The mobilisation of soil phosphorus in surface runoff from intensively managed pastures in south-east Australia

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for the degree of Doctor of Philosophy

Warwick John Dougherty

Department of Soil and Land Systems
School of Earth and Environmental Sciences
University of Adelaide

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Abbreviations

$CaCl_2$-P	–	molybdate reactive P in 10 mM calcium chloride soil extracts
$CaCl_2$-TP	–	total P in 10 mM calcium chloride soil extracts
$CaCl_2$-UP	–	un-reactive P in 10 mM calcium chloride soil extracts
DOC	–	dissolved organic carbon
DRP	–	dissolved (<0.45 µm) molybdate reactive P
DUP	–	dissolved (<0.45 µm) un-reactive P (TDP minus DRP)
EC	–	electrical conductivity
EPC	–	equilibrium P concentration
EDI	–	effective depth of interaction
ICPAES	–	inductively coupled plasma emission spectroscopy
LLD	–	lower limit of detection
LSD	–	least significant difference
NMR	–	nuclear magnetic resonance
OC	–	organic carbon
P	–	phosphorus
P_i	–	soil inorganic P
P_o	–	soil organic P
SE	–	standard error
TDP	–	total dissolved (<0.45 µm) P
TP	–	total soil P
*	–	$P<0.05$ (in statistical analysis and interpretation)
**	–	$P<0.01$ (in statistical analysis and interpretation)
***	–	$P<0.001$ (in statistical analysis and interpretation)

Abstract

The application of substantial quantities of phosphorus (P) has been required to increase productivity on many Australian soils. Unfortunately, these applications have often resulted in increased concentrations of P in surface runoff that contributes to excessive algal growth in surface waters and consequently a decline in their quality. The concentrations of P in runoff from intensively managed pastures are often high (1-5 mg/L) and typically at least an order of magnitude higher than water quality targets. Although a substantial amount of research has been devoted to the problem of P accumulation and mobilisation in arable systems (in which P is typically mobilised by the action of raindrop impact and subsequently transported in particulate form), there has been substantially less research in intensively managed pasture systems. Consequently, there is a paucity of knowledge concerning the fundamental processes and factors responsible for P in runoff from these systems and a dearth of truly effective remedial strategies.

In this thesis, the accumulation of P in soil under intensively managed pastures used for dairying and the processes responsible for its mobilisation in surface runoff were investigated. This research was undertaken at two research sites in South-east Australia, i.e. Camden in New South Wales and Flaxley in South Australia.

A number of factors relating to scale and hydrology may influence the processes of P mobilisation and its concentration in runoff. A comparison was made of the forms and concentrations of P in runoff between a typical rainfall simulation methodology and large runoff plots. The effect of rainfall intensity on the forms and concentrations of P was also investigated. The concentrations of P in runoff from small-scale, high-intensity rainfall simulations were on average 33% lower than those from large plots (approximating hillslopes) although the processes of mobilisation (as evidenced by runoff P forms) were similar. Increasing rainfall intensity resulted in decreasing P concentrations, but similar forms of P. It was hypothesised that changes in hydrological characteristics (residence time and depth of runoff) were responsible for the differences in the P concentrations. A model of P mobilisation (incorporating hydrological and P-release characteristics) was developed and shown to successfully predict runoff P concentrations under a range of rainfall intensities. These findings and the subsequent model were used in the successful modelling of landscape-scale nutrient exports based on rainfall simulation data as part of a separate, but complementary project.

There is anecdotal evidence to suggest that Australian soils are relatively ‘leaky’ in terms of P in runoff compared to soils overseas. Consequently, comparisons of the labile soil P characteristics and soil P-runoff P relationships were made between Australian soils and soils of similar fertility from the USA, UK and New Zealand (using both experimental data and data sourced from the literature). It was concluded that Australian soils leak more P than soils of similar fertility in the USA, UK and New Zealand, although it was beyond the scope of the thesis to make more detailed comparisons between Australian and overseas soils.

The accumulation and mobilisation of P in two soils used for intensive pasture production in Australia were investigated. In intensive pasture systems P accumulated in the shallowest zones of the soil and principally as inorganic P. The concentrations of labile P were 3-5 times higher in the top 0.01 m than in the top 0.1 m. Using a simple model, it was estimated that only the top several mm of soil influence runoff P concentrations. The dominant form of P in runoff was shown to be orthophosphate although in low to moderate fertility soils, dissolved organic P can constitute a substantial proportion of the P in runoff. These results confirm the need to reduce the pool of P available for mobilisation in the immediate topsoil in order to reduce runoff P concentrations.

Because P is stratified, it was hypothesised that one method to reduce the pool of P available for mobilisation is to de-stratify the soil (i.e. mix the topsoil). The effect of this technique on runoff P concentrations was investigated in laboratory and rainfall simulation experiments. These experiments revealed that reductions in runoff P concentrations between 45 and 70% can be achieved by de-stratification of soils under permanent pastures. It was hypothesised that the benefits of de-stratification could be maximised using a combination of information relating to catchment hydrology and the spatial distribution of soil P and that this would result in large reductions in P exports with a relatively small degree of inconvenience to land managers. Given the limited opportunities identified in previous research to reduce P exports in runoff, the strategic utilisation of de-stratification is a potentially important option in water quality management for the dairy industry and warrants further investigation.

Declaration

This work contains no material which has been accepted for the award of any other degree or diploma in a university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text.

I give consent to this copy of my thesis being made available in the University Library.

Components of the research described in this thesis have been published (as listed below). The author acknowledges that copyright of published material contained within this thesis resides with the copyright holders of those works.

Warwick J Dougherty **…………………………………………**

Publications arising from this thesis

- **Dougherty WJ**, Fleming NK, Cox JW, Chittleborough DJ (2004) Phosphorus transfer in surface runoff from intensive pasture systems at various scales: A review. *Journal of Environmental Quality* **33**, 1973-1988.

- **Dougherty WJ**, Smernik RJ, Chittleborough DJ (2005) Application of spin counting to the solid-state P-31 NMR analysis of pasture soils with varying phosphorus content. *Soil Science Society of America Journal* **69**, 2058-2070.

- **Dougherty WJ**, Nash DM, Chittleborough DJ, Cox JW, Fleming NK (2006) Stratification, forms and mobility of phosphorus in the topsoil of a Chromosol used for dairying. *Australian Journal of Soil Research* **44**, 277-284.

Chapter 1 Introduction and synopsis

1.1 Phosphorus, agriculture and the water quality problem

Phosphorus (P) is an essential nutrient for plant growth. Because levels of plant available P are typically low in Australian soils, P has been, and still is, widely applied to Australian soils in order to improve their productivity. Approximately 500 000 tonnes of P are used annually in Australian agriculture (FIFA 2005) at a cost of \$2 to \$5/kg. Whilst P inputs are required for optimal agricultural production, excessive concentrations of P in fresh surface waters can contribute to increased algal growth and consequently a decline in water quality (Sharpley *et al.* 1994; Sharpley and Withers 1994; White 2001). There is a widespread consensus that the quality of coastal surface waters has been degraded by inputs of nutrients from agriculture [e.g. Anon. (1998)]. The National Land and Water Audit reported that 50% of the 75 catchments assessed across Australia exceeded water quality criteria for P (NLWRA, 2001). Algal blooms are conservatively estimated to cost the Australian community \$180-240 million per annum (LWRRDC 1999) as a result of a combination of water treatment costs, impairment of recreation/tourism activities and damage to fishery indsutries. Consequently, as part of various strategies to reduce the incidence of algal blooms, targets have been set to reduce the transfer of P from land to water-bodies (Authority. 1995; Anon. 1998).

The Australian Dairy Industry relies on substantial inputs of P to maintain pasture and milk production. Average annual P fertiliser application to dairy farms was reported to be 44 and 47 kg/ha for dairy farms in Gippsland (Victoria) and coastal NSW, respectively (Nash and Halliwell 1999; Lawrie *et al.* 2004). As a general rule, the application of fertiliser P increases the concentration of P in runoff. Research has revealed that P concentrations in runoff from Australian dairy pastures typically range from 1-5 mg/L (Fleming and Cox 2001; Cornish *et al.* 2002; Nash *et al.* 2005; Dougherty *et al.* 2006b) and are much higher than the typical water quality targets of 0.05-0.10 mg P/L. Although there is a range of factors that may result in P concentrations in runoff from pastures being reduced before the runoff enters a sensitive waterway (Mainstone and Parr 2002), the significance of these factors is very difficult to predict and is highly variable. Therefore, the Australian dairy industry is actively engaged in attempting to reduce the concentrations of P in runoff from grazed pastures.

In order to reduce the concentrations of P in runoff, there is a need to better understand the factors contributing to these high P concentrations. One major factor affecting runoff P concentrations that has been identified in research undertaken in the last decade is that of ‘time since last fertiliser’ application (Nash *et al.* 2005). However, recent improvements in fertiliser management as a result of this research have reduced the significance of this factor (Nash *et al.* 2005) such that other non-specific reasons for high runoff P concentrations now dominate. Improving the understanding of these factors would contribute to the development of management strategies that will reduce runoff P concentrations. This thesis is concerned with these factors and their measurement.

As part of this thesis, a review of the literature was undertaken. The literature review (Chapter 3) was published in the Journal of Environmental Quality (Dougherty *et al.* 2004) at the beginning of the candidature and thus represents a summary statement and review of the understanding (at the time of its publication) of the mobilisation of P and the influence of scale on its measurement. The literature review is presented in this thesis without alteration (apart from formatting). More detailed and updated consideration of the literature is provided in the subsequent experimental chapters.

The literature review examined the soil P cycle, its relationship to the mobilisation of P, the influence of hydrology on the mobilisation of P and the effect of method and scale on the measurement of P mobilisation. The review was undertaken with a specific focus on the processes occurring in intensive pasture systems such as those used for grazing in the dairy industry. Although a number of studies have examined P mobilisation and transport in runoff from intensively managed pastures (Nash *et al.* 2000; Fleming and Cox 2001; Cornish *et al.* 2002; Mundy *et al.* 2003; Barlow *et al.* 2005), these studies were at a range of scales (from laboratory to sub-catchment) and used a multitude of approaches, limiting the integration of these research results (Dougherty *et al.* 2004).

The literature review revealed deficiencies in our understanding of pasture systems with respect to:

- ***The accumulation of P in soil (form and distribution),***
- ***The processes of P mobilisation and subsequent forms of P in runoff, and***
- ***The relationship between the processes of P mobilisation observed using rainfall simulation and those occurring at the hillslope scale*.**

Consequently, the over-arching objectives of this thesis were to, a) investigate the accumulation of P in soil under permanent pastures, b) investigate the mobilisation of this P under a range of conditions (varying soil fertility and differing hydrological conditions) and, c) in light of the information gathered, consider strategies for reducing the concentrations of P in runoff.

As a brief introduction to the research undertaken in this thesis, an overview of the experiments, the questions they addressed and the key findings leading to subsequent research is provided below.

1.2 The experiments

The research was carried out at two sites that are located in key dairying regions of South-east Australia, Camden in New South Wales and Flaxley in South Australia. The soils at both sites are Chromosols (Isbell, 1997) or Haploxeralfs (Soil Survey Staff, 1999) and represent common soil types upon which dairying is carried out.

Perhaps the most widely used method for the study of P mobilisation in runoff is rainfall simulation. However, the results from rainfall simulation experiments may reflect the conditions under which the experiments were undertaken. For example, the intensity of simulated rainfall and the scale at which the rainfall simulations are undertaken can influence results. There has been substantial investigation of rainfall simulation in systems where particulate P exports predominate. However, in pasture systems where dissolved P is most likely the dominant form of P, there has been little study of the effects of rainfall intensity and scale (specifically how P mobilisation under rainfall simulation relates to P mobilisation under natural conditions at the hillslope scale).

The first two experimental chapters in this thesis (Chapter 4 and 5) are concerned with rainfall intensity and scale issues. Chapters 4 and 5 address the following research questions respectively:

- ***What are differences in the processes of mobilisation and concentrations of P in runoff between large-scale low-intensity artificial rainfall simulation events***

(approximating a constant intensity natural rainfall event) and small-scale high-intensity rainfall simulation?
- ***What are the effects of different simulated rainfall intensities on the processes of mobilisation and the resulting concentrations of P in runoff?***

The research showed that whilst method (small-scale high-intensity rainfall simulation vs. large-scale low-intensity rainfall simulation) had little effect on the relative proportions of P mobilised by detachment or dissolution processes, the method did have a significant effect on the concentrations of P in runoff. The absence of an effect of rainfall intensity on particulate P mobilisation is most likely the result of ground-cover intercepting raindrops and reducing their energy before they contact the soil surface. The results of these experiments suggest that rainfall simulation is a robust technique for studying P mobilisation (in pasture systems). However, it was noted that small-scale high-intensity rainfall simulation may provide relatively low estimates of runoff P concentrations.

The intensity of simulated rainfall had little effect on the relative proportions of different P forms in runoff, but did have a significant effect on P concentration; the P concentration decreasing with increasing rainfall intensity. It was hypothesised that the decrease in concentration was the result of differences in residence time of water on the soil and changes in runoff depth. It was concluded that ‘rate limited’ release of P rather than ‘source limited’ release was responsible for changes in runoff P concentrations. A simple model of P release kinetics incorporating residence time and depth effects successfully modelled the effect of changing rainfall intensity. Such findings have important implications for the study of P mobilisation, the interpretation of runoff P measurements and for the setting of soil P regulatory targets on the basis of rainfall simulation measurements.

The experiment in Chapter 4 indicated, in keeping with previous research, that increasing soil P fertility resulted in increased runoff P concentrations. Defining the effect of soil P status on runoff P concentration was fundamental to further detailed study of runoff P concentrations that were undertaken at the Flaxley site. The elucidation of this relationship also contributed to modelling P exports from the sub-catchment in the larger project through which this PhD was funded (i.e. DAS10815 - Flaxley Farmlets: Nutrient loads in run-off water at high stocking densities) and served as the basis for the development and testing of a remedial strategy later in this thesis (Chapter 9). There is anecdotal evidence that runoff P concentrations in Australian soils are higher than those from soils in the USA and UK (i.e.

they are more ‘leaky’). However, there has been little comparison of soil P-runoff P relationships between Australian soils and soils from other continents. In Chapter 6, the following research question is examined:

- ***What is the effect of soil P status on runoff P forms and concentrations?***

The effect of soil P on runoff P was examined using a series of field rainfall simulations at Flaxley. There were significant ($P<0.001$) relationships between various measures of soil P (i.e. Olsen P, $CaCl_2$-P and soil water P) and runoff P (TP and DRP). Even for soils with agronomically optimal soil P status, runoff P concentrations were ~0.25 mg/L and well above typical water quality targets of 0.05-0.10 mg/L. In high P soils, runoff total P (TP) concentrations were almost two orders of magnitude higher than these water quality targets. A comparison of soil P-labile P and soil P-runoff P relationships for a range of Australian soils (from published and un-published sources) with published data for soils from the northern hemisphere suggested that Australian soils are more ‘leaky’ with respect to P. However, wide variations in the methods used in those studies and the need for data to be ‘adjusted’ to account for those different methodologies preclude a definitive comparison. Further examination of this issue is required. However, the logistics involved in comparing Australian and overseas soils were prohibitive from the perspective of this thesis.

An improved understanding of the storage and release of P from soil is a pre-requisite for the development of remedial strategies. Previous research has shown that soil P may be stratified in soils under permanent pasture. This P accumulated in both inorganic and organic forms, the proportions of which presumably influenced the forms of P in runoff. There is little data on these relationships for soils under long-term permanent pasture. A number of researchers have reported that DRP represented a high proportion of runoff P. Other researchers have reported that organic and colloidal forms of P may be important P forms in runoff. However, these studies have typically been at the sub-catchment scale, where a wide range of processes affect P concentrations and forms. To improve our understanding of the mobilisation of P as a function of soil P status, more detailed studies are required. These issues were examined in detail for the Flaxley and Camden sites. The research questions examined in Chapter 7 are:

- ***In what forms and where is P stored in the topsoil under pastures?***
- ***What forms of P are mobilised into runoff and what is their relationship to soil P forms?***

- ***What is the nature of the dissolved P in runoff and what is the effect of soil P status on the characteristics (physico-chemical) of the dissolved P?***

The field studies of soil P distribution revealed that there was substantial stratification of P, the highest concentrations being found in the top 0.01 m of the soil. Examination of the forms of soil P revealed that P accumulates predominantly as inorganic P (P_i), with little or no accumulation of organic P (P_o). The use of re-packed soil trays allowed the detailed examination of the forms of P in runoff from these soils and allowed investigation of the effect of soil P status on these forms. The proportions of dissolved reactive P (DRP) and dissolved un-reactive P (DUP – a surrogate measure of organic P) in runoff were correlated with soil P status and the proportions of P_i and P_o in the soils. Although DRP is the dominant form of P in runoff from soils with very high P status, in runoff from soils with low to moderate P status, DUP can constitute 50% of the runoff P. Further examination of these forms using ultrafiltration revealed that DRP provided a robust estimate of PO_4^-, whilst DUP was comprised low molecular weight (<10 kDa) organic P compounds. Results from this research were published in the Australian Journal of Soil Research (Dougherty *et al.* 2006b). Results relating to the colloidal forms of P were presented at the 2005 Annual Meeting of the Soil Science Society of America (Dougherty *et al.* 2005a).

As an extension to the characterisation of soil P chemistry in Chapter 7, an additional examination of soil P forms was undertaken using a combination of traditional wet chemistry and ^{31}P solid-state NMR. Solid state ^{31}P NMR offers a potentially useful way of characterising soil P and investigating relationships between soil P and runoff P. Whilst liquid-state ^{31}P NMR is commonly used to study soil organic P and provides impressive resolution of organic P forms (Turner *et al.* 2003a), it suffers from only being able to examine alkali-extractable organic P and does not consider inorganic forms of P in soil (Dougherty *et al.* 2005b). The research question examined in Chapter 8 is:

- ***What is the nature of inorganic and organic P in soils as revealed by traditional wet chemistry and solid-state ^{31}P NMR?***

The findings of these investigations were consistent with those of Chapter 7. Difficulties with the solid-state technique limited its application. Nevertheless significant advances in the use of solid state ^{31}P NMR were made that will contribute to further study of soil P chemistry in relation to the mobilisation of P. For example, pre-treatment with HF to remove paramagnetics, as is routinely used in the study of carbon by ^{13}C NMR (Skjemstad *et al.* 1995), showed potential to improve the resolution of P forms by ^{31}P NMR. The results from this research were published in the Soil Science Society of America Journal (Dougherty *et al.* 2005b).

The studies of runoff P forms and the distribution of P forms discussed in Chapter 7 suggest that reducing the quantity of P available for mobilisation is the key to reducing runoff P concentrations. It was hypothesised that in light of the substantial stratification of P in pasture soils revealed in Chapter 8, that de-stratification (i.e. ploughing or a similar technique in order to mix the topsoil) would result in large decreases in runoff P concentration and hence load. Therefore, the final experiment examined the potential benefits of de-stratification. This evaluation was undertaken using a combination of laboratory and rainfall simulation experiments. In Chapter 9, the following questions are examined:

- ***Does de-stratification reduce the concentrations of P in runoff?***
- ***What is the effect of initial soil fertility on the benefits of de-stratification?***

The laboratory and rainfall simulation experiments on re-packed soil trays revealed that de-stratification reduced runoff P concentrations substantially, and that the magnitude of the reduction was related to initial soil P status. For relatively high P soils (Olsen P_{10} ~100 mg/kg), runoff P concentrations were reduced by approximately 70%, whereas for low P soils (Olsen P_{10} ~20-40 mg/kg), the reduction in runoff P concentration was approximately 35%. It is proposed that only relatively small areas of the catchment need to be de-stratified in order to cause large reductions in runoff P concentrations and loads. Furthermore, it is believed that the potentially adverse impacts from erosion resulting from de-stratification can be successfully managed, and that the re-establishment of stratification is a slow process. Data from the Camden experimental site was used to show that there was minimal establishment of stratification over a 3 ½ year period when no fertiliser was applied. However, despite these encouraging results, there is a need to undertake further evaluation of the de-stratification technique in the field at sub-catchment scales.

1.3 Conclusions

This thesis makes a significant contribution to our understanding of the accumulation of P in soils under pasture, the mobilisation of this P and how we measure it. This contribution will advance our conceptual models for use in future research. Advances were also made in the understanding of the processes of mobilisation in relation to the techniques used to study them – hydrological characteristics relating to rainfall having a significant affect on P concentrations. A model was developed that successfully described these effects thus improving the utility of rainfall simulation estimates of runoff P concentrations. The detailed study of the patterns and forms of soil P and the forms of P mobilised in runoff led to the identification of a potentially useful remedial strategy. Subsequently, it was shown that substantial reductions in runoff P concentrations may result from de-stratification of soil P. Given the limited opportunities to reduce P exports, this is an important advance in water quality management for the dairy industry, although it should not be seen as an alternative to careful nutrient management. It was beyond the scope of this thesis to evaluate de-stratification in landscape scale experiments. These issues should be priorities for future research.

Chapter 2 Phosphorus transfer in surface runoff from intensive pasture systems at various scales: a literature review

2.1 Introduction

The inherent phosphorus (P) content of most Australian soils is inadequate to sustain continued agricultural production and so P is added in fertilisers (Holford 1997). Highly productive pastures, e.g. those used for dairying, are significant users and accumulators of P (Nash and Halliwell 1999). In addition to fertiliser P, P may also be imported to pasture systems from external feed sources such as hay and concentrates via faecal matter from grazing livestock (Wu *et al.* 2000).

Concentrations of P in surface runoff from these intensive pasture systems are typically high, being in the range of 1 to 10 mg/L (Greenhill *et al.* 1983; Nash and Murdoch 1997; Nexhip *et al.* 1997; Fleming and Cox 1998). The concentration of P in water is one of the factors limiting productivity in waterways (Wetzel 1983). Consequently, the transfer of P (the collective term for those processes resulting in the loss of P in runoff) from pasture systems to waterways can contribute to the development of toxic algal blooms. There is a general consensus that improved management of P in intensive pasture systems is needed so that P transfers in surface runoff and the subsequent impacts on water quality are reduced and/or minimised.

The significance of P transfer in surface runoff from intensive pasture systems is difficult to assess, because depending on circumstance, either concentration or load can be more or less relevant in terms of impact and assessing the significance of a particular load or concentration is difficult. Furthermore, assessing the importance of P transfer in runoff from intensive pasture systems compared with other sources is difficult because P sources are highly varied within most watersheds. Consequently, the extent of the required reduction in losses of P in surface runoff is difficult to define. It is also difficult to directly link surface water quality measured at the farm or paddock scale to that at the watershed scale. Regulatory authorities generally set water quality guidelines at watershed scale and often use a combination of load and concentration criteria. For example, in a number of Australian coastal watersheds, the general objective is to reduce P losses from agricultural industries – a load based target - (Anon. 1998; 2002c), whereas a more specific water quality target of $P<0.05$ mg/L – a concentration based target - has been set for several watersheds.

There has been a significant investment in research to determine the type and magnitude of processes resulting in P transfer in surface runoff and how management influences this transfer. This research has utilised a wide range of approaches. However, little consideration has been given to the effect of scale and methodology of the research on the processes of mobilisation (the process whereby P is transferred from a P source to the runoff) and subsequent concentrations, and loads of P measured in surface runoff. Small plot studies allow examination of the effect of specific factors on P transfer. Broader scale (e.g., watershed) studies allow quantification of P transfer as a result of general management and landscape factors, but are generally unable to provide detailed information about the effect on P transfer of specific management factors. A mixture of research at a range of scales offers promise of greater insight into the influence and interaction of both management and landscape factors (Haygarth and Jarvis 1999).

Commonly used techniques for measuring runoff P concentration, such as rainfall simulation, may allow prediction of concentrations in runoff at paddock, farm, or broader scales. However, there are almost always differences in the hydrological processes, and therefore the nature of P transfer, at these different scales. For example, runoff coefficients are high and runoff residence times short for rainfall simulation, whereas under natural rainfall at paddock or watershed scale, runoff coefficients are relatively low and residence times relatively long. An understanding of these differences and the factors influencing them may allow P mobilisation and transfer to be examined more effectively. Furthermore, a clearer understanding of landscape processes will contribute to efficient management of P.

This review examines factors affecting P transfer in surface runoff from intensive pasture systems in temperate regions. A conceptual model of P transfer is used as the basis for examining the effects of scale and landscape characteristics on P transfer. Subsequently, the efficacy of predicting P transfer at various scales is also examined. Deficiencies in our understanding and conceptualisation of the scale issue are highlighted and priorities for future research identified.

Phosphorus transfer in surface runoff is specifically examined in this review because, a) in a majority of intensive pasture systems it is the primary pathway for transfer of P off-site and consequently has been the subject of a great deal of research, b) the findings of some of this research are of lesser value than they might have been had ‘scale’ issues been considered more carefully in the design and interpretation of the research, and, c) it is the primary transport pathway dealt with in management tools such as P risk indices.

The fate of P in runoff is strongly influenced by factors such as stream bank erosion, groundwater inflows, and internal cycling within the stream by sediment-water interactions and biological action (Wetzel 1983). The discussion of P mobilisation and transfer in this review is limited to terrestrial processes involved in P transfer and does not deal with processes occurring to P ‘in-stream’. It follows that the use of the term ‘watershed’ refers to those upper areas of watersheds, i.e., low order components of the landscape.

2.2 Conceptual model of P transfer

The development of a conceptual model of P transfer is an important step in understanding the differences in P transfer that may occur at a range of scales. The transfer or loss of P in surface runoff requires there to be a source of P, a process for mobilising this P, and an active transport pathway and agent (Gburek and Sharpley 1998; Djodjic *et al.* 2002). A conceptual model of P transfer that incorporates the source, processes of mobilisation, transport of P, and the factors that influence these was developed by Haygarth and Jarvis (1999). Additionally, the effects of landscape and climate can be incorporated (Figure 2-1). The addition of landscape and climate in the model will aid in the understanding of P transfer, particularly at broader scales.

Simplified conceptual models form the basis of P index or indicator tools that are used to examine the risk of P transfer in runoff [e.g., Gburek *et al*. (2000); Heathwaite *et al*. (2003)]. However, the processes considered in these tools, and the detail in which they are considered differs with the differing objectives of the various tools. For example, Gburek *et al*. (2000) examined the risk of P loss at sub-field scale for individual runoff events, whereas Heathwaite *et al*. (2003) evaluated the risk of P loss from areas of 1 km^2 on an annual basis. The coarser temporal and spatial scales considered by Heathwaite *et al*. (2003) required some simplification of processes involved at the field scale and more detailed consideration of the processes of P delivery downstream than was required by Gburek *et al.* (2000). The conceptual model of P transfer presented in this review considers in detail the range of processes contributing to P transfer in the upper zones of watersheds.

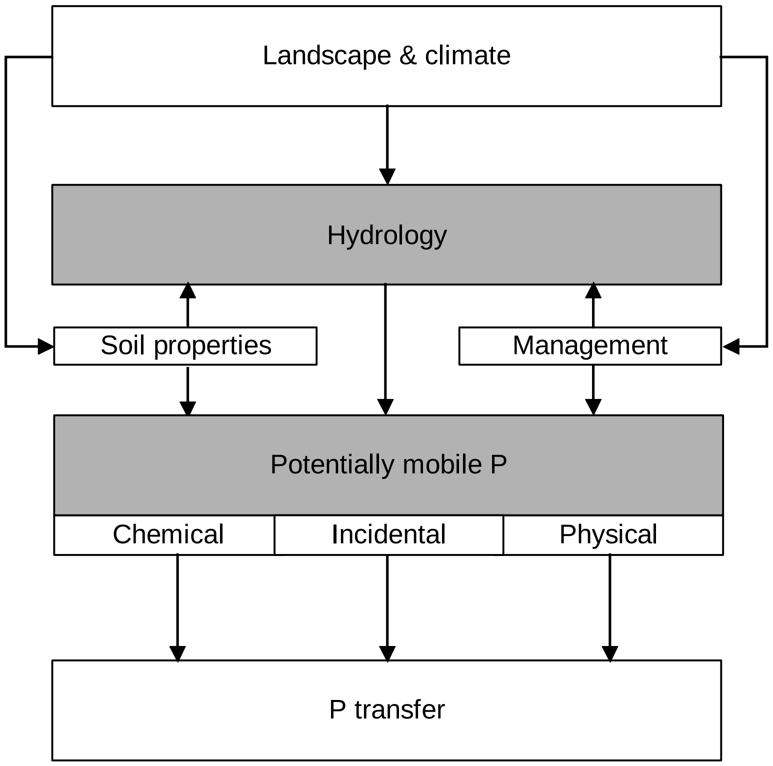

Figure 2-1. Conceptual model of phosphorus (P) transfer (adapted from Haygarth and Jarvis, 1999). The shaded boxes denote the critical transport and source factors without which P transfer will not occur.

2.2.1 Phosphorus sources

In intensive pasture systems, the size of the various pools of P and the turnover rates of these can be large. A general model of the P cycle in pasture systems is illustrated in Figure 2-2. The contribution to runoff P from each of the pools identified in Figure 2-2 is governed by the availability of P within each of them and the rate at which this P can be mobilised. Typically only a small fraction of each pool is available for mobilisation. For example, only 1 to 5 % of total soil P is water soluble (Sharpley 1981; Pote *et al.* 1999).

Fertiliser P is generally surface applied in intensive pasture systems. Immediately following fertiliser P application, the pool of readily soluble soil P is large, but declines rapidly such that changes in soil P are small after 30 days (Bramley *et al.* 1992; Nash and Murdoch 1997;

Barlow *et al.* 1999). This is followed by a continuing slow decline in the readily soluble soil P pool over a number of years (Burkitt *et al.* 2002). The adsorption of P on soil leads to a large increase in P nearest to the surface (Haygarth *et al.* 1998; Sharpley 2003) and importantly it is this part of the soil profile that has the greatest influence on runoff P concentration.

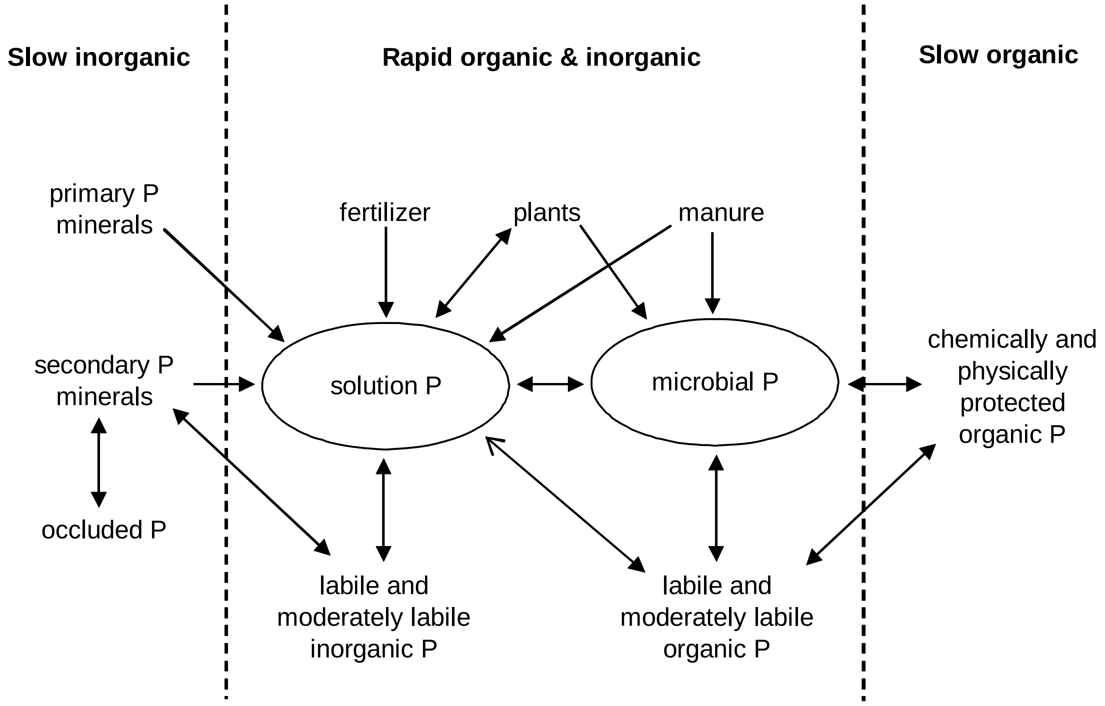

Figure 2-2. The phosphorus (P) cycle in the soil-plant continuum [Leinweber *et al.* (2002)].

A large amount of P in the soil–pasture system can be present in organic forms. Under favourable growth conditions, irrigated pastures can produce 10 to 30 tonnes of dry matter (DM)/ha/yr, equating to an uptake of 30 to 90 kg P ha/yr at a typical plant P content of 0.3 %. Typically in Australian dairy pastures, above ground biomass at any given time is in the range of 1 to 3000 kg DM/ha. Inefficiencies in the utilisation of this pasture will result in a considerable amount of P in plant tissue being deposited on the soil surface as leaf litter. Phosphorus is also found on the surface and within the internal structures of leaf tissue. Typically, water soluble P in pasture material is 10% of total P (Sharpley 1981; Schreiber 1985) although in dried pasture values up to 70% have been reported (Jones and Bromfield 1969). Microbial processes play an important role in mobilisation (mineralisation) and immobilisation of the organic P pool (Bromfield and Jones 1972; Hutchinson and Roper 1985; Perrott *et al.* 1992). Temperature, moisture, and plant growth influence the cycling of P through the microbial pool and the balance between mineralisation and immobilisation and thus soluble soil P.

Deposition of faecal P on intensively grazed pastures can be high. Deposition of faecal P is a function primarily of the grazing intensity (Nexhip *et al.* 1997). High stocking rates may require substantial increases in supplementary feed that not only increase the amount of faecal P deposited on the soil surface but also increase the importation of P (within the supplementary feed). Furthermore, faecal P concentration is affected by dietary composition (Wu *et al.* 2000; Dou *et al.* 2002; Ebeling *et al.* 2002). Increasing dietary P above basal animal requirements increases the P content of faeces, 30 to 60 % of which is water soluble (Wu *et al.* 2000; Dou *et al.* 2002).

2.3 Phosphorus mobilisation

The mobilisation of phosphorus is the transfer of P from the various pools in the soil–plant system into surface runoff. The nature and rate of this transfer and subsequent concentrations of P in runoff are governed by chemical, biological, physical, and hydrological factors. The processes of P mobilisation can be broadly classified into physical (detachment and entrainment of particles containing P, including colloids) and chemical (release of orthophosphate into solution) processes. The mobilisation of P in pasture systems will almost always involve a combination of these two processes. These processes will not only involve the soil, but also other sources of P in the pasture system such as plants or fertiliser. It is important to note that although plant uptake of P can only occur as orthophosphate from soil solution, P mobilised in surface runoff can be derived from any of the pools identified in Figure 2-2. The interaction of water with each of these pools is outlined in Figure 2-3. Rainfall and subsequent runoff interacts with all of the pools, except for those in horizons below the soil surface, which are of primary interest in the leaching of P.

The nature of processes of mobilisation will differ with the contributing source. The interaction of rainfall, infiltrating water, runoff, and the soil–plant system is illustrated in Figure 2-3. Rainfall is first intercepted by the plant biomass and then passes through the usually thin surface organic mat, i.e., the O horizon, if present. Once water reaches the A11 horizon, it either infiltrates or moves laterally as surface runoff depending on the hydrological conditions at the time and the rainfall rate. At small runoff rates, runoff will move laterally largely through the O and A11 horizons. At greater runoff rates, free water may be seen moving over the surface of the O or A11 horizon. Water may also move horizontally and slowly through the A12 horizon [e.g., Stevens *et al.* (1999)].

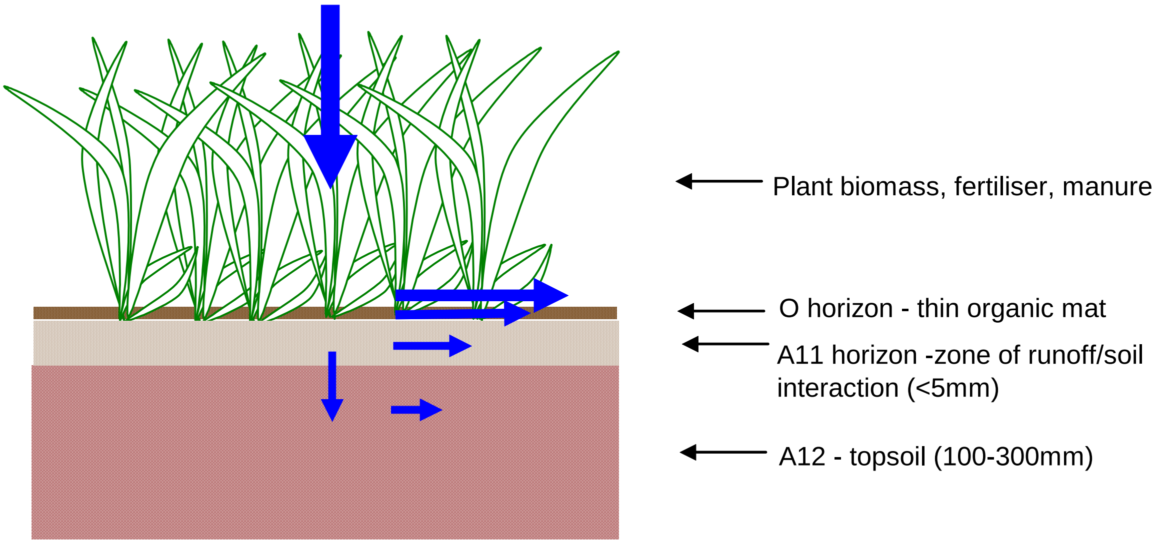

Figure 2-3. Schematic representation of the soil/plant system. Surface runoff travels primarily in the top several mm of soil (A11 horizon), the thin organic mat (O horizon – which may or may not be present), and in a layer above these. The blue arrows denote typical characteristics of water movement. Longer arrows indicate greater velocities, and thicker arrows greater volumes of water moving along the indicated pathway.

The specification of whether the process of mobilisation of P is chemical or physical is not simple. The difficulty in specifying the process arises because of a lack of routine methods for accurately distinguishing ionic phosphate. Instead, operational definitions of the nature of P have generally been employed (Leinweber *et al.* 2002). The most popular fractionation schemes in the study of runoff have involved filtration using 0.45 μm filters to separate particulate (>0.45 μm) and dissolved (≤0.45 μm) P [e.g., Fleming and Cox, (1998); Withers *et al.* (2001)]. Orthophosphate has often been assumed to be the P fraction that is both capable of passing through a 0.45 μm filter and of reacting in the molybdenum blue method (Murphy and Riley 1962). Although this classification is still widely used, the limitations have been acknowledged (Haygarth and Jarvis 1999). This classification suffers from the ability of some of the colloidal particulate matter i.e., particles 1 nm to 2 μm diameter (van Olphen 1977) to pass through 0.45 μm filters (Haygarth *et al.* 1998; McDowell and Sharpley 2001a) and the ability of the molybdenum blue method to solubilise some organic P (Tapachak 1983; Baldwin 1998).

Colloids capable of passing through 0.45 μm filters are common components of soil and include oxides, clay minerals, organic matter, and amorphous material (Goldberg *et al.* 2000). Colloidal materials are notable for their large surface area to mass ratios and the consequent reactivity. Furthermore, these colloids can provide an important transport mechanism for pollutants (Kaplan *et al.* 1996; Saiers and Hornberger 1999). Colloid transport can be promoted by low ionic strengths in the interacting water. Saiers and Hornberger (1999) observed significant increases in movement of colloidal kaolinite when ionic strength was reduced. Soil mineralogy and sodicity will also influence colloidal transport.

Phosphorus in surface runoff from intensive pasture systems is dominated by soluble or fine colloidal material (Nelson *et al.* 1996; Nash and Murdoch 1997; Fleming and Cox 2001). Exceptions to this may occur when livestock remove excessive pasture, exposing the soil, and/or physically disturb the soil surface by trampling (McDowell *et al.* 2003b). This may happen when pasture is over-grazed, and/or excessively wet areas of paddocks are grazed. Other areas where ground cover is likely to be poor and soil trampling occurs are around gates, feed/water troughs, and on livestock tracks (although these tend not to be so prominent in intensive pasture systems). In agricultural systems prone to erosion, such as cropping systems, P in runoff is predominantly in particulate form.

2.3.1 Physical processes of mobilisation

Detachment is primarily a physical process controlled by the availability of energy that can be supplied either as kinetic energy from raindrop impact (Ahuja *et al.* 1982; Torri and Borselli 2000) or from flowing water (Torri and Borselli 2000; Truman *et al.* 2001). In addition, electrical forces can supply energy involved in physico-chemical processes such as slaking or dispersion. Only in the case of dispersion will mineral particles become spontaneously mobilised in water. Particulate matter in surface runoff can range in size from 1 nm to 2 μm (colloidal particles) through to soil aggregates (<10 mm). It is comprised of mineral, organo-mineral compounds, macro organic matter, and soil micro– and macro–fauna.

Inherent properties of the soil-plant system can influence particle detachment and can be illustrated by contrasting a regularly tilled soil with a permanent pasture soil. The tilled soil will often have little or no ground cover and poor aggregate stability because of relatively low organic matter content. In contrast, intensive pasture systems will generally have 100 %

ground cover that intercepts raindrops and therefore reduces the kinetic energy from this source. As noted above, an exception to this may occur when pasture cover is reduced due to livestock activity. The pasture system also provides organic matter that contributes both directly and indirectly to the stabilisation of the soil surface (Loch 2000). The mobilisation of P in particulate forms can also occur as a result of the kinetic energy of surface runoff. Truman *et al*. (2001) observed a linear relationship between runoff rate and sediment yield on arable soils. Similarly, Gabbard *et al*. (1998) observed large increases in sediment transport as a result of increased runoff rates.

The transfer of P is not only a function of the quantity of soil mobilised, but also of the concentration of P in the material transported (Haygarth and Jarvis 1999). This phenomenon is the result of preferential mobilisation of smaller particles, e.g., clays that contain a higher P content than coarse particles, the lower amounts of energy required to transport these particles (Palis *et al.* 1997; Quinton *et al.* 2001), and their slower settling velocities. The ratio of the P content of the eroded soil to that of the bulk soil is known as the enrichment ratio. Enrichment ratios typically range from 1 to 2. Enrichment ratios may also be affected by runoff rate. Quinton *et al*. (2001) observed a disproportionately high loss of P in sediment from small storms. They attributed this to preferential erosion of fine clay particles of high P content during small runoff events, whereas in larger storm events, the greater energy of overland flow transported more coarse material containing relatively lower concentrations of P. Particulate P can also be derived from dust accumulated on plant surfaces (Schreiber and McDowell 1985). This is not likely to be a large component of P losses from soils under pasture. However, it is important to consider because discriminating this source from other sources of P associated with plants is difficult.

2.3.2 Chemical processes of mobilisation

Inorganic phosphorus

The equilibrium between solid phase P (adsorbed or precipitated) and the solution or runoff phase can be represented by a generalised model (Eq. 2-1) where the solid phase is in equilibrium with the solution phase.

$$\text{Solid–phase P} + \text{solution} \Leftrightarrow \text{solid–phase} + \text{solution P} \qquad \text{Eq. 2-1}$$

Increases in the concentration of P in the solution phase (such as may result from fertiliser addition) will also increase the concentration of P in the solid phase. The shift in equilibrium is rate limited, such that increasing the time of reaction between solid–phase P and solution will increase the amount of P in solution (Romkens and Nelson 1974; Sharpley *et al.* 1981a).

Mobilisation (or in some cases immobilisation) of phosphorus can occur from both a stable soil surface (runoff containing little or no sediment) and sediment entrained in the runoff. The concentration of P in the topsoil is particularly important in determining runoff P concentrations because this is where runoff interacts with the soil. As previously noted, P concentrates in the top of the soil in permanent pasture systems, with the highest concentrations being closest to the surface (Haygarth *et al.* 1998; Sharpley 2003). The interaction of surface runoff with soil is greatest at the surface and declines exponentially with depth (Ahuja *et al.* 1981). The depth of interaction varies with slope, rainfall intensity and kinetic energy of rain (Sharpley 1985). Investigation of the depth of interaction has mainly been undertaken in repacked soils lacking natural structure and plants [e.g., Sharpley *et al*. (1981b); Ahuja *et al*. (1982); Ahuja and Lehman, (1983); Hooda *et al*. (2000)]. A number of authors have attempted to simulate the effect of plants (Ahuja *et al.* 1982; Sharpley 1985). Plants can change the processes of soil–water interaction significantly. Plants will reduce the kinetic energy of raindrops, thereby reducing detachment and subsequent mixing of detached material with water ponded on the soil surface. Plants also increase the depth of interaction by reducing runoff velocities and by providing less dense topsoil with greater hydraulic conductivity (Ahuja and Lehman 1983).

The existence of a linear soil P–runoff P relationship has been observed under controlled rainfall simulation conditions by various authors (Sharpley and Syers 1976; Pote *et al.* 1996; Pote *et al.* 1999; Torbert *et al.* 2002). The soil P–runoff P relationship has also been described using a ‘bent stick’ model, the soil P concentration at the bend being known as the ‘change–point’ (McDowell and Sharpley 2001a; McDowell *et al.* 2003c). Soil P–runoff P relationships have been observed to vary significantly at different times and with different soil types (Pote *et al.* 1999). Hesketh and Brookes (2000) found the linear relationship between soil P and P in drainage waters changed over time. Similarly, Gillingham *et al*. (1997) observed a linear relationship for soils with an Olsen P in the 0 to 50 mg/kg range, but the relationship changed with season.

Determination of a soil P–runoff P relationship at broader scales has been less successful. McDowell and Trudgill (2000) found no correlation between soil P and runoff P in a 94 ha watershed of mixed land–use. They attributed the lack of any correlation to unusual rainfall/runoff conditions. Soil P status, processes of mobilisation, and hydrology would most likely be highly variable in such a large area. Their study highlights the effect of hydrology and the challenges that exist in using soil P as a predictor of runoff P concentrations at broad scales.

The best relationships between soil test P and runoff P have been derived in pure soil/pasture systems at small scales where uniformity is high and variability associated with plant biomass, livestock, and manure effects are eliminated. It is hypothesised that there will be large differences in these relationships at different times of the year because of the biological and organic components of the P cycle. Furthermore, the effects of grazing, e.g., changes in biomass P, trampling effects, and faecal deposition by livestock, are difficult to assess in small plots.

It is widely accepted that the kinetics of P release from soils (stable surfaces such as under pasture as well as in mixed soil/water phases in erosive systems) are controlled by diffusion rather than chemical, kinetic rates. Ogdawa and Sparks (1986) examined the effect of different mixing methods on the rate of P adsorption in a number of clay and soil systems. The rate constants for batch experiments in which suspensions of soil were shaken at 180 rpm were approximately 40 times greater than those of either static or continuous flow systems. Furthermore, the activation energies were very low in the static and continuous flow systems and were consistent with diffusion processes (Sparks 1985). In the batch experiments the activation energies were close to those expected from chemical rate–controlled reactions, although they were still within the diffusion–controlled range.

These static and continuous flow systems where solution–soil interaction is relatively small are akin to the situation that occurs under a highly stable soil surface such as in pasture systems. The shaken, batch experiments are more likely to represent mixed solution–soil systems observed under erosive systems examined by various researchers, [e.g., Ahuja *et al.* (1982), Ahuja and Lehman (1983), Sharpley (1985)]. It is probable that there will be large differences between bare soils and stable pasture soils in the effect of parameters such as runoff rate on P concentrations in runoff. The concentration of P in runoff will be a function of the equilibrium between the solid and solution phases. The equilibrium will be determined by three factors, viz., rate of release of P from soil to solution, time of contact, and soil P concentration.

Characterising the processes and quantifying the rates of P release from the soil surface and the changes in these rates under differing conditions may provide a basis for understanding the differences in P mobilisation at different scales. Such studies may assist in explaining the differences in measured P transfer using different techniques, e.g. rainfall simulation on small plots, compared with paddock scale under natural rainfall of much lower intensity.

Organic phosphorus

The contribution to runoff P from plant and manure P has been identified as being potentially significant (Bromfield and Jones 1972; Sharpley 1981; Hutchinson and Roper 1985). Phosphorus leached from plant residues originates from a number of pools. First, plants may have a surface coating of dust particles that is rapidly removed upon rainfall. Secondly, plant surfaces are also coated with a layer of orthophosphate exuded by the plant. Thirdly, there is a slow release of orthophosphate from the cellular component of the plants.

The contribution of P to runoff P from above–ground biomass has primarily been studied using materials such as wheat (*Triticum aestivum* L.) straw, 'hayed off' pasture, or dried and ground plant material. Early research by Bromfield and Jones (1972) examined the leaching of P from 'hayed off' clover (*Trifolium subterraneum* L.) and phalaris (*Phalaris aquatica* L.) mixtures. They found that a large proportion of the P present was water soluble (60 to 70 %) and that approximately 35 and 40 % of this was leached from clover and phalaris, respectively. For a given amount of rainfall, they observed that the amount of P leached decreased with increasing intensity, suggesting that P release at longer times was controlled by a combination of kinetic and diffusion factors rather than kinetics alone.

Surface dust and orthophosphate were lost when wheat straw was leached with simulated rainfall (Schreiber and McDowell 1985). An initial rapid rise in P concentration was observed (associated with surface dust and orthophosphate) followed by a more gradual decline (associated with leaching and diffusion of P from within the wheat straw). Similar results were obtained by Schreiber (1985) who examined leaching of P from wheat straw.

Sharpley (1981) found that application of P fertiliser (50 and 100 kg P/ha) to soil increased the concentration and mass of P leached from the plant canopy. These increases were a result of elevated P concentration in tissue as well as the increase in plant production. The capacity for leaching of P from the plant canopy was regenerated within 24 hours of a leaching event at both 50 and 100 kg P/ha. The concentration of P in runoff derived from plant P was sufficiently high that it suppressed P release from the soil. Furthermore, P in the runoff derived from plants was sorbed by the soil. The proportion of P in runoff that was leached from the plant canopy was greater at lower fertility levels. Sharpley (1981) concluded that modelling of runoff P concentrations should include allowance for contributions from the plant canopy.

Faecal P can contribute to P in runoff (Ebeling *et al.* 2002; Mundy *et al.* 2003). Faecal deposition rates at the soil surface can be high in intensive grazing industries such as dairying, e.g., 20 to 30 kg ha/yr (Nexhip *et al.* 1997; Nash and Halliwell 1999; Mundy *et al.* 2003). Rates of faecal P deposited on the surface are highly dependent on dietary regime (Wu *et al.* 2000) and grazing pressure (Nexhip *et al.* 1997). Increasing concentrations of P in faeces as a result of high P diet increased the concentration of P in runoff under simulated rainfall (Ebeling *et al.* 2002). Mundy *et al*. (2003), however, found that the contribution of faecal P to runoff P was small.

The relative dearth of studies on the effect of organic pools on runoff P is notable. This is a particular issue for intensive pasture–based enterprises where organic matter cycling can be large. The reason for the lack of such studies is not clear. It is likely to be a combination of factors, partly because of the nature of the systems being studied (e.g., bare soils or lack of variability in P pools), the difficulties associated with such studies (e.g., confounding effects of plant biomass and treatments to alter biomass such as grazing), and a lack of resources required to investigate these effects.

2.3.3 Incidental mobilisation

Incidental mobilisation is a variation of both physical and chemical processes of mobilisation and results in high concentrations of P in runoff. Its potential importance has lead to it generally being identified as a distinct mobilisation process (Haygarth and Jarvis 1999). Incidental mobilisation is the direct loss of P from fertiliser or manure sources soon after their application (Haygarth and Jarvis 1999). Phosphorus concentrations in excess of 50 mg/L have been observed in runoff occurring within 24 hours of fertiliser application (Greenhill *et al.* 1983; Nash *et al.* 2000). These high concentrations were attributed to the direct dissolution of highly soluble P from fertiliser granules, or from fertiliser P that was poorly equilibrated with the soil. Incidental losses from dung are not as large and the effect of time since grazing and dung deposition is relatively weak compared to that for fertiliser (Nash *et al.* 2000; Mundy *et al.* 2003). This is because of the relatively low amounts of dung deposited under grazing conditions, compared to fertiliser, and the relatively small surface area of dung exposed (Nash and Halliwell 1999). In colder regions of the Northern Hemisphere where confined livestock operations during winter result in the need to apply large amounts of manure at once, incidental mobilisation of manure P may be important (Preedy *et al.* 2001).

2.4 P transport – pathways and processes

Because the primary focus of this review is on hillslope processes, the following discussion of P transport is limited to hydrological processes and pathways in the headwaters of watersheds.

2.4.1 Hillslope hydrology

The generation of surface runoff generally will be a combination of the infiltration excess and saturation excess models proposed by Horton (1937) and Hewlett (1961) respectively. The infiltration excess model of Horton (1937) proposed that runoff would occur as a result of the rainfall rate exceeding the soil infiltration rate. The saturation excess model of Hewlett (1961) proposed that rainfall infiltrates and subsequently accumulates at various positions in the landscape as a result of sub-surface processes. Consequently, infiltration in these saturated areas becomes negligible and any subsequent rain falling on these areas runs off (Figure 2-4). Both processes were observed to occur in a detailed study of hillslope hydrology and runoff generation by Srinivasan *et al*. (2002). The occurrence of either process in a catchment will depend on climatic, geomorphic, and management factors (Chorley 1978). In intensive pasture systems, infiltration rates tend to be relatively high compared to cropping systems because of the maintenance of ground cover and favourable soil structure that results from high levels of organic matter. These factors will favour the model of runoff generation proposed by Hewlett (1961). An exception to this may occur in high traffic areas, such as near water troughs, around gates, and stock camps, or when compaction and disruption of the surface soil has occurred due to excessive livestock activity when soils are wet.

