Understanding Phosphorus Mobilisation in Surface Run-off from Soils

Bradley J. Mecozzi

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Understanding Phosphorus Mobilisation in Surface Run-off from Soils

Abstract
Managing phosphorus (P) import and export from pastures is a key issue in global agriculture. Knowledge of the amount and mobilisation of nutrients stored in soils can contribute to reducing nutrient runoff to water bodies, optimising soil fertility and improving fertiliser use efficiency. In particular, knowledge gained into the behavior of P can be crucial in developing strategies to prevent the export of nutrients from the soil to nearby water bodies which can lead to the degradation of aquatic environments. In this study, the degree to which P desorption and sorption reactions control the concentration of P in runoff was studied on a well characterised soil from the Camden region of NSW. Twelve runoff trays were constructed and rained upon with solutions of varying P concentrations. Runoff was collected at intervals throughout the runoff events and analysed for reactive P using the molybdenum blue method. Results showed that for the lower rain P concentrations desorption reactions controlled the concentration of P in runoff and vice versa, at the higher rain P levels. As the event continued the soil had less influence and runoff P levels tended to move towards the rain concentration. These results suggest that relatively large P concentrations can be removed from water as it flows over a low P soil. Such insights support the concept that P can be stripped from runoff to prevent its export from the paddock to adjacent water ways and that this can be achieved if farmers maintain a low P buffer zone between their productive pasture and nearby waterways.

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Understanding Phosphorus Mobilisation in Surface Run-off from Soils

by

Bradley J. Mecozzi

A research report submitted in partial fulfillment of the requirements for the award of the degree of

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2013
Abstract

Managing phosphorus (P) import and export from pastures is a key issue in global agriculture. Knowledge of the amount and mobilisation of nutrients stored in soils can contribute to reducing nutrient runoff to water bodies, optimising soil fertility and improving fertiliser use efficiency. In particular, knowledge gained into the behavior of P can be crucial in developing strategies to prevent the export of nutrients from the soil to nearby water bodies which can lead to the degradation of aquatic environments. In this study, the degree to which P desorption and sorption reactions control the concentration of P in runoff was studied on a well characterised soil from the Camden region of NSW. Twelve runoff trays were constructed and rained upon with solutions of varying P concentrations. Runoff was collected at intervals throughout the runoff events and analysed for reactive P using the molybdenum blue method. Results showed that for the lower rain P concentrations desorption reactions controlled the concentration of P in runoff and vice versa, at the higher rain P levels. As the event continued the soil had less influence and runoff P levels tended to move towards the rain concentration. These results suggest that relatively large P concentrations can be removed from water as it flows over a low P soil. Such insights support the concept that P can be stripped from runoff to prevent its export from the paddock to adjacent waterways and that this can be achieved if farmers maintain a low P buffer zone between their productive pasture and nearby waterways.
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1. Introduction

Phosphorus (P) plays a number of indispensable roles not only in natural systems but in human systems crucial for food production and, therefore, our overall survival. Phosphorus is used by plants for the processes of energy metabolism and transport, as well as driving most biochemical processes and growth in plants and animals (Brady and Weil 2008). P is also a major component of deoxyribonucleic acid (DNA) playing crucial roles in inheritance and the synthesis of nucleic acids and membranes (Raghothama and Karthikeyan 2005).

An ever increasing global population means food production is fundamental to our existence yet despite such a high degree of importance in our everyday lives, the finite resources of P are commonly misused and mismanaged in agriculture (Smil 2000). Cordell (2009) suggests that 90% of global demand for P is for food production and that currently around 148 million t of phosphate rock (the main source of P for mineral fertilisers) is consumed per year. Furthermore, many have predicted that existing phosphate rock reserves could be exhausted in 100-250 years (Haygarth, Delgado et al. 2013), (Stewart et al. 2005). Understanding the behavior of P in agriculture is therefore crucial for the ongoing productivity of our food production industries. The role and the importance of P in agriculture are discussed in further detail in the literature review (Chapter 2).

Australian soils, owning to their relative great age and highly weathered status, often have low plant available P levels, and lend themselves to the high usage of P fertilisers to obtain continued high crop yields. In 2011, Australian agriculture used over 4.8 million
t of fertilizer, in which, the approximate content of P was 384,120 t (FIFA 2011). Whilst the benefits of the use of P are clear, in recent years the effects of the loss of some of this added P to runoff and eventually into Australian waterways is becoming of increasing concern. The flow of nutrients from soil to waterways caused by the addition of fertilisers, in concentrations much higher than can be used efficiently by plants, is causing nutrient levels in some of Australia’s waterways to rise and the quality of these environments to fall (Nolan, Lawrance et al. 1995; Alaouze 1999). The increase in nutrient levels in rivers, creeks, lakes and other waterways results in the increased growth of algae and aquatic weeds. Decomposition of the algae and plants can cause a loss in oxygen availability within the water body. The consequent degradation of water quality results in the loss of productivity for all stakeholders including fisheries, recreation, industry and town water supply (Sharpley 1995).

Studies into the behavior of P in soil provide crucial insights into ways of minimising the detrimental environmental impacts of mismanaged P related to runoff and water quality at a local scale. The effects (both economic and environmental) of nutrient flow and the resulting eutrophication of waterways is clear in many areas of New South Wales (Nolan, Lawrance et al. 1995; Alaouze 1999) and indeed in the area of which this study has taken place. Studies on the Nepean River system have shown increases in the concentrations of nutrients as a consequence of anthropogenic inputs, particularly from sewage treatment plant discharges but also from urban and agricultural runoff during storm events (Markich and Brown 1998). Modern agricultural processes in the Nepean area, and indeed globally, need to maintain an appropriate balance between providing
sufficient P to sustain production, and minimising P transfer to prevent its impacts on environmental quality.

In order to achieve better management outcomes, a greater understanding of the behavior of P in agriculture, under various conditions, is important and provides a way of improving the efficiency of use of a resource as important as P. Developing and exploring a means of determining the concentrations of P in runoff from well watered pasture as well as the form and source of this P is crucial for improving agricultural management. Improvements in soil and agricultural management will enable managers to mitigate the effects of eutrophication worldwide as well as minimising the waste of P by farmers who have a financial interest in the efficient use of such fertilisers. Studies like this one provide greater insight into the complex chemical, physical and biological factors which impact on the retention or loss of P (particularly from P desorption) from soils.

