FACTORS AFFECTING PHOSPHATE CONCENTRATIONS IN SURFACE AND SUBSURFACE RUNOFF FROM STEEP EAST COAST HILL COUNTRY

A thesis presented in partial fulfilment of the requirements for the degree of

Masters of Applied Science, Department of Soil Science, Massey University

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1998

ABSTRACT

Eutrophication is a problem receiving much attention within New Zealand and throughout the rest of the world. Problems associated with eutrophication cause major financial, aesthetic and recreational costs to not only commercial and recreational water users but to society in general.

The major nutrient of concern in relation to eutrophication is phosphorus (P) as it is often considered to be the limiting factor. The two major areas from which P enters waterways are point sources and non-point sources. Point sources are relatively easy to identify and quantify. Non-point sources however, are less easy to quantify due to the size of areas from which P is sourced and the number of varying factors which can affect the amount of P which is lost to water-ways.

This study investigated P concentrations in surface runoff and subsurface flow from steep east coast hill country. Factors studied included aspect, soil P status, season and fertiliser addition.

The study was carried out on grazed pasture farmlets, in which there were 'High P' and 'Low P' fertiliser regimes. Each regime had north and south facing aspects. Four sites were used in the study. High P North (HPN), High P South (HPS), Low P North (LPN) and Low P South (LPS). Simulated rainfall was applied to the sites and surface runoff samples were collected and analysed for dissolved reactive phosphate concentration (DRP). Superphosphate fertiliser was then applied at 20 kg P ha^{-1} to each site and the runoff procedure was repeated 7 weeks and 14 weeks after fertiliser application. Subsurface runoff water samples were also collected on the southerly sites during each Run. At the time of each runoff measurement soil samples were collected and analysed for Olsen P, water extractable P and soil moisture content. The soil P retention was also measured for each site.

At each Run the HPN site produced the highest DRP concentrations followed by the LPN site with the southerly sites producing the lowest DRP concentrations. The DRP concentrations in runoff for each site increased between Run 1 and 2 (except for the HPS site) corresponding to fertiliser addition, but interestingly all sites increased markedly in runoff DRP concentration between Run 2 and 3. This corresponded to a time of decreasing soil moisture.

Concentrations of DRP in surface runoff were therefore influenced by a number of factors. These included - fertiliser addition, aspect and season. In general, soils that had previously received large inputs of P fertiliser had higher DRP concentrations in surface runoff than soils with lower fertiliser inputs. The magnitude of this fertiliser effect however, varied with aspect. Generally the impact of fertiliser on DRP concentrations was higher on north facing slopes than on south facing slopes. South facing slopes were wetter and had slightly higher P retention (although in a conventional agronomic sense the P retention across the whole trial was low (< 36 %)). This combination of higher P retention and soil moisture would assist in the immobilisation of added fertiliser P. This was also reflected in the lower P soil test values on the south-facing slopes.

A water extractable P test provided a better correlation with runoff DRP concentrations for individual runoff events than the Olsen P test. Both tests however, provided poor correlations when all of the Runs were combined. This was due largely to the large increase in DRP concentrations in surface runoff in Run 3 with no corresponding increase in soil tests.

There was no apparent relationship between fertiliser regime ie. soil P status, and the concentration of DRP in subsurface runoff. In Run 3 however, there was a marked increase in subsurface DRP concentration for both sites which was consistent with the surface runoff results and supported the theory of soil moisture playing a major role in determining the DRP concentration in water.

The study suggests that the greatest risk of P loss from soil to surface waters will be from northerly aspects with high fertiliser histories during the summer months when soil moisture levels are low.

ACKNOWLEDGEMENTS

I would like to thank the following people and organisations for their help and support which allowed me to complete this project.

My supervisors, Professor Russell Tillman and Dr Allan Gillingham (AgResearch), for their valuable guidance, help, encouragement, patience and support.

The New Zealand Fertiliser Manufacturers' Research Association for providing the postgraduate fellowship.

Lab technicians, Bob Toes, Anne West and Ian Furkert for the many hours of assistance that they provided in the analytical aspects at Massey University.

AgResearch technicians Maurice Gray and Alister Holman for the many hours of help and support that they provided at the Waipawa trial site.

The Holman family for providing me with accommodation and friendship whilst I was in the Hawkes Bay.

Most of all my parents and family who have offered great support morally and financially throughout my varsity 'career' and have helped to steer me in the right direction. Without them none of this would have been possible.

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CHAPTER 1

Introduction

Eutrophication is a problem that has become increasingly prevalent in the last thirty years within New Zealand. Although eutrophication has been an issue of great concern for some time, the introduction of the Resource Management Act (1991) has provided additional stimulus to address the problem.

In most waterways the main area of concern in regards to eutrophication is the phosphate (P) concentration in the water, as it is regarded as being the controlling nutrient in the process. There are two areas from which P enters waterways. These are through point sources (such as pipes) and through non-point sources (such as runoff). The point sources are relatively easy to quantify and consequently methods of control are easier to develop. Non-point sources, however, are not as easy to quantify or control. As pressure is applied to decrease point source discharges, there is also increasing pressure on land-users and supporting industries to control and minimise non-point sources. Added to this is the pressure applied internationally on New Zealand's farming systems to demonstrate their environmental sustainability and to portray a 'clean and green' image.

There has been much work carried out to measure and characterise the losses of P from non-point sources. But due to the large areas involved and variable climatic and soil conditions, accurate estimates are hard to obtain. Therefore more work is needed to obtain data on what are the main factors affecting P loss via non-point sources, the actual concentrations of P entering via non-point sources, and the various means by which P losses can be reduced and controlled.

This study investigates the factors affecting loss of P in runoff from steep East Coast hill country. Factors examined include the relative concentrations of P in surface runoff and subsurface flow, and the effects that fertiliser and aspect have on the P concentration. It is intended that this information will help to give a better understanding of P loss from agricultural land and provide information on possible ways by which P loss can be reduced and controlled.

CHAPTER 2

Literature Review

2.1 Soil Phosphorus and Retention Mechanisms

2.1.1 Phosphorus compounds in mineral soils

In comparison with other major nutrients for growth, phosphorus has a relatively low content within the earth's crust (1100-1200 mg kg^{-1}) (Jackson 1964; Tisdale *et al.* 1985). Likewise the total P content of mineral topsoils is relatively low (50-1100 mg kg^{-1}; Tisdale *et al.* 1985; Brady 1990).

"Inorganic P constituents in mineral soils have generally been classified into two groups, namely calcium phosphates and iron and aluminium phosphates. Among the calcium phosphates, $Ca_{10}F_2(PO_4)_6$ (fluoroapatite), $Ca_{10}(OH)_2(PO_4)_6$ (hydroxyapatite), $Ca_{10}O(PO_4)_6$ (oxyapatite) and $Ca_{10}CO_3(PO_4)_6$ (carbonate apatite) are most abundant while $FePO_4.2H_2O$ (strengite) and $AlPO_4.2H_2O$ (variscite) are the other main P bearing minerals. Inositol phosphates, of which phytic acid is the most significant component, phospholipids, nucleic acids, nucleotides and unidentified sugar phosphates are the principal compounds in the organic P fraction (Morgan 1997). In general, native inorganic sources of P are of little short term consequence to commercial crop production due to their relatively high stability. Although part of the organic P pool may undergo mineralisation (Dormaar 1972), or occur as dissolved materials in the soil water (Ron Vaz *et al.* 1993), the same comment generally applies to the organic fraction" (Morgan 1997).

2.1.2 Phosphorus fertilisation

The need for phosphorus fertiliser to be applied to soils arises from the inability of the relatively small pool of native soil P to supply and maintain adequate amounts of soluble orthophosphate ($H_2PO_4^-$ and HPO_4^-) to the soil solution for satisfactory crop growth and animal performance. Phosphorus fertiliser must therefore be supplied in order to supplement soils with the extra phosphorus required. In principle, this approach is not different from supplying nitrogen (N) or potassium (K) fertilisers. However, the reactions which P fertilisers undergo in soils are quite different from those undergone by N and K fertilisers and result in poor (25% or less) efficiency of recovery of an annual application in the growing crop (Barrow, 1980). In contrast, recovery of N or K fertilisers by crops in the season of application may be as high as 80% (Morgan 1997). Therefore, whereas N and K fertilisers in soils are relatively accessible to crop roots, this is not so for P fertilisers as they quickly undergo complex reactions with various soil constituents which immobilises the P. As a result, P nutrition of field crops is largely dependant on the subsequent release of P from these reaction products to the soil water (Morgan 1997).

2.1.3 Phosphorus retention

The mechanisms by which P fertilisers are converted from a soluble state to a less soluble state are referred to as P retention / P fixation. While the precise sequence of events that occurs after P fertiliser has been applied to soil is unclear, there is a general consensus as to the principal components of the retention process. These are: (I) events associated with the dissolution of the P fertiliser particle; (II) the occurrence of precipitation reactions involving the orthophosphate anion, in which both reactants are initially dissolved in the soil solution; and (III) the occurrence of adsorption reactions, in which only one of the reactants (orthophosphate) is initially in solution (Morgan 1997).

Morgan (1997) states that "Regardless of the pH, all mineral soils contain aluminium and iron oxides and hydrous oxides, which occur as discrete particles or as coatings on other soil particles, especially clay. In addition, amorphous aluminium hydroxy compounds may be present in interlayer locations of expandable aluminium silicates. Such materials are highly efficient at adsorbing $H_2PO_4^-$ ions that may be present in the soil solution, the general view being that retention occurs as a result of exchange between the $H_2PO_4^-$ anion and the hydroxyl (OH^-) ions associated with the iron and or aluminium. Specifically under alkaline conditions in the presence of free calcium carbonate, adsorption of $H_2PO_4^-$ / HPO_4^{2-} on to calcite can also occur by replacement of water, bicarbonate or hydroxy ions present on the calcite particles. Concurrent with these adsorption reactions, $H_2PO_4^-$ ions in solution may undergo precipitation reactions, the nature of which vary with the pH of the soil. Under acidic conditions ($pH<5.0$), the presence of active aluminium, iron or manganese may result in the formation of poorly soluble hydroxy metal phosphates. In contrast, under alkaline conditions, the presence of calcium causes precipitation of dicalcium phosphate anhydrous".

It is generally accepted that the early products of the retention mechanism when fertiliser is applied are only 'relatively' stable and are therefore able to supply adequate amounts of soluble P for early and speedy utilisation by plants. Over time, however, the initial reaction products are altered and while the manner of alteration is not known, there seems to be a general agreement as to the composition of the ultimate products of the fixation mechanism (Sample *et al.* 1980). The stable products of the fixation reaction sequence are octacalcium phosphate, hydroxyapatites and fluoroapatites under alkaline conditions, and strengite and variscite under acid / neutral conditions. Apparently these materials can appear within a matter of months (Sample *et al.* 1980), their rate of production being especially dependent on the prevailing pH.

"In the transition from the 'relatively' stable to the 'stable' state, it is not thought that there is quantitative conversion from one type of P compound to another. Rather, it is more likely that orthophosphate ions which appear during transition are exposed to a number of competing reaction possibilities, including absorption by roots and transport to new sites of reaction by water or cultivation practices. Additional stability of reaction products may also arise from occlusion phenomena or from growth in crystal size of precipitated P compounds" (Morgan 1997).

2.2 Eutrophication

2.2.1 Introduction

Phosphorus is an essential element for plant growth and its input has long been recognised as necessary to maintain profitable crop production. Phosphorus however also increases the biological productivity of surface waters which is more commonly referred to as eutrophication. Although nitrogen (N) and carbon (C) are essential to the growth of aquatic biota, it is P which receives the most attention in relation to eutrophication as it is often considered to be the limiting nutrient. Phosphorus is also considered to be the 'easiest' of the three main nutrients to control due to difficulty in controlling the exchange of N and C between the atmosphere and water and the fixation of atmospheric N by some blue green algae (Sharpley and Rekolainen 1997). As we move from fresh to saline estuaries, through brackish waters, N generally becomes the element controlling aquatic productivity (Thomann and Mueller 1987).

2.2.2 Eutrophication Process

The principal impacts of eutrophication relate to four phenomena: increased aquatic plant growth, oxygen depletion, pH variability, and plant species quality and food chain effects. As a result of these four phenomena such problems as decreased water clarity, algal scums, unsightly decaying algal clumps, and discolouration may occur because of increased phytoplankton population. Large diatoms and filamentous algae can clog water treatment plant filters. In addition the extensive growth of larger plant forms can interfere with recreation, navigation and limit fisheries potential (Sharpley *et al.* 1994).

Phytoplankton settle to the bottom of still waters and their subsequent decay can deplete oxygen and result in the death of desirable fish species. In highly productive streams, algal activity can lead to large diurnal swings of oxygen and pH in buffered waters. The latter can have a deleterious effect on fish by causing a shift of the ammonium ion to the toxic unionised ammonia form (Sharpley *et al.* 1994).

Eutrophication can lead to a shift of the phytoplankton assemblage to noxious species. Some blue-green algae form mats and gas vacuoles, which allow them to form floating mats. Beyond changes in the phytoplankton themselves, shifts in the species types can influence organisms higher up the food chain. For example, some blue-green algae are not a desirable food source for zooplankton. Consequently the appearance of these types of organisms can influence the amount of biomass that is available to the zooplankton, which in turn are a major source of food for fish (Sharpley *et al.* 1994). The whole food chain is therefore effected due to the presence of a certain type of algae lower down the food chain. Other types of blue-green algae associated with eutrophication form potent toxins, which cause taste and odour problems and ultimately effect the potability of the water. Farmers therefore face major economic consequences when they experience stock losses due to drinking contaminated water, and these toxins can also cause a health risk to humans (Kotak *et al.* 1993). In addition to clogging up water filters during treatment, algal blooms can contribute to trihalomethane formation during water chlorination (Palstrom *et al.* 1988).

Eutrophication therefore negatively impacts the aesthetic, recreational and ecological qualities of water ways and consequently has a major financial cost to not only the users of the water ways and the water itself but to society in general.

2.2.3 Sources of Phosphorus

In the USA, point sources of water pollution have been reduced since the late 1960's (Sharpley and Rekolainen 1997). In New Zealand efforts to reduce point sources have only been made in more recent times and many issues have been enforced only since the introduction of the Resource Management Act (1991). However, in both countries water quality problems remain, and as further point source control becomes less cost effective more attention has been directed toward agricultural non-point sources (surface runoff and subsurface flow). Concerns exist not only for the amount of P in streams but also for nitrogen in the form of nitrate and ammonia and other pollutants such as pesticides. However in the case of eutrophication, P is the nutrient which is of major concern due to it being the limiting factor for aquatic biological production.

It is difficult, or almost impossible to attribute non-point sources of phosphorus to any one person or farm, and the losses can be affected by a number of factors. According to Hedley *et al.* (1991), approximately 1 kg of P ha^{-1} yr^{-1} is estimated to be lost by runoff from agricultural land in New Zealand, which is 2-5 times higher than the natural loss rates of phosphorus which occur during the development of some soils. However, the rate of phosphorus loss can change with land use. For instance, up to 6 kg of P ha^{-1} yr^{-1} can be lost from dairy pasture runoff, one of our major agricultural sectors (Sharpley and Syers, 1979a). Less P is likely to be lost from scrub and forestry. There is therefore a major need to identify the exact location and amounts of P which are being released to water ways through non-point sources.