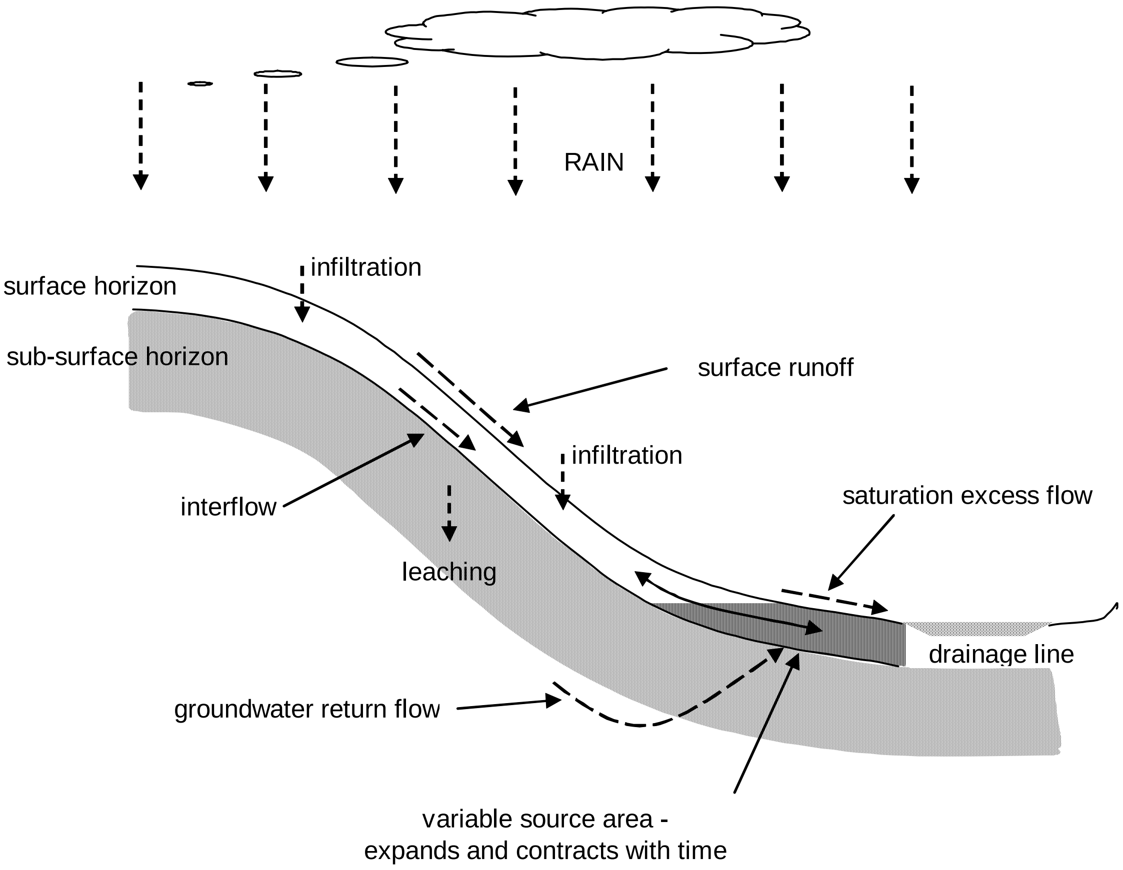

Figure 2-4. Basic components of hillslope hydrology.

Zones of saturation tend to occur in particular segments of the landscape as a function of landscape shape (Figure 2-5). These saturated zones expand and contract with changes in the watershed water balance as shown in Figure 2-6. This expansion and contraction with time is known as the variable source area (VSA) concept (Ward, 1984). These saturated zones will be the predominant source of surface runoff generation. The relative importance of the two processes of runoff generation is highly dynamic. Srinivasan et al. (2002) observed changes in the processes both within and between storm events. The relative importance of various hydrological processes and hence the processes and rates of mobilisation will depend on scale (Table 2-1) and thus are an important consideration in the design and interpretation of research on P mobilisation.

Table 2-1. Hydrological processes and approximate timeframes for their occurrence [adapted from Haygarth et al. (2000a)]

Term	Scale	Generic	Definition	Timescale
Base flow	Sl, F	H	Transfer of water underground in ‘background’ flow conditions, not pathway specific	Hr, D
Bypass flow	So	H	Implies a type of soil water movement – in the case of vertical movement along larger subsoil pathways, e.g., wormholes and fissures, often occurring in unsaturated conditions	Hr, Wk, M
Interflow	Sl, F	H	Lateral flows below the soil surface	Min, Hr
Macropore flow	So	H	As bypass flow, macropores are large enough (<60 μm) to allow gravitational drainage	Min, Hr
Overland flow	Sl, F	G, P	Movement of water exclusively over the soil surface, down slope during heavy rain	Min, Hr
Return flow	Sl, F	H	Where a sub-surface flow pathway emerges at the soil surface	Min, Day
Runoff	Sl, F	H	General hydrologic term describing the lateral movement of water off land above and below ground, causing a short term increase in flow at the watershed outlet	Min, Hr
Sub-surface flow	Sl, F	G	Lateral flows below the soil surface	Min, Hr
Surface runoff	Sl, F	H	As for overland flow	Min, Hr
Throughflow	So, Sl, F	H	General non-specific term describing water movement	na

Sl – slope; So – soil; F – field; H – hydrologic; G – geomorphologic; P – pedologic; Min – minutes; Hr – hours; Day – days; M – months

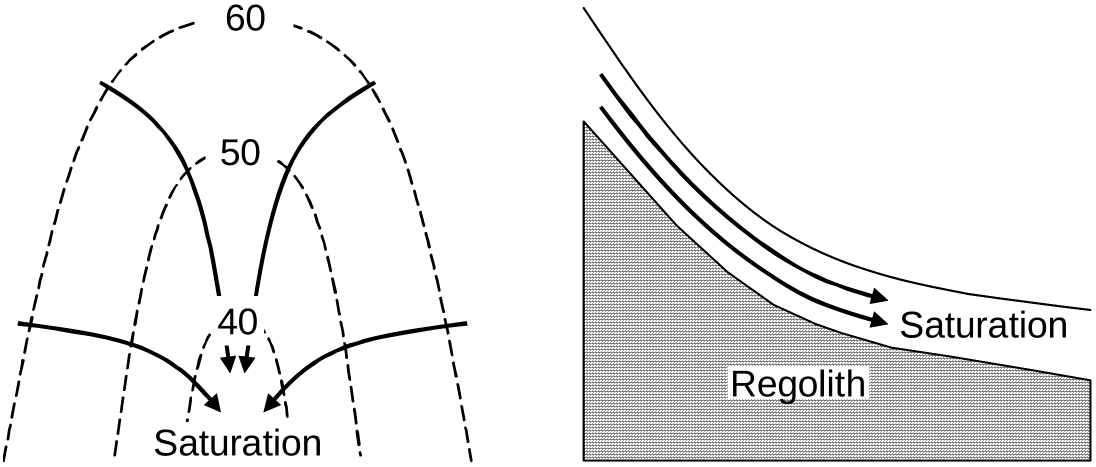

Figure 2-5. Common zones of moisture accumulation in the landscape [adapted from Ward (1984)].

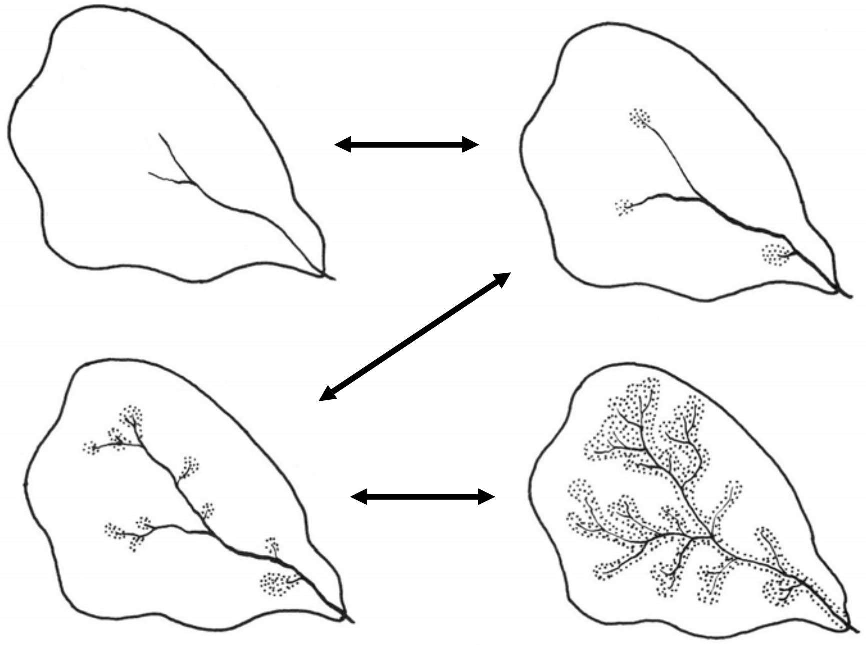

Figure 2-6. Schematic diagram of changing saturation zones during a rainfall event. Saturation zones (indicated by dotted areas) develop, and expand and contract (indicated by reversible arrows) during a rainfall event [adapted from Chorley (1978)].

2.4.2 Major pathways of P transfer

In many temperate regions, e.g., south–east Australia, surface runoff is the major hydrological transport pathway for P (Nash and Murdoch 1997; Fleming and Cox 1998; Stevens *et al.* 1999; Fleming *et al.* 2001) (see Table 2-2). However, under certain conditions sub-surface pathways can be important (Cox *et al.* 2002). Cox and Pitman (2001) observed no overland flow due to low rainfall, consequently groundwater return was the only active hydrological pathway and therefore accounted for the majority of P transported.

Table 2-2. Phosphorus transfer from intensive pasture systems by surface and sub-surface pathways.

Site	Runoff P (mg/L)	Sub-surface P (mg/L)	Load in surface runoff (% of total)	Reference
Flaxley east (Australia)	3.15	0.1	99	(Fleming and Cox 1998)
Flaxley west (Australia)	1	0.33	94	(Fleming and Cox 1998)
Keynes (Australia)	no runoff	~0.3	10	(Cox *et al.* 2002)
Gippsland (Australia)	high	<0.05	na	(Nash and Murdoch 1997; Nash and Halliwell 1999)
Mt Bold east (Australia)	na	na	90	(Stevens *et al.* 1999)
WE-38 (Penn. USA)	na	na	90^A	(Pionke *et al.* 2000)
MCR (Penn. USA)	0.065^B	0.017^C	78^D	(Pionke *et al.* 1996)
Brown (Penn. USA)	0.053^B	0.017^C	84^D	(Pionke *et al.* 1996)

na – not available

^{A}Lower slope position;

^{B}storm event TDP

^{C}average of TDP base and elevated base-flow components

^{D}proportion attributed to storm events

2.4.3 Variable source area (VSA)

There has been limited research specifically examining the VSA concept in relation to P in runoff from pastures. Several studies have examined the nature of these dynamic zones and found that these areas generating runoff are typically only a small part of the landscape. Gburek and Sharpley (1998) observed that only 10 % of a hillslope contributed to runoff. Cornish et al. (2002) also described some evidence for the existence of VSAs in eastern Asutralia. Srinivasan *et al*. (2002) found that these areas can be highly dynamic, such that their location and extent changes both within and between runoff events. Because VSAs often are a small component of the landscape, they are very important in the mobilisation and transfer of P and therefore in managing runoff water quality (Pionke *et al.* 1996; Gburek and Sharpley 1998; Pionke *et al.* 2000). Areas that rarely or never contribute runoff to waterways are relatively unimportant in the study and management of runoff to reduce P transfers off-site.

The identification of areas that do generate runoff may be particularly important for the location of research sites. For example, siting rainfall simulation studies in mid or upper slope positions that infrequently contribute to runoff may lead to inaccurate quantification of P transfer when extrapolations are made to landscapes that include other landforms, e.g., crests, plains, and valley bottoms. Systematic variations in source factors within a landscape may also contribute to such errors in extrapolation. Heathwaite and Dils (2000) and Cornish et al. (2002) observed that runoff P concentrations were greater from plots located further down the slope. In attempting to model runoff P export or concentrations, it is important to understand the runoff generation processes and the spatial and temporal distribution of runoff. Small scale studies, e.g., rainfall simulation, will not be able to provide such information as they only provide a limited spatial and temporal description of P transfer. Modelling non-contributing areas and the use of data generated under conditions vastly different from those occurring in the watershed may provide misleading models of runoff P (Gburek and Sharpley 1998). The study of Srinivasan et al. (2002) highlighted the complexity of studying the dynamics of contributing areas.

Consideration of the contributing areas in a watershed will aid our understanding of the processes of mobilisation. If for instance it is assumed that the whole watershed is contributing runoff, but in reality the contributing area is only 10 % of the total area, the runoff rate in the contributing area is ten times greater than if it is assumed that the whole catchment is contributing. The effect of location and subsequent flow characteristics needs to be considered when designing studies examining P transfer in surface runoff.

The mapping of topographic wetness index (TWI) is an approach that has potential to predict the likely extent of VSAs. The TWI is defined as ln(a/tanbeta), where a is the upslope contributing area per unit contour and tanbeta is the local slope angle. Areas with greater upslope contributing area and that are flatter have a higher TWI and are therefore potentially VSAs. However, the prediction of VSAs is highly sensitive to a number of parameters associated with the models used to derive the ‘a’ and ‘tanbeta’ values (Quinn *et al.* 1997). Further investigation of tools for identifying VSAs is required.

An extension of the VSA concept is that of critical source area (CSA). In this concept, only that part of the landscape generating runoff actually influences P concentrations in the runoff, other parts of the watershed having no influence on runoff quality, irrespective of source factors in these areas. It is these CSAs that should be managed for most efficient reductions in runoff P concentrations. For example, the adoption of practices that reduce P export by 50 % on that 10 % of the watershed generating runoff will lead to a 50 % reduction in P export for minimal change in management. Contrast this with implementation of new management practices across the whole watershed that will still only result in a 50 % reduction in P export but is far more demanding to implement and less likely to be adopted by land managers. The identification of CSAs is critical to the management of water quality whilst minimising the impacts on farm profitability and increasing the likely adoption of such strategies. Careful consideration of the effect of VSA and CSA concepts in designing research is essential.

2.5 Scale and landscape effects on P mobilisation and transport

There is a range of factors that affects the concentrations and loads of P transferred in surface runoff, including source, mobilisation, and transport factors. As previously discussed, hillslope hydrological characteristics vary with scale and time. It follows that measures of P transfer will also differ with scale (Heathwaite and Dils 2000; Nash *et al.* 2002).

In relation to P transfer, scale is often poorly defined and sometimes confused. It is important to differentiate issues purely associated with scale in the sense of size alone, e.g., plots 1 vs. 10 m long, and factors that may actually result, at least partially, from the measurement technique adopted or factors associated with landscape, e.g., change in hydrological processes. A particular difficulty is that a change in scale often results in a change in a range of factors such as hydrological pathways, sources, and measurement methods. These different pathways and differences in hydrology are often lumped together under scale. For example Cornish *et al*. (2002) compared various measures of runoff P concentrations at different scales. This study compared measures of P concentration in runoff from small 1 m^2 plots (with simulated rainfall of 150 mm/hr rainfall), small plots (3 m^2) large plots (30 m^2), paddocks (4 ha), and whole farm (140 ha) under natural rainfall. They concluded that the effect of scale on concentrations of P in runoff was small. Although not specifically defined by Cornish *et al*. (2002), by the nature of the study, their definition of scale included changes in size, hydrology, sources, and in-stream processes. Almost certainly, all of these factors varied among the various scales they studied.

In a similar study, Dougherty (unpublished 2003 - see Chapter 4 in this thesis) compared P concentrations in runoff from small plots (2 m long) nested within larger runoff plots (50 m) across a range of fertility levels. Simulated rainfall was applied at 80 mm/hr to the small plots and at 8 mm/hr to the large plots. Runoff P concentrations were significantly ($P<0.05$) lower (approximately 50%) from the smaller plots. However, the cause of differences in P concentrations could not be attributed specifically to plot size or rainfall intensity effects because the differences in size and rainfall intensity were confounded.

2.5.1 The effects of scale on processes determining P mobilisation

There is a continuum of scales at which P mobilisation and transport have been examined. For convenience they have often been arbitrarily divided on the basis of the most likely processes occurring at each scale. Studies can be categorised as laboratory, profile, plot, field, and watershed scale studies. Whereas laboratory– and profile–scale studies can be clearly differentiated, plot– and field–scale studies are less easily differentiated. Not only will the scale of the study affect the result or processes observed, but changes in scale will result in different topographic features, soil morphological properties, and landscape segments being incorporated within the study. Furthermore, source factors will tend to be more heterogenous at broader scales. Laboratory, profile, and plot studies lend themselves to testing of specific hypotheses whilst controlling variability in source, landscape, and broader scale hydrological processes. Haygarth and Jarvis (1999) proposed that profile and slope/field are the most important scales in agronomic terms and for understanding mobilisation processes. Broader scales, such as the watershed, are more important in terms of understanding the impact of nutrient mobilisation on regional water quality.

Because the distinction between scales is not simple, nor can the advantages and disadvantages of particular scales for studying P transfer be clearly defined. Nash and Halliwell (1999) noted that the use of plots generally involves hydrological isolation at the upslope end of the plots such that plots are drier than they would otherwise be, resulting in greater infiltration at the expense of runoff. Path length has also been proposed as an important determinant of runoff P concentrations (Gascho *et al.* 1998). However, this effect is far from simple because of the complex interaction between path length, flow rate, and therefore contact times. These interactions will be discussed later.

Heathwaite and Dils (2000) observed that P concentration in runoff from small plots was greater the further down a toposequence the plots were located, although they did not attempt to provide a reason for these differences. In a similar demonstration of the effect of hillslope position, Cornish *et al*. (2002) observed increases in P concentrations further down the hillslope from small plots. They attributed this to downslope movement of P–rich material over extended periods of time resulting in increased soil P. Whether this apparent pattern of soil P distribution is common or not and whether there is an influence of such a pattern on runoff water quality is unknown. The areas being examined in both cases were clearly not homogenous and differed systematically with landscape position. In both of these cases, the selection of any one segment of the landscape would have provided quite different estimates of runoff P concentrations from those derived from another segment of the landscape.

Plot studies tend to have one dimensional flow paths, such that surface runoff flows down a uniformly sloping plot with no cross slope. Typically such plots are relatively small and range from a few m^2 to <1 ha. Often plot lengths are in the range of 1 to 100 m. In contrast, watershed or field scale studies often incorporate more complex topography [e.g., Nash and Murdoch (1997); Fleming and Cox (2001)] such that measured concentrations are a combination of mobilisation, transport, and (because of their size) landscape hydrological effects.

A larger study area does not necessarily result in longer flow lengths, rather it may result in more variable path lengths. Contrasting studies in terms of size can be used to illustrate this point. Dougherty (unpublished 2003) studied P mobilisation in large plots of length 50 m and area of 1250 m^2. A contrasting study in terms of scale was that of Fleming and Cox (2001). They studied runoff from a 2.4-ha area with surface interception barriers at the lower end of the monitored area. The average path length of surface runoff (L_o) in these studies can be defined using the following equations (Horton 1945):

$$L_o = \frac{1}{2 \times D_d} \qquad \text{Eq. 2-2}$$

where D_d, the drainage density is defined as:

$$D_d = \frac{\sum L_s}{A} \qquad \text{Eq. 2-3}$$

where $\sum L_s$ is the sum of the stream lengths for the watershed and A is the drainage area of the watershed. Using Eq. 2-2 and Eq. 2-3, average path length on the small plots examined by Dougherty (unpublished 2003) was 25 m. Despite the relatively large area examined by Fleming and Cox (2001), the average path length calculated using Eq. 2-2 and Eq. 2-3 was only 30 m. Furthermore, the nature of mobilisation, transport, and hydrological processes would have been complicated in the study of Fleming and Cox (2001) by highly variable path lengths, complex surface morphology, heterogenous P sources, and variable source areas. It is hypothesised that research at broader scales does not necessarily provide advantages to improving the understanding of the processes resulting in P transfer. The objectives of research must be clearly linked to the scale at which the research is undertaken.

2.5.2 The effect of landscape on processes determining P mobilisation

The effect of incorporating landscape in studies of P transfer is to incorporate landscape scale transport factors and landscape hydrological pathways. At this scale, processes of mobilisation and transfer inevitably become more complex. This almost certainly leads to a decline in the relative amount of information obtained on specific mobilisation processes. However, the combination of a clear conceptual model of the system and landscape being examined and use of statistical techniques, such as non-linear regression, will assist in understanding the various processes resulting in P transfer [e.g., Nash *et al.* (2000)].

At the field scale, anything other than a perfect plane surface with slope in one direction will result in some convergence or divergence of flows and so potentially alter the mobilisation–transport processes. If soil morphological features such as depth to horizon differ within plots, then this may affect plot hydrology and hydrological pathways (Nash *et al.* 2000). Soil physical features such as the presence of macropores may change such that in various parts of the landscape, preferential flow becomes more important (Gachter *et al.* 1998; Cox *et al.* 2000; Cox and Pitman 2001). Landscape position may also affect moisture regimes, with areas lower in the landscape being preferentially predisposed to runoff compared to areas higher in the landscape.

2.5.3 The effect of changing flow conditions on runoff P

In the field there is a wide range of factors that are likely to affect the amount of P desorbed and consequently P concentration in surface runoff. These factors will influence two fundamental properties of P source–water interaction. The first is the contact time between runoff water and P source and the second, the runoff to P source ratio. In addition, factors such as ionic strength and composition will also be affected by these two factors exerting a secondary influence on P concentration. Typical runoff flow velocities are of the order of 0.3-15 cm/sec (Dunne 1978). Presumably because of high hydraulic resistance of pastures, the typical velocities for pastures are at the low end of this range. Increasing slope length will increase the average runoff–soil contact time. Slow flowing water has a greater contact time with P source and so will be expected to have greater concentrations of P in runoff (Haygarth *et al.* 2000). In an examination of scale effects, Gascho *et al*. (1998) compared P concentrations in runoff from plots 3 and 43 m long. Concentrations of soluble P were on average approximately 50 % greater from the large plots than the smaller plots. They attributed this difference to longer residence times on the larger plots.

Fleming and Cox (1998) identified an apparent dilution effect associated with high flow rates for dissolved P. This was likely to have been the result of a combination of wider runoff to soil ratios and shorter contact times. Similarly, McDowell and Trudgill (2000) observed an apparent reduction in P concentrations associated with high flows and an inability of the labile P pool to supply P rapidly to water. Sharpley (1980b) attributed a significant decrease in runoff P concentration with time to the dilution of soil solution P. These data suggest that, whereas soil has a capacity to supply P to runoff to maintain runoff water P concentrations under low to moderate flow conditions, under high flow conditions, the supply of P to solution may be too slow to maintain P concentrations. Conversely, Pionke *et al*. (1996) showed that dissolved P concentration increased above a threshold flow rate. These results were collected from a large, mixed landuse watershed where significant amounts of sediment could be expected to be transported. It may be that the increased dissolved P concentrations are associated with increased sediment loads that will increase the P concentration in runoff, as observed by Sharpley *et al*. (1981b).

2.5.4 Overland flow hydrological theory

It is hypothesised that the basic principles of overland flow hydrology can provide a basis for examining the effect of runoff path length and flow rates. For a given surface runoff pathway, e.g., hillslope, the greatest changes in flow conditions will be associated with changes in volume of runoff. Higher volumes of runoff from higher intensity rainfall will result in a greater depth of flow and higher velocities and therefore wider runoff to soil ratios and shorter soil–water contact times, respectively. For turbulent flows, depth can be estimated by combining the continuity equation:

$$q = D \times V \qquad \text{Eq. 2-4}$$

where q is the unit discharge (m^3/s/meter width), D = mean depth (m) and V = the mean velocity (m/s)

and the Manning equation:

$$V = \frac{D^{0.67} \times S^{0.5}}{n} \qquad \text{Eq. 2-5}$$

where n is the Manning resistance coefficient and S is the slope gradient (m/m)

Eq. 2-4 and Eq. 2-5 can be combined to yield

$$q = \frac{D^{1.67} \times S^{0.5}}{n} \qquad \text{Eq. 2-6}$$

Therefore, depth increases to a 0.6 power of the increase in discharge (q), the rest being attributable to changes in velocity. Therefore for a given slope and Manning resistance coefficient, doubling the unit discharge increases depth by a factor of 1.52 and velocity by a factor of 1.32. It follows that changes in discharge per unit area will increase the solution to soil ratio and decrease the contact time. The following sections will examine the effect of time of contact and solution to soil ratio.

2.5.5 Effect of time of contact and water:soil ratio

The effect of time of reaction on soil P dynamics has been explored in detail primarily in relation to the adsorption of P to soil such as occurs when fertiliser is added to soil. The timeframe of interactions between soil and runoff water are significantly shorter than those typically considered when examining dynamics of added P [e.g., Burkitt *et al*. (2002)]. In surface runoff occurring at the plot to field scale, contact or runoff residence times are in the range of 1 to 60 minutes (see Table 1).

The kinetics of P desorption in batch experiments have been used to explain differences in concentrations of P from rainfall simulation at different intensities on bare soil surfaces (Sharpley *et al.* 1981a). The kinetics of P desorption can be represented by the empirical equation:

$$P_d = K \times P_o \times t^{\alpha} \times W^{\beta} \qquad \text{Eq. 2-7}$$

where P_d is the amount of P desorbed (mg/kg) in time t (s), at a water to soil ratio W, P_o the initial amount of desorbable P present in the soil (mg/kg), and K, α (≤ 1), and β (≤ 1) are constants for a given soil. Sharpley *et al*. (1981a) fit this data to P desorption data acquired using batch experiments in the laboratory for a number of soils that had been recently treated with different amounts of P. The equation tells us that as t increases, P_d increases, but at a declining rate. Similarly, as W increases, P_d also increases, but at a declining rate. The effect of these parameters is shown in Figure 2-7. Figure 2-7 also shows that P_d increases with the amount of P added (or the initial amount of desorbable P present, P_d). Eq. 2-7 can be combined with the following equation:

$$P_c = \frac{P_d}{S} \qquad \text{Eq. 2-8}$$

where P_c is the P concentration in solution and S is the volume of solution such that,

$$P_c = \frac{K \times P_o \times t^{\alpha} \times W^{\beta}}{S} \qquad \text{Eq. 2-9}$$

If the amount of solution with which soil is in contact doubles, W also doubles. Therefore the change in P_c is proportional to W^{β}/S, such that P_c will decrease as a function of the value of β.

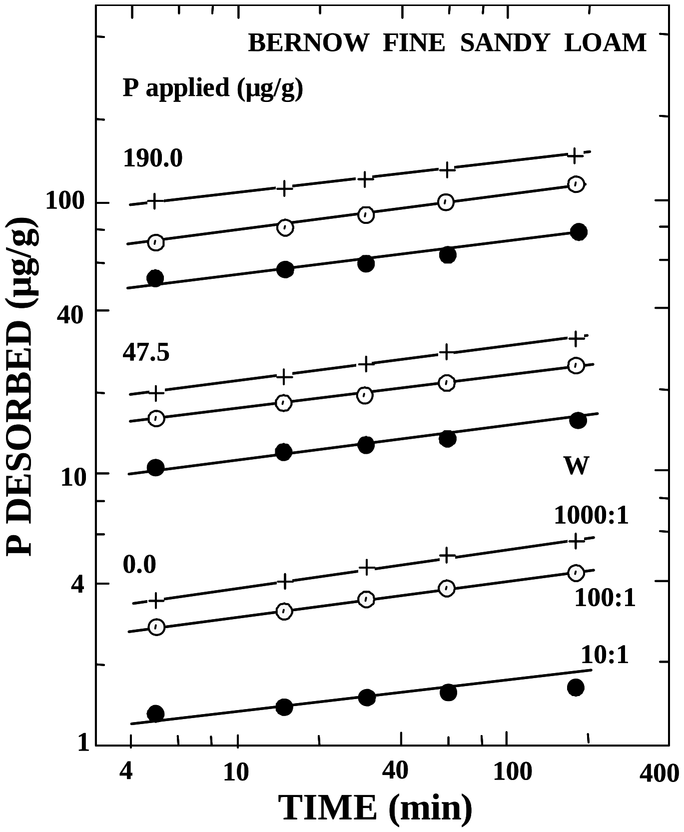

Figure 2-7. Relationship between amount of phosphorus desorbed and time and phosphorus amendment levels and solution to soil ratio (W) (Sharpley *et al.* 1981a)

The utility of such relationships under pasture systems is not clear. There are likely to be substantial differences between the stable pasture systems and the bare soil systems examined by Sharpley *et al*. (1981b) and Ahuja *et al*. (1982) in the development and testing of these relationships. One likely difference will be the solution to soil ratios. The high solution to soil ratios in bare soil situations are unlikely to be applicable for stable systems where pasture and the organic horizon stabilise the soil surface. Sharpley *et al*. (1981b) and Ahuja *et al*. (1982) assumed that the interaction between the runoff and soil phases involved mixing of the two similar to that occurring in batch experiments. However, in pasture systems where sediment concentrations are low or negligible, the solution to soil ratios are most likely to be significantly narrower. This is because the solution–soil interaction is essentially bi-phasic, i.e., water is running over the surface of the soil without any substantial physical mixing. The ‘t’ term in the equation is assumed to be the total time of runoff and ‘W’ the ratio of total volume of runoff to sediment concentration. It may be more appropriate to use the instantaneous ‘W’ value and average residence time of water with soil as the ‘t’ value. If runoff occurred for 30 minutes at 5 mm/hr and interacted with the top 3 mm of soil, the solution to soil ratio would be 0.83. The use of 30 minutes as the ‘t’ term may be inappropriate, rather the average residence time of water in contact with the soil may be more appropriate for pastures.

The effects of flow rates on time of contact and solution to soil ratio, and the subsequent effects on runoff P concentrations, relate primarily to desorption processes of orthophosphate from soil. As previously discussed, P in runoff from pasture systems is derived from a complex combination of sources including adsorbed P, precipitated P, organic P, manure P, and plant P. Whereas some of these sources will conform to the empirical relationships derived by Sharpley *et al*. (1981a), it is possible that not all components contributing P will. An understanding of these relationships and the effect of organic soil P on them is a critical component of understanding P mobilisation in pasture–covered soils and differences with scale.

2.6 Rainfall simulation

Rainfall simulation has been widely used to evaluate the effects of management on erosion and nutrient mobilisation processes and quantities under a wide range of conditions [e.g., Meyer (1965); Loch and Donnollan (1982); Pote *et al*. (1996); Humphry *et al*. (2002)]. A significant advantage of rainfall simulators is that they allow multiple measurements to be made covering a range of conditions over a larger area than is generally possible using conventional measures (Mech 1965; Connolly *et al.* 2002).

Rainfall simulation was originally developed with a view to examining erosion. Therefore issues such as raindrop energy and size distribution were the focus of much of the early research on simulation methods (Meyer 1965). Minimum plot lengths may also be required to simulate various processes occurring in the field. Loch and Donollan (1982) noted that approximately 6 to 12 m were required to observe rilling under rainfall simulation. Pasture systems generally can be regarded as stable systems with little transport of sediment occurring. Because ground cover is usually close to 100 % in these systems, it is reasonable to expect that all raindrops will be intercepted by plant material before they hit the soil surface or by organic material deposited on the soil surface (Torri and Borselli 2000). Consequently, energy input to the soil surface in the form of raindrop impact is reduced to negligible levels. Ahuja *et al*. (1982) and Sharpley (1985) simulated this effect by using screens over soil. They showed that fine screens simulating heavy plant cover dramatically reduced P mobilisation such that sediment levels were negligible.

2.6.1 Rainfall/runoff intensity

Rainfall simulation has been undertaken at rainfall intensities ranging from 50 mm/hr (McDowell and Sharpley 2001a) to 150 mm/hr (Cornish *et al.* 2002). Most commonly, intensities of 80 to 90 mm/hr for 30 to 45 minutes [e.g., Sharpley *et al*. (1981b); Pote *et al*. (1999)] have been used. These rates presumably have been for convenience. High rates allow quick measurements to be made as well as the testing of management effects under extreme conditions when sediment losses, for instance, would be expected to be high (Loch and Donnollan 1982). It follows that at these high rainfall intensities, runoff rates are also high. This is often exacerbated by the practice of pre-wetting soils to minimise initial differences in soil moisture contents (Pote *et al.* 1999; Humphry *et al.* 2002).

Based on the previous discussions of the processes of dissolution and the effect of hydrology, it is logical to question the effect that high rainfall intensities and subsequent runoff rates have on P concentration. Use of rainfall simulation to study P transfer requires consideration of not only the issue of the effects of scale and the processes that are measured, but also the tendency for high rainfall intensities to be used. Sharpley *et al*. (1981a) examined the concentrations of P in runoff at two rainfall intensities. An increase in rainfall intensity from 60 to 120 mm/hr resulted in a reduction of P concentrations by 30 to 40 %. Whereas there has been some examination of the effect of hydrological parameters under rainfall simulation in bare soil (Sharpley *et al.* 1981a; Ahuja *et al.* 1982) there have been no attempts to examine the effect of rainfall simulation intensity on runoff P concentrations under pasture. The limited interaction between soil and overland flow in these highly stable systems is likely to render these situations dramatically different from bare soils. These issues are particularly important if runoff P concentration data derived from rainfall simulations are to be used to accurately model runoff P concentrations at the field or watershed scale.

2.6.2 Plot size (length)

Plot size will have two effects, one on variability (and therefore number of plots required to achieve a given level of statistical confidence) and one on plot length (which will dictate path length and therefore times of travel and duration of contact between P source and water). The effect of increasing plot length is not simple because increasing plot length increases the discharge and therefore the depth of flow, and velocity of runoff. Therefore, increasing plot length increases contact time and P source to soil ratio. However, these increases are not linearly related to plot length, as discussed previously.

2.6.3 Modelling the effect of rainfall simulation parameters

A knowledge of overland flow theory and the models of P desorption previously discussed can be combined to propose a model of the effect of changes of rainfall simulation intensity on runoff P concentration. Based on a simple law of conservation, runoff rates can be defined as follows:

$$\mathrm{RO} = \mathrm{RF} - \mathrm{I} - \frac{dP}{dt} \qquad \text{Eq. 2-10}$$

where RO is runoff rate, RF is rainfall rate, I is infiltration rate, and dP/dt is change in surface depression storage (all units mm/hr). Under steady state conditions, dP/dt can be assumed to be zero. Eq. 2-10 can be used to predict the effect of rainfall intensity on runoff rate under various rainfall rates at Flaxley in the Adelaide Hills, South Australia. Assuming that the infiltration rate of the soil surface is 45 mm/hr, doubling the rainfall rate from 60 to 120 mm/hr will result in a 5-fold increase in runoff rate. A further increase to 180 mm/hr would result in a 9-fold increase in runoff rate compared to that at 60 mm/hr rainfall. The effect of the change in rainfall rate from 60 to 120 mm/hr on P concentration can then be considered using Eq. 2-9 and parameters derived by Sharpley *et al*. (Sharpley *et al.* 1981a). Typical α and β values of 0.2 are used in the following discussion. Increasing the rainfall rate from 60 to 120 mm/hr will increase Q by 5. Assuming constant n and S, based on Eq. 2-5 and Eq. 2-6, D will increase by a factor of 2.6 and t will decrease by a factor of 0.52. Therefore, assuming constant K and P_d,

$$\frac{\mathrm{P}_{120}}{\mathrm{P}_{60}} = \frac{\mathrm{t}_{120}{}^{0.2}}{\mathrm{t}_{60}{}^{0.2}} \times \frac{\mathrm{W}_{120}{}^{0.2}}{\mathrm{W}_{60}{}^{0.2}} \div 2.6 \qquad \text{Eq. 2-11}$$

and,

$$\frac{P_{120}}{P_{60}} = \frac{0.52^{0.2}}{1^{0.2}} \times \frac{2.6^{0.2}}{1^{0.2}} \div 2.6 = 0.41 \qquad \text{Eq. 2-12}$$

where P_{120} and P_{60} are the P runoff concentrations under rainfall intensities of 120 and 60 mm/hr respectively. That is, an increase in rainfall intensity from 60 to 120 mm/hr will decrease runoff P concentration by greater than half. The range of P sources being mobilised may not necessarily conform to simple chemical kinetic effects nor do the runoff conditions under pasture necessarily behave similarly to those from which the equations were derived. Although the above examination of hydrological parameters has been theoretical only and has used only values reported in the literature, it is hypothesised that the above procedures can be used to predict the effect of rainfall simulation parameters under given conditions. It is also proposed that the methodology may be used to more accurately predict runoff at broader scales, e.g., hillslope, using data gathered from rainfall simulation.

2.7 Conclusions

Concentrations of phosphorus (P) in surface runoff from intensive pasture systems are often greater than watershed water quality targets. Consequently, there has been a considerable investment in research to devise strategies to reduce P transfers from these intensive pasture systems. This research has been carried out at a range of scales that can be classified as laboratory, profile, plot, field, and watershed. The research has involved identification of the processes of mobilisation and the effect of various sources of P on P transfer in runoff. Phosphorus in runoff is primarily in dissolved and colloidal forms. Increasing soil P results in an increase in the concentration of P in runoff and the occurrence of runoff soon after application of fertiliser or manure often results in high concentrations of P. The majority of the research has been focussed on inorganic P sources. Less well understood is the effect of organic P pools such as plant biomass, despite the fact that these are frequently identified as making a potentially large contribution to losses of P in runoff.

There has been a growing need to consider P transfer in runoff in a broader context, i.e., the relationship between transfer at finer scales with that at broader scales and the consequent impacts on water quality. The development of conceptual models of P transfer has facilitated the identification of links between source, mobilisation, and transport. A modification to these models has been proposed that includes the effects of climate and landscape. This improves our ability to identify the linkages between source, mobilisation, and transport at the various scales. The concept of ‘scale’ has been poorly defined in the literature. The concept of scale in the context of P transfer is not just one of size, but must also include source, mobilisation, and transport processes, all of which vary with scale. Careful consideration of the effects of scale is essential to understanding and limiting P transfer in surface runoff.

The modified model necessitates a more thorough consideration of the hydrological processes influencing runoff at the landscape scale. Runoff generation in intensive pasture systems in temperate regions generally occurs by a combination of the processes of infiltration excess and saturation excess. The areas of this runoff generation can be highly variable, both temporally and spatially. Yet there has been relatively little attention paid to these factors in the design, siting, and interpretation of research. Although the variable and critical source area concepts are well accepted, the limited research to date has shown that identification of these areas and their relationship to P transfer in runoff is not simple. Use of hydrologic models such as TOPMODEL (Quinn *et al.* 1997) or the Soil Moisture Routing Model (Frankenberger *et al.* 1999) to identify these areas shows promise, although these models require further development and testing in pasture systems.

It is proposed that the conceptual model of P transfer will allow results generated at fine scales, e.g. small plot, to more accurately predict P transfer at paddock and hillslope scales. In addition to outlining a conceptual model to compare scales up to the hillslope, a mathematical basis for predicting scale and methodology effects has been proposed. However, further research is required to examine the relationships between hydrological processes at a range of scales and their impact on the processes and magnitude of P mobilisation. A thorough consideration of scale effects using the conceptual model of P transfer outlined in this paper will facilitate more effective research and consequently, improved strategies for reducing P losses in surface runoff.

Chapter 3 General materials and methods

3.1 Introduction

Various methods were repeatedly used for the experimental work presented in this thesis. In order to avoid repeatedly describing these methods, they are described in detail in this chapter. Thereafter, reference is made to the appropriate sections in this Chapter. Only methods that have been utilised more than once are described, other methods being described in the Materials and Methods section of the relevant experimental Chapter. Where variations of the methods described herein are used in a particular Chapter, these variations are described in the Materials and Methods section of that particular Chapter. A description of the two sites used in this research is also included.

3.2 The study sites

Two study sites were used in the experiments discussed in this thesis. The sites were located in key dairying districts in New South Wales and South Australia (Figure 3-1). Both sites are located in regions that have sensitive waterways that periodically are of poor quality and consequently have been the subject of various actions to improve this water quality.

3.2.1 Flaxley

The site at Flaxley (Flaxley Agricultural Centre) was chosen for this research (Chapters 5, 6, 7, 8, 9) because it was the location of a larger Dairy Australia funded study (DAS10815 - Flaxley Farmlets: Nutrient loads in run-off water at high stocking densities) with which this PhD was associated and through which it was funded. Furthermore, the site had a long history of dairying that has resulted in a wide range of soil P concentrations appropriate for the study of P accumulation and mobilisation. The larger DAS 10815 project examined the effect of different nutrient management strategies on P exports and the possibility of modelling these exports using a combination of simple chemical and hydrological models. The study site used in the PhD is known as ‘Flaxley east’ (referred to simply as Flaxley hereafter) and was a small sub-catchment of 2.4 hectares. It had previously been used in the investigation of processes of P export from a sub-catchment (Fleming and Cox 1998; 2001; Fleming *et al.* 2001).

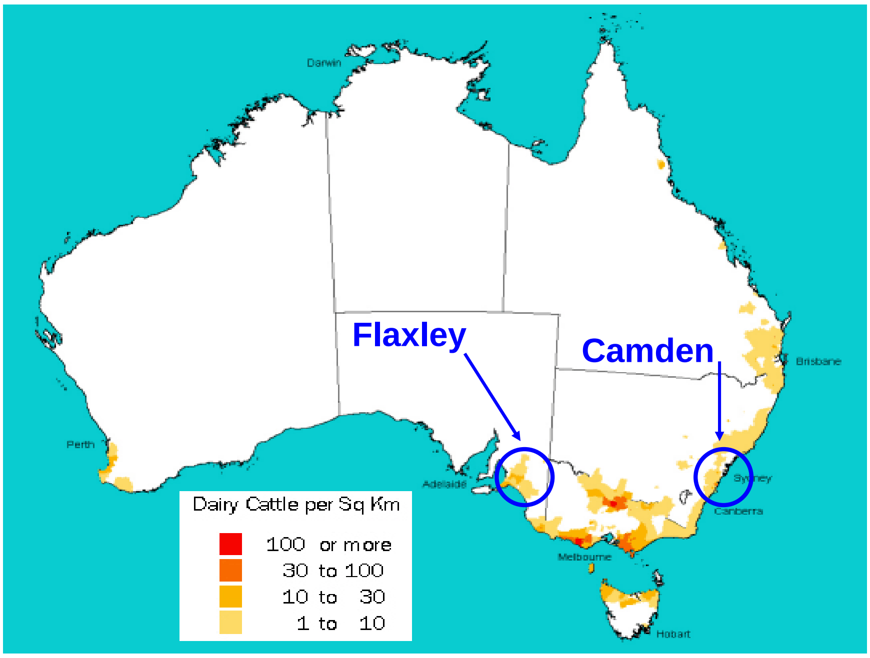

Figure 3-1. Location of the two study sites in relation to dairying regions of Australia (Dairy Australia, 2001). Flaxley – 35^{o} 08'S, 138^{o} 49'E; Camden 34^{o} 06', 150^{o} 42'E.

Flaxley is located in the Adelaide Hills, South East of Adelaide at an elevation of 400 m. Average annual rainfall at the site is 800 mm and is highly winter dominant (Figure 3-2). The runoff season typically extends from July to September. Overland flow is the dominant pathway for P export at this site (Fleming and Cox 1998). The sub-catchment has a relief of approximately 15 m and slopes ranging from 4 to 14%.

The soil at the site is predominantly duplex in nature, with a sandy-loam (10-15% clay) overlying a medium clay sub-soil. A typical soil profile is described in Table 3-1. The pH_{Ca} (1:5; soil:10 mM $CaCl_2$ solution mixture) of the topsoil ranges from 5 to 6 and organic carbon from 4 to 6%. Soil P of the topsoil varies widely as described below. The soil is classified as a Ferric Eutrophic Brown Chromosol (Isbell 1997) or Haploxeralf (Soil Survey Staff 1999).

Until 1985, there were milking sheds adjacent to the sub-catchment resulting in large, but spatially variable inputs of P, most likely via a combination of fertiliser, manure, wash-down effluent and stock feed. Intensive soil sampling within the sub-catchment in 1996 indicated that Colwell P (Colwell 1963) concentrations (0-0.10 m) ranged from 15-441 mg/kg. Since 1996, the sub-catchment has been managed uniformly as part of a larger paddock and has received 15 kg P/ha annually in Autumn in the form of single superphosphate (9% P). However, in the year of the rainfall simulations (2004) no P fertiliser was applied in order to avoid direct fertiliser effects on runoff P concentrations. The pasture at the site is a mixture of perennial ryegrass (*Lolium perenne L.*) and white-clover (*Trifolium repens L.*) with some invasive weed species.

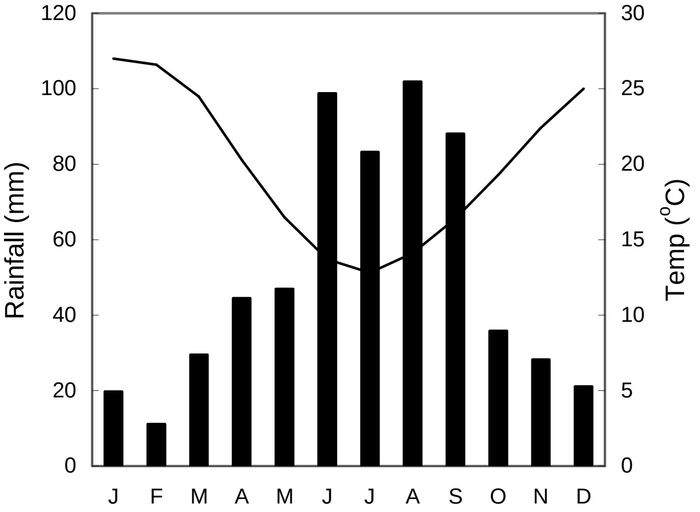

Figure 3-2. Average monthly rainfall and temperature at Flaxley.

3.2.2 Camden

The Camden site was used for studying the effects of scale on runoff P mobilisation (Chapter 4) and the P stratification study (Chapter 7). The site had been established and maintained as part of a Dairy Australia funded project 'Optimising fertiliser P use in NSW – DAN 088'. As part of this study, large runoff plots (1250 m^2) existed that were instrumented to monitor and sample runoff. There were six of these runoff plots that received 0, 20, 20, 40, 40 and 80 kg P/ha/yr but were otherwise treated similarly. The site is referred to as 'Camden' hereafter and has been previously used in the investigation of patterns of P export from a sub-catchment (Dougherty *et al.* 2001).

Camden is located in the Hawkesbury-Nepean Catchment, approximately 80 km south-west of Sydney, at an elevation of 200 m. Average annual rainfall at the site is 794 mm and is slightly summer dominant Figure 3-3. There is no distinct runoff season. During the life of the 3.5 year runoff study, runoff events were evenly distributed, two occurring in each of the seasons of Summer, Autumn, Winter and Spring. The slope of the plots was 5% ± 0.5%.

Table 3-1. Morphological description of typical soil profile in the mid-slope position at Flaxley (Fleming *et al.* 1996). The soil is classified as a Ferric eutrophic Chromosol (Isbell 1997) or Haploxeralf (Soil Survey Staff 1999).

Horizon	Depth (m)	Description
A	0-0.11	Light brownish grey (10YR 6/2) dry, and dark greyish brown (10YR 4/2) moist; fine sandy loam, weak medium sub-angular blocky structure; clear boundary
A_2	0.11-0.25	Greyish brown (10YR 5/2 dry, and dark greyish brown (10YR 4/2) moist; silty clay loam; moderate medium angular blocky structure; clear boundary
B_{21}	0.21-0.51	Reddish brown (2.5 YR) dry, and dark reddish brown (2.5YR 3/4) moist; 35% reddish yellow mottles (7.5YR 6/6) dry; medium clay; moderate medium angular blocky structure parting to strong fine angular blocky; diffuse boundary
B_3	0.51-0.87	A mixture of reddish brown (2.5YR 4/4) with reddish yellow (7.5YR 6/6) dry and of dark reddish brown (2.5YR 3/4) with strong brown (7.5YR 5/6) moist; medium clay; moderate medium angular blocky structure parting to strong fine angular blocky; diffuse boundary
C/B	0.87-1.00	Mixture of reddish brown (2.5YR 4/4) dry, and 45% dark red (10R 3/6) moist; light grey (2.5Y 7/0) and olive yellow (2.5Y 6/8) dry weathered parent material (55%); light clay; moderate medium angular blocky structure for developed soil and massive for weathered parent material

The soil at the site is duplex in nature, a clay-loam (30-40% clay) overlying a medium clay sub-soil. A typical soil profile is described in Table 3-2. The pH_{Ca} of the topsoil ranges from 5 to 6 and organic carbon from 3 to 5%. The soil P status of the topsoil varies widely between the plots as a function of the differential P fertiliser rates. The soil is classified as a Brown Chromosol (Isbell 1997) or Haploxeralf (Soil Survey Staff 1999). Pasture at this site is also a mixture of perennial ryegrass (*Lolium perenne L.*) and white clover (*Trifolium repens L.*).

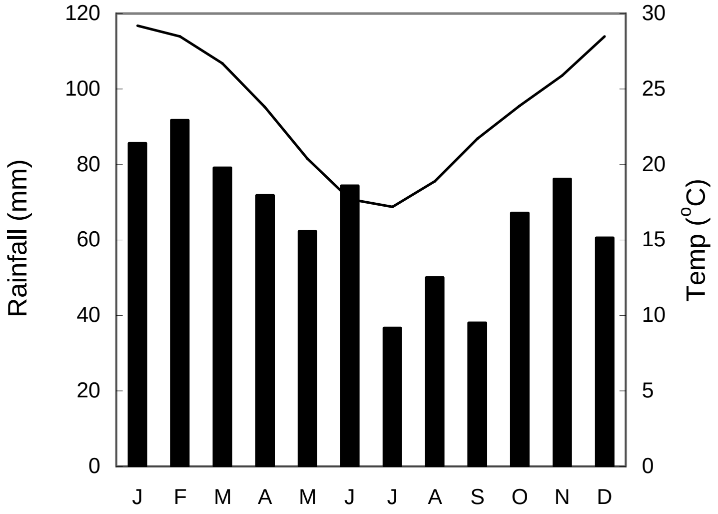

Figure 3-3. Monthly average rainfall and temperature for Camden (80 year average).

Table 3-2. Morphological description of typical soil profile from Camden (Roy Lawrie, NSW DPI pers comm.). The soil is classified as a Brown Chromosol (Isbell 1997) or Haploxeralf (Soil Survey Staff 1999).

Horizon	Depth (m)	Description
A_1	0-0.19	Grey brown (10YR 5/2), loam, hard-setting (4 BR) when dry, moderate pedality (polyhedral), earthy fabric, gradual boundary.
A_2	0.19-0.31	Light grey brown (10YR 6/3), clay loam, earthy fabric, weak pedality, hard-setting (4 BR) when dry, a few ferro-manganiferous concretions, clear boundary.
B_1	0.31-0.59	Dark yellow brown (10 YR 4/4), medium clay, smooth ped-fabric, dense, very hard when dry (5 CR), contains many fine roots, gradual boundary.
B_2	0.59-0.80	Yellow brown and red brown mottled medium clay with slight to moderate amounts of angular grit, rough ped fabric, gradual boundary.
B/C	BC	As above with no grit, smooth ped fabric, diffuse boundary.
C	0.80->1.63	Red brown and grey medium clay, smooth ped fabric, continues to >163 cm.

3.3 Analytical quality assurance

A number of procedures were implemented to ensure the integrity of analytical results. These are outlined briefly below.

All chemical reagents were of ‘AR’ grade. Calibration standards were prepared from these. Phosphorus standards were stored at 4°C and new standards prepared every 4 months. All water used in the preparation of standards, reagents and washing was de-ionised (DI) following a reverse osmosis (RO) treatment.

The dispensing volumes of pipettes and bottle top dispensers were routinely verified. This involved pre-rinsing a pipette tip (in the case of pipetters) and dispensing 5 volumes of liquid, then measuring on an analytical balance (± 0.0001 g) the volume of liquid dispensed 10 times and using the average in all further calculations involving that volume of liquid being dispensed. At all times, pipettes and dispensers were within ±0.5% of their nominated dispensing volume.

Glassware used in the preparation of P standards was ‘A’ grade to maximise accuracy of reagent preparation. All plasticware/glassware used in analytical procedures was soaked overnight in P free detergent (Comprox® – BP Australia), then soaked overnight in RO water prior to acid washing (>1 hour), and then rinsed 3 times with RO water.

Blanks, standards and duplicates were included in all analytical batches. Analytical values for standards were determined to be within 5% of their known values or the analytical batch was rejected and re-analysed.

3.4 Rainfall simulation

The rainfall simulator used in experiments at Flaxley (Chapters 5, 6, 7 and 9) was a rotating disc simulator (Figure 3-4). It was based on a spinning disc with a ‘v-notch’ that allowed water to spray onto the plot when the notch was ‘aligned’ with the spray nozzle. The intensity of rainfall was adjusted by changing the frequency of which the nozzle and notch were aligned. The disc would rotate past the ‘aligned’ position, then stop, before again rotating past the ‘aligned’ position. The time spent in the ‘un-aligned’ position determined the rainfall intensity. The movement of the rotating disc was controlled by a microprocessor (CPU) into which the target rainfall intensity could be programmed. Further details of the simulator and its construction are outlined by Malinda *et al*. (1992).

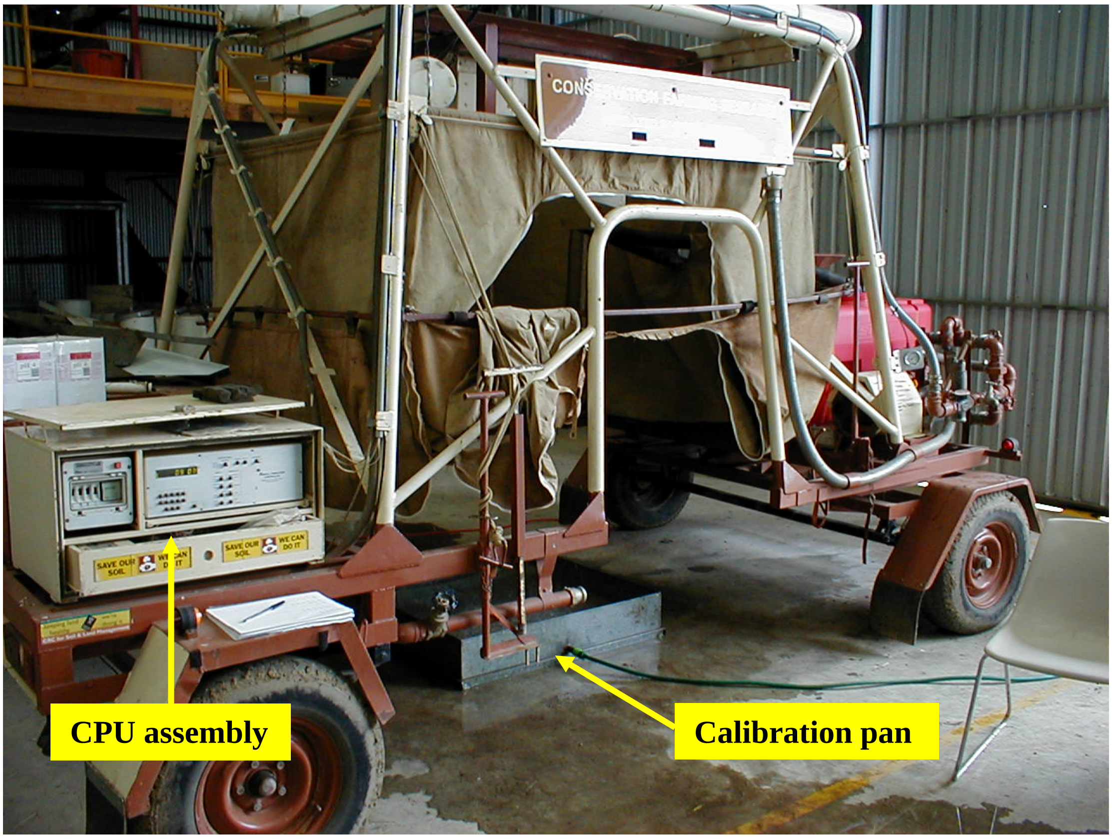

Figure 3-4. Rainfall simulator (Flaxley, SA) during calibration phase.

