</tr>
<tr>
<td>B</td>
<td>Total Load = ( K \left( \sum_{i=1}^{n} \frac{C_i}{n} \overline{Q}_{r} \right) )</td>
<td>Ongley (1973)</td>
</tr>
<tr>
<td>C</td>
<td>Total Load = ( K \sum_{i=1}^{n} \left( \frac{C_iQ_i}{n} \right) )</td>
<td>Rodda and Jones (1983)</td>
</tr>
<tr>
<td>D</td>
<td>Total Load = ( K \left( \sum_{i=1}^{n} C_i \overline{Q}_{r} \right) )</td>
<td>Walling and Webb (1981)</td>
</tr>
<tr>
<td>E</td>
<td>Total Load = ( K \sum_{i=1}^{n} \frac{(C_iQ_i)}{Q_r \sum_{i=1}^{n} Q_i} )</td>
<td>Verhoff et al. (1980)</td>
</tr>
<tr>
<td>F</td>
<td>Total Load = ( K \sum_{i=1}^{n} (C_iQ_i) )</td>
<td>Rodda and Jones (1983)</td>
</tr>
</tbody>
</table>
| G      | Log-Log linear regressions between \( C \) and \( Q \) to estimate P concentrations \( (C_e) \) on the basis of continuous measures of stream flow \( (Q_o) \). \[
\log_{10} C_e = (m \log_{10} Q_o) + b
\]
A correction factor (CF) was applied to account for the inherent underestimation associated with log-log linear regression analysis. | Stevens and Smith (1978) and Ferguson (1986) |
|        | \( s^2 = \sum_{i=1}^{n} \frac{(\log_{10} C_i - \log_{10} C_r)^2}{(n-2)} \) | |
|        | \( CF = \exp (2.65s^2) \) | |
|        | Total Load = \( K \left( \sum_{i=1}^{n} (C_iQ_i) \right) \) | |
Where:

$K$ = conversion factor to take account of time period of record.

$n$ = number of samples.

$C_i$ = instantaneous concentration associated with individual samples (µg l$^{-1}$).

$Q_t$ = instantaneous discharge at time of sampling (m$^3$ sec$^{-1}$).

$\bar{Q}_p$ = mean discharge for period of record using continuous measures of $Q$ (m$^3$ sec$^{-1}$).

$\bar{Q}_e$ = mean discharge for interval between samples (m$^3$ sec$^{-1}$).

$C_e$ = estimate of P concentration from continuous stream flow value.

$Q_e$ = direct measurement or estimate of continuous stream flow (m$^3$ sec$^{-1}$).

$m$ = slope of linear regression

$b$ = intercept of linear regression

Table 6.2: Sampling days during 8 different weekly sampling programmes, when one paired measure of stream flow and phosphorus concentration per week was used to estimate phosphorus load.

<table>
<thead>
<tr>
<th>Sampling Days during weekly Sampling Programmes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group 1</td>
</tr>
<tr>
<td>10$^{th}$ Oct</td>
</tr>
<tr>
<td>18$^{th}$ Oct</td>
</tr>
<tr>
<td>26$^{th}$ Oct</td>
</tr>
<tr>
<td>3$^{rd}$ Nov</td>
</tr>
<tr>
<td>11$^{th}$ Nov</td>
</tr>
<tr>
<td>19$^{th}$ Nov</td>
</tr>
<tr>
<td>27$^{th}$ Nov</td>
</tr>
</tbody>
</table>

6.3.4 Different sampling times

The effect on load estimate accuracy due to sampling at different times of each sampling day was investigated. Load estimates were calculated from values of $Q_i$ and $C_i$ measured at 1.00, 3.00, 5.00, 7.00, 9.00, 11.00, 13.00, 15.00, 17.00, 19.00, 21.00 and 23.00 hours.
6.3.5 Measuring accuracy of P load estimates

The accuracy of each load estimate ($L_{est}$) based on a) different calculation method, b) different sampling strategy and c) different sampling times were determined by comparison to the ‘true’ P load (Equation 6.2).

$$Accuracy\, (\%) = 100 \cdot \left( \frac{L_{est}}{L_t} \right)$$  \hspace{1cm} (Equation 6.2)

Where:

$L_{est}$ = estimated phosphorus load
$L_t$ = ‘true’ phosphorus load

6.4 Results

6.4.1 The contribution of high-flow events to winter phosphorus loads

Temporal changes in P loads during ten consecutive high-flow events in the Pow Burn are shown in Figure 6.1. Larger events delivered greater P loads to Loch Leven. During the largest event, P delivery at peak flow reached 24 kg TP hr$^{-1}$, 21.5 kg PP hr$^{-1}$ and 1.2 kg SRP hr$^{-1}$. ‘True’ P loads for the 10 week study period were 459 kg TP, 78 kg SRP and 351 kg PP. Together, 10 high-flow events contributed 79% (363 kg), 63% (49 kg) and 84% (295 kg) of the ‘true’ TP, SRP and PP loads, respectively, over the 10 week monitoring period (Figure 6.2a). These results show the importance of high flow events in P delivery and transport to Loch Leven. Large storm events were particularly important, as the largest event alone contributed 34% (157 kg), 17% (13 kg) and 39% (136 kg) of the ‘true’ TP, SRP and PP load (Figure 6.2b).
Particulate Phosphorus Load (kg/hr⁻¹)

Total Phosphorus Load (kg/hr⁻¹)

Soluble Reactive Phosphorus Load (kg/hr⁻¹)

Stream Flow at Pow Burn (m³/sec)

Figure 6.1: Temporal changes in phosphorus loads to Loch Leven during 10 consecutive high-flow events in the Pow Burn.

10th Oct 2006
12th Oct 2006
14th Oct 2006
16th Oct 2006
18th Oct 2006
20th Oct 2006
22nd Oct 2006
24th Oct 2006
26th Oct 2006
28th Oct 2006
30th Oct 2006
1st Nov 2006
3rd Nov 2006
5th Nov 2006
7th Nov 2006
9th Nov 2006
11th Nov 2006
13th Nov 2006
15th Nov 2006
17th Nov 2006
19th Nov 2006
21st Nov 2006
23rd Nov 2006
25th Nov 2006
27th Nov 2006
29th Nov 2006
1st Dec 2006
3rd Dec 2006
5th Dec 2006
Figure 6.2a: The contribution of phosphorus loads from high-flow events to ‘true’ P loads between October 10th to December 5th 2006 in the Pow Burn.

Figure 6.2b: The individual contribution of ten high-flow events (A-J) to phosphorus loads between October 10th to December 5th 2006 in the Pow Burn.

6.4.2 Accuracy of phosphorus load estimates using weekly sampling regimes

Estimated phosphorus loads calculated using different weekly sampling regimes, sampling times and calculation methods ranged from 89 to 5028 kg TP (20% - 1095% of ‘true’ TP load), 35 to 4588 kg PP (10% - 1307% of ‘true’ PP load) and 41 to 286 kg SRP (52% - 367% of ‘true’ SRP load). The percentage deviation from the ‘true’ P load for each TP, PP and SRP estimate are shown in Figures 6.3, 6.4 and 6.5, respectively. The sampling frequency that gave the most accurate estimations of P loads varied according to the method of calculation, weekly
sampling group and daily sampling time. Table 6.3 summarises the accuracy of load estimates compared to 'true' P loads.

Table 6.3: Accuracy of load estimations based on weekly sampling regimes. Results account for 7 different calculation methods, 8 weekly sampling groups and 12 different sampling times.

<table>
<thead>
<tr>
<th></th>
<th>TP</th>
<th>PP</th>
<th>SRP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overestimated</td>
<td>102</td>
<td>107</td>
<td>184</td>
</tr>
<tr>
<td>Underestimated</td>
<td>567</td>
<td>562</td>
<td>480</td>
</tr>
<tr>
<td>Equal to 'true' load</td>
<td>3</td>
<td>3</td>
<td>8</td>
</tr>
<tr>
<td>Total No. of Estimates</td>
<td>672</td>
<td>672</td>
<td>672</td>
</tr>
</tbody>
</table>

The probability that P loads would be accurately estimated (i.e. equal to the 'true' P load) using a weekly sampling regime was very small, regardless of the calculation method applied. The vast majority of loads were under-estimated, while a small proportion was over-estimated. Estimates within ±10% of the 'true' TP, PP and SRP load occurred on 48 (7%), 37 (6%) and 85 (13%) of occasions, respectively. Therefore, 93%, 94% and 88% of TP, PP and SRP load estimates had inaccuracies of greater than 10% inaccurate when based on weekly sampling regimes.
Figure 6.3: Percentage deviation from the 'true' total phosphorus load for the period 10th October to 5th December 2006. Load estimates based on 8 different weekly sampling regimes (groups 1-8), 7 different calculation methods (A-G) and different times of sampling within each selected sampling day (1am – 11pm).
Figure 6.4: Percentage deviation from the 'true' particulate phosphorus load for the period 10th October to 5th December 2006. Load estimates based on 8 different weekly sampling regimes (groups 1-8), 7 different calculation methods (A-G) and different times of sampling within each selected sampling day (1am – 11pm).
Figure 6.5: Percentage deviation from the 'true' soluble reactive phosphorus load for the period 10th October to 5th December 2006. Load estimates based on 8 different weekly sampling regimes (groups 1-8), 7 different calculation methods (A-G) and different times of sampling within each selected sampling day (1am – 11pm).
6.4.2.1 Differences between calculation methods

The accuracy of load estimations by different calculation methods were compared by fitting frequency distributions to the raw data using a largest extreme value model (Figure 6.6). Negatively skewed distributions indicate a clear tendency for all calculation methods to under-estimate P loads. On average, methods A, B and F under-estimated TP (-56% to -60%) and PP (-67% to -70%) loads by the most, followed by methods C, D and E for TP (-45% to -50%) and PP (-53% to -60%). Method G under-estimated TP (-40%) and PP (-49%) loads the least. SRP was more accurately estimated than TP and PP loads, with less inaccuracy between estimated and 'true' SRP loads. Methods A, C, D and F, on average, underestimated SRP loads between -18% to -24%, whilst methods B, E and G were the least inaccurate (-11% to -13%). For TP and PP, methods A, B and F showed the least variability between load estimates (indicated by a small tail distribution scale in Figure 6.6). Therefore, although these methods significantly under-estimated TP and PP loads, they were the least likely methods to generate extreme load estimates. In contrast, method C was more likely to generate highly inaccurate estimates, reaching up to 995% and 1207% of the 'true' TP and PP loads in one instance.

6.4.2.2 Differences among weekly sampling groups

Figure 6.7 compares the frequency distributions of the accuracy of load estimates based on 8 different weekly sampling groups. Distributions were negatively skewed for all groups, implying that P loads were most frequently underestimated using \( C_i \) and \( Q_i \) data collected during weekly sampling regimes. On average, TP (-72% to -76%) and PP (-85%) loads were most greatly under-estimated in groups 3 and 4. There was less inaccuracy associated with estimates in groups 2, 6 and 7 but TP and PP loads were still under-estimated (-43% to -56% and -48% to -68%, respectively). The most accurately estimated TP (-28% to -30%) and PP loads (-32 to -39%) were calculated using weekly sampling groups 1 and 5. Similarly, SRP loads were appreciably underestimated in groups 3 and 4 (-23% to -40%), however, the most accurate SRP estimates were in groups 1 and 8 (-2% to +4%).
Figure 6.6: Comparison between frequency distributions of phosphorus load estimate accuracy by 7 different calculation methods (A-G) for a weekly sampling regime. (Note: Loc = peak of distribution, Scale = spread of distribution, n = number of estimates).
Figure 6.7: Comparison between frequency distributions of phosphorus load estimate accuracy, calculated using 8 different weekly sampling groups. (Note: Loc = peak of distribution, Scale = spread of distribution, n = number of estimates).
6.4.2.3 Differences due to variation in time of sampling

Frequency distributions of the accuracy of TP, PP and SRP loads estimated using \( C_i \) and \( Q_i \) values from different times of day for each weekly sampling period clearly showed that load accuracy was affected by the time at which weekly paired measures of \( C_i \) and \( Q_i \) were collected (Figure 6.8). All sampling times resulted in an under-estimation of P loads. In general, early morning values of \( C_i \) and \( Q_i \) (01.00 h and 03.00 h) resulted in the least inaccurate loads for TP (-27% to -28%) and PP (-33% to -35%). In contrast, samples collected at 13.00 h, 15.00 h and 17.00 h yielded the greatest level of inaccuracy for TP (-60% to -65%) and PP (-71% to -77%) loads. For SRP, samples collected at 01.00 h resulted in an average estimate within -7% of the ‘true’ SRP load, while sampling between 11.00 h and 19.00 h resulted in SRP loads approximately -25% of the true load.

6.4.3 Accuracy of phosphorus load estimates by daily sampling regimes

The accuracy of load estimations (expressed as % of the ‘true’ P loads) calculated using daily measures of \( C_i \) and \( Q_i \) at different times of each sampling day and with different methods is shown in Figure 6.9. Estimated loads ranged between 22 - 1891 kg TP (-95% to 312%), 13 - 1503 kg PP (-96% to 328%) and 7 - 276 kg SRP (-91% to 254%). Out of a total of 84 estimates; TP, PP and SRP were accurately estimated on 1, 2 and 3 occasions, respectively (Table 6.4). Total P, PP and SRP loads were estimated within ±10% accuracy on 11 (13%), 8 (10%) and 37 (44%) occasions. Therefore, 87%, 90% and 56% of TP, PP and SRP load estimates had an accuracy greater than ±10%.

<table>
<thead>
<tr>
<th></th>
<th>TP</th>
<th>PP</th>
<th>SRP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overestimated</td>
<td>20</td>
<td>11</td>
<td>26</td>
</tr>
<tr>
<td>Underestimated</td>
<td>63</td>
<td>66</td>
<td>56</td>
</tr>
<tr>
<td>Equal to 'true' load</td>
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<td>7</td>
<td>2</td>
</tr>
<tr>
<td>Total No. of Estimates</td>
<td>84</td>
<td>84</td>
<td>84</td>
</tr>
</tbody>
</table>

Table 6.4: Accuracy of load estimations based on daily sampling regimes. Results comprise 7 different calculation methods and 12 different sampling times.
Figure 6.8: Comparison between frequency distributions of phosphorus load estimate accuracy when stream flow and P concentrations measured at different times of each sampling day (01.00 h to 23.00 h) for a weekly sampling regime. (Note: Loc = peak of distribution, Scale = spread of distribution, n = number of estimates).
Figure 6.9: Percentage deviation from the 'true' phosphorus loads for the period 10th October to 5th December 2006. Loads estimated based on 7 different calculation methodologies (A-G) using daily paired measures of phosphorus concentration and stream flow at different times of the sampling day (1am – 11pm).
6.4.3.1 Differences between sampling methods

Figure 6.10 shows the frequency distribution of estimated P loads calculated using 7 different calculation methods based on a daily sampling strategy. TP, PP and SRP loads were, in general, under-estimated by all calculation methods. Methods A and B under-estimated TP and PP loads the most (-55% to -59%) (-64% to -67%). Results showed that load estimates could be notably over-estimated as well as under-estimated if methods C, D, E or F were applied to daily data sets. Frequency distribution analysis suggested that, on average, method C was the most accurate method for estimating TP (-21%) and PP loads (-26%). However, this method also the most imprecise, having the largest frequency distribution (Figure 6.10). The use of regression relationships between \( C_i \) and \( Q_i \) (method G) did improve the accuracy of TP and PP loads, however, they were still likely to be under-estimated by between -33% and -41%, respectively. Nevertheless, method G was the most precise, showing the smallest frequency distribution. Method G was also particular reliable for estimating SRP loads as, on average, loads were estimated within -7% of the ‘true’ SRP load. Therefore, method G was considered the most reliable method for estimating TP, PP and SRP loads on the basis of daily data.

6.4.3.2 Differences between sampling times

Sampling time can notably affect the accuracy of P load estimates even when sampling frequency is daily (refer back to Figure 6.9). Figure 6.11 compares frequency distributions for TP, PP and SRP load estimates based on 12 different sampling times for a daily sampling regime. Sampling between 11.00 h and 21.00 h resulted in the highest underestimates of TP (-49% to -62%) and PP (-47% to -73%) loads. Load estimates were most accurate using values of TP, PP and \( Q_i \) collected at 1.00 h and 5.00 h (+6% to +10% of ‘true’ TP load) (+5% to +8% of ‘true’ PP load). Similarly, sampling at 23.00 h and between 5.00 h and 9.00 h resulted in the most accurate SRP load estimates (within -3% to 8% of the ‘true’ SRP load), while SRP loads estimated from samples collected between 11.00 h and 21.00 h were less accurate (-16% to -41%).
Figure 6.10: Comparison between frequency distributions of phosphorus load estimate accuracy when estimated by 7 different calculation methods for a daily sampling regime. (Note: Loc = peak of distribution, Scale = spread of distribution, n = number of estimates).
Figure 6.11: Comparison between frequency distributions of phosphorus load estimate accuracy when stream flow and P concentrations measured at different times (1.00 h to 23.00 h) for a daily sampling regime. (Note: Loc = peak of distribution, Scale = spread of distribution, n = number of estimates).
Figure 6.12: Comparison between phosphorus load estimations based on weekly and daily sampling regimes (calculated using 7 different calculation methods and 12 different sampling times).
6.4.4 Comparison between weekly and daily estimated loads

The overall effect of daily and weekly sampling regimes on the accuracy of P load estimated is shown in Figure 6.12. On average, increasing sampling frequency to one daily paired measure of $C_i$ and $Q_i$ reduces load estimation inaccuracy. Average inaccuracy of TP, PP and SRP estimates decreased from -52% to -38%, -61% to -45% and -18% to -14%, respectively. However, compared to 2-hourly sampling, P loads still had a tendency to be notably under-estimated by a daily sampling regime.