2.2.4 Forms of phosphorus lost from agricultural non-point sources

Phosphorus can be lost or transported to water ways in two forms, dissolved P (DP) and particulate P (PP). Particulate P includes P sorbed by soil particles and organic matter eroded during flow events, and generally constitutes the major portion of P transported from cultivated land (Sharpley *et al.* 1992). Runoff from grassland or forest land carries little sediment and is therefore generally dominated by DP. Dissolved P for the most part is readily available for biological uptake. Walton and Lee (1972) reported that soluble phosphorus was essentially 100 % available. However, Stainton (1980) found that soluble P as measured by the molybdate reactive method (Murphy and Riley 1962) is not completely available to support algal growth. This results from a possible reduction in condensed phosphates, hydrolysis of organic P compounds, and reaction with arsenate during analysis, all of which will contribute to an overestimation of the true soluble P concentration. This discrepancy is relatively high for waters of low P concentration, such as are found in lakes, while the percentage error is much lower with concentrations found in streams, rivers and wastewater discharges (Sharpley and Menzel 1987). Where P concentrations are low the discrepancy reported will not be of major consequence in relation to management procedures as it is the water bodies with high P concentrations that are of particular concern.

Particulate P (PP) on the other hand is relatively inaccessible to aquatic biota, and provides a long term source of P. The amount of P that is released from the adsorbed fraction on PP depends largely on the amount of DP in the surrounding water. The direction of the P movement will be governed by the soluble P concentration of the water and the desorbable P content of the sediment material. The rate and extent of P interchange between sediment P and the surrounding water is controlled by the forms of P contained in the sediment and the soluble P concentration of the interstitial water (Sharpley and Menzel 1987). The forms of P contained in the sediment have been reviewed extensively by Syers *et al.* (1973). The potentially mobile forms are P sorbed on hydrous iron and aluminium oxides and calcium carbonate.

In addition to the chemical mobility of the sediment material, its physical mobility will also affect the interchange between particulate and soluble P, and subsequently its bioavailability. The physical mobility of sediment entering a lake will be a function of its texture and lake water temperature and turbidity. The relative densities and temperatures of the inflow and lake water will determine whether sediment enters the surface or bottom waters of the lake. As sediment enters the lake increased water turbidity may reduce the depth of the photic zone. Coarse textured sediments will settle rapidly and be available to algae in the photic zone for short periods only. In contrast, fine textured sediments will remain in the photic zone for a longer period of time. The bioavailability of this sediment will be further increased by the fact that it will be enriched in P compared to coarser material (Sharpley and Menzel 1987).

2.2.5 Methods for measuring P in water

When assessing the contribution of non point sources to an increased rate of eutrophication within our water bodies, it is important to identify the amount of P that is actually available to support aquatic biota. It was thought for a long time that measuring the DP concentration in water ways gave a reliable estimate of the amount of P that was available. As mentioned earlier Walton and Lee (1972) reported that 100% of DP was available to aquatic biota. However, Stainton (1980) reported that not all of the DP found by the molybdate reactive method (Murphy and Riley 1962) is available to aquatic biota. It was also known that some, but not all, of the P adsorbed onto PP can become available. There was therefore a need to develop a method whereby the amount of bioavailable P (BAP) could be measured. Bioavailable P would then be comprised of DP plus PP which is available to support aquatic biota.

Methods using algal assays of 7 to 100 days do not lend themselves to routine analysis due to time restraints (Sharpley 1993). Thus more rapid chemical extractions, using ammonium fluoride, sodium hydroxide and anion exchange resins, have been used to simulate removal of DP and Bioavailable PP (BPP) by algae (Hegemann *et al.* 1983). However the amount extracted depends on the ionic strength, cationic species and pH of the extractant, and the validity of relating the form or availability of P in a chemical extractant to P bioavailability in the aquatic environment is questionable (Sharpley 1993). A simpler method was developed by Menon *et al.* (1989) using iron oxide impregnated filter paper (Fe-oxide strip) as a P sink to adsorb BAP from a sample of runoff, and subsequent removal of P by dilute acid (Sharpley 1993). This method has been shown to be highly correlated to the amount of P utilised by aquatic biota (Sharpley 1993, Menon *et al.* 1989) and is therefore regarded as a useful method for measuring BAP.

2.3 Soil P tests

Many farmers rely on soil testing for P, or other nutrients, to provide them with an indication of the likelihood of an economic return on a fertiliser investment. Soil P tests however, also provide the possibility of assessing the amount of P that is likely to be lost from a soil via surface runoff and subsurface drainage and will subsequently contribute to eutrophication. There is therefore a need to develop a soil testing system that can be used for estimating the potential loss of P as well as the likely economic return that could be gained from fertiliser investment and can subsequently be used to set upper soil P limits so that both economic and environmental concerns are taken into account.

There are then two main issues regarding the level of soil phosphorus: (I) a certain critical level of soil P is needed for economic crop production; and (II) soil P can be lost to the aquatic environment by surface runoff, leaching, and erosion. These two factors must be taken into consideration when setting critical soil test levels (Sibbesen and Sharpley 1997).

Several States in the USA have identified critical or threshold soil test P levels above which the potential for unacceptable P losses in runoff exceeds any crop response concerns. Attempts have been made to base fertiliser management recommendations on these soil P levels (Sibbesen and Sharpley 1997). Within New Zealand there are as yet, no P fertiliser restrictions imposed with regards to the maximum soil P level.

Because of the economic implications of reduced fertiliser and manure applications when based on P rather than crop nitrogen requirements, and lack of supporting documentation relating runoff and soil P, many of the farmers in the USA are contesting the use of soil threshold P levels as a basis for determining fertiliser and manure application rates (Sibbesen and Sharpley 1997). Clearly more information is needed on the relationship between soil P and P losses in runoff as a function of site, P source and management characteristics before any limits should be set. In New Zealand more work is needed to investigate specific soils and situations.

It is however, extremely time consuming and costly to obtain data on DP concentrations in surface runoff and unrealistic to expect that a large database relating soil test P (STP) to DP will be available in the near future. Sibbesen and Sharpley (1997) suggests that one role soil testing laboratories could play in improved soil P management would be to provide predictions of readily desorbed P based on STP and other measured properties such as pH, texture and organic matter content. These data could then be integrated with other information specifically related to surface runoff volume, in order to rate the potential of individual fields to be significant sources of P to nearby waters. Such a test could ultimately be of value in New Zealand.

2.3.1 Soil tests available for correlation

There has been much work conducted over the years investigating the relationship between various STP methods and the amount of P in surface runoff. The investigations have been carried out to find a soil test that will give an accurate estimate of the amount of P that will be lost in surface runoff, and therefore, provide a basis for management strategies to try and minimise losses. As mentioned earlier, it is realised that the level of STP is not the only factor affecting the amount of P that is lost. However, it is one source of information that, when combined with other data, can give an approximation of the amount that will be lost. It is therefore a matter of trying to identify the soil-P test that gives the best correlation with runoff BAP concentrations.

If possible, it would be desirable that the soil test that is used to correlate soil P with runoff BAP concentrations, is also a test that is commonly used by farmers for fertiliser recommendations. Within New Zealand the most common soil test is the Olsen P test (Olsen *et al.* 1954). Overseas, however, there are two other common soil tests used by laboratories. These are, the Mehlich III (Mehlich 1984), and the Bray-Kurtz P1 (Bray and

Kurtz 1945). It would be useful if one of these three routine tests could provide a robust correlation between STP and runoff BAP concentrations because soil testing laboratories are carrying out these tests all the time and it is therefore a simple step to use these data which are already available, to estimate the amount of P which may be lost.

There are however, a number of other tests available that are sometimes used to test for soil P. These include extraction with distilled water (Pote *et al.* 1996), ammonium oxalate (Pote *et al.* 1996), iron oxide impregnated filter strips (Menon *et al.* 1989), sodium chloride (Sharpley *et al.* 1977), as well as the P saturation test (Uunk 1991).

All of the tests mentioned above have been used in various studies relating soil P levels to the amount of P in runoff. Sharpley *et al.* (1977) investigated the relationship between the amount of P extracted from a soil by 0.1 M NaCl shaken for 40 hours and the concentration of DP in runoff. These workers found a direct linear relationship between the amount of P extracted and the DP concentration with a high correlation ($r = 0.98$). Although the soil testing method provided a good relationship and correlation, the method has not been used in subsequent studies.

One of the more interesting studies carried out investigating the relationship between STP and the amount of P in runoff was carried out by Pote *et al.* (1996). The study investigated the relationship between six different STP methods and the dissolved reactive phosphorus (DRP) and BAP concentration in runoff. The six STP methods were the Mehlich III, Bray-Kurtz P1, Olsen, water extractable, Fe-oxide strip, and ammonium oxalate extractable P. All of the tests gave high correlations, but the water extractable, Fe-oxide, and ammonium oxalate extractable tests provided the best correlations ($r > 0.91$) for both DRP and BAP. The study therefore concluded that these three tests give the best precision for predicting DRP and BAP concentrations in runoff. It was not surprising that these three tests would provide the best correlations as firstly, the Fe-oxide strip test closely approximates P actually available to growing algae (ie. the BAP water test) (Menon *et al.* 1989). Secondly the water extractable test should closely resemble the extraction processes in the soil when runoff occurs, and thirdly the ammonium oxalate test dissolves Fe and Al compounds (the compounds to which most P adsorbs) releasing into solution the P that may eventually be desorbed (Pote *et al.* 1996).

Several other studies have shown however, that high correlations can be achieved with tests other than the three with the highest correlations above. A significant relationship between STP analysed by the Mehlich III method and DP in runoff was found by Sharpley *et al.* (1986) and Sharpley (1995). The relationship in these experiments was highly correlated ($r > 0.95$). A similar dependence of the DP concentration of runoff on Bray-Kurtz P1 was found by Romkens and Nelson (1974) ($r = 0.90$).

It has also been found that the water extractable test does not always provide extremely high correlations with DP in runoff. For example Schrieber (1988) found that the correlation was only $r = 0.78$ on 17 Mississippi catchments. Such studies suggest that there are other factors which are important in determining the concentration of P in runoff in different soils. This may be due to varying amounts of clay, Fe and Al oxides, carbonates and organic matter. Sharpley and Rekolainen (1997) found that soils with a Fe oxide strip P content of 200 mg kg^{-1} would support a runoff BAP concentration of 0.53 mg l^{-1} for a clay but 1.65 mg l^{-1} for a sandy loam.

In the Netherlands the P saturation test has been adopted to predict runoff DP concentrations (Sharpley and Rekolainen 1997). The P saturation test assesses to what extent the soil's P retention sites are saturated. The approach works on the principle that the higher a soil is saturated with P (ie. the less sites there are available for further fixation) the more P will be lost in runoff. Conversely if a soil has a relatively low P saturation, then the soil is able to adsorb and fix more P, meaning that less will be lost in runoff.

Recent research in the Netherlands found that a P saturation of between 25-30 % is sufficient to cause runoff DP concentrations which are of concern (Van der Zee *et al.* 1987, 1990, Uunk 1991, Breeuwsma and Silva 1992).

The added advantage of the P saturation approach is that it not only describes the potential for P release from soil but also indicates how close the P sorption sites of a soil are to being saturated. In other words, measuring P saturation both describes the potential of a soil to enrich surface runoff with DP (high degree of P saturation) and also helps to predict how much of the P added in fertilisers will be retained by the soil in a form that is relatively resistant to loss in surface runoff (low degree of P saturation). The method also removes the variability related to soil type which is present in other soil tests (ie. the amount of P measured by other tests is dependent on the soil type).

2.4 Factors affecting the amount of phosphorus lost in runoff

There are various factors that affect the amount of P lost from soil to runoff. There has been much work carried out over the years investigating these various factors as well as ways of estimating how much P is potentially available to be removed in runoff.

Throughout the literature on P loss from soil to runoff water, the overriding factor affecting P loss appears to be the amount of P in soil, in particular the amount of P in the top 20 mm. Work carried out by Ahuja (1990) found that rain drops interact with the soil to a depth of 20 mm. Therefore it is the concentration of P in the top 20 mm that has a major bearing on how much P could be lost.

There have been many soil tests developed to predict how much P will be lost in relation to the amount of P which is available. There are however, many factors that affect the availability of P within the soil to runoff water. Many of the soil tests do not take into account these factors and thus accurate estimates of P loss are not always achieved.

2.4.1 Weathering of native P

All soils have varying amounts of native P, therefore the amount of native P and its rate of weathering can have an affect on the amount of P lost to runoff. The major effect on the amount of weathering is the influence of environmental factors. These include rock type, particle size, temperature and water quality. The rate of chemical weathering shows a positive correlation with the volume of catchment runoff. Dethier (1986) found that where rainfall and runoff was high, the rate of weathering was approximately ten times greater than where runoff was low. Thus, in catchments with a high rate of water throughput, a relatively high rate of P release through weathering might be anticipated (Heathwaite 1997). However, with respect to eutrophication it is the P concentration in runoff water which is important, and if there is a larger volume of runoff it will also mean that the concentration may not increase and will therefore not be an issue of concern.

2.4.2 Erosion

The majority of the P in surface waters that is available to aquatic biota is in the form of DP. However, PP also plays a role in contributing to increased growth of aquatic biota and thus the rate of its loss will have an effect on eutrophication (Sharpley and Rekolainen 1997). Most particulate P is lost from cultivated land, but there is some loss of PP due to erosion, from grassland and forest land. Another source of P which is not always considered, is stream bank erosion. The majority of New Zealand is in pasture or forest so PP losses are generally not of concern. However, in such situations stream bank erosion may provide the major source of sediment in runoff water. In areas such as the East Coast, where erosion is more of a problem losses of PP are an issue of relevance.

2.4.3 Soil type

Retention / fixation of P does not occur to the same extent on all soils, therefore the type of soil plays a major role in determining how much P is potentially able to be lost. Since the adsorption component of the fixation process is associated with the clay and hydrous oxide fractions it follows that P retention will be greater in soils of higher clay content (Brady 1990). In contrast, soils in which inorganic colloids are absent or essentially absent, retain little P (Morgan 1997). The same applies to soils that are predominantly sandy in nature. The presence of kaolinite and calcite increase P retention, the latter more so when it contains a high proportion of iron oxide impurities (Tisdale *et al.* 1985). In general, P retention is at a minimum where soil pH is between 6.0 and 6.5 (Morgan 1997).

The net effect of the presence of organic matter is difficult to assess. Whereas iron and aluminium hydroxy humic complexes have been shown capable of adsorbing P (Wild 1950), organic acid-induced desorption of P from kaolinite and iron/aluminium oxides has also been reported (Nagarajah *et al.* 1970).

2.4.4 Slope length and angle

Work carried out by Ahuja *et al.* (1982) found that the length and degree of angle of slope had an effect on the amount of P that was lost from soil to runoff. It was found that an increase in the slope length produced an increase in DRP concentration in the runoff. Most of the effect of the increase in DRP concentration with increased slope length could be explained by the water to soil ratio which is decreased (as slope length increases more sediment enters the water) and this influences the kinetics of desorption.

Similarly, it was found that an increase in the angle of the slope produced an increase in the DRP concentration measured in the runoff. This was explained by the increased depth of rainfall interaction which increases the amount of P able to be lost.

2.4.5 Duration of runoff event

An investigation by Sharpley *et al.* (1981) into the release of soil phosphorus in relation to the kinetics of desorption found that the DRP concentration in runoff decreased as the period of the runoff event increased. This would be expected due to the most readily available P being removed from the soil early in the runoff event. As time increases only the more tightly fixed P will be left; thus the DRP concentration will decrease.

2.4.6 Temperature

It was found by Barrow (1979), that an increase in soil temperature increased the amount of P in soil solution and thus increased the amount of P that was available for release to runoff. This was explained by the fact that the position of the equilibrium between solution phosphate and adsorbed phosphate moves towards the solution P as the temperature increases. Also, as soil temperature increases, the rate of mineralisation of organic matter also increases releasing more P to the soil solution. Thus it would be expected that as the soil temperature increased throughout the spring and summer, that the potential for loss of P from soil via surface runoff may also increase.