A ‘calibration’ was developed that described the relationship between the ‘programmed’ rainfall intensity and the ‘actual’ rainfall intensity. The ‘actual’ rainfall intensity was determined as the amount of rainfall falling on to a 1 m^2 calibration pan in 20 minutes at a range of programmed intensities. This was then converted to rainfall intensity (mm/hr). Five intensities were used in a randomised order and replicate measurements made. Results of these measurements are shown in Figure 3-5. The 2003 calibration was used for the rainfall intensity experiments in Chapter 5 whereas the 2004 calibration was used for the runoff tray and field simulations in Chapters 6, 7 and 9 respectively.

The coefficient of uniformity of application was estimated by placing small containers at 10 cm spacings in a grid pattern under the rainfall simulator and applying water at a given intensity for a given time. The coefficient of uniformity of application was calculated as:

Coefficient of uniformity = 100 – (σ / Y) Eq. 3-1

where Y is the mean of the volume of water applied to each 1 m^2 area and σ is the standard deviation of the volumes applied to each 1 m^2 area. The co-efficient of uniformity for this simulator was calculated to be 78%.

3.5 Water sample handling and analysis

This section describes the handling and analysis of water samples associated with rainfall simulation, including both the water applied by the simulator and the subsequent runoff water.

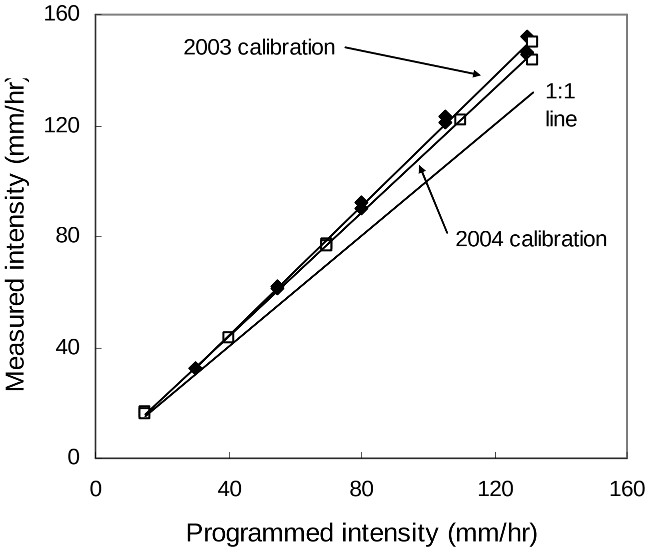

Figure 3-5. Calibration curves for the rotating disc rainfall simulator (Flaxley, SA) calibration curves for 2003 (♦) and 2004 (□). Intensity$_{actual-2003}$ = 1.16 × programmed intensity − 1, $r^2 = 1^{***}$. Intensity$_{actual-2004}$ = 1.12 × programmed intensity − 2, $r^2 = 1^{***}$. Programmed intensity is that entered into the simulator controller.

3.5.1 Sample handling and filtration

For the determination of a range of analytes in runoff, a 250 mL sub-sample was typically collected. Where discrete samples were required at intervals during runoff, only 20 mL sub-samples were collected (to minimise biases in the final composite). Once collected, samples were shaken vigorously (to suspend any sediments and ensure a representative sub-sample was taken) immediately prior to being filtered (<5 mins) in the field using a 0.45 µm prepackaged filter (Sartorius® - Germany). Typically, 12 mL of sample was passed through the filter using a syringe. The first 2 mL of filtrate was discarded to minimise any contamination due to the filter matrix and then the rest of the filtrate collected. The samples on all occasions had very low concentrations of suspended sediment (SS), typically < 100 mg/L (see results sections for various Chapters) such that the samples passed easily through the filters. This precluded the possibility that clogging of the filters resulted in a reduced effective filtration size as more sample was filtered (Gimbert *et al.* 2005).

3.5.2 Runoff sample analysis

Phosphorus analyses were undertaken on both filtered and unfiltered runoff samples.

Dissolved reactive P (DRP)

Molybdate reactive P was determined on filtered samples using the molybdenum blue method of Murphy and Riley (1962) and is referred to as dissolved reactive P (DRP). This method involved the addition of a mixed colour reagent to the sample, allowing colour to develop for 30 min and then reading the absorbance of the sample on a UV-Vis spectrophotometer (Shimadzu® - Japan) at a wavelength of 882 nm in a plastic cuvette (1 cm path-length). A calibration curve was constructed using standards ranging from 0 to 1 mg/L. Blanks and duplicates were included in analytical batches for quality assurance purposes. The colour reagent was made as described in Rayment and Higginson (1992b). Briefly, mixed colour reagent was prepared freshly prior to each analytical run by adding 1.056 g l-ascorbic acid to 100 mL of reagent A, 2 L of which contained 12 g ammonium molybdate, 140 mL sulphuric acid, and 0.2669 g potassium antimonyl tartrate.

Total dissolved P (TDP)

Total P in the dissolved (<0.45 μm) fraction (defined as TDP) was determined using an acidic persulphate digestion technique (Anon. 1995) followed by colorimetric determination (Murphy and Riley 1962). Five mL of sample was pipetted into a plastic 10 mL centrifuge tube, and then 0.66 mL of the digesting reagent was added. The digesting reagent was made by adding 6 g $K_2S_2O_8$ and 5.5 mL concentrated sulphuric acid to a 100 mL flask and making to volume. Samples were then capped and autoclaved at 121^{o}C and 45 kPa for 30 mins. Samples were then cooled and colour reagent added as in the MRP method except that the H_2SO_4 concentration in the colour reagent for this analysis was halved to compensate for the acidity of the digested sample. Samples, blanks and calibration standards were all treated in the same manner.

Dissolved un-reactive P (DUP)

Dissolved un-reactive P was defined as the difference between the TDP and DRP contents of runoff samples. It was used to provide an estimate of the organic P component of the dissolved fraction of runoff (Haygarth *et al.* 1998; Heathwaite *et al.* 2005) although it may also include polyphosphates and some sorbed colloidal P (Hens and Merckx 2002).

Total P (TP)

The total concentration of P and other elements in water was determined on unfiltered samples using acid digestion followed by measurement using ICPAES. Because of possible sediment bound P in the unfiltered sample, a more aggressive acid digestion was considered necessary (compared to that required for determination of TDP) to ensure the solubilisation of all P. Determination of P by colorimetry requires neutralisation of the digest (a task that was often unreliable and excessively time consuming), hence P was determined by inductively coupled plasma emission spectroscopy (ICPAES). The use of ICPAES also allowed other elements to be determined. The detection limit for P by this method was typically 0.03 mg/L. The samples were digested by adding 2 mL of nitric acid to 10 mL of sample and digesting at 160^{o}C for 4 hours. The remaining solution was then made up to 50 mL and submitted for analysis. Blanks were treated in the same manner. Standards used for calibration of the ICPAES were in an acid matrix of similar composition. The ICPAES analyses were conducted at the Waite Analytical Service of the University of Adelaide.

Dissolved organic carbon (DOC)

Dissolved organic carbon was determined by measuring the organic carbon concentration in filtered (<0.45 µm) samples using a Skalar Formacs® (Skalar – Germany) organic carbon analyser. These analyses were undertaken by CSIRO’s Analytical Chemistry Unit.

Suspended sediment (SS)

Suspended sediment was defined as that sediment not passing through a 0.45 µm filter. Although slightly larger pore sizes are sometimes used, (e.g. 1.2 µm), 0.45 µm was adopted in this research to provide consistency with the filter size commonly used to define dissolved P. Suspended sediment was determined by washing and pre-drying a 0.45 µm filter at 40^{o}C for two hours then weighing it (± 0.0001 g). A known volume of runoff (± 0.01 mL) was then passed through the filter under vacuum before the filter was re-dried for two hours and re-weighed. The suspended sediment concentration was calculated using the following equation:

$$SS = \frac{FP_f - FP_i}{V_f} \times 10^3 \qquad \text{Eq. 3-2}$$

where SS is suspended sediment (mg/L), FP_f is dried filter paper weight after filtration (g), FP_i is initial dried filter weight (g), and V_f is the volume of solution passed through the filter (L). The estimated lower detection limit (LLD) of this method was 10 mg/L.

3.6 Soil sampling, handling and analysis

Soil samples were collected for use in rainfall simulation data interpretation and the development of relationships between soil P and runoff P. The shallowest soil depth increments (typically <0.01 m) have been shown to have the greatest influence on runoff P concentrations (Ahuja *et al.* 1981; Sharpley 1985). These were routinely collected and analysed along with 0.10 m increments to allow comparison of the 0.01 m samples with those from the 0-0.1 m depth.

3.6.1 Sampling collection and preparation

Soil samples were typically collected for the 0-0.1 and 0-0.01 m depth increments to provide soil regarded as being related to plant nutrition and runoff characteristics respectively. Soil samples were collected for the 0-0.10 m soil depth by using a push sampler with a 0.02 m diameter tip. The push sampler consisted of a piece of steel tubing with a bevelled end (to allow easy insertion into the soil) mounted on a frame that allowed the operators body weight to be used to push the sampler into the soil. Twenty-five samples were collected on a 0.20 m grid within each rainfall simulation/sampling plot (Chapters 5 and 6). For collection of the 0-0.01 m cores, the same sampling pattern was used. Intact cores were removed and placed on a suitable surface and the 0-0.01 m component collected by sectioning the cores using a sharp knife. At the Flaxley site, there was typically very little pasture mat on the surface allowing easy delineation of the prescribed sampling depths (Chapter 7). At the Camden site a pasture mat was present in places. This was removed prior to sectioning of the cores and the ‘true’ soil-surface was used as the basis for determining the sampling increments (Chapter 7).

Following collection, the soil samples were dried for 48 hours at 40°C and ground to pass through a 2 mm sieve. Sub-samples for total phosphorus (TP), organic phosphorus (P_o) and organic carbon (OC) measurement were further ground to pass through a 200 µm sieve.

3.6.2 Soil sample analysis

Identification of soil sampling depths

In Chapter 7, various depths of soil are referred to, hence a simplified system was adopted to denote the depth in this Chapter. A sub-script suffix is used to denote the depth being referred to. For example, TP_1 refers to total P in the 0-0.01 m depth increment whereas TP_{10} refers to total P in the 0-0.1 m increment. In the other Chapters, the depths being referred to are those discussed in the Materials and Methods for that Chapter.

Olsen P

Olsen P is a commonly used measure of plant available P. Although it was originally developed for use on alkaline soils, it has now become the most commonly used and reliable measure of soil P in the southern Australian dairy industry. For this reason and to allow comparison with overseas studies where it is commonly used, it is the measure of plant available P used in this thesis.

Olsen P (Olsen *et al.* 1954) was determined by shaking 2 g of soil with 40 mL of 0.5 M $NaHCO_3$ (pH 8.5) for 30 minutes, then centrifuging the soil-solution suspension at 3000 rpm for 15 minutes. Samples were then filtered (0.45 µm), neutralised (with HCl) and analysed using the molybdenum blue method as described for DRP.

Calcium chloride extractable P

Calcium chloride extractable P provides a measure of the 'intensity' component of labile soil P (Kuo 1996) and has been shown to be correlated with runoff P concentrations (Pote *et al.* 1996). Calcium chloride extraction was undertaken by shaking 5 g of soil in 25 ml of 10 mM $CaCl_2$ solution for 30 minutes, centrifuging at 3000 rpm for 15 min then filtering through a 0.45 µm filter (Sartorius®, Germany). The filtrate was analysed to determine a number of calcium chloride extractable P fractions. The filtrate was analysed using a molybdenum blue method (Murphy and Riley 1962) described previously and the results reported as $CaCl_2$-P (mg/kg). Total P in the calcium chloride extracts was determined by acidic persulphate digestion as previously described (TDP in runoff) and defined as $CaCl_2$-TP. Un-reactive P in the 10 mM soil extracts was calculated as the difference between $CaCl_2$-TP and $CaCl_2$-RP and was defined as $CaCl_2$-UP and was reported in mg/kg.

Soil water P

Soil water P (SWP) is that P contained in the soil pore water and provides a true measure of the equilibrium soil solution P concentration. Soil water was extracted from moist soil samples by centrifuging the soil using the equipment shown in Figure 3-6 at 3000 rpm for 10 minutes. This procedure typically provided 3-5 mL of solution that was immediately filtered through a 0.45 μm filter and DRP then determined within 1 hour as described previously.

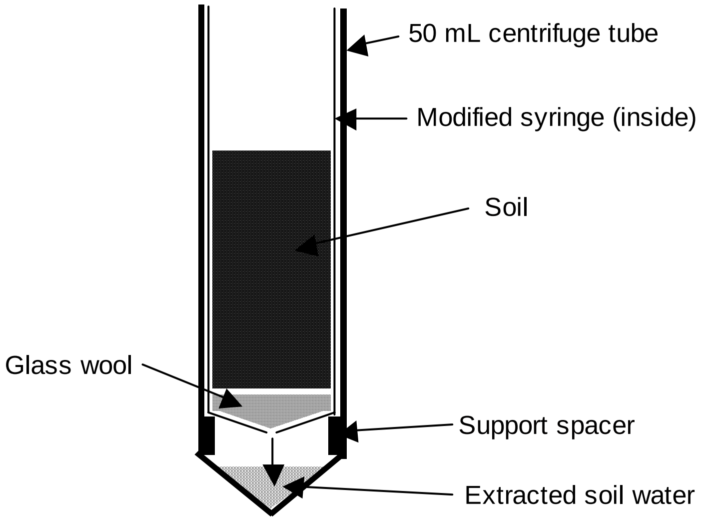

Figure 3-6. Apparatus for extracting soil water from moist soil samples.

Organic and inorganic P

Organic P was defined as the difference between 0.5M H_2SO_4 extractable in unignited and ignited (500^{o}C, 2 hours) samples (Saunders and Williams 1955). Duplicate 500 mg samples were placed in platinum crucibles and ignited in a muffle furnace for 2 hours at 500^{o}C. These and matching un-ignited samples were extracted with 12.5 mL of 0.5M H_2SO_4 for 16 hours. The samples were then filtered (<0.45 μm), diluted 50-fold and P content analysed using the molybdenum blue method as previously described. The ignited sample provided an estimate of total P (for this method) whereas extraction of the un-ignited sample provided an estimate of inorganic P; the difference being an estimate of organic P content.

Total P and elements

Total P and other elements were determined as required using an aqua-regia digest. Five hundred mg of finely ground soil (<200 μm) was weighed out in duplicate into constricted neck digest tubes. To these, 5 ml of aqua-regia (HNO_3:HCl in a 1:3 ratio) was added. Soils were then left overnight before digesting for 2 hours at 160^{o}C. Following digestion, tubes were made up to 50 mL, vortexed and allowed to stand overnight to allow any sediment to settle out. A sample was then analysed using ICPAES.

Organic carbon

A rapid titration procedure based on Walkley and Black (Rayment and Higginson 1992a) was used to determine organic carbon. Finely ground soil (<200 μm, 250 mg) was digested with 10 mL of potassium dichromate (1 M) and 20 mL of sulphuric acid (18 M), heat from the dilution of the sulphuric acid assisting the digestion. Then 200 mL of water, 10 mL of orthophosphoric acid and 0.5 ml of o-phenanthroline was added. The excess chromic acid (that was not reduced by organic matter) was determined by subsequent titration with ferrous sulphate (0.5 N) using o-phenanthroline as an indicator. The ferrous sulphate was added until the solution turned from green to a deep red. The organic carbon content was calculated assuming that 1 mL of 1N potassium dichromate was equal to 3 mg of carbon.

3.7 Ancillary measurements

Ground-cover

Ground cover on rainfall simulation plots was estimated using the transect method of Laflen *et al.* (1981). This involved counting the number of points on a grid spacing of 10 cm that had no ground-cover and expressing this as a percentage of the total number of points counted. On a 1 m^2 plot the total number of points was 121.

Plant biomass

Above ground plant biomass was measured by cutting pasture to a height of 0.02 m. The cut pasture was then dried at 60^{o}C in a forced draught oven for 24 hours and re-weighed. Above ground biomass was expressed as kg/ha dry matter (DM).

Soil moisture

Soil moisture was measured using a Theta™ probe (ΔT Devices, Cambridge UK). This is a ‘capacitance’ type probe that measures soil moisture in approximately the top 7 cm of the soil profile. The theta probe was calibrated by measuring the soil moisture content using the probe then collecting a series of bulk density cores around the measurement point for which bulk density and gravimetric moisture content were determined. The results of this are shown in Figure 3-7.

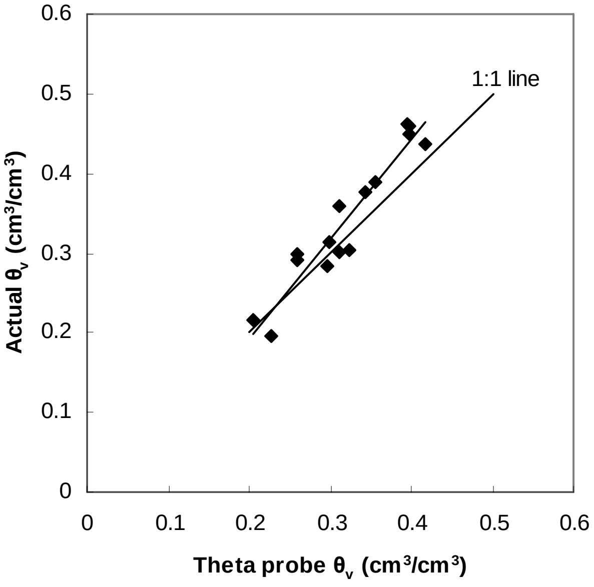

Figure 3-7. Calibration data for theta probe. Actual θ_v = (1.25 × Theta probe θ_v)–0.06, r^2 = 0.91^{***}.

Chapter 4 Processes of P mobilisation and concentrations in runoff – effect of plot scale and rainfall intensity

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4.1 Introduction

Rainfall simulation has been widely used in the study of soil P mobilisation in runoff [e.g. (Sharpley *et al.* 1981b; Pote *et al.* 1999; Torbert *et al.* 2002)]. Rainfall simulation on small plots provides rapid results, is an efficient way to collect data/test hypotheses, allows greater control of conditions (both treatments and rainfall/climate), and is adaptable to a range of research approaches (Meyer 1965). In summary, it is convenient. It has been used to test treatment effects, to study the process of P mobilisation, to develop and calibrate models of runoff P and to set regulatory targets. All of these uses assume that rainfall simulation mimics natural rainfall/runoff conditions to the extent that it is in fact useful for studying the processes of mobilisation and/or developing treatment-response relationships. However, in systems where mobilisation and transport of particulates dominate runoff P losses, it has been shown that rainfall simulation may provide a less than perfect representation of natural mobilisation and transport processes (Loch and Donnollan 1982). Furthermore, the concentration of P in runoff and loads of P exported may also differ from those occurring under natural conditions (Sharpley and Kleinman 2003a). A comparison of P mobilisation and transport in intensively managed pasture systems between rainfall simulation and natural rainfall/runoff at the hillslope scale is lacking.

Rainfall simulation is typically performed on small plots of 1 to 2 m^2 using relatively high rainfall intensities [e.g. 75 mm/hr (Kleinman *et al.* 2004), 150 mm/hr (Cornish *et al.* 2002)] that represent average recurrence intervals (ARI) of between 1 in 2 and 1 in 10 years. These relatively high rainfall intensities allow runoff to be generated in a relatively short timeframe and reduce problems of uniformity of rainfall application that occur at low intensities. However, the use of high intensities also means that the energy inputs to the soil surface are often unrealistically high. This may lead to an increase in the importance of particle detachment and erosion, particularly on bare soils (Humphry *et al.* 2002). The small 'scale' of plots (compared to hillslope scales for example) may also result in artefacts. In order for rilling (a potentially significant form of erosion) to occur, minimum plot lengths are required for sufficient energy to develop in the water such that rilling occurs (Loch and Donnollan 1982; Truman *et al.* 2001). This may not occur on small rainfall simulation plots.

Small plots have hydrological characteristics different to those of the larger landscape that may alter the relative importance of particulate transport. Sharpley and Kleinman (2003a) found that for a given rainfall intensity, larger plots had greater depths of runoff water on the soil surface and greater velocity. This runoff water has greater energy which results in more sediment being transported and hence increases the importance of particulate P export relative to dissolved P. In contrast, an increase in the plot length can result in an increase in the concentration of dissolved P in runoff because of greater contact times between the suspended sediment containing P and the solution phase (Ahuja *et al.* 1982). Similarly, dissolved organic carbon concentrations have been shown to increase with increased reaction time between sediment and water (Valsaraj *et al.* 1996; Tao *et al.* 2000).

In pasture systems with high ground cover percentages, dissolution may be primarily responsible for P mobilisation (Nash and Murdoch 1997). Relatively little consideration has been given to the likely differences in the processes of mobilisation and consequent forms and concentrations of P in runoff between rainfall simulation and hillslope scale runoff in pasture systems. In one example, Cornish *et al*. (2002) compared P in runoff from 1 m^2 rainfall simulation plots (using a hand held watering can and applying water at 150 mm/hr) with natural runoff from 4 and 140 ha areas. Their rainfall simulation experiments provided concentrations of P in runoff that approximated average concentrations (at the 4 ha scale) but were higher than those measured at the 140 ha scale over a 2-year monitoring period. Despite the similarities between the rainfall simulation and larger scale measures of P concentrations, such comparisons are complicated by differences in processes that occur at different scales, e.g. the simulations were almost certainly only measuring surface runoff processes from pasture whereas their larger scale measurements almost certainly incorporated a range of landscape scale hydrological processes. In further comparisons of different size plots by Cornish et al. (2002), there was an apparent increase in soluble P concentrations from 1 to 10 m long plots and then a decrease to the 40 and 140 ha areas. The increase in soluble P at these smaller scales may have occurred because contact time between the P source (i.e. soil and pasture) and the runoff increased allowing greater equilibration and hence higher concentrations of P (Ahuja *et al.* 1982; Nash and Halliwell 1999). As the scale increased from 10 m long plots to 140 ha, the soluble P decrease could have been the result of changing sources of P and changes in hydrology associated with the landscape [as suggested by Cornish *et al*. (2002)]. For example, return flow in lower parts of the landscape may have resulted in a dilution of the overland flow component and a subsequent decrease in P concentrations in the small stream that was monitored. There may have also been sorption of P by sediment mobilised in the small stream or in flow lines in the lower part of the catchment.

The above discussion has highlighted several factors that may affect the results from rainfall simulation. In order to more effectively use rainfall simulation to study natural processes of mobilisation (and the resulting P forms and concentrations), it is necessary to understand how P mobilisation under rainfall simulation relates to or differs from P mobilisation under natural rainfall/runoff conditions. The aims of this experiment were to:

- ***Compare a) the processes of mobilisation, and b) the resultant concentrations, of P in runoff from small-scale, high-intensity rainfall simulations (typical of those routinely used in rainfall simulation investigations) with large-scale, low-intensity rainfall simulations (that approximate natural runoff conditions at hillslope scales).***

The findings of this investigation were intended to help elucidate the processes of mobilisation, inform future studies of P mobilisation and transport using rainfall simulation, and provide an assessment of any artefacts in data derived from the particular rainfall simulation technique being used in this research. The findings were also intended to contribute to the conceptual understanding of P mobilisation.

4.2 Materials and methods

This experiment involved the comparison of P forms and concentrations in runoff from small rainfall simulation plots with those from large plots on which runoff could be generated that approximated natural rainfall/runoff conditions. These two methods are hereafter referred to as LL (**L**arge plot, **L**ow rainfall intensity) and SH (**S**mall plot, **H**igh rainfall intensity). These methods used in the study are described in more detail in the following sections.

4.2.1 Location and site management

This study was undertaken at Camden, 60 km south west of Sydney. The experimental site was part of a larger study examining the effect of different P rates on milk production and runoff quality (Havilah *et al.* 2005). Fertiliser P was applied to grazed ryegrass/clover pastures in Autumn and Spring of each year to achieve annual application rates of 0, 20, 40 and 80 kg P/ha, the 20 and 40 kg P/ha rates being replicated. The plots had been under this management regime for 3.5 years prior to this study.

4.2.2 Runoff plots and rainfall simulations

All rainfall simulations (both LL and SH) were undertaken within large runoff plots (Figure 4-1) that were nested within larger grazing plots. Each LL simulation utilised a whole runoff plot whereas the SH simulations were nested within the plot. The runoff plots were 50 m long and 25 m wide, on an average slope of 5% (± 0.5%) and were located in a mid–slope position. The soils at the site were Ferric Eutrophic Brown Chromosols (Isbell 1997) as described in Chapter 3. Details of the experimental structure for the rainfall simulations are described below in Section 4.2.3.

Water used in the rainfall simulations (both LL and SH) was obtained from the nearby Nepean River. It was necessary to use river water due to the large volumes of water required for the LL simulations (i.e. in excess of 1 ML). Labour constraints restricted the number of simulations that could be undertaken at the SH scale.

Large plot, low intensity (LL) rainfall simulations

For the LL artificial runoff events, bike–shift sprinklers were used to apply water to the whole runoff plot at a rate of approximately 8 mm/hr for 10 hours. These LL ‘artificial rainfall’ events constituted a rainfall event with an average recurrence interval of 1 in 5 years (Pilgrim 1987). The nozzles on the sprinklers were located on frames approximately 0.5 m above the soil surface. They were arranged in order to optimise the uniformity of application. In order to assess the amount of water being applied by each sprinkler, water from the sprinklers was directed into 20 L containers and the time taken to fill the buckets used to calculate flow rates for the sprinklers. The uniformity of application was measured on 2 of the 8 sprinklers on 3 of the plots by placing 10 buckets at 1 m intervals radiating from the sprinkler. Distribution patterns from the each of the sprinklers were used in combination with the sprinkler locations to determine the spatial pattern of water distribution. The coefficient of uniformity of application was calculated as:

$$\text{Coefficient of uniformity} = 100 - (\sigma / Y) \qquad \text{Eq. 4-1}$$

where Y is the mean of the volume of water applied to each 1 m^2 area and σ is the standard deviation of the volumes applied to each 1 m^2 area.

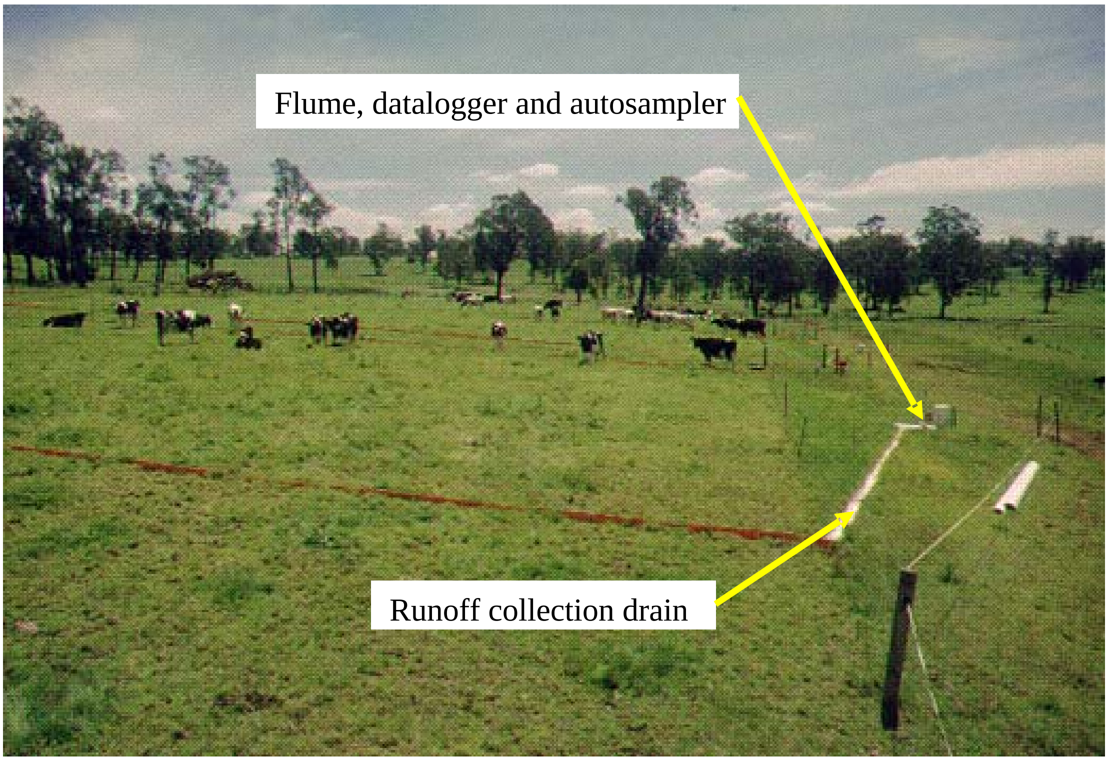


Figure 4-1. Runoff plots at Camden showing the runoff collection drain, and the location of the flow measurement and sampling equipment. The plots were bounded by plastic (orange seen in the photo) inserted vertically into the soil to a depth of approximately 0.2 m to provide surface runon-runoff isolation.

Surface runoff from these large plots was collected in a PVC channel running the width of the plots at their down-slope end. Water was then diverted through an RBC Flume (Clemmens *et al.* 1984) equipped with a pressure transducer (Greenspan® – Milperra, NSW) connected to a datalogger (DataTaker 50® – Rowville, Victoria) which logged data and controlled auto-samplers that collected runoff samples at fixed volume increments (every 1250 L, equivalent to 1.0 mm of runoff).

Large plot, low intensity (LL) rainfall simulations approximate natural runoff events

As part of a separate Dairy Australia funded project monitoring runoff from these large plots (DAN088), natural and artificial runoff events occurred within a short period of each other on two occasions. On the first occasion, the artificial event occurred 7 days prior to the natural runoff event whereas on the second occasion the artificial event occurred 5 days after the natural event (Figure 4-2). As these events occurred in close temporal proximity to each other (and consequently characteristics such as time since fertiliser were very similar), a statistical analysis was undertaken to determine if there were significant differences in runoff DRP concentrations between the two types of events (i.e. natural and artificial). This test was made using a multiple linear regression model using Genstat V6.0 (Lawes Agricultural Institute, Rothamsted, UK) as follows:

$$\mathrm{DRP} = \alpha + (\beta \times \mathrm{CaCl_2 - P}) + (\gamma \times \mathrm{event}) + (\delta \times \mathrm{type}) \qquad \text{Eq. 4-2}$$

where $CaCl_2$-P was the $CaCl_2$ extractable P in the 0-0.01 m increments, ‘event’ was either event 1 or 2, ‘type’ was either natural rainfall or artificial rainfall/runoff (on the large plot scale – coded 1 and 2 respectively in the regression analysis) and α, β, γ and δ are constants. Twenty one data points (there were 3 plots that did not record runoff, one plot on each of three separate occasions) were used in the regression analysis, i.e. six plots, two events and two types of events.

The α, β and γ constants were significant ($P<0.001$) whereas the δ was not ($P>0.05$). The model was highly significant ($P<0.001$) and explained 95% of the variation in the data. This suggests that the runoff DRP concentrations in the LL artificial simulations were not significantly different ($P>0.05$) from those resulting from natural runoff events. There were no significant ($P>0.05$) interactions between the terms. Additional modelling as part of more complex analysis of a larger data set from this site also concluded that there was no significant effect ($P>0.05$) of event type (natural vs. artificial) on runoff P form or concentration (pers. comm. P. Nicholls, NSW Primary Industries).

It was assumed that because of the relatively large size of the LL plots, that they provided an approximation of hillslope scale runoff concentrations. However, it is acknowledged that they may be shorter than a typical hillslope and that they are unlikely to fully represent the range of hydrological processes that occur at the hillslope scale. Nevertheless, because of the likely difficulties associated with obtaining a hillslope with uniform characteristics and being able to generate runoff from it, the comparison being made in this experiment is a reasonable experimental compromise between scale and control of experimental factors.

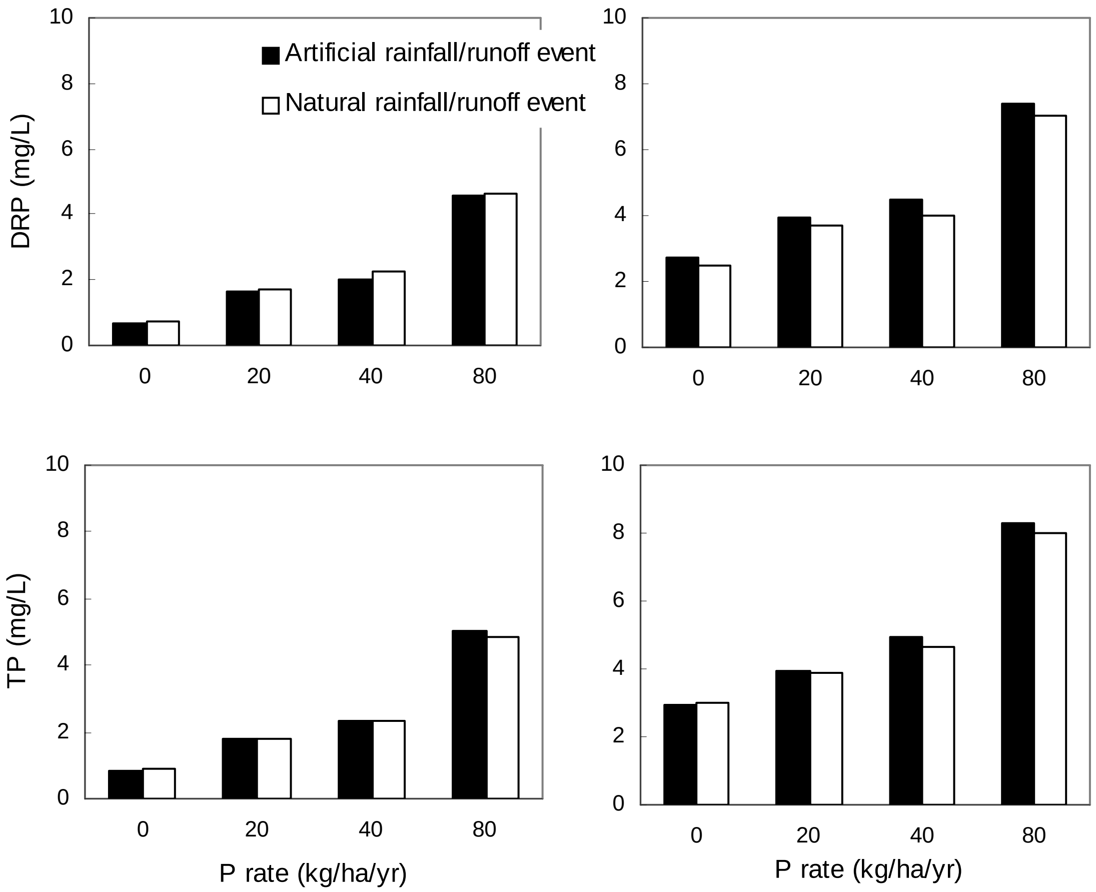
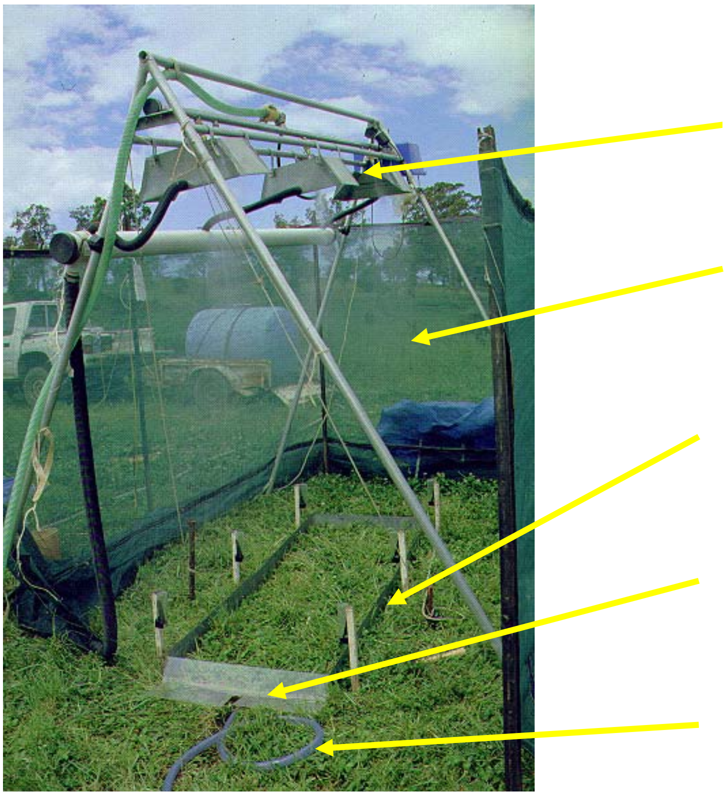


Figure 4-2. Comparison of DRP and TP concentrations in runoff (from large plots) between artificial and natural runoff events (Time 1 – left; Time 2 – right) that occurred within a short time (< ± 10 days) of each other. These occurred on two occasions. There was no significant effect (*P*>0.05) of event type (artificial vs. natural) on DRP nor TP concentration.

Small-scale high-intensity (SH) rainfall simulations

Small-scale high-intensity rainfall simulations were carried out using a swinging boom simulator (Figure 4-3) (Loch *et al.* 2001). Rainfall was applied to an area of 2 × 0.75 m at a rainfall intensity of 80 mm/hr and was continued for 20 minutes after the commencement of runoff. This intensity was chosen as it was typical of that used by other researchers in runoff water quality research (Anon. 2002b) and had been used in previous rainfall simulation research at this site. This intensity approximated a 1 in 10 yr rainfall event for this location (Pilgrim 1987). Runoff from the SH rainfall simulations was collected by a small ‘v’ shaped drain at the bottom of each plot that was subsequently transferred to a collection tank under vacuum. Sub-samples of runoff were taken at fixed runoff volume increments (1.8 L, equivalent to 1.2 mm of runoff) during the runoff event as well as a sub-sample composite from the collection tank at the end of the runoff event. The coefficient of uniformity of rainfall application was measured by placing 121 × 0.05 m diameter pots under the simulator and measuring the volume of water applied to each and calculated using Eq. 4-1.



Swinging overhead nozzles

Shade cloth to deflect wind

Barrier used for hydrological isolation

Runoff collection drain with cover

Suction line for sample collection

Figure 4-3. Swinging boom rainfall simulator used at Camden.

4.2.3 Structure of rainfall simulation experiments

The SH and LL simulations were undertaken on consecutive days. The SH simulations impacted on <3% of the total runoff plot area hence were assumed not to have significantly altered the overall hydrology of the plots for the following LL simulations. Within 3 of the LL plots (plots 1, 3 and 5; 40, 80 and 0 kg P/ha/yr respectively), 4 SH simulations were carried out as shown in Figure 4-4. The simulations were carried out on two occasions, referred to as events 1 and 2, i.e. E_1 and E_2, with different plots being used for the E_1 and E_2 simulations. The E_1 event simulations were undertaken 190 days after the most recent fertiliser application whilst the E_2 event simulations were undertaken 30 days after fertiliser application. The apparent reverse order of these events was the result of the E_1 simulations being undertaken immediately prior to fertiliser application and the E_2 simulations being undertaken ~35 days later (i.e. 30 days after fertiliser application). This timing was necessary to fit in with the management of the larger experiment. Furthermore, as differing days since fertiliser of the two events was not specifically being examined, the different timings served only to provide two events under which the two methods could be compared.

4.2.4 Soil sampling and analysis

Soil samples were collected after both the SH and LL simulations for both the E_1 and E_2 simulations. For the SH simulations, 25 soil samples (0.025 m diameter and 0.01 m deep) were taken on a grid pattern within each rainfall simulation area. For the LL simulations, soil samples were taken by collecting thirty cores (0.025 m diameter and 0.01 m deep) along a permanent sampling transect within each large plot and compositing these. All soil samples were air–dried (40^{o}C) and then ground and passed through a 2 mm sieve. The samples were then stored at 4^{o}C prior to analysis. Soil samples were analysed for 10 mM $CaCl_2$ extractable P as described in Chapter 3 (Materials and Methods).

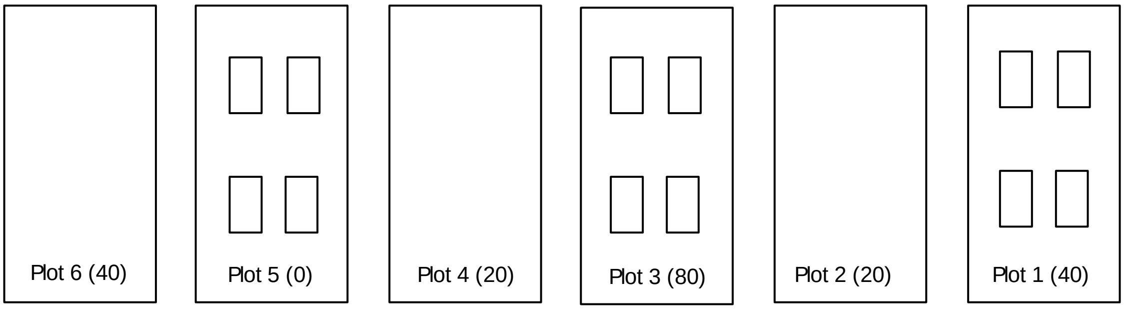


Figure 4-4. Plot arrangement at Camden showing the rainfall simulation plots (SH) nested within the larger (LL) plots (not to scale). The figures in brackets are the P fertiliser rates (kg P/ha/yr) applied to each of the plots.

4.2.5 Runoff sample analysis

Runoff samples were analysed for total P (TP), total dissolved P (TDP), dissolved reactive P (DRP) and dissolved un-reactive P (DUP) using colorimetry and acidic persulphate digestion for the determination of total P as outlined in Chapter 3 (Materials and Methods). The pH, electrical conductivity (EC), dissolved organic carbon (DOC) and suspended sediments (SS) were also determined on each runoff sample. Flow weighted averages for analytes were calculated for each runoff event.

4.2.6 Statistical analysis

The effects of $CaCl_2$-P, method and event number were examined in a multiple linear regression model using Genstat V6.0 (Lawes Agricultural Institute, Rothamsted, UK). Justification and details of the final model used in the analysis are provided in the results section.

4.3 RESULTS and DISCUSSION

4.3.1 General soil characteristics

A summary of the key soil properties at the experimental site is shown in Table 4-1. The soils were slightly acidic and non-saline. Soil Olsen P (0-0.1 m) at the site ranged from 10 mg/kg [below the optimum of 18-22 mg/kg (Gourley 2001)], to 56 that was well above optimal, this range being a consequence of the different P application rates.

Table 4-1. Key chemical characteristics of the runoff plot soil. Figures in brackets are the range of values.

	Depth (m)	
	0-0.01	0-0.10
pH_{Ca}	6.1 (6.0-6.2)	5.6 (5.4-5.7)
EC (dS/m)	0.23 (0.19-0.34)	0.20 (0.14-0.22)
Olsen P (mg/kg)	53 (23-91)	29 (10-56)
$CaCl_2$-P (mg/kg)	13 (4.4-27.6)	5.7 (2.2-12.7)
Texture	Clay loam	Clay loam
Organic carbon (%)	3.2 (2.4-3.1)	2.7 (2.0–3.8)

The major characteristics of the water used in the rainfall simulations are shown in Table 4-2. In all cases, the water was of high quality, having very low concentrations of P, suspended sediments and being of low salinity. The low concentrations of P relative to runoff P concentrations negated the need to adjust runoff P concentrations to account for initial P concentration.

4.3.2 Plot hydrology and runoff

The coefficient of uniformity for rainfall application for the two methods were 65 and 80% for the LL and SH methods respectively. A summary of the rainfall and runoff characteristics is shown in Table 4-3. Runoff rates were much higher for the SH method (43 mm/hr) than for the LL method (2.1 mm/hr), reflecting the much higher rainfall intensity of the SH method. Similarly the runoff coefficients were much higher for the SH method (0.53) than for the LL method (0.2).

Table 4-2. Major characteristics of river water used in rainfall simulations (both SH and LL) for both events (E_1 and E_2); (Figures in brackets are standard errors of means, where values are below LDL, standard errors are not applicable – na)

	Event	
	E_1	E_2
pH	7.88 (0.05)	7.77 (0.05)
EC (dS/m)	0.34 (0.02)	0.28 (0.02)
DRP (mg/L)	<0.05 (na)	<0.05 (na)
TP (mg/L)	<0.1 (na)	<0.1 (na)
SS (mg/L)	<10 (na)	<10 (na)
Al (mg/L)	0.08 (0.01)	0.08 (0.01)
Fe (mg/L)	<0.01 (na)	<0.01 (na)

Table 4-3. Hydrological characteristics of the SH and LL methods for runoff events E_1 and E_2 (Figures in brackets are standard errors).

	Event			
	E_1		E_2	
Method	SH	LL	SH	LL
Rainfall (mm/hr)	76.6 (1.3)	8.5 (0.4)	80.9 (0.9)	9.7 (0.6)
Runoff (mm/hr)	40.4 (0.5)	2.6 (0.2)	40.4 (0.4)	3.5 (0.2)
Runoff CE*	0.24 (0.012)	0.13 (0.019)	0.26 (0.008)	0.09 (0.011)

*Runoff coefficient is the proportion of water applied lost as runoff. The value is the average for the entire runoff event

The substantial differences in the hydrological characteristics were reflected in the hydrographs (Figure 4-5). Runoff occurred rapidly in the SH simulations (after approximately

20 minutes of artificial rainfall), whereas for the LL method it took approximately 8 hours for runoff to commence. For the SH plots, on both occasions, approximately 25 mm of water was needed to be applied before runoff commenced. Whereas for the LL simulations, 28 and 54 mm were required to be applied before runoff commenced in the E_1 and E_2 events respectively.

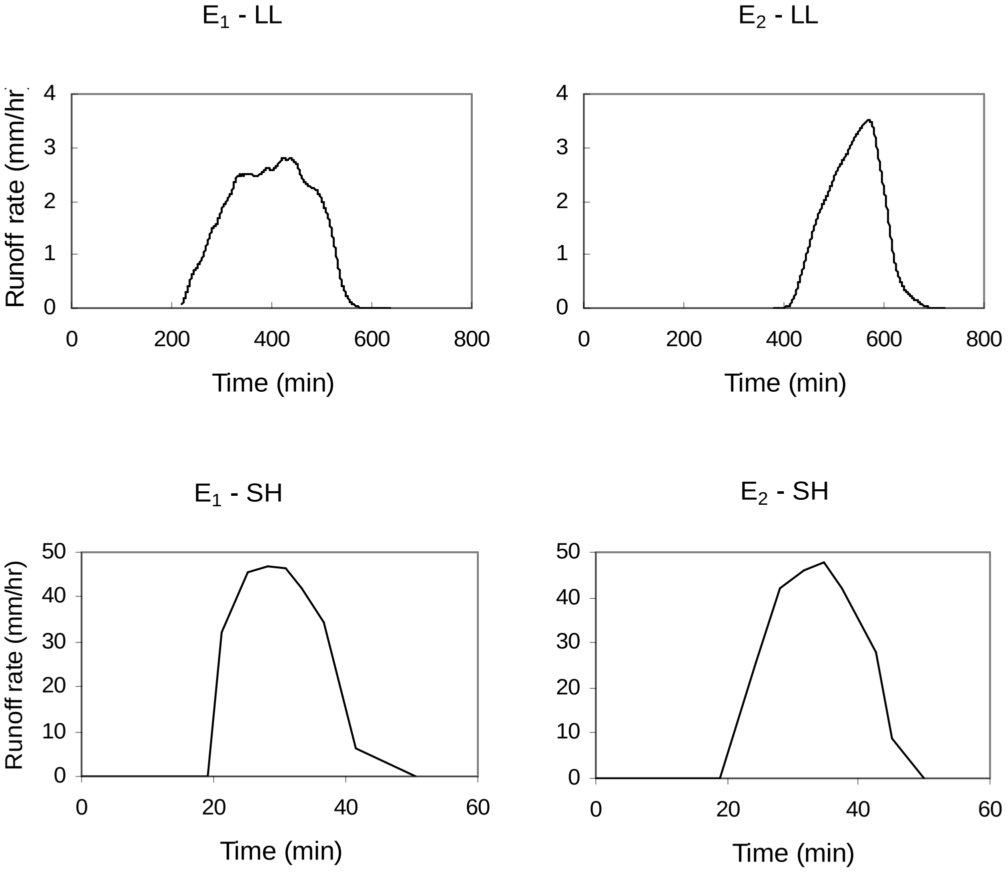


Figure 4-5. Runoff hydrographs (averages across all treatments) from LL and SH methods at E_1 and E_2. Note different y-scales between SH and LL methods. Values are means for all runoff events under each of the conditions specified.

In the case of the SH method, runoff was most likely to have occurred as the result of ‘infiltration-excess’ runoff generation. The rainfall application rate of 80 mm/hr exceeds the infiltration rate of the topsoil that was previously measured to be 23 mm/hr (Burchett 1996). However, for the LL method, the artificial rainfall application rate was low relative to the infiltration rate of the topsoil. Thus, it is hypothesised that the topsoil was saturated before runoff was initiated. Following this saturation, further water could only infiltrate into the B horizon (>0.03 m depth) that had a relatively low hydraulic conductivity of 1 mm/hr (Burchett 1996). This would be classified as a case of saturation excess runoff generation (Nash *et al.*

2002). The difference in the time to initiation between the E_1 and E_2 events in the LL method may have been caused by differences in antecedent moisture contents.

4.3.3 The effect of $CaCl_2$-P, method and event on P in runoff

A preliminary examination of the data indicated that there was a linear relationship between soil P and runoff P as shown in Figure 4-6. This relationship appears to differ between E_1 and E_2, with the slope being greater for E_2. Furthermore, the concentrations of TP appear higher for the LL method than the SH method, and the slope of the soil P-runoff P relationship also appears to be greater for the LL than SH method. The model used to further examine these effects is discussed in the following section.

Model used in the analysis

A model was constructed on the basis of a conceptual model of the processes affecting the mobilisation of phosphorus under the different conditions examined. Runoff P has been shown to be strongly related to soil P (in this experiment $CaCl_2$-P) (Sharpley 1995; Pote *et al.* 1999). Because $CaCl_2$-P provides a measure of the intensity component of P (Kuo 1996) - as does runoff P - a linear relationship was assumed between soil P and runoff P. The SH simulations result in much greater runoff rates and almost certainly shorter residence times (due to their relatively small size), therefore it would be expected that the SH method would result in relatively low runoff P concentration (Ahuja *et al.* 1982; Nash *et al.* 2002). It was hypothesised that this would change the slope of the runoff P response to soil P, therefore, the 'method' effect was modelled as an interaction, i.e. '$\gamma \times CaCl_2\text{-P} \times \text{method}$'. The two events ($E_1$ and E_2) were carried out at 180 and 30 days since fertilisation. A preliminary examination of the data (Figure 4-6) revealed that there were apparently large differences in the slope of plots of DRP against $CaCl_2$-P plots between events E_1 and E_2. Therefore, the effect of the different events was also examined as an interaction term in the model (i.e. '$\delta \times CaCl_2\text{-P} \times \text{Event}$'). The final model used in the statistical analysis was as follows:

$$y_i = \alpha + (\beta \times CaCl_2\text{-P}) + (\gamma \times CaCl_2\text{-P} \times \text{Method}) + (\delta \times CaCl_2\text{-P} \times \text{Event}_i) \qquad \text{Eq. 4-3}$$

where, y is either TP, TDP, DRP, DRP%, PP or SS, $CaCl_2$-P is a measure of soil P, method is either LL and SH (assigned as variable 1 or 2 respectively in the statistical analysis), event is E_1 or E_2 (assigned as variable 1 or 2 respectively in the statistical analysis), and α, γ are δ are constants.

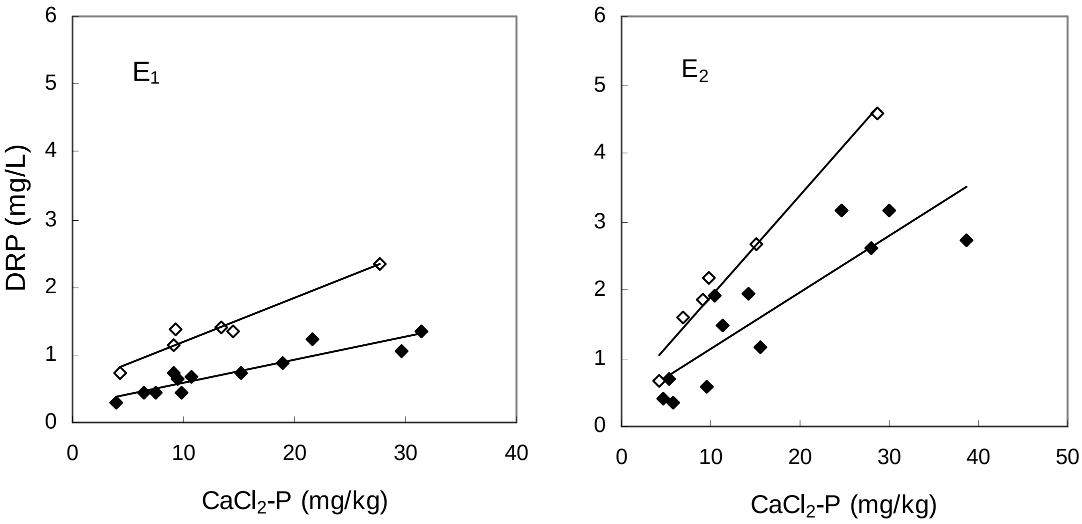


Figure 4-6. Relationship between $CaCl_2$-P (0-0.01 m) and DRP in runoff at E_1 and E_2. (◊ – large-plot, low-intensity - LL; ♦ - small-plot, high-intensity - SH).

Model results – significance of $CaCl_2$-P, method and event on runoff P

There was a significant ($P>0.05$) effect on TP, TDP and DRP of all terms retained in the model listed in Eq. 4-3. Overall model performance (r^2), estimates of the model parameters and their standard errors are shown in Table 4-4.

Table 4-4. Model parameter estimates (Eq. 4-3) for runoff P characteristics. The figures in brackets are standard errors of the terms.