6.5 Discussion

6.5.1 The importance of high-flow events on phosphorus loads

Following the upgrade of sewage treatment works and eliminations of industrial effluents most of the annual P loads to Loch Leven now comes from diffuse P sources. The Pow Burn catchment has been shown to transport an uncharacteristically high percentage of the catchment’s diffuse PP load (see Chapter 4) and high-flow events have been identified as the primary driver of P delivery to the loch (see Chapter 5). This research has further highlighted the importance of high-flow events in P delivery showing that 10 high-flow events contributed 79%, 84% and 63% of the winter TP, PP and SRP loads. The largest event contributed 34%, 49% and 17% of the total TP, PP and SRP load, respectively. This supports the findings of Smith et al., (1991), Edward and Owens (1991), Littlewood, (1993), Sharpley and Rekolainen (1997) and Evans and Johnes (2004) who all commented that relatively few high-flow events contribute the majority of annual P loads. Therefore, accounting for the influence of high-flow events on P transport is crucial when estimating a reliable P load to a water body. In the present study, the accuracy and variability associated with load calculation methods and sampling strategies were investigated. This was achieved by deconstructing a high-frequency data set of 2-hourly measures of stream flow ($Q_i$) and P concentrations ($C_i$). This created a number of artificial data sets that mimicked weekly and daily sampling strategies. King et al. (2005) suggested that sampling frequency must be at least 15 minutes or less in order to obtain a load estimate that was not statistically different from the
'true' load. However, this was dependent on hydrograph characteristics and event duration in a particular catchment. The Pow Burn is not a particularly 'flashy' catchment and small, high-flow events lasted at least 24 hours. Therefore, 2-hourly observed data were considered to be an acceptable reference data set for evaluating the effect of calculation methods, sampling frequency and sampling time on the accuracy and variability of load estimates.

For both weekly and daily sampling strategies, calculation methods A and B showed least variation between load estimates but typically greatly underestimated P loads. Walling and Webb (1985) commented that the degree of underestimation was probably the result of using a time-weighted, rather than a flow-weighted, mean concentration value in the calculation procedure. In this study, methods C, D and E were the most inaccurate as they tended to greatly under-estimate P loads. These methods also had low precision showing large over-estimates as well as under-estimates. On investigation of individual data sets, notable over-estimates were specifically due to the inclusion of high-flow values of \( Q \) and \( C \) in data sets. Results suggest that none of the common interpolation calculation methods are accurate methods for calculating reliable P loads, even when sampling frequency is daily. The common solution to this problem has been to apply extrapolation techniques to account for the variability in \( Q \) and \( C \) values between sampling days (Method G). In this study, when \( \log_{10} Q - \log_{10} C \) linear regression relationships were based on weekly data, the method both under- and over-estimated P loads. Rekolainen et al. (1991) commented how strongly P load estimates for any one year could be significantly influenced by the sampling dates selected. In this study, load estimate accuracy was also found to be dependent on the specific weekly data set chosen to calculate P loads. Log-log linear relationships calculated using daily data did result in more accurate estimates, but still tended towards under-estimation. This was also assumed to be a direct consequence of the specific range of \( Q \) and \( C \) values included in data sets, from which relationships were generated. However, data values in daily data sets did explain the relationship between \( Q \) and \( C \) more efficiently compared to weekly data sets. These results support similar conclusions made by Walling and Webb (1985, 1988) and Webb et al. (1997). While Soerens and Nelson (2002) and Robertson and Roerish (1999) suggest that storm chasing can be the best way of
increasing the precision of daily load estimates, this study suggested that load accuracy was highest when data sets included values of $Q_i$ and $C_i$ from the largest of high-flow events. Data sets that included $Q_i$ and $C_i$ values from some of the smaller high-flow events appeared to result in large over-estimations. This was probably because of an over-estimate of P concentrations at higher flows using a linear log-log regression because P concentrations often decline before peak discharge (Thomas, 1985; 1988; Walling and Webb, 1988; Thomas and Lewis, 1995).

6.5.2 **Sampling programmes must target high-flows events**

When designing a programme to estimate an accurate pollutant load, two key questions are usually addressed (Walling and Webb, 1985; Rekolainen et al., 1991; Johnes et al., 2007). How often should measures of $Q$ and $C$ be taken and second, which load calculation method should be applied. How these questions are addressed are influenced by some common constraints, usually budgets (Johnes, 2007), project goals (concentration versus loads) and desired accuracy with respect to 'true' loads (Tate et al., 1999; King and Harmel, 2003). However, choosing an appropriate approach is difficult because of a lack of information about different sampling strategies and associated errors. The protocol will depend on catchment and hydrological characteristics and the behaviour of the pollutant in question. For example, in catchments where P inputs are dominated by point sources, greatest P concentrations will occur during low flow periods. In contrast, catchments dominated by diffuse P sources, sampling during high-flow events will be much more important. Therefore, a sampling strategy that may suit one catchment will not necessarily be appropriate for another because catchment influences and hydrological conditions differ. It is imperative that the chosen sampling protocol provides sufficient data to accurately measure P loads. This is essential to determine future impacts of pollutants and to allow the effectiveness of management measures which aim to improve water quality to be assessed (Johnes, 2007).

Currently, there is little guidance available for determining suitable high-flow monitoring strategies in small catchments (Harmel et al., 2003) primarily because collecting high-flow event samples by hand is difficult. Travel distances, remote
locations and the unpredictability of high-flow events mean manual sampling is unrealistic. The most reliable and safe method is to use automatic samplers, which can be set to perform time interval, flow-proportional or flow-threshold sampling programmes. Rekolainen et al. (1991) recommended flow proportional sampling above a certain threshold in addition to a small number of samples collected during base-flow conditions. They found this strategy gave the most accurate load estimates because it took into account the relationship between high flows and high P concentrations, which other fixed interval sampling programmes did not. Similarly, Harmel et al. (2003) suggested that flow-threshold sampling was preferable to time-interval sampling and that the flow threshold should be low enough to capture the smallest and quickest events because missing small events substantially increased load estimation error.

However, the most common sampling strategy employed by regulatory authorities involves regular time-interval sampling at a very low frequency (i.e. weekly, monthly). This sampling programme is simple and cost effective but was designed to characterise point source pollution which, until recently, has been the dominant source of P causing water quality problems. Now that diffuse P sources dominate in many rural catchments (including Loch Leven), periodic grab sampling must be supplemented with high-flow event monitoring (King et al., 2005). To achieve the most accurate estimates of P loads, data collection should be at a daily frequency and the largest high-flow events should be targeted by sampling protocols if the relationship between $Q$ and $C$ is to be most reliable. The use of automatic samplers and online analysers allow the collection of data which results in the most accurate loads possible, they are costly to buy and maintain. There can also be problems with sample storage prior to nutrient analysis (Kotlash and Chessman, 1998) and increased analysis costs due to high numbers of samples. To balance budget constraints and sampling requirements, Harmel and King (2005) suggest the best option for accurate load estimation is to conduct flow-proportional (i.e. predetermined increments of flow volume), composite sampling because this was found to increase sampling capacity without a significant effect on sampling error. In the absence of continuous flow recording equipment (which interfaces with an automatic / online sampler), a variable time-interval sampling strategy may
adequately represent true loads where flow-threshold or flow-proportional sampling is not possible (Harmel et al., 2003). However, adequate knowledge of specific catchment and hydrological characteristics are required. Johnes (2007) suggests that a stratified sampling programme with daily sampling on the 35 highest flow days, combined with weekly sampling during the remainder of the year returns load estimates with low inaccuracy.

6.6 Conclusion

Diffuse P pollution contributes significantly to water quality impairment in many rural catchments. As such, regulatory authorities must now focus on monitoring, controlling and reducing the delivery of diffuse P to receiving water bodies, particularly as this is one of the main requirements of the Water Framework Directive. It will be necessary for regulatory personnel to monitor the delivery of P to receiving water bodies during high-flow events because these events contribute the majority of the annual P load to a water body. Event sampling is also vital in order to implement successful management programmes and to assess the effectiveness of mitigation measures (Tate et al., 1999). However, many researchers have emphasised the difficulty of collecting and analysing high numbers of event samples (Rekolainen et al., 1991; Miller et al., 2000; Harmel et al., 2002; King and Harmel, 2003; Agouridis and Edwards, 2003) because sampling design is driven by budgetary constraints rather than project goals (Johnes, 2007). Consequently, the main challenge is designing an infrequent monitoring programme that provides the best possible data whilst minimising cost. However, there remains little guidance or information for determining suitable settings for high-flow monitoring in small watersheds (Harmel et al., 2003). It is recommended that, prior to the implementation of a sampling programme, some knowledge is gained regarding a catchment’s high-flow event characteristics, for example, the duration, flow ranges and how P responds during these events. This information will aid the implantation of suitable monitoring programmes designed to estimate a truly representative P load, whilst meeting economic constraints. This study further suggests that interpolation calculation methods should be avoided and the common log-log
extrapolation procedure of Stevens and Smith (1978) and Ferguson (1986) applied when only infrequent data is available. This is because the common interpolation methods are unlikely to give reliable P load estimates even when sampling frequency is daily. Furthermore, the accuracy of the extrapolation method can be improved by including $C_i$ and $Q_i$ values only from the largest high-flow events as the relationship between $C_i$ and $Q_i$ is explained more precisely.
7 Sediments as Sources or Sinks of Phosphorus

7.1 Introduction

Research into P transport during high-flow events inferred that settled stream bed sediments were an important source of sediment-associated P to Loch Leven during early high-flow events (refer to Sections 5.7.6 and 5.7.7). A range of studies have shown that sediments in aquatic systems can participate in the process of phosphate buffering (e.g. House and Dennison, 1998; House and Warwick, 1999). Stream sediments can often act as a temporary P sink and possibly maintain water column soluble reactive P (SRP) concentrations at approximately the sediment equilibrium P concentration (Taylor and Kunishi, 1971; Klotz, 1988). This is because they have the ability to sorb or desorb P (Klotz, 1988; Froelich, 1988). This buffering capacity is greatest under low flow conditions when there is a relatively long contact time between the sediments on the bed and the water in the river or stream. A large buffering capacity also occurs where the sediment surface area to water volume ratio is high (Jarvie et al., 2005). Benthic sediments, therefore, play a vital role in the regulation of SRP concentrations in the water column (Klotz, 1988; Haggard et al., 1999) and in the delivery of P through fluvial systems to standing water bodies (Owens and Walling, 2002). The regulation of SRP by sediments could help minimise ecological changes that may occur when SRP concentrations in a stream or receiving water body (such as a lake) are elevated.

Historically, high SRP concentrations in streams and rivers have been caused by point source P inputs. However, now that point sources are under stricter regulation, continually increasing P concentrations are being related to diffuse source P inputs (Carpenter et al., 1998). Diffuse sources generally represent P inputs from sediment sources and land use activities, e.g. agricultural land and fertiliser application (Haggard et al., 1999). A substantial and important source of diffuse P in many rural catchments is often delivered into water courses associated with sediment in surface runoff caused by heavy rainfall. Therefore, surface runoff can deliver and deposit large quantities of sediment into water courses which can be retained in the fluvial system for many months (Poinke and Kunishi, 1992; Walling et al., 1997;
Smith et al., 2006). In rivers, the interaction of P with suspended and bed sediment largely determines the concentration of SRP in the water column (House et al., 1995). Jarvie et al. (2005) propose that diffuse sediment sources could, therefore, provide the ‘missing link’ between eutrophication impacts at times of ecological sensitivity and sediment-associated diffuse P delivered to stream channels during high-flow events. It will be in the ecologically sensitive months that SRP from accumulated sediment sources could be released. Therefore, it would be advantageous to know if river bed sediments and sediments entering aquatic systems in runoff act as P sources or sinks, especially during times of greatest ecological risk (Jarvie et al., 2005).

The objectives of this study were:

- To examine stream bed sediment characteristics related to their potential uptake and release of SRP in two contrasting stream environments in the Loch Leven catchment.
- To determine if stream bed sediments in the two contrasting streams were acting as sources or sinks of water column SRP.
- To establish if suspended bed sediments could buffer increasing SRP concentrations that are often observed during high-flow events.

### 7.2 Site description

Stream bed sediment was collected at different times of the year (January, April, July and October) from the Pow Burn and the Camel Burn in the Loch Leven catchment (Figure 7.1). The Pow Burn catchment drains an area of 11.72 km$^2$, whilst the Camel Burn is a much smaller catchment, draining 2.09 km$^2$. In both rural catchments, agriculture dominates the land use and population density is very low. There are no regulated point source inputs (sewage treatment works or industrial effluents) entering either stream. The Pow Burn is the larger of the two streams, being deeper and faster flowing compared to the Camel Burn. Due to the differences in flow regime the sediment composition between the two streams was also different. The Pow Burn is dominated by sands and pebbles, with fine sediments only
accumulating in areas of slack flow or aquatic vegetation stands. In contrast, the smaller, shallower Camel Burn was dominated by fine silt. Accumulation of large amounts of fine sediment was due to lower flows and large masses of in-channel vegetation.

Figure 7.1: Location of the Pow Burn and Camel Burn in the Loch Leven catchment and location of sediment sample points.

7.3 Methods

7.3.1 Stream flows

An automatic, continuous stream flow gauge was operated by SEPA on the Pow Burn and recorded stream flow every 15 minutes (refer to Chapter 5, Figure 5.3). Continuous stream flow data was not available from the Camel Burn. However, based in intermittent measures of stream flow at the Camel Burn, stream flow was highly correlated with stream flow at the Pow Burn ($r^2 = 0.90$) (refer to Chapter 4, Figure 4.6). Estimates of continuous stream flow at this site were, therefore, calculated using equation 7.1.
\[ \log Q_{Cc} = (0.942 \times \log Q_{Pb}) - 0.9443 \]  
(Equation 7.1)

Where:

\( Q_{Cc} \) = Steam flow at the Camel Burn, m\(^3\) sec\(^{-1}\).

\( Q_{Pb} \) = Stream flow at the Pow Burn, m\(^3\) sec\(^{-1}\).

7.3.2 **Water sample analysis**

Duplicate stream water samples were collected in clean, acid washed 250 ml polyethylene bottles. Water samples were stored in the cold and dark until transportation to the laboratory for analysis. Upon arrival at the laboratory, unfiltered water samples were analysed for total phosphorus (TP) and filtered water samples (Whatman® GF/C 0.45 μm) analysed for soluble reactive phosphorus (SRP) after the methods of Murphy and Riley (1962). Analysis of water samples took place within 4 hours of collection. Temperature, pH and dissolved oxygen were measured in the water column at each site at the time of sediment sampling.

7.3.3 **Sediment sample analysis**

Three sediment samples were collected along a transect in the Pow Burn and Camel Burn. Sediment was collected from the upper 5 cm using a Maitland corer. To minimise small particle loss on collection of sediment a flow hindering device was placed directly upstream of the sampling point to slow water velocity. Stream sediment was not exposed to the air after collection, in order to reduce the potential for physiochemical changes that could occur due to drying. Drying of sediments may induce increased phosphate affinity due to changes in organic, Fe and Al surface complexes and nutrient flushes following cell lysis (Stutter *et al.*, 2007). Sediment samples were stored in the cold and dark until transportation to the laboratory for analysis of the equilibrium phosphate concentration (EPC\(_0\)), labile P content and particle size analysis. In the Pow Burn catchment, a single sediment sample was also collected from a pipe that allowed drainage of nearby land during periods of rainfall. This runoff was discharged directly into the Pow Burn. A 30 L sample of runoff was
collected in 3 x 10 L plastic buckets and transported back to the laboratory for analysis.

Prior to sediment analysis, the top 5cm layer of the sediment cores were sieved through a 2 mm aluminium sieve. Sediments (including the runoff sample) were then left to settle under controlled conditions (in the dark at 4°C ± 2°C) before the clear supernatant was siphoned off. The supernatant was then centrifuged at 2500 rpm and any fine sediment collected was added back to the original sediment sample. All wet sediment samples were subsequently kept in sealed glass containers in the cold and dark at 4°C (± 2°C) during times of storage to minimise biological activity. Labile P analysis took place within 1 day of collection, whilst EPC₀ analysis was performed within 7 days of collection. Separate sediment samples were also frozen for particle size analysis.

7.3.4 Theory of the equilibrium phosphorus concentration (EPC₀)

A measure of the sediments EPC₀ has often been used to determine whether sediments are acting as a source or sink of P, or are in equilibrium with respect to P exchange in the water column (House and Dennison, 1998; House and Dennison, 2000). When water column SRP concentration is greater than sediment EPC₀, sediments adsorb P from the water column and act as a P sink, but when stream water SRP concentration is lower than the sediment EPC₀, sediments release P and act as a P source. EPC₀ is achieved when sediments are neither sorbing nor desorbing P from the water column (Taylor and Kunishi, 1971). Therefore, the EPC₀ is the concentration of the dissolved P in the water column when there is neither net sorption nor desorption of P by the stream sediment.

7.3.5 Method for measuring equilibrium phosphorus concentration (EPC₀)

On arrival at the laboratory, sediment samples were wet sieved using a 2 mm, clean aluminium sieve. In order to retain the smallest sediment fraction in the sample after wet sieving, the remaining suspension of water and sediment was centrifuged at 2500 rpm for 5 minutes and drained of excess water. It was appropriate to sieve sediment samples prior to EPC₀ analysis because the best P
absorption performance of sediment occurs in this size fraction (Hwang et al., 1976; House and Denison, 2000). The sieved sediment samples were analysed to determine \( EPC_0 \) using a modified protocol of Taylor and Kunishi (1971). Bulk phosphorus solutions of 0, 250, 500, 1000 and 2500 \( \mu g \) l\(^{-1}\) were prepared in 2 mM CaCl\(_2\) solution. Solutions were made up from a 100 mg l\(^{-1}\) KH\(_2\)PO\(_4\) solution (where 0.2195g KH\(_2\)PO\(_4\) was dissolved in 500 ml of distilled water). For each sample site, approximately 1.0 g of wet (sieved) sediment was added to a clean, acid-washed 50 ml analysis tube with 45 ml of P concentration. Solutions were shaken for 24 hours in an end over end shaker at 10\(^\circ\)C (± 1\(^\circ\)), in the dark, in a controlled environment chamber unit. Following the 24 hour incubation period, the final SRP concentration was determined after filtering the sample through a Whatman\textsuperscript{\textregistered} 0.45 \( \mu m \) GF/C filter. Analysis was performed in triplicate.

\( EPC_0 \) (measured in \( \mu mol \) l\(^{-1}\)) was calculated by plotting the relationship between the change in the amount of SRP sorbed after a 24 hour incubation, against the concentration of SRP in solution after 24 hours, and fitting an isotherm to the data using a least squares method (Figure 7.2) (House and Dennison, 2000; Jarvie et al., 2005). In this study, the P exchange by sediments was expressed as a Freundlich isotherm (Hwang et al., 1976; Taylor and Kunishi, 1971). The Freundlich model is derived from \( \Delta N_a = K_f C^n_i \), where \( K_f \) is the Freundlich sorption constant and \( n \) is a constant. The intersecting point (\( EPC_0 \)) of the sorption – desorption graph on the x-axis (\( Y = 0 \)) represented the zero point of P exchange at which no net desorption or sorption of P occurred (Ekholm, 1994). For the purpose of comparison to other sediment measures in this study, \( EPC_0 \) values were converted into \( \mu g \) l\(^{-1}\).