2.4.7 Surface cover and characteristics

The nature of the surface cover and the shape of the surface soil have been found to have an effect on the amount of P lost from soil to runoff. In work carried out by Ahuja *et al.* (1982), and Ahuja *et al.* (1983) it was found that an increase in surface vegetation cover such as vegetation decreased the DRP concentration in surface runoff. This was explained by increased surface cover decreasing the velocity of the raindrops and therefore reducing the depth of the rainfall-soil interaction. In contrast when there was an increase in the amount of ridges and clods on the surface of the soil the concentration of DRP in runoff increased. This was thought to be a direct result of the increased soil and water interaction caused by increased turbulence due to an increase in macropores.

2.4.8 Soil moisture

In an investigation on the chemical composition and ionic strength of soil solutions from New Zealand topsoils by Edmeades *et al.* (1985), it was found that soil moisture content played a major role in the concentration of ions in soil solution. The study investigated several macronutrients- calcium, magnesium, potassium, sodium, ammonium and nitrate, and found that the concentration of the ions increased as soil moisture content decreased. Although phosphate was not investigated in this study it is possible that the same effect occurs. As in the case of temperature, a decrease in moisture can also mean that the cell walls of plant material are broken down and subsequently some of the P within them can become available to runoff water. If this is the case then it is likely that, as the soil moisture decreases over spring and summer, there will be an increase in the P concentration in soil solution and thus an increase in the potential for P loss. This theory is supported by the results of Cooke (1988) who found an increase in the DRP concentration in runoff over the summer months.

2.5 Subsurface loss of P

Phosphorus transport via subsurface pathways is far less well documented than that in relation to surface runoff. This may be a result of both the difficulty in measurement and the general assumption that this pathway is quantitatively less important than surface delivery. In fact, for a long time it was assumed that little or no P was lost via subsurface flow, due to the fact that P is relatively well retained by soils. It was also assumed that if any was lost then it would be in such small quantities and concentrations that it would not have a major effect on eutrophication. It is however, now known that only very small concentrations of dissolved P are required to cause accelerated growth of aquatic biota and cause problems.

Most subsurface transport of P is assumed to be in the soluble fraction, where typical concentrations of soluble P percolating through soil are of the order of 0.1 mg l^{-1} orthophosphate, even where surface soil P concentrations are high (Withers 1994). Recent research suggests that other P fractions may also be transported via this pathway (Dils and Heathwaite 1996). For example, for a single storm event it was found that the soluble inorganic fraction in the subsurface and near-surface flow formed only 10 % of the total P export in the subsurface flow for both undrained and tile drained plots. Particulate P formed the bulk of total P mobilised for this event.

For subsurface pathways, the link between land use and P export is less clearly defined than that for surface runoff. Below the ground surface, soil characteristics and P transformations along flow pathways become relatively more important in characterising P loss. Transformations include readsorption of dissolved P by soil particles (Sharpley *et al.* 1982) and are part of the dynamic and labile nature of certain P fractions (Heathwaite 1997).

Soil characteristics are also important in defining the rate of water movement through soil pores and in indicating potential for chemical and biological modification of the P load. For example, sandy and peaty soils may have a high leaching potential with regard to P, owing to minimal retention through adsorption, a process which is important in soils with a higher clay content. Research also suggests that organic P compounds may be more readily transported through the soil relative to inorganic P, but this may be soil specific, for example, in peaty soils (Williams and Edwards 1993).

Soil structure will influence P fractionation through its indirect control of the length of contact time between percolating water, soil water, and soil particles. In this context, macropores, which exist in structured soils or develop through cracking during dry periods, enable rapid bypass through the soil. This will reduce the contact time between soil and percolating water. There is evidence to suggest that water moving through soil fissures may show elevated P concentrations (Dils and Heathwaite 1996, Sharpley and Rekolainen 1997). Bypass or macropore flow will probably transport P in a form similar to that recorded in surface runoff, however, it does not require the high rainfall intensity and duration events characteristic of overland flow conditions. Thus P may be transported by macropore flow in relatively small storm events. Similar arguments exist for artificial drainage pipes, which act effectively as large, more or less permanent, macropores in the soil (Heathwaite 1997).

An investigation by Heckrath *et al.* (1995) of the relationship between Olsen P in the surface soil and P concentrations in subsurface water was carried out on the Broadbalk experiment in Rothamsted. The Broadbalk experiment is a continuous wheat experiment where for more than 150 years either no P, or P in the form of farmyard manure, or inorganic fertiliser has been applied. There is therefore a range of Olsen P values in the plow layer (0-230 mm) of 5-100 mg kg^{-1} soil. The investigation found that a simple linear split-line model described the relationship very well for all drainage events. It was found that up to an Olsen value of 60 (the change point) P was retained strongly in the plow layer. Above this value P losses in the drainage water were much higher and closely related to the level of Olsen P. The data therefore suggested that P loss in drainage water will be minimal up to a certain Olsen P value above which losses can rapidly increase.

2.6 Reducing P losses from non-point sources

It is accepted that it is neither feasible nor economic to control all non point sources of P. However it is possible through some land management practices to reduce the load of P in surface waters. Management essentially needs to focus on identifying 'hot spots' where P loss is likely to be greatest, and targeting these areas for reductions (Heathwaite 1997).

There are essentially two ways to approach the management of P loss from agricultural land. These are through either source management which involves managing soil P inputs and outputs, or through transport management, which involves controlling the movement of P in runoff water. If possible it is more logical to try and fix the problem from the source rather than trying to minimise the effects once the P has entered the runoff water. Source management is more likely to provide a better soil P management strategy whereby soil P levels will not exceed levels required for optimum crop production. Source management also has the potential to reduce the loss of P via subsurface drainage, which transport management techniques are less able to achieve.

2.6.1 Source management

Source management involves targeting soil susceptible to P loss, and using soil tests based on environmental rather than agronomic considerations to determine P application and suitable application methods. Environmental concern has forced many countries and States in the USA to consider the development of recommendations for P applications and catchment management based on the potential for P loss in runoff, as well as crop P requirements. A major difficulty in the development of these recommendations has been the identification of soil test P levels that are high enough to raise concerns about the potential for unacceptable levels of P loss in runoff.

Establishing these levels is often a highly controversial process, for two reasons. First, the database relating soil test P to runoff P is limited to a few soils and crops and there is often a reluctance to rely upon data of this type generated in other regions, due to variations in P loss between different soil types (Brady 1990). Second, the economic implications of establishing soil test P limits which may limit fertiliser and manure applications are significant. In many overseas areas, dominated by animal based agriculture, there simply is no economically viable alternative to land application of manure. Likewise, most of New Zealand's pastoral agriculture is reliant on inputs of fertiliser to make it economically viable. A lot of New Zealand's hill pasture would grow very little grass without fertiliser inputs and present production levels would eventually become unsustainable.

Once soil P limits, at which there is a risk of P loss at an unacceptably high level, have been reached, there is a need to reduce or omit further P applications by either fertiliser or manure so that further losses of P will be reduced. There may however, be only a limited time period over which P applications can be omitted on soils with high soil test P without affecting yield. Withers *et al.* (1994) found that after three years of withholding P-fertiliser on P rich calcareous soils in England, crop yields of cereals were significantly reduced. It may therefore be more appropriate to reduce P application rates on certain soils rather than omit P altogether. Small amounts of placed starter fertiliser for vegetable cover crops have reduced the need for much larger P applications being broadcast (Costigan 1988) and a similar strategy may be appropriate for other crops. This then raises the issue of the method of application of P fertiliser and manure. If fertiliser and manure is applied in split dressings it will reduce the likelihood of large losses of P if a large runoff event occurs directly after P application. Applying P at times of the year when there is a reduced risk of a large runoff event occurring will also minimise losses of P.

2.6.2 Transport management

Transport management involves minimising the amount of P-enriched surface runoff reaching surface waters, and reducing loss of particulate P through erosion. In many grassland catchments, livestock are often grazed on riparian land owing to its proximity to watering sites and the unsuitability of such land for other uses unless it is drained. Where this is the case, there is virtually no buffer between the land and the stream. This means that little transformation or trapping of P exported from the land is possible before it enters the stream. Runoff from grazed riparian areas may contain high concentrations of P in various fractions, especially around feeding and watering areas (Dils and Heathwaite 1996). Consequently riparian land needs to be managed carefully to control P losses. Heathwaite (1997) recommends using a 10 m wide buffer strip between agricultural land and adjacent water courses. The success of this approach depends on the mechanisms by which P is transported from land to stream (Muscutt *et al.* 1993). If the major P fraction is particulate, or at least surface runoff derived, buffer zones need to trap and retain sediment associated P. In this case, factors such as the roughness coefficient of the vegetation in the buffer zone are critical. Vegetation characteristics will vary seasonally and it will be important to coincide maximum vegetation trapping efficiency with the main periods of P export. Unfortunately, P export in surface runoff will primarily be associated with periods of high rainfall, commonly in winter months. This coincides with periods where vegetation cover and trapping efficiency may be least.

Other practices that can be implemented to try and reduce P loss and are mainly relevant to cropping, include, contour cropping which involves planting crops against the slope to try and trap runoff, the formation of terraces, and conservation tillage. Forming terraces are an expensive option to begin with, however, they have been shown to be effective at reducing P loss (Sharpley and Rekolainen 1997). Conservation tillage also has the potential to increase DP and BAP losses compared to conventional tillage, due to the accumulation of crop residues and added P at the soil surface which provide a source of P to runoff (Sharpley and Smith 1994). This option therefore is not always successful. These practices however, are generally more efficient at reducing PP than DP. They therefore only trap and remove a small portion of the total P which is entering surface waters (Sharpley and Rekolainen 1997). Transport reduction options are therefore only minimal and their success and applicability in many areas is questionable.

2.7 Conclusions

Eutrophication is therefore a problem which is being faced by not only New Zealand, but many other countries throughout the world. Phosphorus is the major limiting nutrient involved in eutrophication and as point sources are being reduced, particular attention is being focused towards non-point sources of P. As most of New Zealand's agriculture is pastorally based and relies on inputs of P fertiliser to sustain production, the relative effects of fertiliser and the farming system on P concentrations in runoff is of particular concern.

There are a number of tests available for measuring the P content in surface waters, however, the most relevant is the bioavailable P test which measures the amount of P available to aquatic organisms. Much work has been carried out investigating the ability of many P soil tests to predict the amount of P in runoff water. For individual circumstances many of these tests provide relatively good estimates of the amount of P that is likely to be lost via runoff. However many of the studies have shown that it is not only the soil test P level that affects runoff P concentrations but a combination of several factors to do with soil type and climatic conditions.

Of the methods available for control and minimisation of non-point sources of P, relatively few are of relevance to the New Zealand farming situation. Most of the methods are only effective at removing PP and as most of New Zealand agriculture is pastorally based the major losses of P are in the form of DP rather than PP. Further options therefore need to be investigated.

CHAPTER 3

3.1 Introduction

The amount of phosphate entering water ways is an area of concern for farmers, councils and the public as a whole in relation to its effect on accelerating eutrophication of surface waters. Of particular interest is the amount of phosphorus entering water-ways from surface runoff and subsurface flow. There exist a number of tests which measure the phosphate content in water, including the bioavailable phosphate test (BAP), particulate phosphate (PP), dissolved reactive phosphate (DRP), and total phosphate (TP). This study chose to use the DRP test to analyse the amount of P in the simulated surface runoff and subsurface flow generated on four sites of varying aspect and soil P content.

Simulated rainfall was applied to the four sites and surface runoff and subsurface flow data was collected over three runs carried out before fertiliser application, and on two occasions after fertiliser application. The concentrations of DRP in surface runoff and subsurface flow data are presented and compared in this chapter.

3.2 Materials and Methods

3.2.1 Site Description

The research was conducted on a fertiliser trial located in the Central Hawkes Bay in New Zealand. The trial is large scale (48 Ha) and located about 4 km west of the Waipawa township on dry, steep hill country. The trial site has an average rainfall of about 900 mm being wet in the winter and dry in the summer. The soil type is Waipawa silt loam (Rocky Recent soils). This averages about 60 cm in depth and overlies white argillite rock which is exposed on some ridges.

Soil moisture levels generally increase until July then decline before being recharged with autumn and winter rain. The ridges within the trial run east to west and therefore all of the aspects on the trial can be classified as northerly or southerly. The soil on the south aspects is at a higher gravimetric moisture content than that on north aspects at all times. The difference ranges from about 5 % in the summer (ie. 15 and 10 % respectively) to about 20 % in the winter (ie. 55 and 35 %).

The trial includes two phosphorus fertiliser regimes. The 'High P' regime operates on a soil Olsen P level of 28, while the 'Low P' operates on a soil Olsen P of 9 (paddock averages). The 'High P' paddocks had an application of 500 kg/ha of triple superphosphate (20 % P) applied in September 1994 to increase the Olsen levels to the desired operating level of 28.

3.2.2 Runoff Measurements

Four sites were chosen, consisting of two northerly faces and two southerly faces. One of each of the two north and south facing aspects had either a 'Low P' or a 'High P' fertiliser regime applied to it over a three year period. The four faces could then be classified as High P North (HPN), Low P North (LPN), High P South (HPS), and Low P South (LPS).

At each site 8 plots (2m×2m) were randomly located on 20° slopes. Preliminary work suggested that 20° was a suitable slope that allowed ease of access while still being steep enough to induce sufficient runoff and be classed as steep hill country. Soil samples were then taken from each plot and the Olsen P of the top 20mm was measured. Out of the 8 plots the three with Olsen P values furthermost from the mean value were omitted from the trial. On the remaining 5 plots at each site the modified "Amsterdam" rainfall simulator provided rainfall to a $0.55m^2$ area from a horizontal tray fitted with drippers and a mesh screen to fragment raindrops into realistic sizes (Bowyer-Bower and Burt, 1989). The $0.55m^2$ plot (1.09m ×0.5m with the plot length downslope) was formed on the upslope and both sides by metal walls driven into the soil surface. The downslope boundary was formed by a metal collecting trough extending the width of the plot and seated in a trench across the slope. The trough had a metal lip embedded 20mm below the soil surface into the upslope wall of the trench which was sealed to prevent subsurface leakage into the trough. On the southerly aspects a second trough was placed 80mm below the soil surface to catch subsurface water. Preliminary work showed that subsurface runoff could only be collected on the southerly aspects due to the soils on the northerly aspects being too dry and taking too long to wet up sufficiently for subsurface flow to occur.

At each runoff measurement site the main plot (measuring 2m×2m) was marked out and split into two subplots side by side running the full length of the main plot downslope. The runoff subplot was randomly selected and the other used for soil sampling in order to avoid affecting the hydrologic properties of the actual runoff plot by taking soil samples.

Simulated rainfall was applied to the plots at a rate of 50mm per hour for one hour. Surface runoff was collected every 5 minutes for the first 30minutes. Subsurface runoff was collected every 10 minutes for 60 minutes on the southerly slopes. Each water sample was analysed for dissolved reactive phosphate (DRP) content.

Surface runoff was measured in three different runs. Run 1 was at the start of June 1997. Superphosphate was then applied at a rate of 20kg P/Ha to all of the plots at the end of July. The fertiliser was sieved to a size less than 2mm and greater than 0.5mm to ensure that the fertiliser was spread evenly over the whole plot. Fertiliser was applied at the end of July. Run 2 was then carried out seven weeks after fertiliser application and Run 3 14 weeks after application.

3.2.3 Dissolved Reactive Phosphate analyses

Each runoff water sample was filtered through a Sartorius 0.45 micron cellulose acetate filter paper. A 20ml aliquot of filtrate was then pipetted into a 50ml volumetric flask and 10ml of Murphy and Riley solution (Murphy and Riley 1962) was added and the solution made up to volume with distilled water. The solutions were left for 30 minutes and analysed on a UV/visible spectrophotometer at 712nm.

