Thesis for Masters Degree by Research

Phosphorus Behaviour and Availability within a Chemically Loaded Soil

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Submission Date July 2007

Contents

Summary

The aim of this thesis was to investigate the behaviour of Phosphorus (P) in a constructed Reed Bed Treatment Systems (RBTS).

P availability to plants is a complex area, and one that as yet is not fully understood. Plant available P has been supplemented by man since the 19th century, however, the recommended rates of fertilisation even now are often vague and uncertain, and consideration as to how fertiliser application rates are related to plant available P is often not given. Long-term studies of P requirements are expensive and time consuming and the information gained from these experiments is usually not transportable to other soils or crops.

Environmental considerations are increasingly important as awareness is growing of the impact of relatively low levels of P can have on receiving waterways, and the consequences of over fertilisation can be critical to certain ecosystems. The majority of studies carried out on wetland soils have been to investigate their ability to remove or reduce P from receiving waters. This work studied the behaviour of P in these soils, the pools that are favoured under saturated conditions and how these pools can be related to predicting the P fertiliser requirements of such systems. A review of the available literature was also performed which gave the necessary background to the importance of P in this kind of system.

The current analytical techniques available were reviewed to assess how useful these are in predicting P requirements, and the limitations involved with the different methods, and why these particular techniques are used.

An experiment was carried out to investigate the distribution of P in a sandy loam soil under saturated conditions using a modified fractionation procedure for a control and a trial treating high

ammoniacal solution from the coke making process from the Whyalla Steelworks. Due to the unusual nature of this man-made system the Hedley fractionation procedure was chosen to gain a greater understanding of how P behaves in this unique system. Both systems were planted with *Phragmites Australis*. Monitoring of the P levels leached from this system was performed to account for the total P. Time and resource limitations determined the final form of the experiment and due to the location access to university resources and support was limited.

Monitoring of the treatment of ammoniacal solution by the trial RBTS was performed focusing on three main constituents of the solution. The results of this monitoring were reported and potential treatment mechanisms discussed.

Modelling techniques have been used for predicting P behaviour and requirements, some more accessible than others depending on the requirements involved however, more work needs to be done in this area to develop a simple and easy to use system. Using a modelling software package LEACHN designed by Dr J Hutson originally to model Nitrogen in soils modified for P in non wetland soils, it was possible to compare the predicted behaviour of P with the experimental results obtained by the fractionation experiment.

Declaration

'I certify that this thesis does not incorporate without acknowledgment any material previously submitted for a degree or diploma in any university; and that to the best of my knowledge and belief it does not contain any material previously published or written by another person except where due reference is made in the text.'

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Angela Stokes

1. Literature Review

Introduction

The aim of this literature review is to collate the available information on how phosphorus (P) behaves in both wetland and upland soils. There are a large number of publications on P in agricultural soils, but it would appear that the reactions and pathways of phosphorus are still not fully understood.

P is needed by every living cell and is frequently the most limiting macronutrient in most Australian soils, its availability in the Earths crust is finite at approximately 0.12%. P exists in soil in many different forms and levels of availability. It is important to understand how these forms or pools of P are related, and what mechanisms are involved in P moving between these pools.

P availability to plants is complex and not fully understood. Plant available P has been supplemented by fertilisers since the 19th century, however the basis for recommending rates of fertilisation are often vague, and the relationship between fertiliser application rates and plant available P indices is often not defined. Long-term studies of P requirements are expensive and time-consuming and the information gained is difficult to extrapolate to other soils or crops.

Environmental considerations are increasingly important as awareness has grown of the impact P can have on receiving waterways at relatively low levels. The consequences of excess P application can be critical to certain ecosystems. In reality avoiding excess P application is difficult. It is an issue which can be considered from either an agricultural or environmental viewpoint as excess application often depends on individual site characteristics and soil properties. P behaves conservatively in soil and aquatic environs in as much as it does not suffer any loss to the atmosphere, however, it exists in forms

and fractions that can differ in terms of their reactivity, solubility, transferability and eventually their bioavailability.

The current available analytical techniques were also reviewed to assess how useful these are in predicting P requirements of soils, the limitations involved with some of the more widely used methods, and why these particular techniques are preferred.

The transport mechanisms which define the flow pathways between soil and waterways presents a further source of complexity, in that depending on their nature and location they can either inhibit or promote the loss of P from soil to water. Limiting P losses is a high priority in areas where there is the risk of environmental impact. Modelling techniques have been used; some approaches are better than others depending on the requirements and processes involved, but more work needs to be done in this area before simple and user-friendly systems can be developed.

1.1 The Importance of Phosphorus

Phosphorus is an essential nutrient playing an important role in energy transformations in all living organisms. Phosphorus has many functions in the growth, development and structure of cells, with the highest levels of P being found in actively growing cells. Phosphorus in its oxidised state is the critical part in higher energy compounds such as nucleotides and phosphorylated carbohydrates. High energy phosphorus compounds are involved in nearly every major biochemical reaction and are used for storing energy from exergonic reactions – transporting energy to other reaction sites, and forcing endergonic reactions (Stevenson,1986).

Most Australian soils are P deficient, although there are a few important exceptions in northern New South Wales and south-eastern

Queensland. The unusual features of geological and pedological histories of the continent have lead to many strongly leached, highly weathered, low fertility soils. Even younger soils have been derived from parent material affected by earlier P-depleting weathering cycles. There are very few P-rich parent materials such as basalt, or morainic deposits available for soil formation. The average P content for Australian soils is 0.03%, which when compared to American soils around 0.04-0.10%, is very low indeed. Therefore the addition of P fertiliser is essential for the economic growth of crops (Costin and Williams, 1983).

1.1.1 Types of Phosphorus found in soil

There are many types of P found in soils, the most available form is orthophosphate associated with minerals in the soil (Lindsay 1979). These inorganic P constituents in mineral soils can generally be classified into two groups based on the most significant contribution to P solubility, namely: calcium phosphates, and iron and aluminium phosphates. Among the calcium phosphates: $Ca_{10}F_2(PO_4)_6$ (fluorapatite), $Ca_{10}(OH)_2(PO4)_6$ (hydroxyapatite), $Ca_{10}O(PO_4)_6$ (oxyapatite) and $Ca_{10}CO_3(PO_4)_6$ (carbonate apatite) are the most abundant. $FePO_4.2H_2O$ (strengite) and $AlPO_4.2H_2O$ (variscite) are the other main P-bearing minerals.

In general, native inorganic and organic sources of soil P are highly stable and of little short-term consequence for commercial crop production. Organic P compounds in mineral soils can be found in the form of inositol phosphates, of which phytic acid is the most significant component, and phospholipids, nucleic acids, nucleotides and unidentified sugar phosphates. However, part of the organic P pool may undergo mineralisation or occur as dissolved materials in the soil solution.

P retention in soils can occur in many ways, chemisorption, anion exchange, sorption, physical adsorption, specific adsorption and non-specific adsorption.

1.1.2 The common factors in all mineral soils.

All mineral soils contain aluminium and iron oxides and hydrous oxides, which occur as discrete particles or as coatings on other soil particles, especially clay. In addition, amorphous aluminium hydroxy compounds may be present in interlayer locations of expandable aluminium silicates. Such materials are highly efficient in adsorbing phosphate ($H_2PO_4^-$) anion and hydroxyl (OH^-) ions associated with the iron and/or aluminium. Under alkaline conditions in the presence of free calcium carbonate ($CaCO_3$), adsorption of $H_2PO_4^-/HPO_4^{2-}$ on to calcite can also occur by replacement of water, bicarbonate (HCO_3^-) or OH^- ions present on the calcite particles.