### 7.3.6 Labile phosphorus and total phosphorus content of sediments

The amount of P that was loosely sorbed to the sediments was assessed using a modified chemical extraction method of Pacini and Gächter (1999) using ammonium chloride (NH\(_4\)Cl). Ammonium chloride extractable P is, hereafter, termed labile P. One gram of wet sediment was transferred to a clean, acid washed 50 ml centrifuge tube and 25 ml of 1.0 M NH\(_4\)Cl added. Samples were agitated by a rotational shaker for 2 hours in the dark at room temperature. After shaking, the
extract was decanted and the extraction repeated. The final extractant was then centrifuged at 2500 rpm for 5 minutes before being filtered through a 0.45 µm Whatman® glass fibre filter for SRP determination after the method of Murphy and Riley (1962). The average dry weight of sediment in each sample was quantified by differential weighing and drying (at 105°C) (APHA, 1998). The total P content of sediment was determined by suspending a known weight of sediment into a known volume of distilled water. The sample was then digested in a sulphuric acid / potassium persulfate solution and autoclaved at 121°C for 30 minute before determination of SRP (Refer to Chapter 3 for detailed description of the method).

![Graph]

**Figure 7.2:** Example of phosphate sorption determination at 10°C in the dark, used to calculate the EPC_0 of sediments. (Note: EPC_0 is when there is no absorption or desorption of P from the sediment, x = 0).

### 7.3.7 Sediment particle size analysis

Particle size analysis was performed by the Analytical Services Group of the Chemistry Department at the University of Edinburgh. Ten to 15 g of sediment sample was wet sieved through a series of sieves to obtain the fractions > 1 mm. These fractions (plus the material <1mm) were dried and weighed in order to
determine the percentage contribution in each size fraction. The fine material (<1 mm) was then analysed by laser diffraction using a Beckman Coulter LS particle size analyser. Sediment size categories were based on the Wentworth Scale: Clay/Silt (0.35-63 μm), very fine and fine Sand (63-250 μm), medium and coarse sand (250-1000 μm) and very coarse sand (1000-2000 μm).

7.4 Statistical analysis

Data were assessed for normality of distribution using the Anderson-Darling test of homogeneity. To normalise distributions, absolute data values were log transformed, whilst proportion values were arcsine-square root transformed to normalise data distribution where necessary (Zar, 1999; MacDonald, 2008). Where residuals were normally distributed, differences between sampling sites and months were evaluated using two-way analysis of variance (ANOVA). Differences between treatment levels were assessed using Tukey’s multiple comparison tests. Where data transformation did not result in normality of distribution, non-parametric Kruskal-Wallis tests were applied. In all cases, significance was set at p = 0.05. Relationships among variables were investigated using Pearson’s product moment correlation of normally distributed data or non-parametric Spearman’s rank correlations when data transformation did not normalise residual distribution.

7.5 Results

7.5.1 Physico-chemical characteristics at sample sites

Despite the close proximity of the Pow Burn and Camel Burn and the similarities in land use in their catchments, the hydrology and channel morphology was different at each location (refer to Section 7.2). Table 7.1 summarises the physico-chemical conditions at each stream during the time of sediment sampling.
Stream discharge at the time of sediment sampling was recorded at each site at the time of sediment sampling and ranged between 0.06 m\(^3\) sec\(^{-1}\) and 0.416 m\(^3\) sec\(^{-1}\) at the Pow Burn and 0.038 m\(^3\) sec\(^{-1}\) to 0.08 m\(^3\) sec\(^{-1}\) at the Camel Burn. Base flow at the Pow Burn, therefore, was much higher than at the Camel Burn. Physico-chemical properties of the two streams were similar but SRP concentrations during base flows were higher in the Pow Burn compared to the Camel Burn (Table 7.1).

At the time of sediment sampling, water column SRP concentrations ranged from 29.88 µg l\(^{-1}\) to 52.68 µg l\(^{-1}\) in the Pow Burn and 14.55 µg l\(^{-1}\) to 24.55 µg l\(^{-1}\) in the Camel Burn.

### 7.5.2 Hydrological conditions prior to sediment sampling

Figure 7.3 shows the hydrological conditions in each catchment prior to sediment collection. Sediment sampling took place at different times of the year to account for temporal variability of sediment characteristics due to differences in climatic conditions and stream flows. Sediment sampling in January took place immediately after a few months of winter high-flow events. Sampling in April took place approximately two weeks after a number of average high-flow events. Base flow levels were continuing to decrease during this period. It was anticipated that sediment sampling in the summer would allow for a long period of base flow and, therefore, settlement of sediment along the stream beds. However, the summer of
2007 was particularly wet and a number of small high-flow events occurred prior to summer sampling in July. Sampling in October was after a relatively long period of low base flow (approximately 10 weeks), however, a large event in August would have washed substantial quantities of settled sediment out the streams.

Figure 7.3: Stream flow at the Pow Burn and Camel Burn during 2007 and times of sediment sampling. (Note: different flow scales on y-axis).

7.5.3 Particle size distribution at sediment sampling sites

Figure 7.4 shows the average \((n = 3)\) composition of the sediment cores collected from the Pow Burn and Camel Burn at different times of the year. Medium/coarse sands (250 \(\mu\)m to 1000 \(\mu\)m) dominated the sediment composition at the Pow Burn, being present in significantly higher proportions than at the Camel Burn \((F(3,16) = 26.42, p < 0.001)\). Very coarse sands (1000 \(\mu\)m to 2000 \(\mu\)m) did not contribute much to the < 2 mm sediment composition at either site, but were significantly greater in quantity at the Pow Burn \((F(3,16) = 8.43, p = 0.01)\), again reflecting the different flow conditions between streams. The sediment at the Camel Burn primarily consisted of clay/fine silts (0.35 \(\mu\)m to 63 \(\mu\)m) and fine sands (63 \(\mu\)m to...
to 249.5 μm) throughout the year, except in January. In January, the clay/silt fraction was lower and there was a larger amount of medium and coarse sands in the sediment. This was probably due to winter high-flow events flushing fine clays/silts out of the stream. Otherwise, clays and silts were present in significantly higher proportions in the Camel Burn, compared to the Pow Burn (Clay/Silt, $F_{(3,16)} = 24.28$, $p < 0.001$) (Fine Sands, $F_{(3,16)} = 17.21$, $p = 0.001$). This reflected the lower flow range, the smaller catchment size and the high levels of sediment trapping due to large lotic macrophyte stands. There were no significant differences between particle size distributions between seasons at either site ($p > 0.05$). All sediment collected from the runoff sample consisted of particle sizes in the clay/silt size range (0.35-63 μm).

### 7.5.4 Equilibrium phosphorus concentrations and soluble reactive phosphorus concentrations in the water column

Mean monthly EPC$_0$ in the Camel Burn ranged from 25.84 μg l$^{-1}$ to 105.47 μg l$^{-1}$ compared to 12.71 μg l$^{-1}$ to 45.39 μg l$^{-1}$ in the Pow Burn (Figure 7.5). On all sampling occasions, sediment EPC$_0$ were significantly higher in the Camel Burn compared to the Pow Burn ($F_{(1,16)} = 22.41$, $p < 0.001$). Higher EPC$_0$ at the Camel Burn were probably due to greater levels of diffuse particulate-P on the stream bed (Jarvie et al., 2005). However, there were no significant differences between EPC$_0$ measured at different times of the year at either sample site ($F_{(3,16)} = 1.49$, $p = 0.249$). At the Camel Burn, EPC$_0$ concentrations were greater than ambient water column SRP concentrations throughout the year, indicating that sediments were acting as a P source. In contrast, EPC$_0$ concentrations at the Pow Burn were generally lower than water column SRP concentrations, implying that these sediments were acting as a P sink (Figure 7.5). Sediments appeared to be in equilibrium with the ambient water SRP concentration in the Pow Burn in July. Soluble reactive P concentration in runoff was considerably lower than EPC$_0$. Therefore, sediments entering streams in runoff would release SRP into the Pow Burn on discharge.
Figure 7.4: Sediment particle size distribution in sediment samples (<2000 µm) collected from the Pow Burn and Camel Burn during 2007. (Error bars show the standard error of the mean, n =3).
Figure 7.5: Sediment equilibrium P concentration, labile P and total P content and soluble reactive P concentrations in the water column at the Pow Burn and Camel Burn at different times of the year. (Error bars indicate standard error of the mean, n = 3).
Mean sediment labile P (LP) and total P (TP) content in the Pow Burn ranged from 5.05 μg g⁻¹ to 55.31 μg g⁻¹ and 426 μg g⁻¹ to 1473 μg g⁻¹ (dry weight), respectively. Mean monthly LP was greatest in January; however, this result was attributed to one of the sediment replicates having a much greater LP content than the other two. This was thought to be due to (a) the higher proportion of fine silt and/or (b) the uptake of P by fine sediments (refer to Appendix A.4, Figure A.4.1). Regardless, statistically there were no differences between sediment LP and TP concentrations at different times of the year at the Pow Burn (Kruskal-Wallis) (LP, H = 3.82, p = 0.282) (TP, H = 5.46, p = 0.141). Sediment LP did not significantly differ between sampling months, which indicated that P uptake by sediments was potentially not occurring, perhaps due to competition for SRP with stream biota during spring/summer and early autumn months. At the Camel Burn, mean sediment LP and TP concentrations ranged from 1.26 μg g⁻¹ to 8.30 μg g⁻¹ and 757 μg g⁻¹ to 4373 μg g⁻¹ (dry weight), respectively. Sediment LP concentrations in the two streams were not significantly different (Kruskal Wallis) (H = 0.85, p = 0.356). Given that sediments at the Camel Burn were concluded to be a P source, low sediment LP concentrations further confirm this. However, sediment TP concentrations were significantly higher (H = 10.83, p = 0.001) reflecting the larger percentage of silts and fine sands at the Camel Burn and fine sediment settlement. There were significant differences between sediment P content measured at different times of the year. Sediment LP and TP were found to be significantly lower in January (Kruskal-Wallis) (LP, H = 9.36, p = 0.025) (TP, H = 8.74, p = 0.033). This was probably due to flushing of fine sediments out of the stream by winter high-flow events and desorption of sediment LP into the water column.

Sediment TP concentrations in runoff (3348 to 3625 μg g⁻¹) were comparable to those measured in the Camel Burn due to dominance of fine clay/silt particles. Sediment LP concentrations, however, were appreciably higher than those measured in bed sediments (93 to 109 μg g⁻¹). Runoff, therefore, can be considered a major source of readily available (labile) P.
7.5.6 Relationships between equilibrium phosphorus concentrations, sediment phosphorus content and sediment particle size

Sediment EPC\textsubscript{0} was not related to any of the sediment size fractions at the Pow Burn or Camel Burn (Table 7.2a). Similarly, sediment LP in the Pow Burn was not correlated with any sediment particle size. However, sediment LP at the Camel Burn was significantly and positively correlated with the clay/silt sediment fraction and significantly, negatively correlated with the medium/coarse sand fraction (Table 7.2b).

Table 7.2a: Correlations between sediment EPC\textsubscript{0}, sediment phosphorus content and sediment particle size ($r = $Pearson’s product moment correlation, $r_s = $Spearman’s rank correlation, *Significant correlation).

<table>
<thead>
<tr>
<th></th>
<th>Clay/Silt</th>
<th>Fine Sands</th>
<th>Medium to Coarse Sands</th>
<th>Very Coarse Sands</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pow Burn</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EPC\textsubscript{0}</td>
<td>$r = 0.079$</td>
<td>$r = 0.048$</td>
<td>$r = -0.019$</td>
<td>$r = -0.239$</td>
</tr>
<tr>
<td>$p = 0.808$ &amp; $p = 0.881$ &amp; $p = 0.952$ &amp; $p = 0.454$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TP\textsubscript{s}</td>
<td>$r_s = 0.308$</td>
<td>$r_s = -0.077$</td>
<td>$r_s = -0.147$</td>
<td>$r_s = 0.692$</td>
</tr>
<tr>
<td>$p = 0.331$ &amp; $p = 0.812$ &amp; $p = 0.649$ &amp; $p = 0.013^*$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LP\textsubscript{s}</td>
<td>$r_s = -0.161$</td>
<td>$r_s = -0.238$</td>
<td>$r_s = 0.224$</td>
<td>$r_s = -0.350$</td>
</tr>
<tr>
<td>$p = 0.618$ &amp; $p = 0.457$ &amp; $p = 0.484$ &amp; $p = 0.265$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Camel Burn</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EPC\textsubscript{0}</td>
<td>$r = -0.008$</td>
<td>$r = 0.481$</td>
<td>$r = -0.231$</td>
<td>$r_s = -0.084$</td>
</tr>
<tr>
<td>$p = 0.981$ &amp; $p = 0.113$ &amp; $p = 0.470$ &amp; $p = 0.795$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TP\textsubscript{s}</td>
<td>$r_s = 0.608$</td>
<td>$r_s = 0.105$</td>
<td>$r_s = -0.490$</td>
<td>$r_s = -0.477$</td>
</tr>
<tr>
<td>$p = 0.036^*$ &amp; $p = 0.746$ &amp; $p = 0.106$ &amp; $p = 0.117$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LP\textsubscript{s}</td>
<td>$r = 0.752$</td>
<td>$r = 0.353$</td>
<td>$r = -0.679$</td>
<td>$r_s = -0.361$</td>
</tr>
<tr>
<td>$p = 0.005^<em>$ &amp; $p = 0.261$ &amp; $p = 0.015^</em>$ &amp; $p = 0.248$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 7.2b: Correlations between sediment EPC\textsubscript{0}, water column SRP and sediment phosphorus content ($r = $Pearson’s product moment correlation, $r_s = $Spearman’s rank correlation, *Significant correlation).

<table>
<thead>
<tr>
<th></th>
<th>SRP\textsubscript{w}</th>
<th>TP\textsubscript{s}</th>
<th>LP\textsubscript{s}</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pow Burn</strong></td>
<td>EPC\textsubscript{0}</td>
<td>$r_s = 0.194$</td>
<td>$r_s = -0.077$</td>
</tr>
<tr>
<td>$p = 0.545$ &amp; $p = 0.812$ &amp; $p = 0.366$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Camel Burn</strong></td>
<td>EPC\textsubscript{0}</td>
<td>$r_s = -0.158$</td>
<td>$r_s = 0.137$</td>
</tr>
<tr>
<td>$p = 0.084$ &amp; $p = 0.672$ &amp; $p = 0.109$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
7.5.7 Phosphorus sorption potential of sediment in surface runoff

During the high-flow periods, substantial quantities of surface runoff, rich in clay and silt particles, also enter streams in the Loch Leven catchment. Figure 7.6 shows that runoff sediments had high EPC$_0$ concentrations and would act as a P source unless water column SRP concentrations were maintained at greater concentrations than sediment EPC$_0$ (i.e. at peak concentrations during high-flow events). Runoff would also transport large quantities of readily exchangeable, LP into streams, which would probably be released into the water column as dissolved P. The concentration of LP in the runoff sample was considerably greater than concentrations measured from bed sediments (Figure 7.5 and Figure 7.6). However, sediment TP content in runoff was comparable to sediment TP content in the Camel Burn.

![Diagram showing sediment equilibrium P concentration, labile P and total P content and soluble reactive P in runoff entering the Pow Burn in January 2007.](image)

**Figure 7.6:** Sediment equilibrium P concentration, labile P and total P content and soluble reactive P in runoff entering the Pow Burn in January 2007 (Error bars indicate standard error of the mean, n = 3).
7.6 Results summary

In summary, the results of this study have found that:

1. Sediments in the Pow Burn were dominated by medium/coarse sands (250 to 1000 μm), whilst sediments at the Camel Burn and in surface runoff were dominated by clays and silts (0.35 – 63 μm).

2. During base flow SRP concentrations, sediments in the Pow Burn acted as a P sink, whilst sediments in the Camel Burn and in runoff acted as a P source.

3. Sediment EPC₀ were significantly lower in the Pow Burn compared to the Camel Burn, possibly reflecting the higher clay/silt content of sediment at the Camel Burn. However, EPC₀ were not correlated with any sediment size fraction or water column SRP concentration in either stream.

4. Sediment LP was similar at each site, but TP levels were significantly higher in the Camel Burn, again reflecting the higher clay/silt content. Sediment LP and TP content were significantly, positively correlated with the clay/silt sediment fraction at the Camel Burn, whilst sediment TP was significantly, negatively correlated with medium and coarse sands in the Pow Burn. At the Camel Burn, sediment LP and TP were significantly lower in January compared to other sampling months.

5. In the runoff sample, sediment TP was much greater than the Pow Burn sediments but comparable to levels in the Camel Burn. Sediment LP in runoff, however, was considerably greater than levels measured in stream bed sediments.

7.7 Discussion

A number of studies have provided some information regarding the interaction of sediments in fluvial systems with the overlying water column with respect to P (Klotz, 1988; House et al., 1995; House and Warwick, 1998; Haggard et al., 1999; Jarvie et al., 2005; Stutter et al., 2007). These studies have concluded that the way in which stream sediments interact with P in the water column, i.e. uptake and release, play a pivotal ecological role in buffering water column SRP concentrations and the
export of P to downstream environments and receiving water bodies (McDowell and Sharpley, 2003; Smith et al., 2006). This study has shown that there are significant differences between the P sorption characteristics of two different streams in the Loch Leven catchment. Due to these differences, stream bed sediments are both important in providing a natural P buffering capacity in some areas (i.e. being a P sink), whilst being a source of P in others.