3.2.4 Sequential water extractions

A 1g sample of soil was placed into a centrifuge tube and 20ml of distilled water was added to the soil and the mixture weighed. The mixture was then shaken on an end over end shaker for 30 minutes and centrifuged at 9000 rpm for 1 minute. The solution was decanted off and filtered under suction through a Watman No. 6 filter paper. A 4ml aliquot of the filtrate was placed into a 50 ml volumetric flask and 32 ml of water was added followed by 10 ml of Murphy and Riley solution (Murphy and Riley 1962). The solution was made to volume and left for 30 minutes before being read on a UV/visible spectrophotometer at 712 nm. Distilled water was then added to the remaining soil and water mixture in the centrifuge tube until it was at the original weight and the procedure was repeated until five sequential extractions were complete.

3.3 Results and Discussion

The results of the runoff experiment are presented below, firstly as a comparison between sites for each run and then as a comparison between runs for each site.

3.3.1 DRP concentrations in runoff for Runs 1,2 and 3

There was a general trend of decreasing DRP concentration with increasing time of collection (Figs 3.1, 3.2 & 3.3). This observation agrees with work carried out by Sharpley *et al.* (1981) who measured the DRP concentration in runoff at five minute intervals over a 30 minute period, as was the case in this study. The only two exceptions to this trend are the HPN site for Runs 2 and 3. In these two cases the concentration increased by 0.13 mg dm^{-3} and 0.33 mg dm^{-3} for Run 2 and Run 3 respectively.

In Run 1 (Fig 3.1) it appears that the magnitude of drop from the initial concentration to the final concentration was dependent on the maximum concentration recorded. The sites underwent declines of 0.70 mg dm^{-3}, 0.40 mg dm^{-3}, 0.33 mg dm^{-3} and 0.16 mg dm^{-3} for the HPN, LPN, HPS and LPS sites respectively. This trend however, was not followed in any of the other Runs with the drop in concentration being variable between all of the sites and Runs.

The average DRP concentrations in the runoff for Run 1 (Fig 3.1) show that the HPN slope had a maximum DRP concentration in the runoff of 1.32 mg dm^{-3} compared with 0.66 mg dm^{-3} for the HPS and LPN sites, and 0.28 mg dm^{-3} for the LPS site. This is a trend displayed throughout all of the Runs (Figs 3.1, 3.2 & 3.3), ie. the HPN site having the highest maximum DRP concentration, followed by the LPN site. The LPS and HPS sites had the lowest maximum DRP concentrations. This trend is backed up by the average flow weighted DRP concentrations (Table 3.1). These show that southerly aspects had the lowest DRP concentrations, the one minor exception being the HPS site which had an average flow weighted DRP concentration of 0.39 mg dm^{-3} compared to 0.37 mg dm^{-3} for the LPN site in Run 1. The overriding theme then, appears to be that aspect was at least as important as fertiliser history in determining P loss in runoff.

Of particular note in these results (Figs. 3.1, 3.2 & 3.3) is the behaviour of the HPS site. In Run 1 the HPS site produced results very similar to the LPN site. After the application of fertiliser between Run 1 and 2, the HPS produced runoff which had a considerably lower maximum DRP concentration than the LPN site. This is supported in the average flow weighted data which shows that in Run 1 the HPS had an average of 0.39 mg dm^{-3} compared with 0.37 mg dm^{-3} for the LPN site. In Runs 2 and 3 though the comparisons are 0.25 mg dm^{-3} and 1.12 mg dm^{-3} for the HPS site versus 0.79 mg dm^{-3} and 1.82 mg dm^{-3} for the LPN site.

Table 3.1 Average flow weighted DRP concentration (mg dm^{-3}) in surface runoff for Runs 1, 2 & 3.

Site	Run 1	Run 2	Run 3
LPN	0.37	0.79	1.82
HPN	1.05	1.13	3.29
LPS	0.20	0.25	1.03
HPS	0.39	0.25	1.12

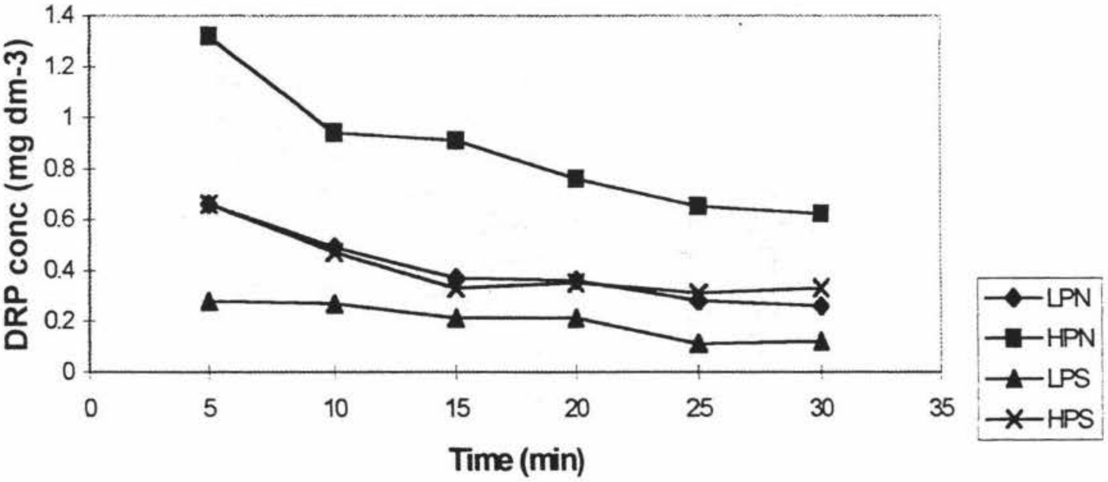

Fig 3.1 Average DRP concentration in runoff over time for Run 1

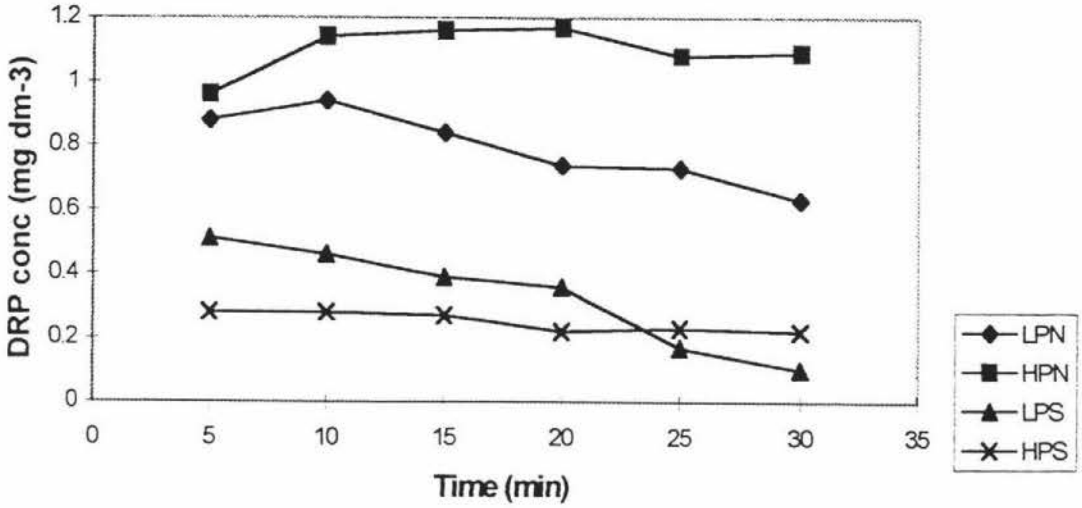

Fig 3.2 Average DRP concentration in runoff over time for Run 2

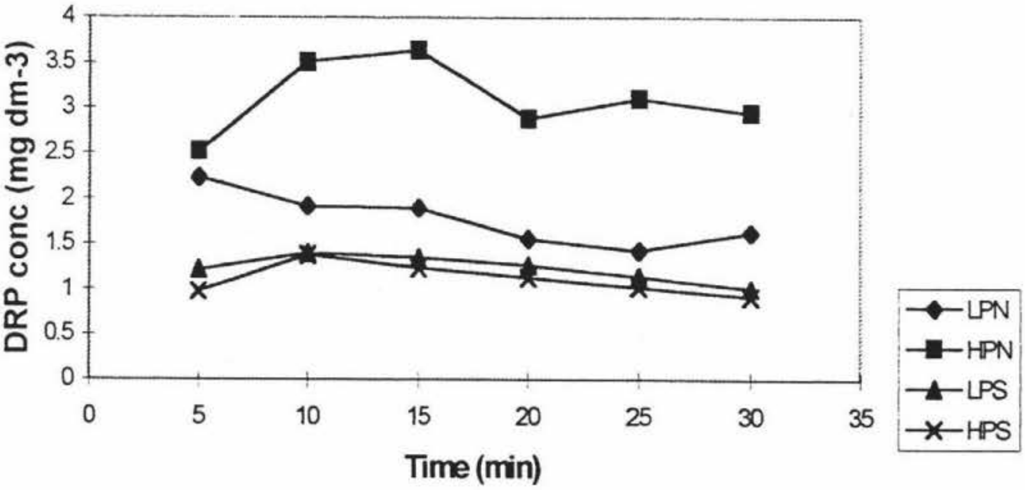

Fig 3.3 Average DRP concentration in runoff over time for Run 3

3.3.2 DRP concentrations in subsurface flow for Runs 1, 2 & 3.

A complete set of data was not able to be obtained in Run 1 (Fig 3.4) due to low flow volumes throughout the whole sampling period. Samples were collected for 40 minutes on the LPS sites and 50 minutes on the HPS sites. The time of collection started when subsurface flow first occurred in sufficient volumes for collection and ended after 60 minutes of rainfall. The time plotted in Fig 3.4 represents the time from when subsurface runoff collection commenced rather than the rainfall period.

There was a general trend similar to that found in the surface runoff (Figs. 3.1, 3.2 & 3.3) of an overall decrease in DRP concentration as time of collection increased (Figs. 3.4, 3.5 & 3.6). The only exception to this was the LPS site in run 1 (Fig 3.4). DRP concentrations from the LPS site underwent an overall increase of 0.03 mg dm^{-3}, however, the collection time for this site was only 40 minutes and the data set is not complete.

There does not seem to be any real pattern as to which site produced the higher DRP concentrations in the subsurface flow. In Runs 1 and 2 the LPS site produced the higher maximum DRP values, whereas in Run 3 the HP site produced the highest maximum DRP value. This is supported by the average flow weighted DRP concentrations (Table 3.2).

The DRP concentrations recorded all lie within values found by Heckrath *et al.* (1995) who measured DRP concentrations in tile drains under continually cropped wheat fields.

Table 3.2 Average flow weighted DRP concentration (mg dm^{-3}) in subsurface flow.

Site	Run 1	Run 2	Run 3
LP	0.22	0.24	0.54
HP	0.18	0.13	0.74

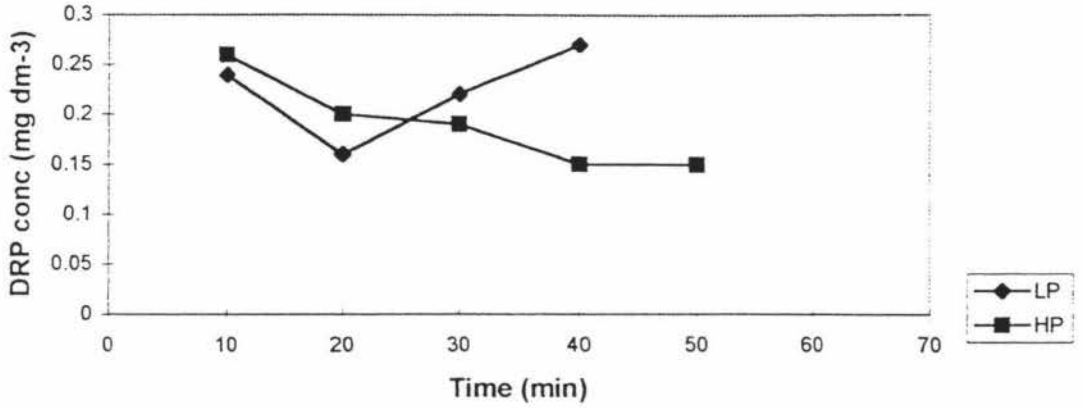

Fig 3.4 Average DRP concentration in subsurface flow over time for Run 1

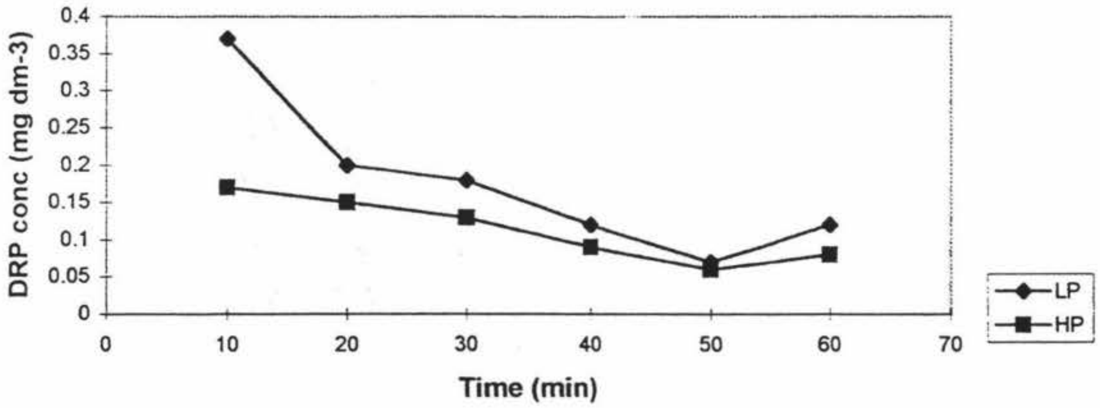

Fig 3.5 Average DRP concentration in subsurface flow over time for Run 2

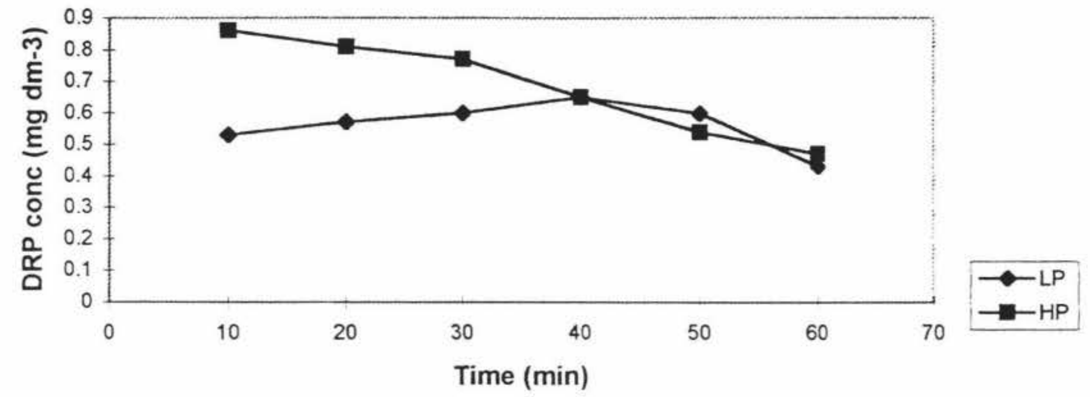

Fig 3.6 Average DRP concentration in subsurface flow over time for Run 3

3.3.3 DRP concentrations in surface runoff from the LPN, HPN, LPS and HPS sites.

Comparison between Runs for each site (Figs. 3.7, 3.8, 3.9 & 3.10) revealed a general trend for DRP values at each site to increase with each successive Run. The exceptions to this are the HPN and HPS sites where runoff DRP concentrations decreased between Run1 and 2. In the case of the HPN site however, the decrease was small and in fact the average flow weighted DRP values (Table 3.1) showed an increase in average DRP values between Run 1 and 2 for this site.