	TP	TDP	DRP
model r^2	0.93^{***}	0.96^{***}	0.95^{***}
α	0.583^{**} (0.142)	0.4886^{***} (0.095)	0.389^{**} (0.104)
β ($CaCl_2$-P)	0.068^{**} (0.022)	0.060^{**} (0.015)	0.069^{***} (0.016)
γ ($CaCl_2$-P × Method)	-0.067^{***} (0.009)	-0.056^{***} (0.006)	-0.059^{***} (0.007)
δ ($CaCl_2$-P × Event)	0.079^{***} (0.009)	0.069^{***} (0.006)	0.068^{***} (0.007)

* - $P<0.05$

** - $P<0.01$

*** - $P<0.001$

The relationship between each of $CaCl_2$-P, method and event and the adjusted runoff DRP (partial residuals) are shown in Figure 4-7. The parameter DRP is presented in these figures as it represented the majority of P in the runoff (consequently plots of TP, TDP and DRP were all very similar) such that differences in TP concentrations between methods is almost exclusively due to differences in DRP (see discussion below). The effect of $CaCl_2$-P on runoff DRP is shown in Figure 4-7a which is consistent with the positive relationship between soil P and runoff P reported widely in the literature (Sharpley 1995; Pote *et al.* 1996; Torbert *et al.* 2002).

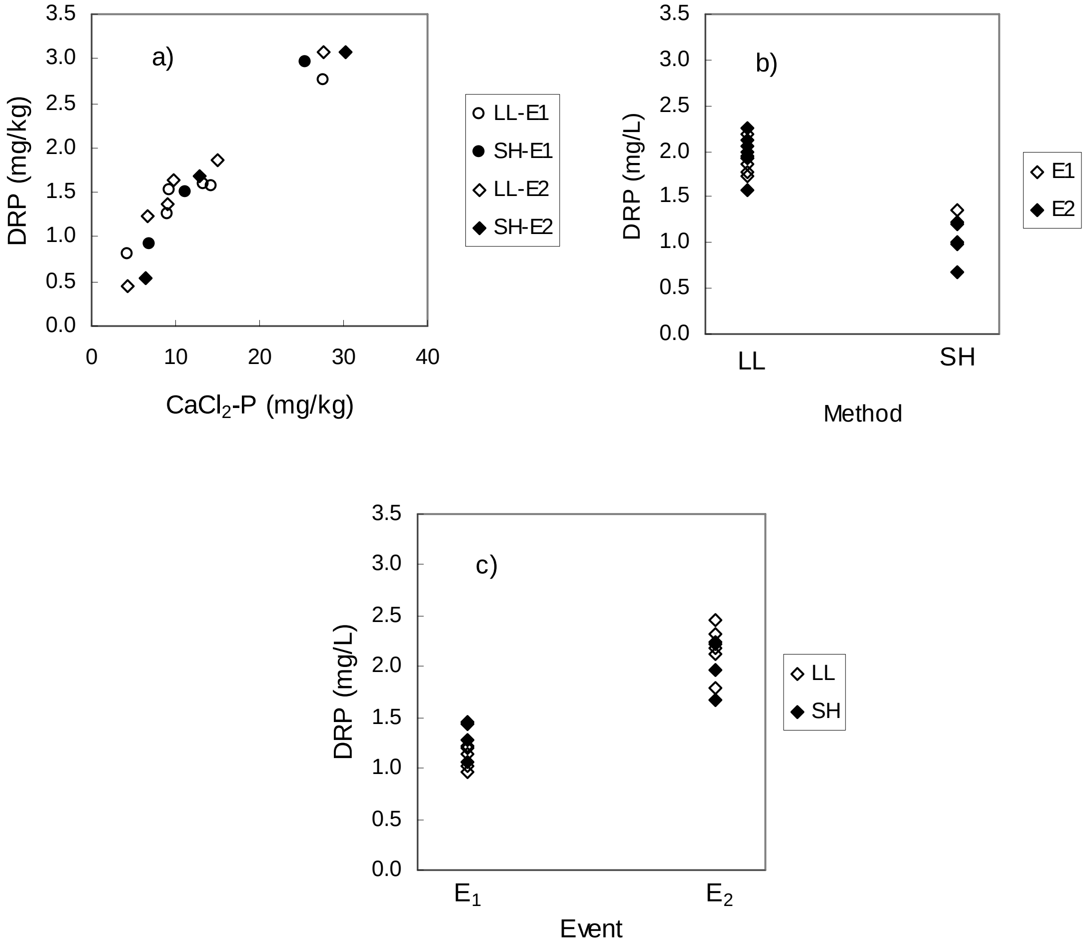


Figure 4-7. Relationship between adjusted (partial residuals) dissolved reactive phosphorus concentrations in runoff and, a) soil $CaCl_2$-P (0-0.01 m), b) simulation method (LL - large plots - low intensity; SH - small scale - high intensity), and c) event (E_1 and E_2)

The SH method results in lower concentrations of DRP in runoff (Figure 4-7b), the concentrations of P in runoff from the SH method being on average across all simulations 67% of that from the LL method. There was no significant effect ($P>0.05$) of method on PP or SS concentrations. Consequently, the major difference in TP concentration between the methods was the result of differences in DRP concentrations. The proportion of TP as DRP was 84%, there being no significant effect ($P>0.05$) of method on this proportion. Similarly, the proportion of TP as TDP was 95%, there being no significant effect (*P*>0.05) of method on these proportions.

Sharpley and Kleinman (2003b) reported that greater runoff flow rates, because of bigger contributing area from larger rainfall simulation plots (10 m long) than small plots (2 m long), resulted in higher concentrations of particulate P due to the higher runoff rates being able to transport more particulate matter. Conversely, their larger plots had lower DRP concentrations, which they attributed to the re-adsorption of DRP by the suspended sediment. In contrast, there was no significant effect (*P*>0.05) of method (SH vs. LL) on the PP or SS concentrations from the plots studied in this experiment, the average concentrations of PP and SS being 0.22 and 74 mg/L respectively. Despite the relatively high intensity and runoff rate of the SH method, the relative proportions of P forms transported in runoff have not been significantly altered by method (i.e. dissolved P was the dominant form of P in runoff irrespective of the method). This dominance of dissolved P is consistent with a number of studies that have shown DRP accounting for 80-90 % (Nash and Murdoch 1997; Dougherty *et al.* 2006b; Dougherty *et al.* 2006c).

There were higher runoff DRP concentrations from the second runoff event (Figure 4-7c). This is consistent with event 2 being only 30 days after fertiliser application, compared to 180 days after fertiliser application for event 1. However, as the adjusted DRP for the two events (Figure 4-7c) has taken into account the effect of $CaCl_2$-P, this suggests that $CaCl_2$-P doesn’t predict differences in runoff P concentrations resulting from the ‘time since fertiliser effect’ or other differences between events 1 and 2.

The effect of methodology has important implications for the use of rainfall simulation data as a basis for modelling runoff P export from catchments and setting of soil P targets for environmental protection. Where soil P-runoff P relationships derived using rainfall simulation are to be used in P export models, the possibility that rainfall simulation provides relatively low estimates of runoff P concentration as indicated in this experiment needs to be considered. Furthermore, differences in absolute runoff volumes and runoff coefficients may also result in unrealistic estimates of P exports. Where the soil P-runoff P relationship derived from rainfall simulation is to be used to set soil P targets, this implication of relatively low-estimates of runoff P concentration also needs to be considered. McDowell *et al*. (2003c) used soil P-runoff P relationships derived from rainfall simulation to set target soil P levels for New Zealand that would result in runoff P concentrations that met water quality targets. If the rainfall simulation data from the SH method were used for this purpose, much higher soil P targets would be set to achieve a given runoff P concentration than would be the case if the LL methodology were used in setting these targets. Therefore, rainfall simulation should be used cautiously for setting soil P levels to achieve particular water quality objectives.

The origin of ‘method’ effects on runoff P concentrations

The trends in runoff P concentration within a runoff event can provide clues as to the reasons for the differences in concentrations between the two methods examined. A decline in P concentrations within an event may suggest either a depletion of the pool of P supplying P to runoff or dilution effects associated with increasing runoff rates within the runoff event (Sharpley 1980a; Ahuja and Lehman 1983). At higher runoff rates, the decline due to depletion or the dilution effect would be expected to be greater, providing a possible explanation for the differences in runoff P concentrations between methods (Ahuja 1982).

In contrast, a constant concentration of P during a runoff event coupled with differences in the concentration between methods (in the case of this experiment) would provide an indication that there is some mechanism limiting the rate at which P can be mobilised, and because of the differences in runoff rates, there is a ‘rate limited’ dilution of runoff P.

In the case of this experiment, the concentrations of DRP (the dominant form of P) do not decline substantially with time (Figure 4-8), suggesting that the most likely reason for the differences in runoff P concentrations is not a source limitation, but rather a rate-limited mobilisation of P. The influence of these processes on runoff P concentration is further explored in the following Chapter.

4.4 Conclusions and implications

There was a significant ($P<0.01$) effect of method (LL vs SH) on the concentrations of TP, TDP and DRP in runoff. The use of small scale, high intensity (SH) rainfall simulation resulted in estimated runoff P concentrations that were 33% lower than those from large scale-low intensity (LL) rainfall simulation. There was no significant effect ($P>0.05$) of method on the proportions of the various forms of P contained in runoff (i.e. DRP was the dominant form of P in runoff >80% whereas PP accounted for only 7% of runoff P). Thus, the small-scale, high-intensity simulations represented the processes of P mobilisation well, but provided relatively low estimates of runoff P concentration.

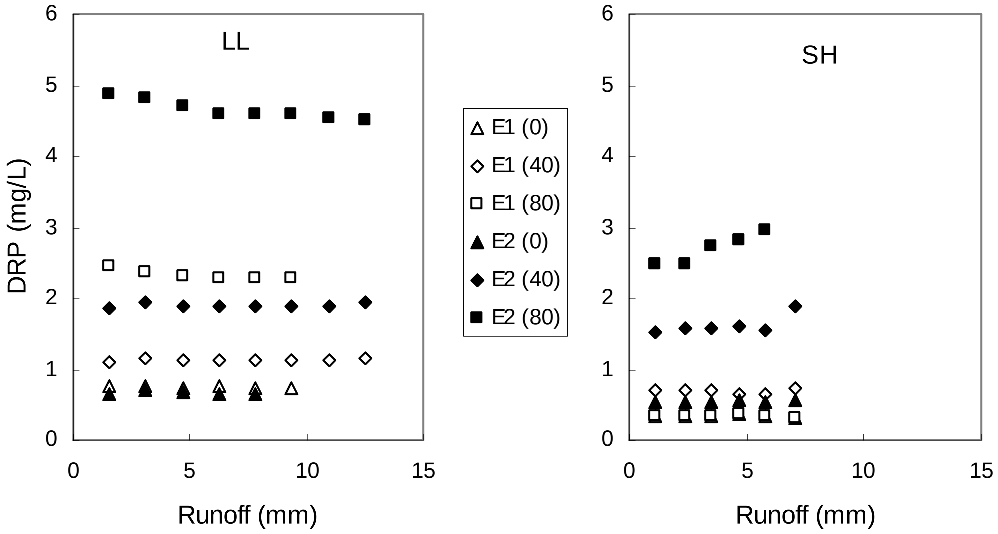


Figure 4-8. Concentration of DRP during runoff events E_1 and E_2 for both LL and SH methods. The numbers in brackets refer to the P application rate of the runoff plots.

The relatively constant DRP concentrations during events, suggests that difference in DRP concentrations between the methods was not due to limitations on the amount of P able to be mobilised, but rather was due to limitations on the supply of P from the source to runoff. It is hypothesised that the transfer of P from P sources to the runoff is an equilibrium reaction that is influenced by the equilibration time (longer time resulting in a greater equilibration and hence higher runoff P concentrations) and the ratio of the volume of runoff water to the P source (the wider the ratio, the longer taken to achieve equilibrium runoff P concentrations). This hypothesis is examined in more detail in the following Chapter.

Before using rainfall simulation estimates of runoff P concentration for either modelling catchment scale exports of P, or setting soil P targets to achieve water quality criteria, it is important to consider the effect of the rainfall simulation method. Failure to do so may result in inaccurate model predictions (where rainfall simulation data are used to parameterise catchment scale models) or unexpectedly high concentration of P in runoff from hillslope scales (where rainfall simulation data are used to set water quality targets).

Chapter 5 The effect of rainfall intensity on the processes of P mobilisation and the resultant concentration of P in runoff

5.1 INTRODUCTION

In the previous chapter, it was shown that the proportion of various P forms (viz. dissolved vs. particulate) in runoff from small-scale, high intensity rainfall simulation were similar to those contained in runoff from large plots approximating natural runoff conditions at the hillslope scale. However, small-scale, high-intensity rainfall simulation provided relatively low estimates of P concentration. This has implications for the development of models of P mobilisation and export and the setting of water quality targets. Therefore, understanding the influence of rainfall intensity on these processes and the resulting concentrations is desirable. Such an understanding would also help elucidate the processes controlling the mobilisation of P under intensively managed pastures.

The use of small plots and relatively high intensities, which is almost exclusively the practice in rainfall simulation, may result in a number of artefacts. For example, as shown in the previous chapter (Chapter 4), rainfall simulation may provide estimates of runoff P concentrations that are relatively low compared to those occurring at the hillslope scale under natural rainfall-runoff conditions. There is also evidence in the literature to suggest that rainfall intensity and plot size will affect forms and concentrations of P in runoff (Sharpley *et al.* 1981b; Ahuja *et al.* 1982; Sharpley and Kleinman 2003a). However, this literature relates to runoff systems in which the concentrations of P in runoff are largely controlled by suspended sediments and where particulate P is an important component of runoff P. These systems contrast with intensive pasture systems in Australia in which the dominant form of P in runoff is likely to be dissolved, and particulate P and suspended sediments are insignificant.

Increasing the rainfall intensity generally leads to an increase in runoff rate. This increased runoff rate results in an increase in the velocity of the runoff water and increase in its depth (Nash *et al.* 2002). Thus, the residence time of the runoff water will decrease and the increase in depth leads to a widening of the runoff volume to P source ratio. In model systems, an increase in equilibration time of soil P and a solution and a narrowing of solution to soil P ratio leads to increases in P solution concentration (Barrow 1979; Sharpley *et al.* 1981a). Similarly, in runoff situations it has been proposed that an increase in runoff residence time will lead to an increase in attainment of equilibrium between the soil P source and runoff (Ahuja *et al.* 1982; Nash and Halliwell 1999). Conversely, an increase in the depth of runoff water on the soil surface will result in a slower attainment of equilibrium. These observations have been made in systems where suspended sediments play a major role in controlling runoff P concentrations [e.g. (Sharpley *et al.* 1981b; Ahuja *et al.* 1982; Sharpley and Kleinman 2003a)]. The effect of rainfall intensity on residence time, depth of runoff and subsequent P concentrations has not been examined in pasture systems where particulate P and sediments do not play a large role in P transport, as was shown to be the case in the previous Chapter and by other researchers (Nash and Murdoch 1997; Fleming and Cox 1998).

Understanding the effects of different rainfall intensities on P mobilisation and runoff P concentrations will aid in the interpretation of rainfall simulation data. Improving the understanding of the effect of simulated rainfall intensity on runoff P concentration may serve as the basis to increase the utility of rainfall simulation data in landscape scale modelling of P exports. For example, if soil P-runoff P relationships derived from rainfall simulation are to be used in catchment scale P export models, they may require adjustment to account for the methodological effects. This adjustment can be made either on the basis of an understanding of the methodological effects, or an empirical calibration of the model to fit measured data. The former method is more attractive as it potentially negates the need for expensive and often lengthy monitoring exercises to calibrate catchment scale P export models.

It is hypothesised that changes in rainfall intensity will alter runoff P concentrations because of differences in plot hydrology. Therefore, the aim of the research presented in this Chapter, was to:

- ***Investigate the effect of varying simulated rainfall intensities (when ground cover is high) on the processes of P mobilisation and on the concentrations of P in runoff.***

The investigations in this Chapter are presented in two sections. The first section is concerned with the effect of rainfall intensity on runoff P forms and concentrations. The second section is concerned with subsequent testing of a physically based model to explain the rainfall intensity effects observed in the experimental section. These are then followed by a conclusion.

5.2 Materials and methods - rainfall intensity effects on P form and concentration

This experiment was undertaken at the Flaxley site on a Chromosol that had been used for dairying for the last 30 years. Initially it was planned that a ‘direct’ approach to investigating the effect of residence time and depth of runoff on runoff P concentrations would be used. This would involve applying water at the up-slope end of small plots using a device to distribute applied water across the width of the plots so that it would flow evenly down the plots. Water could then be applied at different rates to achieve various depths and velocities. This would allow a direct examination of the effect of hydrological parameters (residence time and depth) on P concentration such as used by various authors, e.g. (Barlow *et al.* 2004). However, preliminary experiments found that achieving uniform flow was very difficult and water almost always concentrated into 1 or 2 dominant flow paths. This situation would be distinctly different to that occurring under natural conditions where saturation excess causes runoff to flow more evenly across the surface and the whole soil surface serves as a source of P available to be mobilised. Therefore, a rainfall simulator was used to apply water at different rates that would result in different depths of water and residence times. Visual observations on the plot during rainfall simulation/runoff indicated that this technique substantially reduced the problem of preferential flow paths and ensured that P was being mobilised from all sources.

Rainfall simulations were undertaken at rates ranging from 20 to 150 mm/hr (20, 40, 67.5, 95, 122.5 and 150 mm/hr), each treatment being randomly allocated to a single plot in each of four blocks (i.e. a randomised complete block design). The lowest rainfall intensity was based on the need to generate runoff within a reasonable time-frame and taking into consideration likely soil infiltration rates (estimated infiltration rate was 10 mm/hr). Rainfall simulation was undertaken using a rotating disc simulator as described in Chapter 3 (General Materials and Methods) that applied artificial rainfall to 1 m^2 plots. Water was collected at the down-slope end of the plots using a vacuum collection system that transferred water to collection and sampling facilities. The application of water via artificial rainfall raises the possibility that differing rainfall application rates changed the depth of interaction due to different degrees of disturbance of the soil surface due to raindrop impact (Sharpley 1985). It was assumed that this would not occur due to the heavy pasture cover protecting the soil surface from direct raindrop impact.

5.2.1 Soil sampling and analysis

Soil samples were taken from each plot 1 hour after the completion of the rainfall simulation. This involved collecting 25 cores (0-0.01 m depth) within each plot that were then composited to form a single sample for each plot. These samples were dried and prepared prior to determination of $CaCl_2$-P using the methods described in Chapter 3 (General Materials and Methods).

5.2.2 Runoff sampling and analysis

Discrete sub-samples (10 mL) of runoff were collected at 5 minute intervals during the runoff events (including a sample at the commencement of runoff) as well as a 100 mL composite being collected at the end of the event. All runoff samples were filtered immediately following collection using 0.45 µm filters (Sartorius® - Germany). Samples were subsequently analysed for DRP using the method described in Chapter 3 (General Materials and Methods). Runoff composites were also analysed for TP, TDP and SS as per the methods in Chapter 3 (General Materials and Methods).

5.2.3 Statistical analysis

The effect of rainfall simulation intensity on runoff P concentrations was tested using ANOVA (Genstat V6.1 - Lawes Agricultural Trust, Rothamsted) with intensity (n=6) and block (n=4) being the factors in the analysis. Subsequently, an exponential decay regression was fitted to the data to describe the effect of intensity on runoff DRP concentration as follows:

$$\mathrm{DRP} = a + \left(b \times e^{-ci}\right) \qquad \text{Eq. 5-1}$$

where DRP is the average concentration of DRP in the runoff (mg/L), ‘i’ is rainfall intensity (mm/hr), and a, b and c are constants. The effect of intensity on average time of residence

(T_{av}) and average depth of water on the surface (D_{av}) was described using a power function of the form:

$$T_{av} \text{ (or } D_{av}) = a^{bi} \qquad \text{Eq. 5-2}$$

where ‘i’ is rainfall intensity (mm/hr), and a and b are constants.

5.3 Results and discussion - rainfall intensity effects on P form and concentration

5.3.1 Effect of rainfall intensity on runoff P mobilisation

P form and concentration

Rainfall intensity had a large effect on the hydrological and chemical characteristics of runoff. The major chemical characteristics of runoff for each of the rainfall intensities are shown in Table 5-1. There was a significant effect of rainfall intensity on the concentrations of TP, TDP and DRP ($P<0.05$) but no significant effect on PP and SS ($P>0.05$). The dominant form of P was DRP, accounting for 94% of TDP. The effect of rainfall intensity on DRP concentration in runoff is shown in Figure 5-1.

Table 5-1. Runoff chemical characteristics for various rainfall intensities. Numbers followed by the same letter are not significantly different (*P*>0.05).

Rainfall intensity	TP	TDP	DRP	DUP	PP	SS	DRP[A]
mm/hr	mg/L						%
Intensity effect	***	***	***	ns	ns	ns	ns
20	2.40^a	1.76^a	1.53^a	0.23	0.64	100	87
40	1.92^b	1.10^b	1.02^b	0.08	0.82	126	93
68	1.21^c	0.78^c	0.68^c	0.10	0.43	92	87
95	1.10^c	0.54^{cd}	0.53^{cd}	0.01	0.56	88	98
123	1.04^c	0.55^{cd}	0.54^{cd}	0.01	0.49	116	98
150	0.92^c	0.43^d	0.43^d	0.00	0.47	117	100

[A] % of TDP

The concentration of DRP at an intensity of 20 mm/hr is 3.6 times that at 150 mm/hr. One of the most commonly used rainfall intensities is 80 mm/hr, based upon the USA rainfall simulation protocol (Anon. 2002b). Use of this intensity, would estimate the runoff DRP concentration at this site to be 0.60 mg/L, compared to 1.53 mg/L at the 20 mm/hr rate.

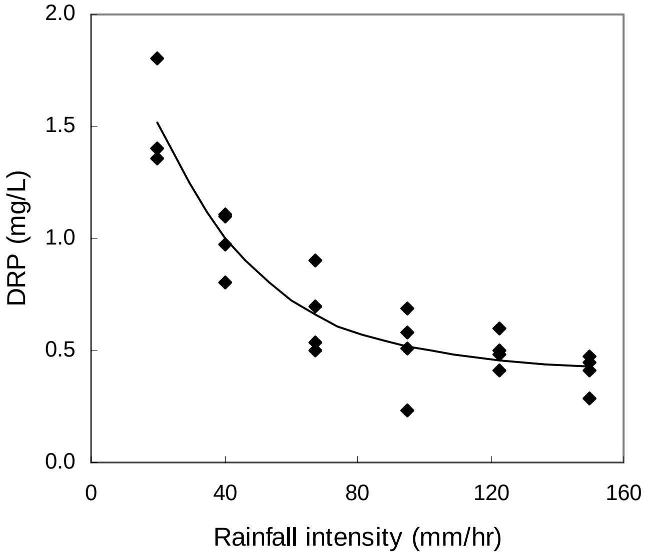


Figure 5-1. Effect of rainfall intensity on mean DRP concentration in runoff. DRP = 0.44 + 2.04e$^{-0.0315x}$. r^2 = 0.87***).

Hydrology

The application of higher rainfall rates resulted in substantial changes in runoff hydrological characteristics (Table 5-2 and Figure 5-2). The time to initiation of runoff decreased significantly (P<0.001) as rainfall rate increased, although there was no significant (P>0.05) change in the amount of water required to initiate runoff. Higher rainfall intensities resulted in a large increase in runoff rate, with runoff rates varying from 4 mm/hr to 118 mm/hr for the 20 and 150 mm/hr rainfall intensities respectively. The runoff rate associated with the 20 mm/hr rainfall is similar to the typical runoff rates of 1-5 mm/hr at the sub-catchment scale reported by Fleming *et al.* (2001) for the Flaxley study site, whereas the high runoff rates associated with the rainfall intensity of 150 mm/hr are approximately 30 times higher than those reported by Fleming *et al*. (2001). Increasing the rainfall intensity resulted in significantly shorter runoff residence times and increasing depth of water (Figure 5-3). Average residence time (T_{av}) decreased from 7.8 to 0.8 min as intensity increased from 20 to 150 mm/hr. The greatest change in residence time and depth occurred between 20 and 40 mm/hr (Figure 5-3 and Table 5-2).

Table 5-2. Summary of key hydrological characteristics at different rainfall intensities. Numbers followed by the same letter are not significantly different (*P*>0.05). Note that the runoff and infiltration rates are averages calculated over the duration of the runoff event.

Rainfall intensity (mm/hr)	Time to runoff (min)	Rainfall to runoff (mm)	Runoff rate (mm/hr)	Infiltration rate (mm/hr)	Total runoff (mm)	Residence time (T_{av}) (min)
Intensity effect	***	ns	***	***	***	***
20	17^{a}	5.7	4^{a}	16^{a}	2^{a}	7.8^{a}
40	8.6^{b}	5.7	27^{b}	13^{a}	13^{b}	2.8^{b}
68	3.9^{c}	4.4	41^{c}	27^{b}	28^{c}	2^{b}
95	3.4^{c}	5.3	65^{d}	30^{b}	45^{d}	1.9^{b}
123	2.7^{c}	5.6	87^{e}	36^{b}	61^{e}	0.9^{c}
150	2.3^{c}	5.7	118^{f}	32^{b}	84^{f}	0.8^{c}

P loads in runoff

There was a highly significant (*P*<0.001) effect of rainfall intensity on the loads of P contained in runoff (Table 5-3). This large increase in P load with increasing intensity occurred despite the decrease in runoff P concentrations. This large effect of rainfall intensity on P loads necessarily limits the use of rainfall simulation for calculating export coefficients (e.g. kg/ha of P) for use in modelling of either P exports from hillslopes or larger scales.

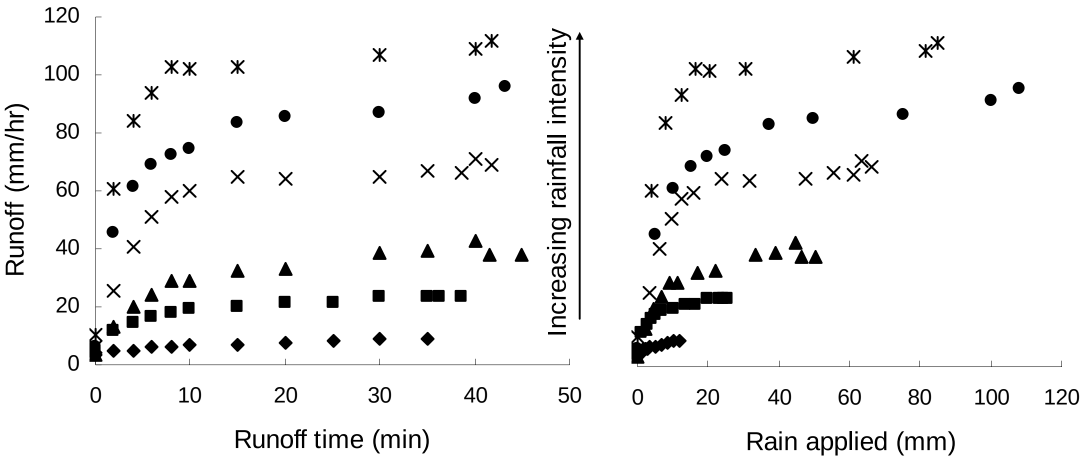


Figure 5-2. Runoff rates (average of four replicates) for each of the rainfall intensities as a function of time and applied rainfall. ♦ - 20 mm/hr; ■ – 40 mm/hr; ▲ - 67 mm/hr; × - 95 mm/hr; ● – 122 mm/hr; * - 150 mm/hr.

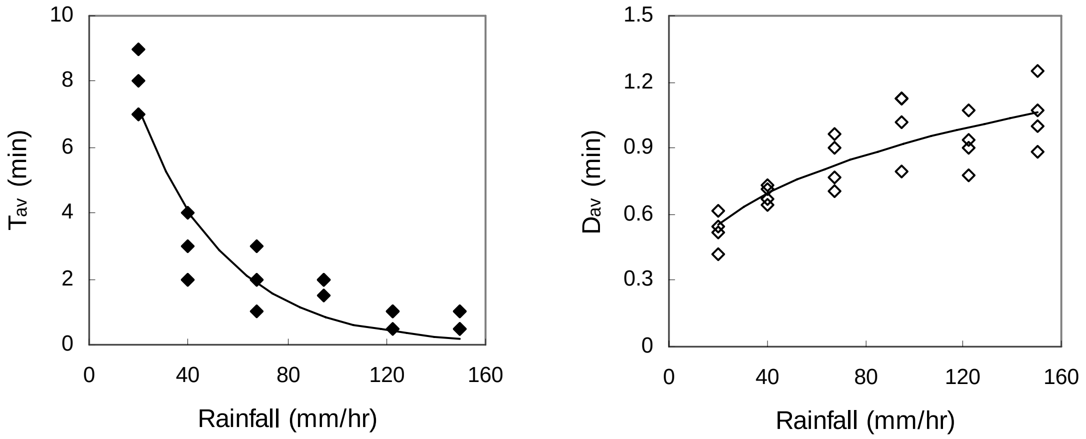


Figure 5-3. The relationship between rainfall intensity and average residence time (T_{av} - ♦) and average depth (D_{av} - ◊) of runoff on 1 m^2 plots. $T_{av} = 12.63e^{-0.0282x}$. $r^2 = 0.93^{***}$; $D_{av} = 0.2111x^{0.3224}$, $r^2=0.98^{***}$.

5.3.2 Is P mobilisation source or rate limited?

There was a significant and large effect of rainfall intensity on the concentration of P in runoff. This effect on P concentration can be accounted for by one of two explanations. These are that the supply of P from the soil into the runoff is either constrained by a ‘source’ or a ‘rate’ limitation. The possible role of these limitations is examined in the following section.

Table 5-3. Means of loads of runoff P forms as a function of rainfall intensity. Numbers followed by the same letter are not significantly different (*P*>0.05).

Rainfall intensity mm/hr	TP	TDP	DRP	DUP	PP	SS
	mg/m^2					
Intensity effect	***	***	***	***	*	***
20	4.3^{a}	3.3^{a}	3.1^{a}	1.1^{a}	0.25^{a}	159^{a}
40	25.0^{b}	14.6^{b}	12.9^{b}	10.4^{a}	1.75^{ab}	1041^{ab}
68	34.0^{bc}	22.9^{bc}	18.7^{bc}	11.1^{a}	4.27^{bc}	1962^{bc}
95	51.1^{cd}	25.6^{c}	22.5^{cd}	25.6^{b}	3.07^{abc}	3005^{cd}
123	64.0^{de}	36.9^{d}	30.8^{de}	27.1^{b}	6.07^{c}	3889de
150	77.0^{e}	38.0^{d}	34.0^{e}	36.7^{b}	4.07^{bc}	4692^{e}

In the case of a ‘source’ limitation, there is only a fixed quantity of P available to be mobilised. During a runoff event, the size of this pool will decline due to continual removal of P by runoff such that the concentration of P in runoff will also decrease with time (Ahuja *et al.* 1983). At a higher rainfall intensity or runoff rate, the decline in P concentration during a runoff event is likely to be more rapid as a greater mass of P is removed per unit time.

The other explanation for the differences in P concentrations is that of a ‘rate’ limitation. In the case of a rate limitation, the rate of transfer of P between the P source and runoff is limited by P release or diffusion (Ahuja and Lehman 1983; Sharpley and Ahuja 1983) such that increasing the runoff rate results in a dilution of the P being mobilised. Assuming that the pool of P available to be mobilised is not being depleted, then for a given runoff rate, the concentration of P in runoff should be constant (during an event) under a rate limited situation.

Evidence suggesting which of these mechanisms (either source or rate) is responsible for the observed effect of rainfall intensity on runoff P concentrations can be found in plots of concentration and runoff rates as a function of time. The relationship between concentration and time are presented with the P concentrations normalised to allow comparison of the relative changes (Figure 5-4). There is little change in concentration with time for the 20 mm/hr rate, whereas there is an initial large decrease with time for the 150 mm/hr rate followed by a relatively constant concentration.

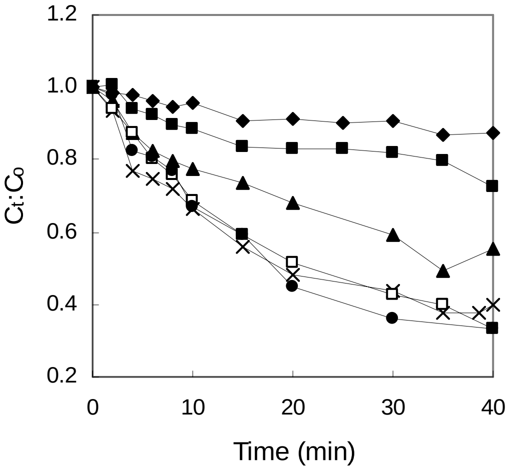


Figure 5-4. Change in DRP during an event (points are averages of four replicates). Data are normalised relative to the DRP concentration at time zero of the rainfall intensities. ♦ - 20 mm/hr; ■ - 40 mm/hr; ▲ - 67 mm/hr; □ – 95 mm/hr; × - 122 mm/hr; ● – 150 mm/hr.

Therefore, it is hypothesised that the mobilisation of P is a two stage process. In Figure 5-5 the normalised concentrations of P and the runoff rates for the 20 and 150 mm/hr rates are shown. The initial decline in the P concentration – particularly evident for the higher rainfall intensity – may be associated with either a source or rate limitation. In the case of the source limitation, it may be that there was a highly soluble pool of P which was rapidly depleted. Running the low intensity simulations for a long period of time in order to see if depletion occurred in them may have helped confirm or reject this hypothesis. Unfortunately this was impractical as the times required for this to occur would have been of the order of >6 hours each based on the depletion rate for the 150 mm/hr intensity.

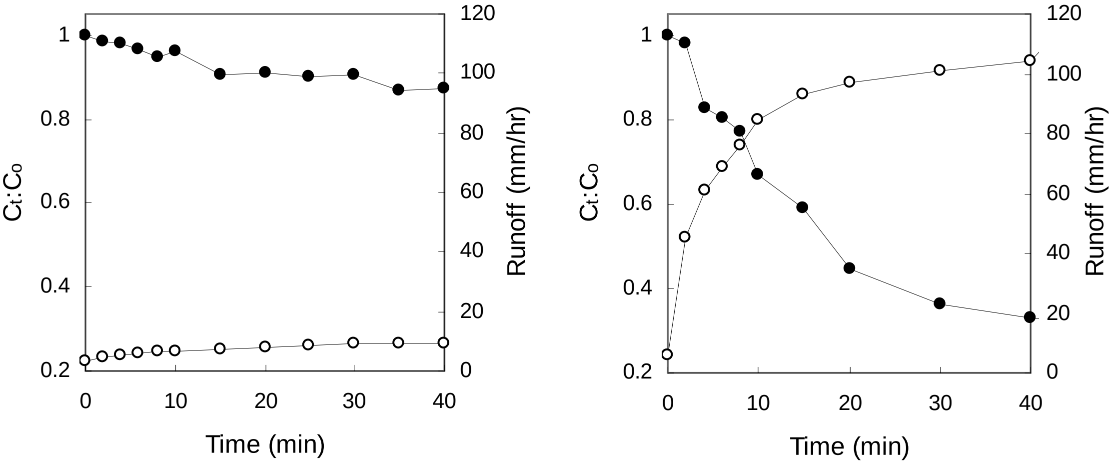


Figure 5-5. Changes in runoff rates (○) and relative P concentration (●) in runoff (C_t/C_o = concentration at time 't' relative to that at time = 0) after the commencement of runoff for rainfall intensities of 20mm/hr (left) and 150 mm/hr (right). Data are average of four replicates.

The alternative reason for the initial decline is a rate limitation associated with changes in hydrology. The increase in runoff rate during the early phase of the runoff events would have resulted in changes in residence times, depth of water, and thus the degree of equilibrium between the P source and the runoff water.

However, once the runoff rate becomes relatively stable (>20 mins), then the P concentration also becomes relatively stable. This suggests that in this second phase of the runoff event, the rate of supply of P is constant, which is consistent with a rate limitation. Similar patterns are exhibited for all rainfall intensities. The P concentrations in these latter phases change little with time but they do increase with decreasing rainfall intensity.

It is therefore hypothesised that the differences in P concentration are the result of the combination of hydrological factors and the kinetics of P release. This hypothesis is examined in the following section.

5.4 Materials and methods - modelling hydrological effects on runoff P concentrations

This second part of Chapter 5 involves the evaluation of a simple chemical kinetic model to explain the differences in P concentrations observed in the first part of this Chapter as rainfall intensity increased. This model is then also tested on the data from Camden presented in Chapter 4.

It was firstly assumed that the primary mechanism of P mobilisation was the diffusion of P from the soil. Secondly, it was proposed that this diffusion occurs across the stable runoff:soil boundary into the runoff rather than the more commonly proposed mechanism whereby P diffuses from soil particles in a turbulent mixed soil:runoff suspension at the soil surface [e.g. (Ahuja *et al.* 1982; Sharpley 1985; Vadas and Sims 2002)]. This latter mechanism is most likely to occur in bare soils where raindrop impact disturbs the soil surface.

In order to examine the possibility that P in sediment entrained in runoff was controlling runoff P concentrations (rather than diffusion from the stable surface as proposed) a batch de-sorption experiment was undertaken. This involved shaking dried topsoil (0-0.001 m) from the study site (Olsen P - 64 mg/kg; $CaCl_2$-RP - 23 mg/kg) at two soil:solution ratios (representing two suspended sediment concentrations, i.e. 200 and 2000 mg/L) and removing sub-samples at each of 1, 10, 100 and 1000 minutes. The sub-samples were then analysed for DRP.

The results of this batch shaking experiment (Figure 5-6) showed that for typical runoff sediment concentrations (approximately 100 mg/L) and short sediment-runoff contact times (<10 minutes) that only low concentrations of P (i.e. <0.1 mg/L) resulted (Figure 5-6). Furthermore, examination of the soil surface during rainfall simulations revealed an essentially sediment-free runoff solution flowing over the soil surface (Figure 5-7). There was no temporary entrainment of sediment or a mixing zone evident as would occur in bare soils. Therefore, it was concluded that the process of P mobilisation in rainfall simulation/runoff from our pasture plots was not desorption of P from entrained sediment. Therefore the assumption that the mobilisation of P is a diffusion or desorption type process at the soil/runoff interface was considered reasonable. Confirmation of this assumption allowed examination of the effect of changes in residence time and depth of runoff using kinetic descriptions of P release as described below in the following ‘Background Theory’.

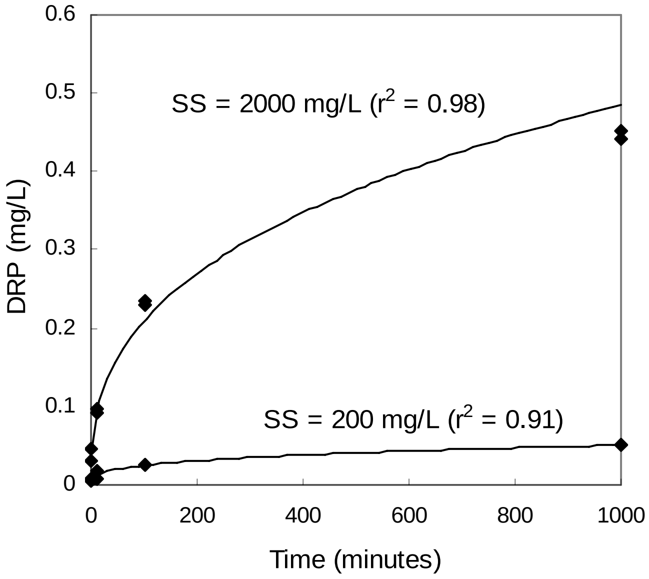


Figure 5-6. The effect of time and suspended sediment (SS) concentration on the concentration of DRP in solution.

Figure 5-7. Shallow runoff flowing over the soil surface during rainfall simulation illustrating the stability of the soil surface and the protection from raindrop impact afforded by the pasture biomass. (Pasture was pushed aside to allow this photo to be taken).

5.4.1 Background theory

The kinetic descriptions of P mobilisation involved modification of an equation proposed by Sharpley *et al*. (1981a). Sharpley *et al.* (1981a; 1981b) proposed a relatively simple model to explain the transfer of P from soil to runoff. This model is more sophisticated than partitioning coefficient type approaches [e.g. earlier versions of FHANTM (Fraisse and Campbell 1997) and GLEAMS (Leonard *et al.* 1987)] in that it allows for the effect of time and solution:soil ratios which have been shown to be important factors influencing solution P concentrations (Barrow 1979). Sharpley's model assumes that there is a turbulent soil:water layer at the soil surface that results in the dissolution of P and its subsequent transfer into overland flow. The model of P desorption proposed by Sharpley *et al.* (1981a) is:

$$P_d = KP_0 t^{\alpha} W^{\beta} \qquad \text{Eq. 5-3}$$

where P_d is the amount of P desorbed into solution (mg/kg), P_0 is the amount of P in the soil (mg/kg), W is the solution:soil ratio, t is the time of equilibration, and K, α and β are constants. When applied to de-sorption of P from soil into runoff, the model needs to include a term specifying the amount of soil from which P is being desorbed (as the P_d term is mg of P desorbed per kg of soil). Therefore Eq. 5-3. becomes:

$$P_d = KSP_0 t^{\alpha} W^{\beta} \qquad \text{Eq. 5-4}$$

where P_d is the P desorbed (mg), S is the amount of soil (kg) interacting with the runoff. Furthermore, the concentration of P in solution can be defined as:

$$P_c = \frac{P_d}{V} \qquad \text{Eq. 5-5}$$

where P is the concentration of P in runoff (mg/L) and V is the volume of solution (L). Therefore, substituting Eq. 5-4 into Eq. 5-5, the concentration of P in solution is described by:

$$P_c = \frac{K P_0 S t^{\alpha} W^{\beta}}{V} \qquad \text{Eq. 5-6}$$

Although the model was originally developed for use in situations where a turbulent runoff soil mix occurred in runoff, it is hypothesised that an analogy can be used in stable runoff systems with some modifications of the assumptions regarding the parameters (Dougherty *et al.* 2004). Firstly, Sharpley (1985) concluded that if a surface seal forms (from raindrop impact on bare soils) then the depth of runoff/soil interaction becomes very small. In stable soil systems such as in pastures (i.e. where little sediment is entrained in runoff and the soil surface is stable - akin to a surface seal) then the effective depth of interaction can be assumed to be small, (e.g. only of the order of mm of soil depth), and therefore W (soil:solution ratios) is relatively small (e.g. <1). For example, Sharpley (1985) reported EDI to reduce to as small as 0.23 mm when mesh was used to simulate plant cover that reduced rainfall drop impact. Therefore in the application of the model, the W term will represent the ratio of the amount of water on the surface with the amount of soil with which it is interacting. Secondly, in contrast to the original and more common use of ‘t’ (Vadas *et al.* 2002), this term in the modelling of runoff P from these stable soil systems can be equated with the time that the runoff is in contact with the soil [i.e. the residence time which is the time it takes it to flow from its point of origin to the point in which it is no longer in contact with the P source - in this case the stable soil surface (Sharpley *et al.* 1981b; Dougherty *et al.* 2004)]. It is this time that determines how much P is in solution, not the total time of the runoff event as is more commonly used [e.g. (Vadas *et al.* 2002)].

It is hypothesised that if the depth of overland flow (D_{av}) and the time for it to flow across the plot (residence time - T_{av}) is known, an estimate of the amount of P desorbed and consequently the concentration of P in the runoff can be made. Given that the primary interest lies, at this stage, not in the absolute concentrations, but rather in predicting differences between rainfall intensities, the following equation can be used to compare concentrations:

$$\text{Ratio of concentrations} = P_1 : P_2 \qquad \text{Eq. 5-7}$$

where P_1 and P_2 are the concentration of P in runoff water from two methodologies resulting in different hydrological properties (and hence equilibration times). If Eq. 5-6 is substituted into Eq. 5-7, and assuming that K and P_o and S will be the same for a given site irrespective of methodology, then Eq. 5-7 becomes:

$$P_1 : P_2 = \frac{\left(\frac{t_1^{\alpha}}{t_2^{\alpha}}\right) \times \left(\frac{W_1^{\beta}}{W_2^{\beta}}\right)}{\frac{V_1}{V_2}} \qquad \text{Eq. 5-8}$$

The t, W and V parameters are all a function of runoff hydrology and their measurement/estimation are described below. V is estimated as the volume (or depth) of water on the soil surface rather than the total volume of runoff as used in other versions of the model [e.g. (Sharpley *et al.* 1981a; Vadas *et al.* 2002)]. The α and β parameters are a function of soil properties and their derivation is described in the following sections.

It is important to note that because P is not only diffusing into the solution that is leaving the plots as runoff, but is also diffusing into the water that is infiltrating into the soil, then some of the P is being 'lost' into the soil. For the above methodology to be useful, the rate of water and P infiltrating into the soil must be the same between methodologies being considered. If this is not the case then the P infiltrating into the soil will need to be accounted for. Statistical analysis confirmed that there was no significant effect ($P>0.05$) of rainfall intensity on infiltration rate, although there was some evidence for an increase. Nevertheless, it was concluded that the assumption of no change in infiltration was satisfied.

5.4.2 Measurement and/or derivation of hydrological parameters for rainfall simulations

Measurements were made of average runoff residence times using potassium bromide (KBr) as a tracer. Potassium bromide at a concentration of 1000 mg/L was introduced to the mid-point of the plots once runoff had reached steady state. Runoff was then collected every 30-60 seconds and samples analysed for bromide concentration using a bromide selective electrode (Orion$^{®}$, Thermo Corp, USA). The time (secs) to peak bromide concentration (T_{pk}) was determined visually from plots of time against bromide concentration. The average flow velocity (V_{av} - m/s) was calculated using:

$$V_{av} = \frac{L_{Br}}{T_{pk}} \qquad \text{Eq. 5-9}$$

Where L_{Br} is the distance (m) upslope from the plot exit at which the Bromide was injected into the overland flow. Hence, the average residence time of water on the plots (T_{av} - secs) was calculated as:

$$T_{av} = \frac{L}{V_{av}} \qquad \text{Eq. 5-10}$$

where L is the length (m) of the plot. The T_{av} value for each plot was then later used in modelling P concentration differences between different rainfall intensities in Eq. 5-8. Simple engineering hydrological equations were used to estimate the other hydrological parameters that couldn’t be measured directly. Depth of water at the outflow of plots was estimated after rearrangement of Mannings equation:

$$Q = \frac{D^{1.67} \times S^{0.5}}{n} \qquad \text{Eq. 5-11}$$

to give:

$$D = \left[\frac{Q \times n}{S^{0.5}}\right]^{0.61} \qquad \text{Eq. 5-12}$$

where D is depth (m), Q is flow rate (m^3/s), n is Mannings coefficient and S is slope (m/m). Then D can be substituted into the continuity equation:

$$Q = V \times D \times W \qquad \text{Eq. 5-13}$$

where Q is the flow rate (m^3/s), V is velocity (m/s) and D is depth (m), and W is the width (m). The V_{av} and T_{av} parameters derived in Eq. 5-9 & Eq. 5-10 were used in conjunction with the above hydrological equations described above to estimate the W and V parameters for use in Eq. 5-9. It was assumed that the depth of interaction was constant such that the change in W was simply a function of the depth of water on the plot surface. For a sandy loam, Sharpley (1985) showed that at relatively low slopes (e.g. <8%), the effective depth of interaction was relatively insensitive to changes in rainfall intensity.

5.4.3 Derivation of P release kinetic parameters

In order to derive the α and β parameters for use in Eq. 5-9, 100 intact cores were collected (0.1 m diameter and 0.05 m deep) from the site at which the simulations were undertaken. This involved inserting ‘pvc’ tube with a sharpened cutting edge into the soil and carefully digging out the tube and intact soil core so as to not disturb the integrity of the soil. They were capped on the bottom end and sealed around the edges with paraffin wax to eliminate edge effects (Figure 5-8). The soil was slowly wet up to saturation over a period of six hours, water was ponded on the surface at various depths and the cores shaken on a reciprocating shaker for various times (t) before sampling the ponded water from the surface. This water was filtered (0.45 μm filter) and DRP determined as per Chapter 3 (General Materials and Methods). Five shaking times (1, 3, 9, 30, and 81 minutes) and four different depth of water (0.001, 0.002, 0.005 and 0.010 m) were used in a factorial design with four replicates.

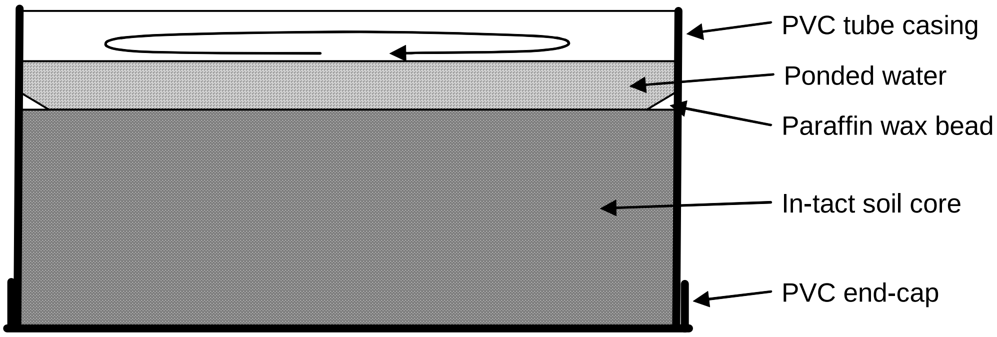


Figure 5-8. Cross section of intact core arrangement for determining α and β parameters for use in eq. [6].

Assuming that the depth of soil which was contributing P remained constant while the depth of water changed, the values of the β parameter can be determined from a regression where the depth values are used as the ratio W changes simply as a function of the change in depth. The α and β parameters in Eq. 5-3 were determined using non-linear least squares regression in SPSS v12.0.1 (Systat, Chicago, Illinois). P_0 was defined as the $CaCl_2$ extractable P (mg/kg) in the top 5 mm of each core and W was the depth of water (mm) as previously discussed.

Because the routine use of intact cores to derive α and β values is not practical, the utility of deriving α and β values using batch equilibrium experiments (i.e. shaking as is typically used to estimate α and β values) was evaluated by comparing α and β values derived by the intact core methodology with those derived using batch equilibration methodology. This batch equilibration methodology involved using various solution:soil ratios (W=1, 2, 5 and 10) and equilibration times (T = 1, 3, 9, 27 and 81) similar to those used in the intact core experiment. A composite of the top 5 mm of soil from all of the intact cores was used in this experiment. Fourty mL of water was shaken with various amounts of soil (as required to achieve each of the solution:soil ratios). Samples were centrifuged, filtered (<0.45 μm) and DRP determined as described in Chapter 3 (General Materials and Methods). The α and β parameters were again determined using least squares regression in SPSS v12.0.1 (Systat, Chicago, Illinois).

5.4.4 Statistical analysis

In order to compare the predicted effect of rainfall intensity on runoff P concentration using the above methodology with the measured effect of rainfall intensity, an analysis of variance analysis was undertaken (Genstat v6.1, Lawes Agricultural Institute, Rothamsted) with factors being rainfall intensity (n=6) and methodology (n=2; actual and predicted) with 4 replicates.

5.5 Results and discussion - modelling hydrological effects on runoff P concentrations

The batch equilibration experiment and visual examination of the soil surface during rainfall simulation indicate that P is not mobilised from soil entrained in the runoff, rather it is mobilised from the stable soil surface. Consequently it was assumed that the factors resulting in differences in P concentration as a result of different rainfall intensities were related to different runoff:soil contact times (T_{av}) and wider soil:runoff ratios (W). This is an important assumption, because runoff T_{av} and W were not independent, but rather dependent variables in the original experimental design. Consequently the approach to predicting such differences in P concentrations as described in the Materials and Methods section was tested using the data presented in Part 1 of this Chapter.

The regression used to determine the α and β values was highly significant ($P<0.001$) as were each of the individual terms. The α and β values derived from the intact core experiments were 0.40 (SE 0.07) and 0.35 (SE 0.05). The α and β values are well above the average values reported by Sharpley (1981a) for a range of soils. The α and β values derived from the batch shaking experiment were 0.13 (SE 0.01) and 0.55 (SE 0.03) respectively. The batch equilibrium experiment gives a much smaller α value than does the intact core methodology. It is hypothesised that this is because of the much more intimate contact between the soil and solution resulting in more rapid attainment of equilibrium.

The α and β values derived from the intact cores were used to predict the concentration of P (as DRP) in runoff at various rainfall intensities relative to the average concentration of DRP at a rainfall intensity of 20 mm/hr. Average values of T_{av} and W derived in the statistical analysis of the rainfall intensity experiment were used in the modelling using Eq. 5-8. The results of this modelling are shown in Figure 5-9. There was no significant difference

(P>0.05) between the measured and modelled data. There were some differences, particularly at higher intensities when the data were plotted on a runoff rate basis.

Because the concentrations used were flow weighted averages for the runoff events, there may have been some error associated with the changing concentrations during runoff events as shown in Figure 5-5 (i.e. the first phase of P mobilisation). As previously discussed, this decrease in runoff P concentration in the early part of the runoff events when the hydrology was changing rapidly was particularly pronounced for the high rainfall intensities. This may contribute to the greater difference between measured and predicted ratios at these intensities as the equations being examined relate to the ‘rate limited’ phase of P mobilisation (i.e. the second phase).

It was therefore hypothesised that the predicted and measured DRP concentrations associated with the last 5 minutes of the rainfall simulations (when relatively constant runoff rates and P concentrations occurred as shown in Figure 5-5) may be more closely related. When the model was re-run for these conditions, there was much greater agreement as shown in Figure 5-10.

Thus, the effect of rainfall intensity on runoff P concentrations was modelled successfully on the basis of runoff hydrology and the kinetics of P release. This model may serve as a useful basis for comparing the differences between small-scale, high-intensity rainfall simulation and hillslope scale estimates of runoff P concentrations, thus overcoming some of the difficulties in extrapolating from the plot to the field scale (Beven 1995). Future development and testing of this revised version/application of the model could include the capability to predict actual runoff P concentrations.