7.7.1 Correlations between sediment particle size and equilibrium phosphorus concentrations

In general, EPC$_0$ at the Camel Burn were higher than at the Pow Burn, ranging between 25 µg l$^{-1}$ and 105 µg l$^{-1}$ and 12 µg l$^{-1}$ to 45 µg l$^{-1}$, respectively. Similar EPC$_0$ were reported by Jarvie et al. (2005) from sediments in the Hampshire Avon and Lower Wye catchments, where EPC$_0$ values ranged between 1.86 µg l$^{-1}$ and 177 µg l$^{-1}$. It was hypothesised that differences between particle sizes were responsible for higher EPC$_0$ at the Camel Burn and in surface runoff. Whilst the Pow Burn was dominated by medium/coarse sands, the Camel Burn was heavily dominated by the fine clay/silt fraction. This corresponded with the smaller catchment size, lower flow regime and higher abundance of in-stream channel vegetation in the Camel Burn. Many studies have reported that the fine bed sediment fraction (< 2 mm) is most geochemically reactive in terms of P sorption (De Willigen et al., 1982; Jarvie et al., 2005), whilst the very fine sediment fraction (< 1000 µm) is considered to be the particle size which is often most highly correlated with EPC$_0$ and P release and uptake (Klotz, 1988; Haggard et al., 1999; Haggard et al., 2004). However, it was surprising to find that significant correlations between sediment EPC$_0$ and sediment particle size were not found in either stream. These results suggest that factors other than sediment particle size could be responsible for determining sediment EPC$_0$ in both the Pow Burn and the Camel Burn.
7.7.2 Correlations between sediment particle size and sediment phosphorus content

The Camel Burn had significantly higher concentrations of TP and LP compared to the Pow Burn. At the Camel Burn, both LP and TP were significantly, positively correlated with the silt/clay fraction of sediment at the Camel Burn. Therefore, higher P content in the Camel Burn was almost certainly due to the greater percentage of the clay/silt fraction. Interestingly, there were no correlations between sediment P content and particle size at the Pow Burn. A range of studies have reported finding positive correlations between sediment P content and the percentage of fine sediment due to the increased surface area on which P can be adsorbed (Meyer, 1979; Mallet, 1998; Wang et al., 2006). However, Haggard et al. (1999) and House and Dennison (2002) reported finding no significant correlations between these parameters, despite the expectation to doing so. The results of this study suggested that factors other than sediment particle size were responsible for determining the P content of sediments in the Pow Burn.

7.7.3 Correlations between equilibrium phosphate concentrations and water column soluble reactive phosphorus

There were no significant correlations between sediment EPC$_0$ and SRP concentrations in the water column in this study. McDowell et al. (2001), Haggard et al. (2004), Jarvie et al. (2005), Popova et al. (2006) and Haggard et al. (2007) have all shown significant correlations between sediment EPC$_0$ and water column SRP concentrations. However, these positive correlations were due to effluents from sewage treatment works increasing sediment EPC$_0$ and LP concentrations, as well as water column SRP concentrations. Neither the Pow Burn nor the Camel Burn receives point source P inputs from sewage treatment works or industrial effluents. However, Haggard et al. (1999) and House and Dennison (2002) did not find significant correlations in their studies, therefore this result is not unheard of. The absence of correlations between sediment EPC$_0$ and water column SRP concentrations are most likely explained by the fact that many abiotic and biotic
factors are known to influence strong controls on sediment P sorption (Reddy et al., 1998) and water column SRP concentrations (Haggard et al., 2007). Therefore, it is unlikely that benthic sediments acted alone to regulated and/or maintain sediment EPC₀ and water column SRP concentrations in either stream.

### 7.7.4 Sediments as sources or sinks of phosphorus

As previously stated, the use of sediment EPC₀ values provides us with useful information about how sediments will respond when placed in contact with freshwater of known SRP concentration (Jarvie et al., 2005). In this study, the water column SRP concentrations in the Pow Burn were only approximately equal to the sediment EPC₀ during July. This was due to slightly higher sediment EPC₀ values. However, small high-flow events immediately before sediment sampling resulted in the clay/silt content of sediment being at its lowest. This suggested that other factors prompted equilibrium to occur. Given the time of year, biotic uptake of P was the mostly likely explanation. At all other times, sediment EPC₀ was lower than base flow water column SRP concentrations in the Pow Burn, indicating sediment P uptake. In the Camel Burn, there was no indication that water column SRP and sediment EPC₀ were in equilibrium at any time of the year. Water column SRP concentrations were lower than sediment EPC₀, therefore, sediments at the Camel Burn were a P source. Lottig and Stanley (2007) suggest that fine sediments often become P sources because in the absence of scouring floods they quickly lose their P uptake due to saturation. In contrast, sands require less velocity than silts to be mobilised, therefore, sediments in the 1-2 mm size fraction could optimise P uptake and sediment turnover. This size fraction was more dominant in the Pow Burn and could possibly maintain a stable, long term P buffering mechanism.

Jarvie et al. (2005) suggests that the inequality between water column SRP and sediment EPC₀ happens because water residence times over the sediment are not long enough to allow equilibrium to be reached. Alternatively, or in conjunction to this proposal, sediment EPC₀ values represent an integrated measure of SRP exposure over a long time scale, whilst river water SRP fluctuations are over shorter timescales. High stream discharges may also account for non-equilibrium due to
high suspended sediment concentrations (House et al., 1995). The Meteorological Office published data that indicated that the winter of 2006 (i.e. the winter leading up to the first sediment sampling) was especially wet in East Scotland, with monthly rainfall between October 2006 and January 2007 being up to 68% greater than the 1961-1990 monthly rainfall averages. In addition, monthly rainfall from May to August 2007 was up to 49% above the 1961-1990 monthly averages (refer to Figure A.4.2 in Appendix A.4). As such, high-flow events in the Loch Leven catchment were prevalent during the sampling year, even in summer (Figure 7.3). These high-flow events and associated high suspended sediment concentrations could also be responsible for sediments in the Pow Burn and Camel Burn not reaching equilibrium with SRP concentrations in the ambient water column.

However, on the basis of this study, stream bed sediments should facilitate the reduction and increase of water column SRP concentrations in the Pow Burn and Camel Burn, respectively (under base flow conditions). Given this conclusion, it was interesting to note that base flow water column SRP concentrations were higher in the Pow Burn. This could reflect the dominance of larger sediments in the Pow Burn that have less P uptake capacity, differences in catchment SRP sources or the very high abundances of lotic macrophytes in the Camel Burn which could reduce water column SRP substantially. Mainstone and Parr (2002) argued that growth rates and standing crops of primary producers can influence stream water SRP, even at concentrations <10 μg L⁻¹. The large stands of macrophytes in the Camel Burn could, therefore, indirectly affect sediment P dynamics and water column SRP. However, Haggard et al. (1999) suggest results of this nature imply that sediments are not the primary regulator of water column SRP concentrations.

**7.7.5 Abiotic and biotic factors control sediment phosphorus uptake and release**

Abiotic factors that regulate sediment P sorption characteristics include sediment P binding strength, organic matter content (Smith et al., 2005), ionic strength (Ryden and Syers, 1975; Bowden et al., 1977; Wang et al., 2006), iron and aluminium oxides and cation exchange capacity (Bowden et al., 1977; Walling and Morehead, 1987) and sediment temperature and redox conditions (House and
Dennison, 2002). Originally, these abiotic processes were thought to dominate the control of ambient P, especially in fine sediments (Klotz, 1988; Froelich, 1988). However, recent work has highlighted the importance of biological processes in the potential uptake and release of P by sediments (Smith et al., 2005; Haggard et al., 2007) as well as influencing SRP concentrations in the surrounding water column. Khoshmenesh et al. (1999) reported that biotic processes can account for up to 43% of dissolved P adsorbed from the water column. Haggard et al. (1999) cited that sediment bacteria are also an important mechanism for the mediation of P dynamics in fluvial systems. Elwood et al. (1981), Mainstone and Parr (2002) and Gainswin et al., (2006) also provided conclusive evidence that the presence of microbial communities, biofilms and aquatic macrophytes helped control dissolved P concentrations in sediment and the water column.

Streams are often heterogeneous ecosystems, being composed of a range of particle sizes from fine silts to large boulders. Differences in sediment sizes can affect P concentrations by shifting the balance between abiotic and biotic processes (Lottig and Stanley, 2007). Therefore, it is reasonable to assume that both biotic and abiotic processes determine water column SRP concentration in both the Pow Burn and the Camel Burn. Lottig and Stanley (2007) commented that in streams that were dominated by fine sediments P retention was unlikely to be attributed to biotic processes. This is due to small sediments providing a relatively unstable substrate for the establishment of biota because they are readily mobile. Therefore, fine sediments are expected to limit biotic uptake. Consequently, abiotic processes were likely to explain most of the variability in sediment P dynamics in the Camel Burn, further explaining why significant correlations between sediment P content and particle size were found.

In contrast, biotic uptake has been seen to account for over 50% of P retention in streams dominated by coarse particles such as sand, gravel and pebbles (Lottig and Stanley, 2007). Duffer and Dorris (1966) observed that larger, more stable sediments can be efficiently and quickly colonised by microbial and algal communities, whilst offering less surface area for abiotic P sorption. With this in mind, biotic processes were likely to play an important role in sediment P dynamics in the Pow Burn. This would explain why there were no significant correlations.
found between sediment P content and particle size in this stream. However, further investigations would be required to confirm this. In addition, few studies have investigated how the two processes interact together to determine sediment and water column P concentrations. This still remains uncertain.

7.7.6 The effect of high-flow events on phosphorus uptake and release

Studies by McDiffett et al. (1989) and House and Warwick (1999) concluded that P supply in a river is often governed by the re-suspension of settled stream-bed sediment. This is especially the case in downstream catchments where sediments are more likely to accumulate. Phosphorus - discharge hysteresis analysis revealed that re-suspension of bed sediments provided a rapidly delivered P source to Loch Leven during early autumn high-flow events (refer to Chapter 5). During the rising limb of hydrographs SRP concentrations also increased, reaching concentrations considerably greater than those experienced during base flows. In such circumstances, the patterns of P uptake or release of stream bed sediments may change, i.e. sediments that would usually act as a buffer to water column SRP may become P saturated and no longer provide a natural P buffering capacity. Conversely, if high enough peak SRP concentrations are reached, sediments that usually act as a P source may become a P sink. Further investigation would be needed to positively conclude if re-suspended sediments do act or continue to act as P sinks during high-flow events in these streams.

7.8 Conclusion

Research of the type undertaken during this study is important for understanding how phosphorus cycling between the water column and sediment phases change. This is particularly important in freshwater environments that suffer from eutrophication as a result of point and diffuse P sources. This study has shown that water-sediment dynamics are essential in controlling river-water SRP concentrations under low flow conditions. The results further suggested that abiotic and biotic processes probably acted together to regulate P uptake and release.
Fine sediments in the Camel Burn were found to be a source of P under low flow conditions. Sediment EPC$_0$ and P concentrations at this site were high due to the deposition of large amounts of fine, diffuse source sediment. These areas of fine bed sediment were originally anticipated to act as a P sink due to greater surface area and P binding capacity, but conversely, they were found to release SRP into the water column. The management implication of this is that during low flows, areas of fine bed sediment may increase eutrophication impacts. Such sediments were only likely to act as P sinks when water column SRP concentrations reached >100 $\mu$g l$^{-1}$ or when fresh sediments were newly deposited. In the absence of point source effluents, concentrations of > 100 $\mu$g l$^{-1}$ would unlikely to occur under low flow conditions. In contrast, areas of coarse sediment in the Pow Burn had low EPC$_0$ concentrations and were found to provide a P sink because they were below water column SRP concentrations. However, this abiotic regulation capacity would be limited due to the large particle size bit it was concluded that coarse sediments may help reduce water column SRP concentrations as they could probably support larger biotic communities in spring/summer months compared to fine sediments. The importance of sediment P sorption and desorption remains to be clarified.
8 Phosphorus Bioavailability during High-Flow Events

8.1 Introduction

The loss of bioavailable particulate P (BAPP) from agricultural soils is one of the primary causes of freshwater eutrophication in rural areas (Sharpley et al., 1995; Fang et al., 2002). Although, SRP is often taken to be the measure of the minimum amount of P available for freshwater algae (Boström et al., 1988) it is likely that a fraction of P associated with particulate matter could also be algal available (Ekholm, 1998; Uusitalo et al., 2000). Currently, most water quality studies are based on measures of total P (TP) or SRP, but TP is probably an over-estimate of TBAP, whilst SRP is probably an under-estimate (Ellison & Brett, 2006). It has been suggested that a more accurate measure of total bioavailable P (TBAP) may be the sum of SRP and the amount of bioavailable PP (BAPP). Even though TBAP may be more difficult to determine than TP and SRP, it may be a more accurate estimate of long term P availability to aquatic macrophytes and algae (Boström et al., 1988; Randall et al., 1998) and of water quality conditions in lakes and streams (Ellison & Brett, 2006). In rural catchments, large quantities of PP normally enter water courses during periods of heavy rainfall and high surface runoff, attached to eroded soils and suspended sediments (Sonzogni et al., 1982). A large proportion of the annual PP load entering a lake is often transported during just a few major events (Brett et al., 2005; Ellison & Brett, 2006). However, the exact magnitude and importance of sediment associated P will vary greatly among individual rivers and will be influenced by local catchment characteristics and varying hydrological conditions. In catchments where PP inputs to a water body are greater than dissolved P inputs, knowledge regarding the potential bioavailability of PP transported during high-flow events could help facilitate catchment management aimed at improving poor water quality (Fang et al., 2002; Sharpley et al., 2002; Uusitalo et al., 2003; Nakajima and Okubo, 2003). Therefore, this study has assessed the bioavailability of P associated with sediments (referred to as bioavailable particulate P, BAPP) transported during high-flow events in the Loch Leven catchment. The main objectives of the study were to:
• Determine the temporal variability of BAPP and describe delivery patterns during high-flow events and;
• Estimate the proportion of the annual TP and PP load that could be considered potentially bioavailable once deposited into the loch.

8.2 Methods

8.2.1 Study site and sample collection

Hach Lange® automatic water samplers were located on the bank of the Pow Burn stream in the Loch Leven catchment (Figure 8.1). The samplers collected in-stream water samples (500 ml) every 2 hours over the hydrograph of all high-flow events between 10th October and 5th December 2006. Care was taken to ensure that the monitoring set-up allowed the collection of reliable chemistry data sets, with special attention given to the positioning of the sample nozzles within the water column. Nozzles were elevated above the river bed by securely attaching them to large concrete blocks, thereby minimising potential interference from suspended river bed sediments was minimised. Figure 5.4 in Chapter 5 provides details the monitoring set up.

Figure 8.1: Location of Pow Burn monitoring site within the Loch Leven catchment.
8.2.2 Phosphorus analyses of water samples

Total P (TP), total soluble P (TSP) and soluble reactive P (SRP) analyses were performed within 48 hours of sample collection. Total P was measured in unfiltered water sample using a sulphuric acid / potassium persulfate digestion to convert all forms of P to orthophosphate (PO₄-P) and then analysed as SRP. Soluble reactive P was determined following the molybdate blue method of Murphy and Riley (1962), using a 4 cm flow cell and a Phillips PU8620 Series UV/VIS/NIR single beam spectrophotometer at 882nm. Orthophosphate concentration was determined using a linear regression equation determined by the absorbance at 882 nm of known phosphorus standards. Total soluble P was determined the same way as TP but using a filtered (Whatman GF/C 0.45μm) sample. Particulate P (PP) was estimated by subtracting TSP from TP. Chapter Two gives a detailed description of analysis techniques.

8.2.3 Total suspended sediments

Total suspended sediments in the water samples were measured following standards methods outlined by the American Public Health Association (1996). Known volumes of sample were filtered through pre-washed and dried Whatman® 0.45 μm GFC filter papers and dried to a constant weight in an oven at 103 to 105°C. Filter papers were removed from the oven and allowed to cool to a constant weight in a sealed desiccator (containing silica crystals). The TSS concentration was determined using Equation 8.1.

\[
TSS \ (mg \ L^{-1}) = \frac{(A - B) \cdot 1000}{V} \quad \text{(Equation 8.1)}
\]

Where:

\( A \) = weight of filter paper and dried sediment, mg
\( B \) = weight of filter paper, mg
\( V \) = volume of water filtered, ml
8.2.4 Bioavailable phosphorus analysis of suspended sediments

Total bioavailable P (TBAP) is defined as the sum of immediately available P (SRP) and the P associated with particulate matter that can be transformed into an available form by naturally occurring processes (Boström et al., 1988). These processes can be chemical (e.g. dissolution), physical (e.g. desorption) or biological (e.g. enzymatic degradation). Many methods have been suggested in the literature regarding the best methods for assessing BAPP but an algal bioassay is the usual experimental approach. This involves culturing algal cells under controlled environmental conditions in a medium that contains P supplied by soil or sediment, followed by an assay of P assimilated by the algae. However, assays are often performed in a method-specific chemical environment that might be unfavourable for certain P mobilisation processes (Boström et al., 1988). Also, they mostly involve culturing a single algal species (commonly Scenedesmus spp. or Selenastrum spp. is used), even though the utilisation of specific P compounds is known to vary among species. Although algal assays are considered the most reliable method of giving an accurate measure of BAPP, they are expensive and time consuming. As such, their use is often limited especially when there are a large number of samples to be analysed (Hegemann et al., 1983).

Other options for assessing BAPP are P-sink methods such as iron oxide (FeO) impregnated paper strips (Sharpley et al., 1991; Sharpley, 1993; Dils and Heathwaite, 1998) or anion exchange resins (AER) (Uusitalo, 2003; Uusitalo and Ekholm, 2003). FeO strips placed in a P solution scavenge SRP and any BAPP. In a similar manner, different types of AER selectively prefer one or several different types of ions. Dowex resins, for example, are designed specifically for the separation of P from liquid media and are the most commonly used resins in P bioavailability studies. Essentially, the FeO strip and AER act as near infinite sinks for P (Van der Zee et al., 1987). By reducing the dissolved P concentration to negligible levels, a diffusion gradient is created that promotes desorption of P from soil surfaces (Pettersson et al., 1988; Bramley and Roe, 1993). In this manner, these methods mimic the action of P uptake by plants (Menon et al., 1989). Using FeO
strips, Sharpley (1993) found that BAPP from field runoff was very closely related to the growth of P-starved *Selenastrum capricornutum* over a 29 day incubation period ($r^2 = 0.92$ to 0.96). It was assumed that measurable ‘FeO-P’ provided an accurate estimate of the BAPP in runoff samples. Similarly, Hanna (1989) found a strong relationship between algal P uptake and extractable P from field runoff samples using anion exchange resins ($r^2 = 0.83$). Another alternative to algal bioassays is chemical extractants (Dorich et al., 1985; Psenner et al., 1988; Farmer et al., 1994; Pacini and Gächter, 1999; Nakajima and Okubo, 2003) such as 0.1 M sodium hydroxide (NaOH) (Sagher et al., 1975; Sonzogni et al., 1984; Dorich et al., 1984, 1985; Boström et al., 1988; Sharpley et al., 1991, 1993 and Nakajima and Okubo, 2003). This measure is described as ‘potentially’ bioavailable PP as it is often determined by the ability of algae to assimilate the P attached to the sediment. Sagher et al. (1975) demonstrated that, essentially, all of the P in Wisconsin lake sediment that was extractable with 0.1 M NaOH was assimilated by algae during 28-day algal assay incubation. Dorich et al. (1984) also reported that inorganic P extracted from suspended sediments using 0.1 M NaOH was strongly correlated with 2-day and 14-day algal available P ($r = 0.89$ and $r = 0.95$, respectively). The study concluded that the 0.1 M NaOH extraction was routine, rapid and free from most interference. It also offered a reliable alternative to algal bioassays. Similarly, Sonzogni et al. (1984), Sharpley et al. (1991) and Sharpley (1993) demonstrated that TBAP in runoff corresponded to the SRP concentrations and the fraction of inorganic PP obtained by extraction with 0.1 M NaOH.