The main point of note at all sites (Figs. 3.7, 3.8, 3.9 & 3.10) is that Run 3 produced the highest maximum DRP values by a considerable margin. The average flow weighted DRP values (Table 3.1) in Run 3 were approximately three times higher than the next highest value for nearly all of the sites. It would have been expected after the application of fertiliser between Runs 1 and 2, that the average flow weighted DRP concentrations would have increased, as was the case for the LPN, HPN and LPS sites (Table 3.1). It was not expected though, that there would be a further significant increase between Runs 2 and 3. This would tend to suggest that there was some factor other than fertiliser application overriding the amount of P which is being lost from the soil to the runoff.

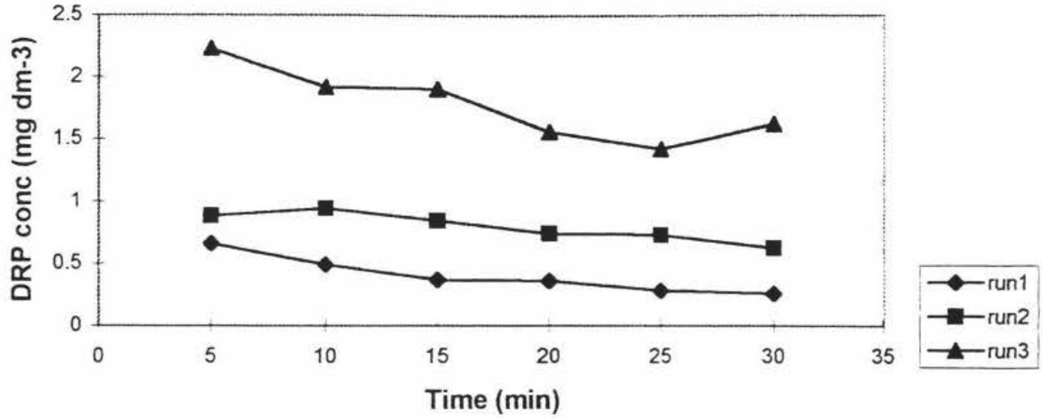

Fig 3.7 Average DRP concentration in runoff over time for LPN

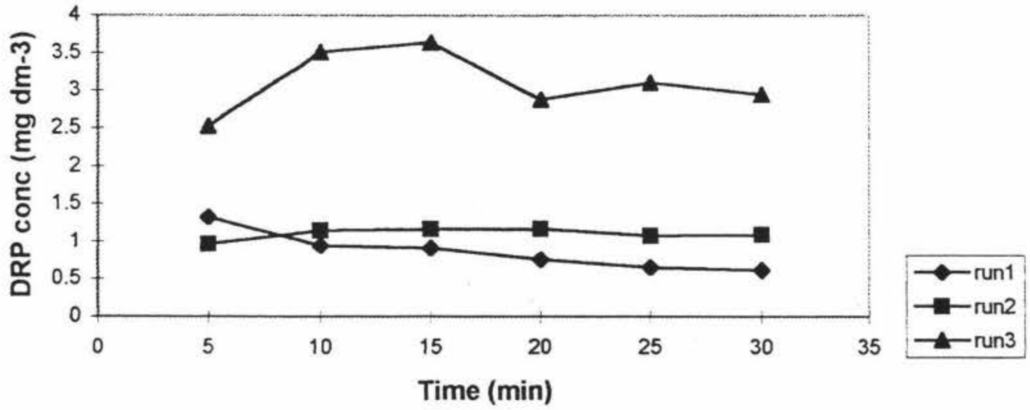

Fig 3.8 Average DRP concentration in runoff over time for HPN

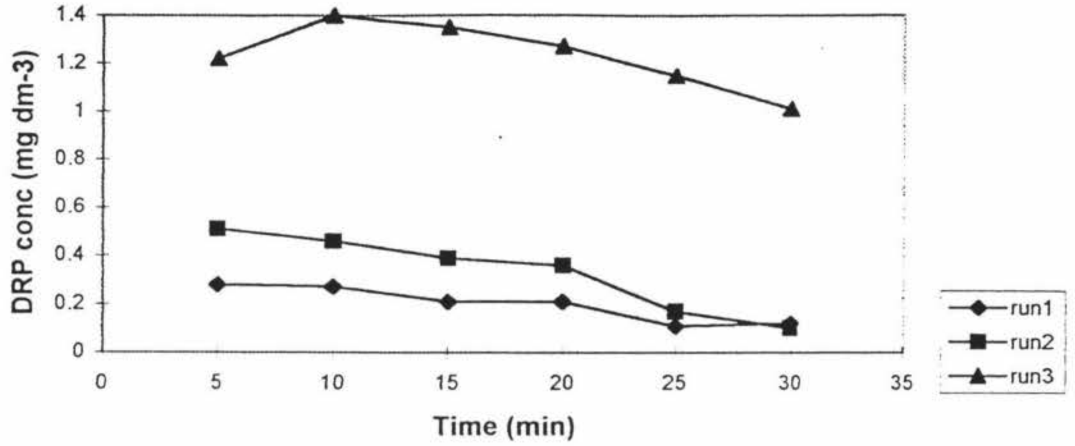

Fig 3.9 Average DRP concentration in runoff over time for LPS

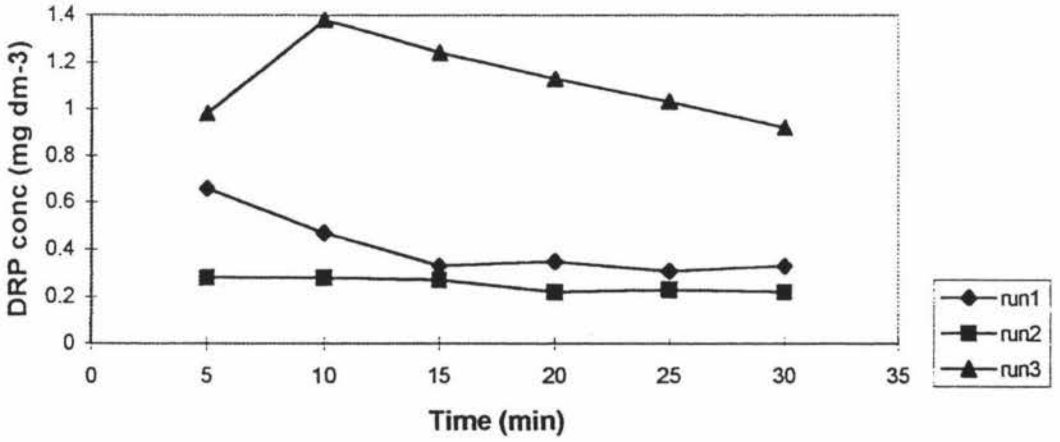

Fig 3.10 Average DRP concentration in runoff over time for HPS

3.3.4 DRP concentration in subsurface flow for the LP and HP sites

The subsurface flow results (Figs 3.11 & 3.12) showed a similar trend to that for the surface runoff results, with Run 3 producing higher DRP concentrations than Runs 1 and 2. The pattern in the HP site is the same as the pattern for the surface runoff results on that site. Both sets of data (Figs. 3.10 & 3.12) show that there was a decrease in maximum DRP values between Runs 1 and 2 which then increased for Run 3. The results for the LP site (Fig. 3.11) illustrate how, due to the incomplete nature of the data set in Run 1 it is more difficult to comment on the variation between Run 1 and 2. It can be seen that in both Run 1 and Run 3 the DRP concentrations increased up to the 40 minute mark. Thereafter though, concentrations in Run 3 decreased to produce an overall decrease in the DRP concentration from the initial to the final concentration. The main point of note however, is that for both the LP and HP sites there was a major increase in DRP concentrations between Run 2 and 3.

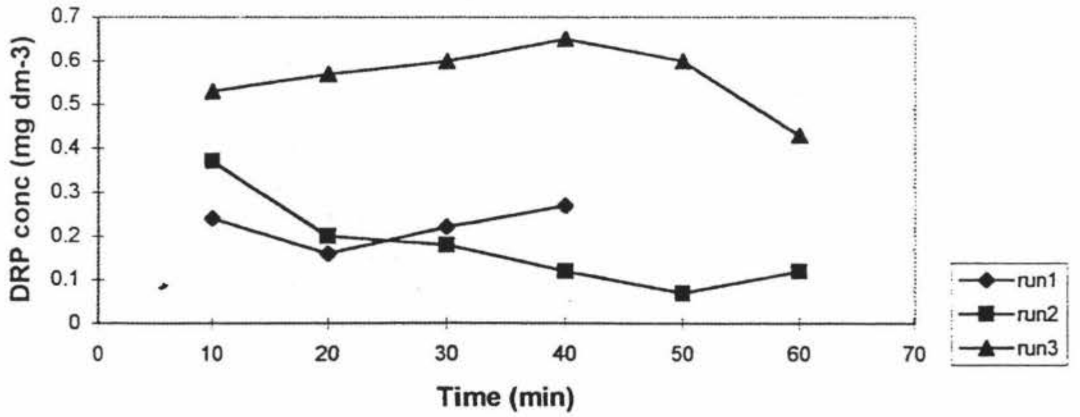

Fig 3.11 Average DRP concentration in subsurface flow over time for LP

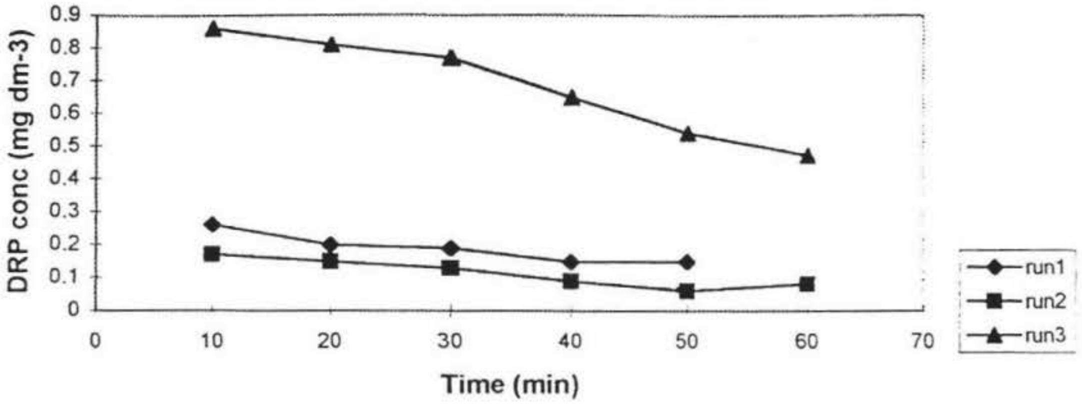

Fig 3.12 Average DRP concentration in subsurface flow over time for HP

3.3.5 Sequential extractions

A similar pattern to that found in the water runoff data (Figs. 3.1, 3.2 & 3.3) can be seen in the sequential water extractions (Figs 3.13 & 3.14). A drop in P concentration occurred as the number of extractions increased. This is similar to the drop in DRP concentrations as the time of runoff collection increased, recorded in the surface runoff results. It is also evident that the HPN site produced the highest P concentration, followed by the LPN site, with the HPS and LPS sites producing the lowest P concentrations. The exception to this was the HPS site in Run 1 which produced P concentrations similar to those from the LPN site. This same phenomenon was seen in the surface runoff for Run 1 (Fig 3.1). All of the sites showed an increase in P concentration in the sequential water extractions after fertiliser application. This was to be expected, however, it was not displayed by the HPN and HPS sites in the surface runoff data.

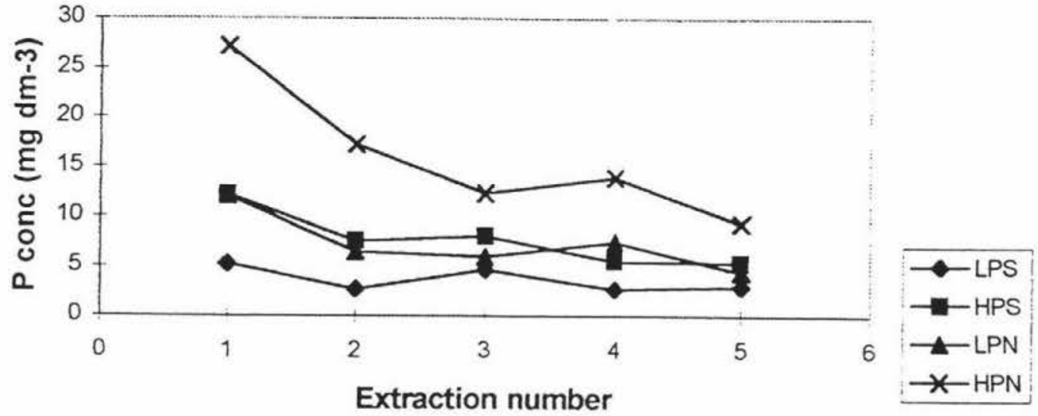

Fig 3.13 Water extractable P concentration vs. extraction number for sequential extractions before fertiliser application.

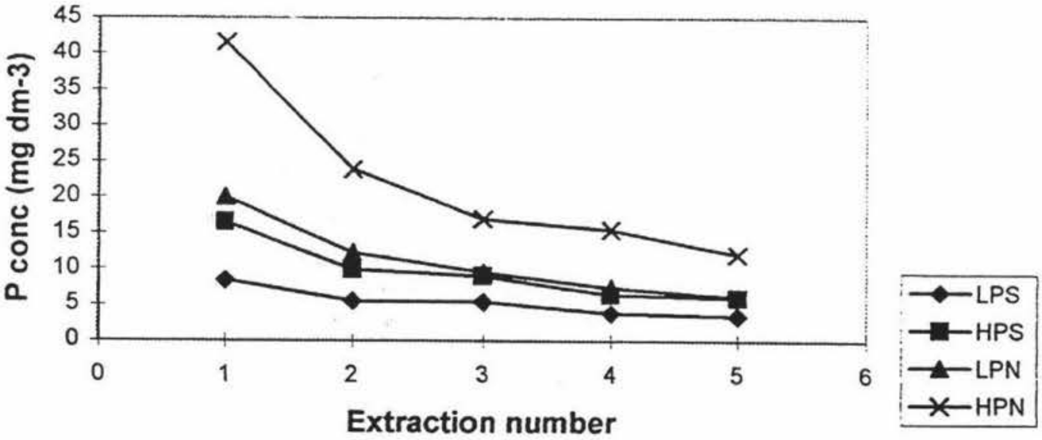

Fig 3.14 Water extractable P concentration vs. extraction number for sequential extractions after fertiliser application

3.4 Conclusion

It has been shown that the DRP concentration in the runoff decreased as the time of collection increased. The implications of this are that the shorter runoff events are likely to produce a higher average DRP concentration than runoff events of longer duration due to DRP concentrations being lower at the end of the longer events.

The HPN site produced the highest surface runoff DRP concentrations in all of the runs followed by the LPN site with the southerly sites producing the lowest surface runoff DRP concentrations. Aspect therefore seems to have a bearing on the amount of P that will be lost with the northerly aspects losing more P than the southerly aspects.

With the exception of the HPS site all of the sites experienced an increase in average flow weighted DRP concentrations in surface runoff between Run 1 and 2. This is to be expected as fertiliser was applied between these Runs. The surprising point however, was the major increase in DRP concentrations for all sites between Run 2 and 3. The increase was less for the southerly sites. This possibly suggests that there is some other factor overriding the fertiliser effect in determining how much P is being lost.