1.1 Significance of this research

A large amount of time has been dedicated to the study of P use and behavior in agricultural systems. This is especially true of the processes that result in the transfer of P from the plant soil continuum to major waterways and further, in regards to the effects of this P on the overall health of such a waterway (Withers and Haygarth 2007; Haygarth, Delgado et al. 2013), (Zhang et al. 2013). However, several areas require more research, not least the forms of P released from soil and the mechanisms by which it is lost. In particular, studies into the contribution of P desorption from surface
soil into runoff are few and far between. This study attempts to fill this knowledge gap as a means of increasing the efficiency of nutrient management practices.

1.2 Aims

This study aims to determine the quantities of P in runoff during controlled trials as an empirical assessment of what would happen under field conditions. The knowledge gained will:

- contribute to the understanding of P mobility in agricultural soils in particular by:
  - investigating the degree to which P desorption and sorption reactions control the concentration of P in runoff from well watered pasture in controlled simulated trials;
  - determining the change in runoff P concentration over time and assessing how quickly P concentration in this runoff becomes stable.
- provide insight into means of stripping P from runoff to prevent its export from the paddock to adjacent water ways.

1.3 Outline of report

Following this introduction, the behaviour, mobilisation and importance of P in agriculture are explored in a review of relevant literature. This review provides the background knowledge to help inform the scope of the study and assist with identification of appropriate methods and interpretation of data. The soil collection and runoff analysis methods are then described and the results of the analyses and a discussion of their significance follow. These results are discussed and compared with
several similar studies which provide supporting evidence for the findings. Implications
of the findings for management strategies and the potential for limiting P loss to
waterways are explored. Suggestions are made for future studies and management
practices.
2. Literature Review

2.1 The importance of P in soils and the environment

Phosphorus is an essential element utilised by all life forms and is primarily conserved in soils and sediments. Among the nutrient elements, P is second only to nitrogen in its impact on the productivity and health of both terrestrial and aquatic ecosystems (Raghothama and Karthikeyan 2005). Phosphorus is an essential component in adenosine triphosphate (ATP) which plays a crucial role in energy metabolism and transport, driving most biochemical processes and growth in plants and animals (Brady and Weil 2008). P is also a major component in DNA and RNA, and hence plays crucial roles in genetic inheritance as well as the biosynthesis of nucleic acids and membranes in plants (Raghothama and Karthikeyan 2005).

Despite its vital importance to biology, plants have to strive hard to obtain P from soil. This is primarily due to the fact that the total quantity of P in most native soil is low and, much of the P is in forms that are unavailable to plants.

2.1.1 The importance of P in Agriculture

The development of sustainable land management practices for all ecosystems requires a fundamental understanding of the chemical, biological and physical processes in soils that affect the availability of P to plants (Pierzynski and Gehl 2005). This being the case, P deficiency is considered one of the major limitations to crop and pastoral production (Raghothama and Karthikeyan 2005). Much of the Australian continent experiences this nutrient deficiency as the inherent P content is at a level that is
inadequate to sustain continued intensive agricultural production. This has led to P being widely applied to Australian soils in order to improve their productivity (Ryan 2010). In some natural systems around the world, P is cycled naturally, through the plant-soil continuum, but in most agricultural systems, soil P is removed in the crop or animal biomass and therefore must be replaced if P deficiencies are to be avoided (Leinweber et al. 2002).

Mineral fertilisers and animal manures are the main products applied to agricultural land to raise soil P levels and maintain crop yields (Leinweber et al. 2002). These P inputs are primarily designed to increase and maintain soil P and replace P removed from the soil. P is a non-renewable resource and, as such, these continued inputs are necessary to sustain the productivity of agricultural systems and satisfy the consumption needs of an ever increasing global population. As P is a finite resource however, with many predicting supplies could be exhausted within 100-250 years (Haygarth, Delgado et al. 2013), (Stewart et al. 2005), it is important that the most efficient means of P replacement, in soils, are chosen by landowners.

Whilst the benefits of adding P to the soil are clear, problems occur when P is applied in levels that are in excess of the amounts required for optimum plant growth (Leinweber et al. 2002). The small amounts of P lost from the soil (Figure 1) can have severe impacts on water quality in receiving catchments.
2.1.2 The issues associated with P fertiliser - the importance of good P management

Continued input of P fertiliser into agricultural systems above the levels required by crops or pasture is leading to a build-up of P in the soil and an increased risk of environmental damage from P loss to water. Frequently, the practices designed by landowners to increase biological productivity of their soils will also increase the biological productivity of the waters draining these soils (Sharpley 1995) and will accelerate eutrophication (the enrichment of waterways that stimulates excess plant and algal growth) in surface waters. In the past, nutrient pollutants have been mostly derived from point sources such as sewerage or stormwater outlets from urban areas; but in recent years, efforts have been made and infrastructure put in place to reduce
nutrient flow through these pathways (Sharpley 1995). Now the focus for many is on nutrient flow, especially P flow, from agriculture to water bodies, such as lakes and rivers but also eventually to ocean waters. Agriculture has been identified in a number of studies as the major source of nutrients, with one USA study finding that 50% (lakes) and 60% (rivers) of nutrient pollution was derived from nearby agricultural zones (Daniel, Sharpley et al. 1998).

Smil (2000) determined that the worldwide anthropogenic loss of dissolved P from land is roughly equal to the natural rate which suggests better P management is required in a general agricultural sense. Smil (2000) also stated that catchments heavily fertilised by a combination of manures and phosphates may be discharging several kg of P/ha every year. Surface water concentrations of P between 0.01 and 0.02 mg/L are considered critical values above which eutrophication is accelerated (Daniel, Sharpley et al. 1998) meaning that most agricultural discharges would lead to some degree of nutrient enrichment in water bodies. These surface water concentrations are considerably lower than concentrations of P in soil solution critical for plant growth (0.2-0.3 mg/L) (Daniel, Sharpley et al. 1998), which suggests that even relatively small losses of agricultural P to waters may contribute to undesirable eutrophication. It is, however, problematic to restrict the losses to the point where they do not cause such a problem.

2.1.3 Consequences of runoff

The degradation of waterways that results from the receipt of P enriched runoff from agricultural zones is detrimental to a range of activities and stakeholders. The increased growth of algae and aquatic weeds and the oxygen shortages caused by their
decomposition, impact on fisheries, recreation, industry, drinking water (Sharpley 1995) and the overall aesthetics and amenity of an area. Modern agricultural processes need to maintain an appropriate balance between providing sufficient P to sustain production, and minimising P transfer to prevent its impacts on environmental quality. This will only be achieved by developing further understanding of the way P interacts with soil and the environment based on continued research. This study aims to contribute to our better understanding of soil-P-water interactions.