Investigating BAPP during high-flow events would involve processing a large number of samples over a very short time interval. Therefore, a technique that was simple, fast, reliable and cheap was required due to the quick turn around of sample collection and the limited volume of samples collected during this research. However, a standard method for assessing BAPP from water samples does not exist, so it was necessary to make a judgement regarding the most appropriate method in this case. Table 8.1 summarises the advantages and disadvantages of using alternative techniques compared to algal bioassays (Boström et al., 1988). In this study, a modified method using a single chemical extraction (0.1 M NaOH) was chosen to assess BAPP. The technique followed the general methodology proposed
by Dorich et al. (1985) but modifications were made. These are detailed and explained in the following sections.

8.2.5 Modified method to determine bioavailable particulate phosphorus

The method of collecting and assessing the BAPP content of small quantities of suspended sediment, as described by Dorich et al. (1985), were modified as shown in Table 8.2. These modifications allowed the potential bioavailability of P from suspended sediments, isolated from water samples collected during high-flow events, to be determined. The modifications were also compatible with laboratory equipment and available resources. Calculation of BAPP and the TBAP concentrations in water sample is described by Equations 8.2 to 8.4. Firstly, the mass of BAPP extracted from one gram of suspended sediment was determined (Equation 8.2). The BAPP concentration (µg l\(^{-1}\)) in the original water sample was then calculated (Equation 8.3). Finally, the TBAP concentration in the original water sample was determined by adding the estimated BAPP concentration to the SRP concentration (Equation 8.4).

\[
\text{BAPP (µg g}^{-1}\text{ dry weight TSS) = } \frac{\text{SRP}_{ex}V}{W_t} \quad \text{(Equation 8.2)}
\]

\[
\text{BAPP (µg l}^{-1}\text{) = } \frac{\text{BAPP(µg g}^{-1}\text{)}}{\text{TSS (g l}^{-1}\text{)}} \quad \text{(Equation 8.3)}
\]

\[
\text{TBAP (µg l}^{-1}\text{) = BAPP (µg l}^{-1}\text{) + SRP}_w \quad \text{(Equation 8.4)}
\]

Where:

\text{SRP}_{ex} = \text{Concentration of SRP in extractant (0.1M NaOH) solution, µg l}^{-1}\text{ }

\text{V = Volume of extractant solution, L}

\text{W_t = Dry weight of extracted sediment, g}

\text{TSS = Total suspended sediments, g l}^{-1}\text{ }

\[ SRP_w = \] Concentration of SRP in water sample from which suspended 
 sediment was isolated, \( \mu g L^{-1} \).

Table 8.1: Advantages and disadvantages of assessing bioavailable phosphorus in 
water and sediment samples using different techniques.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron Oxide Impregnated</td>
<td>- A relatively non-destructive procedure that utilises the capacity of the iron sink to withdraw P from the sediment on the basis of the sorption / desorption equilibrium.</td>
<td>- The acid digestion of the paper strip can desorb the iron-associated P and can result in an over-estimation of BAPP.</td>
</tr>
<tr>
<td>Strips</td>
<td>- Highly correlated with the growth of P starved algae during a fixed assay period.</td>
<td>- Requires pre-concentration of suspended sediment and a fixed sediment to solution ratio.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- The attachment of suspended sediment particles to the strip has been reported to result in over estimates of BAP (Ekholm and Yli-Halla, 1992; Dils and Heathwaite, 1998).</td>
</tr>
<tr>
<td>Anion Exchange Resins</td>
<td>- A relatively non-destructive procedure that utilises the sorption / desorption equilibrium to exhaust desorbable P.</td>
<td>- AER are not capable of extracting all of the PP assimilated by algae during an assay, therefore estimated underestimate BAPP.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Shows un-specificity of sorption for orthophosphate P over other anions and restricted P sorption capacity (Uusitalo, 2003).</td>
</tr>
<tr>
<td>Chemical Extractant (0.1 M NaOH)</td>
<td>- A rapid procedure, with the analysis of P in the extract routine and free from most interference (Dorich et al., 1985).</td>
<td>- Considered a destructive, non-specific analysis technique by some researchers.</td>
</tr>
<tr>
<td></td>
<td>- Highly correlated with the growth of P starved algae during a fixed assay period.</td>
<td>- Samples require pre-concentration before extraction, which is time consuming and complicates analysis.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Requires fixed sediment to solution ratio.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Estimated BAP using this method is often an over-estimate of algal available P.</td>
</tr>
</tbody>
</table>

### 8.3 Pre-study experiments

Any potential effects of method modifications were investigated in pre-study experiments that were performed to address the following issues:

- Digestion of filter papers may release P into the extractant solution.
- Digesting different weights of suspended sediment in a fixed volume of extractant would alter the sediment: solution ratio.
- Sample storage may affect the determination of BAPP.
Table 8.2: The original methodology proposed by Dorich et al. (1985) for the determination of algal available (bioavailable) phosphorus from suspended sediments and modifications for use in this study.

<table>
<thead>
<tr>
<th>Method Step</th>
<th>Dorich et al., (1985)</th>
<th>Modifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Water sample collection</td>
<td>Collected in 2.5 L glass containers at the peak of the storm hydrograph.</td>
<td>Collected in 500 ml polyethylene containers every 2 hours during the storm hydrograph.</td>
</tr>
<tr>
<td>2. Sediment separation</td>
<td>Sediments concentrated by continuous flow centrifugation and re-suspended in known volume of distilled water</td>
<td>Sediments collected by filtration through pre-washed 0.45 µm Whatman® GFC filter papers.</td>
</tr>
<tr>
<td>3. Phosphorus extraction</td>
<td>Re-suspended sediment extracted with 0.1 M NaOH (17 hr) using an extractant to sediment ratio of 500:1</td>
<td>Sediments retained on filter papers extracted with 0.1 M NaOH (17 hr) using a range of extractant to sediment ratios.</td>
</tr>
<tr>
<td>4. NaOH-P determination</td>
<td>SRP determined in the 0.1 M NaOH extract after method of Murphy and Riley (1962).</td>
<td>No modification.</td>
</tr>
<tr>
<td>5. Other analysis</td>
<td>Total P content of original water sample.</td>
<td>TP, TSP, SRP, TPP and TSS concentration of original sample.</td>
</tr>
<tr>
<td>6. Sample storage</td>
<td>Sediment samples stored for 2-14 days after re-suspension in distilled water.</td>
<td>Original water samples stored for 2 days after collection, prior to any separation procedure.</td>
</tr>
</tbody>
</table>

8.3.1 Filter papers as an additional source of phosphorus

Dorich et al. (1985) separated suspended sediment from water samples using continuous flow centrifugation. As this method was not available during the current project, suspended sediment was separated from water samples by filtration through pre-washed Whatman® 0.45 µm glass fibre filter paper. The collected sediment had to be extracted with the filter paper, so it was important to determine if the filter papers would be an additional source of P during the extraction process. This was investigated as follows: 12 Whatman® 0.45 µm glass fibre filters were pre-washed and cleaned by soaking in distilled, deionised water for 2 hours before being placed into separate, clean (acid washed and distilled water rinsed) polypropylene centrifuge tubes with 10 ml of 0.1 M NaOH. The filter papers were then 'extracted' in an end-over-end shaker in the dark for 17 hours at room temperature (18°C ± 3°C). As a
control, 3 centrifuge tubes containing only 10 ml of 0.1 M NaOH under placed the same conditions. After extraction, the samples were centrifuged at 2500 rpm for 5 minutes to separate the filter paper residue. The extractants were then analysed for SRP after the methods of Murphy and Riley (1962). Results showed that filter papers did release an additional source of P during extraction with 0.1 M NaOH; concentrations ranged between 32 \( \mu \text{g l}^{-1} \) and 48 \( \mu \text{g l}^{-1} \). Phosphorus concentrations in the control tubes remained below the detection limit of the spectrophotometer (2.0 \( \mu \text{g l}^{-1} \)). It was clear that this additional source of P would need to be accounted for when determining the BAPP concentration of sediments. As suspended sediments would be extracted in association with the filter paper through which the sample was filtered, it would not be possible to determine the exact contribution of P from each individual filter paper used. The most appropriate option was that the average concentration of P released from three clean filter papers, extracted separately, should be subtracted from the final SRP concentration of each extractant for each batch of sediments (Equation 8.5).

\[
\text{BAP}_{\text{ex}} = \text{SRP}_{\text{ex}} - \text{SRP}_{\text{fp}} \quad \text{(Equation 8.5)}
\]

Where:

\( \text{BAP}_{\text{ex}} \) = Bioavailable P in extractant solution, \( \mu \text{g l}^{-1} \)

\( \text{SRP}_{\text{ex}} \) = Concentration of SRP in extractant solution, \( \mu \text{g l}^{-1} \)

\( \text{SRP}_{\text{fp}} \) = Mean SRP concentration extracted from three clean filter papers, \( \mu \text{g l}^{-1} \)

8.3.2 The effect of varying solution to sediment ratio and sample storage

Dorich et al. (1985) determined a relationship between BAPP and 0.1 M NaOH extractable P, using a consistent solution to sediment ratio of 500:1. In order to maintain a consistent solution to sediment ratio, the dry weight of collected sediment to be chemically extracted would need to be pre-determined and the extractant volume adjusted in each case. As drying and weighing sediment prior to chemical extraction could lead to changes in the determined P bioavailability, it was
not ideal to separate and pre-dry sediments before extraction (Sharpley, pers. comm.). For this reason, and to keep analysis rapid and simple, a fixed volume of extractant was used to digest varying quantities of sediment. This resulted in varying solution to sediment ratios for different samples. Previous studies had suggested that changes in the solution to sediment ratio could result in inaccurate determination of BAPP as this alters the kinetic equilibrium between the sediment and extracting solution (Dorich et al., 1985). It was, therefore, important to determine whether varying the solution to sediment ratio, rather than using the proposed 500:1 ratio, would affect the estimation of BAPP. In addition, although every effort would be made to analyse samples for BAPP within 48 hours of collection, there was a possibility that some samples might need to be stored for longer before analysis. These issues were investigated as follows. One large stream water sample (10 litres), high in suspended sediment was collected from the Pow Burn during a period of high stream flow. TSS, TP, TSP, SRP and PP concentrations of the sample were determined within 2 hours of collection. The sample was then split into three sub-samples and stored in a dark refrigerator (5°C ± 1°C). Sub-sample 1 was stored for 1 day, sub-sample 2 for 4 days and sub-sample 3 for fifteen days. After the appropriate storage time, BAPP was determined at five different solution to sediment ratios (500:1, 670:1, 1300:1, 3000:1 and 5500:1) by filtering different volumes (110, 80, 40, 20 and 10ml, respectively) of mixed water sample through Whatman® 0.45 μm glass fibre filter papers. The collected sediments were then extracted in acid washed, distilled water rinsed, 15 ml polypropylene centrifuge tubes containing 10 ml of 0.1 M NaOH, on a rotational shaker for 17 hours at room temperature in the dark. The BAPP concentration was determined as previously described.

Figure 8.2 shows the estimated BAPP content of sediment extracted using different solution to sediment ratios and storage times.
Results were assessed with a Two-way ANOVA (with replication) \((n = 3)\) (Dytham, 2005). There were significant differences between the solution to sediment ratio \((F = 6.78, p = 0.001)\) and storage time \((F = 5.0, p = 0.013)\). Investigation of 95% confidence intervals indicated that BAPP was significantly lower when samples had been stored for 15 days and when extracted at a solution to sediment ratio of 5500:1. However, Sharpley et al. (1991) found that different solution to sediment ratios between 500:1 and 50 000:1 did not significantly affect the estimation of BAP from field runoff samples.

### 8.3.3 Final modified method to determine bioavailable phosphorus of suspended sediments

As a result of the investigations detailed in the previous sections, the following conclusions were drawn. First, filter papers introduced an additional source of P during chemical extraction of BAP from suspended sediments. To account for this, 3 clean filter papers would be digested during each batch extraction of suspended sediments, and the mean filter paper SRP concentration would be
subtracted from the final extractant SRP concentration. Secondly, extracting suspended sediments at different solution to sediment ratios did not affect the reliable estimation of the BAPP sediments, using ratios between 5500:1 and 500:1 so long as sample storage did not exceed 4 days. Figure 8.3 summarises the final laboratory methods for determining the BAPP content of suspended sediments.
Water Sample

Suspended sediment from known volumes of water sample collected on clean Whatman® 0.45 µm GFC filter papers.

Filter papers with suspended sediment extracted in 10 ml 0.1 M NaOH for 17 hours, in the dark at room temperature.

3 x clean filter papers extracted in 10 ml 0.1 M NaOH for 17 hours, in the dark at room temperature.

Extractants centrifuged at 2500 rpm for 5 minutes

Extractants filtered through clean Whatman® 0.45 µm GFC filter papers and collected.

SRP concentration (µg l⁻¹) of extractants determined after Murphy and Riley (1962)

Absorbance (882 nm) measured on a spectrophotometer in a 4 cm cuvette or flow cell. Phosphorus concentrations in samples estimated using a regression equation determined from the absorbance values of known SRP standards solutions made in 0.1 M NaOH.

BAP content of suspended sediment in original water sample determined.

Total Suspended Sediments (x 3)

Total P
Total Soluble P
Soluble Reactive P
Total Particulate P

Dry weight of suspended sediment collected from known volumes of original water sample (x 3).

Figure 8.3: Final methodology for determining the potential bioavailable phosphorus content of suspended sediments.
8.4 Data Analysis

Some data in this study has already been presented and discussed in Chapter 5. However, to characterise and discuss the bioavailability of PP during high-flow events, some is repeated here (e.g. stream flows, TP, PP and TSS concentrations). Temporal changes in BAPP and TBAP were summarised and compared to stream water TP, PP and TSS concentrations. Relationships between these parameters during high-flow events were assessed by correlation analysis. Residuals were not normally distributed and log₁₀ transformation of data did not normalise distribution. Therefore, non-parametric Spearman's rank correlation analysis was applied.

The % of PP that could be considered to be potentially bioavailable was determined using Equation 8.6.

\[
\text{% of PP bioavailable} = 100 \cdot \left( \frac{\text{BAPP}}{\text{PP}} \right)
\]

(Equation 8.6)

Where:

- \( BAPP \) = measured concentration of bioavailable P of suspended sediments, \( \mu g \text{ L}^{-1} \).
- \( PP \) = measured concentration of particulate P (TP-TSP) in stream water, \( \mu g \text{ L}^{-1} \).

Changing temporal patterns in BAPP and TBAP were assessed by classifying hysteresis plots as no hysteresis, weak/strong clockwise or weak/strong anticlockwise hysteresis.

8.4.1 The 'Pollutogram' analysis approach

Another potential analysis method developed by Rossi et al. (2005) is the 'pollutogram' approach, which has been used to describe the delivery of TSS during storm-water discharges and from combined sewage overflows (Figure 8.4). Because TSS and P often behave in a similar manner during high-flow events (refer back to Chapter 5) there may be potential to use the 'pollutogram' approach to describe P dynamics during high-flow events in the Pow Burn. Stutter et al. (2008) have
recently used this analysis approach to compare the behaviour of P during different high-flow events in a north east Scottish rural catchment. Calculating \( \beta \) values describes the delivery dynamics of P during high-flow events. \( \beta \) values of \(<1\) indicate early transport of P, whilst \( \beta \) values \( >1 \) suggest most P was transported at the end of a high-flow event. If \( \beta \) value = 1 it means that pollutant concentrations stay constant for the duration of the high-flow event (Figure 8.4). For this study, \( \beta \) values were obtained by fitting curves to real data using the same approach as Stutter et al. (2008) (Equation 8.7). The applicability and reliability of this technique as a method of investigating P delivery during high-flow events is investigated further in this study.

\[
F(x) = x^\beta
\]

(Equation 8.7)

Where:
\( F(x) \) = the fraction of the total mass of the determinant during the high-flow event.
\( x \) = the total mass of water during the high-flow event.
\( \beta \) = a coefficient representing the relationship between the determinant mass and water volume over time which can be plotted as the cumulative proportion of water transported.

Figure 8.4: Evolution of TSS concentrations and flows during a rain event, and evolution of the TSS cumulative mass vs. cumulative flow ('pollutogram') (from Rossi et al., 2005).
8.5 Results

8.5.1 Temporal changes in bioavailable phosphorus concentrations during high-flow events

BAPP and TBAP concentrations were monitored every 2 hours during 9 high-flow events in the Pow Burn between October and December 2006. These events are labelled A-F and H-J and were previously described in Chapter 5 (Figure 5.6). Figures 8.6a, 8.6b and 8.6c show temporal changes in TP, PP, BAPP and TBAP concentrations during these 9 events. Box and whisker plots summarise flow and concentration data for each event (Figure 8.6).

BAPP and TBAP concentrations during high-flow events ranged from 4.0 to 1112 µg l\(^{-1}\) and 18.0 to 1185 µg l\(^{-1}\), respectively. Mean BAPP and TBAP concentrations ranged from 45 to 169 µg l\(^{-1}\) and 99 to 244 µg l\(^{-1}\), respectively. Mean event BAPP ranged between 1395 to 1901 µg g\(^{-1}\) dry weight with measured individual contents ranging between 112 to 4634 µg g\(^{-1}\) dry weight (Figure 8.6). Peak BAPP and TBAP concentrations during storm events coincided with peak concentrations of TP, PP and TSS. Spearman's rank correlation analysis confirmed that there were very strong, highly significant linear relationships between TP, PP, BAPP, TBAP and TSS concentrations in all high-flow events (Table 8.3). BAPP and stream flow were highly and significantly correlated during 8 out of 9 monitored events, but not during event J. This was due to there being no relationship between stream flow and TSS concentrations during this particular event. BAPP concentrations were, therefore, highly dependent on the TSS concentrations being transported through the stream.
Figure 8.5a: Temporal changes in stream flow, total P (TP), particulate P (PP), bioavailable PP (BAPP), total bioavailable P (TBAP) and total suspended sediments (TSS) during the course high-flow events in the Pow Burn (October 2006). (Note different y-axis scales).
Figure 8.5b: Temporal changes in stream flow, total P (TP), particulate P (PP), bioavailable PP (BAPP), total bioavailable P (TBAP) and total suspended sediments (TSS) during the course high-flow events in the Pow Burn (October to November 2006). (Note different y-axis scales).
Figure 8.5c: Temporal changes in stream flow, total P (TP), particulate P (PP), bioavailable PP (BAPP), total bioavailable P (TBAP) and total suspended sediments (TSS) during the course high-flow events in the Pow Burn (November to December 2006). (Note different y-axis scales).
Figure 8.6: Mean measures (with maximum and minimum values shown as error bars) of phosphorus, total suspended sediment concentrations and stream flow during nine high-flow events in the Pow Burn.
Table 8.3: Range of Spearman’s rank correlation coefficients and significance values between measured phosphorus fractions, TSS and flow during all nine high-flow events in the Pow Burn.