Concurrent with these adsorption reactions, $H_2PO_4^-$ ions in solution may undergo precipitation reactions, the nature of which varies with the pH of the soil. Under acid (<5.0) conditions, the presence of active aluminium, iron or manganese may result in the formation of poorly soluble hydroxy metal phosphates (e.g. $Al(OH)_2H_2PO_4$). In contrast under alkaline conditions, the presence of active calcium causes precipitation of dicalcium phosphate anhydrous (Morgan, 1997).

1.2 The Phosphorus Cycle

Figure 1.1 below, depicts a simple soil-based view of the P cycle. Phosphate inputs can represent the weathering of rocks or the addition of man made fertilisers. In the soil the phosphate is absorbed on clay surfaces and organic matter and becomes immobilised. Plants dissolve ionised forms of phosphate. Herbivores obtain P by eating

plants, and carnivores by eating herbivores. Herbivores and Carnivores excrete phosphorus as a waste product in urine and faeces. P is also released back into the soil when plant and animal matter decomposes and the cycle repeats.

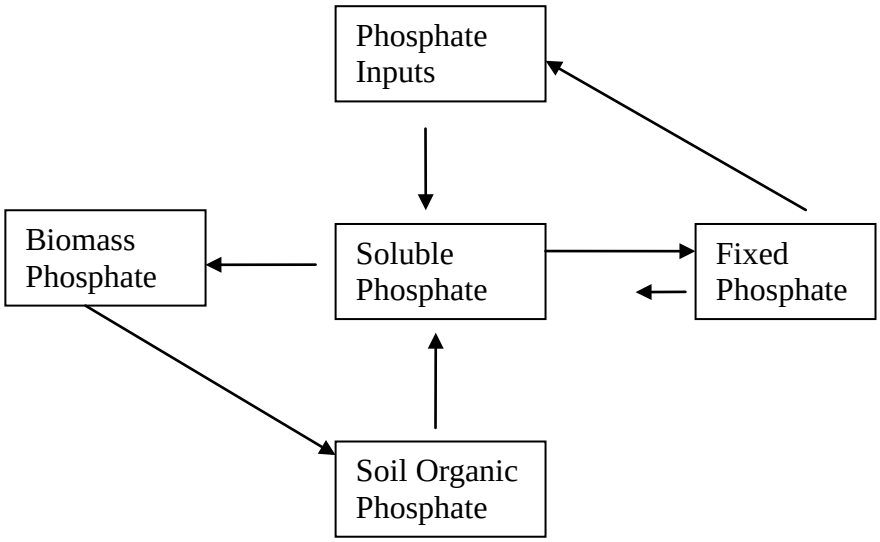


Figure 1.1 A simple soil based view of the P cycle.

Another way to view P in the soil would be the identification of all its forms and pathways. Although it would be useful to be able to determine all of the P compounds in soil individually, it is not possible because of the complexity of the chemistry of soil P. However, it is possible to define classes of soil P compounds by using extractants that remove them from soil material, and this can tell us how available these classes or pools of P are to the plant. A simplified version of the P pools is shown in figure 1.2.

Phosphorus Pools in Soil

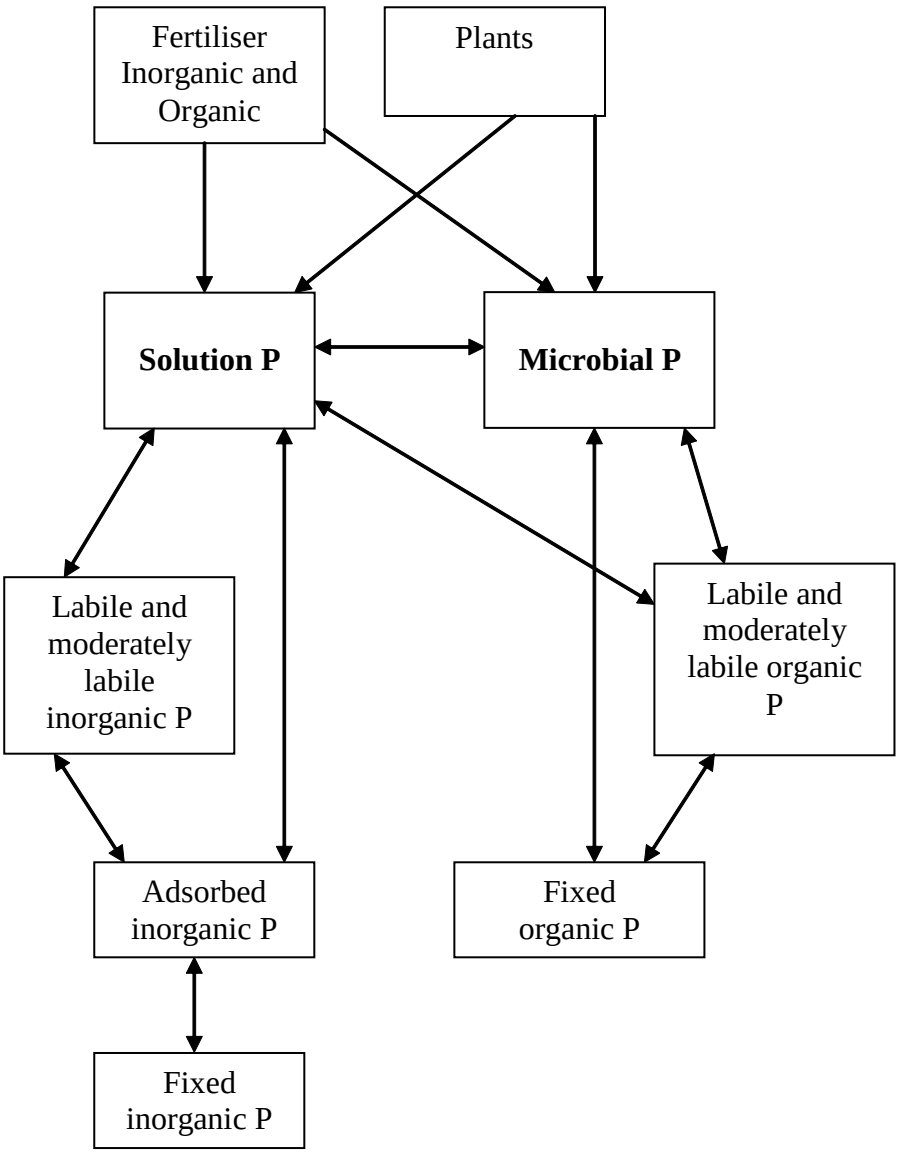


Figure 1.2: The pools represent the measurable fractions in terms of extractability; the arrows represent the interactions between pools (double headed arrows do not represent reversible reaction pathways).

1.2.1 Phosphorus Pools

Soil P exists in inorganic and organic forms. Inorganic P (Pi) forms are usually hydrous sesquioxides and amorphous and crystalline Al and Fe compounds in acidic, non-calcareous soils, and Ca compounds in alkaline, calcareous soils. Organic P (Po) forms include relatively labile phospholipids, nucleic acids, nucleotides and inisotol phosphates, while more resistant forms of P are comprised of humic acids (Sharpley and Rekolainen, 1997). The lability of these forms of P is defined by the extent to which extractants of increasing acidity or alkalinity applied sequentially can dissolve P.