2.2 The behaviour of P in soil

The interaction between biological, chemical and physical properties and processes, together with the history and intensity of land use and management of an area determine the forms, concentrations, dynamics and mobility of P in the soil (Condron 2004).

2.2.1 P Quantities and forms in soil

P in natural systems originates from the weathering of soil minerals and other geological material such as phosphate rich rocks. Through chemical and physical weathering, P becomes solubilised and is either accumulated by plants and animals, altered and stored as inorganic and organic forms in the landscape or it is removed from soil and deposited as sediment in waterways (Condron 2004). In intensively managed agricultural ecosystems, P is typically supplied in large amounts via fertiliser inputs as previously discussed. This system of addition, use and removal or recycling is known as the soil P cycle (Figure 1), a complex cycle heavily influenced by a number of factors such as the forms of P present, the amount of biological activity in the soil, soil
chemistry (e.g., pH) and environmental factors such as soil moisture and temperature (Pierzynski and Gehl 2005).

The total P concentration in soils generally ranges from 50 to 3000 mg/kg, with 50-70% found in inorganic forms in mineral soils; in organic soils, however, 60-90% of total P is found in organic forms (Condron 2004). Minerals weather to release P into the soil solution and the type of mineral that does this varies between soils. In unweathered or moderately weathered soils, the main form of inorganic P is calcium phosphates. In areas of intense weathering calcium phosphates and other basic minerals leach from soils and precipitates with iron and aluminium then form and become the main source of soil P in these cases (Pierzynski and Gehl 2005). Iron and aluminium oxyhydroxides are also common in highly weathered soils and can either further release P (very slowly) for use by plants or bind and store P (more likely) through chemical reactions known as sorption and desorption (discussed further later) (Pierzynski and Gehl 2005). These inorganic forms of P are dissolved or desorbed from mineral forms into solution in the form of primary or secondary orthophosphates, depending on soil pH, and these are the forms readily available for uptake by plants (Pierzynski and Gehl 2005). A soil solution P concentration of greater than 0.2 mg P/L is widely regarded as the concentration needed to achieve optimum intensive plant growth (Daniel, Sharpley et al. 1998; Pierzynski and Gehl 2005), but lower concentrations tend to be the norm in most agricultural systems.

The solution P derived from the breakdown of the sources mentioned above is taken up, utilised and stored by plants. In natural ecosystems, this P is eventually cycled back into the soil when the plant dies or drops leaves, branches and roots or through the addition
of animal manures or bio solids. Common forms of organic P in soil include inositol phosphates, phospholipids, phosphoglycerides and phosphate sugars (Pierzynski and Gehl 2005). With time, much of the organic P returned to the soil by natural processes is broken down (mineralised) by microorganisms and converted to soluble and inorganic forms of P (Pierzynski and Gehl 2005) (accessible to plants) at a rate that is determined by the type of organic matter and the nature of the soil (Figure 2).

Figure 2: The transformations and transport of organic P in the soil system (Pierzynski and Gehl 2005).

In agricultural systems, most of the P accumulated by a plant is lost to the soil when the plant is removed upon harvest, but some is returned to the soil via crop residues. In
animal based agriculture, plant P, in the form of grain and other feeds, is transformed into manure (by livestock) and returned to the soil. Organic by-products, such as manures, are commonly used across a wide variety of situations to return or increase P concentrations in soil; however, because these by-products may be added frequently over relatively small areas, soil P can build up to values of environmental concern. It is for this reason that finding more environmentally sound and efficient ways of returning P to soil is a significant issue in soil management.

2.2.2 Addition of P - what happens to added P?

Both organic and inorganic sources of P such as commercial fertilisers, manures, biosolids or even industrial by-products (e.g., sugar mill mud) are added to the soil to ensure that P deficiency does not inhibit plant growth (Pierzynski and Gehl 2005). The form of added P is important, as the behaviour of P in soil will in some ways be dictated by the form added.

Commercial P fertilisers are common sources of inorganic P, and are produced by an industrial process where phosphate rock is reacted with an acid (Leicam et al. 2005). These fertilisers are chosen for situations where intensive crop based agriculture is taking place, and a rapid growing cycle is required and harvest is soon followed by re-sowing. Animal manures, biosolids and composts are sources of organic P and may be used on less intensive agricultural system as a lower cost means of reusing these by-products effectively to add P to soil. These sources, however, normally contain much lower concentrations of P than commercial fertilisers.
Once added to soil, P can behave in a number of ways. Inorganic P can become fixed by way of precipitation into a mineral form or by sorption reactions (Frossard, Condron et al. 2000). Inorganic P can also become solubilised by way of mineral dissolution and desorption reactions. Soil organic P transformations are primarily mineralisation-immobilisation reactions performed by soil microorganisms (Frossard, Condron et al. 2000), and also the simple uptake of solution P by plants.

2.2.3 Sorption and desorption reactions

Sorption is the term used to describe the transfer (in this case) of P from solution form to a solid phase in soil and involves the formation of a chemical bond between a phosphate anion and a soil colloid (Pierzynski and Gehl 2005). Solution P is not thermodynamically stable in the presence of soil and so undergoes these reactions, largely with metal oxyhydroxides and aluminosilicate clays, to form less soluble, more stable compounds (Pierzynski and Gehl 2005). These reactions largely take place on the surface of soil constituents such as clays and oxyhydroxides and result in the retention of P in the soil. After the initial surface reaction, where either ligand or anion exchange between the solution P and soil particle occurs, the P moves slowly to the interior of the particle or is buried by the growth of particles or their adhesion and such become less accessible to plants (WA Department of Agriculture 2003).

The amount and rate of P sorption varies with the concentration of P in soil, the pH, the clay and Fe/Al content as well as depth in the soil column and past soil management practices (WA Department of Agriculture 2003). In summary, acidic soils with low
concentrations of P and organic matter and high clay and Fe/Al content typically have the greatest P sorption capacity.

Desorption refers to the release of soil P from the solid phase, mentioned above, into the soil solution via diffusion arising from a concentration gradient. This process occurs when soil P solution concentrations become very low as a result of runoff, leaching or uptake by plants or microbes. In the case of plants, active uptake of P by root hairs causes the concentration of P nearby to decrease. This drives the desorption process whereby P is released from the soil particles (by diffusion) into solution (WA Department of Agriculture 2003).

2.2.4 Dissolution, Mineralisation and Precipitation of P in soil

Perhaps the simplest transformation of P in soil is the weathering of primary minerals containing P to slowly release orthophosphate to the soil (Pierzynski and Gehl 2005) via dissolution. The reverse of this process is the precipitation of secondary minerals from saturated soil solutions, i.e., the formation of insoluble, solid compounds in soil.