<table>
<thead>
<tr>
<th>Flow (m$^3$ sec$^{-1}$)</th>
<th>TP (µg l$^{-1}$)</th>
<th>PP (µg l$^{-1}$)</th>
<th>BAPP (µg l$^{-1}$)</th>
<th>TBAP (µg l$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>0.720 - 0.926</td>
<td>P &lt; 0.001</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PP</td>
<td>0.620 - 0.938</td>
<td>0.931 - 0.997</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>0.620 - 0.938</td>
<td>P &lt; 0.001</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BAPP</td>
<td>0.257 - 0.936</td>
<td>0.868 - 0.965</td>
<td>0.891 - 0.995</td>
<td>X</td>
</tr>
<tr>
<td>0.257 - 0.936</td>
<td>P &lt; 0.001</td>
<td>P &lt; 0.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TBAP</td>
<td>0.617 - 0.885</td>
<td>0.826 - 0.985</td>
<td>0.814 - 0.975</td>
<td>0.826 - 0.988</td>
</tr>
<tr>
<td>0.617 - 0.885</td>
<td>P &lt; 0.002</td>
<td>P &lt; 0.001</td>
<td>P &lt; 0.001</td>
<td></td>
</tr>
<tr>
<td>TSS</td>
<td>0.246 - 0.967</td>
<td>0.794 - 0.963</td>
<td>0.840 - 0.971</td>
<td>0.837 - 0.964</td>
</tr>
<tr>
<td>(mg l$^{-1}$)</td>
<td>P = 0.19/</td>
<td>P &lt; 0.001</td>
<td>P &lt; 0.001</td>
<td></td>
</tr>
<tr>
<td></td>
<td>P &lt; 0.001</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

8.5.2 Estimated total bioavailable phosphorus loads

Actual % bioavailability of PP ranged from 14% to 95%. Average % BAPP during high-flow events ranged between 26% and 43%. Figure 8.7 shows the temporal changes in % BAPP during high-flow events. Although there could be great temporal differences in PP bioavailability, in general, bioavailability remained fairly constant over the hydrographs. There were no significant correlations between % BAPP and stream flow or TSS.
Figure 8.7: The percentage of particulate phosphorus that could be considered potentially bioavailable, delivered to Loch Leven during various high-flow events.
Using average values of PP bioavailability, it is possible to estimate the potential amount of sediment associated P that could become bioavailable once delivered to Loch Leven. For example, 351 kg PP was transported by the Pow Burn to Loch Leven between 10th October to 5th December 2006 (Chapter 6). Therefore, 91 kg to 151 kg of the 351 kg PP load could be considered a bioavailable source of P. The SRP load during those 10 weeks was 78 kg. Therefore, the TBAP load can be estimated to be 78 kg SRP plus the BAPP load, which estimated TBAP to be between 169 kg and 229 kg (Figure 8.8). Similarly, the PP load delivered during 10 high-flow events alone (not including base flow contributions) was 291 kg. Therefore, between 76 kg and 125 kg of the PP load could be considered bioavailable, along with 51 kg of SRP. The TBAP load is estimated to have been between 126 kg and 175 kg (Figure 8.8). Lastly, the annual PP load to Loch Leven in 2005 was 4.11 t. Between 1.07 t and 1.77 t of PP was a source of bioavailable P, along with the 2.68 t of SRP. The TBAP load in 2005, therefore, was estimated to have been between 3.75 t and 4.45 t (Figure 8.8).

![Figure 8.8: Estimated minimum and maximum bioavailable phosphorus loads during different survey periods (TBAP = total bioavailable P = SRP + BAPP).](image)
8.5.3 Hysteresis patterns of bioavailable phosphorus

The directions of hysteresis (clockwise and anti-clockwise) indicate the relationship between stream flows and P transport during high-flow events. Hysteresis patterns of TP, PP, SRP and TSS during high-flow events have already been presented and evaluated in Chapter 5. In this section, hysteresis patterns of TBAP and BAPP concentrations (μg l⁻¹) and the BAP content of suspended sediments (BAPP, μg g⁻¹ dry weight) are investigated. Hysteresis patterns during monitored events are shown in Figure 8.9. Table 8.4 summarises the dominant hysteresis directions for BAPP and TBAP during 9 high-flow events in the Pow Burn. Because of the close correlations between TSS, TP, PP, BAPP and TBAP, hysteresis patterns were the same for BAPP and TBAP as reported for TP and PP in Chapter 5 (Section 5.6.7).

Table 8.4: Hysteresis patterns between total suspended sediments and various phosphorus fractions and stream flow during nine high-flow events in the Pow Burn. (C = strong clockwise, c = weak clockwise, a = weak anti-clockwise hysteresis).

<table>
<thead>
<tr>
<th>Event</th>
<th>Max. Flow (m² sec⁻¹)</th>
<th>TSS (mg l⁻¹)</th>
<th>TP (μg l⁻¹)</th>
<th>PP (μg l⁻¹)</th>
<th>SRP (μg l⁻¹)</th>
<th>BAPP (μg l⁻¹)</th>
<th>TBAP (μg l⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.207</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>C</td>
</tr>
<tr>
<td>B</td>
<td>0.301</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>C</td>
</tr>
<tr>
<td>C</td>
<td>0.416</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>C</td>
</tr>
<tr>
<td>D</td>
<td>3.820</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>C</td>
</tr>
<tr>
<td>E</td>
<td>0.462</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>C</td>
</tr>
<tr>
<td>F</td>
<td>0.259</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>C</td>
</tr>
<tr>
<td>H</td>
<td>0.719</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>C</td>
</tr>
<tr>
<td>I</td>
<td>0.775</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>C</td>
</tr>
<tr>
<td>J</td>
<td>0.564</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>C</td>
</tr>
</tbody>
</table>
Figure 8.9: Hysteresis patterns of bioavailable particulate phosphorus (µg l⁻¹ and µg g⁻¹) and total bioavailable phosphorus (µg l⁻¹) during nine high-flow events in the Pow Burn between October and December 2006.
In summary, early autumn high-flow events displayed strong clockwise hysteresis loops, indicating that concentrations were higher on the rising limb of the hydrograph compared to the falling limb. The patterns of hysteresis for BAPP and TBAP changed after the largest high-flow event (event D): clockwise hysteresis weakened (event E) and anti-clockwise patterns became dominant (event F). Similar to TSS, TP and PP, this indicated P ‘wash-out’, where concentrations of BAPP and TBAP start to recede before stream flow. Later high-flow events revealed more complex hysteresis loops due to multiple flow peaks and changing P sources.

BAPP (μg g⁻¹ dry weight) hysteresis patterns were also investigated (Figure 8.9). Generally, the BAPP content of suspended sediments was high at the beginning of each event and levelled out towards the end. Spearman’s rank correlation analysis suggested there were no strong relationships between the BAPP content of suspended sediment and BAPP concentrations in the water in 7 out of the 9 events ($r_s = -0.381$ to 0.265, $p > 0.05$). However, significant correlations occurred during event C ($r_s = 0.538$, $p < 0.05$) and I ($r_s = 0.844$, $p < 0.001$). This was due to peak BAPP concentrations coinciding with peak sediment BAPP content, which did not occur during other events. Normally, BAPP (μg l⁻¹) was highest near peak flows, whilst BAPP (μg g⁻¹) was highest near the start of each event.

8.5.4 Analysis of phosphorus fractions in ‘pollutograms’

Plots of cumulative mass versus cumulative discharge are shown in Figure 8.11. An example of measured and modelled pollutants during high-flow event A is shown in Figure 8.10. Pollutogram plots of measured and modelled pollutants for all remaining high-flow events are present in Appendix A.5.
Figure 8.10: Pollutograms and estimated $\beta$ values for total suspended sediments (TSS), total P (TP), particulate P (PP), soluble reactive P (SRP), bioavailable particulate P (BAPP) and total bioavailable P (TBAP) during high-flow event A (October 2006) in the Pow Burn.
Figure 8.11: Pollutograms for nine consecutive storm events in the Pow Burn catchment.
Modelled values of β for TSS and P fractions during each high-flow event are summarised in Table 8.5.

Table 8.5: Rapidity of total suspended sediment and phosphorus delivery based on modelled pollutogram β values during 9 consecutive high-flow events in the Pow Burn.

<table>
<thead>
<tr>
<th>Fastest delivery (low β values)</th>
<th>Slowest Delivery (high β values)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A E D H B J I C F</td>
<td></td>
</tr>
<tr>
<td>TSS</td>
<td></td>
</tr>
<tr>
<td>TP</td>
<td></td>
</tr>
<tr>
<td>PP</td>
<td></td>
</tr>
<tr>
<td>SRP</td>
<td></td>
</tr>
<tr>
<td>BAPP</td>
<td></td>
</tr>
<tr>
<td>TBAP</td>
<td></td>
</tr>
<tr>
<td>Corresponding β Value</td>
<td></td>
</tr>
<tr>
<td>TSS</td>
<td>0.38 0.53 0.59 0.62 0.64 0.64 0.66 0.73 0.88</td>
</tr>
<tr>
<td>TP</td>
<td>0.48 0.62 0.66 0.67 0.69 0.73 0.73 0.78 0.86</td>
</tr>
<tr>
<td>PP</td>
<td>0.40 0.52 0.59 0.59 0.63 0.64 0.68 0.76 0.82</td>
</tr>
<tr>
<td>SRP</td>
<td>0.74 0.76 0.77 0.84 0.90 0.92 0.92 0.92 0.97</td>
</tr>
<tr>
<td>BAPP</td>
<td>0.39 0.55 0.55 0.57 0.57 0.58 0.63 0.72 0.86</td>
</tr>
<tr>
<td>TBAP</td>
<td>0.38 0.53 0.59 0.62 0.64 0.64 0.66 0.73 0.88</td>
</tr>
</tbody>
</table>

To recap, the β value indicates whether most of the P mass arrived predominantly at the beginning (β values of <1) or at the end of the high-flow event (β values >1), whilst a β value of 1 means pollutant concentrations stay constant during the high-flow event. For SRP, modelled β values ranged between 0.74 – 0.97. Early events (A-C) had the lowest β values (0.74 – 0.77) suggesting that SRP delivery was fastest during early season events. Soluble reactive P β values were greater during later events suggesting that SRP delivery became constant as high-flow events continued to occur in the catchment (i.e. increasing β values towards β = 1). Increasing β values showed that changes in the pathways of SRP delivery occurred between early and later events. Modelled β values for TSS, TP, PP, BAPP and TBAP ranged between 0.38 – 0.88, 0.48 – 0.85, 0.40 – 0.82, 0.39 – 0.86 and 0.38 – 0.88, respectively. However, the pollutograms presented in Figure 8.10 show discrepancies between the modelled and observed data for particulate related P fractions and TSS. Soluble reactive P delivery dynamics during high-flow events,
however, was reliably modelled. These results suggest that $P$ values may not be a reliable way to describe and compare differences in $P$ delivery dynamics between high-flow events. Therefore, conclusions have not been drawn on the basis of these results. This is considered further in the discussion section.

8.6 Results summary

In summary, this study has shown that:

- BAPP and TBAP concentrations during high-flow events were higher than during base flow conditions. Concentrations were sufficiently high enough to contribute high concentrations of bioavailable $P$ to Loch Leven.

- BAPP and TBAP concentrations were significantly correlated with stream flow during all high-flow events ($r_s = 0.617$ to $0.885$, $p < 0.001$). TBAP and BAPP were also strongly and significantly correlated with TSS, TP and PP concentrations ($r_s = 0.794$ to $0.997$, $p < 0.001$).

- PP bioavailability ranged, on average, between 26% and 43% during high-flow events. There were no correlations between stream flow and % BAPP. % BAPP remained reasonably constant over the high-flow event hydrographs.

- Using SRP loads as a measure of $P$ bioavailability underestimates the overall bioavailable $P$ load. True TBAP loads were estimated to be between 91 – 169 kg greater than the minimum bioavailable $P$ load (or SRP load) for the period between period of 10th October to 5th December 2006. Similarly, the TBAP load during 10 high-flow events was between 76 – 126 kg compared to an SRP load of 51 kg. And finally, the estimated annual TBAP load in 2005 was between 3.75 – 4.45 tonnes, compared to 2.68 t of SRP.

- BAPP and TBAP exhibited the same hysteresis patterns as TSS, TP and PP in high-flow events due to strong and significant correlations between these parameters. Hysteresis was strongly clockwise during early autumn events, tending towards weak clockwise and complex patterns during later events. Event F was the only event to display weak anti-clockwise hysteresis, although the pattern of delivery was complex due to multiple discharge..
peaks. Hysteresis patterns of BAPP content of suspended sediments (µg g⁻¹) showed that P content was generally higher during the early stages of the rising limb of the hydrograph, declining quickly after the start of each event.

- The pollutogram method successfully described SRP delivery dynamics during high-flow events in the Pow Burn. Estimated β values indicated that SRP delivery was fastest during early events and tended towards constant delivery during later events (β = 0.74 to 0.98). Particulate related P fractions (TP, PP, BAPP and TBAP) and TSS, however, were not reliably modelled by this analysis approach.

8.7 Discussion

It is been suggested that using SRP concentrations is likely to result in an under-estimation of P bioavailability in waters receiving surface runoff (Ekholm, 1998; Uusitalo et al., 2000; Ellison and Brett, 2006) and that measures of bioavailable P provide the most accurate assessments of conditions in streams and lakes (Butkus et al., 1988; Ekholm and Krogerus, 2003). This is because a varying proportion of inorganic PP may desorb and be added to the immediately bioavailable P pool (Uusitalo et al., 2000). High-flow events are very important for transporting PP in large quantities due to the mobilisation of sediments in surface runoff (Brett et al., 2005). During this research, it has been shown that the majority of P transported during high-flow events in the Pow Burn catchment is in the particulate form, mostly probably bound to eroded agricultural soils. The transport of PP from agricultural catchments is particularly important due to the application of P based fertilisers, which can significantly increase soil P content (Heckrath et al., 1995).

This work has also shown that a major portion of the annual PP load is delivered to Loch Leven in just a few high-flow events. In almost all of the water samples analysed during high-flow events in the Pow Burn, peak flow PP concentrations were 80% and 95% of the TP concentrations. During all events the PP concentration was significantly and positively correlated with TSS (see Section 5.6.2). Therefore, the relative importance of SRP as a source of bioavailable P reduced as the TSS concentration in stream flow increased due to increasing PP
concentrations. Therefore, not taking into account the bioavailable portion of PP during periods of high turbidity (i.e. high-flow events) almost certainly leads to an under-estimation of P bioavailability (Uusitalo et al., 2000).

8.7.1 Bioavailability of particulate phosphorus during high-flow events

During high-flow events, mean concentrations of BAPP and TBAP ranged between 45 – 169 µg l⁻¹ and 99 – 244 µg l⁻¹, respectively. Concentrations were consistently greater than critical TP values above which eutrophication can be accelerated (10 µg l⁻¹ and 20 µg l⁻¹) (Vollenweider and Kerekes, 1980). These concentrations were higher than the annual mean target value of 40 µg l⁻¹ TP set for Loch Leven by the Loch Leven Catchment Management group to minimise eutrophication (LLCMP, 1993). Furthermore, the Water Framework Directive has more stringent TP targets. A shallow, high alkalinity loch like Loch Leven must achieve targets of 32 µg TP l⁻¹ in order to achieve a good to moderate status (Carvalho et al., 2006). Consequently, it is clear that high-flow events are critical in delivering a source of bioavailable PP at concentrations that could contribute to poor water quality in Loch Leven.

BAPP (as a % of PP concentrations) in the Pow Burn ranged between 13% and 96% during the high-flow events, with mean event % BAPP being between 26% and 43% of the total PP concentrations. Several other studies have also reported a large variation in measured % BAPP. Rydin and Rast (1989) found that around one third of P associated with suspended sediment was potentially biologically available. Similarly, Dorich et al. (1984), Sharpley et al. (1992) and Ekholm and Krogerus (2003) reported % BAPP ranging between 5% and 69% in different agriculture catchments. Ekholm and Krogerus (2003) reported % BAPP was mostly <20% in forested catchments, whilst Auer et al. (1998) reported values between 5% and 48% in multiple land-use catchments. Consequently, differences in % BAPP are attributed land-use and soil particle size (Pacini and Gachter, 1999). Reynolds and Davies (2001) reported that fine silts and clays are normally higher in BAPP content than coarser soil particles. Therefore, the variability of % BAPP measured during this study was not considered unusual and was characteristic of soils and sediments.
originating from agricultural land. It could be hypothesised that finer sediments should dominate the early part of hydrographs as they are more mobile and transported more readily. However, particle size analysis on suspended sediments collected during high-flow events was not performed and a relationship between % BAPP and sediment particle size could not be determined. This requires further investigation.

8.7.2 Hysteresis and delivery patterns of bioavailable phosphorus during high-flow events

Hysteresis patterns of TSS, TP, PP and SRP during high-flow events have already been discussed in Section 5.8.4. Hysteresis patterns for BAPP and TBAP will be discussed here, although many of the conclusions drawn in Chapter 5 are applicable to BAPP and TBAP. First, BAPP and TBAP concentrations were higher on the rising limb of the hydrograph, with concentrations mostly decreasing before peak stream flow. This pattern of sediment delivery corresponded to strong clockwise hysteresis during the first few high-flow events (A-D). The strength of hysteresis weakened with increasing numbers of high-flow events. This reflected changing sediment sources, timing of delivery and transport distances. It was concluded in Chapter 5 that within-channel and bank sediments were most likely to be the dominant sediment source during early events. This explained the rapid increase in TSS and PP concentrations before peak stream flows. Slower delivery of sediment from more distant sources within the catchment (e.g. surface runoff and soil erosion) would account for weakening clockwise hysteresis during later high-flow events and anticlockwise hysteresis when events occurred in quick succession. Because of the strong correlation between TSS and PP, it was not surprising that BAPP and TBAP showed the same hysteresis patterns as TSS, TP and PP described in Chapter 5.