1.2.2 Inorganic Interactions

Phosphorus sorption occurs primarily by the covalent bonding of phosphate ions to hydrous oxides of cations. There are many reactions involving cations in soils however the discussion here is limited to those cations that significantly contribute to P solubility (Lindsay 1979). In alkaline soils calcium carbonate as well as iron oxides are involved with P sorption, liming acid soils to pH 6.5 increases P availability by enabling iron and aluminium phosphates to convert to calcium phosphates. In the pH range 6 – 6.5 several phosphate minerals can coexist, these include varisite, strengite, $CaHPO_4.2H_2O$, $CaHPO_4$ and $Ca_4H(PO_4)_2$ (Lindsay 1979). This appears to be the pH range in which phosphates are most available to plants. Desorption will also occur usually from the more labile pools releasing P back into the soil solution.

1.2.3 Organic Interactions

Organic P can generally be defined as chemically bound phosphates such as inisotol phosphate. For the purposes of this P pool

classification this definition works well. However Iyamuremya et al (1996b) questions this assumption stating that organic macromolecules can desorb from the soil matrix and consequently act as carriers for P in environments where it would otherwise be immobile. To date not all organic forms of P in soils have been characterised and there is still a lot of debate about the involvement of Fe and Al in the association between organic matter and P. Organic P can be released back in to the soil solution by mineralisation as discussed in the previous section and hydrolysis from more labile pools.

1.2.4 Plant Interactions

P concentration in the soil solution and the rate of diffusion of P are well known factors in the transport of P from the soil to the plant roots. The ability of the plant roots to create P concentration gradients is vital. Diffusion distance is small, therefore the size of the root system and the formation of root hairs are factors in making the soil P positionally available. Plants with extensive root systems of finely branched, small diameter roots will have a competitive advantage for P absorption over species with larger diameter, less branched root systems. The presence of root hairs will also increase the ability of a plant to access P.

The mobility of P in soil is low compared with other plant nutrients because of the generally low solubility of phosphate compounds and the strong P-binding capacity of soil material. Plant roots, therefore, have a 'contact problem' relative to both soil and applied P. A plant root gets most of its P from within 2 mm of the root surface during the period of active P uptake (Sibberson and Sharpley, 1997). Therefore the larger the surface area of the root system the greater the P uptake.

Evidence has been found that plant roots may cause the release of P from undissolved sources. The depletion of the soil solution encourages P desorption from the soil matrix. Also, changes in the pH in the area around the roots from differential uptake of cations and anions affects solubility of soil phosphate.

The flooding of soils has been found to increase the availability of P in acid soils (Lindsay 1979). The pH of the reduced soils generally rises toward neutral increasing the solubility of iron and aluminium phosphates. Then, as the redox potential decreases it is possible for strengite and varisite to convert to vivianite ($Fe_3(PO_4)2.8H_20$). It has been observed (Lindsay 1979) that a rice plant is still able to obtain sufficient P under highly reduced conditions. At the roots of a flooded system the redox potential is higher than that of the bulk soil due to the O_2 supplied through the plant's stem.

Organic P is an important fraction of soil P, but, because roots take up P in the form of orthophosphate, any organic P compounds in the soil solution must first be mineralised before the uptake can happen. The area in the immediate vicinity of the roots known as the rhizosphere can differ from the bulk soil in terms of its pH, CO_2 partial pressure, enzyme activity and cation and anion activities (Jungk, 1987), and it is processes that occur in this zone that determine the immediate availability of P to the plants roots.

1.2.5 Fertiliser Interactions

The mechanisms by which P fertilisers in mineral soils are converted from a soluble state to a less soluble state are referred to as P retention or P fixation. The precise sequence of events is not fully understood but there is a general consensus as to the major components of the retention mechanism. These are associated with the dissolution of the P fertiliser particle where precipitation of the orthophosphate anion

occurs, the anion will either react with Fe, Al or Ca cations within the solution or will undergo adsorption on to the soil surface (Morgan, 1997). The exact pathways are dependent on the fertiliser used and the inclusion of cations in the fertiliser product (Lindsay 1979).

The initial products of the retention mechanism are weakly sorbed and can therefore supply sufficient amounts of soluble P for immediate use by crops. Over time however the initial reaction products are altered, and while the manner of alteration is unknown there seems to be general agreement as to the composition of the ultimate products of the fixation mechanism. Available evidence indicates that the strongly held products of the fixation reaction sequence are octacalcium phosphate, hydroxyapatites and fluorapatites under alkaline, calcareous conditions, and strengite and variscite under acid/neutral conditions. These materials can appear within a matter of months, their rate of production being primarily dependent on the prevailing pH (Morgan, 1997).

1.3 Fertilisation

1.3.1 History of Fertilisation in Australia

From 1900 improvements in cereal yields occurred due to improved farming practices and the use of superphosphate, a man made fertiliser produced by mixing phosphate rock with sulphuric acid. The continued use of P fertiliser has remained essential. The general consensus has been that when soluble phosphate is added to soil a rapid conversion to insoluble forms occurs, the added P remains close to the application point and is not easily removed or moved by leaching. Residues accumulate in the soil and eventually only maintenance levels of P will need to be added. Unfortunately this is not the case for most Australian soils which are likely to be dependent on P fertilisers in spite of accumulation.

Phosphate fertilisers come in various forms: from slag obtained from the steel industry, finely ground phosphate rock up to single, double or triple superphosphates. Compound fertilisers such as ammonium phosphates, nitrophosphates and metaphosphates are used in advanced agricultural systems. All of these except for slag are prepared from phosphate rock, this is the only readily available economically viable source (Cook, 1983).

1.3.2 Manufactured Products

There are a number of fertiliser products available. The most well-known are described below.

Superphosphate is made by the reaction of finely ground phosphate rock and sulphuric acid. A simplified version of the reaction process is as follows:

$$3[Ca_3(PO_4)_2].CaF_2 + 7H_2SO_4 + 3H_2O \rightarrow$$
$$7CaSO_4 + 3Ca(H_2PO_4)_2.H_20 + 2HF + 2H_2O$$

Tricalcium phosphate in phosphate rock is converted to hydrated monocalcium phosphate. Calcium sulphate is mixed in, and hydrogen fluoride (HF) is removed. The reaction is exothermic and the heat drives off large amounts of H_2O (steam). The amount of sulphuric acid added is less than the theoretical needed to ensure the product remains free of uncombined phosphoric acid or sulphuric acid (either acid will cause the product to become hygroscopic and cause caking). Therefore, a small amount of dicalcium phosphate dihydrate appears in the product and some undecomposed phosphate rock (Toy and Walsh, 1987). Triple superphosphate does not have the calcium sulphate by-product.

Monocalcium phosphate monohydrate is prepared by the decomposition of phosphate rock with phosphoric acid instead of sulphuric acid.

$$3[Ca_3(PO_4)_2].CaF_2 + 7H_3PO_4 + 5H_2O \rightarrow 5Ca(H_2PO_4)_2.H_20 + HF$$

This contains approximately 44-46% phosphate (Toy and Walsh, 1987).