The subsurface flow results follow generally the same trend as the surface runoff results with a decrease in DRP concentration as the time of collection increased. There was however, no pattern as to which site produced the highest DRP concentrations for each Run. The results though, do show a major increase in DRP concentrations between Run 2 and 3, similar to that seen in the surface runoff results, indicating perhaps that the same factor is operating in the subsurface flow as is affecting the surface runoff P concentrations.

CHAPTER 4

4.1 Introduction

There are several factors that affect the amount of P which could be lost via surface runoff and subsurface flow. This study examines various soil factors which may relate to the amount of P loss in runoff and the soils reaction to fertiliser application over time.

Soil samples were collected at the time of each run and the Olsen P, water extractable P and soil moisture were measured. This chapter presents the results of these tests and attempts to analyse the effect of aspect and fertiliser application on these soil parameters.

4.2 Materials and Methods

4.2.1 Olsen P

A 1 gram (g) sample of soil was placed into a centrifuge tube and 20ml of 0.5M $NaHCO_3$ was added to the soil. The mixture was shaken on an end over end shaker for 30 minutes. The mixture was then centrifuged at 9000 rpm for 1 minute. The solution was decanted off and filtered under suction through a Watman No. 6 filter paper. A 4ml aliquot of the filtrate was then placed into a 50 ml volumetric flask. Thirty two ml of water was added followed by 10 ml of Murphy and Riley solution (Murphy and Riley 1962). The solution was then made to volume and left for 30 minutes before being read on a UV/visible spectrophotometer at 712 nm.

4.2.2 Phosphate Retention

A 5g sample of soil was weighed into a centrifuge tube, 25ml of P solution was added and then shaken in an end over end shaker for 16 hours. The tubes were then centrifuged at 8000 rpm for 5 minutes. A 2 ml aliquot of solution was pipetted into a 50ml volumetric flask and 12.5 ml of nitric-vanomolybdate reagent was added and the solution made to volume with distilled water. The solution was then left for 30 minutes and read on a UV/visible spectrophotometer at 420nm.

4.2.3 Water Extractable Phosphate

A 1g sample of soil was placed into a centrifuge tube and 20ml of distilled water was then added to the soil. The mixture was shaken on an end over end shaker for 30 minutes and centrifuged at 9000 rpm for 1 minute. The solution was then decanted off and filtered under suction through a Watman No. 6 filter paper. A 4ml aliquot of the filtrate was placed into a 50 ml volumetric flask and 32 ml of water added followed by 10 ml of Murphy and Riley solution (Murphy and Riley 1962). The solution was then made to volume and left for 30 minutes before being read on a UV/visible spectrophotometer at 712 nm.

4.2.4 Soil Moisture

Soil cores were taken from the measurement sites to a depth of 75mm. The soil was weighed and placed in an oven at 105°C over night. The soil was then weighed again and the gravimetric soil moisture content was calculated by the difference in weight.

4.3 Results and Discussion

4.3.1 Soil Moisture

The average soil moisture contents on each site for the three Runs (Table 4.1) show that the northerly sites had a lower moisture content than the southerly sites. For Run 1 the northerly sites had an average moisture content of 31.0 % with 48.5 % for the southerly sites. The difference in Run 2 was similar with 32.4 % with 51.7 % for the north and south aspects respectively. In Run 3 however the magnitude of the difference was much smaller with the northerly sites averaging 19.9 % as against the 24.4 % for the southerly sites. The overall trend was for a slight increase in the average soil moisture between Run 1 and Run 2 followed by a significant decrease between Run 2 and Run 3.

Table 4.1 Average soil moisture content (%) on each site at the time of the three Runs.

Site	Run1	Run2	Run3
LPN	30.7	32.4	18.9
LPS	46.2	47.2	23.9
HPN	31.3	32.3	19.9
HPS	50.7	56.1	24.8

4.3.2 P retention

Phosphorus retention in New Zealand soils may be divided into three classes: low (0-30 %), medium (31-85 %) and high (86-100 %) (McLaren and Cameron 1996). The soils on the northerly aspects fall in the low category while the soils on the southerly aspects fall in the medium category (Table 4.2). Although the P retention on both aspects is generally low (the southerly aspect soils are in the lower part of the medium category), the southerly aspects are likely to retain more P compared to the northerly sites, and consequently it might be expected that runoff P losses would be greater from the northerly sites than the southerly.

Table 4.2 P retention in the top 20 mm soil depth for the four sites

Site	LPN	HPN	LPS	HPS
Retention (%)	10.4	16.4	36.6	34.0

4.3.4 Olsen P to 80mm depth at Run 1.

The average soil Olsen P levels at 20 mm intervals to 80 mm depth for each site before fertiliser application are presented in Table 4.3. There is a significant difference in the Olsen P values at the 0-20 mm depth between the aspects with the same fertiliser treatments. The LPN site had an average Olsen P in the 0-20 mm interval of 27.5 mg dm^{-3} compared with 13.0 mg dm^{-3} for the LPS site. The LPN site also had a higher Olsen value at the 20-40 mm depth of 12.2 mg dm^{-3} versus 9.7 mg dm^{-3} for the LPS site. The difference was not apparent at depths below 40 mm, with similar Olsen values being recorded at both sites. The same phenomenon occurred on the High P treatment with the HPN site having an Olsen value of 88.4 mg dm^{-3} compared to 61.3 mg dm^{-3} for the HPS site at the 0-20 mm depth. This effect continued into the 20-40 mm depth with Olsen values of 45.3 mg dm^{-3} and 29.3 mg dm^{-3} for the HPN and HPS sites respectively. As in the Low P treatments the trend was not followed below the 40 mm depth with no major difference between the HPN and HPS sites.

The differences in Olsen soil test values between aspects are likely to be due to differences in the soil moisture content, (Table 4.1) as well as differences in P retention (Table 4.2).

Before the fertiliser trial started three years ago the Low P treatments and the High P treatments had the same Olsen P values. Therefore the differences in the Olsen P values have been achieved with the addition of fertiliser in the three year period. The major difference in the Olsen values between the treatments is likely to have been achieved with the initial application of 500 kg ha^{-1} of 20% P triple superphosphate to the High P treatment. The difference in soil Olsen P between the 'High P' and 'Low P' treatments is significant down to the 80 mm depth, with the High P treatment having approximately double the Olsen P value of the Low P treatment at both the 40-60 mm and the 60-80 mm depth intervals.

Table 4.3 Average Olsen P values (mg dm^{-3}) at 20 mm depth intervals for each site before fertiliser application.

Site	0-20 mm	20-40 mm	40-60 mm	60-80 mm
LPN	27.5	12.2	9.5	7.8
LPS	13.0	9.7	9.4	7.3
HPN	88.4	45.3	23.5	14.1
HPS	61.3	29.3	19.0	13.4

4.3.5 Olsen P changes in the 0-20 mm soil depth

All of the sites except for HPS, showed a similar increase in the Olsen P value (top 20 mm) between Run 1 and Run 2 (Table 4.4). This presumably resulted from the addition of fertiliser P at 20 kg P ha^{-1}. The LPN, LPS and HPN sites increased by 19.0 mg dm^{-3}, 24.0 mg dm^{-3} and 17.4 mg dm^{-3} respectively. The HPS site however, increased by only 7.2 mg dm^{-3}. All of the sites then showed a decrease in the Olsen P value between Run 2 and Run 3. It should be noted that the HPS site exhibited the lowest decrease (1.5 mg dm^{-3}) in Olsen values between these runs after having the lowest increase between Run 1 and Run 2. The decrease in the other sites was 16.9 mg dm^{-3}, 10.8 mg dm^{-3} and 30.2 mg dm^{-3} for the LPN, LPS and HPN sites respectively. This trend shown by all of the sites is similar to that reported by Gillingham *et al.* (1997) on a nearby trial site where an initial increase in Olsen P values after fertiliser application was followed by a decrease back towards the original value.

Table 4.4 Average Olsen P values (mg dm^{-3}) in the 0-20 mm soil depth for each Run.

Site	Run1	Run2	Run3
LPN	27.5	46.5	29.6
LPS	13.0	37.0	26.2
HPN	88.4	105.8	75.6
HPS	61.3	68.5	66.0

4.3.6 Water extractable P changes in the 0-20 mm soil depth

The average water extractable P in the top 20 mm for the three Runs (Table 4.5) increased between Run 1 and Run 2 at all of the sites. The LPN, LPS, HPN and HPS sites increased by 9.2 mg dm^{-3}, 2.7 mg dm^{-3}, 12.7 mg dm^{-3} and 4.2 mg dm^{-3} respectively. The increase in the amount of water extractable P on the northerly sites was markedly more than the increase on the southerly sites. Between Run 2 and Run 3 the water extractable P in the northerly sites decreased by 7.7 mg dm^{-3} and 11.4 mg dm^{-3} for the HP and LP treatments respectively. The southerly sites however increased by 1.4 mg dm^{-3} and 0.3 mg dm^{-3} for the LP and HP treatments respectively.

Table 4.5 Average water extractable P values (mg dm^{-3}) in the 0-20 mm soil depth for each Run.

Site	Run1	Run2	Run3
LPN	12.5	21.7	14.0
LPS	6.3	9.0	10.4
HPN	26.6	39.3	27.9
HPS	12.9	17.1	17.4

4.4 Conclusion

At the time of Runs 1 and 2 the southerly sites had much higher soil moisture levels than the northerly aspects (difference of 15-20 %). In Run 3 when the soil moistures were generally lower the difference between aspects was reduced (4-5 %).

The Olsen P changes in the 0-20 mm soil depth are consistent with what would have been expected with all of the sites undergoing an increase between Runs 1 and 2 due to the application of fertiliser, and then a subsequent decrease back towards the original value for Run 3. Of note however, is the difference in the Olsen values between aspects with the same fertiliser treatment (27.5 mg dm^{-3} and 13.0 mg dm^{-3} for the LPN and LPS sites respectively and 88.4 mg dm^{-3} and 61.3 mg dm^{-3} for the HPN and HPS sites respectively at Run 1). This can possibly be attributed to two factors, one is the difference in P retention between the aspects and the second is the difference in soil moisture between the aspects, which combined could cause the northerly aspects to have higher Olsen values than the southerly aspects.

The water extractable results follow largely the same pattern as the Olsen P results except that the southerly sites increase in water extractable P between Runs 2 and 3 while the northerly sites decrease. Of note is that while the Olsen P value for the HPS site at the time of Run 1 were considerably higher than for the LPN site, the water extractable P results at the same time were similar for the LPN site and the HPS site. In Run 2 the LPN results were in fact higher than the HPS site. The difference in P retention and soil moisture between the aspects is again likely to be related to the variation between the aspects.

CHAPTER 5

Correlation of runoff data with soil tests

5.1 Introduction

Results presented in previous sections show that there are indeed differences in DRP concentrations in runoff between the four sites, and between the three runs. The results also show that various soil properties vary between each site and each run. This chapter attempts to correlate the soil test data with the runoff data and explain what the main factors are that affect the amount of P that is lost from soil to surface waters.

5.2 Results and Discussion

5.2.1 Runoff DRP concentration in relation to Olsen P

The correlation between the flow weighted DRP concentrations in runoff and the Olsen P (top 20 mm) (Table 5.1) decreased with each Run. The correlation was relatively poor to begin with in Run 1 ($r = 0.72$) and decreased thereafter to $r = 0.43$ in Run 3. Apart from a decrease in the r^2 value, regression between Olsen values and DRP concentrations produced reasonably similar equations for Run 1 and Run2 except for a slight decrease in the Y intercept in Run 2 (Figs 5.1 & 5.2). This decrease is likely to have been caused by the HPS site which had a decrease in average DRP concentration in Run 2 although the Olsen P values had increased. It should be noted though that the increase in the Olsen P value due to fertiliser application between Run 1 and Run 2 at this site was the smallest of all the sites suggesting that there is some factor operating on this site that is not operating on the other sites.

The major point of note when comparing the three runs however, is the increase in the DRP concentrations for Run 3 (Table 5.2) at the same time as Olsen P values declined (Table 5.2). This resulted in a regression equation with a greater slope and higher Y intercept (Fig 5.3) than for Runs 1 and 2. This tends to suggest that there is a factor overriding the Olsen P values in determining how much P is being lost in surface runoff.

This concept can be further demonstrated by the comparison of Olsen P values and DRP values in Run 3 (Table 5.2). The LPN and LPS sites have similar Olsen P values of 29.6 mg dm^{-3} and 26.2 mg dm^{-3} respectively, yet they produced different DRP values of 1.82 mg dm^{-3} and 1.03 mg dm^{-3} respectively. The LPS and HPS sites produced similar DRP concentrations of 1.03 mg dm^{-3} and 1.12 mg dm^{-3} respectively, yet they have Olsen values of 26.2 mg dm^{-3} and 66.0 mg dm^{-3}. This can perhaps be partly explained by difference in P retention between the sites (Table 4.2) which would cause the southerly sites to retain more P than the northerly sites despite having similar Olsen P values. Although the difference in P retention between the aspects in agronomic terms is low (13.4 % vs 35.3 % for the northerly and southerly aspects respectively) it may be that it has major consequences on environmental processes- such as P loss in runoff. These data plus the overall correlation of Olsen P values and DRP concentrations for all three runs (Table 5.1) which showed a very poor correlation (r = 0.28). This suggests that the Olsen P value in the top 20 mm of soil is not a reliable way of estimating the amounts of DRP that can be lost in surface runoff.

Table 5.1 Correlation coefficients for Olsen P, water extractable P and soil moisture content with average flow weighted DRP values for each Run.

Site	Olsen P	Water extractable	Soil moisture
Run 1	0.72	0.80	-0.38
Run 2	0.60	0.80	-0.70
Run 3	0.45	0.71	-0.59
Combined data	0.28	0.44	-0.77

Table 5.2 Average Olsen P values and average flow weighted DRP concentrations in runoff for each site at each Run.

Site	Run 1		Run 2		Run 3	
	Average Olsen P (mg dm^{-3})	Average DRP conc (mg dm^{-3})	Average Olsen P (mg dm^{-3})	Average DRP conc (mg dm^{-3})	Average Olsen P (mg dm^{-3})	Average DRP conc (mg dm^{-3})
LPN	27.5	0.37	46.5	0.79	29.6	1.82
LPS	13.0	0.20	37.0	0.25	26.2	1.03
HPN	88.4	1.05	105.8	1.13	75.6	3.29
HPS	61.3	0.39	68.5	0.25	66.0	1.12

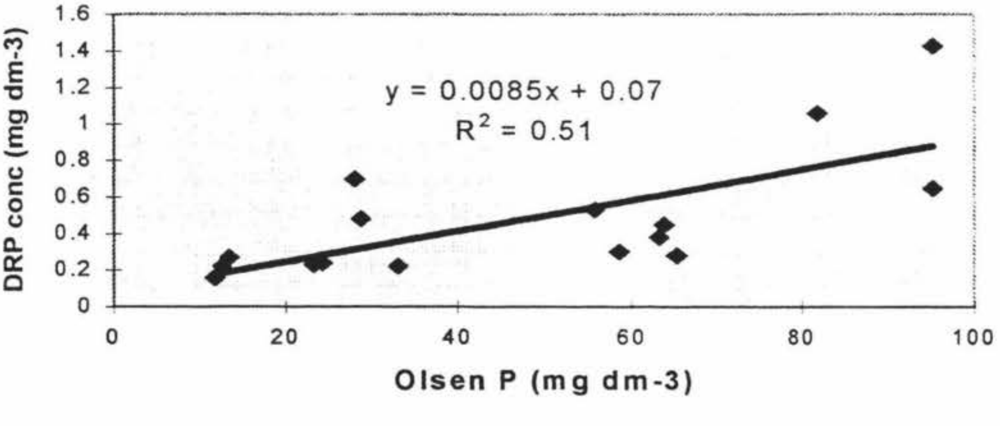

Fig 5.1 Average flow weighted DRP concentration in runoff vs. Olsen P in top 20 mm for Run 1.