Hysteresis patterns were also investigated for the BAP content of suspended sediments (BAPP, µg l⁻¹) during high-flow events. During most high-flow events, BAPP content was highest at the beginning of the hydrograph, generally decreasing before peak discharge. Again, this is probably because sediments transported at the start of high-flow events are finer and more mobile and have a higher affinity for
binding P. Stutter et al. (2008) suggested that bed sediments are often high in BAPP because of the fine, silt nature and greater surface area. However, understanding the causes of changing BAPP content is very complex due to varying sediment sources (McDowell and Wilcock, 2004), selective processes of erosion and transport, differences in sediment surface binding capacity (Lookman et al., 1995), seasonal biological cycling (Steegan et al., 2001) and the action of physical and chemical processes as the sediment travels downstream.

8.7.3 Using the ‘pollutogram’ approach to assess phosphorus delivery patterns during high-flow events

Stutter et al. (2008) applied the ‘pollutogram’ approach (after Rossi et al., 2005) to assess the characteristics of P delivery during high-flow events in a Scottish agricultural catchment. Rossi et al. (2005) designed this analysis technique to describe the delivery of TSS from urban catchments and combined sewer overflows during rain events. Because more than 80% of polluting compounds (including nutrients) are associated with TSS during wet weather events (Chebbon, 1992) it was anticipated that this method may be suitable to compare P delivery during high-flow in the Pow Burn. However, when modelled and measured P loads were compared (see Figure 8.10) delivery patterns of particulate related P were not reliably predicted during high-flow events in the Pow Burn. However, SRP loading patterns were. Therefore, this approach may not be appropriate for assessing P delivery during high-flow events in rural catchments, most likely because sediment sources and the factors that determine TSS and P delivery from urban catchments differ to rural catchments. Perhaps the most notable difference is that urban catchments have a much greater proportion of impervious areas. Therefore, runoff waters and associated pollutants are conveyed more efficiently and much more rapidly into watercourses compared to rural catchments. Furthermore, the delivery of TSS at the beginning of rain events in urban areas stems from storm-water, wastewater and sediments in combined sewer systems. Rossi et al. (2005) also included the influence of treatment devices on TSS delivery dynamics (e.g. combined sewage overflows and storm-water storage tanks). These types of treatment devices are used to treat or retain runoff before it enters the receding environment and these are not usually present in rural catchments. Finally,
Rossi et al. (2005) validated their model against first flush studies. Research presented in Chapter 5 has clearly demonstrated that TSS and P delivery during high-flow events is different during later events compared to the first flush events. For these reasons, using the pollutogram approach to compare P delivery during high-flow events in rural catchments may not be appropriate. Nevertheless, estimated β values did support conclusions drawn from a visual assessment of P hysteresis patterns.

8.7.4 The importance of determining particulate phosphorus bioavailability

This study showed that winter high-flow events delivered a large proportion of the winter PP and sediment loads to Loch Leven. Although winter is not an ecologically sensitive time, environmental conditions in summer months could promote the transformation of PP delivered by winter high-flow events (Heathwaite, 1997). Potentially bioavailable P is unlikely to contribute to the bioavailable P pool when SRP concentrations in the loch are high. However, during the algal production period, SRP concentrations may drop below sediment equilibrium phosphate concentrations (EPC₀) allowing potentially bioavailable PP to be desorbed. Therefore, high-flow event PP could help to maintain high internal SRP loads and impede the speed of recovery Loch Leven. A number of studies have reported little reduction in lake productivity with reduced P inputs and have attributed this to an increased bioavailability of P entering lakes, as well as internal recycling of P (Logan, 1982; Young and DePinto, 1982; Gray and Kirkland, 1986). James and Barko (1991, 1993) showed that PP loads retained in a lake contributed considerably to the P budget via diffusive fluctuation as a function of redox potential and pH. This process sustained high algal growth in the summer when external PP loading was small. They also reported that PP derived from agricultural soils contributed to high concentrations of biologically labile P during internal loading processes. Spears (2006) recently showed that internal P loads from the loch's bed sediments have been critical in maintaining poor water quality in Loch Leven, despite significant reductions in external P loads. This has important implications for management. If sediments were a negligible source of BAPP, then erosion control measures in the
catchment would do little to reduce the eutrophication problems in the loch. However, because it has been shown that sediments could contribute to the bioavailable P pool, measures to reduce the PP transport from the catchment should be a primary management strategy for improving water quality in Loch Leven.

8.8 Conclusion

This research has shown that concentrations of BAPP and TBAP entered Loch Leven during high-flow events at concentrations that would promote algal growth and poor water quality. On average, 26–43% of PP delivered to Loch Leven during winter high-flow events was potentially bioavailable. Hence, SRP is not an accurate estimation of total bioavailable P because the major proportion of TP entering Loch Leven is delivered as PP. Although not immediately bioavailable, PP could contribute to poor water quality during ecologically sensitive times, when conditions in the loch promote P desorption. This information assists the design of eutrophication control measures, which should be targeted specifically to the characteristics of catchment runoff and the properties of receiving waters. In the Loch Leven catchment, management actions should aim to reduce the P content of catchment sediment sources, as well as reducing sediment erosion and PP delivery during winter months. Such measures may be an effective way of decreasing losses of bioavailable P from catchment soils.
9 Final Summary

It has long been recognised that phosphorus (P) in freshwater bodies has resulted in water quality problems and eutrophication in many parts of the world. Increasing inputs of P to freshwaters has resulted in a significant rise in the number of water bodies defined as having poor water quality under the EU Water Framework Directive. The main sources of P to aquatic environments are defined as either ‘point’ or ‘diffuse’, both of which contribute P to water bodies in the soluble and particulate forms to varying degrees (Haygarth and Jarvis, 1999). Dissolved forms of P normally dominate in aquatic environments where there are substantial inputs of P from point sources (Muscutt and Withers, 1996; Neal et al., 2000). However, in rural catchments that are dominated by agriculture, diffuse sources of P are often the greatest contributors of P being transported through streams and rivers (McDowell and Sharples, 2002). The introduction of the EU Water Framework Directive into UK legislation has been particularly important in initiating research that investigates characteristics of diffuse pollution. The research presented in this thesis has investigated the contributions of diffuse P to Loch Leven, highlighting the importance of high-flow events on the delivery of diffuse source P to the loch. A summary of the findings and conclusions of the research is presented below.

9.1 Annual phosphorus loads to Loch Leven in 2005

In an attempt to improve water quality in Loch Leven, external P loading to from the catchment was reduced from approximately 20 t TP y⁻¹ in 1985 to 8 t TP y⁻¹ in 1995. The repeat of the loadings survey in 2005 (performed as part of this research) showed that the amount of P entering the loch was estimated to be 7.69, 3.57, 2.68 and 4.11 tonnes of TP, TSP, SRP and PP, respectively. Although the annual TP load to Loch Leven has not notably decreased over the past ten years (-0.3 t), the contribution of P from point and diffuse sources has changed. In 1995, SRP and PP loads contributed 63% and 37% of the annual TP load, whilst in 2005 SRP and PP loads contributed 37% and 56% (the remaining 7% being soluble un-reactive P). This was attributed to the efficient management of point P sources which continue to reduce SRP loadings. Therefore, PP is now the dominant P source.
to Loch Leven. Because high PP loads are often associated with P-laden sediments in rural catchments, the need to focus future catchment management on controlling diffuse P sources is emphasised. However, such sources are difficult to address as they tend to be highly temporally and spatially variable and occur throughout the whole catchment area. Consequently there is an urgent need to gather detailed information relating to specific diffuse P sources. This information will enable efficient restoration and management measures to be put in place to address the loss of diffuse P from across the catchment. Results from the 2005 annual P loading survey indicated that the greatest PP loads were delivered to Loch Leven during winter months (October, November and December) when rainfall, river flows and P concentrations in the catchment were elevated. Therefore, one of the most important research requirements identified was the need to improve the understanding of the temporal and spatial nature of diffuse PP transport within individual catchments.

9.2 The influence of high-flow events on phosphorus transport

In many parts of the world, including the UK, the intensity, frequency and duration of high-flow events has been increasing as a result of climate change (Ekström et al., 2005; Fowler et al., 2005; Hennessy et al., 1997; Hulme et al., 1998; McGuffie et al., 1999; Jones and Reid, 2000; Karl et al., 1995; Osborn et al., 2000; Osborn, 2002;). This is expected to be having a direct impact on the transport of P, by increasing the mobilisation of diffuse P sources to water bodies. Qualitative and quantitative information concerning P transport during high-flow events will, therefore, help to inform measures to reduce P loads and subsequently improve the water quality of P receiving environments.

A study of ten consecutive high flow events in the Pow Burn in the Loch Leven catchment between October and December 2006 showed that P transport during high-flows was dominated by the PP fraction, which was associated with high suspended sediment concentrations. This was due to large amounts of surface runoff and subsequent high stream discharges. However, larger events did not result in the highest measured P concentrations, probably because the magnitude of P response is determined by other factors as well as stream flow. For example, rainfall intensity
and duration and the antecedent conditions prior to high-flow events appeared to be important factors determining P responses during high-flow events.

Hysteresis analysis indicated that P from a range of different P sources were transported during periods of heavy rainfall and high river flow. In early season high-flow events, within-channel sediments and riparian soils were easily and rapidly mobilised and were a significant P source. However, during later high-flow events, these sources were depleted and less mobile P sources transported from further within the catchment became more important. Hysteresis analysis also showed the importance of antecedent conditions to SRP sources as the magnitude of SRP response was often much smaller when events quickly succeeded one another. It appeared that the fast succession of high-flow events resulted in the depletion of both available SRP and PP sources.

As well as highlighting the importance of high-flow events for P transport in the Pow Burn catchment, this research suggested that un-regulated point source P inputs occurred in the Pow Burn catchment. Localised nutrient impacts in streams are often attributed to these chronic point P sources (Jarvie et al., 2003). Neal et al. (2005) commented that reduction of un-consented nutrient transfers could help restore good water quality on an individual tributary basis. Therefore, in addition to high-flow event P transfers, a much better understanding of the contribution of these additional P sources is required for the successful targeting and control of nutrient inputs at the local catchment scale (Edwards and Withers, 2008). It is suggested that specific P sources are investigated at a smaller, more local scale in order to identify catchment 'hot spots' and maximise the success of diffuse P reduction management measures.

9.3 Uncertainties associated with calculating nutrient loads

A pre-requisite for water quality research, nutrient export modelling and efficient catchment management is that sampling programmes provide an accurate representation of 'true' P loads (Dolan et al., 1981; Walling and Webb, 1982; Rekolainen et al., 1991; Kronvang and Bruhn, 1996; King et al., 2005; Johnes, 2007). Statistical sampling theory suggests that smaller sampling intervals produce
more accurate estimates of P loads (Haan, 2002; Harmel and King, 2005). This is because short-lived high-flow events are captured that can contribute the majority of annual P loads (Walling and Webb, 1981; Walling and Webb, 1996; Phillips et al., 1999; Jordan et al., 2007). Therefore, in catchments where diffuse P sources dominate, the exact influence of these events need be included when calculating a 'truly' accurate P load. In spite of this, there has been little progress in increasing in regulatory programmes, even though it will be vital in order to meet the requirements of the Water Framework Directive.

The accuracy and variability associated with P load calculation methods and sampling strategies were investigated by deconstructing a high-frequency data set of 2-hourly measures of stream flow and P concentrations collected in the Pow Burn between October and December 2006. A number of artificial data sets were created mimicking weekly and daily sampling strategies. Loads estimated using these datasets showed that common interpolation methods were unlikely to give reliable P load estimates even when sampling frequency was daily. Thus it was concluded that, in catchments where continuous stream flow data were available, extrapolation procedures still give the most accurate load estimates on the basis of infrequent sampling. The accuracy of extrapolation methods could be improved by including data from the largest high-flow events. However, there remains little guidance or information available to assist in determining suitable thresholds for high-flow monitoring in small watersheds (Harmel et al., 2003). Therefore, it is recommended that, prior to the implementation of a sampling programme, some knowledge should be gained regarding the high-flow event characteristics (i.e. duration of rainfall, flow ranges, expectant length of runoff) in order to design a monitoring programme to estimate a representative P load, within economic constraints.

9.4 Sediments as sources or sinks of phosphorus

Historically, high soluble P concentrations in streams and rivers have been caused by point source inputs. However, now that point sources are under stricter regulation, continually increasing P concentrations are related to diffuse source inputs (Carpenter et al., 1998). Diffuse sources generally represent P inputs from
sediment and land use activities, e.g. fertiliser application (Haggard et al., 1999). In the Loch Leven catchment, a substantial amount of diffuse P is delivered into water courses associated with sediment in surface runoff. During such events, large quantities of sediment can be deposited into water courses and retained in the fluvial system for many months (Poinke and Kunishi, 1992; Walling et al., 1997; Smith et al., 2006). In rivers and streams, the interaction of P with suspended and bed sediments can determine the concentration of SRP in the water column at low flow (House et al., 1995). Jarvie et al. (2005) proposed that these diffuse sediment sources could provide the ‘missing link’ between eutrophication at times of ecological sensitivity and sediment-associated diffuse P delivered to stream channels during high-flow events. It will be in the ecologically sensitive months that SRP from such sources could be released. Therefore, it would be advantageous to know if different sediment sources act as P sources or sinks, especially during times of greatest ecological risk.

Stream bed sediments from two contrasting stream environments were collected from the Pow Burn and the Camel Burn at different times of the year (January, April, July and October). Sediment characteristics relating to their potential uptake and release of SRP were measured; equilibrium phosphate concentration (EPC₀), labile P (LP), total P (TP) and sediment particle size. Medium/coarse sands (250 μm to 1000 μm) dominated the sediment composition at the Pow Burn, being present in significantly higher proportions than at the Camel Burn. In contrast, the sediment at the Camel Burn primarily consisted of clay/fine silts (0.35 to 63 μm) and fine sands (63 μm to 249.5 μm) and were present in significantly higher proportions compared to the Pow Burn. Fine bed sediment was hypothesised to act as a P sink due to greater surface area and P binding capacity. In contrast, it was inferred that the bed sediments in the Camel Burn released SRP into the water column during low flow conditions because sediment EPC₀ were higher (25.84 μg l⁻¹ to 105.47 μg l⁻¹) than ambient water SRP concentrations (at the time of sampling). In contrast, bed sediments of the Pow Burn were found to act as a P sink, as sediment EPC₀ were lower (12.71 μg l⁻¹ to 45.39 μg l⁻¹) than ambient water SRP concentrations. Sediment EPC₀ was found not to be related to any of the sediment size fractions at in either stream. Sediment LP was similar at each site, but TP levels
were significantly higher in the Camel Burn, again reflecting the higher clay/silt content. Low sediment LP concentrations (1.26 μg g$^{-1}$ to 8.30 μg g$^{-1}$) at the Camel Burn supported the conclusion that sediments were releasing SRP, rather than adsorbing. It was hypothesised that fine sediments were only likely to act as P sinks when fresh sediments were deposited or when water column SRP concentrations exceeded $\sim$100 μg l$^{-1}$. In contrast, areas of coarse sediment were found to provide a P sink, although uptake capacity would be highly limited due to the large particle size.

The management implication of these findings is that fine, settled bed sediments are releasing SRP into the water column during low flows, potentially increasing the risk of within-stream eutrophication in ecologically sensitive months. The subsequent re-suspension of settled bed sediment high in SRP during winter could result in the transport of large quantities of sediment-associated P to Loch Leven. In the loch, where water residence times are long, the extent to which these bed sediments supply P to the water column in summer will govern the relative importance of agriculture as an eutrophication source (Jarvie et al., 2006). Spears et al. (2006) provided evidence that internal P loading from the loch’s sediments continued to drive the occurrence of algal blooms. Therefore, to reduce eutrophication risks in the loch, catchment management must significantly reduce the delivery and accumulation of sediment associated P.

9.5 Phosphorus bioavailability during high-flow events

The loss of bioavailable P (BAP) from agricultural soils is one of the primary causes of freshwater eutrophication in rural areas (Sharpley et al., 1995; Fang et al., 2002). In the Loch Leven catchment, research has shown that the majority of P enters the loch during winter months, primarily attached to eroded sediments during high-flow events. Fang et al. (2002), Nakajima and Okubo (2003), Sharpley et al. (2002) and Uusitalo et al. (2003) suggested that in catchments where PP inputs to a water body are greater than dissolved P inputs, site-specific knowledge regarding the potential bioavailability of PP transported during high-flow events could help in the formulation of measures to reduce poor water quality. Therefore, in this study, the
bioavailability was assessed of P associated with suspended sediments collected during high-flow events in the Pow Burn, a tributary to Loch Leven. The results showed that bioavailable PP (BAPP) and total BAP (BAPP + SRP) entered Loch Leven during high-flow events at concentrations that would promote algal growth and poor water quality. On average, 26 – 43% of PP and 34 – 62% of TP delivered to Loch Leven during winter high-flow events was a potentially bioavailable source of P. Although not immediately bioavailable, PP could contribute to poor water quality in Loch Leven during ecologically sensitive times, when conditions in the loch promote P desorption. Hence, catchment management actions should work towards reducing the P content of sediment sources as well as reducing the loss of sediments from the catchment during winter months.

9.6 Implications of presented research

The results of the research presented in this thesis have provided evidence that the transfer of P within a catchment is highly dynamic both spatially and temporally. To be successful, catchment management plans need to take this variability into account when assessing the ecological risks of excessive nutrient transfer from land to water. To do this, P monitoring programmes need to be at a high enough resolution for this natural spatio-temporal variability in nutrient transfer as a result of high-flow events, to be taken into account. Regulatory authorities must, therefore, move towards using cost-effective, high-frequency sampling programmes that adequately represent high-flow events if they are to improve the accuracy of P load estimates calculated using extrapolation methods.

Future work in the Loch Leven catchment should now aim to identify very specific contributing P source areas (e.g. hot spots of disproportionate P loss from fields and farmyards) and the relative contribution of these sources to P inputs to the loch. Information at a micro-catchment scale, whether experimental, routine monitoring or modelling studies, would bring fresh evidence of the extent of agricultural P losses and the importance of different transport pathways. This information will facilitate the implementation of much improved, better targeted and more cost effective catchment management initiatives that will have a greater impact
on reducing P transfers from the land to water. To improve the success of catchment initiatives designed to address diffuse pollution problems in other rural catchments, research of a similar nature to that performed at Loch Leven would be beneficial.
10 References


and Effects of Phosphorus. Report for the Environmental Protection Agency, Trinity College Dublin.