1.3.3 Organic Phosphorus Sources

Organic P fertilisers have been used for centuries as the P source for crops. Even with the advancement of P technology and processes, organic P sources from animal manures, including composts and sewage sludge are still important. In terms of fertiliser management the major differentiating factor is P availability. Analysis can be performed on these sources and a P availability coefficient can be produced determining available P as a portion of total P. Phosphorus from manure or sludge should be comparable to P from inorganic fertiliser.

The P contained in organic P sources is a combination of inorganic and organic P. Essentially, all of the inorganic P is in the orthophosphate form, which is the form taken up by growing plants. Around 45-70% of manure-P is inorganic P, and the remainder is made up organic P. Much of the organic P is easily decomposed in soil, however, factors such as soil moisture and soil pH have a bearing on the P mineralisation rate. The final decomposition product is orthophosphate P compounds.

It is generally thought that there should be no difference in P fertiliser sources as long as the nutritional analysis differences are taken into

account and P fertiliser recommendations are the same regardless of the P fertiliser source. There have been some studies that suggest under acid conditions in high P fixing soils that organic fertiliser such as manure or alfalfa will behave differently from inorganic fertilisers (Iyamuremya, et al 1996).

1.3.4 Predicting Fertiliser Requirements

Soil P tests are used in many countries as a basis for fertiliser recommendations. The small size of the sample relative to the area sampled presents problems for representative sampling. A range of extractants are used to extract what is often referred to as plant-available P from soil. However, these extractants, with the exception of water, are destructive in their action and can extract P from different soil pools. Extractants have been selected because, in field experiments, they have been shown to give a reasonable correlation between extracted P and uptake, dry-matter yield and crop response to added fertiliser P where soil P is relatively low.

In many countries there is a wide variation of methods used for soil P analyses as well as strategies for making P fertiliser recommendations. This makes it difficult to develop any kind of international correlation of data. It is also evident that P recommendations can vary between countries at the same soil-P levels obtained using the same test method (Tunney et al., 1997).

In Australia, two methods of predicting P fertiliser requirements have been widely used. The first is to calibrate soil P tests with crop responses, by using a wide selection of soil tests against yield responses. A high correlation between soil test and yield response indicates that the soil test is correctly estimating the effect of P buffer capacity on P availability to a particular crop grown on a particular group of soils. Tables have been developed for use as guidelines for fertiliser application rates from this information (Moody and Bolland, 1999). The second method is to measure quantity of P in the soil, for which the Colwell method is regularly used as well as for measuring buffer capacity (Moody and Bolland, 1999). This quantity is correlated with yield response and buffer capacity to give a critical value for each buffer class or for specific soils.

As will be seen in the next section, this apparently simple interpretation of fertiliser requirements is much more complex.

1.4 Fate of P after fertilisation

1.4.1 Initial reactions of fertiliser.

The need to supplement soils with P fertilisers arises from the inability of the relatively small pool of native soil P to supply and maintain adequate amounts of soluble orthophosphate ($H_2PO_4^-$ and HPO_4^{2-}) to the soil solution for crop growth. After entering into the soil solution P fertilisers are usually quickly immobilized by reactions with various soil constituents. As a result, P nutrition of crops is largely dependent on the release of P from these reaction products back in to the soil solution.

In the transition from the available to the fixed state, there is no simple quantitative conversion from one type of P compound to another. Rather it is more likely that orthophosphate ions that appear during transition are exposed to a number of competing reaction possibilities, including absorption by roots and transport to new sites of reaction by water or cultivation practices.

Some studies indicate that movement of fertiliser P away from the initial reaction site is limited to a few centimetres or so, others show deeper penetration of fertiliser P in the profile (Sui et al., 1999). Presumably, over time P can diffuse outwards and downwards from the uppermost soil layers, resulting in more uniform distribution in the profile as a whole. Assuming that the part of the redistribution process occurs in the solution phase, downward movement of P raises the issue of soluble P loss from the soils in subsurface leaching (Morgan, 1997). It is this issue which is of particular interest to the

project described in section 2, as it was important to understand the risks of P loss in effluent discharge.

1.4.2 Reactions of P fertiliser in the soil

Adsorption of P increases the negative charge of soils, i.e. increases the cation exchange capacity (CEC). This can be useful in managing variable charge soils with little permanent change in the overall charge, which can be useful in reducing or preventing leaching. This increase in negative charge does not have a big effect on the soil pH. Addition of phosphate to soil is usually as a salt such as a dihydrogen phosphate ion KH_2PO_4. Phosphate can behave as a Lewis acid to form a ligand; if adsorption of a phosphate ligand by a soil increased charge by exactly one unit, this charge would be balanced by the removal of a cation from the solution phase, which in turn would result in no change of pH. In reality it appears that the process is dependent on the pH of the system and the concentration of electrolyte in solution. Most measurements (Barrow, 1983) indicate the charge increase is less than one unit, i.e. the charge is only slightly balanced by the removal of a cation from the soil solution. The remainder could be balanced by the displacement of hydroxyl ions, the result of which should be a slight rise in the pH. P fertiliser is not neutral - superphosphate is acidic - so the net change in pH is very small.

The phosphate anion requires a balancing cation, the simplest being calcium, and because Australian soils are often deficient in sulfur, superphosphate is a very good way of supplying this sulfur. Other important cations such as zinc and cadmium can be placed in the soil using P fertilisers as a carrier.

1.4.3 Longer Term Effects

Australian soils that lack P are often low in organic matter because of the low plant growth potential. By adding P to these soils and increasing plant growth, soil organic matter, organic carbon, nitrogen, sulphur and P increases. An increase in organic matter has several effects on the soil properties, such as an increase in CEC, although this is likely to be quite small, and a decrease in pH. These effects have been widely observed and are certainly linked to accumulation of organic matter. The mechanisms involved are uncertain; it could be due to a build up of solid-phase organic acids or due to transformations of nitrogen, such as the oxidation to nitrate. It is an important issue as a low pH can result in limited production in certain soils.

Increased P status occurs when P fertiliser is added, because the P added remains in soil for extended periods of time. However the longer the P remains in the soil the less available it is to plants, which explains the need for continual P applications to Australian soils. Removal of P occurs with the removal of crops or pasture and redistribution by animals to drinking holes. The amount removed is generally much lower than the amount applied during fertilisation. (Other mechanisms include the loss of P to water but this is dealt with in more detail in section 1.7).

Efficiency of P uptake by plants depends on a number of factors, such as soil properties, soil management and environment. Plant uptake of P increases if soil temperature, moisture and nutrient status increase. P amendments in either organic or inorganic forms are necessary for most agricultural soils in order to maintain adequate available levels of soil P in a form which can be used by the plant. Amounts will be dependent on plant and soil type. The availability of P to crops is reduced by complexation in soil with Ca at a high pH, by Fe and Al at a low pH, and by high clay content. Liming may increase P

availability in soils by stimulating mineralisation of organic P, or may decrease P availability by the formation of insoluble Ca phosphates at pH >6.5. In other situations liming can increase P availability by increasing the pH. A fall in pH or the increase in biological activity in the rhizosphere including vesicular-arbuscular mycorrhizal associations (a symbiotic relationship between roots and fungus) with plant roots, can considerably enhance P uptake, especially on low P soils (Sharpley and Rekolainen, 1997).