Mineralisation is a process whereby the decomposition of organic compounds (from manures, bio-solids, etc.) by microorganisms in the soil results in the release of inorganic P into the soil. These reactions are achieved through the work of enzymes released by microorganisms and roots with enzyme production increasing when P concentration is low (Pierzynski and Gehl 2005). Mineralisation of organic P sources is largely controlled by the amount of carbon in the soil as it is the carbon levels in soil that will determine the amount of microbial activity. Microorganisms can also take available
P from the soil and alter it into biochemical compounds essential to their survival, thus competing with plants for the pool of available P.

2.2.5 Bioavailability of P

As noted above, solution P, the main source of P for plants, usually has concentrations between 0.01 and 3.0 mg/L (Frossard, Condron et al. 2000). This, however, is a far lower concentration than most plants store in their tissues (often in the range of 0.1-0.9% dry matter), i.e., P uptake is an active process. Uptake from solution provides only part of what the plant requires and the rest of the required P must be obtained from the solid phase in soil by a combination of the physical and biological processes mentioned above and in section 2.2.6. As such, the availability of soil P to plants depends partially on the balance between the rate of mineralisation and immobilisation of soil P, which is in turn related to the amount of microbial activity. The factors that affect the amount of microbial activity (temperature, moisture, pH and aeration) will therefore affect the bioavailability of P to plants. Shigaki and Sharpley (2011) found that the main soil characteristic affecting soil P availability to plants was the P sorption maximum, which is a function of pH, clay, organic C, Fe and Al contents.

The forms of P utilised for plant uptake are the $\text{H}_2\text{PO}_4^-$ and $\text{HPO}_4^{2-}$ ions (Whitehead 2000). The rate of uptake of these two ions is determined by their concentration in the soil solution surrounding the roots and also partly by the rate of movement of the ions towards the root surface (Whitehead 2000). Plant demand for P varies between species and throughout the lifecycle. The rate of movement through soil is usually slow due to P becoming immobilised via precipitation and adsorption by soil constituents such as
clays and metal oxyhydrides. As a result, P uptake is considered to be primarily controlled by the rate of root growth and the number of root hairs (Whitehead 2000), rather than by P transport to the root surface by mass flow.

2.2.6 The role of mycorrhizal fungi in supplying P to plants

Mycorrhizal fungi are present around the root systems of most plants in terrestrial ecosystems and crop production systems, mediating interactions between the roots and the soil (George et al. 1995). This mycorrhizal symbiosis is based on the exchange of carbon from the plant in return for P and other mineral nutrients from the fungus (George et al. 1995). Schactman et al. (1998) suggest that the access of roots, colonised by mycorrhizal fungi, to P can be 3 to 5 times higher than in non mycorrhizal roots. It is this symbiotic relationship which enables the plant to compete more successfully with other soil organisms for nutrients and in doing so support its own growth. This increase in availability is due to the development of a network of external hyphae, which absorb and translocate phosphate and other mineral nutrients from the soil to the root more efficiently than the plant can achieve alone (Harrison 1997). Many studies have shown that improvements in growth, health and stress resistance of mycorrhizal plants are considerable (Harrison 1997, Schactman et al. 1998).

2.2.7 P measurement methods and interpretation

The main goal of most soil P testing is to identify the optimum soil test P concentration required for crop growth and from this the amount of fertiliser required to be added; the economic benefit of doing so can also be calculated (Sims 2000). To do this, we
chemically extract an amount of P that is proportional to that which will be available to
the crop during the growing season (Sims 2000).

As previously mentioned, much of the P that is potentially available to plants in soil
solution is quite low and, as such, the assessment of plant available P therefore
depends mainly on the measurement of P stored in the soil solids that can become
plant available. The methods that have been developed are based on dissolving or
extracting the P from the soil using an extracting solution (Whitehead 2000) such as
sodium bicarbonate or sulfuric acid. There are many of these soil P tests available, each
using a differing extract and each designed for use on soils with certain characteristics.
One such test is the “Olsen P” test which is based on the use of a pH 8.5, 0.5M
NaHCO$_3$ solution to decrease the solution concentrations of soluble Ca$^{2+}$ (by
precipitating it as CaCO$_3$) and soluble Al$^{3+}$ and Fe$^{3+}$ (by forming Al and Fe
oxyhydroxides) (Sims 2000). Eliminating these compounds increases the solubility of P
which can then be effectively measured in solution. The “Olsen P” test does not extract
all the potentially available P but it does provide a means of categorising soils in terms
of plant available P, and is used in this way as a basis for fertiliser recommendations
(Sims 2000).

Other P testing methods including “Colwell P” test (which also uses sodium
bicarbonate) and the “Bray 2” soil test (which uses ammonium fluoride and hydrochloric
acid) rely on similar chemical reactions to extract P.

Once test results are obtained, fertiliser rate recommendations are developed using
crop response data that have been obtained within a region with similar soils, cropping
systems, and climatic conditions (Sims 2000). To be effective, the results of the tests must be calibrated to the soils and cropping systems in place in the geographical region of interest.

### 2.3 Mobilisation of P in surface runoff

The mobilisation of P is its transfer from the various pools in the soil–plant system into surface runoff (Dougherty et al. 2004).

#### 2.3.1 Mechanisms for loss of P from soils - Physical vs. Chemical

P is inevitably lost from the soil-plant system. The nature and rate at which this loss occurs depends on a number of factors. The soil chemistry (e.g., pH), degree of biological activity (i.e., soil microorganisms), the soils physical characteristics (i.e., clay vs. sand content), and the hydrology (i.e., rainfall and runoff patterns) of an area all play a role in determining the rate and concentration of P in runoff. Dougherty et al. (2004) classified the processes of P mobilisation and transfer into two broad categories: physical (which involves the detachment and entrainment of whole soil particles containing P), and chemical (which involves the release of P into solution). These processes not only involve P contained in the soil but also added P from manures, fertilisers and plant remains.

The upper section of Figure 3 illustrates rainfall flowing across the surface of the soil that can either dissolve and transport P in solution (chemical mechanism) or pick up and transport entire soil particles or colloids and with them the sorbed P they contain (physical mechanism). In intensive pastures where ground cover is near 100%, P in
surface runoff consists mainly of soluble P or fine soil particles. In areas where ground cover is limited due to overgrazing/trampling, or around paths, gates and feed troughs, P in runoff is predominantly in particulate form (Dougherty et al. 2004).