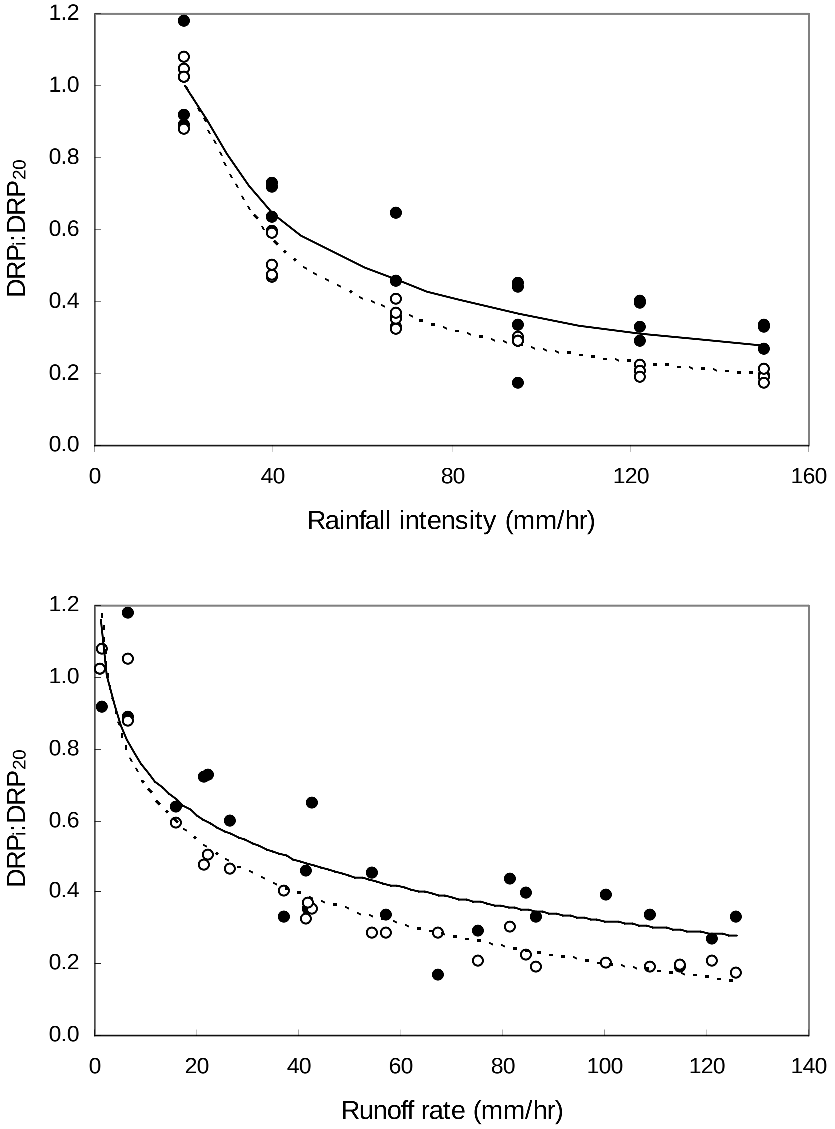


Figure 5-9. Relationship between actual (● & solid line) and predicted (○ & dashed line) average runoff DRP concentration relative (at various intensities) to that at an intensity of 20 mm/hr (i.e. DRP_i:DRP_{20}) as, a) a function of rainfall intensity, and b) as a function of runoff rate.

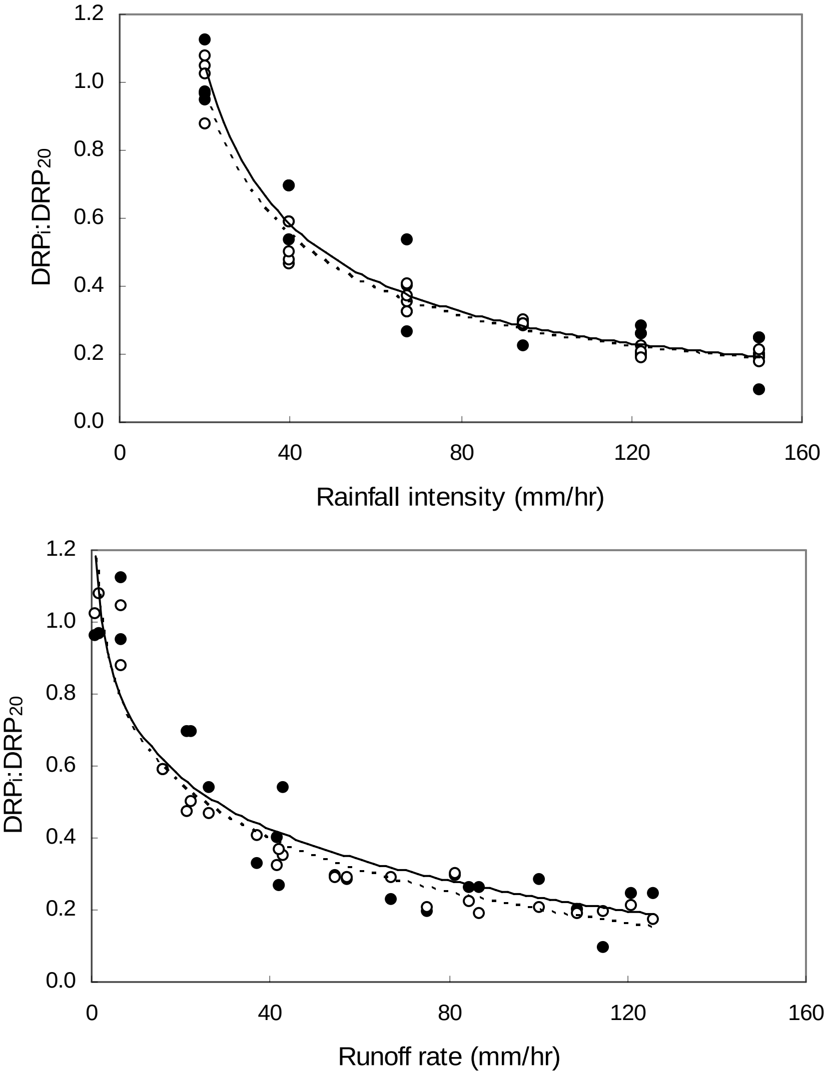


Figure 5-10. Relationship between actual (● & solid line) and predicted (○ & dashed line) concentration of DRP (under constant hydrological conditions during the last 5 minutes of runoff) relative to that at an intensity of 20 mm/hr (i.e. DRP_i:DRP_{20}) as, a) a function of rainfall intensity, and b) as a function of runoff rate.

5.5.1 Prediction of the relationship between rainfall simulation and hillslope runoff P concentrations - Camden

The model has been shown to successfully predict the relative differences in P concentrations arising from different hydrological conditions associated with different rainfall intensities. It is the obvious extension of this to consider the success of the model in predicting the differences in runoff P concentrations between rainfall simulation and larger scales such as a hillslope. The data gathered and presented in Chapter 4 from the Camden site offer such an opportunity. The α and β parameters could not be determined for intact cores (these were not available), so were estimated using soil packed into 0.05 m diameter tubes to a depth of 0.02 m. The soil was a composite from all of the plots at Camden and was packed to a bulk density of 1 g/cm^3. The methodology used to calculate α, β and K was the same as that described for Flaxley in Section 5.4.3. The α, β and K parameters were estimated to be 0.35 (SE 0.13), 0.19 (SE 0.05) and 0.056 (SE 0.011).

Hydrological parameters for the Camden rainfall simulations were not directly measured so had to be estimated using the hydrological equations presented earlier in this Chapter. The average residence time (min) was estimated to be 26.50 (SE = 4.90) and 1.31 (SE = 0.04) minutes for the large plot-low intensity (LL) and small plot-high intensity (SH) simulation respectively. The average depth of runoff on the surface was 0.9 (SE 0.02) and 0.8 (SE 0.03) mm for the LL and SH simulations respectively. The ratio of DRP concentrations between the LL and SH plots (i.e. $DRP_{LL}:DRP_{SH}$) was modelled using Eq. 5-8. The comparison of the modelled and measured ratio of P concentrations between the LL and SH plots (i.e. $DRP_{LL}:DRP_{SH}$) is shown in Figure 5-11. There is a significant relationship ($P<0.01$) between the predicted and actual $DRP_{LL}:DRP_{SH}$ values, although the model over-estimated the ratio of the P concentrations between the two methods by approximately 30%. This error is most likely associated with the estimation of the α and β parameters and the estimation of the hydrological parameters. Nevertheless, this suggests that this model also has the potential to predict hillslope runoff P concentrations.

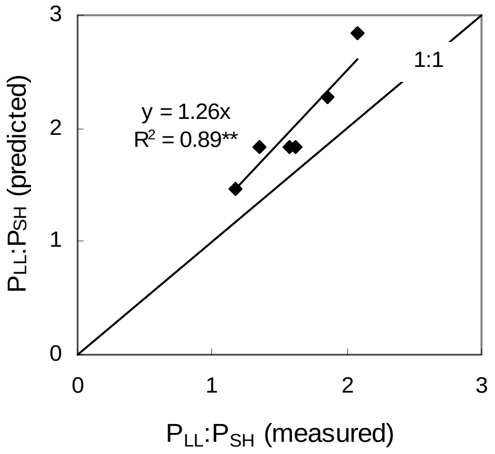


Figure 5-11. Comparison of the measured and predicted ratios of runoff DRP between the Camden large plot-low intensity (LL) and small plot-high intensity (SH) rainfall simulations.

5.5.2 Sensitivity analysis and limitations of this modelling approach

Sensitivity analysis of the model

In order to examine the 'robustness' of the model, a simple sensitivity analysis of the model was undertaken by adjusting the two hydrological parameters (i.e. the runoff rate and Mannings 'n' coefficient). The results of this analysis are shown in Figure 5-12. There is relatively little effect of change in Mannings 'n'. This is an important finding because the estimation of Mannings 'n' for very shallow flows is problematic (Diaz 2005). Also Manning's 'n' changes with depth, the value increasing with decreasing depth due to increasing drag of the bed and increasing resistance of vegetation (Diaz 2005). This is reflected in the extreme values of Mannings 'n' calculated for the very lowest rainfall intensity and flow rate. Such slow flows and shallow depths are only likely to occur in small plots, the accumulation of runoff from hillslope would result in deeper flows with greater velocity. In such circumstances the Mannings 'n' value would approach the more typical range of 0.05-0.2 (Engman 1986; Anon. 2002a). The correct estimation of runoff rate appears to be much more important than the estimation of Mannings 'n' (Figure 5-12), particularly at low runoff rates where the effect on residence time is relatively large (Figure 5-2 and Table 5-2).

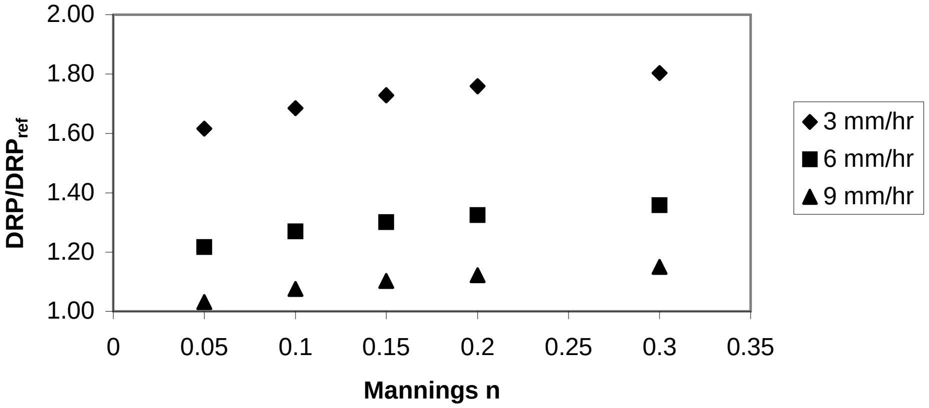


Figure 5-12. Sensitivity analysis of several key combinations of parameters in the model. The y-axis (DRP/DRP_{ref}) is the DRP concentration relative to that at 20 mm/hr.

Limitations

Whereas the estimation of hydrological parameters and model that has been used here provides a relatively simple means of predicting some of the effects associated with methodology of P runoff P measurement, the methodology does have a number of limitations.

It is a simple lumped parameter model (i.e. factors such as depth are simplistic averages for the plot), Mannings ‘n’ values do not change and it relies on empirical estimates of runoff coefficients. Whilst these may provide a reasonable approximation at such small scales as 1m^2 plots, they are likely to be less reliable at larger scales. More complex numerical solutions may need to be developed to better model some of these important parameters, particularly for broader scales where simplistic averages may provide even greater sources of error.

The simple core experiments used for the estimation of α and β are for a single fertility level only and required empirical derivation. In the use of the kinetics modelling approach in erosive type systems, numerous authors have derived relationships for predicting α and β based on easily measurable soil properties, (e.g. clay content, organic carbon, Fe) (Sharpley 1983; Vadas and Sims 2002). If the model proposed here is to be more widely used, similar procedures for estimating α and β may need to be developed for pasture systems.

5.6 Conclusions

This study has shown that rainfall simulation is a robust technique for studying the processes of P mobilisation in runoff on soils with pasture cover. There was little difference in the proportions of various P forms in runoff with changing rainfall intensity. There is however a large and significant effect of simulated rainfall intensity on the concentrations of P in runoff. Therefore, the selection of rainfall intensity and the subsequent runoff P concentrations are likely to be critical in the accurate modelling of runoff P concentrations using rainfall simulation derived relationships between soil P and runoff P. There was also a large effect of rainfall intensity on the loads of P contained in runoff. Consequently, rainfall simulation experiments should not be used to predict the export of nutrients from hillslopes or catchments without a thorough understanding of the implications of the method of generating the data.

The data presented provide useful insights into the mobilisation of DRP (the dominant form of P in runoff) in runoff under rainfall simulation. Mobilisation occurred as a two-stage process, with an initial decline in P concentration followed by relatively stable P concentrations. The initial decline in P concentration may have been due to either changing hydrology in the initial stage of the runoff events or a depletion of the pool of P being mobilised. It was proposed that the change in P concentration with intensity in the second stage was the result of a combination of differences in residence times and depths of runoff water (resulting from the different intensities). Relatively high rainfall simulation rates result in very short runoff residence times and subsequently low P concentrations. The use of low rainfall simulation intensities results in relatively long residence times and consequently higher P concentrations.

A simple model (utilising runoff hydrological characteristics and a parameterised model of P release kinetics) was tested to evaluate this hypothesis. The utility of such a model for ‘adjusting’ rainfall simulation data for rainfall intensity effects was also investigated. Predictions using this model were in close agreement with data from the rainfall simulation experiment. This supports the hypothesis that the hydrological/kinetics parameters were responsible for differences in runoff P concentrations and that such an approach has the potential for ‘correcting’ rainfall simulation P concentrations so that they better reflect those likely to arise from overland flow over hillslope scales.

Further testing of the model on the Camden data from Chapter 4 also demonstrated the success of the model. There was a significant relationship between modelled and measured data, although the model was over-estimating the difference between the large scale-low intensity and the small scale-high intensity simulations by approximately 30%. This may have been caused by the need to estimate a number of hydrological parameters and use chemical kinetic parameters from the Flaxley site.

It is worth noting that the effect of variations in intensity of natural rainfall at the hillslope scale is likely to be much smaller than that of variations in simulated rainfall on small rainfall simulation plots. The estimates of runoff residence times in the large runoff plots were are of the order of 25 minutes. The laboratory equilibration experiments showed that there were relatively large differences in runoff P concentrations when runoff residence times varied between 1 and 5 minutes, but suggest that at longer times such as >20 minutes that there is relatively little difference. As the large plots are likely to represent the small end of the hillslope scale and therefore runoff residence times would be commonly in excess of 30 minutes, it is reasonable to expect that variations in natural rainfall intensity and subsequent differences in runoff residence times will have little affect on runoff P concentrations.

Further development of the modelling approach would improve the utility of rainfall simulation as a tool for parameterising catchment scale models of diffuse P losses and for setting target soil P concentrations. The effect of factors relating to hydrology should be considered in the interpretation and use of rainfall simulation estimates of runoff P concentration in future research.

Chapter 6 The effect of soil P status on runoff P concentrations

6.1 Introduction

In the previous two chapters (Chapters 4 and 5), the combined effect of hydrology and chemical kinetics on P mobilisation was examined. The concentration of P in the soil can also have a substantial effect on the concentration of P in runoff. The addition of phosphorus to soil can lead to increases in the export of P in surface runoff. Concentrations of P in runoff can increase by orders of magnitude under certain conditions. Quantifying the influence of P additions or accumulations on runoff P concentrations is fundamental to the development of strategies aimed at reducing this P.

The export of P in surface runoff occurs in two modes [i.e. ‘systematic’ and ‘incidental’ (Haygarth and Jarvis 1999; Nash *et al.* 2005)]. The incidental mode is typically the result of the coincidence of fertiliser or manure application and rainfall/runoff and typically results in high concentrations of P (Austin *et al.* 1996; Preedy *et al.* 2001). The concentrations of P arising from this mode are inversely related to the time between fertiliser or manure P application and the occurrence of runoff (Nash *et al.* 2005). On the other hand, the systematic mode arises from the mobilisation of P from soil and pasture and is responsible for the more frequently observed relatively low concentrations of P in runoff. Because the systematic mode occurs more frequently than the incidental mode, it may be responsible for a substantial proportion of annual P exports.

Numerous authors have shown that the P concentration in the systematic mode is related to soil P [e.g. Sharpley (1995); Pote *et al*. (1999)]. There are two major potential sources of P that contribute in this mode, these being soil P and above ground biomass P. Although, leaching of P from the pasture biomass can make a considerable contribution to P losses, it is reasonable to conclude that the soil controls the runoff P concentration via processes of de-sorption and re-sorption of P (Sharpley 1981). Therefore, understanding the effect of soil P status on runoff P concentration is fundamental to the study of P mobilisation and identification of strategies to reduce P concentrations in runoff. Fleming and Cox (2001) developed a model of P export for the Flaxley study site based upon hydrological factors. However, they noted that despite the predictive success of their model, that consideration of the soil P-runoff P relationship at this site may make a valuable contribution to the modelling of P export. Furthermore, they noted that despite the fundamental nature of such relationships, there was limited data available for Australian soils. Definition of soil P effects on runoff P concentration form the basis for the source components of numerous risk assessment methodologies (Sharpley *et al.* 2003; Heathwaite *et al.* 2004) and therefore the implementation of remedial or preventative management strategies.

The existence of a relationship between soil P and runoff P has been demonstrated using rainfall simulation for both environmental (e.g. water soluble P, calcium chloride extractable P) and agronomic (e.g. Olsen or Bray P) type soil P tests [e.g. (Sharpley 1995; Pote *et al.* 1999)], despite agronomic soil P tests generally using chemical extractants variously designed to mimic plant extraction of soil P. In a recent review of North American literature (Vadas *et al.* 2005) it was proposed that a single extraction coefficient could be used to predict P mobilisation across a wide range of soils and conditions. The use of a single extraction coefficient for studies at various sites was successful for both agronomic soil tests (Bray and/or Mehlich P) and environmental type tests (i.e. degree of phosphorus saturation).

If a single extraction coefficient successfully predicts runoff P concentration, it simplifies the modelling of runoff P concentrations in research and policy tasks, and the identification of high runoff P risk areas in risk assessment. Until the recent research of Vadas *et al*. (2005), it was widely assumed that variation in a range of soil properties and conditions meant that individual soil P-runoff P relationships needed to be derived for each soil or site (Pote *et al.* 1999; Torbert *et al.* 2002; Melland 2005). Although the research of Vadas *et al.* (2005), suggests that a single extraction coefficient may be applicable to soils in the USA, there is anecdotal evidence that runoff P concentrations from Australian soils are high compared to those reported overseas. This would suggest that a different coefficient may apply to Australian soils. Of all the studies examined by Vadas *et al*. (2005), the highest DRP concentration reported was approximately 2 mg/L with the large majority of runoff P concentrations being less than 0.75 mg/L, despite an extreme range of soil P values. In Australian studies, runoff P concentrations (excluding those influenced by the incidental mode) appear to be relatively high. Mundy *et al*. (2003) reported runoff DRP concentrations of >0.5 mg/L on moderately fertile soils (Olsen P - 33 mg/kg). Fleming and Cox (2001) reported TDP concentration being typically >1 mg/L. Nash *et al*. (2000) reported TP concentrations typically greater than 2 mg/L for Olsen P of 17-40 mg/kg. Greenhill *et al*. (1983) reported DRP of >1 mg/L for two sites with Olsen P of 17 mg/kg. Because the majority of these studies were performed on small sub-catchments or large irrigation bays, their direct comparison with the data of Vadas *et al*. (2005) is problematic for a number of reasons. Firstly, as suggested in Chapter 4, rainfall simulation - as used in the majority of studies examined by Vadas *et al*. (2005) – may provide relatively low estimates of runoff P concentrations compared to those occurring at the hillslope or catchment scale. Secondly, the complexity of hydrology and contributing areas in catchment studies make the relationship between average catchment soil P and runoff P concentration difficult to establish (McDowell and Trudgill 2000; Styles *et al.* 2006).

Identification of Australian runoff P data that were collected under rainfall simulation and their comparison with each other and the data of Vadas *et al*. (2005) would provide a useful preliminary evaluation of the single extraction coefficient concept. Given the wide range of soils examined by Vadas *et al*. (2005) it is expected that a range of Australian soils may also exhibit similar soil P-runoff P relationships. Therefore, the aims of the research presented in this Chapter were to:

- ***Define the soil P – runoff P relationship for the Flaxley site and compare this with published and unpublished data from Australia and overseas including that of Vadas et al. (2005).***

6.2 Materials and methods

6.2.1 Soil P mapping

In order to maximise the range of soil P values included in the study of the soil P-runoff P relationship (and for later consideration of the likely benefits of a remedial strategy - see Chapter 9), it was necessary to have knowledge of the spatial distribution of soil P at the study site. In order to achieve this, a soil surface P map was produced. A 25m grid sampling was undertaken. Sampling points were located using GPS for later use in ArcGIS® (ESRI, California). At each sampling location, 25, 0-0.01 m and 25, 0-0.10 m cores were taken and each of these individual sets of 25 cores were composited to form a 0-0.01 and 0-0.10 m soil composite for each sampling location (74 in total). Soil samples were prepared and Olsen P and $CaCl_2$-P determined as described in Chapter 3 (General Materials and Methods). A surface soil P map was then produced using ArcGIS® and a locally weighted splining function (Davies *et al.* 2005a).

6.2.2 Rainfall simulation

In order to define the soil P-runoff P relationship, rainfall simulations were undertaken using the rotating disc rainfall simulator described in Chapter 3 (General Materials and Methods). Because the objective of this study was to examine the relationship between soil and P in runoff from pasture-soil systems (where ground cover is typically close to 100%), the location of simulations was constrained such that sites were used that had only 100% or near to ground cover, and each of these sites were visually checked to ensure that there was no evidence of recent (<12 months) manure deposition within the simulation areas. Simulations on sites with low ground cover would have resulted in a change of processes of mobilisation from dissolution to sediment detachment and erosion (Sharpley 1981). Given that the predominant mechanism of P mobilisation in pastures is dissolution (Nash and Halliwell 1999) this was considered undesirable. Manure P was avoided as it would be expected that the presence of a locally concentrated source of P within small plots would have unduly influenced the runoff P concentration and resulted in a substantial incidental P component (Preedy *et al.* 2001).

Artificial rainfall was applied at a rate of 30 mm/hr such that runoff occurred for 20 minutes. Following cessation of runoff, a runoff composite sub-sample was taken and filtered (<0.45 μm) immediately. A composite soil sample (0-0.01 m) was collected from each plot 1 hour after runoff ceased. Soil water was then extracted from each of these soil samples using the centrifugation method described in Chapter 3. The extracted and filtered soil water was analysed for molybdate reactive P and is referred to hereafter as soil water P (SWP). The soil was then prepared for soil analysis including Olsen P and $CaCl_2$-P as described in Chapter 3 (General Materials and Methods). Bray P (Bray and Kurtz 1945) was also determined on the soil samples. This involved extracting 7 g of soil with 49 mL of 0.03M NH_4F for 60 sec followed immediately by vacuum filtration (Whatman #42) and determination of molybdate reactive P as per Chapter 3 (General Materials and Methods).

6.2.3 Ancillary measurements

A number of ancillary measurements were also made. These included measures of soil moisture prior to simulation using a Theta probe® (Delta T devices, Cambridge, UK) and estimates of ground cover (Laflen *et al.* 1981).

6.2.4 Comparison of Flaxley soil and runoff data with other data

Additional published and unpublished Australian and international data were gathered for comparison with the Flaxley soil P relationships (Olsen P vs. $CaCl_2$-P) and soil P-runoff P relationships. The comparisons of soil P measures (Olsen P vs. $CaCl_2$-P) were made on data gathered from the literature in which the same method of determining $CaCl_2$-P was used (i.e. a 30 minute extraction at a 1:5 soil:solution ratio).

Different rainfall intensities and different sampling depths were used in the derivation of the soil P-runoff P relationships that were examined. Because of the effects of these variations in methodology on the soil P-runoff P, data were adjusted to account for these differences. All soil P data were adjusted where necessary to approximate the relevant soil P values for the 0-0.02 m increment. The 0-0.02 m increment was selected as the common basis as Vadas *et al*. (2005) used soil data from sampling depths ranging from 0-0.02 to 0-0.05 m. The adjustments to soil P values to account for different sampling depths was undertaken using the ratios of P in various depth increments described later in Chapter 7. Soil P in the 0-0.05 m increment was assumed to be 0.8 times that in the 0-0.02 m increment whereas soil P in the 0.01 m increment was assumed to be 1.25 times that in the 0-0.02 m increment.

Similarly, all runoff P concentrations were adjusted to approximate the runoff P values that would be derived at 80 mm/hr. These adjustments were made using the effect of intensity investigated in Chapter 5. Specific details of these adjustments are described below. No formal statistical comparison was made between the data sets because of the approximations involved in the various adjustments described below. A single regression was fitted to the combined Australian data for both Bray P and the degree of phosphorus sorption saturation (DPS). In fitting this regression, the runoff DRP data were square root transformed to ensure approximately constant residual variance. The regressions were then back-transformed for presentation. Visual qualitative comparisons were made between the Australian data and that of Vadas *et al*. (2005).

Soil P-runoff P relationships of Vadas *et al*. (2005)

For comparison with the Flaxley data and other Australian data, the spread of data for the Bray P-DRP and degree of phosphorus saturation-DRP relationships described by Vadas *et al*. (2005) were estimated visually and plotted on the relevant figures.

Soil P-runoff P relationships of Cornish *et al*. (2002)

These measurements were made at rainfall intensities of 150 mm/hr on pastures used for dairying. The DRP values reported by Cornish *et al.* (2002) were therefore increased by a factor of 1.53 based on the effect of intensity reported in Chapter 5. Soil Bray P values (0-0.05 m) were adjusted to 0.02 m equivalents using an adjustment factor of 1.25 based on data derived in Chapter 7. Degree of phosphorus sorption (DPS) was estimated from a relationship between Bray P and DPS derived from the Camden research site (unpublished data - Dougherty) that was located on similar soils derived from the same parent material and only several kilometres from the study site of Cornish *et al*. This relationship was DPS = ((lnBrayP) × 4.36)-5.759 (r^2=0.78***; n =24).

Soil P-runoff P relationships of Dougherty (unpublished)

These data were gathered from a Chromosol and Vertosol in the Camden (NSW) region. Fertiliser had been applied to these sites 9 months prior to rainfall simulation that were carried out at a rate of 80 mm/hr. Soil sampling depth was 0-0.02 m. Therefore no adjustments were made to this data set.

Soil P-runoff P relationships of Melland (2005).

These rainfall simulations were undertaken on P fertilised pastures used for grazing of sheep. Soil sampling depth was 0-0.05 m; therefore soil P values were multiplied by a factor of 0.8 to represent 0-0.02 m values. The DPS for these soils were predicted from a relationship between Olsen P and DPS. This relationship was DPS = (0.205 × Olsen P) + 2 (r^2=0.92***, n=23) (Melland 2005).

6.2.5 Statistical analysis

Simple descriptive statistics of soil and runoff characteristics (mean, median, minimum, maximum and standard deviation) for the Flaxley rainfall simulations were produced using Excel (Microsoft Corp.) functions. Relationships between soil P measures were examined using Genstat v6.0 (Lawes Agricultural Trust Rothamsted, UK). Residuals were checked visually to confirm the existence or otherwise of normally distributed residuals. Where this condition was not satisfied the dependent data were log-transformed (in the case of Olsen P) or square root transformed (in the case of the $CaCl_2$-P). Final regressions applied and reported were those observed to have approximately normally distributed residuals. The transformed data and regressions as well as back-transformed relations are presented.

6.3 Results

6.3.1 Flaxley site characteristics

There was large variation in soil P values in the 0-0.01 m soil increment at the study site (Figure 6-1). Olsen P (0-0.01 m) values measured in the preliminary soil P mapping ranged from 21 to 180 mg/kg. The soil P map shown in Figure 6-1 was used to assist in the identification of appropriate sites for rainfall simulation, the aim being to distribute rainfall simulations across the study site whilst encompassing a wide a range of soil P fertility levels.

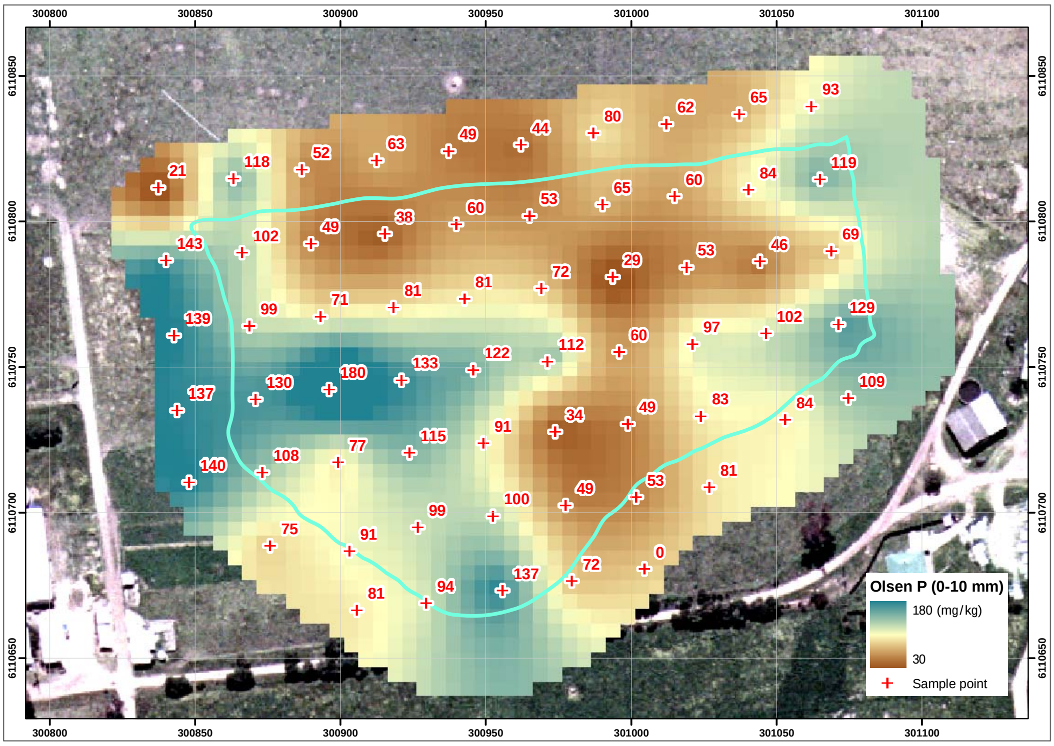


Figure 6-1. Olsen P (0-0.01 m) map of Flaxley east. Numeric descriptors on the map are Olsen P values at the sampling points.

6.3.2 Rainfall simulation characteristics

Simulations were undertaken over a period of 3 months. The first 40 simulations were undertaken over a six week period in July and August of 2004. The remaining 15 simulations were undertaken in September 2004. The delay of the second set of simulations was the result of technical problems with the simulator. The water used for rainfall simulation was from a rainwater tank. This water was of high quality, its average (separate samples were analysed from the rainwater tank for each day of simulation) chemical characteristics being:

TP	TDP	DOC	Fe	pH	EC
———	mg/L	———		-	µS/cm
<0.05	<0.05	6.1	<0.05	7.45	0.04

The simulations were generally undertaken when the soil moisture content was very high, average soil moisture content (0-7.5 cm) was 0.46 cm^3/cm^3 (Table 6-1). Such conditions were expected to be conducive to the generation of runoff by the process of saturation excess rather than infiltration excess (Zheng *et al.* 2004). It is this process of saturation excess that is hypothesised to be the dominant mechanism of runoff P generations at this site (Fleming *et al.* 2005). The last 15 simulations were undertaken after a slightly drier period when the soil moisture content was lower (average 0.37 cm^3/cm^3) than for the other simulations (0.49 cm^3/cm^3). A summary of the hydrological characteristics of the runoff events is presented in Table 6-1.

Table 6-1. Summary of the hydrological characteristics of the rainfall simulations.

	Infiltration^A	Runoff^A	Runoff coefficient	Soil moisture
	——— (mm/hr)	———		(cm^3/cm^3)
Mean	15.7	14.3	0.29	0.46
Median	14.9	15.1	0.31	0.46
Min	2.3	1.4	0.03	0.28
Max	28.6	27.7	0.56	0.66
SE	3.6	4.5	0.15	0.10

^{A}these were constant rates once approximate hydrological equilibrium was attained during the events

Runoff occurred soon after the commencement of rainfall application, (typically within 15 mins or the application of 7.5 mm rainfall) due to the high soil moisture contents. On average, approximately 18 mm of rainfall was applied to runoff plots, of which 30% ran off, the rest infiltrating. Steady state infiltration on these sites (measured as the difference between application and runoff rates once the runoff rate was constant) was 16 mm/hr.

The soil P status (0-0.01 m) of the rainfall simulation sites varied widely (Table 6-2), Olsen P ranging from a low 13 to a very high 158 mg/kg. This was a similar range to that revealed in the preliminary soil P mapping exercise and based on relationships derived in Chapter 7 equates to Olsen P_{10} of approximately 8-100 mg/kg. Ground-cover was high (>95%) for all simulations and pasture biomass (dry-weight) ranged from 390 to 1690 kg/ha. There was no significant ($P>0.05$) relationship between plant biomass and soil P content. This was consistent with the Olsen P content being either at or above the optimal Olsen P_{10} value of 18-22 mg/kg for pasture growth (Gourley 2001) in 94% of simulations.

Table 6-2. Summary of soil characteristics (0-0.01 m) at sites used for the rainfall simulations.

	Olsen P	$CaCl_2$-P	Soil water P
	—— (mg/kg)	——	(mg/L)
Mean	77	8.81	2.67
Median	78	8.51	2.07
Min	13	0.49	0.13
Max	158	30.65	8.51
SE	36	6.51	2.16

A summary of the basic chemical characteristics of the runoff is presented in Table 6-3. Phosphorus in the runoff from the plots was predominantly (average 72 %) dissolved (i.e. <0.45 µm). The DRP fraction accounted for 86 and 62 % of the TDP and TP respectively. These values are similar to those reported in earlier Chapters and by Fleming *et al.* (1996). The DUP component accounted for 12 % of TP and 17 % of TP and TDP respectively. There was no significant relationship ($P>0.05$) between suspended sediment and biomass or ground cover, indicating that mobilisation of sediment was not the result of direct raindrop impact (a finding consistent with that of Chapter 5).

Table 6-3. Summary of runoff chemical characteristics.

	TP	TDP	DRP	DUP	pH	EC	DOC	SS
	———	mg/L	———	———	——	µS/cm	— mg/L —	
Mean	1.34	0.96	0.83	0.16	7.33	120	48	153
Median	1.13	0.68	0.60	0.14	7.38	110	45	130
Min	0.09	0.06	0.04	0.00	6.78	60	18	38
Max	4.54	3.92	3.88	0.62	7.61	270	103	541
StDev	1.07	0.92	0.90	0.14	0.18	43	18	106

6.3.3 Relationship between soil P measures

Flaxley

There were significant (P<0.001) relationships between all soil P measures. The relationships between Olsen P, $CaCl_2$-P and SWP are shown in Figure 6-2. The relationship between Olsen P and $CaCl_2$-P and Olsen P and SWP were both best described by a curvilinear relationship although the degree of curvilinearity was only weak compared to that observed in other studies [e.g. Koopmans *et al.* (2002)], whereas the relationship between $CaCl_2$-P and SWP was linear.

A split-line relationship (or bent-stick model) has frequently been used to describe the relationship between Olsen P and $CaCl_2$-P [e.g. (McDowell and Trudgill 2000; McDowell and Sharpley 2001a; Vadas *et al.* 2005)]. Such a relationship implies that as the quantity of P in the soil (measured by Olsen P) increases, there is a distinct point at which the solubility of P or intensity component of soil P (measured by $CaCl_2$-P) changes such that it increases more rapidly than below this point. This point is known as the ‘change point’. However, the common use of a split-line model has largely been for reasons of convenience (McDowell and Sharpley 2001a) because it allows a ‘threshold’ to be defined above which the increase in the potential risk of P loss is greater than that below it. This provides a convenient management tool (i.e. because P status below the change point is often regarded as being acceptable from the perspective of the balance between agronomic and environmental objectives, whereas a soil P status above the change point provides an undesirable environmental risk). From a statistical standpoint, the fitting of a split-line model to the Olsen P – $CaCl_2$-P relationship would, in the case of the data presented in this thesis, violate the assumption of a constant mean-variance relationship required for fitting of regressions.

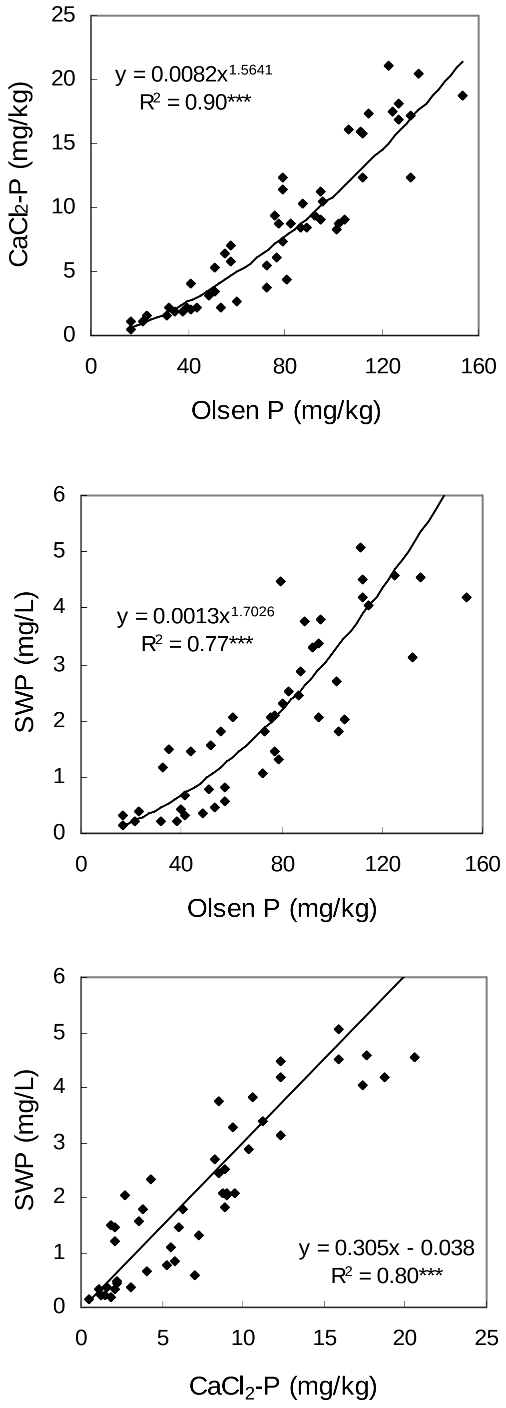


Figure 6-2. The relationship between the various measures of soil P (0-0.01 m) for the rainfall simulation soils.

The use of a curvilinear model to describe the Olsen P (quantity) vs. $CaCl_2$-P (intensity) is consistent with a continuum of sorption site affinities (White and Taylor 1977; Barrow 1983) and a gradual decrease in the affinity of sorption sites for P with increasing additions of P

(Barrow 1983; Barrow *et al.* 1998; Koopmans *et al.* 2002). In contrast, the bent-stick approach implies a sudden decrease in the affinity of sorption sites for P at some point.

The relationship between $CaCl_2$-P and SWP was linear. This is consistent with these two measures of labile P incorporating the intensity components of soil P (Kuo 1996). The concentration of P in the soil water was high in these soils, with DRP concentrations ranging from 0.13 to 8.5 mg/L. Typically, soil solution P concentrations of 0.003 to 0.3 mg P/L are found in arable soil (Moody *et al.* 1995; Pierzynski *et al.* 2005). Similar ranges of SWP to those observed in the Flaxley soils were reported by Webb *et al*. (2004) in the top 20 mm of soil under highly fertile pastures used for grazing of dairy cows in Victoria (Australia). The data of Webb *et al*. (2004) suggest that there may also be a substantial concentration of un-reactive P in the soil water that may be mobile. The relative significance of this pool and its mobility in the Flaxley soils is considered in more detail in Chapter 7.

Comparison with other soils

When compared to soils examined by other authors (Hesketh and Brookes 2000; McDowell and Trudgill 2000; McDowell and Sharpley 2001a; McDowell *et al.* 2003c), the Flaxley site soils have much higher concentrations of labile P ($CaCl_2$-P) for given Olsen P values (Table 6-4). The exception to this is the Camden site (discussed in Chapter 4). Compared to the soils from the UK and USA, the Australian soils appear to have 2-5 times greater labile P. These differences are particularly pronounced in the mid P status range of Olsen P – 60 mg/kg. This is particularly important as this is the most likely range of ‘problem’ soils in Australia from a water quality perspective. Reasons for these differences are discussed in Section 6.3.5.

6.3.4 Soil P-runoff P relationships

The relationships between the various measures of soil P and runoff TP and DRP are shown in Figure 6-3, Figure 6-4 and Figure 6-5. There was a significant (P<0.001) relationship between each of the 3 soil P measures and runoff TP and DRP. In all cases the relationships on the natural scale were curvilinear in nature. Such a curvilinear relationship for Olsen P vs. DRP is again consistent with a decreasing affinity of sorption sites for P with increasing quantity of P in the soil [i.e. a typical quantity-intensity relationship (McDowell and Sharpley 2001a)] and reflects the nature of this relationship in the soil extractions discussed previously.

Table 6-4. Comparison of labile soil P (measured as $CaCl_2$-P) at Olsen P contents of 20, 60 and 100 mg/kg for the Flaxley soils with that of other soils reported in the literature. The same analytical methods were used in all soils considered. The soils have been ranked in approximately decreasing order of $CaCl_2$-P.

Olsen P (mg/kg)	20	60	100	Reference
Site/location		$CaCl_2$-P (mg/kg)[A]		
Camden - NSW	4.3	10.5	13.4	- Chapter 7 -
Flaxley (41-55)	1.5	6.9	13.12	- na -
Flaxley (1-40)	1.5	3.8	5.97	- na -
Denbigh, UK	0.75	1.5	- na -	(McDowell and Sharpley 2001a)
Pukemutu – NZ	~ 0.5	~ 1.25	~ 4.5	(McDowell *et al.* 2003c)
Devon UK	~ 0.5	~ 1.2	~ 2.25	(McDowell and Trudgill 2000)
Broadbalk UK	~ <0.05	~ 1	- 4 -	(Hesketh and Brookes 2000)
Devon, UK	~ 0.25	~1	~2.25	(McDowell and Trudgill 2000)
Mataura - NZ	~ 0.5	~ 0.5	~ 3.0	(McDowell *et al.* 2003c)
Woodlands -NZ	~ 0.2	~ 0.5	~ 1.3	(McDowell *et al.* 2003c)

[A] the use of '~' denotes that these values were estimated from published data as per reference

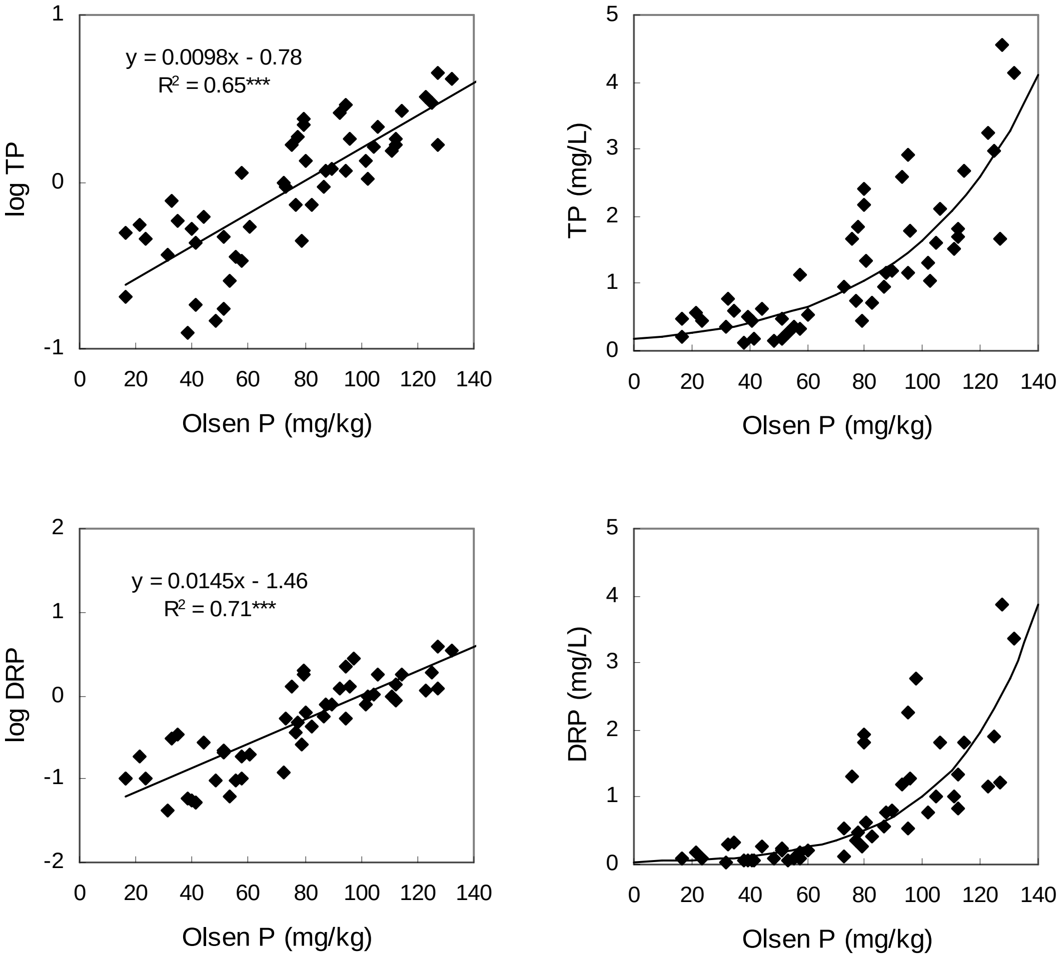


Figure 6-3. Relationships between Olsen P (0-0.01 m) and runoff TP and DRP for the Flaxley field rainfall simulations. The transformed data used for regression analysis and the resulting relationship are shown on the left whereas the corresponding back-transformed relationship with the original un-transformed data are shown on the right.

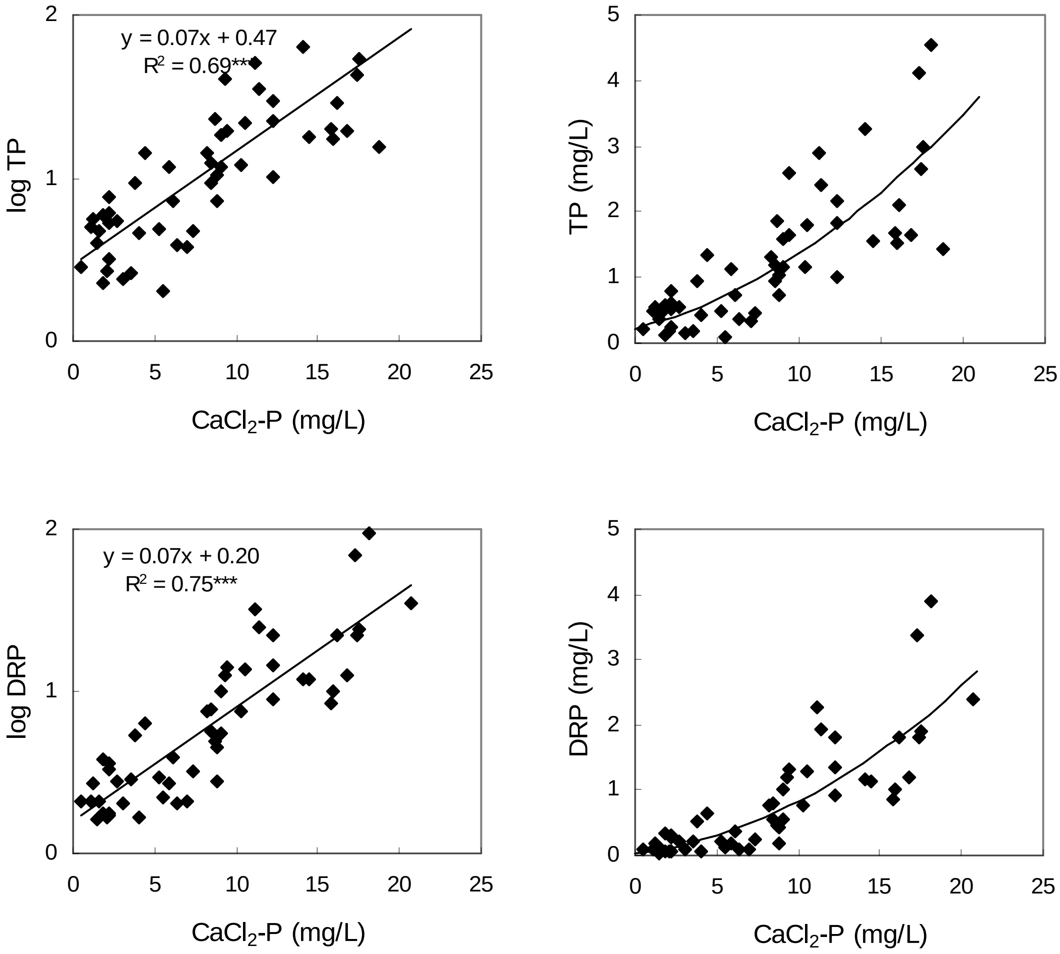


Figure 6-4. Relationship between $CaCl_2$-P (0-0.01 m) and runoff TP and DRP for the Flaxley field rainfall simulations. The transformed data used for regression analysis and the resulting relationship are shown on the left whereas the corresponding back-transformed relationship with the original un-transformed data are shown on the right.

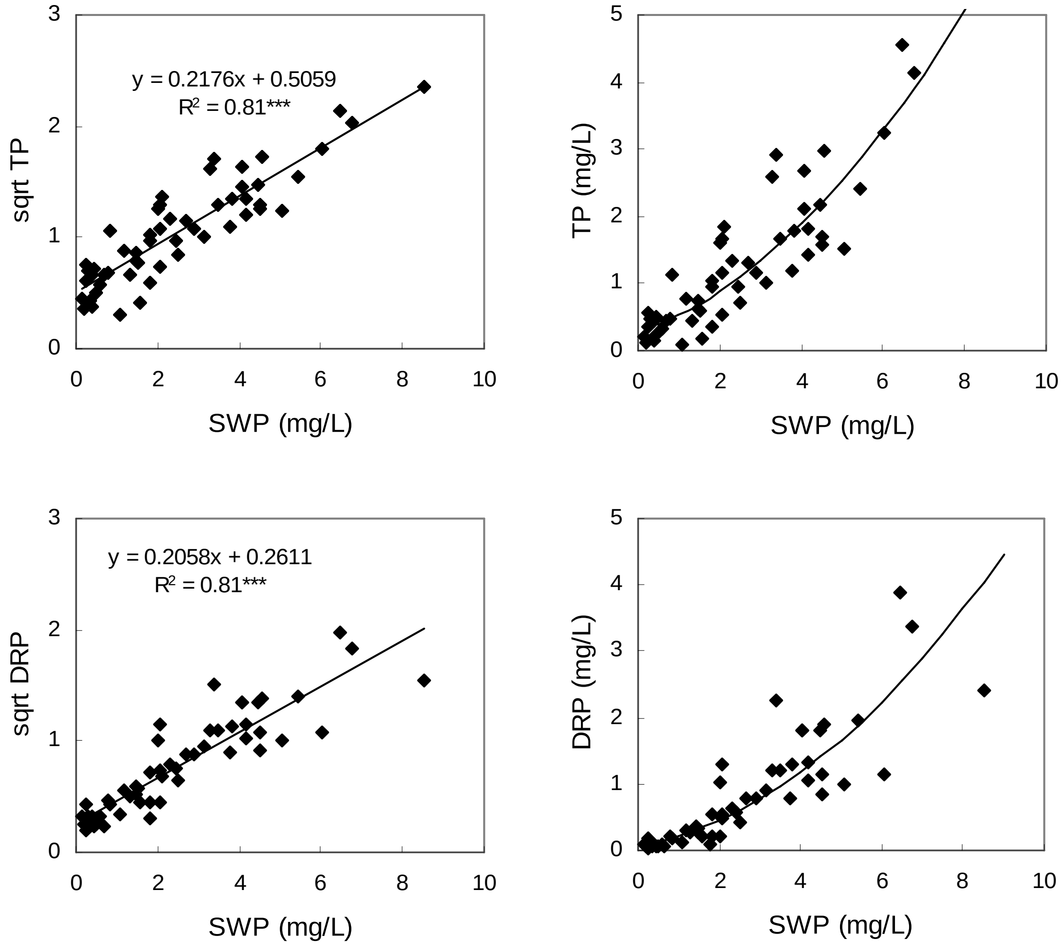


Figure 6-5. Relationship between SWP (0-0.01 m) and runoff TP and DRP for the Flaxley field rainfall simulations. The transformed data used for regression analysis and the resulting relationship are shown on the left whereas the corresponding back-transformed relationship with the original un-transformed data are shown on the right.

6.3.5 Comparison of Australian and North American soil P - runoff P relationships

A comparison of the data revealed in the literature and from unpublished sources is shown in Figure 6-6 and Figure 6-7. The approximate limits of the data reported by Vadas *et al*. (2005) are represented by the shaded areas. The body of Australian data available for comparison with North American relationships derived by Vadas *et al*. (2005) was limited. There was a highly significant relationship (P<0.001) between both DPS and Bray P and runoff DRP concentrations for the combined Australian soils. Although highly significant, only 43 and 54% of the variation was explained by the Bray P and the DPS respectively. This ‘low explanation’ of the variation is not surprising given the wide range of methods used and the need for ‘adjustments’ to data as outlined in the methods. Nevertheless, the significance of the relationships between soil P and runoff P does suggest that the single coefficient extraction concept requires further examination for Australian soils. The existence or otherwise of a single extraction coefficient would have important implications for runoff P risk assessment methodologies currently under development for Australian grazing industries (Smith *et al.* 2005).