Immobilisation in organic matter occurs as the amount of organic matter increases this action, this can be a useful immobilisation, as over time the organic material will breakdown releasing the P back into the soil for reuse.

Continuing reactions occur between soil and phosphate. The fertiliser will usually be applied as a band near the seed, the P is thought not to move very far. When P fertiliser is first added to soil most of the P is quickly removed from the soil solution and continues to be removed over a long period of time. The rate at which this occurs is often fast to begin with and then slows. The supply of P to plant roots is dependent on the diffusion rate. In turn the diffusion rate is dependent on the P content of the soil solution resulting in higher P application rates of fertiliser to keep the available P levels high. The proportion of available P is sometimes used as a measure of the efficiency of the fertiliser, however Barrow (1983) found that in practice a sorption index has usually been used. Sorption at a constant concentration is reciprocally related to the proportion of P in solution. Similarly the amount of fertiliser required is reciprocally related to the efficiency of fertiliser use. Phosphorus requirements increase as adsorption increases.

Soils differ as to how much P fertilisation they require by virtue of their P sorption capacity. However, it is not as simple as knowing the levels of P sorbing components in the soil. P continues to react with

the soil over time resulting in the proportion of P in the soil solution decreasing and therefore the potential rate of movement to the plant roots decreasing. In other words the fertiliser becomes less effective over time resulting in the need for further fertilisation.

1.4.4 Reaction Rates

Experiments have shown that the reaction rate of P immobilisation is very slow. Evidence suggests that P builds up within soils over many years, however, until this level becomes fairly high P fertiliser will still need to be added to ensure sufficient available P for crops. An accelerated study by Barrow (1983) on the rate of P adsorption showed a marked slowing down of P adsorption over time, but also indicated that the proportion of P that remains effective is independent of the level of P application.

There are many factors influencing the generally slow rate of P reaction, the most influential is temperature, for every rise of $10^{o}C$ the rate increases threefold. This allows the speeding up of the reaction for laboratory trials. Field results are still difficult to estimate because temperature also accelerates desorption. Barrow (1983) reported that in one study of non calcareous soils the interrelation between P adsorbed (Ps), concentration (c) and time (t) could be described by the following equation:

$$Ps = ac^{b1}t^{b2}$$

a, b1 and b2 are coefficients.

There are many important differences between soils, therefore the residual value of P fertiliser is likely to be very different. Some soils will require lower levels and others will require higher levels, resulting in some controversy over the subject of the application of P

fertiliser. Caution must be taken when extrapolating data or observations from one soil to another even in the same region.

Barrow proposed two ways of viewing the issue of P fertilisation. The first is to only replace the amount of P removed by a crop and assume that the P in the fixed form will then return to the available pool if there is insufficient P in the available pool. The second is that over time the P in the available pool will be further adsorbed over time and that unless extra P is added there will be a continual reduction in the P available pool.
If we consider the reaction between P, soil and plant uptake as being time dependent, then a soil is P deficient when the rate of supply to plant roots is less than the rate required for optimum growth. Application of low levels of fertiliser will achieve an adequate rate but over time the rate decreases and more P is needed. Alternatively a large amount of P could be added which will last over a number of years.

1.4.5 Differences between Inorganic and Organic Amendments

It is thought that P fertiliser additions, whether inorganic or organic, will contribute the same available forms to the soil providing the P test levels are the same. However, differing behaviours between inorganic and organic binding should be taken into account. There have been several studies into this area.

One such study by Iyamuremya et al (1996a) showed that adding increasing rates of manure or alfalfa to high P fixing soils increased the pH and decreased the exchangeable Al, sorption capacity and amount of P adsorbed. Therefore organic residues may be used in very acid soils as a substitute for conventional P amendments. Indications are that the role of the organic amendments in reducing P sorption is not attributable solely to the reduction in the exchangeable

Al. This suggests additional mechanisms are involved in the P sorption reduction from organic amendments. One mechanism could be the release of phosphate from decomposing organic residues. Also, organic amended soils have been found to release significant amounts of sulphate and fluoride, which are complexing agents for Al and Fe.

A further study by Iyamuremya et al (1996b) compared the pools between inorganic amended soils and organic amended soils using the Hedley fractionation method. This study concluded that organic residues rich in total P (manure and alfalfa) affected the distribution of P fractions of soils. Bioavailable P and the fractions that largely react with Al and Fe increased in all soils treated with manure and alfalfa. With few exceptions inorganic amendments did not significantly affect P distribution.
The minimal effects of inorganic amendments on P distribution showed that simply changing the chemistry of the soil in terms of pH and exchangeable metals did not affect redistribution of P among P fractions. Therefore changes observed for organic amendments in reducing P sorption were not only a reduction of exchangeable Al or increased pH, but were also caused by complexation of surface sites of P sorption (chemisorbed P).

A previous study by Selles et al (1995) using a Hedley Fractionation method, found that the residual fertiliser from inorganic P amendments tended to accumulate mainly in the more labile forms such as resin-Pi, microbial P and bicarbonate Pi.

It is generally accepted that P in soils moves as orthophosphate and as such is involved in most of the current transport models. However, Dolfing et al. (1998) found that Al and Fe bonding to carbon are likely to be different from those currently accepted. Suggesting that there may be a role for Fe and Al in binding P to the organic matter in the soil and this could then play a role in controlling the movement of P through the soil. Dolfing et al. (1998) proposed two categories of P:

defined operationally as organic, chemically bound P, and P bound to the organic backbone of humic substances via Al and Fe bridges. Any details of the molecular mechanisms involved are as yet scarce. However, this does highlight the evolving nature of our understanding of the P cycle and in turn the classification of P pools.

1.4.6 Penetration of Phosphorus into the soil profile

The primary mechanism of loss of P from the soil is through sediment-laden surface run off. Therefore there is a need to know the distribution of P in the organic and various inorganic phases in order to predict the impact of P run off on aquatic environments.

Long-term no-till management shows an increase in the availability of immobile nutrients such as P in a thin layer 0-5cm below the soil surface, along with an accumulation of organic carbon. Therefore the distribution of P into organic forms has become an interesting area of research (Essington and Howard, 1999). It could be that Po may play an important role in the maintenance of a readily available source of P and slow cycling of P in no-till managed soils. Essington and Howard's (1999) paper aimed to compare the influence of no-till with disk-till on plant available P, by splitting P into inorganic and organic phases, and the speciation of Pi into operationally defined chemical pools as a function of P fertilisation rate and depth in long-term tillage plots. In this study the pools focused on were loosely bound and soluble, non-occluded Al-bound, non-occluded Fe-bound, occluded-reductant soluble and Ca-bound.

Soil Pi was found predominantly in the non-occluded Fe and occluded-reductant soluble fractions. The results of this particular paper found that conservation tillage probably has no effect on soil P fertility. However, localisation of the influence of tillage on P speciation near the soil surface indicates that the form of P, which has

the potential to be lost through surface runoff, is an important soil chemical characteristic. Speciation influences bioavailability, therefore any change in P speciation could affect the aquatic environments that receive run off.