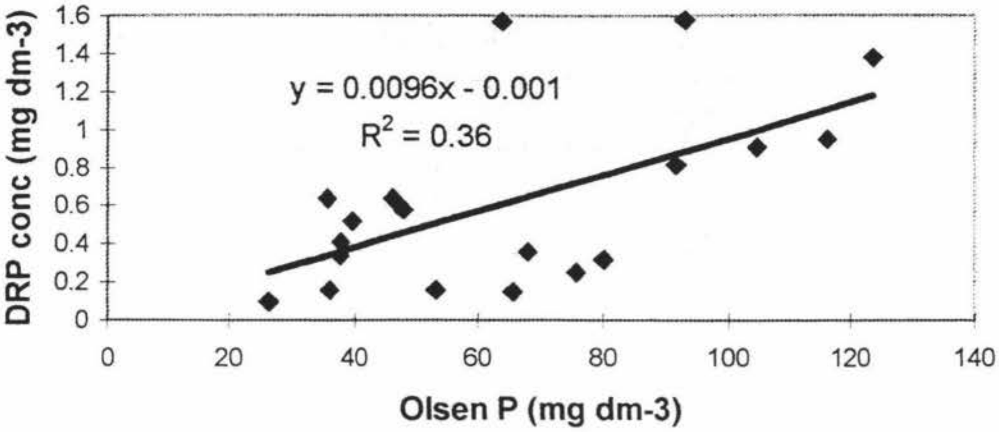

Fig 5.2 Average flow weighted DRP concentration in runoff vs. Olsen P in top 20 mm for Run 2.

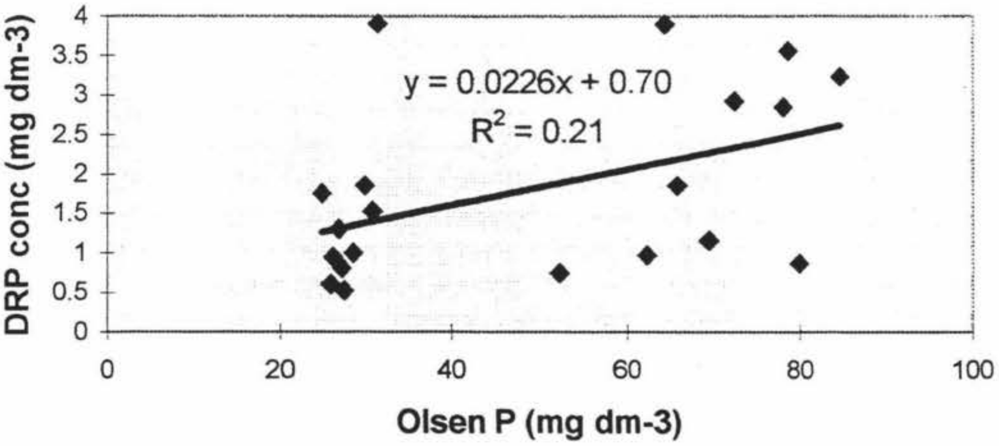

Fig 5.3 Average flow weighted DRP concentration in runoff vs. Olsen P in top 20 mm for Run 3

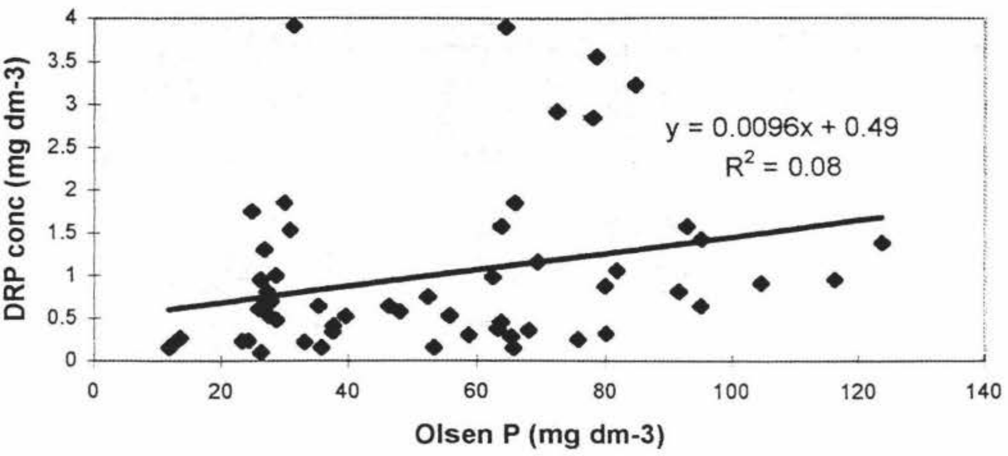

Fig 5.4 Average flow weighted DRP concentration in runoff vs. Olsen P in top 20 mm for all three runs.

5.2.2 Runoff DRP concentration in relation to water extractable P

The water extractable P test provided a better correlation with average flow weighted DRP concentrations than did Olsen P values (Table 5.1). The correlation between water extractable P and DRP concentration reached a maximum of r = 0.80 for Runs 1 and 2 and decreased to r = 0.71 for Run 3. This is similar to the results of Pote *et al.* (1996), who studied the correlation between a range of soil tests and DRP concentrations in surface runoff. In that study all of the tests provided better correlations (r > 0.85) than those found in this study, but the water extractable test was also found to correlate better than the Olsen test. This can also be seen in Table 5.3 where average water extractable P values and average flow weighted DRP concentrations relate well in Runs 1 and 2 (except for the HPS site in run 2). For example in Run 1 the LPN and HPS sites produce similar DRP concentrations. The Olsen P tests for the LPN and HPS sites vary greatly with values of 27.5 mg dm^{-3} and 61.3 mg dm^{-3} respectively. The water extractable tests however produced similar results of 12.5 mg dm^{-3} and 12.9 mg dm^{-3} for the LPN and HPS sites respectively.

As in the case of the Olsen P test, regression analysis produced similar equations for Runs 1 and 2 (Figs 5.5 & 5.6). However, Run 3 again produced DRP concentrations that were much higher than for Run 1 and 2 which lead to a regression equation with a greater slope (Fig 5.7) than for Runs 1 and 2 (Figs 5.5 & 5.6).

The major increase in DRP concentration for Run 3 appears to be independent of the water extractable P test. This can be seen by the northerly sites undergoing major decreases in water extractable P between Run 2 and Run 3 whilst the southerly sites had slight increases, yet the DRP concentrations for all sites increased substantially (Table 5.3). This different behaviour in Run 3 lead to the overall correlation between water extractable P and average flow weighted DRP concentrations in runoff (Table 5.3) being considerably less than the correlations for each individual run. Thus, while there appears to be a close relationship between the water extractable soil P and DRP concentrations in surface runoff at a given time, the same relationship cannot be used to predict DRP concentrations throughout the year.

Table 5.3 Average water extractable P values and average flow weighted DRP concentrations in runoff for each site at each Run.

	Run 1		Run 2		Run 3	
Site	Avg water extract P (mg dm^{-3})	Average DRP conc (mg dm^{-3})	Avg water extract P (mg dm^{-3})	Average DRP conc (mg dm^{-3})	Avg water extract P (mg dm^{-3})	Average DRP conc (mg dm^{-3})
LPN	12.5	0.37	21.7	0.79	14.0	1.82
LPS	6.3	0.20	9.0	0.25	10.4	1.03
HPN	26.6	1.05	39.3	1.13	27.9	3.29
HPS	12.9	0.39	17.1	0.25	17.4	1.12

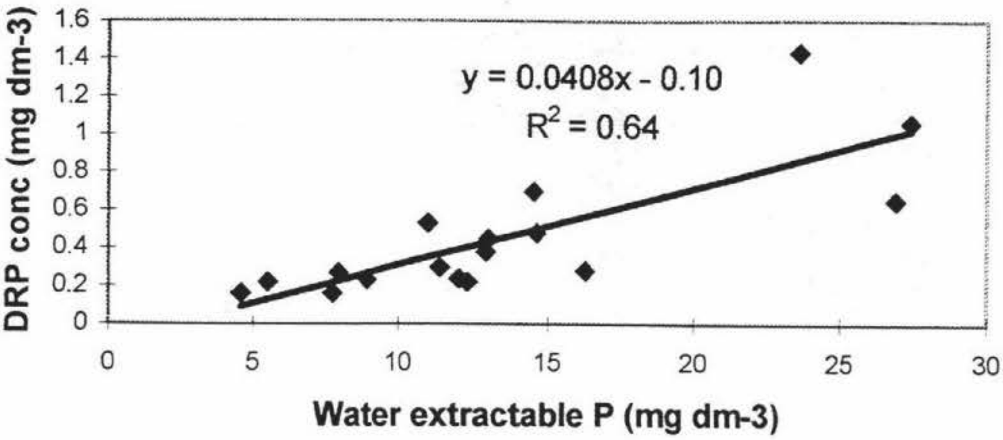

Fig 5.5 Average flow weighted DRP concentration in runoff water vs. water extractable P in the 0-20 mm soil depth for Run 1.

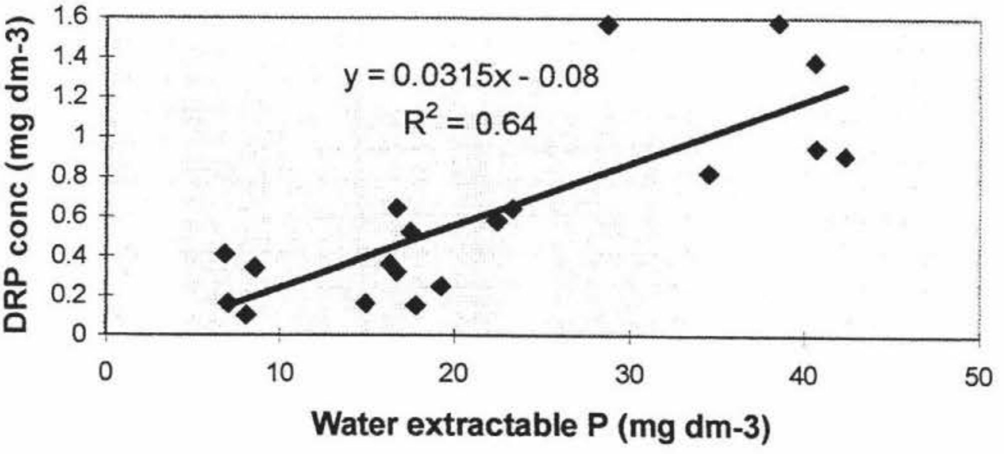

Fig 5.6 Average flow weighted DRP concentration in runoff water vs. water extractable P in the 0-20 mm soil depth for Run 2.

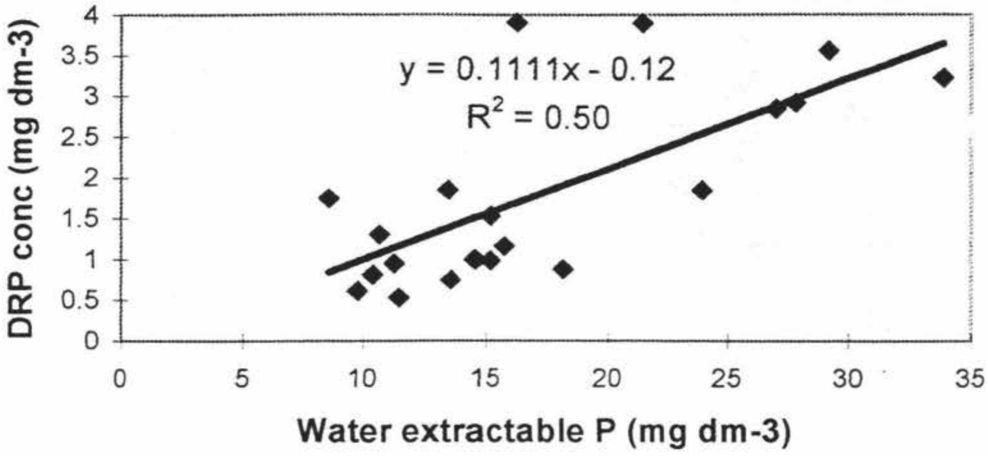

Fig 5.7 Average flow weighted DRP concentration in runoff water vs. water extractable P in the 0-20 mm soil depth for Run 3.

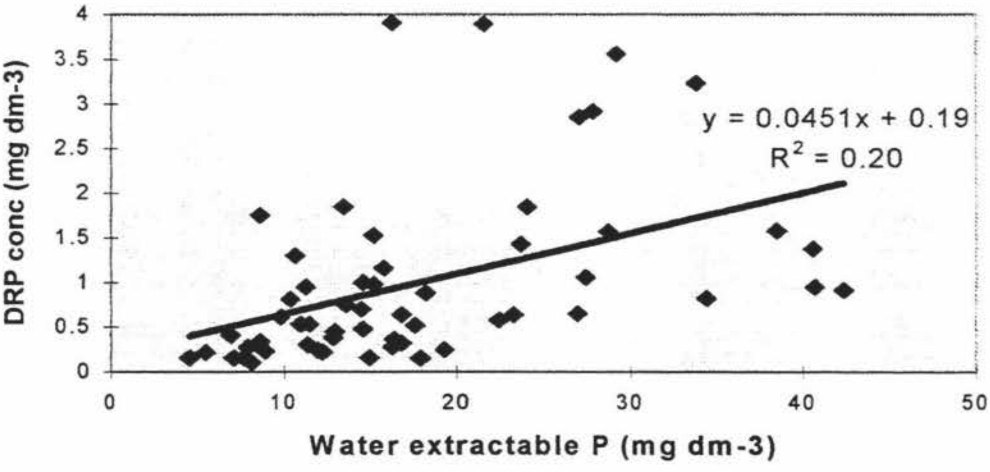

Fig 5.8 Average flow weighted DRP concentration in runoff vs. water extractable P in the 0-20 mm soil depth for all three runs.

5.2.3 Runoff DRP concentration in relation to soil moisture.

The correlations of average flow weighted DRP concentrations with soil moisture content for each run separately (Table 5.1) give negative r values that are all less (in absolute value) than those derived for water extractable P, but are similar to the values obtained in the correlation of Olsen P with DRP concentration. The lowest soil moisture correlation is in Run 1 ($r = -0.38$) and the highest value is in Run 2 ($r = -0.70$) before dropping again in Run 3 ($r = -0.59$). The major point of note however, is the overall correlation for all three runs combined ($r = -0.77$).

Although the correlation for each individual Run was low the overall correlation for all runs combined was much better than for either the Olsen or water extractable tests. This is further demonstrated in Table 4 where in Run 3 there is a major increase in the DRP concentration which is accompanied by a major drop in soil moisture for all of the sites.

This may explain why the Olsen P and water extractable P tests displayed no major increase between Runs 2 and 3, yet DRP concentrations increased dramatically. The soil moisture factor apparently overrides the soil P test effect when soil moistures reach low levels. This is also consistent with the northerly faces having lower soil moistures than the southerly faces for each run, whilst producing the highest DRP concentrations (except for HPS in Run 1). As mentioned earlier, P retention is likely to cause the southerly aspects to retain more P than the northerly aspects. This factor plus the moisture factor could combine to cause the northerly faces to produce runoff with a higher DRP concentration than the southerly aspects.