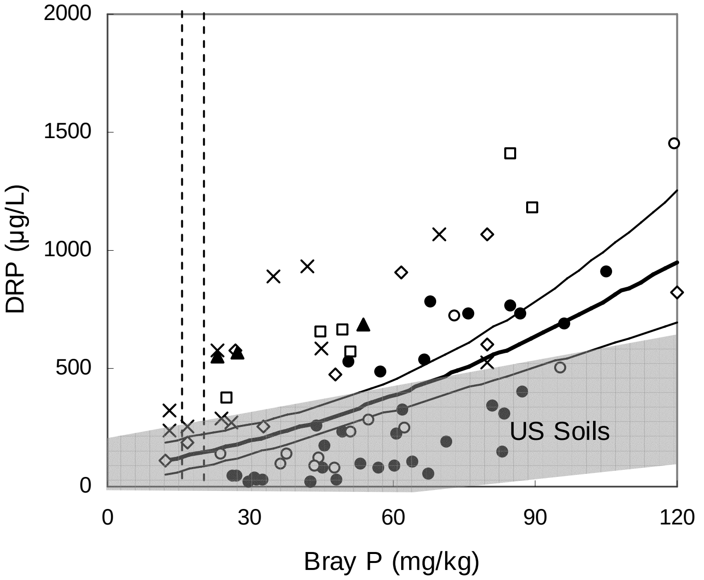


Figure 6-6. Relationship between Bray P (0-0.01 m) and runoff DRP for the Flaxley site and several other Australian studies. The shaded area represent the approximate range of values reported by Vadas *et al.* (2005) from North American runoff studies. ● – Flaxley field simulations; ○ Flaxley tray simulations; ▲ – Narellan NSW (Cornish *et al.* 2002); × - Vertosols - Camden NSW (Dougherty unpublished); □ Chromosols - Camden NSW (Dougherty unpublished); ◊ Camden rainfall simulations (Chapter 4). The vertical dashed lines indicate the approximate optimal value of Bray P for plant growth.

At relatively low Bray P and DPS values, the Australian runoff P concentrations were similar to those for the USA data. However, at relatively high Bray P and DPS values, the concentrations of P in runoff from the Australian soils appeared to be substantially higher than those of the northern hemisphere. It may be that because Vadas *et al.* used soil sampling depths between 0.02 and 0.05 m (compared to the 0.02 m depth for the Australian soils) that in fact the difference is greater as the USA soils would lie further to the right. For the Australian soils, the relationships were best described by curvilinear functions such that at higher soil P values the rate of increase in DRP is greater. This contrasts with the American data collated by Vadas *et al.* (2005) that reveal linear relationships between soil P and runoff

DRP. Unfortunately there is little additional data available to compare the properties of the North American soils and the Australian soils. Available data are from a wide range of methods that make comparisons difficult at best. The range of studies examined by Vadas *et al.* (2005) also covered much wider soil P ranges. For example, Bray P ranged from almost 0 to 800 mg/kg. In contrast, the Bray P values for the Australian soils examined only ranged up to 130 mg/kg. For any given soil P value, there was a comparable range of runoff DRP concentrations for both the Australian and North American studies. This range was of the order 700 μg/L of DRP.

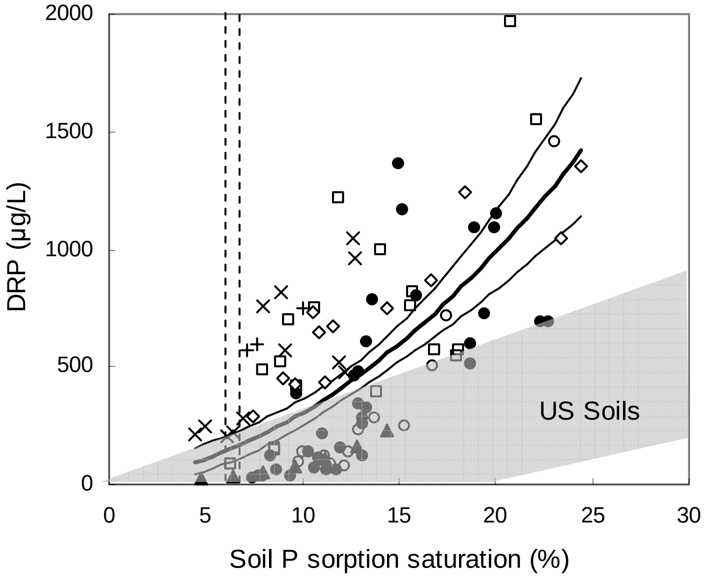


Figure 6-7. Relationship between degree of P sorption saturation (adjusted to 0-0.01 m) and runoff DRP for the Flaxley site and several other Australian studies. The shaded area represent the range of values reported by Vadas *et al.* (2005) from North American runoff studies. ● – Flaxley field simulations; ○ Flaxley tray simulations; + – Narellan NSW (Cornish *et al.* 2002); ♦ - Western Victoria multiple sites (Melland 2005);× - Vertosols - Camden NSW (Dougherty unpublished); □ Chromosols - Camden NSW (Dougherty unpublished); ◊ Camden rainfall simulations (Chapter 4). The vertical dashed lines indicate the approximate optimal value of DPS for plant growth.

The data suggest that a single relationship may have potential to be used to predict runoff P concentrations from pasture systems. This is similar to the conclusion of Vadas *et al.* (2005). However, it would appear that there may be a difference in the nature of the relationship between Australian soils and the North American study sites, Australian soils producing higher runoff P concentrations for a given soil P value. The reason(s) for this apparent difference in the soil P-runoff P relationship are not clear. A wide range of factors such as scale or rainfall simulation methodology (Ahuja *et al.* 1982; Sharpley and Kleinman 2003a; Dougherty *et al.* 2004), inherent soil chemical properties (Sharpley 1995; Cox and Hendricks 2000; Penn *et al.* 2005), timing and magnitude of P amendment in relation to the runoff event (Preedy *et al.* 2001; Nash *et al.* 2005) and hydrology (Pote *et al.* 1999; Zheng *et al.* 2004) may all influence the soil P-runoff P relationship. As all of the data points considered were derived using similar rainfall simulation and soil sampling procedures (or adjustments to correct for such factors) then methodology should not be a major factor in the differences between the Australian and the USA soils. Similarly, because none of the sites considered had fertiliser recently applied, then timing of fertiliser was not a major influence.

There may be more fundamental reasons for the differences. Such fundamental differences may lie with soil P chemistry. There is a higher concentration of P in the labile P pool of the Australian soils compared to soils from the Northern Hemisphere (see Table 6-4) suggesting that fundamental differences in soil P chemistry may be responsible for at least part of the difference. Penn *et al*. (2005) observed that runoff P concentrations could be influenced by mineralogy. They observed that soils with ratios Al-bearing minerals to kaolinite >0.5 had a significantly lower concentration of DRP in runoff for a given soil water soluble P level compared with soils with a ratio <0.5. Australian soils tend to be dominated by kaolinite whereas North American and European soils often have higher proportions of 2:1 clay minerals (Norrish and Pickering 1983). This suggests that part of the reasons for the higher concentrations of P in runoff and labile fractions may indeed be due to differences in mineralogy. Further comparison of the fundamental soil properties is needed for a wide range of soils from both Australia and overseas. This comparison could involve simple chemical, mineralogical and biological examination of the soils and also include rainfall simulation experiments using uniform methodologies.

6.4 Conclusions

There was a significant (*P*<0.001) relationship between various measures of soil P and runoff TP and DRP for the Flaxley site. This relationship was curvilinear for all of the soil P measures. The Flaxley soils (this Chapter) and Camden soils examined in Chapter 4 appear to be more ‘leaky’ than soils from the UK and North America. At given Olsen P values, $CaCl_2$-P was higher for Australian soils than for soils in the USA, UK and New Zealand. Similarly, Australian soil-pasture systems appear to have higher runoff P concentrations than runoff from North America soil-pasture systems. The data suggest that at least part of the reason for higher runoff P concentrations from Australian soils lies in differences in the fundamental chemical properties of the Australian soils, the origins of which may be mineralogical composition. However, there may also be differences in the other potential sources of runoff P such as plant biomass, soil organic P and manure P.

Given the likely increasing significance of the ‘systematic’ component of P exports in runoff from Australian pastures [at the expense of the incidental component as farmers improve the timing of fertiliser application (Nash *et al.* 2005)], improving the understanding of the fundamental soil P properties in relation to mobilisation of P in runoff warrants further attention. An improved understanding of this would contribute to the development of strategies designed to reduce runoff P concentrations. The accumulation of P in two Australian Chromosols used for dairying and its subsequent mobilisation in runoff is examined further in the following chapter.

Chapter 7 Stratification, forms and mobility of phosphorus in the topsoils of Chromosols used for dairying

7.1 Introduction

The data presented in the previous Chapters have highlighted the processes of mobilisation that result in high concentrations of P in runoff from intensively managed pastures. In order to further understand the reasons for these high concentrations, there is a need to better understand the chemistry of P in the soil that results in these high P concentrations.

In dairying, substantial quantities of P are applied to the soil surface of pastures via fertiliser, the recycling of P in manure and senescing plant material. In a survey of 7 farms near Sydney (New South Wales), P inputs ranged from 13 to 137 kg P/ha/yr and net accumulation from 1 to 127 kg P/ha/yr (Lawrie *et al.* 2004). In the Gippsland (Victoria) the average fertiliser P application rate for a dairy farm is 44 kg/ha/yr (Drysdale 1998) with estimated net P accumulation approximately 30 kg P/ha/yr (Nash and Halliwell 1999). These substantial inputs of P coupled with minimal soil disturbance and the strong affinity of soil for P, result in the preferential accumulation of P at the immediate soil surface (Sharpley *et al.* 1993; Kingery *et al.* 1994; Haygarth *et al.* 1998; Sharpley 2003). It is this immediate soil surface that has the greatest influence on runoff P concentrations (Ahuja *et al.* 1981; Sharpley 1995; Pote *et al.* 1999; McDowell *et al.* 2003c).

The forms of P in runoff have been shown to vary as a function of the forms of P in the soil from which they are mobilised (Nelson *et al.* 1996; McDowell and Sharpley 2001b; Heathwaite *et al.* 2005). Most P in runoff from dairy pastures in Southern Australia is in a dissolved (<0.45 μm) form (Nash and Murdoch 1997; Fleming and Cox 1998) that is difficult to control (Nash 2002) and is highly bio-available. Orthophosphate has been identified as important components of this dissolved P (Halliwell *et al.* 2000), but colloidal P [i.e. P associated with particles of size 1 nm to 1 μm can also make a major contribution to the P transported in runoff (Haygarth *et al.* 1995; McDowell and Sharpley 2001b; Hens and Merckx

2002; Heathwaite *et al.* 2005)]. This colloidal P can be composed of organic and inorganic material (Hens and Merckx 2002).

The forms of P in soil, (viz. the proportions of organic and inorganic P - P_o and P_i respectively) vary greatly. A study of 15 sites under pasture in eastern Australia (McLaughlin *et al.* 1990) revealed that organic P ranged from 35 to 65% of the total soil P. A relationship between total soil P and P forms has been variously reported, the majority of P accumulating as inorganic P [e.g. Steward and Oades (1972) ; Curtin *et al.* (2003)]. Whilst inputs of P from mineral fertilisers are inorganic, even the P in plant litter and manure (that make a large contribution to soil surface P inputs) can be composed of >70% inorganic P on soils with high P status (Jones and Bromfield 1969; Turner and Leytem 2004).

A number of studies have investigated the forms of P in the top 0.05-0.30 m of the soil profile (McDowell and Condron 2000; McDowell *et al.* 2002; Lawrie *et al.* 2004) and the relationship between soil P status and P concentration in runoff (Sharpley 1995; Pote *et al.* 1999). However, there has been no comprehensive examination of the relationships between soil P status (i.e. fertility), the forms of soil P (organic vs. inorganic) in the zone of soil/runoff interaction and the P forms mobilised in surface runoff from high fertility soils under pasture. Furthermore, there has been little detailed examination of the stratification of P in the top 0.10 m of the soil, despite the large potential reduction in runoff P exports that may result from de-stratification (Nash and Halliwell 1999; Sharpley 2003).

Improving the understanding of the pattern and forms of P accumulation and the consequent forms of P mobilised will improve the understanding of the processes of mobilisation and assist in formulating management strategies to reduce P exports. Therefore, the aims of the investigations described in this Chapter were to:

- ***Determine the effect of soil P status (i.e. P fertility level) on the forms of P in the immediate topsoil (0-0.01 m),***
- ***Investigate the vertical distribution of P in the top 0.10 m of the soil, i.e. the degree of stratification,***
- ***Examine the forms of P in runoff.***

The soils used in the experiments were from the two sites previously described in this thesis, a) the Flaxley site in South Australia, and b) the Camden site in New South Wales. Previous research has shown that surface runoff is the predominant pathway for P transport (Fleming and Cox 1998), hence the investigations were restricted to the topsoil and its influence on P transported in surface runoff.

7.2 Methods

7.2.1 Soil sampling[1]

Flaxley

Prior to soil sampling for this study, the site had not been fertilised for 10 months and had not been grazed for approximately five months over summer because of low summer rainfall. Composite soil samples were collected within the sub-catchment from 26 sampling locations approximating a grid pattern. In order to facilitate soil sampling and accurate sectioning of soil cores, 1 m^2 areas at each sampling location were pre-wet with 50 mm of water ($P < 0.05$ mg/L) over a 2 hour period, 1 week prior to sampling. This equated to rainfall in a typical ‘break of season’ event at this site. Twenty-five cores (0.02 m diameter) were taken within each of these 1 m^2 areas and cut into four sections in depth increments of 0-0.01, 0.01-0.02, 0.02-0.05, and 0.05-0.10 m. At each sampling location, the 25 cores for each increment were composited. In addition, 25 samples of the 0-0.10 m increment were collected at each location and composited to enable comparison of the soil properties for each of the increments with the standard agronomic soil P measure [i.e. Olsen P (Olsen *et al.* 1954), 0-0.10 m].

Camden

Prior to soil sampling at the Camden site, fertiliser had not been applied for 6 months. Composite soil samples were collected within each of 6 plots along a permanent sampling transect. Thirty cores (0.02 m diameter) were taken along these transects and cut into four sections in depth increments of 0-0.01, 0.01-0.02, 0.02-0.05, and 0.05-0.10 m. For each plot, the 30 cores for each increment were composited. In addition, 30 samples of the 0-0.10 m increment were collected for each plot and composited to enable comparison of the soil

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[1] Because various sampling depths are used in this Chapter, subscripts are used to denote the sampling depth of the measure being discussed. These sub-scripts are for the sampling depth in cm, for example, Olsen P_1 refers to the Olsen P content of the 0-0.01 m increment.

properties for each of the increments with the standard agronomic soil P measure [i.e. Olsen P (Olsen *et al.* 1954), 0-0.10 m].

7.2.2 Soil preparation and analysis

Following collection, the soil samples were prepared for analysis as described in Chapter 3 (General Materials and Methods). Sub-samples for total and organic phosphorus (P_o) and organic carbon (OC) measurement were further ground to pass through a 200 μm sieve.

All soil samples were analysed for organic carbon, $CaCl_2$-P. Topsoil samples (0-0.01m) were analysed for $CaCl_2$-TP, $CaCl_2$-P and $CaCl_2$-UP (by difference), total P, inorganic and organic P, Olsen P. The 0-0.1m increments were analysed for Olsen P, $CaCl_2$-P.

Multi-point P sorption isotherms were determined for the 0-0.01m increments of selected samples. These were constructed by shaking soil (10:1 solution:soil) for 17 hours at 20^oC with solutions containing 0, 10, 30, 50, 70 and 100 mg P/L and then measuring the final concentrations and calculating the P sorbed (mg/kg) from the solution. The relatively small number of equilibrating concentrations was a consequence of the limited amount of soil available due to the shallow sampling depths and the need to conserve soil for further studies. The equilibrium phosphorus concentration (EPC) was calculated using regression as the final concentration of P (in the equilibrating solution) on the isotherms at which there is no net sorption nor desorption of P.

7.2.3 Calculation of the effective depth of interaction (EDI)

In order to evaluate the importance of stratification of P upon P mobilisation a knowledge of the depth of soil with which runoff interacts with the soil is useful. The EDI provides such an estimate.

The EDI concept was developed to provide a description of the depth of soil from which P in runoff was being mobilised (Ahuja *et al.* 1981). The contribution of soil to the P being mobilised in runoff declines exponentially with depth. In rainfall simulation experiments on a Ruston fine sandy loam, Ahuja (1981) demonstrated that the contribution of P from soil at 5 mm depth was an order of magnitude lower than that at the immediate soil surface. The EDI was defined as the thickness of soil in which the degree of interaction was uniform and equal to that at the surface. Whilst there has been considerable attention to the determination of the EDI in bare soils (Ahuja *et al.* 1981; Ahuja and Lehman 1983; Sharpley 1985), there has been little examination of this concept for pasture soils. The EDI can be calculated using a modified version (Sharpley 1985) of the P desorption equation examined in Chapters 4 & 5 as follows:

$$P = \frac{K \times P_o \times EDI \times \rho \times t^{\alpha} \times W^{\beta}}{V} \qquad \text{Eq. 7-1}$$

where P is the runoff P concentration (mg/L), P_o is a measure of the initial soil P (mg/kg) – in this case $CaCl_2$-P, EDI is the effective depth of interaction (mm), ρ is the soil bulk density (g/cm^3), t is the runoff residence time (min), W is the runoff depth to EDI ratio, V is the volume of runoff (L), and K, α and β are constants. The EDI was calculated for the Flaxley and Camden sites using Eq. 7-1. Data from the runoff trays (this Chapter) and field simulations (Chapter 6) from Flaxley and from the Camden site (Chapter 4) were used to determine the EDI at these sites. The calculation of the EDI was carried out by solving Eq. 7-1 for EDI based on the runoff data using least squares linear programming (in Excel's 'solver' function).

7.2.4 Runoff generation and collection

Flaxley

Twelve re-packed soil trays were constructed as described in McDowell *et al.* (2003c) to examine the relationship between the concentration and form of P in soil and runoff. Trays were constructed from plywood to be 0.20 m wide, 1.00 m long and 0.125 m deep, except for the down-slope end where the trays were only 0.10 m deep to allow runoff to exit the trays and be collected for measurement of runoff volume and rate and sub-sampling for analysis. Soil was packed into the trays to a depth of 0.10 m and sown to ryegrass as described below.

The soils used in the runoff trays were collected from a sub-set of the sampling locations at the Flaxley site described above. Soils encompassing a wide range of soil P status were used. In order to best reflect P forms and concentrations in the zone of soil-runoff interaction (<0.01 m), soil for repacking in the trays was collected separately for the 0-0.01 and 0.01-0.10 m depth increments. Prior to packing, soil was ground and passed through a 6 mm sieve. Further drying of the soil was not undertaken as there had not been any substantial rain for several months and the soils were effectively dry. For each of the trays, the soil from the 0.01-0.10 m increments was packed at a bulk density of 1.10 g/cm^3 following which the 0-0.01 m increment was re-packed on top at a density of 1 g/cm^3. The trays were sown to ryegrass (*Lolium perenne L*) and grown in a glasshouse for four months prior to the rainfall simulation experiments.

Rainfall simulations were undertaken using the rotating disc rainfall simulator described in Chapter 3 (General Materials and Methods). Rainfall was applied at an intensity of 30 mm/hr and continued until runoff had occurred for 20 minutes, resulting in the application of rainfall for approximately 30 minutes in total on average. This combination of intensity and duration was equivalent to a 1 in 3 year event for the study site (Pilgrim 1987). A 250 mL sub-sample of the runoff was collected for filtration and analysis (see following section). Following the simulations, 10 cores (0-0.01 m) were collected from each tray to provide a composite for each tray. These soils were prepared and analysed for Olsen P, P_o and P_i as previously described.

Camden

The generation of runoff and subsequent collection of runoff samples from the Camden site was carried out as described in Chapter 4. Briefly, this involved rainfall simulation at 8 mm/hr on large plots (50 × 25 m), runoff samples then being collected at prescribed runoff intervals.

7.2.5 Runoff analysis

A sub-sample of runoff from each tray (Flaxley) or runoff plot (Camden) was collected and filtered (<0.45 µm, Sartorius® - Germany) immediately after the cessation of runoff. Each sample was analysed for total dissolved P (TDP), dissolved reactive P (DRP) dissolved un-reactive P (DUP - defined as the difference between TDP and DRP), suspended sediment (SS) and dissolved organic carbon (DOC) as outlined in Chapter 3 (General Materials and Methods).

7.2.6 Ultrafiltration of runoff samples

The use of 0.45 µm filters to define phosphorus is arbitrary and substantial amounts of colloidal material pass through such filters (Hens and Merckx 2001; Heathwaite *et al.* 2005).

In order to provide more detailed physical fractionation of P forms in the runoff samples, samples from five of the runoff trays (selected to provide a range of runoff P concentrations) and five of the Camden runoff plots (there was insufficient sample from one of the plots) were subject to a more detailed filtration procedure.

Initially 1.2 μm glass fibre filters were used to delineate the upper limit of the colloidal size range. However, examination of these using scanning electron microscopy revealed substantial retention of <1 μm particles even though the suspended sediment load was low and only small volumes of sample (50 mL) were passed through these filters. Similar findings were reported by Gimbert *et al.* (2005).

The 1.0 μm (the upper size limit of colloids), and 0.10 μm fractions were isolated by centrifugation using Stokes Law to determine the appropriate centrifuging time and speed to separate these fractions. This involves calculating the centrifugation time based on the following equation:

$$t = 6300 \times 10^{6} \times 0.010019 \times \left[\frac{\log \frac{r_o}{r_i}}{(\mathrm{rpm} \times 1.6 \times \mathrm{dia.})} \right] \qquad \text{Eq. 7-2}$$

where t is time (min), r_o and r_i are the radius (cm) of the bottom and top of the solution being centrifuged in the solution, rpm is the revolution per minute and dia. is the desired particle cutoff diameter (μm).

The samples were then filtered through 100, 10 k-Dalton (kDa) membranes (YM Series, Amicon, Germany) in order to further examine the nature of colloidal (1 μm to 1 nm) and sub-colloidal (<1 nm) fractions. These filters had approximate exclusion diameters of 30, 3 nm respectively according to Turner *et al.* (2004).

Ultrafiltration was undertaken within 6 hours of sample collection for the Flaxley soils. The Camden soils were stored frozen at -20^{o}C prior to ultrafiltration. The ultrafiltration through the 100 and 10 kDa filters did not include the addition of NaCl as described in Turner *et al.* (2004) and Shand *et al.* (2000) as preliminary experiments showed that there was only a slight increase in P concentration with increasing volume for the 100 and 10 kDa filters. Whilst

NaCl could have been added to these samples as is often done (Shand *et al.* 2000; Turner *et al.* 2004), changes in ionic strength are likely to have substantial impacts on the size and conformation of colloids and thus effect the size distribution of P, DOC and other constituents (Ghosh and Schnitzer 1980; Stevenson 1996).

Following filtration a sub-sample of each filtrate was analysed for RP[2] and TP[2] and OC[2]. The size distribution of colloids in the solutions was also examined using a NiComp® 370 particle size analyser. However, in all cases (even for the <1 μm fraction) the samples were below the detection limit of the instrument.

7.2.7 Statistical analysis

The effect of depth on $CaCl_2$-P and OC was tested using ANOVA with depth (n=4) as the main factor and Olsen P_{10} (0-0.10 m) of the respective samples/plots (Flaxley n=26; Camden = 6) as a covariate in the treatment structure. This analysis was carried out using Genstat 6.1 (Lawes Agricultural Trust, Rothamsted).

Relationships between soil properties (0-0.01 m increment) for the samples for both sites were examined using least-squares linear and non-linear regression using SPSS v12.0.1 (Systat - Chicago, Illinois). Linear regression was used to examine the relationships between: a) soil total P_1 and soil P forms (P_o and P_i), b) total P and C:P_o ratio and total P and OC, c) Olsen P_{10} (0-0.10 m) and $CaCl_2$-P in each of the depth increments and d) Olsen P_1 and DUP in runoff. Differences in the accumulation of P in the various depth increments were tested by comparing the slopes of the regressions of Olsen P (0-0.10 m) against $CaCl_2$-P for each of the individual depth increments.

The relationship between soil organic P (%) and DUP (%) in 10 mM $CaCl_2$ extract of soils was investigated using linear regression. A log-log transformation was required to provide normally distributed variance before examining this relationship. Non-linear regressions were used to examine the relationship between Olsen P (independent variable) and the degree of stratification (defined as the ratio $CaCl_2$-P_1:$CaCl_2$-P_{10}), DUP (%) in 10 mM $CaCl_2$ of soils and DRP in runoff from the rainfall simulation trays (dependent variables). The relationships were examined using the following non-linear equation:

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[2] The terminology for describing runoff analytes is altered here as all samples are regarded as dissolved. For instance RP is used to refer to reactive P rather than DRP, the size fraction being specified where necessary.

$$\text{Dependent variable} = \alpha + \beta_1 \times e^{(\beta 2 \times \text{Independent variable})} \qquad \text{Eq. 7-3}$$

where α, β_1 and β_2 are constants. For all statistical analyses, residuals were examined graphically to check that they were distributed normally with constant variance. Unless specified otherwise, all units used in the analyses were either mg/kg for soil or mg/L for runoff solutions.

7.3 Results

7.3.1 General soil properties

The soils at both sites varied widely in their P fertility status. Olsen P_{10} ranged from 15 to 97 mg/kg (average - 42) at Flaxley and from 10 to 56 mg/kg (average – 29) at Camden (see Table 4.1). The Olsen P values at both sites encompassed the agronomically optimal Olsen P_{10} value of 18-22 mg/kg for intensive pasture production (Gourley 2001).

A summary of the key soil properties of the 0-0.01 m increments is shown in Table 1. Organic carbon in the top 0.01 m was very high (Hazelton and Murphy 1992) and the soils were strongly acidic. There was a significant ($P<0.01$) relationship between total soil P and Olsen P and $CaCl_2$-P (Figure 7-1) for both sites. Both soils have similar baseline total P values (i.e. approximately 800 mg/kg). However, the labile component (as estimated by $CaCl_2$-P) is relatively high for the Camden soil. This difference may be the result of the more recent applications of P on the Camden soil or differences in soil chemistry. The differential accumulation of P at the Camden site has occurred over a period of 3 ½ years whereas this accumulation has occurred over approximately 20-30 years at the Flaxley site.

The sorption properties of the soils changed substantially in response to accumulation of P. Typical P sorption isotherms are shown for four of the soils from each of the sites (only four are illustrated for clarity) in Figure 7-2. For both soils, the addition of P results in depression of the sorption capacity at particular P concentrations. The Camden soils exhibited lower sorption maxima and also clearly showed a depression of sorption maxima with increasing TP_1 values. There was also a significant ($P>0.01$) relationship between TP_1 and EPC (data not shown) and Olsen P_1 and EPC for both sites (Figure 7-3). Importantly, there were very large differences in the form of these relationships and the magnitude of EPC between the two sites.

The higher EPC values for the Camden soils are consistent with the greater lability of P in these soils discussed in Chapter 6.

Table 7-1. Key properties of the 0-0.01 m soil increments (averages of 26 sampling locations). The figures in brackets are the range of values.

	Site	
Parameter	Flaxley	Camden
pH_{Ca}	5.67 (5.43-6.10)	5.8 (5.5-6.1)
Olsen P (mg/kg)	65 (28-146)	45 (14-88)
$CaCl_2$-P (mg/kg)	4.24 (0.31-11.59)	8.28 (2.13-18.41)
Organic P (mg/kg)	516 (420-693)	563 (550-581)
Organic P (%)	43 (23-63)	58 (41-75)
Total P (mg/kg)	1229 (632-1901)	1045 (676-1490)
Organic carbon (%)	6.1 (5.2-7.6)	6.7 (5.5-8.0)
Carbon:Organic P ratio	119 (96-147)	122 (100-145)

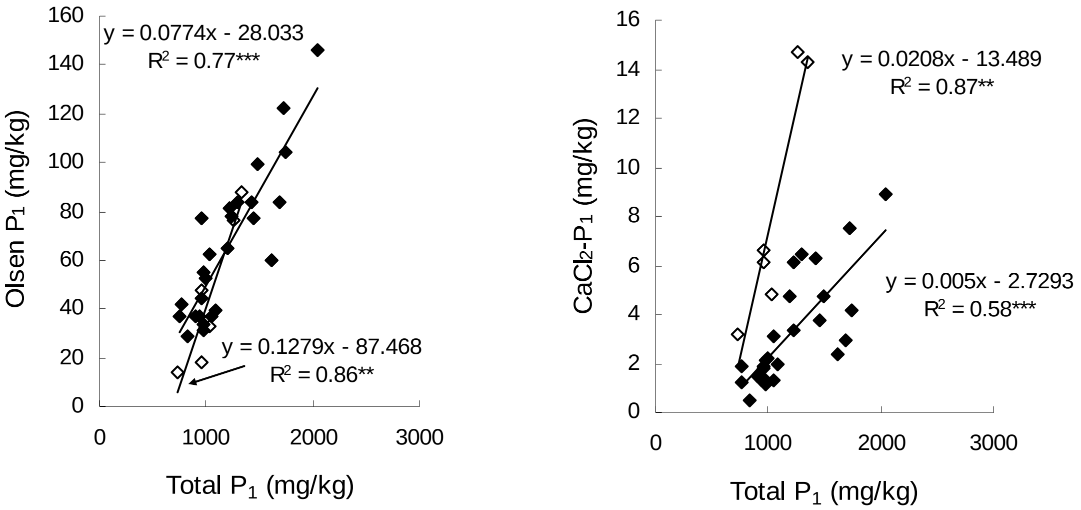

Figure 7-1. The relationship between total P and Olsen (left) and $CaCl_2$-RP (right) in the 0-0.01m increment of the Flaxley (♦) and Camden (◊) soils.

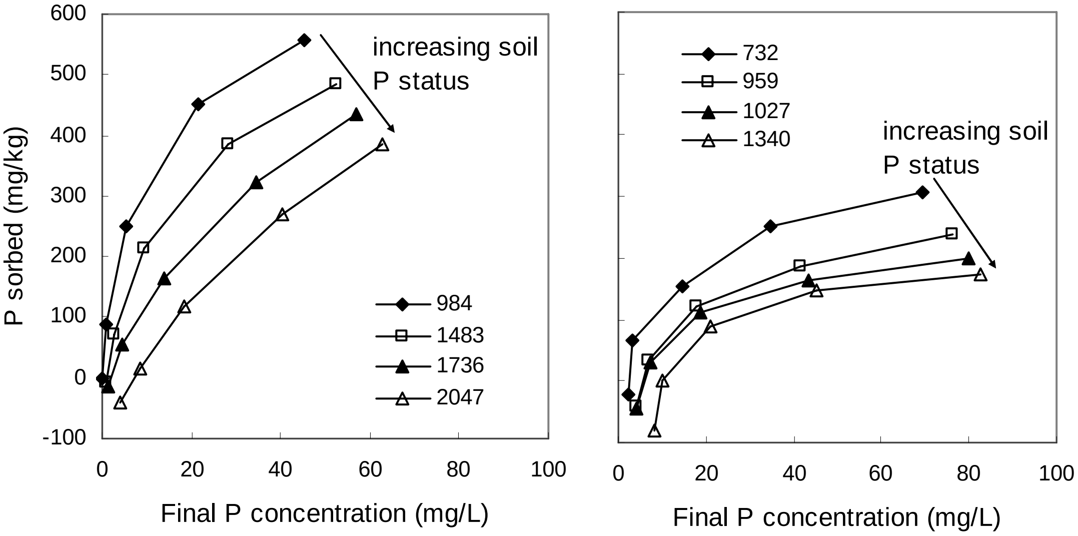

Figure 7-2. P sorption isotherms for selected Flaxley (left) and Camden (right) soils (0-0.01 m). The numbers in the legends refer to the corresponding total P_1 values.

Organic carbon increased with increasing fertility for both Camden and Flaxley ($P<0.01$) (Figure 7-4). The organic carbon is high in all cases, irrespective of soil fertility. The Camden soil had higher OC for a given fertility level. This was most likely a reflection of the continual fresh inputs of organic matter (due to irrigation and more evenly distributed rainfall though-out the year at Camden) on these soils throughout the year, compared to the seasonal inputs on the Flaxley soil.

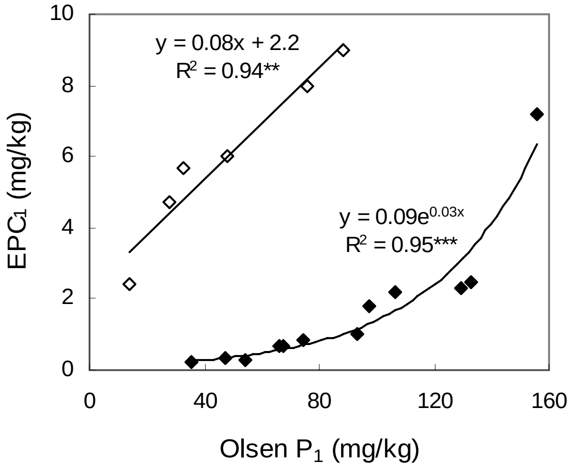

Figure 7-3. The relationship between Olsen P and EPC in the 0-0.01 m increment of the Flaxley (♦) and Camden (◊) soils.

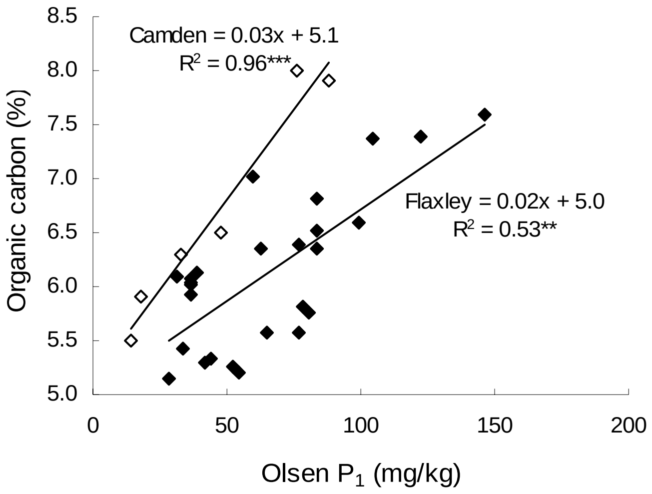

Figure 7-4. Relationship between soil P status (Olsen P) and organic carbon for the Flaxley (♦) and Camden (◊) soils.

7.3.2 Soil P forms

Significant linear relationships between total soil P and P_o ($P<0.01$) and P_i ($P<0.001$) in the 0-0.01 m increment were observed for the Flaxley site but there was no relationship between total soil P and P_o on the Camden soil (Figure 7-5). Phosphorus (0-0.01 m) accumulated predominantly as P_i, the slope of the relationship between total P and P_i being 0.83 (SE 0.03) for Flaxley and 0.99 (SE 0.05) for Camden. Only relatively small increases in P_o were observed across the range of total soil P for Flaxley, the slope of this relationship being 0.17 (SE 0.03), and there was no relationship ($P>0.05$) for Camden. Consequently, for both soils, the proportion of P_o decreased with increasing total soil P concentrations (Figure 7-5b). For Flaxley, at the lowest total P concentration, P_o accounted for 63% of the total P, whereas at the highest total P it only accounted for 26%. For Camden, at the lowest total P concentration, P_o accounted for 75% of the total P, whereas at the highest total P, P_o only accounted for 41%. The lack of a detectable accumulation of organic P in the Camden soil may be the result of the relatively short timeframe over which these plots had been run, i.e. 3 ½ years, which may not be sufficient to see a substantial increase in the organic P pool.

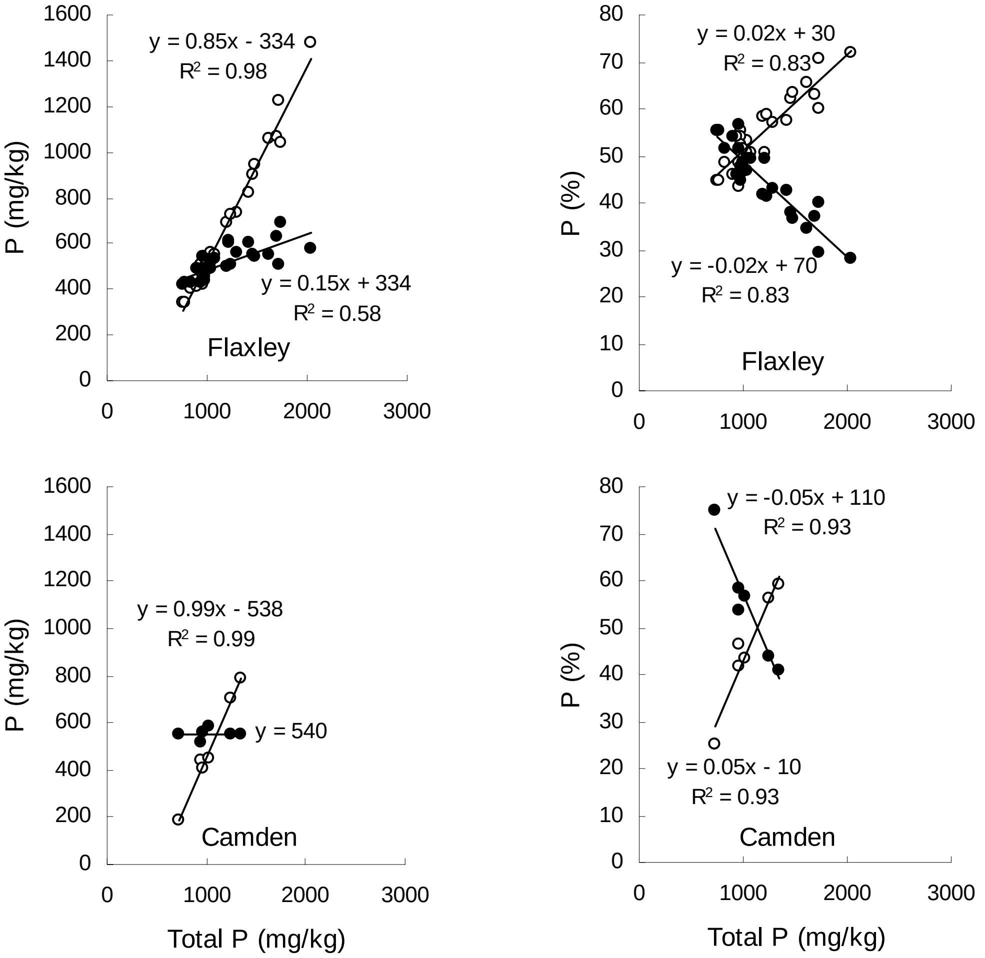

Figure 7-5. Relationship between concentrations of total soil P and organic (P_o - ●) and inorganic (P_i -○) forms of P in the top 0.01m of soil (left), and proportions of organic and inorganic P in the top 0.01 m of the soil expressed as percentages of total soil P (right).

One possible explanation for the wide range of P_o values reported by other researchers may lie with the amount of P previously added to the plots. Although Turner *et al.* (2003b) did not specifically examine the relationship between total P and P_o and P_i, their data revealed a significant relationship between total P and P_o and P_i. However, there was no significant relationship between total soil P and the proportions of P_i and P_o, each accounting for ~50% of total soil P. This lack of a relationship may be related to the wide range of soils they examined and hence the wide range of climatic and management histories.

7.3.3 P stratification

The soils exhibited marked stratification of $CaCl_2$-P at both sites and all sampling locations [i.e. the concentration of $CaCl_2$-P was highest in the top 0.01 m and decreased with depth

(*P*<0.001)]. Typical depth-$CaCl_2$-P profiles for the Flaxley and Camden sites are shown in Figure 7-6. $CaCl_2$-P (mg/kg) in the 0-0.01 m increment was on average 5.8 and 8.7 times greater than in the 0.05-0.10 m increment for the Flaxley and Camden sites respectively (Table 2).

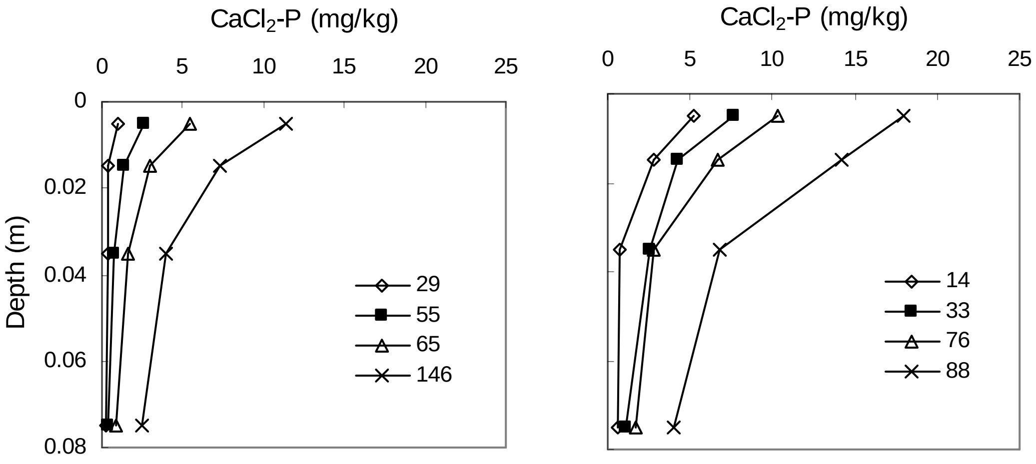

Figure 7-6. Examples of depth distribution of $CaCl_2$-P for Flaxley (left) and Camden (right) soils. The values on the legends are the corresponding Olsen P values (0-0.1 m).

For both sites there was a significant relationship between Olsen P_{10} and $CaCl_2$-P for each of the individual depth increments reflecting the accumulation of P in each of the increments. The slopes of each of the regressions between Olsen P (0-0.10 m) and $CaCl_2$-P (0-0.01, 0.01-0.02, 0.02-0.05 and 0.05-0.10 m) were significantly different (*P*<0.05). The slopes of the regressions between Olsen P (0-0.10 m) and $CaCl_2$-P are shown in Table 7-2. These data illustrate the preferential accumulation of P (in this case $CaCl_2$-P) in the immediate topsoils.

Table 7-2. Slope and significance of relationship between Olsen P_{10} and $CaCl_2$-P for each of the depth increments sampled. (figures in brackets are standard errors of slopes).

Depth (m)	Flaxley	Camden
0.000-0.010	0.092** (0.009)	0.314** (0.04)
0.010-0.020	0.062** (0.006)	0.252*** (0.03)
0.020-0.050	0.040** (0.003)	0.137*** (0.01)
0.050-0.100	0.027** (0.002)	0.072*** (0.01)

The degree of stratification (measured as $CaCl_2$-P_1:$CaCl_2$-P_{10}) decreased with increasing soil P status. This is reflected in the significant (*P*<0.001) relationship between degree of stratification and soil fertility (Olsen P; 0-0.10 m) (Figure 7-7). The $CaCl_2$-P_1: $CaCl_2$-P_{10} was highest (i.e. approximately 0.65), at low fertility levels and decreased to approximately 0.2 at higher fertility levels for Flaxley whereas at Camden the $CaCl_2$-P_1: $CaCl_2$-P_{10} ranged from 0.47 at the lowest fertility level to 0.28 at the highest fertility level. This means for Flaxley that at the lowest fertility level, 65% of the $CaCl_2$-P in the top 0.10 m was present in the top 0.01 m and at the highest fertility level, only 20% of the $CaCl_2$-P was present in the top 0.01 m.

The substantial stratification of $CaCl_2$-RP suggests that reductions in runoff P concentration may be achieved as a result of de-stratification (i.e. mixing of the topsoil), as proposed by Sharpley (2003). Clearly, any such reductions will be a function of site specific characteristics such as hydrology and soil P status. Sharpley (2003) observed on average an 80% decrease in Mehlich P concentration of the 0-5 cm depth as a result of mixing, i.e. de-stratifying the top 20 cm of the soil, and consequently observed a large reduction in dissolved P concentrations in runoff. The results for Flaxley and Camden suggest that the magnitude of the benefit of de-stratification would be a function of both soil P status (because of its relationship with degree of stratification) and the relationship between soil P and runoff P concentration. Those soils with higher soil P status would experience a smaller percentage decrease in soil P concentration in the top 1 cm as a result of de-stratification than those soils with lower P. However, the *actual* decrease in runoff P concentrations from mixing would likely be largest at high fertility levels. The effect of de-stratification on soil surface P, runoff P concentrations and its implications at a sub-catchment scale are considered in Chapter 9.

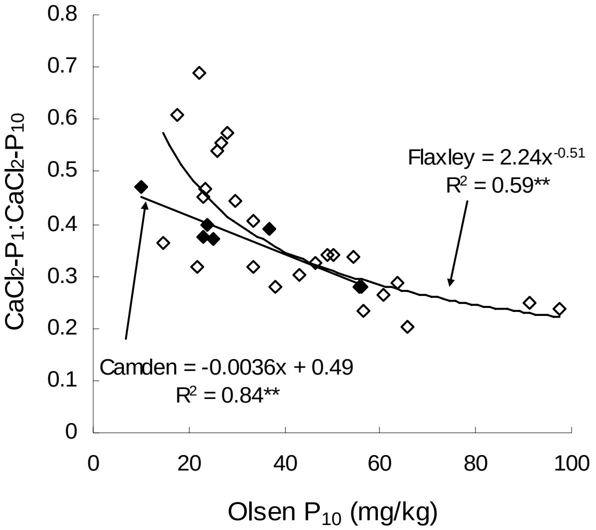

Figure 7-7. Relationship between soil fertility (expressed as Olsen P; 0-0.10 m) and degree of P stratification for the Flaxley (◊) and Camden (♦) soils (expressed as ratio of $CaCl_2$-P mass in the 0-0.01 m increment to that in the 0-0.10 m increment, i.e. $CaCl_2$-P_1: $CaCl_2$-P_1).

7.3.4 Labile soil P forms

Changes in the soil P composition (P_o vs. P_i) were mirrored in the composition of the dissolved P (<0.45 µm) in the 10mM $CaCl_2$ soil extracts. There were significant (*P*<0.001) linear relationships between P_o (%) and DUP (%), and Olsen P and DUP (%) for soils at both sites. As P_o and Olsen P contents increased, so did the DUP (%) in the 10 mM $CaCl_2$ extracts. As soil fertility increased, the majority of the increase in the $CaCl_2$-TP occurred as $CaCl_2$-P. At low fertility levels, DUP accounted for a substantial proportion of $CaCl_2$-TP. In the Flaxley soils this was >50%, whereas in the Camden soils it was ~50%. However, at high soil fertility levels, $CaCl_2$-P became the dominant form of $CaCl_2$-TP. The effect of fertility on the composition of P in the calcium chloride extracts was much more pronounced for the Flaxley soil than the Camden soil (Figure 7-8). Nevertheless, for both low to moderate fertility soils at both sites, DUP is a significant proportion of soluble P. A similar trend in the composition of soil extracts following application of a wide range of P rates was observed by McDowell and Sharpley (McDowell and Sharpley 2001b). They reported a large decrease in $CaCl_2$-UP (%) in soil extracts as P was added to soils, although they did not attempt to specifically relate this to forms of P in soil.

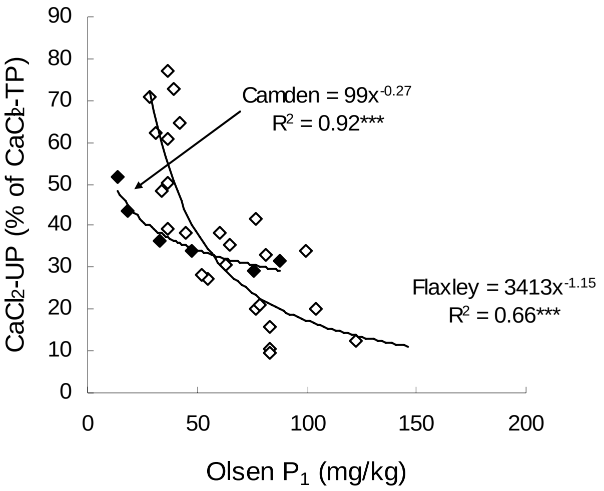

Figure 7-8. Relationship between Olsen P_1 and the proportion of $CaCl_2$ extractable P present as $CaCl_2$-UP (un-reactive P) of the 0-0.01 m increments of the Flaxley (◊) and Camden (♦) soils.

7.3.5 Effective depth of interaction

The average estimated EDI was 2.5, 1.3, and 1.2 mm for the Flaxley runoff trays, Flaxley field simulations and Camden runoff plots respectively. These values are comparable to other values reported in the literature. For example Sharpley (1985) reported a wide range of EDI values, from approximately 1.5 to 13 mm. When Sharpley used screens to simulate plant cover (and its effect of reducing raindrop impact and disturbance at the soil surface) the values of EDI decreased to below 1 mm. The larger values calculated here reflect the lack of surface disturbance and mixing compared to the bare surfaces traditionally observed when examining the EDI (Ahuja *et al.* 1981; Sharpley 1985). This lack of mixing means that a greater EDI is required to generate a given runoff P concentration. The small EDI values reported here highlight the importance to runoff P of soil P in the immediate topsoil (<0.01 m) under pastures and indicate that reducing P in this zone is likely to be an important step in reducing runoff P concentrations.

7.3.6 The physical and chemical distribution of P in runoff: the effect of soil P status.

Runoff samples from soils encompassing a wide range of soil P status from both the Flaxley and Camden sites were examined. The runoff samples from Flaxley were those generated from runoff trays whereas those from the Camden site were from field runoff plots. The Olsen

P_1 in the Flaxley runoff trays ranged from 35-156 mg/kg and $CaCl_2$-P_1 from 2.56-19.49 mg/kg. Olsen P_1 at the Camden site ranged from 14-99 mg/kg and $CaCl_2$-P_1 from 3.19 to 14.67 mg/kg. For soils from both sites, there was a significant relationship ($P<0.001$) between Olsen P and runoff DRP (Figure 7-9). For the Flaxley site, at high Olsen P concentrations, runoff DRP increased more rapidly per unit of Olsen P than at low Olsen P concentrations whereas the relationship between soil P and runoff P was linear at Camden. There was also a negative relationship ($P<0.001$) between DUP in runoff (% of TDP) and Olsen P for both sites (Figure 7-9), Dissolved un-reactive P (%) decreasing with increasing Olsen P. There was also a significant positive linear relationship ($P<0.01$; $r^2 = 0.50$) between soil P_o (%) and runoff DUP (%).

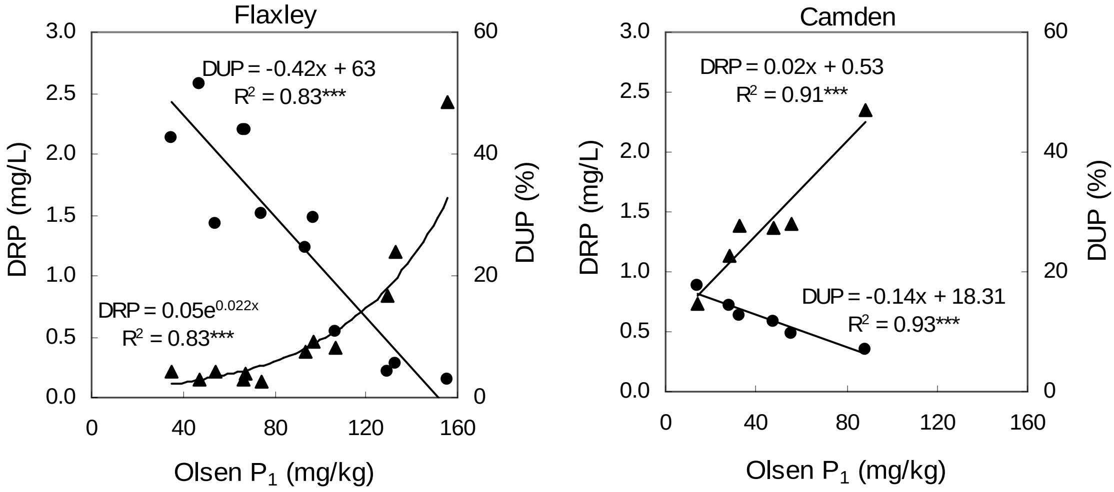

Figure 7-9. Relationship between Olsen P (0-0.01 m) and P concentrations and form (DUP% of TDP) in runoff from Flaxley (left) and Camden (right). Dissolved reactive P (mg/L DRP - ▲) and dissolved un-reactive phosphorus (% DUP - ●). Note that the scales are the same for both sites.

There is clearly a large difference in the relationships between Olsen P and DRP for the soils from the two sites. This can be attributed to a number of factors. The first is that the conditions under which runoff was generated were quite different. It has already been demonstrated that small-scale rainfall simulations at high rainfall intensity can under-estimate runoff P concentrations (Chapter 4), such that the Flaxley runoff P concentrations could reasonably be expected to be under-estimates. Data from Chapters 4 & 5 indicate that this underestimate is about 50%. Another likely factor is that inputs of P have been higher more recently at the Camden site and there has been relatively little time for P and soil to equilibrate. This is reflected in the plots of total P_1 vs $CaCl_2$-P_1 (Figure 7-1) and Olsen P_1 vs $CaCl_2$-P_1 (Figure 7-5) that show that there are much higher concentrations of Olsen and

$CaCl_2$-RP for given total soil P levels at Camden than Flaxley. However, it should be noted that the rate of this reaction of P with soil is rapid in the first month or so (Nash *et al.* 2005) and continues more slowly after this time (Bramley *et al.* 1992; Burkitt *et al.* 2002). The data presented in Chapter 4 also support this continuing slow decline in fertiliser effect.

At all soil fertility levels including the lowest for both sites, runoff DRP was above typical water quality guidelines (i.e. $P<0.05$ mg/L). As previously mentioned, (at least for the Flaxley soil), the concentrations measured under rainfall simulation are likely to be relatively low compared to those that may occur in overland flow from natural rainfall at the hillslope scale. Therefore, the contribution to P exports from low P soils should not be ignored, although high P soils should be a priority for remedial management. Importantly, these low P soils include those in the agronomically optimal Olsen P_{10} range of 18-22 mg/kg.

7.3.7 Ultrafiltration of runoff samples and the importance of colloidal P[3]

The runoff samples selected for ultra-filtration for both sites encompassed a wide range of P and DOC concentrations (Table 7-3). The results of ultrafiltration of these samples are shown in Figure 7-10 (Flaxley) and Figure 7-11 (Camden).

Table 7-3. Phosphorus and carbon contents of samples subject to ultrafiltration.

Flaxley			Camden		
	TDP	DOC		TDP	DOC
ID	mg/L		ID	mg/L	
T4	0.24	21	KA5	0.82	26
T6	0.33	22	KA4	1.03	22
T13	0.63	18	KA6	1.46	20
T18	1.28	21	KA2	1.54	24
T19	2.53	26	KA3	2.53	22

The majority of each of the analytes that were in the <1 µm fraction, were also in the <10 kDa fraction. Figure 7-12 shows the proportions of each of the analytes that are in each of the size ranges. Of the TP, RP, UP and OC that was in the <1 µm fraction, on average, 94, 95, 90 and

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[3] The terminology for describing analytes is altered here as all samples are regarded as dissolved. For instance RP is used to refer to reactive P rather than DRP, the size fraction being specified where necessary.