1.5 Phosphorus Interactions in Wetlands

1.5.1 Natural Wetlands and Flooded Soils

P is frequently the most limiting macronutrient in wetland ecosystems. Most municipal and agricultural wastewater discharges contain elevated P concentrations compared to levels that will stimulate excessive or nuisance algal growth in downstream receiving waters. Therefore, the P assimilation capacity of wetlands used for treatment is important. Due to the high biological importance of P, wetland ecosystems have developed mechanisms for trapping and recycling P entering a wetland system. It is readily inter-converted from organic to inorganic forms and forms chemical complexes with organic and inorganic ligands, which in turn may be adsorbed or precipitated within wetland soils. P typically forms insoluble complexes with oxidised Fe, Ca and Al in aerobic wetland soils. Under anaerobic conditions much of this bound P becomes soluble and more available for plant uptake and for diffusion from the soil system. If an aerobic surface soil horizon occurs within the wetland, soluble P may be retained or trapped within the wetland sediments until it is biologically cycled (Kadlec and Knight, 1996).

P may be directly adsorbed onto clays located within and under wetlands. This adsorption is strongest under low pH conditions. In some instances, incoming P sorbed to particulates settles rapidly and is effectively buried as this form of the nutrient. However, exchangeable sorbed P is available for further cycling. Soluble reactive P often persists longer, but not in oligotrophic wetlands.

Some portion of the P bound in wetland sediments may eventually be recycled through plant uptake and either reburied as organic P or lost in the wetland outflow.

Trends for wetland soil can be categorised in three ways: in acid soils P may be fixed by aluminium and iron; in alkaline soils P may be fixed by calcium and magnesium; and reducing conditions can lead to solubilisation of iron minerals and the release of P precipitates. If free sulphide is present due to sulphate-reducing conditions, iron sulphide can form and stop iron mineralisation of P. Sulphide produced in wetlands by sulphate reduction, interferes with Fe-phosphate binding in soils and sediments, due to the formation of Fe-sulphides causing phosphate to be released in to marine and freshwater sediments (Lamers et al., 1998).

Two important physical processes for P removal in wetlands are sedimentation of particulate P and sorption of soluble P. Incoming particles may contain P in available and unavailable forms. The particles may contain weakly bound P, which could easily be dissolved in to the soil solution. However, if the particles contain P as insoluble minerals or fixed organophosphorus complexes, it may be permanently removed by sedimentation. All wetland soils have a capacity to sorb P, but that capacity is quite variable.

P dynamics in flooded soils involves complex processes, therefore it is very difficult to evaluate possible P availability to aquatic biota and potential losses to the environment. An increase and subsequent decrease in solution P is often observed after flooding events. This has been linked to changes in Fe compounds in particular poorly crystalline Fe oxides. Redox potential controls Fe reduction while pH directs the dissolution-precipitation of Fe compounds, and consequently P sorption-desorption in flooded soils (De Mello et al., 1998).

P loading to the system, hydraulic retention time, and soil physico-chemical properties regulates the P sorption capacity of stream sediments and wetland soils. Generally, inorganic P added at concentrations considerably greater than those present in the interstitial water of sediments or soils is retained, whereas at low P loadings, wetlands soils/stream sediments can release P.

Reddy et al (1998) described many of the P sorption mechanisms in wetland soils and sediments as similar to those in upland soils, with some important differences. Thus, Al and Fe oxides and hydrous oxides and calcium carbonate sorb P in both upland and wetlands soils. However, depending on the mineralogy, oxidation-reduction changes in soils and sediments can significantly alter P solubility and sorption mechanisms. Iron compounds can play especially important roles in wetland soils, streams and sediments. Hydrated iron oxides associated with Al and organic matter in gel complexes have been shown to control inorganic P sorption in lake sediments. Wetland vegetation and residues can further complicate the system by inducing wide variations in dissolved oxygen and pH levels, as well as serving as major sinks or sources for soluble P. Some systems include soils and environmental conditions that yield wide ranges in P sorption capacities. Description of P mobility in wetland soils and stream sediments in such a basin requires knowing the buffering capacity of the soils and sediments and the factors regulating P sorption and the release capacity. In an ideal world, various P sorption parameters would be closely related to selected physico-chemical properties of the soils and sediments, which would make management of these systems easier.

1.5.2 Constructed wetlands

As can be noted from the above discussion the majority of interest in the behaviour of P in wetland and flooded soils is focused on the use

of these systems as a sink for P. Very little work has been done on the requirements of these systems for P fertilisation, although it is acknowledged that they are often deficient in P as a nutrient.

For constructed wetlands built for industrial treatment purposes, P fertilisation is valuable especially when the waste stream does not contain P. Often in these systems the soil is an upland soil, as in the case of the reed bed treatment system at the Whyalla Steelworks in South Australia that treats high ammoniacal liquor from coke ovens that does not contain any P. The soil in this particular system is a sandy loam, with a very low level of organic material. Fertilisation is necessary for this system to support the *Phragmites Australis* reeds which are grown in the system. As there are no recommendations for fertiliser addition levels it was necessary to investigate the fate of P in this system under both chemically loaded conditions and under water addition only. The results of this investigation will be discussed in Section 2 of this report.

1.6 Current analytical techniques

A useful analytical method for P needs to be simple, extract sufficient P to be measurable, and be of a type that can be related to the pool, which can be deemed plant available, and not extract significant amounts of non plant available pools.
The determination of soil-available P is not a straightforward process. Two basic reasons for this were described well by Tiessen and Moir (1993).

First, the methods used for determination of available P in an agronomic context never measure the quantity of P available to a crop, but rather they measure a pool of soil P that can be related to the plant available P. The relationship is established over years of agronomic experimentation and the testing of fertiliser responses using regression

equations. These regression equations relate plant performance to measured soil P levels, or indicate levels of P deficiency, giving a potential P fertiliser requirement. Results obtained using this method are often not transferable from one soil or crop to another, and different equations are established by soil testing services for varying crops and soil types. This approach can break down completely when natural ecosystems are examined because of the small measurable pools, and where P cycling rather than pool size is a major determining factor of annual productivity.

Second, P availability needs to be defined with respect to an external sink such as a plant community or crop. Plants differ in their ability to extract P from soils due to differences in rooting systems, mycorrhizal associations, and growth rates. Since the available P pool is constantly changing through reactions such as dissolution or desorption, and mineralisation, the pool size will be very time dependent.

1.6.1 Common extraction methods

Many extraction methods are available. The most common methods are the alkaline bicarbonate extract of Olsen et al (1954), and Colwell (1963), and the acid ammonium fluoride extract (Bray and Kurst, 1945) with a number of modifications. Another popular method is a lactate extraction (Egner et al., 1960). The lactate and the bicarbonate extractions are based on the theory that plant roots produce CO_2 which forms bicarbonate in the soil solution, and also produces organic acids similar to lactate that may make the soil P more soluble. It is assumed that these extractants will simulate the action of the plants root and give a good indication of the plant-available P.

The bicarbonate method (Olsen et al., 1954) and many of the modifications of this method have been used successfully on both acid

and alkaline soils. The available P is extracted using a solution of sodium bicarbonate at a pH of 8.5 with extraction times ranging from 30 minutes up to 16-hours (Colwell, 1963). The 30-minute extraction is useful to obtain a quick turnaround of samples but the 16-hour extraction time is more reproducible and provides a more complete extraction. Interference from organic matter dissolved in the solution is often eliminated by sorbing the organic matter onto activated acid washed charcoal which has been added to the extract.