Physical transfer can be by way of sedimentation or detachment whereby soil particles are mobilised by some external energy such as a raindrop impact or flowing water (Pierzynski and Gehl 2005), (Leinweber 2002). Particulate matter in surface runoff can be either colloidal particles (1 nm to 2 um), or soil aggregates of sizes less than 10 mm (Dougherty et al. 2004). The process of physical mobilisation becomes increasingly common on pastures that are heavily grazed where the soil surface becomes exposed: gully and rill erosion further accelerate the rate of physical transfer. This is in contrast to well pastured sites where plant cover will intercept raindrops or slow the flow of surface runoff, and as a result, limit the amount of physical detachment of soil particles. Smil (2000) considers that grasslands and forests have negligible soil erosion rates compared to land planted to annual crops and as such suggests that up to 90% of all soil erosion from cropped land is a consequence of losing canopies, leaf litter and the dense roots of native vegetation.

Most of the P lost from soils is by way of physical surface processes, such as, erosion and overland flow, associated with recent rainfall events (Pierzynski and Gehl 2005). In terms of chemical mobilisation, however, dissolution is the main process whereby P is chemically mobilised and involves the water sitting on the surface of the soil or flowing slowly, allowing P to desorb into solution and be transported away.
2.3.2 Studying P release: past experiments

Rainfall simulation is widely used to evaluate the effects of land management on erosion, nutrient mobilisation and quantities at a range of different conditions (Dougherty et al. 2004). Nash et al. (2004), Miller et al. (2006), and Wright et al. (2006) all employed rainfall simulators to study P mobilisation and release rates at various scales. This technique is frequently used as it seems to be a simple means of allowing multiple measurements to be made whilst being able to easily alter the test conditions.
Dougherty et al. (2004) suggested that such tests produce the best results for the relationship between soil P and runoff when undertaken at small scales. This is due to the fact that small scale pure soil pasture systems have a high uniformity and the effects of rainfall variations, biomass, livestock and fertiliser differences are minimised.

2.4 Summary of key points

The small amounts of P lost from the soil can have severe impacts on water quality in receiving catchments. For this reason it is important to understand the behaviour of P in soil, the reasons for its mobilisation and possible means of preventing P loss to the environment. Rainfall simulation is a simple and effective way of studying such processes on a small scale and to develop a greater understanding for future management.
3. Materials and Methods

This chapter presents details on the methods of collection and preparation of the soil used for the experiment. The raining and sampling processes as well as the specific analysis techniques used to determine the concentration of P in runoff are also explained.

3.1 Soil Sampling and Preparation

For the purpose of determining the influence of P sorption from surface soil on subsequent runoff, a single well-characterised soil was selected for the study. The site selected for the collection of soil was a flat paddock, previously used as grazing pasture for a dairy farm located in Camden, south-western Sydney (0288843E, 6224579N). A bulk sample (500 kg) of topsoil (0-10 cm) was collected from the chosen site by firstly using a rotary hoe to loosen the soil from a small strip of pasture. A gauge was used to ensure the correct depth (0-10 cm) of soil had been reached and the desired amount was then collected and placed into bins. A smaller sample (50 kg) of 0-2 cm topsoil was also collected, this time by hand, in areas where there was little grass cover in order to ensure an accurate collection of topsoil at the desired depth.

The soils collected were cleared of large unwanted vegetation and left to dry for several days. Once dry, each bulk soil sample was separately passed through a 4 mm sieve to ensure only fine soil remained. This soil was then thoroughly mixed to ensure homogeneity. Grass clippings small enough to fit through the sieve also found their way into the treated soil, so perhaps future methods should include another sifting process perhaps at 2 mm to prevent this from occurring.
An XRF (X-ray florescence) spectroscopy was carried out on a sample of 0-10 cm soil and also a sample of 0-2 cm soil. For this test approximately 5.5 grams of crushed, fine, homogenous powder was combined with about 10 drops of polyvinyl alcohol binder in a paper cup using a wooden stirrer. After mixing, the sediment was placed in an hydraulic press where the sediment was pressed at 2500 p.s.i. forming a robust pellet. The pellets were left in the oven at 80°C for a period of 2-3 days and then weighed. Each sample was placed into the chamber of an energy dispersive X-ray fluorescence spectrometer, where they were analysed against a suite of calibration standards.

A standardised procedure used in numerous previous studies including Dougherty et al. (2011) was followed in the construction of 12 plywood runoff boxes [100cm long, 20 cm wide, 10 cm deep (front), 12.5 cm deep (sides and rear)] to contain the soil for the rainfall simulation trial (Figure 4).

Figure 4: Constructed runoff trays following known procedures and showing soil packed to the lowest edge.
The collected bulk soil (0-10 cm) was packed to just below the front edge of each box and watered to near saturation to allow the soil to suitably compact to a bulk density approximating that occurring in the field. Additional soil was added where required to ensure little subsidence occurred upon subsequent additions of water. Dougherty et al. (2004) suggest that the concentration of P in the topsoil is particularly important in determining runoff P concentrations because this is where the runoff interacts with the soil the most. Phosphorus concentrates in the topsoil in permanent pasture systems with the highest concentrations being closest to the surface and as such the interaction of surface runoff with the soil is greatest at the surface and declines exponentially with depth (Dougherty et al. 2004). It is clear that there is a much higher P content in the 0-2 cm samples and with this research in mind, an approximately 1 cm layer of topsoil (0-2 cm material) was placed over the top of the bulk soil to replicate the variations in soil characteristics between these two layers in the field and thus further ensuring a more accurate representation of field conditions was achieved. The repacked boxes were watered and left over night on a level surface to settle before sowing (see Figure 4).

Boxes were hand sown at a rate 5 times that of the recommended rate, with a commercially bought lawn mix consisting of a combination of fescue, cocksfoot, ryegrass and bent grass. Seeds were lightly raked into the surface soil. The boxes were then placed in an area of full sun and watered every second day until the grass had reached a height of approximately 10 cm and a consistent vegetative covering had formed to prevent the loss of topsoil. After a week of growth 2 g (corresponding to a rate of 100 kg/ha) of urea was evenly spread over the surface of the soil in each box to boost growth.
3.2 Rainfall Simulation

A drip rainfall system was chosen as the best means of replicating a rainfall event in a pastoral setting (Bowyer et al. 1989). The set up involved a rectangular Perspex simulator, containing many plastic tubes with fishing line inserts, which ensured a consistent drop formed at the head of each tube. The simulator was supported 1 metre above the ground and a holding container above the simulator was constantly fed water so as it maintained a constant 'head', ensuring near constant water pressure.

Figure 5: (Left) Rainfall simulator during calibration phase, showing collection containers and raining simulator. (Right) Final simulation set up during uniformity testing, showing holding container, runoff boxes and gutter system.