Appendix A.1

Detailed Laboratory Methods

A.1.1 Analytical Solutions and Reagents for Soluble Reactive Phosphorus Analysis

Prior to phosphorus analysis, stock solutions and reagents were prepared as follows:

**2.5M Sulphuric Acid (H$_2$SO$_4$)**
Using a 25ml volumetric pipette, 70ml of concentrated analysis grade sulphuric acid was added to 350ml distilled water (placed in an ice bath). Distilled water was added until a final volume of 500ml was reached. Solution was stored in a glass bottle in the dark at room temperature.

**Ammonium Molybdate Solution**
This solution was made fresh at the beginning of every batch of samples analysed. Thirty ml of ammonium molybdate solution was sufficient for most sets of batch analysis, therefore 1.2g of ammonium molybdate was dissolved in 30ml distilled water and added in appropriate volumes to the mixed reagent (see Table A.2.x).

**Ascorbic Acid**
This solution was made fresh at the beginning of every batch of samples analysed. For the SRP mixed reagent for filtered water samples, the required weight of ammonium molybdate was dissolved in a known volume of distilled water and added to the final SRP reagent solution (see Table A.2.x). For the SRP mixed reagent for digested (TP/TSP) water samples, the required weight of ammonium molybdate was dissolved in a known volume of distilled water and added to the final SRP reagent solution (see Table A.2.x).

**Potassium Antimonyl Tartrate (PAT)**
0.274g of PAT was dissolved in 100ml distilled water. The solution was stored in a dark glass bottle in the dark at room temperature for a maximum of 3 months.

A.1.2 Total Phosphorus and Total Soluble Phosphorus Reagents

For total phosphorus (TP) and total soluble phosphorus (TSP) analysis, the following solutions were also required:

**Potassium Persulphate**
This solution was made fresh at the beginning of every batch of samples analysed. One hundred ml of solution was sufficient for each batch of analysis; therefore 8g of potassium persulphate was dissolved in 100ml distilled water.

**30% H$_2$SO$_4$**
This reagent was prepared by adding 30 ml of concentrated analysis grade sulphuric acid to 70ml distilled water (in an ice bath). After cooling, the solution was stored in a glass bottle in the dark at room temperature for a maximum of 3 months.
transferred to a glass storage bottle and stored in the dark at room temperature for a maximum of 3 months.

**Soluble Reactive Phosphorus Mixed Reagent**

For the determination of SRP in a water sample, 1ml of reagent was added to 5ml of filtered water sample. The required volume of reagent varied between analysis batch but was determined from the following table (Table A.1.1):

**Table A.1.1:** Recipe table for SRP mixed reagent for filtered water samples.

<table>
<thead>
<tr>
<th>Reagent Volume (ml)</th>
<th>2.5M Sulphuric Acid (H₂SO₄) (ml)</th>
<th>Ammonium Molybdate (ml)</th>
<th>PAT (ml)</th>
<th>Ascorbic Acid (g)</th>
<th>Distilled Water (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>25</td>
<td>7.5</td>
<td>2.5</td>
<td>0.3</td>
<td>15</td>
</tr>
<tr>
<td>100</td>
<td>50</td>
<td>15</td>
<td>5</td>
<td>0.6</td>
<td>30</td>
</tr>
<tr>
<td>150</td>
<td>75</td>
<td>22.5</td>
<td>7.5</td>
<td>0.9</td>
<td>45</td>
</tr>
<tr>
<td>200</td>
<td>100</td>
<td>30</td>
<td>10</td>
<td>1.2</td>
<td>60</td>
</tr>
</tbody>
</table>

For the determination of SRP in digested water samples (TP/TSP), 1ml of reagent was added to 5ml of filtered or unfiltered water sample. The required volume of reagent varied between analysis batch but was determined from the following table (Table A.1.2):

**Table A.1.2:** Recipe table for SRP mixed reagent for digested water samples.

<table>
<thead>
<tr>
<th>Reagent Volume (ml)</th>
<th>2.5M Sulphuric Acid (H₂SO₄) (ml)</th>
<th>Ammonium Molybdate (ml)</th>
<th>PAT (ml)</th>
<th>Ascorbic Acid (g)</th>
<th>Distilled Water (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>13.5</td>
<td>7.5</td>
<td>2.5</td>
<td>0.3</td>
<td>26.5</td>
</tr>
<tr>
<td>100</td>
<td>27</td>
<td>15</td>
<td>5</td>
<td>0.6</td>
<td>53</td>
</tr>
<tr>
<td>150</td>
<td>40.5</td>
<td>22.5</td>
<td>7.5</td>
<td>0.9</td>
<td>79.5</td>
</tr>
<tr>
<td>200</td>
<td>54</td>
<td>30</td>
<td>10</td>
<td>1.2</td>
<td>106</td>
</tr>
</tbody>
</table>

**A.1.3 Phosphorus Standards**

For a 100mg (PO₄-P ¹⁻¹) standard stock solution, 0.2195g of potassium dihydrogen orthophosphate (KH₂PO₄) was dissolved in 500ml distilled water in an acid washed 500ml volumetric flask. Stock solution was stored in a glass bottle in a dark fridge (5°C ± 2°C) for up to 3 months. From this stock solution, 100 µg l⁻¹, 200 µg l⁻¹, 300 µg l⁻¹ and 400 µg l⁻¹ working standards were prepared before each batch of analysis. From the spectrophotometer absorbance values of the standard solutions, a linear regression equation was used to determine the phosphorus concentrations in the unknown samples collected during field studies (Figure A.1.1).
A.1.4 Analytical Solutions and Reagents for Silica Analysis

Prior to silica analysis, stock solutions and reagents were prepared as follows:

**Acid Ammonium Molybdate**
0.34g ammonium molybdate was dissolved in 100ml of distilled water. One ml of concentrated analytical grade hydrochloric acid (HCl) was then added. The solution was stored in a plastic bottle in the dark at room temperature for a maximum of 3 months.

**Oxalic Acid / Sulphuric Acid Reagent**
0.9g of oxalic acid was dissolved in 245ml of distilled water and 4.5ml of concentrated analytical grade sulphuric acid (H$_2$SO$_4$) solution. The solution was stored in a plastic bottle in the dark at room temperature for a maximum of 3 months.

**Silica Mixed Reagent**
The mixed reagent for the determination of SRS was made fresh at the beginning of each set of batch analysis using the volumes in Table A.1.3.

**Table A.1.3:** Recipe table for SRS mixed reagent.

<table>
<thead>
<tr>
<th>Reagent Volume (ml)</th>
<th>Oxalic / sulphuric acid mixture (ml)</th>
<th>Distilled Water (ml)</th>
<th>Ascorbic acid (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>30</td>
<td>30</td>
<td>0.45</td>
</tr>
<tr>
<td>120</td>
<td>60</td>
<td>60</td>
<td>0.9</td>
</tr>
<tr>
<td>180</td>
<td>90</td>
<td>90</td>
<td>1.35</td>
</tr>
<tr>
<td>240</td>
<td>120</td>
<td>120</td>
<td>1.8</td>
</tr>
</tbody>
</table>
A.1.5 Silica Stock Solution and Standards

For a 100mg SiO$_2$ l$^{-1}$ stock solution, 0.0313g of Na$_2$SiF$_6$ was dissolved in 100ml distilled water in an acid washed 100ml plastic volumetric flask. Stock solution was stored in a plastic bottle in a dark fridge (5°C ± 2°C) for up to 3 months. From this stock solution, 5 mg l$^{-1}$ and 10 mg l$^{-1}$ working standards were prepared before each batch of analysis. From the spectrophotometer absorbance values of the standard solutions, a linear regression equation was used to determine the SRS concentrations in the unknown samples collected during field studies (Figure A.1.2). Figure A.1.3 details the laboratory procedure which was followed to determine the SRS concentrations within water samples.

![Graph showing a linear regression equation and standard curve for SiO$_2$ concentration.](image)

**Figure A.1.2:** Example of SiO$_2$ standard curve and regression equation used to determine unknown SRS concentration of samples.
Water Sample

Filtered
(0.45 μm Whatman GFC)

One ml of filtered water sample added to clean plastic test tube.

One ml of acid ammonium molybdate solution added to test tube and allowed to stand for 10 minutes.

Three ml of SRS mixed reagent added to test tube and allowed to stand for 30 minutes.

Absorbance of samples measured on a spectrophotometer at 810nm using a 1cm cuvette or flow cell. Silica concentrations in samples estimated using a regression equation determined from the absorbance values of known SRS standards solutions.

Figure A.1.3: Standard laboratory procedure for the determination of soluble reactive silica in water samples.
A.1.6 Equilibrium Phosphorous Concentration (EPCo)

Approx 1 g wet sediment weighed into 15 x clean weighing boats

Wet sediment added to 50 ml centrifuge tube with:
- 3 x 45 ml 0 µg P l⁻¹
- 3 x 45 ml 250 µg P l⁻¹
- 3 x 45 ml 500 µg P l⁻¹
- 3 x 45 ml 1000 µg P l⁻¹
- 3 x 45 ml 2500 µg P l⁻¹

Shake for 24 hour on orbital shaker at 160 rpm at 10°C temperature in dark (in a controlled environment chamber)

Remove 10 ml aliquot from each flask and filtered through Whatman GF/C 0.45 µm filter

Soluble Reactive Phosphorus Concentration determined (Murphy and Riley, 1962)

Figure A.1.4: Step by step method for determining the equilibrium phosphate concentration of river bed sediments.

A.1.7 Labile Phosphorus Extraction

Labile phosphorus was extracted from river bed sediments after the methods of Falmer et al. (1994).
Figure A.1.5: Step by step instructions for the extraction of labile phosphorus from river bed sediments.
A.1.8 Bioavailable Phosphorus Extraction

The bioavailable phosphorus fraction was extracted from stream bed sediments after the method of Sharpley et al. (1991).

**Figure A.1.6:** Step by step instructions for the extraction of bioavailable phosphorus from river bed sediments.
A.2 Annual Loading Survey Measured Phosphorus Concentrations

Remaining figures from the Loch Leven annual phosphorus loading survey are presented in this section, as reported in Chapter 3.

**Loch Outflow (L)**

![Graph showing phosphorus concentrations at the outflow of Loch Leven.](image)

**Figure A.2.1:** Phosphorus concentrations at the outflow of Loch Leven.

**Gairney Water, Tributary (Gu)**

![Graph showing phosphorus concentrations at a small tributary of the Gairney Water.](image)

**Figure A.2.2:** Phosphorus concentrations at a small tributary of the Gairney Water.
Figure A.2.3: Phosphorus concentrations at the Gairney Water at upstream and downstream locations.
Figure A.2.4: Phosphorus concentrations at the South Queich at upstream and downstream locations.
Figure A.2.5: Phosphorus concentrations at the North Queich at upstream and downstream locations.
Figure A.2.6: Phosphorus concentrations at the Foccy Burn in the North Queich catchment.

Figure A.2.7: Phosphorus concentrations at the Hatton Burn in the North Queich catchment.
Figure A.2.8: Phosphorus concentrations at the Camel Burn at an upstream location and a downstream location which received fish farm effluent.
Figure A.2.9: Average chlorophyll$_a$, total phosphorus and soluble reactive phosphorus concentrations in Loch Leven in 2005. (Data provided by the Centre for Ecology and Hydrology).
A.3 Water Sample Stability Trials

A.3.1 Methods

In order to investigate the effect of sample storage on SRP concentrations, 18 x 500 ml polyethylene bottles from the EPIC® water sampler were cleaned with and soaked in phosphate-free detergent (Decon®) for 24 hours and then rinsed twice with distilled, deionised water. A large water sample (10 litres) was collected from the Pow Burn during a period of high flow and immediately brought back to the laboratory. The sample was well mixed and split into 2 equal sub-samples. One sub-sample was spiked with potassium di-hydrogen phosphate (KH$_2$PO$_4$) to increase the initial SRP concentration (Group B) whilst the other sub-sample was left untreated (Group A). The experiment was performed as detailed in Figure A.3.1.

Figure A.3.1: Experimental design to test the effects of sample storage on SRP concentrations of water samples collected by an automatic water sampler located on the Pow Burn.
A.3.2 Results

Initial SRP concentration of water samples in groups A and B ranged from 40.95 μg l⁻¹ to 44.68 μg l⁻¹ and 252.15 μg l⁻¹ to 258.95 μg l⁻¹, respectively. These concentrations represented approximate SRP concentrations measured at the Pow Burn during periods of base flow and high flow. Figure A.3.2 shows the changes in SRP concentrations after 24, 48 and 96 hours. Table A.3.1 details the results of paired t-tests. In summary, the results of the experiment showed that for water samples with both high and low initial SRP concentrations, there was no significant difference between concentrations measured at 0 hours and after 24 and 48 hours storage in EPICS sampler water bottles. However, SRP concentrations were significantly lower after 96 hours storage in both test groups.

\[\text{Figure A.3.2: Mean concentrations (± SE of the mean, } n = 3) \text{ of soluble reactive phosphorus in water samples determined after 24, 48 and 96 hours storage in EPIC®} \]
polythylene sampler bottles (Group A = Low initial SRP concentrations and Group B = high initial SRP concentrations).

Table A.3.1: Significance values for paired t-tests between low (group A) and high (group B) initial SRP concentrations after 24, 48 and 96 hours storage outside during winter weather conditions (0-7°C).

<table>
<thead>
<tr>
<th>Test Group</th>
<th>Comparison</th>
<th>Significance value of paired t-test</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0 hours v 24 hours</td>
<td>p = 0.730</td>
</tr>
<tr>
<td>A</td>
<td>0 hours v 48 hours</td>
<td>p = 0.074</td>
</tr>
<tr>
<td>A</td>
<td>0 hours v 96 Hours</td>
<td>p = 0.037</td>
</tr>
<tr>
<td>B</td>
<td>0 hours v 24 hours</td>
<td>p = 0.822</td>
</tr>
<tr>
<td>B</td>
<td>0 hours v 48 hours</td>
<td>p = 0.056</td>
</tr>
<tr>
<td>B</td>
<td>0 hours v 96 Hours</td>
<td>p = 0.01</td>
</tr>
</tbody>
</table>

A.3.3 Discussion

House and Warwick (1998) commented that it was the first 24 hours that was the most critical period for SRP sample stability, and that beyond 24 hours there was consistent losses of SRP from less than half of their samples. This pre-experimental study demonstrated that although slight fluctuations in SRP concentrations were observed during sample storage, on average, the changes were not significantly different from initial concentrations if analysed within 48 hours of sample collection. Therefore, storage of water samples for up to 48 hours before SRP analysis was tolerable and was unlikely to have any noticeable effect on measured SRP concentrations. Kotash and Chessman (1998) commented that a larger proportion of SRP would be most likely be adsorbed from samples of low initial SRP concentrations, compared to more concentrated samples. This was also found to be the case in this experiment. However, the importance of SRP losses during storage will depend on the objectives of a particular study. For example, in a study investigating the effect of storm events on P concentrations, temporal changes are likely to be great enough to overcome the effects of sample storage. Similarly, for a study investigating the effect of storm events on P loads, concentrations are likely to be high enough that small percentage losses of SRP would have little effect on loading calculations (Kotash and Chessman, 1998). Therefore, sample preservation is not always a requirement, especially considering that the estimation of loadings is usually associated with many other sources of error (Walling and Webb, 1985; Johnes, 2007). It was concluded that sample preservation was not required during winter storm event sampling on the Pow Burn, so long as samples were analysed within 48 hours of sample collection.
A.4 Sediments as a Sink or Source of Phosphorus

Figure A.4.1: Comparison between sediment labile phosphorus content and percentage of the clay/silt fraction (0.035 – 63 μm) in three sediment cores from the Pow Burn in January 2007.

Figure A.4.2: The percentage rainfall above or below the monthly 1961 to 1990 monthly average in East Scotland (data obtained from the Meteorological Office (http://www.metoffice.gov.uk/climate/uk on 03/03/2007)).
Appendix A.5

A.5 Sediment Phosphorus Bioavailability – ‘Pollutograms’

Figure A.5.1: Pollutograms and estimated β values for total suspended sediments (TSS), total P (TP), particulate P (PP), soluble reactive P (SRP), bioavailable particulate P (BAPP) and total bioavailable P (TBAP) during high-flow event A (October 2006) in the Pow Burn.
Figure A.5.2: Pollutograms and estimated $\beta$ values for total suspended sediments (TSS), total P (TP), particulate P (PP), soluble reactive P (SRP), bioavailable particulate P (BAPP) and total bioavailable P (TBAP) during high-flow event B (October 2006) in the Pow Burn.
Figure A.5.3: Pollutograms and estimated β values for total suspended sediments (TSS), total P (TP), particulate P (PP), soluble reactive P (SRP), bioavailable particulate P (BAPP) and total bioavailable P (TBAP) during high-flow event C (October 2006) in the Pow Burn.
Figure A.5.4: Pollutograms and estimated $\beta$ values for total suspended sediments (TSS), total P (TP), particulate P (PP), soluble reactive P (SRP), bioavailable particulate P (BAPP) and total bioavailable P (TBAP) during high-flow event D (October 2006) in the Pow Burn.
Figure A.5.5: Pollutograms and estimated $\beta$ values for total suspended sediments (TSS), total P (TP), particulate P (PP), soluble reactive P (SRP), bioavailable particulate P (BAPP) and total bioavailable P (TBAP) during high-flow event E (October 2006) in the Pow Burn.
Figure A.5.6: Pollutograms and estimated $\beta$ values for total suspended sediments (TSS), total P (TP), particulate P (PP), soluble reactive P (SRP), bioavailable particulate P (BAPP) and total bioavailable P (TBAP) during high-flow event F (November 2006) in the Pow Burn.
Figure A.5.7: Pollutograms and estimated $\beta$ values for total suspended sediments (TSS), total P (TP), particulate P (PP), soluble reactive P (SRP), bioavailable particulate P (BAPP) and total bioavailable P (TBAP) during high-flow event H (November 2006) in the Pow Burn.
Figure A.5.8: Pollutograms and estimated $\beta$ values for total suspended sediments (TSS), total P (TP), particulate P (PP), soluble reactive P (SRP), bioavailable particulate P (BAPP) and total bioavailable P (TBAP) during high-flow event J (November 2006) in the Pow Burn.
Figure A.5.9: Pollutograms and estimated β values for total suspended sediments (TSS), total P (TP), particulate P (PP), soluble reactive P (SRP), bioavailable particulate P (BAPP) and total bioavailable P (TBAP) during high-flow event J (December 2006) in the Pow Burn.