71% respectively passed through the 10 kDa filter for the Flaxley samples and 92, 95, 53 and 64% for the Camden samples. Only in the case of OC (for both soils) and UP (for Camden) was there any substantial reduction in concentration upon filtration of samples through the 10 kDa filter (i.e. these were in the 100 to 10 kDa fraction). Material that passes through the 10 kDa filter can be classed as non-colloidal (Thurman 1985) (i.e. it can effectively be classed as dissolved - although the classification of the lower size limits are also somewhat arbitrary).

The high proportion of DRP in the <10 kDa fraction is consistent with DRP being an estimate of orthophosphate. In the Camden samples, there is some DUP in the larger fractions but no DOC suggesting that this DUP is inorganic rather than organic in this case. The similarity in the distribution of DUP at Flaxley , particularly in the two smaller size fractions suggest that the DUP is largely organic P. Dissolved un-reactive P is routinely used as an estimate of organic P in solution [e.g. Haygarth *et al*. (1998); Heathwaite *et al*. (2005)] although it may also include polyphosphates and some colloidal P (Hens and Merckx 2002). There was a strong similarity in the proportions of DUP, DOC and Fe in the 100-10 kDa fraction of the Camden soil. Dolfing *et al*. (1999) and Nelson *et al*. (1996) suggested that these similarities in proportion are indicative of associations of Fe, P and C in the runoff. In contrast, there was a lack of concordance of the Fe with P and C in the 100-10 and <10 kDa fractions for the Flaxley soil, suggesting little association between Fe and P or C. The UP in the <10 kDa fraction of the samples would seem most likely to be organic P, as evidenced by its concordance with OC removal, and the lack of iron in this fraction. Similar patterns of P, Fe and C distribution between size fractions were observed in runoff from a sandy soil by Nelson *et al*. (1996).

The carbon that passed through the 10 kDa filter is likely to be in the form of low molecular weight compounds such as fulvic acids or organic P compounds. Fulvic acids are a common component of dissolved soil organic carbon (Tan 2003). More detailed investigation of these sub-colloidal forms of P and the role of organic P cycling in P exports is warranted, particularly in relation to low to moderately fertile soils that are likely to constitute a large proportion of dairying areas.

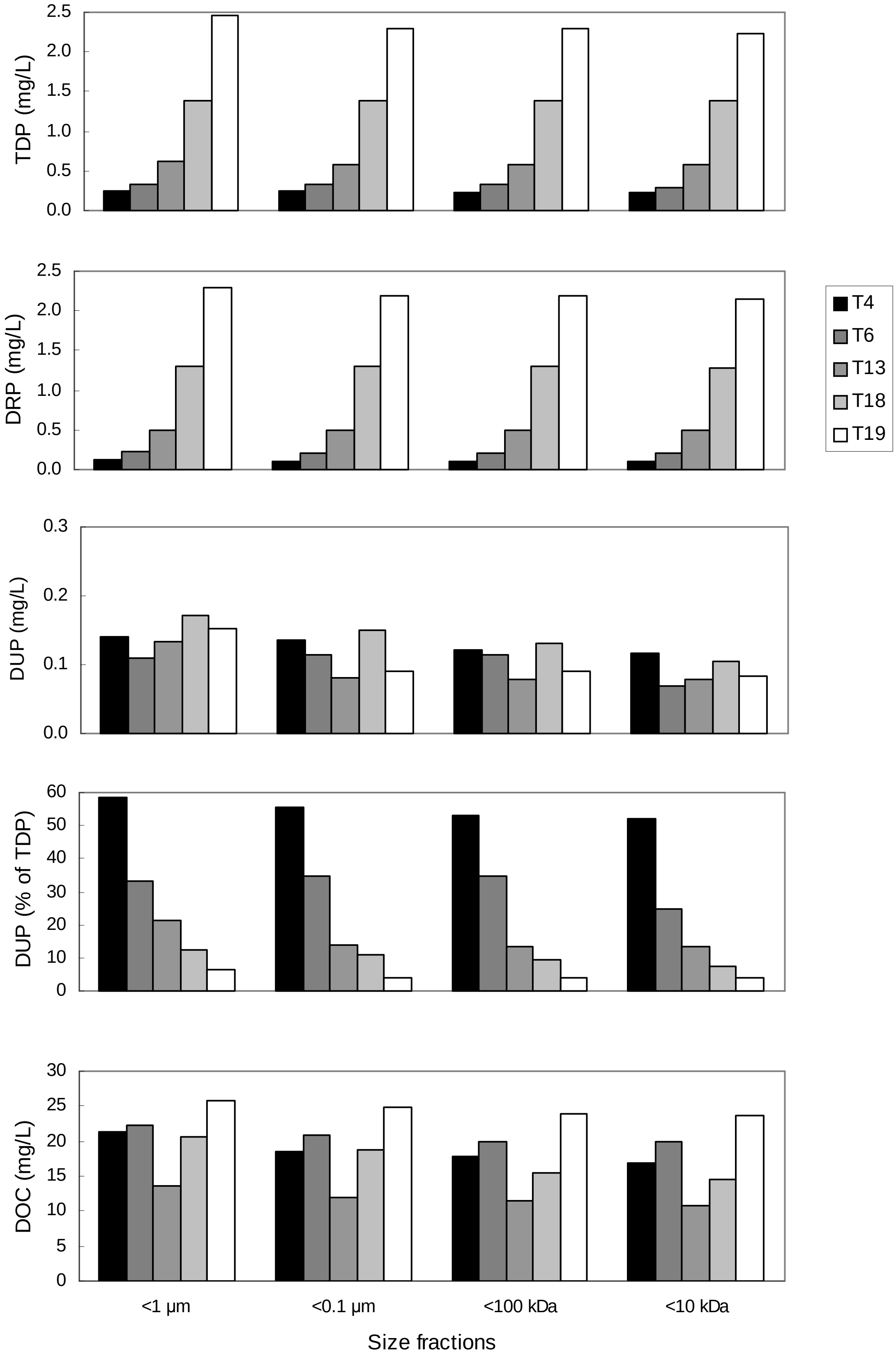

Figure 7-10. Phosphorus concentrations and forms in various size fractions of the Flaxley runoff samples. The legend refers to the sample identifier in Table 7-3.

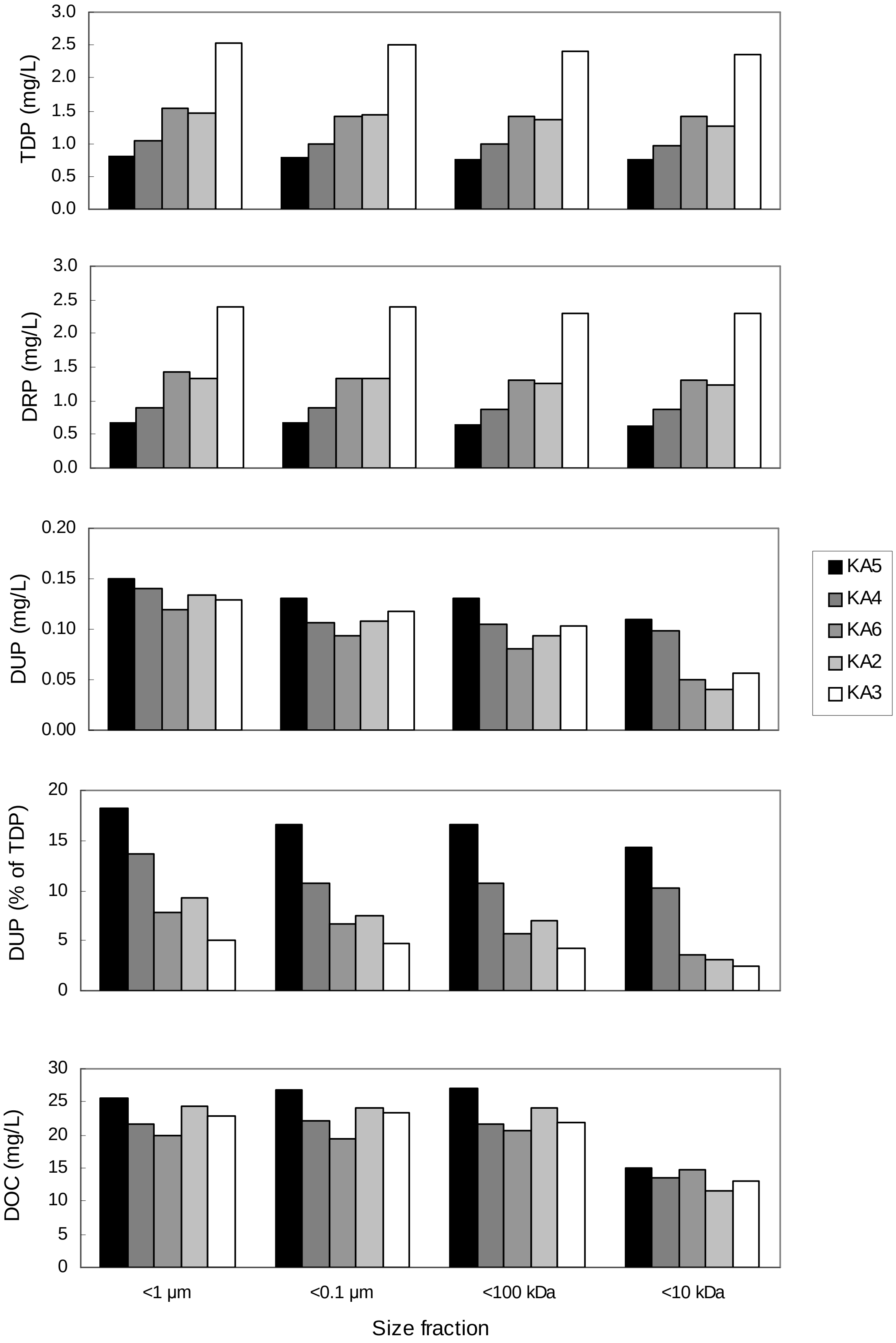

Figure 7-11. Phosphorus concentrations and forms in various size fractions of the Camden runoff samples. The legend refers to the sample identifier in Table 7-3.

Colloids have been shown to play an important role in the transport of P in surface runoff by other authors (Haygarth *et al.* 1997; Turner *et al.* 2004; Heathwaite *et al.* 2005). However, in the case of the Flaxley and Camden soils, the majority of the P and OC in runoff that passed through a 1 µm filter, also passed through a 10 kDa filter and can therefore be classified as ‘sub-colloidal’ P (Figure 7-12). This confirms the hypothesis that dissolution (i.e. mobilisation of dissolved forms of P) is indeed the dominant mechanism of P mobilisation from soil into runoff from under intensively managed pastures. This confirms the assertion that in intensive pasture systems, the aim of remedial strategies should be to reduce the P available for mobilisation (Nash *et al.* 2005), rather than strategies to trap P once it is mobilised (e.g. buffer or filter strips).

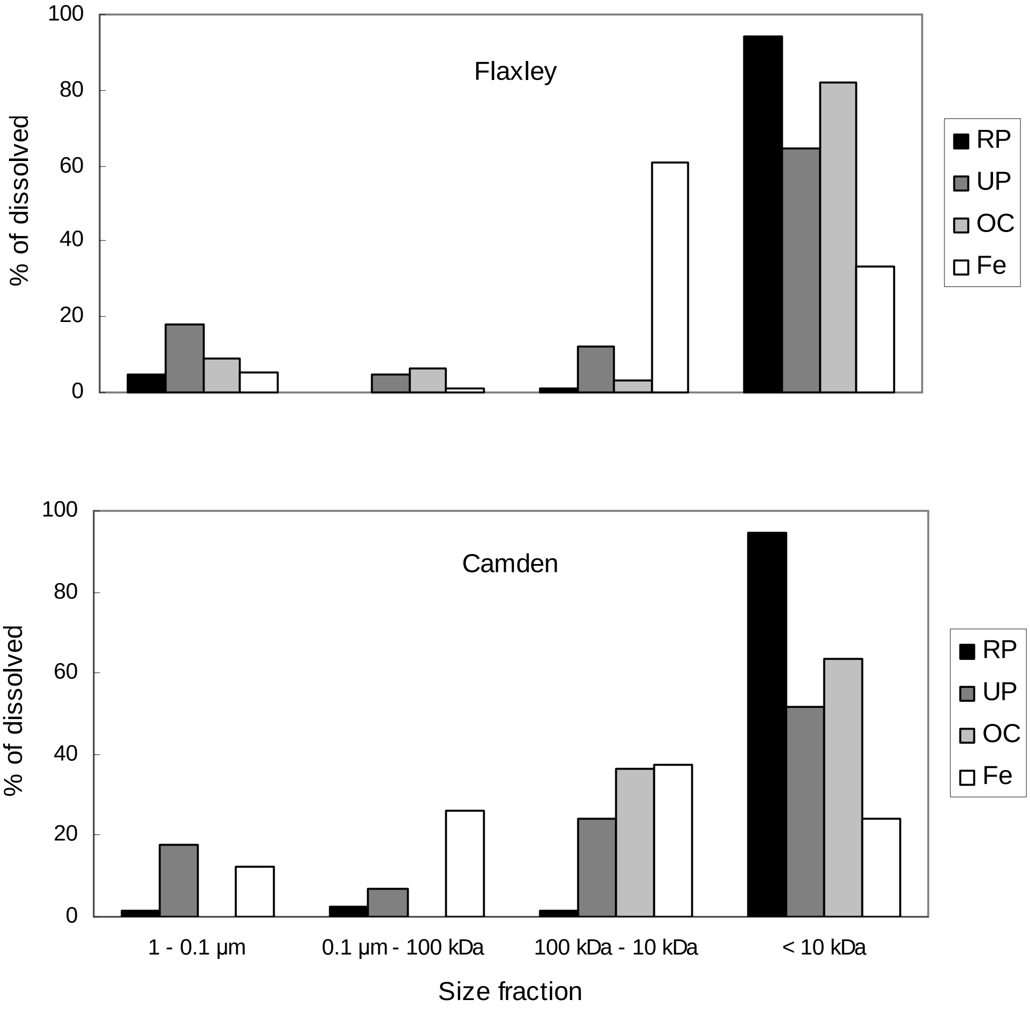

Figure 7-12. Proportion of analytes in various size ranges (average of 5 samples at each site) in runoff samples from Flaxley and Camden. Standard error bars are not shown as they were <1% for all analytes and all size ranges.

7.4 Conclusions

The proportions of P_o and P_i in the topsoil under intensive pastures vary widely. These proportions are strongly related to the soil P status, low P soils containing predominantly P_o, whereas high P soils contain predominantly P_i. The change in the forms of soil P altered the relative importance of mobilisation processes as evidenced by the change in forms of P mobilised as soil P status changed. Dissolved un-reactive P (DUP) can be an important form of P in runoff. DUP was the dominant form (>50%) of dissolved P in runoff from low P soils at Flaxley, whereas dissolved un-reactive P accounted for <20% of the dissolved P in high P soils. However, at Camden, DUP was relatively unimportant as a component of runoff P, irrespective of soil P status. The study indicates that colloidal forms of P and C in runoff from soils under pasture are minimal. There was little DRP or DUP in the colloidal fraction of any of the runoff samples examined, with the majority of P (and DOC) being in sub-colloidal fractions. Therefore, from soils under pasture, dissolution of P (whether DRP or DUP) was most likely the dominant process of P mobilisation.

Given that dissolution of P is the dominant process of mobilisation (viz. particle detachment or erosion), that runoff P concentrations are strongly related to soil P concentration, the pronounced stratification of soil P (measured as $CaCl_2$-P), and that the top several mm of the soil profile are likely to be the predominant source of the P mobilised, it is proposed that de-stratification (i.e. mixing of the soil by cultivation for example) may substantially reduce runoff P concentrations. The degree of $CaCl_2$-P stratification is strongly related to soil P fertility. Consequently, the potential benefits of de-stratification are likely to be related to soil P fertility, catchment hydrology and the interaction between these. This combined with the curvilinear (exponential) relationship between soil P and runoff P means that de-stratification is likely to result in relatively large decreases in runoff P concentration where runoff occurs on high P soils compared to that occurring on low P soils. As these high P soils are a priority for remedial action (to reduce concentrations of P in runoff originating from them), de-stratification may be a useful strategy on such soils. The potential benefits of de-stratification are investigated further in Chapter 9.

Future studies of P mobilisation should give consideration to the effect of changing fertility on the forms of P mobilised. Further research is also needed to investigate under what conditions organic P is an important component in runoff.

Chapter 8 Examination of soil P forms using solid-state ^{31}P NMR

8.1 INTRODUCTION

It was shown in Chapter 7 that the proportions of organic and inorganic forms of phosphorus (P) varied greatly in the soils examined. These forms of P play a variable role in soil P transformations, pasture production and the mobilisation of P in surface runoff. Numerous techniques have been employed to study these forms and their cycling in soil. Such techniques include wet chemical analysis, sequential fractionation, isotopic labelling, and solid-state and solution ^{31}P NMR spectroscopy. Phosphorus-31 NMR has been successfully employed in the identification of a wide range of organic and inorganic P compounds in solution. However, there has been relatively little use of solid-state ^{31}P NMR to study soil despite the potential advantages of being able to examine P compounds in-situ without prior manipulation.

Nuclear magnetic resonance (NMR) spectroscopy is an ideal analytical technique for differentiating and quantifying elements in different chemical environments. It is particularly well suited for P characterisation because the ^{31}P nucleus is NMR-sensitive (more so than ^{13}C or ^{15}N), has 100% natural isotopic abundance, and has a nuclear spin of ½, that ensures relatively easy detection and spectral interpretation. Two different modes of ^{31}P NMR spectroscopy – solution and solid-state – have been applied to P characterisation in soils and related materials. Each mode has inherent advantages and disadvantages.

Studies of soil P using NMR have mainly utilised solution NMR. Solution NMR spectra provide much better resolution than solid-state NMR spectra, enabling clearer differentiation of chemically similar species. Solution ^{31}P NMR spectroscopy has been widely used to differentiate and quantify classes of organic P molecules found in soils [see, for example, (Cade Menun and Preston 1996; Mahieu *et al.* 2000; Makarov *et al.* 2004; Turner 2004; Turner and Richardson 2004)]. Impressive resolution is possible using this technique, for example, a range of chemically similar inositol phosphates can be differentiated (Turner and Richardson 2004). However, in most studies, differentiation of only broad classes of organic

P compounds, such as orthophosphate monoesters and diesters, phospholipids and phosphonates, has been achieved (Cade Menun and Preston 1996; Mahieu *et al.* 2000; Makarov *et al.* 2004). The obvious drawback to solution NMR is that only soluble species can be detected. These soluble species represent a highly variable proportion of total soil P, e.g. 16.1 – 99.6% and are typically a mixture of organic and inorganic species (Cade Menun *et al.* 2000). Furthermore, the high pH required to solubilise most of the organic matter may cause hydrolysis of sensitive phosphate esters (Makarov *et al.* 2002; Turner *et al.* 2003a).

The obvious attraction of solid-state NMR spectroscopy for the analysis of soil is that soil is (for the most part) a solid and a solid-state technique avoids the problems inherent with insoluble species and aggressive extractants. Solid-state ^{31}P NMR spectroscopy has found application mainly in the characterisation of inorganic P in soil (Hinedi *et al.* 1989; Frossard *et al.* 1994; McDowell *et al.* 2002; McDowell *et al.* 2003a), although some researchers have used it to characterise organic P (Newman and Condron 1995; Condron *et al.* 1997). The main disadvantage of solid-state ^{31}P analysis is that the spectra lack the resolution of solution spectra (Shand *et al.* 1999). Furthermore, paramagnetic species, especially Fe, can limit the quantitative potential of solid-state NMR analysis of soils. This limitation has been studied in depth for solid-state ^{13}C NMR analysis of soils [see, for example, (Kinchesh *et al.* 1995; Dai and Johnson 1999; Smernik and Oades 2000b; a)]. Although the potential for paramagnetic species to compromise quantitation in solid-state ^{31}P NMR analyses has been recognised (Hinedi *et al.* 1989; Frossard *et al.* 1994; Condron *et al.* 1997; McDowell *et al.* 2002; McDowell *et al.* 2003a; Hunger *et al.* 2004), the issue of quantitation has not been considered in depth in previous ^{31}P NMR studies. Although spin counting has been widely used in solid-state ^{13}C (Smernik and Oades 2000b; a) and ^{15}N (Smernik and Baldock 2005) to quantify observability, it has not previously been applied in ^{31}P NMR analyses of soil

In this chapter, chemical methods and solid-state ^{31}P NMR analyses are used to examine P forms (both organic and inorganic) in a sub-set of the soils sampled from the sub-catchment being examined in this study. The eight soils examined had a wide range of P contents, but otherwise similar chemistry. The aim of this Chapter was to:

- ***Determine the forms of P in the soils identifiable in the cross polarisation (CP) and direct polarisation (DP) ^{31}P NMR spectra using a combination of NMR spectroscopy and wet chemistry, and investigate the observability of these P forms using spin counting.***

8.2 MATERIALS AND METHODS

8.2.1 Site description and soil sampling

The soils examined were from the Flaxley site and were a sub-set of those used in Chapters 6 & 7. As discussed in the previous Chapter, the surface horizon has the greatest influence on the processes of P mobilisation in surface runoff, hence the samples examined were the 0-0.01 m increments.

The soil samples for examination were from the upper, mid and lower slope positions of the landscape (designated U, M and L respectively). At each of these positions in the landscape, samples of low, medium and high P fertility were selected (designated L, M and H respectively), except for the upper part of the landscape where no low-fertility, surface horizon was available. Samples are identified by their slope position followed by their fertility level (e.g. U-H refers to the soil from the upper part of the landscape with a high P status). Sampling was undertaken at the end of summer when there was minimal pasture growth and no pasture mat, precluding the possibility that the soil samples were contaminated with large amounts of un-decomposed plant material. Samples were dried and passed through a 2 mm sieve. A sub-sample of each of the soils was ground to pass a 200 μm sieve for use in all analyses except for pH, EC and Olsen P, for which the < 2 mm fraction was used.

8.2.2 Soil analysis

Soils were digested in a nitric-perchloric acid mixture (6:1) at 160°C (Olsen and Sommers 1982) and concentrations of elements, including P, measured by ICPAES. The organic P content of the soils was determined using two different methods, the ignition method of Saunders and Williams (1955) and a sequential extraction using concentrated H_2SO_4 and NaOH (Bowman and Moir 1993). The ignition method involved extracting both a sample of soil ashed at 500°C and an un-ashed sample in 0.5M H_2SO_4, the difference being defined as organic P. As is the case for most chemical extraction methods, the ignition method of Saunders and Williams is subject to a number of possible sources of error. Consequently, organic P was also measured by the method of Bowman (1993) by extracting the soil with concentrated H_2SO_4 followed by 0.5 M NaOH.

Olsen P, organic carbon, pH and EC were determined as outlined in Chapter 3 (General Materials and Methods). Oxalate extractable aluminium (Al), iron (Fe) and P were separated by shaking 1 g of soil in 100 mL acid ammonium oxalate for 4 hr in the dark (Ross and Wang 1993) and measuring the concentrations in the filtered supernatant by ICPAES. The degree of P saturation was calculated as $P_{ox}/(Fe_{ox}+Al_{ox})$ (Hooda *et al.* 2000). Organically-complexed Fe was determined by extraction with Na-pyrophosphate (Ross and Wang 1993). This involved shaking 0.3 g of soil with 30 mL of 0.1 M Na-pyrophosphate for 16 hr, centrifuging (15 000 g) and analysis of the supernatant by ICPAES.

The M-H soil was subjected to more detailed analysis to assist in the interpretation of spectrum features. NaOH-EDTA extraction was undertaken using the method of Cade-Menum and Preston (1996). Five g of soil was shaken with 100 mL of 0.25 M NaOH-0.05 M Na_2EDTA for 16 hr, centrifuged at 1500*g*, and the supernatant filtered, frozen (–20^{o}C), and then freeze-dried. The soil residue was dried at 40^{o}C, ground and passed through a 2 mm sieve. Hydro-fluoric (HF) acid was used to isolate organic matter by removing inorganic soil components (Skjemstad *et al.* 1995). Briefly, 2.5 g of soil was shaken with 50 mL of 2% hydrofluoric acid solution for periods of 1 h (five times), 16 h (three times) and 64 h (once). Between treatments, samples were centrifuged, the supernatant discarded and replaced with fresh 2% hydrofluoric acid solution. Following the final treatment, the residue was rinsed three times with de-ionised water, and then freeze-dried.

8.2.3 NMR Spectroscopy

The NMR spectroscopy component of this research was undertaken with advice provided by Dr Ron Smernik of the University of Adelaide. Solid-state ^{31}P NMR spectra were acquired with magic angle spinning (MAS) and high-power ^{1}H decoupling on a Varian Unity INOVA 400 spectrometer with a Doty Scientific supersonic MAS probe at a ^{31}P frequency of 161.9 MHz. Samples were packed into 7 mm diameter cylindrical zirconia rotors with Kel-F end-caps and spun at 5 kHz at the magic angle. Free induction decays were acquired with a sweep width of 50 kHz. A total of 1216 data points was collected for all spectra, representing an acquisition time of 12 millisec. All spectra were zero-filled to 131072 data points and processed with a 100-Hz Lorentzian line broadening and a 0.010-sec Gaussian broadening.

Chemical shifts were externally referenced to ammonium dihydrogen phosphate ($NH_4H_2PO_4$) at 0.72 ppm (Frossard *et al.* 2002).

Phosphorus-31 CP NMR spectra of the whole soils and soil fractions represent the accumulation of 20000 scans, except for the HF-treated residue of soil M-H (10000 scans), and were acquired using a 1 millisec contact time and a 1 sec recycle delay. Preliminary variable contact time experiments (data not shown) on soil L-H showed that signal intensity was maximised at a contact time of 1 millisec. Preliminary inversion-recovery experiments (data not shown) on soil L-H showed that this recycle delay was sufficient to avoid saturation. The total acquisition time for ^{31}P CP NMR spectra was around 6 hr (3 hr for the HF-treated residue of soil M-H).

Phosphorus-31 DP NMR spectra of the whole soils and soil fractions represent the accumulation of 2700-5000 scans and were acquired using a 20 sec recycle delay. The total acquisition time for ^{31}P DP NMR spectra was around 15-28 hr. The ^{31}P DP NMR spectra were corrected for a broad background signal by subtracting the ^{31}P DP NMR spectrum acquired for an empty rotor (there was no such background signal for ^{31}P CP NMR spectra). The effect of the recycle delay on signal intensity for ^{31}P DP NMR spectra of soil L-H and fractions of soil M-H is shown in Figure 8-1. In all cases, the signal intensity at a recycle delay of 20 sec was 87-97% of the signal intensity at a recycle delay of 100 sec. Thus, while a recycle delay of 20 sec is insufficient to completely avoid signal loss through saturation for these whole soils and soil fractions, saturation is unlikely to cause signal loss of more than 15%. Longer recycle delays were considered impractical as they would require either very long run times, or the acquisition of fewer scans that would adversely affect signal-to-noise ratios. Previously published ^{31}P DP NMR spectra of soils and related materials have employed recycle delays of 0.1-20 sec (Hinedi *et al.* 1989), 0.5 sec (McDowell *et al.* 2002; McDowell *et al.* 2003a), 20 sec (Frossard *et al.* 1994); (Frossard *et al.* 2002), and 60 sec (Hunger *et al.* 2004).

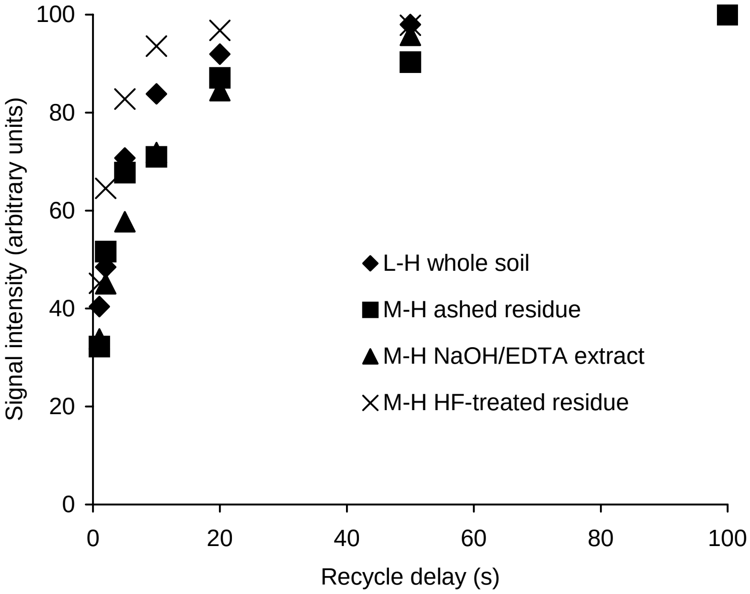

Figure 8-1. Effect of recycle delay on ^{31}P DP NMR signal intensity for soil L-H, the ashed residue of soil M-H, the NaOH-EDTA extract of soil M-H and the HF-treated residue of soil M-H.

Phosphorus-31 spin counting experiments were performed using a modification of the ^{13}C spin counting method of Smernik and Oades (2000b). Ammonium dihydrogen phosphate was used as an external intensity standard (i.e. the $NH_4H_2PO_4$ spectrum was acquired separately to those of the samples). The $NH_4H_2PO_4$ ^{31}P CP NMR spectrum was acquired in 16 scans, using a 1 millisec contact time and a 10 sec recycle delay. Preliminary variable contact time experiments showed that signal build-up was essentially complete by 1 millisec. Preliminary experiments in which the recycle delays were varied between 1 sec and 100 sec showed that this recycle delay was sufficient to avoid saturation. The $NH_4H_2PO_4$ ^{31}P DP NMR spectrum was acquired in one scan after equilibration for 1000 sec (16.7 min). Preliminary experiments in which the recycle delay was varied between 1 sec and 5000 sec showed that a 1000 sec equilibration was required to avoid saturation. For CP spin counting experiments, differences in spin dynamics between the sample and the $NH_4H_2PO_4$ standard were accounted for using the method of Smernik and Oades (2000b), except that a variable spin lock rather than a variable contact time experiment was used to determine $T_{1\rho}$H (Smernik *et al.* 2002). The $T_{1\rho}$H relaxation rate for $NH_4H_2PO_4$ was found to be 120 millisec. The $T_{1\rho}$H relaxation rate for soil L-H was found to be 3.33 millisec; this value was used in the $T_{1\rho}$H correction for all of the other soils and soil fractions. Uncertainty in the precision of P_{obs} values is estimated to be ±10% CP and ±15% in DP (Smernik and Oades 2000b).

8.3 RESULTS AND DISCUSSION

8.3.1 Wet chemical P analyses

The soils were slightly acidic, non-saline and had a wide range of Olsen P contents (Table 8-1), reflecting the highly varied nature of their management in the past. The Olsen P concentrations (0-0.01 m) ranged from 29 to in excess of 100 mg/kg. The corresponding 0-0.10 m Olsen P concentrations (data not shown) ranged from approximately 20 to 70 mg/kg. These concentrations are typical of those found in soils used for intensive pasture production in south-east Australia and are similar to or above the agronomic optimum Olsen P value (0-0.10 m) of 18-22 mg/kg (Gourley 2001). The organic carbon content of the soils was high, a consequence of both the highly productive nature of these soils and the shallow sampling depth.

Table 8-1. Summary of key soil sample properties

Soil	pH[A]	EC[A] µS/cm	OC[B] %	Olsen P mg/kg	DPS[C] %	Fe_{tot}[D,E] %	Fe_{org}[E, F] %
L-L	6.66	155	4.4	44	8	1.46	0.20
L-M	6.96	440	6	83	12	1.64	0.17
L-H	6.90	380	7.2	146	19	1.4	0.27
M-L	5.99	107	5.2	29	8	0.98	0.40
M-M	6.42	93	5.6	65	14	1.61	0.24
M-H	6.60	83	5.5	133	27	1.04	0.18
U-M	6.58	280	6.5	99	17	0.92	0.18
U-H	6.53	440	7.3	143	27	0.86	0.25

[A] 1:5 soil:water extract

[B] Determined by chromic acid digestion and colorimetric titration with $FeSO_4$

[C] Degree of phosphorus saturation: $[P_{ox}/(Fe_{ox}+Al_{ox})]\times100$ (Hooda *et al.* 2000)

[D] Determined by digestion with HNO_3-$HClO_4$ at 160°C

[E] Expressed as percentage of soil mass

[F] Organically complexed Fe determined by extraction with Na-pyrophosphate (Ross and Wang 1993)

Total and organic P contents varied widely (Table 8-2). Total P contents ranged from 702 to 2166 mg/kg. Total P content determined by 0.5 M H_2SO_4 extraction of ignited soils were very similar to total P contents derived by HNO_3-$HClO_3$ digestion. On average, total P estimated by the ignition method was 4% higher than that of the HNO_3-$HClO_4$ digestion. Organic P estimated by the ignition procedure was on average 8% higher than that estimated by the H_2SO_4-NaOH extraction. There was a significant relationship ($P<0.01$) between the total P content and the percentage of P present as organic P determined by both the ignition method and sequential extraction methods. In soil M-L, which has the lowest total P content, organic P (estimated by ignition) accounted for 46% of total P. In soil L-H which has the highest total P content, organic P (estimated by ignition) accounted for 28% of total P. The corresponding percentage of organic P estimated by the H_2SO_4-NaOH extraction was 48 and 25% for the M-L and L-H soils respectively. The low P soils have approximately equal amounts of organic and inorganic P. In contrast, inorganic P accounts for 70-74 % of the P in the high P soils.

Table 8-2. Summary of soil P fractions (figures in brackets are % of total).

Soil	P_{tot}^{A}	P_{tot}^{B}	P_{org}^{C}	P_{org}^{D}
	mg/kg			
L-L	942	1052	438 (42)	348 (37)
L-M	1707	1692	630 (37)	695 (41)
L-H	2166	2046	573 (28)	545 (25)
M-L	702	930	428 (46)	338 (48)
M-M	1137	1196	501 (42)	418 (37)
M-H	2098	2146	641 (30)	590 (28)
U-M	1331	1442	552 (38)	449 (34)
U-H	2100	2150	584 (27)	678 (33)

[A] Determined by digestion with HNO_3-$HClO_4$ at 160°C

[B] Determined by extraction of ignited soil with 0.5M H_2SO_4

[C] Organic P as percentage of total P determined by extraction of ignited soil with 0.5M H_2SO_4

[D] Organic P determined by sequential H_2SO_4 and NaOH extraction as % of total P determined by digestion with HNO_3-$HClO_4$ at 160°C (Bowman 1989).

8.3.2 Comparison of ^{31}P CP and DP NMR spectra for soil M-H

The ^{31}P CP and DP NMR spectra for soil M-H are compared in Figure 8-2. As is standard practice in the presentation of NMR spectra, the ^{31}P CP and DP spectra of soil M-H shown in Figure 8-2 have been scaled to maximise clarity such that the highest peak of the central resonance in each spectrum is the same height. The vertical scales in Figure 8-2 are thus unrelated. The CP spectrum of the whole soil consists of a series of broad resonances. The resonance centered at –1.6 ppm is the central resonance, whereas the other resonances are artifacts called spinning side-bands (SSBs) – denoted by the asterisks. These SSBs appear because the rate of magic angle spinning was insufficient to overcome the broadening caused by chemical shift anisotropy (CSA).

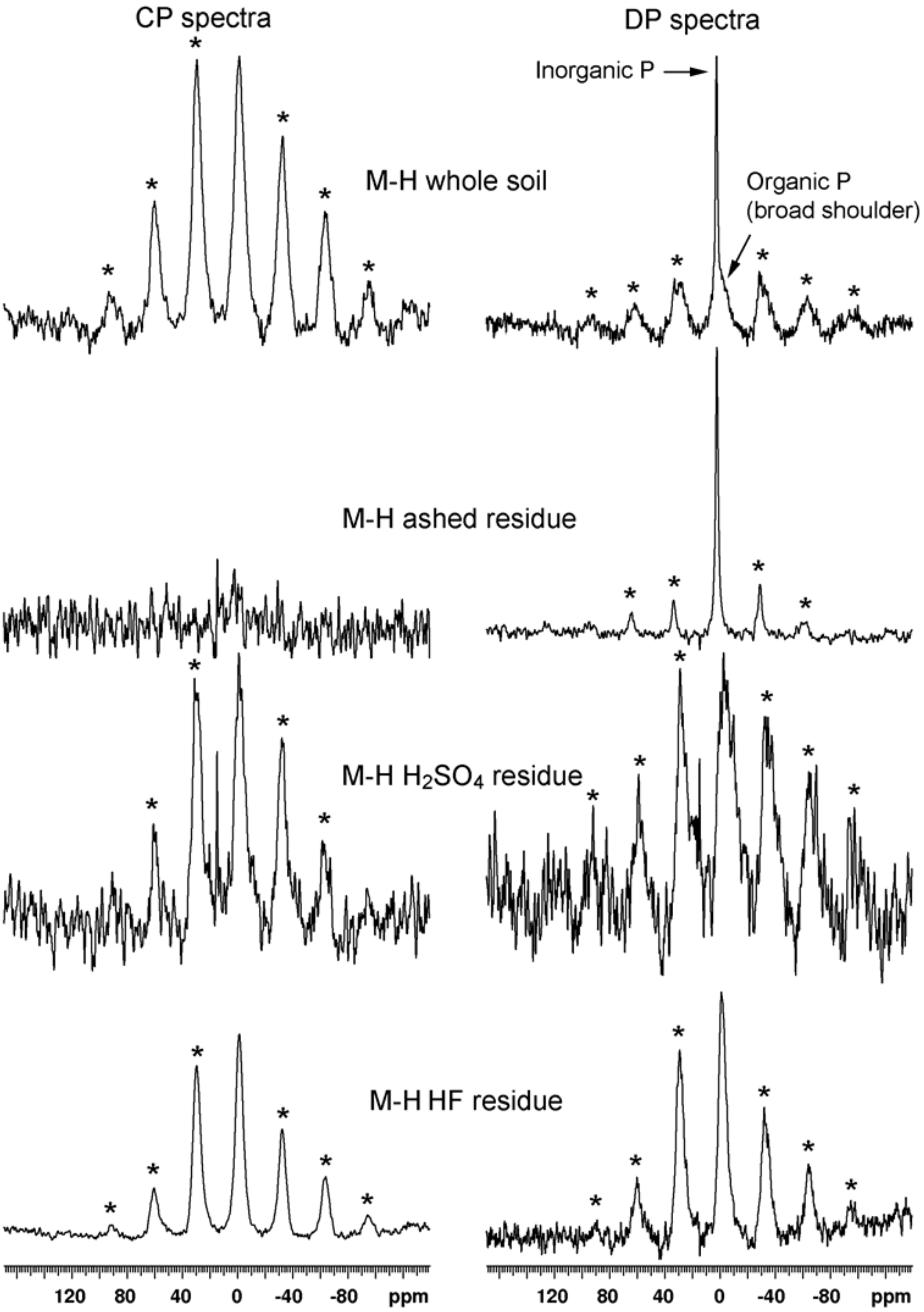

Figure 8-2. ^{31}P CP and DP NMR spectra of soil M-H, and H_2SO_4 treated, ashed and HF treated residues of soil M-H. Spinning side-bands are marked with an asterisk (*).

In the solid-state, chemical shift is a function of the orientation of the observed atom and its chemical environment to the applied magnetic field (i.e. it is anisotropic). Rapid spinning at the magic angle removes the CSA broadening, collapsing the signal into a much sharper resonance at the average (isotropic) chemical shift. If the spinning rate is less than the size of the CSA, then multiple resonances are produced – a central resonance at the isotropic chemical shift, and SSBs at integer multiples of the spinning rate. Under the conditions the spectra were run (9.4 T field, 5 kHz spinning rate) SSBs appear every 31 ppm in ^{31}P spectra. The envelope of SSBs approximates the shape and extent of the anisotropic (non-spinning) resonance. Therefore, the ^{31}P nuclei that give rise to the CP spectrum in Figure 8-2 have a CSA of around 250 ppm. Previously reported solid-state ^{31}P NMR spectra of soils and sewage sludge have exhibited CSA of similar magnitude (Hinedi *et al.* 1989; Frossard *et al.* 1994; Condron *et al.* 1997; McDowell *et al.* 2003a).

The central resonance (and also each SSB) of the ^{31}P CP spectrum of the whole soil is broad and featureless – no differentiation of different P types is apparent in this spectrum. The central resonance is 8.5 ppm wide at half-height, and around 20 ppm wide at its base.
In contrast, the ^{31}P DP NMR spectrum of whole soil M-H (Figure 8-2) contains both sharp and broad resonances. The broad resonances appear to correspond with those detected by CP, both in terms of the broad lineshape and the extent and shape of the SSBs. The central peak of the sharp resonance is centered at 2.7 ppm, 4.3 ppm downfield of the broad resonance detected by CP. This resonance has a width at half-height of approximately 1.8 ppm (i.e. it is nearly five times narrower than the resonances detected by CP). Spinning side-bands for the sharp peak of the central resonance are less prominent, indicating that the P species that give rise to it have much lower chemical shift anisotropy.

It would thus appear that two different types of P are detected in the ^{31}P DP NMR spectrum, and that only one of these two types of P is detected by CP. In order to assign these two distinct P types, solid-state ^{31}P NMR analysis was applied to soil fractions generated during the wet chemical determination of organic and inorganic P and the residue after HF treatment of soil M-H.

The procedure of Saunders and Williams (1955) used to determine the organic P content involved first ashing the soil at 500°C to convert all P to inorganic forms. Because ashing removes all organic carbon, the residual P must be inorganic. The ^{31}P DP NMR spectrum of soil M-H after ashing (but before H_2SO_4 extraction) contains only the sharp resonances with small SSBs (Figure 8-2). No signal could be detected in the ^{31}P CP NMR spectrum of soil M-H after ashing. Therefore, this sharp resonance present in the ^{31}P DP spectra of both the ashed residue and the whole soil was assigned to inorganic P.

Shaking the soil with 0.5 M H_2SO_4 for 16 hr nominally removes inorganic P and leaves organic P intact. The ^{31}P NMR spectra (both CP and DP) of the residue of soil M-H after H_2SO_4 extraction contain only the broad resonances with prominent SSBs (Fig. 2). It is proposed that these broad resonances are due to organic P. This is consistent with the findings of Shand et al. (1999), who found that organic P gave rise to broad ^{31}P NMR resonances in a large range of soils. However, the effect of extraction with 0.5M H_2SO_4 on organic and inorganic P is not entirely straightforward. Firstly, the extraction may hydrolyse some organic P. This may result in the extracted soil containing less organic P than the whole soil. Secondly, some native P minerals may be resistant to this treatment, such that inorganic P may still be present in the residue resulting from the H_2SO_4 extraction. However, the similarity of the organic P contents estimated by the H_2SO_4 extraction, the sequential H_2SO_4-NaOH extraction, and NaOH-EDTA extraction (data not shown) suggest that these potential deficiencies of the H_2SO_4 extraction are not major sources of error in the estimation of organic P content. Furthermore, some imprecision in the isolation of organic and inorganic P in the method of Saunders and Williams does not invalidate the interpretation of the ^{31}P CP and DP NMR spectra and the subsequent assignment of organic and inorganic P.

Further evidence for the assignment of the broad resonances in the whole soil to organic P is provided by examination of the HF treated residue of soil M-H. De-ashing with hydrofluoric acid (HF) is commonly used to concentrate organic matter and remove paramagnetic impurities prior to ^{13}C NMR analysis of organic matter (Skjemstad *et al.* 1995). Soil M-H was treated with HF and subsequent wet chemical analysis of the HF-treated material confirmed that the majority of the P in the residue was organic P (98%) as defined by the method of Saunders and Williams (1955). The ^{31}P CP and DP NMR spectra of the HF-treated residue of soil M-H are very similar to those of the H_2SO_4 residue, apart from the improvement in signal-to-noise ratio. As the HF treatment dissolved all inorganic soil components, the P remaining in the HF residue must be organic in nature. Thus, the broad resonances in the CP and DP spectra of the HF residue must be from organic P.

Therefore, based on the evidence provided by spectra from the ashed sample, the H_2SO_4 extracted residue, and the HF treated residue, it is concluded that the broad resonances observed in the CP and DP spectra of the whole soils are indeed due to organic P. This differentiation of organic and inorganic P found here has rarely been reported in solid-state ^{31}P NMR analyses of whole soils and related materials. Indeed, many solid-state ^{31}P NMR studies do not assign any NMR signal to organic P (Hinedi *et al.* 1989; Frossard *et al.* 1994;

McDowell *et al.* 2002; McDowell *et al.* 2003a), or mention organic P only briefly (Frossard *et al.* 2002; McDowell *et al.* 2003a; Hunger *et al.* 2004). Newman and Condron (1995) could not differentiate organic and inorganic P in ^{31}P CP NMR spectra of dairy pond sludge, although circumstantial evidence pointed towards the majority of the resonance coming from organic P. Condron et al. (1997) reported similar results for soils and soil humic acids. Benitez-Nelson et al. (2004) used spectral de-convolution to apportion the solid-state ^{31}P NMR spectra of sediments to broad P groups including organic and inorganic P. They made broad assignments of orthophosphate, P esters and phosphonates based on chemical shift derived by spiking of their samples with known compounds. Precise identification of the mineral phase detected in the ^{31}P DP NMR spectrum is difficult given the dependence of ^{31}P chemical shift on variables such as pH and the purity of the mineral (Hunger *et al.* 2004). More detailed identification of the organic P is restricted by the broadness of the organic P resonance. This is in contrast to the detailed characterisation of organic P possible in solution ^{31}P NMR spectra of soil extracts, where line-widths are at least two orders of magnitude smaller (Cade Menun and Preston 1996; Mahieu *et al.* 2000; Makarov *et al.* 2004; Turner and Richardson 2004).

It should be noted that the finding that inorganic P gave rise to sharp resonances with relatively small SSBs in the ^{31}P DP NMR spectrum may be particular to these soils, and may not be true in general. On the other hand, the results appear to confirm the contention of Shand et al. (1999) that organic P always gives rise to broad resonances with prominent SSBs. The potential to differentiate inorganic and organic P by solid-state ^{31}P NMR as proposed is a key advance in the use of NMR for the study of soil P.

8.3.3 Spin counting

Given the differentiation of organic and inorganic P in the ^{31}P DP NMR spectra of the whole soil, it would be tempting to use spectral de-convolution to quantify the proportion of each as is commonly used in solution ^{31}P NMR [e.g. (Turner *et al.* 2003b; McDowell and Stewart 2006)]. However, this would only be a measure of the relative amounts of *NMR signal* produced by each of the components. Either or both of these P types may be under-represented in the NMR spectra, perhaps to differing degrees, and there may be other types of P that are essentially undetected by either technique. Therefore, an essential pre-cursor to the use of spectral de-convolution is confirmation that the NMR spectrum is quantitative (i.e. the majority of the P in the sample being analysed must be detected by ^{31}P NMR). This requires a way to gauge how much of the total P in the sample is actually detected in each ^{31}P NMR spectrum. Spin counting provides such a gauge.

The degree to which solid-state NMR spectroscopy can provide quantitative information on soil chemistry has been widely debated, especially with regards to soil C chemistry (Frund and Ludemann 1989; Kinchesh *et al.* 1995; Preston 1996; Mao *et al.* 2000; Smernik and Oades 2000b; c; Keeler and Maciel 2003). Two potential causes of quantitation problems in solid-state ^{31}P NMR spectra of soils are widely recognised – close association with paramagnetic ions, especially Fe (Hinedi *et al.* 1989; Frossard *et al.* 1994; Condron *et al.* 1997; McDowell *et al.* 2002; McDowell *et al.* 2003a; Hunger *et al.* 2004), and remoteness of ^{31}P nuclei from nearest ^{1}H neighbours, which affects only CP spectra (Frossard *et al.* 1994; Condron *et al.* 1997; Hunger *et al.* 2004).

That quantitation can be achieved at all from NMR spectra is a consequence of a fundamental NMR property – that, under suitable conditions, each nuclear spin of a given isotope (e.g. ^{31}P, ^{13}C or ^{15}N) produces the same quantum of NMR signal, regardless of its chemical environment. This is not true for other spectroscopic techniques, such as infra-red or ultra-violet spectroscopy, for which different chromophores (the chemical structures that give rise to the signal) have different sensitivities. However, the potential for NMR to provide quantitative characterisation of soil chemistry is often limited because the properties of the soils themselves are not consistent with the “suitable conditions” required for producing quantitative NMR spectra. The two main problems are interference by paramagnetic species present in the soil, and low sensitivity, which can make it impossible to obtain a quantitative NMR spectrum on a practical timescale, even when it is theoretically possible to do so given unlimited spectrometer time.

Spin counting is a convenient way to gauge the potential “quantitativeness” of an NMR spectrum. The causes of NMR quantitation problems have a common feature – they all *decrease* the amount of NMR signal produced by the affected nuclei. Spin counting simply calibrates the amount of NMR signal produced by a sample against that of a standard, with the result, the “NMR observability” or P_{obs}, expressed as the amount of NMR signal per unit mass of the nucleus in the sample divided by the amount of NMR signal per unit mass of the nucleus in a reference material.

The results of spin counting on the ^{31}P CP and DP spectra of the whole and treated soil fractions are shown in Table 8-3. The P_{obs}(CP) values for the whole soil were in the range 7-12%, indicating that only around 10% of potential NMR signal for these soils was detected using this technique. The P_{obs}(DP) values were higher by a factor of 2.0-2.7, ranging between 16% and 28%. These values may be slightly affected by signal saturation, which would result in an underestimation of P_{obs}(DP) by up to 15% (see 8.2.3 Materials and Methods). In any case, it is clear that the majority of P in all of the soils was “undetected” even in the DP spectra.

Table 8-3. ^{31}P NMR observability in whole and treated soil fractions measured by spin-counting.

	P_{obs}(CP) (%)	P_{obs}(DP) (%)
Soil L-L whole	10	27
Soil L-M whole	7	19
Soil L-H whole	8	16
Soil M-L whole	10	21
Soil M-M whole	10	23
Soil M-H whole	9	21
Soil U-M whole	11	28
Soil U-H whole	12	24
Soil M-H H_2SO_4 residue	10	20
Soil M-H ashed residue	0	10
Soil M-H NaOH-EDTA residue	14	43
Soil M-H NaOH-EDTA extract	14	78
Soil M-H NaOH-EDTA extract (neutralised)	24	72
Soil M-H HF residue	73	77

The P_{obs}(DP) value for the ashed residue of soil M-H was 10%, about half the value of 21% determined for the corresponding whole soil (Table 8-3). This result suggests that the organic P converted to inorganic P by ashing is not subsequently detected in the ^{31}P DP NMR spectrum. In contrast, the P_{obs}(DP) value for the residue of H_2SO_4 extraction was 20%, which is very similar to P_{obs}(DP) for the whole soil (21%).

Another advantage of spin counting is that it facilitates a more meaningful comparison of corresponding CP and DP spectra. As previously noted, the ^{31}P CP and DP spectra of soil M-H shown in Figure 8-2 are scaled so that the highest peak of the central resonance in each spectrum is the same height. The vertical scales in Figure 8-2 are thus unrelated, and although the broad resonances present in each of the spectra have very similar chemical shifts, line-shapes and patterns of SSBs, their relative intensities, i.e. heights, cannot be compared meaningfully across the two techniques in this representation. This is the way corresponding CP and DP spectra are usually presented [see, for example, (Frossard *et al.* 1994; Condron *et al.* 1997; Frossard *et al.* 2002; McDowell *et al.* 2002). In Figure 8-3, Figure 8-4 and Figure 8-5, corresponding CP and DP spectra are presented in a way that allows direct comparison between the two techniques (although not between soils as each of these have been scaled differently for clarity). This was achieved by representing the vertical scale of the CP spectra to take account of the greater sensitivity of the CP technique. The ratio of signal detected by the two techniques (CP:DP) for the spin counting standard was 1.82:1. Allowing for this and the larger signal losses in the soil CP spectra caused by its more rapid $T_{1\rho}H$ relaxation rate (see 8.2.3 Materials and Methods section), the soil ^{31}P CP spectra were scaled down by a factor of 1.37 relative to the ^{31}P DP spectra to facilitate direct comparison of the spectra on the vertical scale.

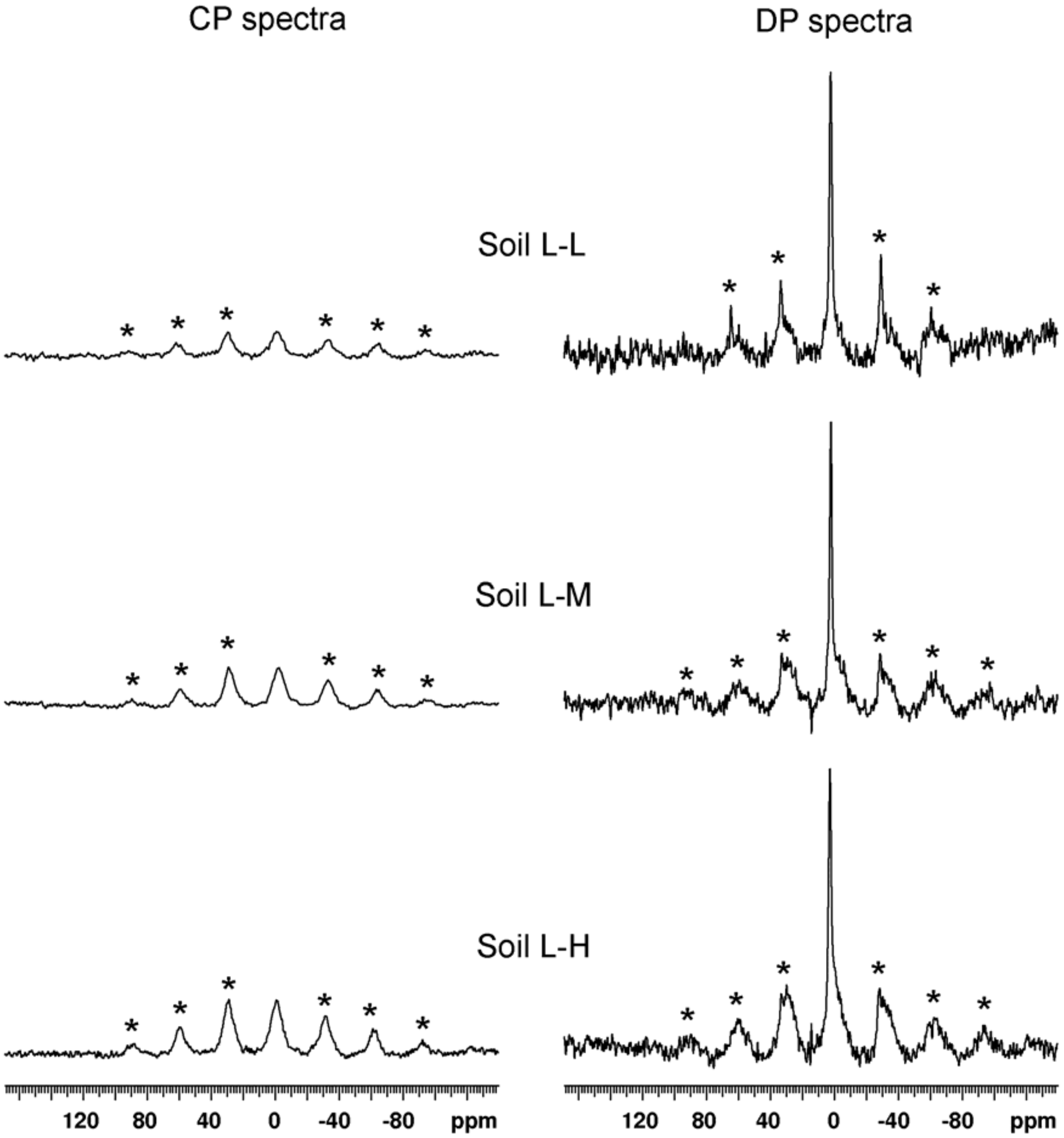

Figure 8-3. ^{31}P CP and DP NMR spectra of soils from lower elevations of the experimental site, M-L, M-M and M-H. The vertical scales have been adjusted to allow direct comparison between corresponding CP and DP spectra for each soil (see text). Spinning side bands are marked with an asterisk (*).