The acid ammonium fluoride extract (Bray and Kurtz, 1945) has been widely used on acid and neutral soils. The relatively low acid strength and the importance of acidity for the extraction mechanism make this method unsuitable for calcareous or strongly alkaline soils that would neutralise the acidity and eliminate the standard test conditions. This test is a purely chemical test therefore rather than being interpreted in terms of plant function it is more useful to interpret the results in a quantitative estimate of P availability that will be affected to a greater or lesser extent by the soil's P buffering capacity.

Iron-oxide-impregnated paper strips have been in use for some time. They were first introduced in 1983 and have undergone many evaluations and improvements (Sharpley, 1993; Guo et al., 1996). This method uses the iron oxide coating on the strips as a sink for P, simulating the adsorption mechanisms in action at the interface of the soil and root surface. As the iron oxide adsorbs the P from the solution, the P concentration reduces, and the P equilibrium between soil solution and soil moves in favour of mobilising available P into solution from the soil. This is a milder extraction than either Bray or Colwell and therefore less likely to mobilise P that is unavailable to plants. Myers et al. (1997) developed a quick-and-easy method for producing iron oxide strips and also found that they could be stored for later use.

Probably the most simple and versatile method for assessing P status is the anion exchange membrane (AEM) method (Schoenau and Huang, 1991). This method uses a sink for solution inorganic P, which offsets the equilibrium between dissolved and soluble inorganic P. Exchangeable P as well as some of the more soluble precipitated P forms will enter the depleted solution and be absorbed by the resin. Several variations of this method have been developed incorporating differing extraction times and anionic forms (Cooperband et al., 1999; Myers et al., 1999). Cooperband et al. (1999), found that anion exchange membrane sorption of Pi and Po can be as close as 100% of the total soluble P if concentrations are high. More complex Po compounds such as phytate may be closer to 90% recovery; this is still a high recovery rate. AEMs were also found to effectively recover biologically immobilized Pi released upon chloroform fumigation.

Available P is a functional concept as opposed to a measurable quantity therefore there is no simple and direct measurements available. Plant available P is the amount of P taken up by a plant during a specific period of time such as a growing season. The plant obtains P through its roots or the root symbionts from the soil solution. Available P is made up of both the current solution P, and P which will enter the soil solution during the period used to define availability (Tiessen and Moir, 1993).

1.6.2 Sequential Extractions

Phosphorus undergoing long term transformations can be measured with sequential extractions, which first remove labile P and then gradually the more stable forms. Hedley et al. (1982) developed a P fractionation method aimed at quantifying labile Pi, calcium associated Pi, iron and aluminium associated Pi, as well as more stable forms of Po. The Hedley Fractionation method involves the removal of the most biologically available Pi using an anion exchange resin.

Next the labile Pi and Po sorbed on to the soil surface, along with a small amount of the microbial P are removed using a 0.5M $NaHCO_3$ extract. A duplicate of this sample is then treated with $CHCl_3$ before the 0.5M $NaHCO_3$ extract, the extra Pi and Po extracted is considered to originate from the lysed microbial cells. Using this duplicate sample, treated with $CHCl_3$, an extraction using 0.1M NaOH is performed to remove Pi and Po held more strongly by chemisorption to Fe and Al compounds of the soil surfaces. The use of ultrasonification on the 0.1M NaOH extraction that enables the extraction of Pi and Po held on the internal surfaces of soil aggregates. An acid extract of 1M HCl is used to remove mainly apatite-type minerals, but this could also extract occluded P in more weathered soils. Finally the more chemically stable Po forms and relatively insoluble forms are dissolved by oxidation and acid digestion using H_2SO_4 and H_2O_2.

To determine the Pi content in all of these extracts, the method of Murphy and Riley (1962) is used. The total P content is determined by digesting a portion of the Hedley extracts with acidified ammonium persulphate, and then performing the Murphy and Riley (1962) method. The organic P is then calculated by the difference between Pi and total P.

Many variations on this method have been developed but the basic fractions have not changed significantly. While the reason for the fractionation is to separate the different P pools according to their lability, any chemical extraction can at best approximate the biological functions involved in the natural environment. This is due to the many complex interactions continually taking place in the soil, many of which are still unclear.

It may be possible to relate the techniques (such as Colwell) used for assessing plant available P, and assuming that you accept these pools as being plant available, with the total P found in the various pools

using the sequential fractionation schemes which may give some indication as to which pools are accessible by the plant.

1.6.3 Microbial analysis

Soil microbial biomass is also a dynamic force driving soil P cycling. Having a good method to estimate P in soil biomass (Pm) is useful for understanding the P cycle and for characterising bioavailable fractions of P. The most common method uses 0.5M $NaHCO_3$ bicarbonate; in a recent study this bicarbonate method was compared with two alternative methods for estimating Pm. The methods compared were iron oxide paper strips, and resin membrane (Myers et al., 1999). For microbial estimation, duplicate samples are used, one treated with a biocide and one untreated. The difference was an estimate of Pm.

A recovery factor Kp (Hedley and Stewart, 1982) is often used to improve the accuracy of Pm estimates, but this factor is not easily transported between soils as there is still uncertainty about the types of fungi and bacteria used for the calibration being representative of the indigenous microbes in the soil being tested. This variability has convinced some researchers to leave the Kp factor out when reporting Pm estimates. The advantages of the resin membrane over the iron oxide papers is that it is conveniently commercially available which may in turn reduce the variability experienced by different laboratories producing individual batches of iron oxide papers (Guo et al., 1996). In the study carried out by Myers et al. (1999) the results using these alternative methods were found to have greater precision than the bicarbonate method for estimating Pm. However, more research is required into these alternative methods to assess the transportability between different soil types.

1.7 Environmental impacts of Phosphorus losses

1.7.1 What Is Eutrophication ?

Eutrophication is a natural geological process, which involves a body of water such as a lake, and organic life, such as fish, insects, shellfish, bacteria, algae and aquatic plants. Organic life develops and multiplies over the years, and eventually the bottom of the lake accumulates the remains of this organic life and other sediments. Eventually the lake will become very shallow and change into a marshland or swamp and then maybe become dry land. Generally this would occur over thousands of years, particularly for a large body of water. However, large influxes of nutrients can accelerate the process of eutrophication.

One of the most used indicators of eutrophication is the algal bloom. Algae are small plants that live suspended or free floating in water. The most common species is blue-green algae, some are blue-green in colour others are pale green-yellow and some red. Bacterial decomposition of the accumulated dead algae causes an unpleasant smell. Many of the dead cells settle slowly decaying further on the bottom of the water body. It is this bacterial decay that consumes large amounts of the dissolved oxygen, so much so that at times the normal diffusion of oxygen from the air to the water is not sufficient. The oxygen depletion that follows kills fish promoting the growth of even more weeds and algae (Toy and Walsh, 1987).
All plant and animal cells contain approximately 3-5% P in both organic and inorganic forms. For eutrophication other nutrients are essential too, but P can often be the limiting factor in some situations. Most P accumulation is caused by point sources such as sewage containing human effluents and detergents. Land drainage and agricultural run off also contribute, these being more difficult to control. Here the focus will continue to be on the soil-water interactions.

1.7.2 Phosphorus Transport Mechanisms

Loss of P from land can occur in three ways:

1. as dissolved or particulate P in surface runoff: P picked up by rainwater or flooding which flows over the land surfaces to streams or rivers,
2. as dissolved or particulate P in subsurface runoff: P picked up by water that enters the soil profile and moves through the soil to streams or rivers without ever reaching the main water table,
3. as dissolved or particulate P in flow to groundwater: P picked up by water that passes to the water table and which is subsequently discharged to streams, rivers or lakes as seepage (Morgan, 1997).