To calibrate the system, 12 small containers were placed under the rain simulators in a symmetrical fashion (see Figure 5), and were left to catch rain for a period of 15 minutes. The volume in each container after this period was measured and recorded, allowing for a conversion to calculate rainfall intensity (mm/hr).
3.3 P Uniformity Testing

For the purpose of allocating subsequent treatments, a test of background runoff P concentrations for each tray was undertaken. Each runoff tray was given enough water the morning of the test to ensure the soil was thoroughly saturated before being placed under the simulators. This procedure meant that there was not a long period of time between the initiation of rain and the commencement of runoff. Two boxes were placed under each of two simulators (see Figure 5), using timber and bricks to ensure they were sitting at a gradient of 5% and were then covered by a plastic sheet. The simulators were filled with tap water and allowed to reach the rainfall intensity determined in the calibration testing. At this stage the plastic sheeting was lifted and rain began to fall on the boxes. A separate timer was started when runoff was visible on each box and rain was allowed to continue for 30 min thereafter. All runoff was collected from each box using a simple gutter system which fed into a nearby bucket. The total volume collected and the time at which runoff started was recorded for each box. A small amount of each collected runoff sample was filtered and frozen for future analysis.

3.4 P in rain testing

For this, the main test of this project, the same rainfall simulators were used as in the above test and the soils in the runoff trays were pre-wet the night before the testing. Six P concentrations (0, 0.075, 0.15, 0.3, 0.6 and 1.2 mg/L) were selected to be the concentrations of P in the solution used to rain upon the runoff trays (Table 1). This range of values was selected as they were considered to represent concentrations experienced in the environment. Using the results from the initial tray uniformity testing,
one high and one low concentration tray was randomly allocated to each of the 6 treatments. Raining solutions were made up from a standard solution of P (1000 mg/L) into 50 L bins, using the ratios listed in Table 1, and a sample of each was collected for testing.

3.75 ml of 1000 mg/L stock in 50 L water = 0.075 mg/L solution
7.5 ml of 1000 mg/L stock in 50 L water = 0.15 mg/L solution
15 ml of 1000 mg/L stock in 50 L water = 0.3 mg/L solution
30 ml of 1000 mg/L stock in 50 L water = 0.6 mg/L solution
60 ml of 1000 mg/L stock in 50 L water = 1.2 mg/L solution

Table 1: Volumes used in preparing raining solutions.

These solutions were thoroughly mixed they were then added to the simulators (with the selected pair of runoff trays beneath) and raining was initiated. Once runoff was observed a timer was set for 40 min and a sub-sample of the runoff taken every 5 min. The remaining runoff was collected in a bucket so a composite sample could be taken at the end of the 40 min. All sub-samples and a sub-sample of the composite were filtered (0.45 µm) immediately and frozen for later analysis.

The overall runoff rate and volume were not recorded but observations indicated that the rate of rainfall, runoff and the overall volume of runoff were very consistent between the simulators and between the individual runoff trays. The only thing that varied slightly between trays was the time until runoff started and this may have been due to the fact that some of the trays used later in the day had had more time to dry out than those used first.
3.5 Solution P sample analysis

Run off samples for each tray were analysed in the laboratory using the molybdenum blue method - widely used to approximate inorganic P - based on Murphy and Riley (1962). This method involved the addition of a mixed colour reagent to the sample, allowing colour to develop for 30 minutes and then reading the absorbance of the sample on a spectrophotometer. Known standards (0, 0.5, 1, 1.5, 2, 2.5 mg/L) were used to create a calibration curve for the analysis and an independent standard used for verification.
4. Results and Discussion

The investigation was a proof of concept study and as a result the inferences and conclusions that can be drawn are somewhat tentative, but nonetheless will help increase knowledge about the behaviour and transport of P in soil and as such help improve the management of P as a limited resource.

4.1 Soil properties

The soil for this study was taken from a former dairy pasture system which has returned to a dry land (unirrigated) system in the past 10 years. The soil itself is a Haplic Eutrophic Brown Chromosol (Isbell 2002) with an A1 horizon to 25 cm, having about 30 % clay and a pH in CaCl₂ of ~4.7. Organic carbon is ~1.5 % and it has an ECEC of ~12 (cmol+/kg). Colwell P analysis shows a concentration of ~26 mg/kg (Dougherty 2006).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>XRF Code</th>
<th>P (ppm)</th>
<th>S (ppm)</th>
<th>Cl (ppm)</th>
<th>V (ppm)</th>
<th>Cr (ppm)</th>
<th>Ni (ppm)</th>
<th>Cu (ppm)</th>
<th>Zn (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-10cm</td>
<td>HONS839</td>
<td>402</td>
<td>457</td>
<td>474</td>
<td>89</td>
<td>57</td>
<td>65</td>
<td>25</td>
<td>35</td>
</tr>
<tr>
<td>0-2cm</td>
<td>HONS840</td>
<td>683</td>
<td>731</td>
<td>96</td>
<td>84</td>
<td>53</td>
<td>70</td>
<td>24</td>
<td>53</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>As (ppm)</th>
<th>Se (ppm)</th>
<th>Rb (ppm)</th>
<th>Sr (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>1</td>
<td>71</td>
<td>64</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>61</td>
<td>70</td>
</tr>
</tbody>
</table>

Table 2: XRF data for the Camden soil.
An XRF analysis performed on the Camden soil showed a higher concentration of P and S in the top 0-2 cm of soil than in the 0-10 cm sample (Table 2). This confirms the concentration of P in the uppermost soil layers is greater, and validates the method of placing a layer of the 0-2 cm soil on the surface of the trays. All other elements displayed show that there are no unusual chemical features in the selected soil.

4.2 Tray uniformity

Initial uniformity testing for each runoff tray was carried out and the results of these tests (Table 3) used to allocate individual trays to each treatment. A high and low initial concentration tray was allocated to each treatment; this may contribute to some of the variations in concentrations between replicates as reported later in Figure 7.