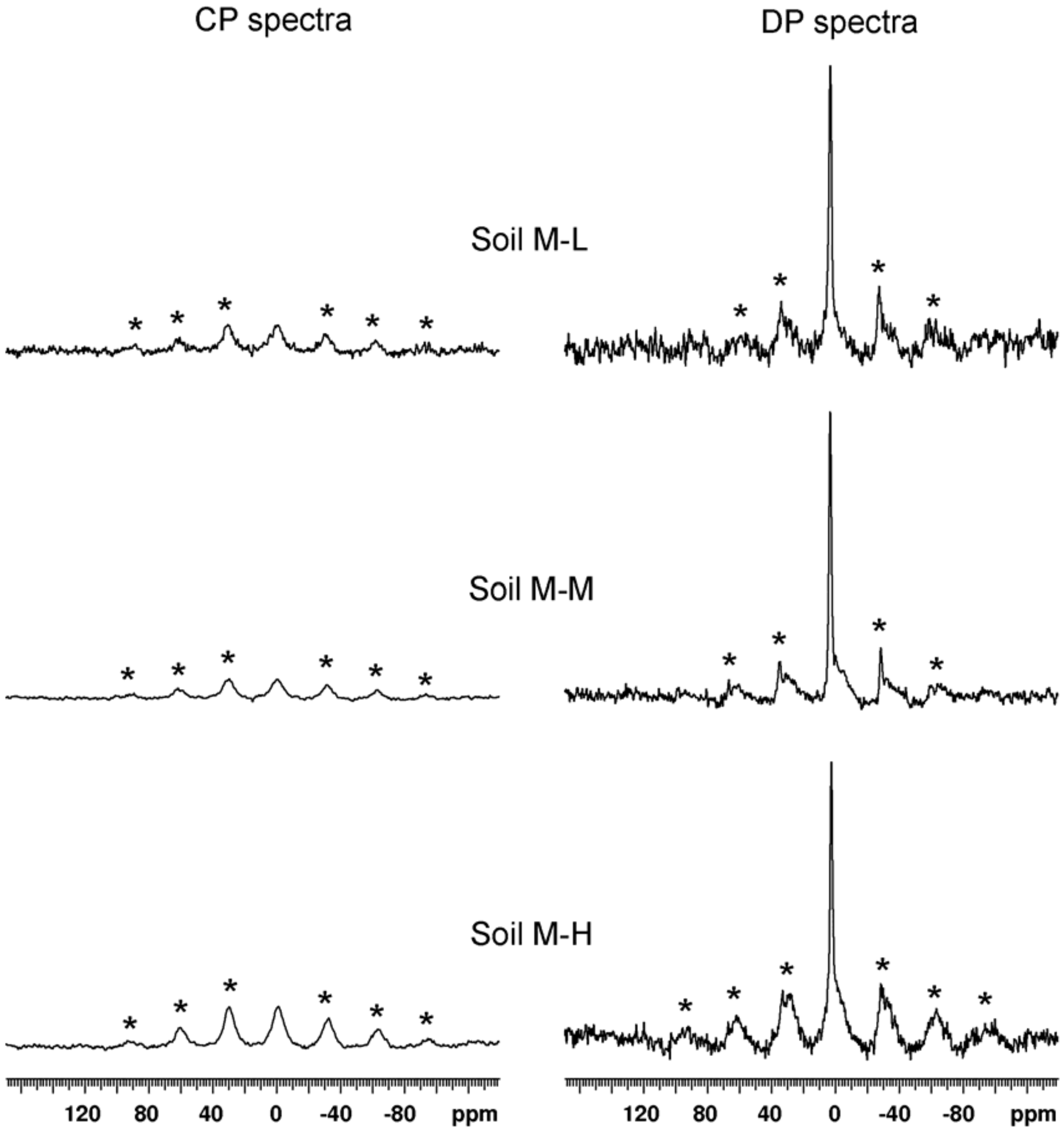

Figure 8-4. ^{31}**P CP and DP NMR spectra of soils from intermediate elevations of the experimental site, M-L, M-M and M-H. The vertical scales have been adjusted to allow direct comparison between corresponding CP and DP spectra for each soil (see text). Spinning side-bands are marked with an asterisk (*).**

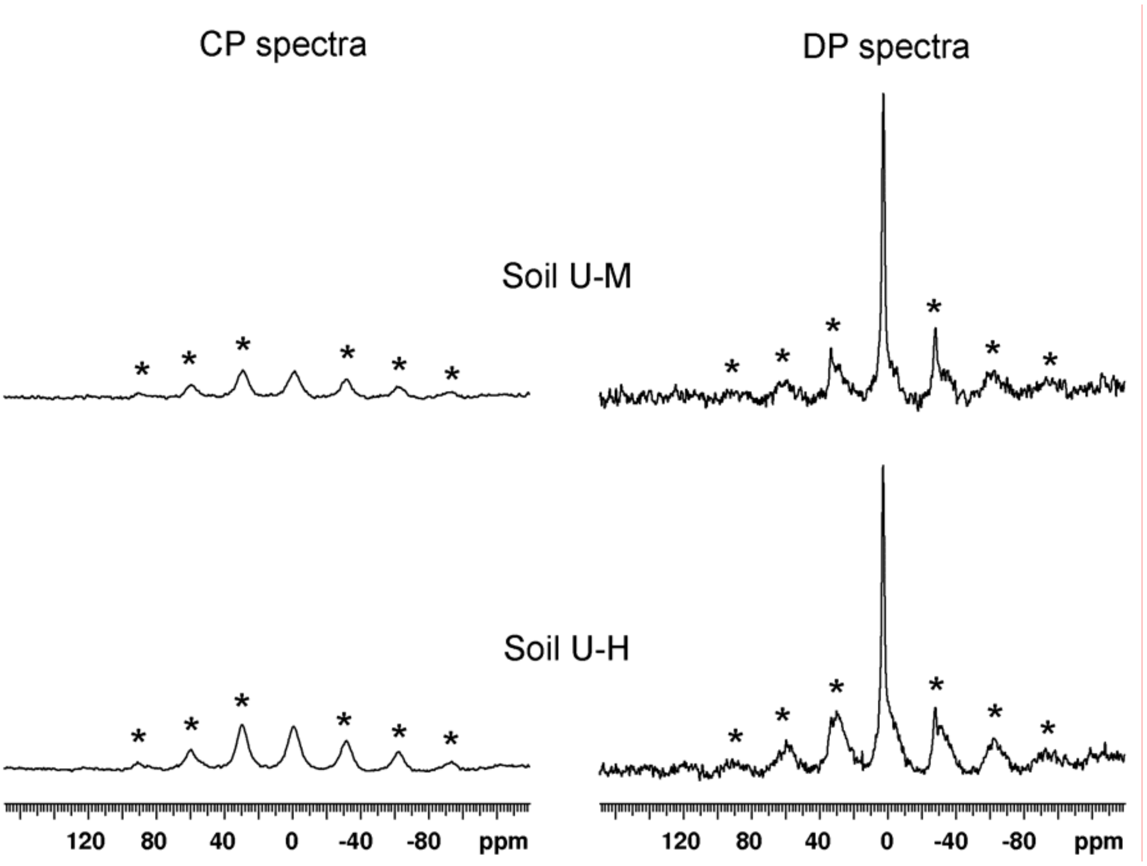

Figure 8-5. ^{31}P CP and DP NMR spectra of soils from the upper elevations of the experimental site, U-M and U-H. The vertical scales have been adjusted to allow direct comparison between corresponding CP and DP spectra for each soil (see text). Spinning side-bands are marked with an asterisk (*).

The broad resonances (which are attributed to organic P) seen in corresponding ^{31}P CP and DP spectra in Figure 8-3, Figure 8-4 and Figure 8-5 are of nearly equal intensity, indicating that the P species that give rise to them are seen with very similar sensitivity by both techniques. Although the ^{31}P NMR spectra of all the soils exhibit the same general features (each contains sharp inorganic P resonances with small SSBs and broad organic P resonances with prominent SSBs) there do appear to be differences in the relative contribution of these two types of signal (Figure 8-3, Figure 8-4, Figure 8-5). In particular, spectra from the soils with higher P contents contain relatively more signal derived from organic P (i.e. the broad resonances). However, wet chemical analyses indicate that organic P constitutes a smaller proportion of total P for the high P soils (Table 8-2). This apparent contradiction most likely results from a difference in the observability of P between the samples (i.e. either the NMR observability of organic P is higher for the high P soils, or the observability of inorganic P is lower for the high P soils). The increasing saturation of reactive Fe sites with P [i.e. inorganic P, as total P content increases (see Table 8-1 and Table 8-2)] is likely to contribute to the reduction in the relative observability of inorganic P in the high P soils. This finding highlights the risks of trying to quantify different P types by integrating NMR spectra without taking into the account possible differences in their NMR sensitivity.

8.3.4 The effect of paramagnetic iron on NMR observability

The presence of paramagnetic species, especially Fe, is the most likely cause of the low NMR observability of ^{31}P nuclei in these soils. Paramagnetic species can affect NMR observability it two ways: (i) they can cause non-selective signal loss by affecting magnetic field homogeneity, and (ii) they can cause selective loss of signal for nuclei in close contact with the paramagnetic centers. Smernik and Oades (2000b) provided an example of the first case, in which the NMR observabilities of physical mixtures of cellulose and paramagnetic salts were determined. Addition of 3.3% and 8.1% Mn decreased both CP and DP observability of ^{13}C nuclei by around 30% and 60%, respectively. The decrease in NMR observability affected all resonances equally. The most abundant paramagnetic element present in the soil studied here is iron (0.86-1.64%, Table 8-1). The concentration of Mn in these soils is around two orders of magnitude lower (data not shown), and at these concentrations Mn is unlikely to have a substantial effect on NMR observability via this mechanism.

To test whether the paramagnetic species present in the soil affect the NMR observability of remote ^{31}P nuclei, a physical mixture of soil L-H (357 mg) and $NH_4H_2PO_4$ (15 mg) was prepared. The P_{obs}(CP) and P_{obs}(DP) values for the added phosphate salt were 96% and 84%, respectively, showing that the bulk magnetic properties did not substantially affect the observability of ^{31}P nuclei in the added phosphate salt.

Much lower concentrations of paramagnetic species can affect NMR observability when there is contact between the paramagnetic species and the observed nuclei at the molecular level. For example, the NMR observability of ^{13}C nuclei in pectin was decreased by 80% when complexed paramagnetic Cu^{2+} was present at a concentration of 11.9% (Smernik and Oades 2000a), whereas the observability of ^{13}C nuclei in cellulose was unaffected when 9.8% Cu^{2+} was added in a physical mixture (Smernik and Oades 2000b). Hinedi *et al.* (1989) reported that a range of Fe and Mn phosphate minerals produced no signal at all in ^{31}P DP NMR spectra. McDowell *et al.* (2002; 2003a) also assumed that Fe phosphates were not visible in ^{31}P DP NMR spectra and thus used wet chemical techniques to calculate Fe phosphate contents to supplement the Ca and Al phosphate contents determined by NMR.

To test whether closely-associated Fe is responsible for the low NMR observability of P in the whole soils, extraction with NaOH-EDTA (traditionally used for solution ^{31}P NMR analysis) was undertaken. Treatment with NaOH solubilises organic P while the EDTA, a strong chelating ligand, increases the efficiency of P extraction from soils by chelating the cations that may bind P (Cade Menun and Preston 1996; Turner and Richardson 2004). Treatment of soil M-H with NaOH-EDTA resulted in a residue containing 255 mg/kg of inorganic P and 249 mg/kg organic P. The freeze-dried NaOH-EDTA extract contained 2110 mg/kg inorganic P and 555 mg/kg organic P.

The solid-state ^{31}P CP and DP NMR spectra of the residue and extract fractions from NaOH-EDTA extraction of soil M-H are shown in Figure 8-6. The ^{31}P CP NMR spectrum of the residue is very similar to the corresponding CP spectrum of the whole soil and the H_2SO_4 residue (Figure 8-2). This similarity is consistent with the results of the wet chemical analysis that shows that there is still a substantial proportion of organic P in the residue. The ^{31}P DP NMR spectrum of the residue is also similar to the corresponding DP spectrum of the whole soil (Figure 8-2), except that the broad organic P resonances appear to be less intense. This reduced intensity can be attributed to the reduced organic P concentration in the residue relative to the whole soil.

The P_{obs}(CP) value for the NaOH-EDTA residue was 14% (Table 8-3), slightly higher than the P_{obs}(CP) values for the corresponding whole soil (9%) and the H_2SO_4 residue (10%). The P_{obs}(DP) value for the NaOH-EDTA residue was 43% (Table 8-3), approximately double the P_{obs}(DP) values for the corresponding whole soil (21%) and the H_2SO_4 residue (20%). This indicates that either the P in the fraction not extracted by NaOH-EDTA had a higher NMR observability than the fraction that was extracted, or that NaOH-EDTA extraction removed paramagnetic species from the residue fraction that were compromising NMR observability. The ^{31}P CP NMR spectrum of the freeze-dried NaOH-EDTA extract is very different in appearance to the corresponding CP spectrum of the whole soil. The chemical shift of the central resonance in the CP spectrum of the NaOH-EDTA extract is 11.3 ppm, considerably downfield of the central resonances in the CP spectrum of the whole soil (-1.3 ppm). Furthermore, the SSBs are much less prominent in the ^{31}P CP NMR spectrum of the NaOH-EDTA extract than in the corresponding CP spectrum of the whole soil. The ^{31}P DP NMR spectrum of the NaOH-EDTA extract is similar in appearance to the corresponding CP spectrum, but has slightly less intense SSBs. The downfield shift is most likely the result of the change in pH (Hunger *et al.* 2004).

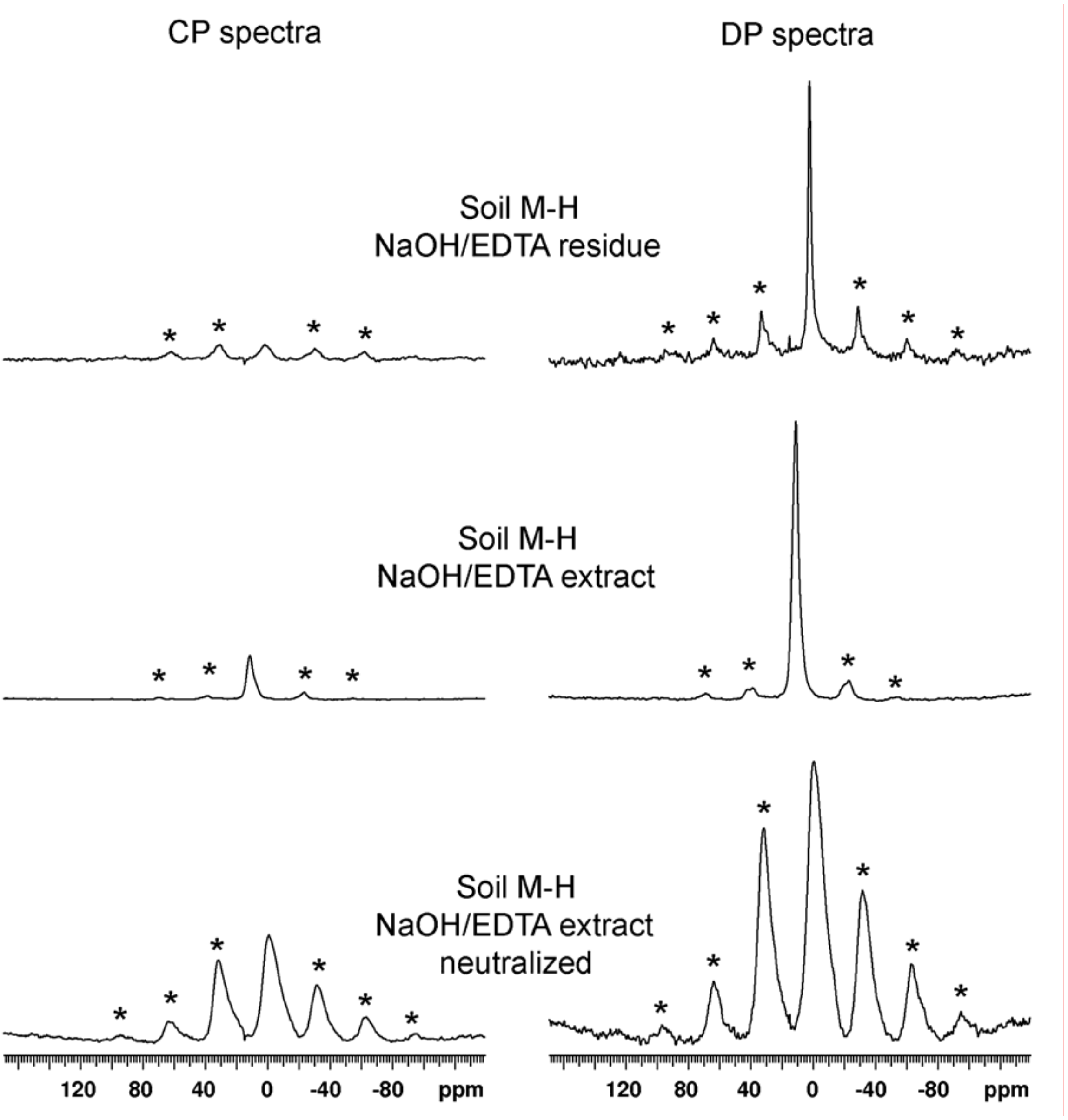

Figure 8-6. ^{31}P CP and DP NMR spectra of residue and extract (un-amended and neutralised) fractions from NaOH-EDTA extraction of soil M-H. The vertical scales have been adjusted to allow direct comparison between corresponding CP and DP spectra for each soil fraction. Spinning side-bands are marked with an asterisk (*).

To examine the effect of pH on the chemical shift and SSBs, a sub-sample of the freeze-dried extract was neutralised by first dissolving it in de-ionised water and then adding HCl until the pH was reduced to 5.9. The neutralised sample was subsequently freeze-dried. The neutralised, freeze dried NaOH-EDTA extract contained 1944 mg/kg inorganic P and 386 mg/kg organic P. The neutralisation of the extract resulted in a small change in the proportions of inorganic P (83%) and organic P (17%) relative to the untreated NaOH-EDTA extract, and a small decrease in the total P concentration, attributable to the addition of chloride ions. The P_{obs}(CP) was 24%, which is considerably higher than that for the untreated extract. At least part of the increase in P_{obs}(CP) can be attributed to increased protonation of the phosphate groups in the soils, i.e. because CP relies of transfer of magnetization from ^{1}H to ^{31}P nuclei, the increase in the degree of protonation of the weakly acidic phosphate ions and esters brought about by a decrease in pH, increases the concentration of ^{1}H nuclei in close proximity to ^{31}P nuclei, and hence increases P_{obs}(CP). The P_{obs}(DP) was 72%, which is similar to that of the untreated NaOH-EDTA extract.

Both the ^{31}P CP and DP NMR spectra of the neutralised, freeze-dried NaOH-EDTA extract are very different in appearance to the corresponding spectra of the untreated freeze-dried NaOH-EDTA extract. In both the spectra of the neutralised extract, the SSBs are much more prominent. The ^{31}P CP NMR spectrum for the neutralised freeze-dried NaOH-EDTA extract is similar to that of the whole soil. However, the ^{31}P DP NMR spectrum for the neutralised freeze-dried NaOH-EDTA extract contains much more prominent SSBs than does the DP spectrum of the whole soil. Both the whole soil and the neutralised freeze-dried extracts have similar total P contents (2098 and 2330 mg/kg respectively) and in both cases are dominated by inorganic P. The most likely explanation for the differences in appearance of the ^{31}P DP spectra of the whole soil and neutralised NaOH-EDTA extract is that they contain quite different inorganic P minerals. This is not surprising considering that the inorganic P present in the latter is the result of dissolution of the original soil P minerals, followed by a modified precipitation during freeze-drying.

Both the soil residue and freeze-dried extract resulting from treatment with NaOH-EDTA have substantially higher P_{obs} (both CP and DP) than the corresponding whole soil. This can be attributed to the strong affinity of EDTA for Fe, and the subsequent displacement of P. Consequently, less of the P is in close proximity to Fe and there is a substantial increase in the observability of P (particularly inorganic P).

The P_{obs}(CP) and P_{obs}(DP) values for the HF-treated residue of 73% and 77%, respectively (Table 3), were the highest of any of the treated soil fractions, providing further evidence that closely-associated paramagnetic Fe is the main cause of poor NMR quantitation for the organic P in these soils. As previously noted, ~17% of the soil Fe is associated with organic matter. However, it should be noted that only 12% of P present in the whole soil was recovered in the HF-treated residue. This accounts for only 41% of the organic P in the whole soil. By contrast, the recovery of C on HF treatment for this soil was 91%. The most likely cause of the low recovery of organic P is that majority of organic P may be have been in small, soluble molecules held in the soil by association with clay minerals and iron oxides, and was released into solution during HF treatment. In other words, it may be that the organic matter lost during HF treatment, which represented only 9% of soil carbon, may have been disproportionately rich in P.

8.4 CONCLUSIONS

Using a combination of CP and DP ^{31}P NMR and selective extractions, broad classes of P (i.e. organic and inorganic) have been observed in the NMR spectra of the soils examined. This is consistent with the data for a broader set of soils (Chapter 7). Organic P was identified as broad resonances with prominent spinning side bands (SSBs), whereas inorganic P appeared as sharp resonances with smaller SSBs. Although organic and inorganic P have been identified in the spectra of the whole soil samples, the use of spin counting showed that only small proportions of P in the samples was observed. On average, only 9 and 22% of total P could be observed using CP and DP respectively. The poor observability of P by ^{31}P NMR is probably due to interference from paramagnetic ions. In the soils examined, iron in intimate contact with P rather than iron in the bulk soil was identified as being responsible for the poor observability of P. These findings highlight the risks of trying to quantify different P types by integrating NMR spectra without taking into the account possible differences in their NMR sensitivity. Unfortunately though, there was no differentiation within the two broad groups, such that more detailed differentiation of organic or inorganic forms of P could be made. This contrasts with the resolution possible in solution state studies (Turner *et al.* 2003c; a).

It was beyond the scope of this project to undertake the further developments required to improve the information that can be obtained using solid-state ^{31}P NMR. It is recommended that spin counting be routinely used in solid-state ^{31}P NMR analyses of soils, and that P_{obs} values be reported. Furthermore, in the further development of solid state ^{31}P NMR, methods should be utilised that allow the P_{obs} of the various forms of P identified to be assessed. Significant improvements in the information garnered from solid-state ^{31}P NMR analysis of soil will come not from improving resolution – there are fundamental limitations here – but in using information contained in non-frequency parameters, such as observability, chemical shift anisotropy, and relaxation rates.

Chapter 9 Evaluation of de-stratification to reduce runoff P concentrations

9.1 Introduction

In the previous chapters and in research carried out by others, it is clear that concentrations of P in runoff can be excessively high and need to be reduced. These excessive concentrations of P result from a combination of processes classified as ‘incidental’ and ‘systematic’ (Haygarth and Jarvis 1999). Incidental mobilisation of P is that which occurs from specific events such as the application of fertiliser or grazing just prior to a runoff event. The high concentrations of P often associated with these incidental processes represent a departure from the baseline or systematic concentration of P in runoff. The concentrations of P in runoff from these incidental type events can range from 10-50 mg/L (Greenhill *et al.* 1983; Nash *et al.* 2005). Improved management of fertiliser so that it is not applied when the chances of runoff are high has been cited as reducing the significance of these events in P export (Nash *et al.* 2005).

Although the concentrations of P arising from incidental processes are very high, their occurrence is not as frequent as the P concentrations that reflect the systematic (or background) processes. This is because these systematic processes occur for all runoff events. Even when no fertiliser is applied to grazed dairy pastures and Olsen P levels are well below optimal from an agronomic standpoint, concentrations of P in runoff can still be in the range of 0.5-3 mg/L (Austin *et al.* 1996; Cornish *et al.* 2002). Therefore, reducing the magnitude of P concentrations arising from these systematic processes is also important. These systematic processes involve the mobilisation of P from the soil-pasture system.

In Chapter 7, it was shown that the concentrations of P in the top 0.01 m of soil are substantially higher than those in the top 0.1 m. Furthermore, the depth of soil with which runoff interacts was shown to be <<0.01 m. As soil P under permanent pastures (such as those used for dairying) is highly stratified, it was proposed in Chapter 7 that de-stratification of soil P (i.e. mixing of the topsoil to reduce or eliminate stratification) may reduce runoff P concentrations. An investigation of the potential benefits of de-stratification on manured soils (Sharpley 2003) showed that by de-stratifying a high P soil, large reductions in runoff P concentrations were possible. In Chapter 7 it was proposed that the effect of de-stratification on soil surface P would be a function of the soil P status due to changing degree of stratification with changing soil P status.

De-stratification would typically be undertaken by cultivating soils by means such as disc ploughing, rotary hoeing or power harrowing. These techniques would mix the soil thoroughly, maximising the likely benefits of the technique. However, they would also result in a temporary loss of productivity of the treated pasture and may represent an erosion risk (Sharpley 2003). This increased erosion risk may negate the potential benefits of de-stratification although it is proposed that this is a manageable risk.

In humid regions, a number of studies have found that only small areas of the landscape generate runoff (Sharpley *et al.* 1999; Davies *et al.* 2005b; Melland 2005). These areas are termed variable source areas (see Chapter 2 for a more detailed discussion). Hydrological modelling based on the VSA concept in the Flaxley sub-catchment (Davies *et al.* 2006) suggests that a small proportion of the landscape is responsible for the majority of runoff. It is worth noting that the modelling approach used by Davies et al. (2006) made an *a priori* assumption that the VSA concept was in fact valid. Soil moisture measurements in this catchment through the winter of 2004 showed that soil moisture was related to position in the landscape (Davies and Dougherty unpublished 2004), providing equivocal support for the assumption of VSA hydrology. The combined effect of runoff volume and runoff P concentration predicted by the model define the key P exporting zones. Large runoff volumes or concentrations on their own do not necessarily constitute key P exporting zones. In the Flaxley east catchment, the intersection of runoff generating areas with areas of moderate to high soil P status may mean that only small parts of the catchment are responsible for the majority of P exported in runoff (Figure 9-1) (Davies *et al.* 2005a; Dougherty *et al.* 2006a). Clearly, a small area dominates P losses (this is the CSA). This area is associated with applications of P from effluent in the past, and so in some senses can be regarded as anomalous, although such ‘hotspots’ of P in paddocks or in the landscape are not uncommon (Pionke *et al.* 2000; Page *et al.* 2005). It is such areas of the landscape that may be the most efficient to target for remedial management actions (Pionke *et al.* 2000).

Given the stratification of soil P and the limited extent of the CSA in the Flaxley sub-catchment, the aims of this experiment were to:

- ***Quantify the effect of soil de-stratification on runoff P concentrations at a range of soil fertility levels and consider the potential effect of de-stratification on P export for the Flaxley East catchment.***

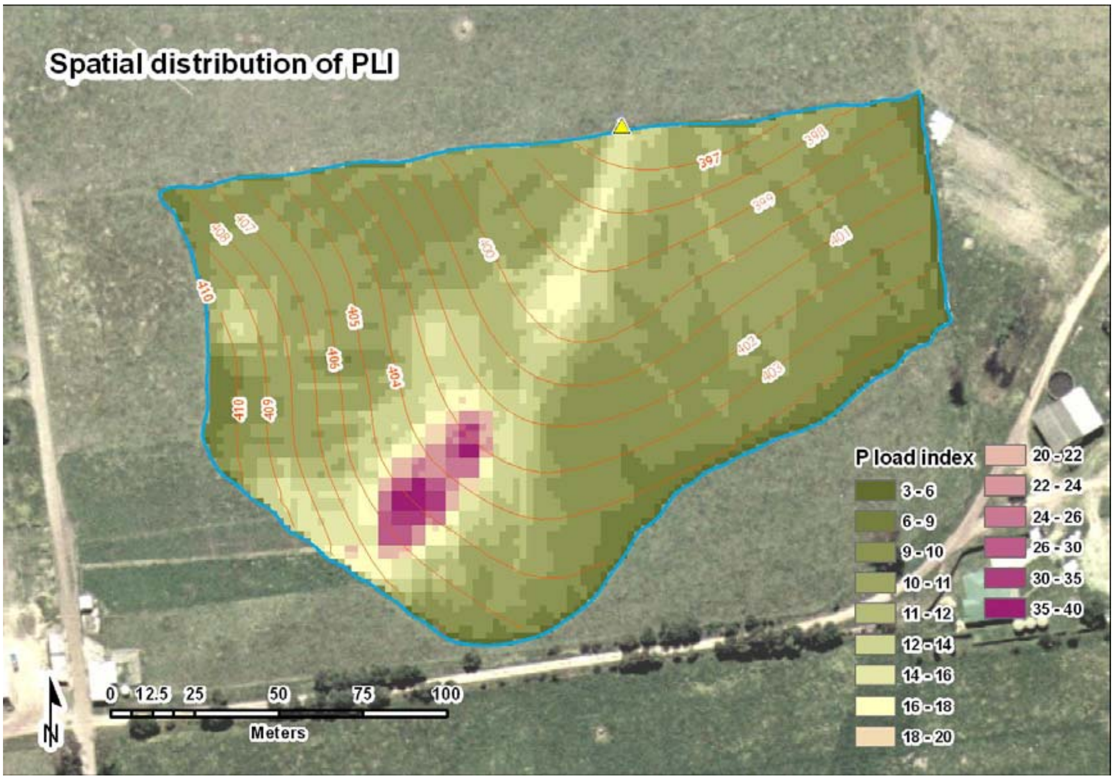

Figure 9-1. Spatial contribution to modelled P load exported in runoff from Flaxley East (Davies *et al.* 2005b). The phosphorus load index (PLI) is a relative measure of the contribution of particular areas of the landscape to P export, higher PLI representing a greater contribution.

9.2 Material and methods

9.2.1 Laboratory incubation

As a preliminary step in the evaluation of the effect of de-stratification, its effect on soil P was investigated in a laboratory experiment. Samples of each of the 0-0.01, 0.01-0.02, 0.02-0.05 and 0.05-0.10 m depth increments from Flaxley (collected as part of Chapter 7) were mixed in proportion to their masses contained in each of the depth increments for 9 sampling locations at Flaxley east. These samples were then incubated in the dark at 20^{o}C, 60% field capacity for 4 weeks. As control treatments, the 0-0.01 m increments for each of the locations were also incubated under the same conditions. All of the soil samples were then dried and Olsen P and $CaCl_2$-RP determined as described in Chapter 3.

9.2.2 De-stratification in runoff trays

Twenty-two runoff trays were prepared as described in Chapter 7. These were re-packed so as to simulate stratification (as would occur in the field). Briefly this involved sampling and re-packing of the 0-0.01 and 0.01-0.1 m increments separately. These trays represented a range of Olsen P_1 concentrations from 21 to 124 mg/kg. All of these trays were sown to a ryegrass/clover pasture and allowed to grow for 2 months prior to commencement of this experiment.

A sub-set of the trays (11) was de-stratified that represented a wide range of soil P status. This was undertaken by tipping the soil and pasture out of the trays, mixing it and then re-packing it into the trays and re-sowing it with pasture. The pasture was then grown for two months. Rainfall simulations were then undertaken 2 months later using the rainfall simulation methodology described in Chapter 7 (i.e. rainfall intensity 30 mm/hr, continued until 20 minutes of runoff had occurred). The trays had approximately 100% ground cover at the time of simulation.

Simulation immediately after de-stratification was deemed un-necessary as there would obviously be significant sediment loss under rainfall simulation (Sharpley 2003). The management of this sediment loss in relation to the implementation of de-stratification at the sub-catchment scale is considered in the Results and Discussion Section of this Chapter.

9.3 Results and discussion

9.3.1 Laboratory incubation

The laboratory incubation experiment resulted in a large reduction in Olsen P and $CaCl_2$-P concentrations for the de-stratified soils (Figure 9-2). The magnitude of the reductions was a function of initial soil fertility, the greatest change (%) occurring for the lower fertility soils. This is consistent with the higher degree of stratification for the low P soils reported in Chapter 7.

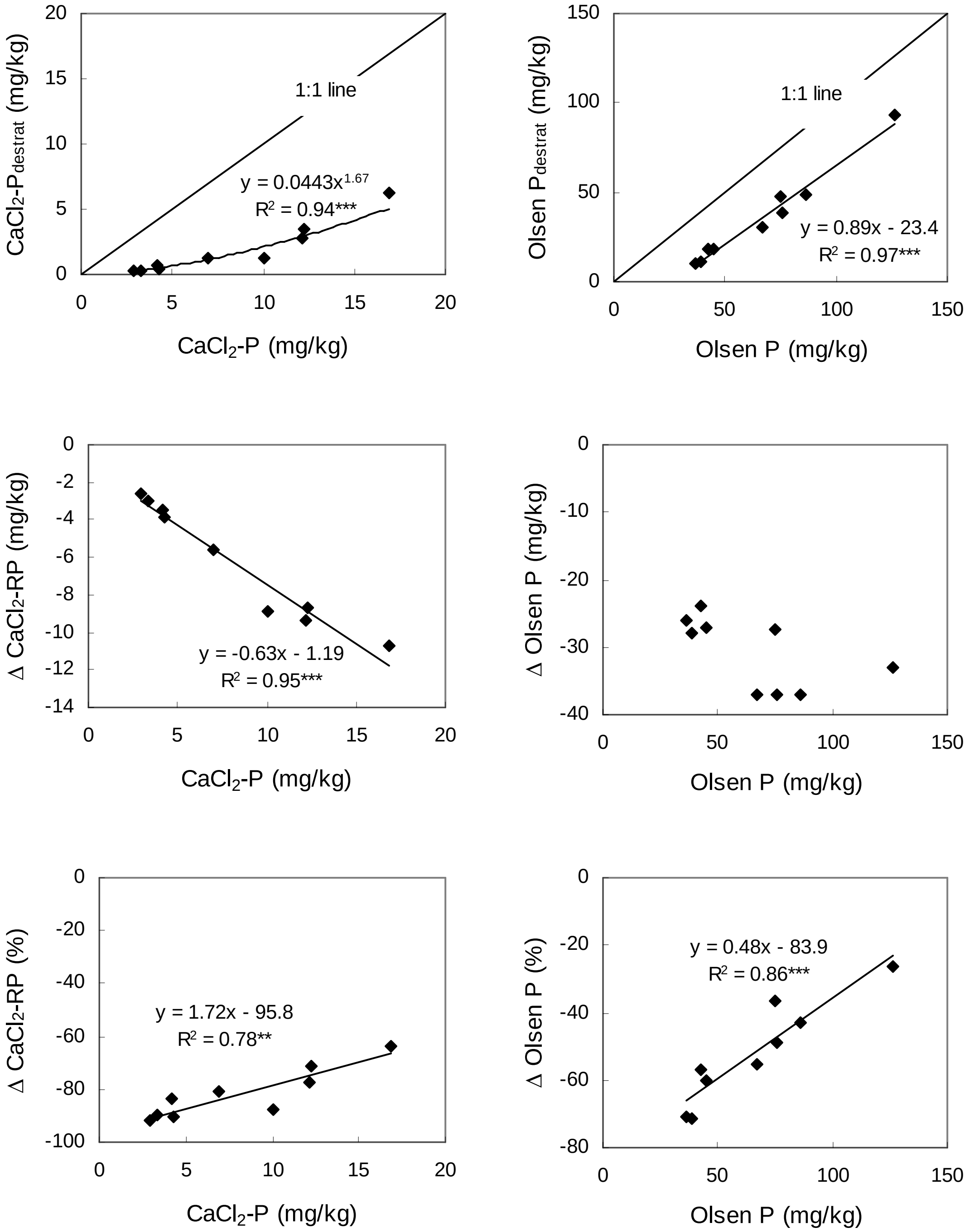

Figure 9-2. Effect of de-stratification on soil properties from laboratory incubation experiments. Data on the x-axis are the values of $CaCl_2$-P and Olsen P in the 0-0.01 m increment prior to de-stratification (i.e. the control values), whereas the values on the y-axis are the soil P values and changes associated with de-stratification.

On average, de-stratification resulted in a 52 and 82% reduction in Olsen P and $CaCl_2$-P concentrations in the top 0-0.01 m increment (the zone of soil/runoff interaction as demonstrated in Chapter 7). The greater reduction in the $CaCl_2$-P can be attributed to the fact that Olsen P extracts more of the ‘quantity’ component of soil P whereas $CaCl_2$-RP measures the ‘intensity’ component (Kuo 1996).

9.3.2 De-stratification in runoff trays

Mixing the soils in those trays selected for de-stratification resulted in a reduction in the concentration of $CaCl_2$-P in the top 0.01 m. Figure 9-3 shows the degree of stratification ($CaCl_2$-P_1:$CaCl_2$-P_{10}) for the stratified and de-stratified soils. The degree of stratification in the trays is lower than that measured in the field (Chapter 7). This may be because there was diffusion of P from the top 0.01m into the deeper soil as there was a distinct boundary between the P rich top 0.01 m and the low P deeper soil due to the method of creating stratification in the trays. This contrasts to the stratification occurring in the field where there was a gradual decline in soil P in the deeper soil (Chapter 7).

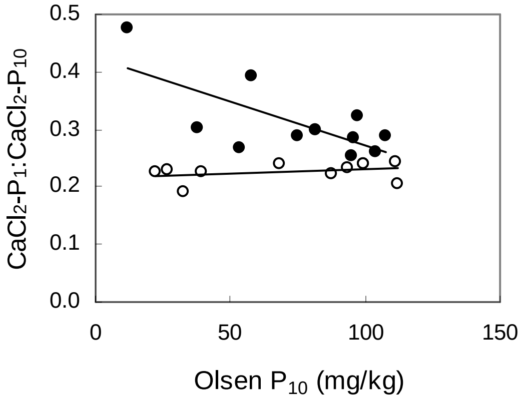

Figure 9-3. The degree of stratification ($CaCl_2$-P_1:$CaCl_2$-P_{10}) of stratified (●) and de-stratified (○) soils as a function of soil P status.

The de-stratification of soil resulted in lower concentrations of TP in runoff (Figure 9-4). The regressions of Olsen P_{10} vs runoff P (DRP, TDP and TP) were significantly different ($P<0.01$) between the stratified and de-stratified soils. The effect of de-stratification resulted in relatively large absolute decreases in runoff P concentrations at the highest Olsen P concentrations. For example, at an Olsen P_{10} of 110 mg/kg, runoff TP was approximately 1.7 and 0.6 mg/L for the stratified and de-stratified soils respectively, a decrease in runoff P concentration of approximately 65%. At Olsen P_{10} less than 40 mg/kg, the difference in runoff P concentrations between stratified and de-stratified soils was relatively small.

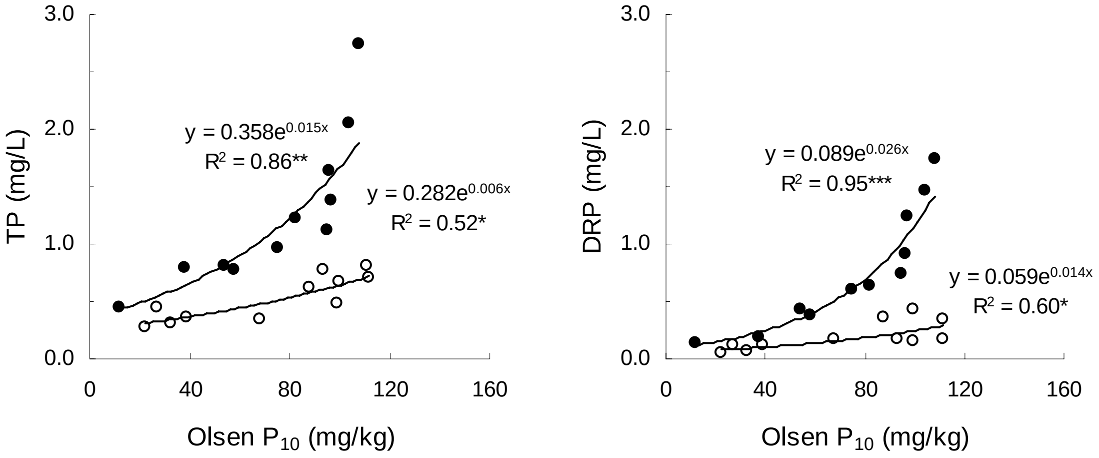

Figure 9-4. The relationship between soil P (Olsen P_{10}) and runoff TP (left) and DRP (right) for stratified (●) and de-stratified (○) soils.

9.3.3 Possible limitations on the benefits of de-stratification

The data show that there are substantial potential reductions in runoff P resulting from de-stratification. However, a number of factors may negate these benefits. The first of these is the mobilisation of much greater amounts of particulate P due to raindrop impact on bare soil after cultivation (used to de-stratify the soils). Sharpley (2003) showed in rainfall simulation experiments that total P concentrations could be higher in runoff from de-stratified soils in the first 2-3 months after de-stratification due to mobilisation of particulate P. However, the use of de-stratification in only limited parts of the landscape (as proposed in the introduction) and the climate at Flaxley offers possibilities to reduce this erosion. Buffer strips are highly effective at reducing particulate transport. For example, Tate *et al.* (2000) observed that suspended sediment loads decreased by between 50-90% when 10 m grassed buffer strips were used to filter runoff. The presence of grassed areas below the areas proposed for de-stratification at Flaxley would most likely substantially reduce the off-site movement of any P containing sediment entrained in runoff.

The de-stratification operations may also be timed to minimise the likelihood of runoff occurring before the pasture is re-established. Flaxley has a distinctly winter dominant rainfall-runoff season. Carrying out de-stratification and re-sowing pasture at the end of the rainfall-runoff season when soil moisture is still sufficient to allow pasture establishment may mean that pasture can be established when the chances of runoff are relatively low, thus reducing the overall risk of mobilisation of sediment.

The other issue that needs consideration is that of the re-establishment of stratification. If soil P is stratified, then it might be reasonable to assume that the further addition of P would allow stratification to re-establish. Stratification of soil P arises from the addition of fertiliser, manure and the action of plants in drawing soil P from below the surface and re-deposition of this phosphorus on the surface (Nash and Halliwell 1999). On soils with Olsen P values higher than the agronomic optimum, there is no need for further addition of fertiliser P in the short-term. Hence this is not likely to contribute to the re-establishment of stratification. Data from the runoff plots at Camden provide an insight into the likely significance of manure and plant P in the re-establishment of stratification. Nutrient budgets were calculated for these plots using data for pasture consumption, nutrient content of pasture, time spent on the paddocks, P consumed in other areas such as the milking shed and feed-pads (pers. comm. Helena Warren, NSW DPI). These nutrient budgets were calculated for 3 ½ years of grazing. Soil samples were also gathered at the beginning and the end of this 3 ½ year period.

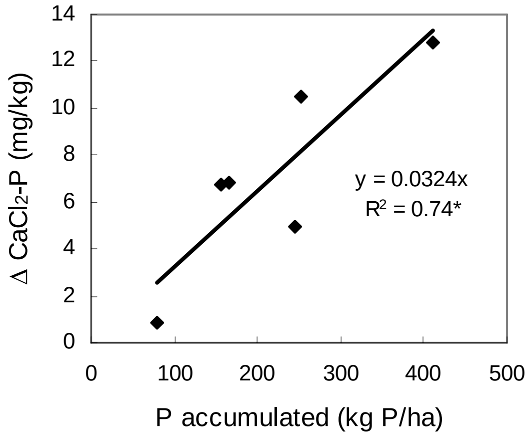

Figure 9-5. The relationship between P accumulation and the change in soil P.

The relationship between P applied and the change in soil P is shown in Figure 9-5. The data in the figure equate to plots that had 0, 20, 40 and 80 kg P/ha applied annually. All of the plots accumulated approximately 20-25 kg/ha/yr P from manure deposition. The plot with the smallest $\Delta CaCl_2$-P was that which had no P applied whereas that with the largest $\Delta CaCl_2$-P was that having had 80 kg P/ha applied annually. The relationship indicates that when P fertiliser is not applied there is little re-establishment of stratification, whereas the application of P fertiliser significantly increased the soil P (i.e. the increase in soil P that would influence runoff P occurred primarily because of the application of fertiliser, not P containing manure or senescing plant material).

9.4 Conclusions

The preliminary experiments undertaken in this thesis suggest that de-stratifying high P soils (e.g. those >Olsen P_{10} of 50 mg/kg) under permanent pasture (such as used by the dairy industry) may have the potential to reduce the concentrations of P in runoff. De-stratification of high P soils in re-packed runoff trays from the Flaxley sub-catchment resulted in decreases of runoff P concentrations of >60%. Given the difficulties in reducing runoff P concentrations from high fertility areas using other means, this technique warrants further assessment.

It is proposed that effectiveness of de-stratification in reducing P exports would be maximised if combined with knowledge of the landscape hydrology and the spatial distribution of P. The benefits of de-stratification need evaluation in a range of landscapes, including those not exhibiting VSA hydrology and under permanent pastures. The ability to identify the hydrologically active components of the landscape and high fertility areas needs further development. Further developments in technology such as remote sensing may allow more cost effective identification of these (Hergert 1998; Schmugge *et al.* 2002).

Despite evidence provided in this thesis suggesting that accumulation of P and stratification are primarily the result of fertiliser P application, more research is required to confirm this assertion. From an industry perspective, de-stratification should not be seen as the only solution to excessive runoff P concentrations. Rather, de-stratification represents one of a number of possible tools in a broad P management strategy that should aim to minimise the accumulation of P in the first instance.

Chapter 10 Conclusions and industry implications

The high concentrations of P contained in runoff from intensively managed pastures in Australia and the need to better understand the reasons for these excessive concentrations was highlighted in the initial literature review. Consequently, the experimental component of this thesis has examined the influence of hydrology and soil P chemistry on the forms and amounts of P mobilised in surface runoff from soils under permanent pasture. This was carried out at two sites in major dairying districts (Camden, NSW and Flaxley, SA). Subsequent to this research and its findings, the effect of de-stratification of soil P on runoff P was evaluated.

10.1 Summary of findings

Rainfall simulation is widely used in the study of P mobilisation. Evaluation of this technique showed that it is a useful tool for examining the processes of mobilisation. A comparison of small-scale, high intensity rainfall simulation with large-scale, low intensity rainfall simulation (approximating natural rainfall/runoff at the hillslope scale) was undertaken. Both methods yield runoff of similar composition in terms of P forms. However, the small-scale, high-intensity rainfall simulation method provides relatively low estimates of runoff P concentrations. It was concluded that rainfall simulation is a robust technique for investigating the processes of P mobilisation under intensively managed pastures, although it should not be assumed that it will provide quantitative estimates of P concentrations or P exported in runoff. Rainfall simulation data should be used with caution when parameterising models, setting target soil P concentrations and in calculating runoff P exports. For example, McDowell *et al*. (2003c) used soil P-runoff P relationships derived by rainfall simulations to set target soil P concentrations. The soil P values they proposed are likely to be overestimates and not provide the level of water quality protection intended.

Phosphorus mobilisation under rainfall simulation was shown to be a two-stage process. The factors controlling the first phase could not be confirmed. Either they were depletion/dilution of the P source or rate-controlled release of P. However, it was hypothesised that the changes in hydrological characteristics combined with the kinetics of P release controlled the P concentrations in the second phase of P mobilisation. To consider the hypothesis that these factors were responsible for changes in P concentrations, a simple physically based model that considered changes in residence time and runoff depth was tested. This model explained >90% of the variation in runoff P concentrations arising from changes in rainfall intensity in the second phase of P mobilisation. The model explained 85% of the variation in flow-weighted means in the runoff events. When tested on the experimental data from the small-scale, high-intensity vs. large-plot, low-intensity experiment, the model over-estimated the differences between the methods by ~30%. This overestimation may have been due to the need to estimate several of the required parameters.

Subsequently, the P release characteristics of the Flaxley soil were examined and compared with those of the Camden soil, other Australian soils (from published and unpublished sources) and various overseas soils (using published data). The soils at Flaxley and Camden appeared to be more ‘leaky’ with respect to P than soils of similar fertility from overseas. Concentrations of labile P ($CaCl_2$-P) were much higher for these two soils than for other soils with comparable P status. When soil P-runoff P relationships from various Australian sites were compared with published data, it appeared that the Australian soils again tend to be more ‘leaky’. These findings highlight the need to understand the accumulation and mobilisation of soil P.

The accumulation and mobilisation of P were examined for soils with a wide range of soil P status at the Flaxley and Camden sites. The composition of soil P at the two sites varied widely and was related to soil P status. The P in low P soils was predominantly organic, whereas in high P soils it was predominantly inorganic. There was very little organic P accumulation at either site, although organic P (and carbon) concentrations were high, raising the possibility that some sort of organic P equilibria had been attained. The relative importance of the various forms of mobile changes with soil P status, runoff P containing a greater proportion of organic P at low fertility levels. For the Flaxley soil, organic P in runoff constituted 50% of P at low fertility, whereas for the Camden soil this was 10% or less. Most of the P in runoff is sub-particulate and sub-colloidal (i.e. it is truly dissolved), irrespective of whether it is inorganic or organic P. Consequently, remedial strategies that are based on physical trapping of sediment associated pollutants are unlikely to be effective.

Phosphorus that did accumulate in the soil under permanent pastures did so primarily at the immediate soil surface (i.e. soil P was highly stratified). The concentration of P in the top 0.01 m was substantially higher than that in the top 0.1 m. Exacerbating the effect of this stratification on runoff P concentrations, was the fact that P was shown to be predominantly mobilised from the top couple of millimetres of the soils.

These findings suggested that de-stratification represented a possible remedial option. Laboratory and rainfall simulation experiments were undertaken to examine this method and showed that de-stratification did reduce runoff P. However, the success and magnitude of the benefit of de-stratification was a function of soil fertility. Reductions of runoff P concentrations in excess of 60% were observed when high P soils were de-stratified. However, only small reductions were observed for low P soils. It was concluded that de-stratification of soil P would provide large reductions in runoff P concentrations on the high P soils at Flaxley.

It has been proposed that VSA hydrology occurs at Flaxley (Davies *et al.* 2006) such that lower parts of the landscape generate the majority of runoff (although at this point in time there is only limited evidence for such hydrology existing). In this thesis, it was proposed that knowledge of soil P distribution and landscape hydrology may mean that only small parts of the landscape may need to be managed by de-stratification. For the Flaxley study catchment, it was proposed that the intersection of the dominant runoff generating zone with areas of high P status means that large reductions in P export may be achieved with little inconvenience to the land manager. Furthermore, it was proposed that the potential problems associated with de-stratification (i.e. the temporary erosion risk and the re-establishment of stratification) were manageable and unlikely to provide significant impediments to the success of this technique.

10.2 Future research

The concentrations of P in runoff from intensively managed pastures are often well above desirable limits. The need to develop strategies to reduce these is critical to the sustainability of these industries.

Previous research has suggested that inorganic P is by far the most important form of runoff P. However, the research contained in this thesis has demonstrated that organic P can be a substantial component of runoff P in low to moderate fertility soils, but that its importance may vary between soils. The importance of organic P at Flaxley is a novel finding and the importance of organic P in runoff from other sites warrants further investigation. Future methodology for studying runoff P should include provisions to examine the importance of organic P. The cycling of organic P in relation to P mobilisation should also be considered.

The point at which soil P concentration becomes excessive from a runoff water quality perspective is not clear. A preliminary comparison of the soil P-runoff P relationships between several Australian sites and those reported in the literature from North America suggest that Australian soils are more ‘leaky’ with respect to P. The reasons for this are not clear and further examination of this issue is required to confirm (or otherwise) this phenomena. If Australian soils are indeed more ‘leaky’, an improved understanding of the factors controlling P release from these soils may contribute to the development of remedial strategies. The relationship between agronomically and environmentally optimal soil P requires further consideration. Data in this thesis shows that runoff P concentrations are relatively insensitive to changes in soil P until very high soil P levels are reached for the Flaxley site, whereas for the Camden soil there is a simple linear relationship between soil P and runoff P.

The observation of substantial vertical stratification of soil P highlighted the potential benefits that may arise from de-stratification of soil P. Rainfall simulation experiments in re-packed soil trays further highlighted these potential benefits but further research is required to evaluate this technique in a landscape context, including the role of landscape hydrological processes and P mobilisation/immobilisation. Techniques to more reliably and cheaply identify the spatial variation in landscape hydrology and soil P status require investigation. Recent developments in remote sensing offer the possibility to map soil moisture and P status. A better understanding of landscape hydrology may also improve ‘P risk indexing’ systems currently being developed for the Australian grazing industries.

The use of solid state ^{31}P NMR in this thesis was novel and resulted in several important advances in this technique. Although fundamental in nature, further development of techniques such as solid state ^{31}P NMR to examine soil P chemistry offer the potential to improve our understanding of P cycling in soil-pasture-runoff systems.

In summary, P in intensively managed pasture systems accumulates in the worst possible zone of the soil from a water quality perspective (i.e. the top several centimetres) from which it then moves into runoff via a process of diffusion. The dominance of dissolved P indicates that strategies that will reduce the labile pool of P in the top several millimetres of soil are best suited to reducing runoff P concentrations. Evaluation of one such technique (i.e. de-stratification of soil P by mixing) has shown that it has significant potential to provide a simple and quick but sustainable solution to the problem of excessive runoff P concentrations. However, further work is needed to evaluate the technique and its application at the landscape scale. However, the dairy industry should also consider the likely benefits of management strategies that avoid accumulation of P in the zone of runoff/soil interaction by reducing inputs.

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