Increased DRP concentrations in runoff due to decreased soil moisture levels agrees with work carried out by Edmeades *et al.* (1985) who found that macronutrient concentrations increased in soil water as soil moisture decreased. Although P was not studied in that investigation it is possible that a similar phenomenon operates for P as for other macronutrients. A possible explanation for DRP concentrations increasing as soil moisture decreased, is that as the soil dries out P is mineralised and some of the P which would normally be locked up in cell structures in organic matter and soil micro-organisms is made available to the runoff water. This phenomenon could explain why there was no major difference in the soil test P concentrations between Run 2 and 3 yet there was a major increase in DRP concentrations. Before a soil is analysed it is dried and sieved to less than 2 mm particle size. This process essentially breaks down some of the organic matter and soil micro-organisms and some of the P within them is then available for analysis. The same effect could be taking place in the field when the soil moisture drops dramatically. Therefore the soil tests measure P that is not normally available to runoff water when the soil moistures are high, but does become available as soil moisture decreases. This explains the increase in slope of the regression line in Run 3 compared to Runs 1 and 2 for the water extractable P test (0.11, 0.03 and 0.04 for Runs 3, 2 and 1 respectively).

Another factor which could operate in conjunction with soil moisture to cause a major increase in the DRP concentration in Run 3 is soil temperature. At the time of Run 3 the soil temperature would have been much higher than it was at the time of Runs 1 and 2. Work carried out by Barrow (1979) found that as soil temperature increased the soil solution P concentration also increased. Therefore an increase in soil temperature which is going to coincide with a decrease in soil moisture is also likely to cause an increase in the DRP concentration of the runoff.

Table 5.4 Average soil moisture values and average flow weighted DRP concentrations in runoff for each site at each Run.

Site	Run 1		Run 2		Run 3	
	Avg Soil moisture (%)	Average DRP conc (mg dm^{-3})	Avg Soil moisture (%)	Average DRP conc (mg dm^{-3})	Avg Soil moisture (%)	Average DRP conc (mg dm^{-3})
LPN	30.7	0.37	32.4	0.79	18.9	1.82
LPS	46.2	0.20	47.2	0.25	23.9	1.03
HPN	31.3	1.05	32.3	1.13	19.9	3.29
HPS	50.7	0.39	56.1	0.25	24.8	1.12

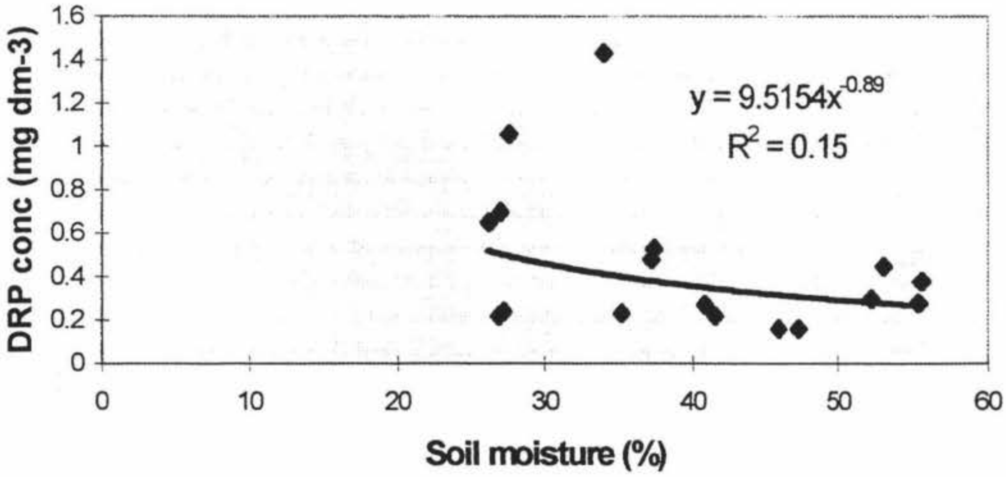

Fig 5.9 Average flow weighted DRP concentration in runoff vs. gravimetric soil moisture for Run 1.

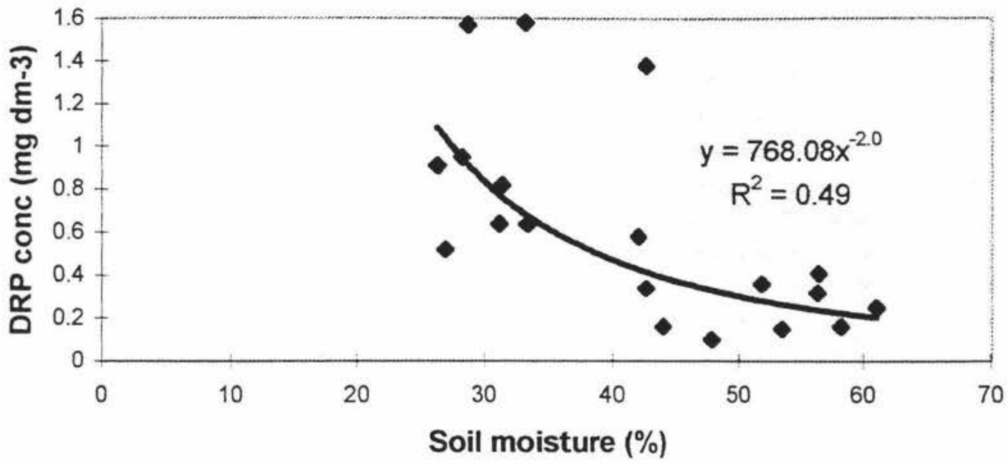

Fig 5.10 Average flow weighted DRP concentration in runoff vs. gravimetric soil moisture for Run 2.

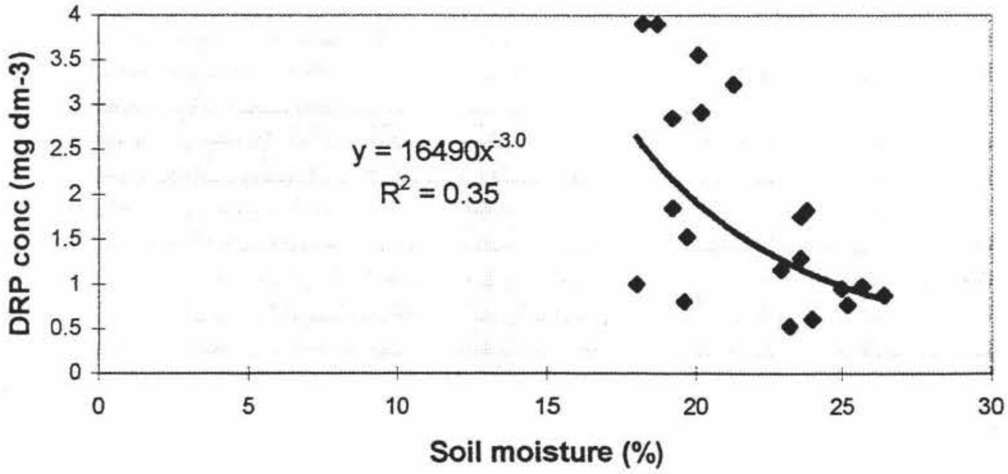

Fig 5.11 Average flow weighted DRP concentration in runoff vs. gravimetric soil moisture for Run 3.

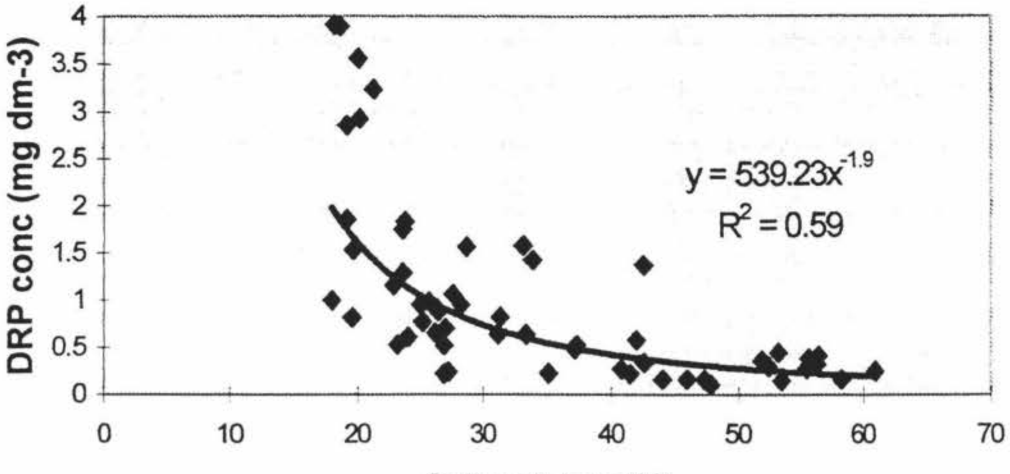

Fig 5.12 Average flow weighted DRP concentration in runoff vs. gravimetric soil moisture for all three Runs.

5.2.4 Subsurface flow in relation to Soil P.

It was assumed that the soil region in which the subsurface runoff samples were being collected from (20-80 mm) would only undergo very minor P concentration changes over the period of the study, due to fertiliser not being expected to have an influence below the 20 mm depth. Soil samples at depths greater than 20 mm were then only collected at the time of Run 1 instead of for every run as was the case for the surface soil. Only the Olsen P test was performed on this soil and, as was shown in surface runoff, the correlation between Olsen P and DRP concentrations in water was low. In hindsight it would have been preferred that the water extractable P test was carried out on these soil samples as well.

There appears to be no relationship between average Olsen P in the 20-80 mm soil depth interval and the average flow weighted DRP concentration for any of the runs (Table 5.5). The HP site has a much higher average Olsen P value than the LP site (8.8 mg dm^{-3} and 20.6 mg dm^{-3} for the LP and HP sites respectively) yet in Runs 1 and 2 the LP site produces subsurface flow with a higher average DRP concentration than the HP site. This was reversed in Run 3. Sharpley and Rekolainen (1997) reported that the pathway and rate of flow of water through the subsoil had a major effect on the concentration of P in subsurface water. They found that the faster that water flowed through the subsoil, the higher was the concentration of P in the water. If the LP site had more soil cracks for preferential flow than the HP site it could be that this could cause the LP site to produce higher DRP concentrations than the HP site whilst still having much lower general soil P levels. Olsen P levels however, were shown to have a limited effect on the amount of P in water and because the LP sites had a much lower Olsen P value than the HP site it cannot be assumed that the HP sites should produce the highest DRP concentrations. Therefore preferential flow is only one possible explanation for increased DRP concentrations in the LP site.

As in the surface runoff results, Run 3 produced subsurface flow with a much higher DRP concentration than for the previous two runs. This effect is likely to be due to the drop in soil moisture which was found to have a major effect on the amount of P available to surface runoff water. Without full soil tests though for each run it is not possible to comment on whether soil P levels varied in the testing period and any variations in DRP concentrations such as in Run 3, can only be assumed to be the result of similar factors to those which effected the surface runoff concentrations.

Table 5.5. Average Olsen P in the 20-80 mm interval and the average flow weighted DRP concentrations in subsurface flow for Runs 1, 2 & 3.

Site	Avg Olsen P (mg dm^{-3}) 20-80 mm	Avg DRP conc		
		Run 1 (mg dm^{-3})	Run 2 (mg dm^{-3})	Run 3 (mg dm^{-3})
LP	8.8	0.22	0.24	0.54
HP	20.6	0.18	0.13	0.74

5.3 Conclusion

The Olsen P test correlated poorly with surface runoff DRP concentrations in individual runs and also using the overall combined data. In contrast the water extractable test correlated relatively well with surface runoff DRP concentrations for each individual Run, but correlated poorly when all of the runs were combined. For both tests the poor correlation with the combined data is a result of the large increase in DRP concentrations between Runs 2 and 3, during which time both soil tests either decreased or remained the same. Comparison of soil conditions existing at Runs 2 and 3 reveals a major difference in soil moistures, with all sites being markedly drier at Run 3 compared with Run 2. This suggests that soil moisture level may be an important factor determining DRP concentrations in runoff.

The soil moisture correlated relatively poorly with the DRP concentration in runoff for each individual run. However, the soil moisture correlated much better than either the Olsen test or the water extractable test when all data are combined. Therefore soil moisture appears to have had a major effect on the amount of P that is lost from soil to surface runoff. The likely causes of this are that as the moisture level drops, P mineralisation occurs and subsequently P that would otherwise be retained in cell matter is made available to runoff water. As the soil moisture drops, the soil temperature is also likely to rise which moves the adsorption-desorption equilibrium reactions in the direction of desorption and subsequently more P will be released.

Although the soil moisture, overall, correlated better than the Olsen P test and the water extractable P test, on the individual runs, the water extractable P test provided the best correlation. If a soil test was going to be developed to estimate possible losses of P from soil via runoff, it would need to take into account both the soil P concentration and the soil moisture as well as perhaps the soil temperature as it appears that it is a combination of all of these factors which determines P loss. It is difficult to comment on which factor is dominant in determining P loss. The HPN site which produced the highest DRP concentrations had a combination of both the highest soil P concentration and lowest soil moisture content. The fact that the LPN site produced the next highest DRP concentrations perhaps suggests that it is the moisture factor which has the greatest influence, but it must also be remembered that the northerly sites had a lower P retention level and this would also contribute to the northerly sites producing the highest DRP concentrations. A point of note however, when comparing the influence of fertiliser addition and a decrease in soil moisture is that the decrease in soil moisture produced a greater increase in DRP concentration than did the addition of fertiliser. When developing a test, a combination of all of these factors will be required to give an accurate estimate of P losses from soils such as that used in this study.

It is not possible to comment on the correlation between subsurface flow DRP concentration and subsoil P concentrations as soil tests were not taken at the time of each run. A point of note however, is that in Run 3 the subsurface DRP concentration increased as it did for the surface runoff. The same factors that affected the surface runoff are therefore likely to be operating on the subsurface flow water as well.

No subsurface runoff was able to measured on the northerly aspects as they were too dry. It can therefore be expected that subsurface movement of P on the northerly aspects will be insignificant in regards to P loss.

CHAPTER 6

Conclusion

The results of this study indicate that the concentrations of DRP in surface runoff are influenced by a number of factors. These include - fertiliser addition, aspect and season. In general, soils that have received large inputs of P fertiliser have higher DRP concentrations in surface runoff than soils with lower fertiliser inputs. The magnitude of this fertiliser effect however, varies with aspect. Generally, the effect of fertiliser on DRP concentrations was higher on north facing slopes than on south facing slopes. South facing slopes were wetter and, in this study, had slightly higher P retention (although in a conventional agronomic sense the P retention across the whole trial was low (< 36 %)). The difference between the aspects however, may be important in relation to runoff P concentration measurements. This combination of higher P retention and soil moisture would assist in the immobilisation of added fertiliser P. This was also reflected in the lower (Olsen and water extractable) P soil test values on the south-facing slopes.

The important influence of soil moisture was again demonstrated by the very high DRP concentrations observed in Run 3 which was carried out early in summer when the soils were very dry. This suggests that the greatest risk of P loss from soil to surface waters will be from northerly aspects with high fertiliser histories during the summer months when soil moisture levels are low. This is consistent with the observation that the highest DRP concentrations in the runoff were recorded on the HPN site during Run 3 (average flow weighted concentration of 3.29 mg dm^{-3}).

Unfortunately this coincides with the time of the year when eutrophication is a greater problem. During the summer months water flows in rivers are low and water temperatures are high. This leads to increased algal blooms, increased macrophyte growth, and depleted oxygen levels which can cause fish kills. The summer months in the region of the trial also have high intensity rain storms which are likely to cause large runoff events. Potential P losses from soil to water are therefore greatest during the time of year when P concentrations in surface waterways are a problem. This makes the task of controlling non-point sources of P all the more difficult and raises concern as to whether control methods such as reducing fertiliser inputs will be effective.

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