<table>
<thead>
<tr>
<th>Tray number</th>
<th>P Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.156</td>
</tr>
<tr>
<td>2</td>
<td>0.156</td>
</tr>
<tr>
<td>3</td>
<td>0.219</td>
</tr>
<tr>
<td>4</td>
<td>0.232</td>
</tr>
<tr>
<td>5</td>
<td>0.147</td>
</tr>
<tr>
<td>6</td>
<td>0.189</td>
</tr>
<tr>
<td>7</td>
<td>0.208</td>
</tr>
<tr>
<td>8</td>
<td>0.120</td>
</tr>
<tr>
<td>9</td>
<td>0.156</td>
</tr>
<tr>
<td>10</td>
<td>0.230</td>
</tr>
<tr>
<td>11</td>
<td>0.149</td>
</tr>
<tr>
<td>12</td>
<td>0.188</td>
</tr>
</tbody>
</table>

Table 3: Initial runoff tray uniformity data.
4.3 Rain simulation results

Measured rainfall P concentrations were generally close to the target concentrations set out in the experimental design (see Table 4). The concentrations of P in the collected runoff solutions were quite low (in most cases) such that measured concentrations may be subject to analytical errors that may have contributed to the variations in the observed relationships.

<table>
<thead>
<tr>
<th>Target rainfall P conc. (mg/L)</th>
<th>Measured rainfall P conc. (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.075</td>
<td>0.04</td>
</tr>
<tr>
<td>0.15</td>
<td>0.12</td>
</tr>
<tr>
<td>0.3</td>
<td>0.25</td>
</tr>
<tr>
<td>0.6</td>
<td>0.54</td>
</tr>
<tr>
<td>1.2</td>
<td>1.25</td>
</tr>
</tbody>
</table>

Table 4: Rain solution concentrations.

Flow rates were not measured during this experiment so in calculating mean event concentrations we assumed constant runoff rates as a first approximation of mean event concentrations. As will be discussed below this assumption probably impacts little on the broader implications of interpreting the data using mean P concentrations. Future studies should measure runoff rates to enhance the strength of any inferences.

Examined first was the relationship between the P applied and the P in runoff (Figure 6) and it was determined that runoff concentrations vary substantially during a rainfall event. Following this, interest was principally the effect of the addition of solution
containing P and whether, depending on concentration, sorption or desorption reactions were dominant. The change in P concentrations, i.e.: delta concentration; (runoff P concentration minus rainfall P concentration) was plotted against rainfall P concentration (Figure 6). It appears that when delta concentrations (conc. final – conc. initial) are >0 desorption is occurring and when <0 sorption is occurring.

Figure 6 suggests that even with very short residence times relatively large P concentrations can be reduced substantially from runoff as it flows over a low P soil. At the lower added P concentrations (≤ 0.075 mg/L) a degree of desorption occurs whereby soil P is mobilised into the runoff resulting in a runoff P concentration higher than was present in the rain. The opposite appears to be true of the higher rained P concentrations. Here P present in the rain is strongly sorbed by the soil and the resulting runoff is of a concentration less than that contained in the rain. The extent of this sorption process however is constrained by reaction time which is likely to be itself constrained by the short residence time of runoff on the plots and thus in contact with the soil. As such, the amount of P sorbed by the soil is limited by hydrological factors, that is, the interaction of the water and the soil throughout the trial.

The ‘x’ intercept in Figure 6 represents the background concentration of P in the soil and it is at this point where rained P will runoff at the same concentration (Pin=Pout). This is the case because, at this point, there is nothing to drive the process (no concentration gradient) one way or the other in terms of reaching equilibrium.
The relationship between the P applied and the P in runoff over time for each of the trays and rainfall P concentrations is presented in Figure 7. Although runoff/flow rate was not measured in this study, it is widely accepted that in controlled rainfall simulations there will be variations in the runoff rate throughout the duration of the rainfall event (Dougherty 2006). The runoff concentration over time plots in Figure 7
reveal that this difference in flow rate plays a role in the concentration of P in runoff.

Dougherty (2006) altered rainfall intensity and Figure 8 depicts that rainfall intensity had a significant effect on the chemical characteristics of the runoff.

At the beginning of any runoff event, the runoff rate is relatively low, there is a shallower depth of flow and thus the water has a longer residence time within the soil (Dougherty 2006). At the end of the runoff event the opposite is true, i.e. the flow rate and depth are greater and the residence times shorter. Dougherty (2006) similarly found that increasing the rainfall intensity (equivalent to the faster flow of the water as the event continues) resulted in significantly shorter runoff residence times and increasing depth of flow (Figure 8).
Figure 7: Runoff P concentration over time plots for each treatment.
Figure 8: The effect of varying rainfall intensity on the mean DRP (dissolved reactive phosphorus) concentration. (Source: Dougherty 2006)

All of the plots in Figure 7 suggest that as the rainfall event progresses the runoff P concentration moves towards the concentration of the added solution. This is perhaps due in part to the fact that there is insufficient time for the soil and runoff to equilibrate as residence time decreases as the event proceeds. This is especially evident in the 0.075 mg/L and 0.6 mg/L plots and these two graphs are possibly the best representation of the reactions taking place.
Figure 9: Runoff P concentration plots over time for the 0.075 and 0.6 mg/L treatments.

Both replicates of the 0.6 mg/L trial sorbed P more strongly at the start of the rainfall event than at the conclusion. This could either be due to the short term blocking, or occupation of sorption sites as the P floods the system when it is added quickly in a higher concentration. Alternatively as the event progresses, the hydrology of the plots changes and this is perhaps the more likely reason as to why runoff concentrations vary during the event. When the event begins only a small amount of the added water runs off, as infiltration is high initially. As the soil reaches saturation, effectively all of the water runs off the plots; consequently, towards the end of the event, there is a greater depth of water which flows more quickly across the surface of the soil.
The plots to which 0.6 mg/L P rainfall was added had runoff P concentrations that were much lower than the rain concentration at the start of the event due to the reasons mentioned above. The water appears to be sitting for long enough to allow much of the added P to be sorbed by the soil, allowing the water to return to the background P concentration of the soil. The runoff P concentration then increases as the event continues as the flow rate increases and residence time is reduced. The water in this case is not in contact with the soil for as long and there is less time for the P concentration to move toward equilibrium or the background concentration for the soil. For these reasons the runoff concentration is moving towards the concentration of the added solutions as the soil has begins to have less influence.

In the 0.075 mg/L plot, the initial runoff P concentration is much higher than the rain concentration; however, as the event progresses the concentration moves back towards the rain concentration. Again this is due to the hydrology of the soil; at the start the water has a higher residence time and has more time for P to equilibrate. Dougherty (2006) also found that an increase in runoff residence time will lead to an increase in attainment of equilibrium between the soil P source and runoff. Here a degree of desorption occurs as P moves out of the soil so as the water can reach the background concentration. At the end of the event there is less chance for these desorption reactions to occur and we see a decrease in concentration. The increase in the depth of runoff water on the soil surface will result in a slower attainment of equilibrium (Dougherty 2006) and thus lower runoff P concentrations.
Figure 10: Change in P concentrations against P added and theoretical 1:1 line.

The 1:1 line depicted in Figure 10 represents the theoretical runoff concentrations where the soil has had no influence (P initial=P final). The difference between this 1:1 line and the experimental curve can be considered the diffusion limitation gap. The experimental results do not follow this line (and always runoff at a concentration equal to the rain concentration) because the soil cannot release or take in enough P to allow that to occur. This process could either be rate or source limited; however, there was a
constant source of P in the rain solution in this experiment; therefore, it is almost certainly limited by the rate (of diffusion). This is in contrast to Dougherty’s (2006) trial where only a fixed amount of P was available to be mobilised and the size of the pool declined due to the continual removal and dilution of the available P. Figure 10 shows that the size of the gap (between the experimental curve and 1:1 line) tends to increase as higher P concentrations are rained on the soil either due to short term blocking of sorption sites or due to that fact that there is so much P available that sorption sites are quickly taken up.

The insight that relatively high P concentrations can be stripped from water when it flows over low P soil - even with very short residence times - could be of particular importance to understanding P dynamics at a paddock, farm and or landscape scale. In a farm situation high concentrations are observed in runoff from laneways, cattle camps and water troughs, all areas, which due to their frequency of use, receive increased inputs of P (from dung). A study by Lucci et al. (2010) found that DRP (dissolved reactive phosphorus) export was much greater (per unit area) from both laneway and trough areas compared with the greater pasture areas and that these sources need to be addressed in management decisions. However, in terms of the relative contributions of P from various parts of a dairy farm although there were large spikes from laneways and other high use areas, due to their relatively small size they perhaps contribute only a small part to the total P loss to our waterways. This study by Dougherty (pers comm.) although suggesting that laneways and high P ‘hotspots’ only generate a portion of P losses to waterways, states that this total amount could be reduced further by diverting high P water through low P soils.
Thus if a dairy farm P ‘hotspot’ produced a runoff P concentration of 0.2 mg/L from a rainfall event and this water flowed over an adjacent low P soil, the data in this study suggests that around half of this P can be stripped from the water. This is the case even with the very short residence times in this experiment (around 2 min). In another study by Dougherty (2006) residence times were over 25 min for pasture plots that were 25 metres in length. This being the case one could expect that on the paddock scale, where paddocks could be many hectares in size, large concentrations of P that runoff from hotspots would largely be returned to background concentrations.

Similar studies have hypothesised that running high P water over low P soil will load this low P soil up with P. However, it is unlikely that this added runoff will impact on the low P soil in the short to medium term. A typical runoff P concentration from a high P soil is around 2 mg/L P and an average runoff for some areas is 100 mm per year. This being the case, it only represents 2 kg P/ha being lost. If runoff from 10 ha of land runs over a buffer/filter strip of 1 ha then the loading rate might be 20 P/ha (pers. comm. Warwick Dougherty). A lot of soils on the east coast of Australia would cope with this sort of loading for at least 10-20 years before sorption was seriously impacted and it is logical that the lifetime could be prolonged by harvesting P from these buffer strips.

Furthermore the data would support the use of vegetated buffer strips as a means of preventing P transport from paddock to waterways. Vegetated buffers are widely used in agricultural production for reducing agricultural nonpoint source pollution. Many studies suggest that vegetated buffers are effective in removing pollutants from runoff, Zhang et al. (2010) successfully captured the relationship between buffer width and pollutant removal efficiency (Figure 11). The Zhang et al. (2010) study suggests a well vegetated
buffer zone with a width of around 30 metres removes more than 85% (under favourable slope conditions) of all studied pollutants (N,P, pesticides and sediment), even the dissolved forms.

Figure 11: The relationship between buffer width and pollutant removal efficiency.

In most cases there would be no input of P into such vegetated buffer zones, other than runoff-run-on, and as such you could predict that the P content of those soils would be lower than any adjacent high input dairy pasture systems. As such P could be effectively stripped from runoff based on the results of this study just conducted. The ability to predict the optimal buffer zone for any given area therefore can be assisted by the results of this study.
5. Conclusions and recommendations

The high nutrient concentrations contained in runoff from intensively managed pastures in Australia and the need to better understand the reasons for this nutrient loss was highlighted in this study. Consequently, the experimental component of this thesis has examined the influence of hydrology and soil P chemistry on amounts of P mobilised in surface runoff from soils in a small scale experiment. As a result of this research farmers and decision makers may be better informed as to selecting techniques to minimising nutrient loss and its effect on the environment.

5.1 Conclusions

Rainfall simulation is widely used in the study of P mobilisation and this experiment showed that it is a useful tool for examining the processes of mobilisation. One of the original aims of this study was to use rainfall simulation to contribute to the understanding of P mobility in agricultural soils. The results of this work achieved this to a degree, showing that changes in the hydrology of runoff trays throughout a rainfall event control the concentration of P contained in the runoff. It was evident that the hydrology of the tray determined the reactions taking place between soil and water and as a result the concentration of nutrients in the associated runoff. Adding phosphate to the system in the rain, although few other studies have done this, provided an insight into the reaction of a low P soil to high P surface water flowing over it. As such, the experiment added to our understanding of the transport of P from high P areas on a dairy farm, such as feed troughs and laneways. The knowledge gained will help design means of limiting nutrient export to the environment. Similarly the results will aid in the
interpretation of rainfall simulation data in the future to make studying P mobilisation an easier process.

The second aim was to provide insight into means of stripping P from runoff to prevent its export from the paddock to adjacent water ways. The study has shown that relatively high P concentrations can be stripped from water when it flows over low P soil. This knowledge can therefore be used to help farmers illustrate and understand means of reducing the nutrient content of runoff from their pasture systems. Reductions in runoff P concentrations arising from high P zones can occur rapidly and maintaining low P buffer zones adjacent to pasture systems can have a large impact on reducing P export to the environment.

5.2 Recommendations

While this was a preliminary study, useful insights into the methodology of carrying out such studies were gained. For example, this study confirms the likely ability of buffer zones to mitigate high P runoff and thus it is recommended that landowners maintain a low P buffer zone between their productive pastures and adjacent waterways as a means of stripping nutrients from runoff waters. Assessment of possible designs/contents of such buffer zones should be investigated.

Future experiments will benefit from addressing deficiencies identified in the methods used in this study and as a result improve the efficiency and overall value of information gained. Improvements should include:

- a broader range of soil P concentrations,
• more thorough monitoring of hydrological aspects of runoff, such as flow rate changes during the events and average residence times.

These two latter measurements would allow depths of water on the surface to be calculated at different times during the event and allow more detailed modelling of P sorption and desorption kinetics.
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