Phosphorus is transported in both dissolved (DP) and particulate (PP) forms. Particulate P includes P sorbed by soil particles and organic matter eroded during rainfall or flooding, and constitutes the major proportion of P transported from cultivated land. The runoff from grass or forestland carries less sediment therefore is generally dominated by DP. While DP is, for the most part, immediately available for biological uptake, PP can provide a long-term source of P for aquatic biota. The bioavailability of PP can vary from 10 to 90%, depending on the nature of the eroding soil. Together, DP and bioavailable PP constitute bioavailable P (BAP) or P available for uptake by aquatic biota (Sharpley and Rekolianen, 1997).

P loads transported from catchments are a function of catchment hydrology, in terms of timing of surface runoff, soil P content, and the amount of P added as fertiliser or manure. In most cases, P exported from catchments occurs in surface rather than subsurface runoff, although it is recognised that in some regions more P is transported in drainage waters. However the P concentration in water percolating through the soil profile is likely to be small, due to sorption of P by P

deficient subsoils. Exceptions occur in acid organic or peaty soils, where the adsorption affinity and capacity for P are low, due to the predominantly negative charged surfaces, and the complexing of Al and Fe by organic matter. Similarly, P is more susceptible to movement through sandy soils with low P sorption capacities, in soil which has become waterlogged, leading to conversion of Fe(III) to Fe(II) and the mineralisation of organic P; in this case preferential flow occurs through macropores and earthworm holes. Because of the variable path and time of water flow through a soil with subsurface drainage, factors controlling DP in subsurface waters are more complex than for surface runoff.

1.7.3 Surface Runoff

The literature relating the level of P in soil to that in surface run off is limited. Routine soil-P test methods have not been fully evaluated for their ability to predict P concentrations in surface runoff. Romkens and Nelson (1974) reported a linear relationship between level of soil-test P and concentration of DP in surface runoff, using simulated rainfall. This has been confirmed by others in more recent research (Sharpley, 1995; Sharpley et al., 1978).

It has been shown that there is a greater potential for release of DP to surface runoff as soil test P increases. However, the relationship between soil test P and DP concentration of surface run off has varied between studies in terms of the cropping system and the soil type. Differing ratios and contact time between water and soil during runoff could have affected these relationships. Differences can also be noted between grassland and cultivated land, for the same level of soil test P, generally less P was dissolved from the grassland. This difference may result from less contact of surface runoff with the surface soil for grass than for other crops, due to a greater vegetative cover and surface soil protection by grass (Sibberson and Sharpley, 1997).

For a given level of soil test P, the concentration of P maintained in surface runoff will be influenced by soil type. This is because of differences in P buffering capacity between soils, caused by varying levels of iron and aluminium hydroxyoxides, clay, carbonates, and organic matter. This is why care must be taken when using soil test P as the sole criterion for determining the potential for P enrichment of surface runoff from subsequent fertiliser or manure applications.

Sharpley (1995) reported that in the Netherlands the national strategy is to limit P entry into both surface water and groundwater. One of the approaches for accomplishing this goal is the identification of a soil P saturation level, above which P application rates should not exceed crop removal rates. The P saturation approach is based on the fact that the potential for soil P desorption increases as sorbed P accumulates in soil. To determine the critical level of soil P accumulation, Dutch regulations have set a critical limit of 0.1mg /L as DP in groundwater at the depth equal to the mean highest water level. The degree of accumulation is expressed in terms of the phosphate saturation (%), given by:

$$\text{P sorption saturation} = \frac{\text{Extractable soil P}}{\text{P sorption capacity}} \times 100$$

The units of extractable soil P and P sorption capacity are unit mass of DP for a given soil (mg/kg). In the Netherlands, extractable soil P and P sorption capacity are determined from the content of oxalate-extractable P, Al and Fe of non-calcareous soils. A Phosphorus sorption of 25% has been established as the critical value above which the potential for P leaching becomes unacceptable.

P saturation describes the effect of soil type on the differential release of soil P to surface runoff better than common soil P test measures. An added advantage of the P saturation approach is that it not only

describes the potential for P release from soil but also indicates how close the P sorption sites of a soil are to being saturated. The added complexity of this approach in terms of obtaining a reliable estimate of soil P sorption capacity, compared with standard soil test methods, may limit its acceptability at the present time (Sibberson and Sharpley, 1997).

Less information is available on the relationship between soil P and bioavailable P (BAP) in surface run off, including eroded sediments. Bioavailable P consists of DP and a fraction of the PP available for uptake by algae. The transport of bioavailable PP in surface runoff and sediments is dependent on both erosion potential and surface soil P content.

Surface soil resin strip P content, thought to have had a strong theoretical justification for use in estimating BAP, may not on its own be a reliable estimate of the potential for transport of BAP in surface runoff and erosion from agricultural land (Sharpley et al., 1995). An estimate of erosion is certainly more important (Sibberson and Sharpley, 1997).

More recent studies have been looking at the leaching potential of manure and compost amendments in order to reduce the potential of P run off from non point sources (Sharpley and Moyer, 2000). It may be possible in future to develop guidelines for application rates and methods, but more work on the potential soil interactions will need to be carried out in conjunction with the development of these methods.

1.7.4 Predicting Leaching Potential

Many soils have a very high adsorption capacity for P, usually far exceeding the quantities of P added as manures and fertilisers, therefore, it has been considered for a long time that leaching losses of

P from soil to water are negligible in the majority of cases. However, the concentrations of P required to trigger eutrophication in fresh water are extremely small according to Brookes et al. (1997) around 0.02-0.035 mg/l P, other predict it to be as low 0.01 mg/l P.

P leaches easier from organic soils than from mineral soils. Based on the Langmuir equation, phosphate saturation degree (PSD) might be related to the partitioning of P between the solid and the solution phase in soils (Brookes et al., 1997):

$$PSD = \gamma Kc / (1+(\gamma Kc))$$

where: PSD = phosphate saturation degree of the soil profile between the soil surface and the groundwater table.

γ = the ratio between total fixed P and reversibly adsorbed P, usually assumed to be about 3

K = Langmuir adsorption constant, measured as 1.13 l/mg

c = MRP (molybdate reactive P) concentration in the groundwater at the reference level (mg/l –P)

The above equation can allow the determination of critical levels of P saturation in soils in terms of maintaining acceptable P concentrations in the groundwater.

P movement down the soil profile as a result of drainage water can vary widely from negligible to a few mg/l, in arable and grasslands and often even higher in organic soils. In terms of fertiliser loss the costs involved are insignificant, however, in terms of the risks of eutrophication to the receiving water ways the costs may be very high indeed.

Brookes et al. (1997) suggested that the accumulation of P in the soil profile could lead to an increased loss of P in drainage water. A simple indicator is required which can predict the soil P

concentrations at which the risk of leaching becomes significant in different soil types (Brookes et al., 1997). For sandy soils, tests showed that the P sorption capacity and the particle size distribution of the total soil profile down to the groundwater table was a good indicator of the risk of P losses by drainage. Further tests on clay loams showed that until a critical concentration of soil Olsen P was reached, there was not much movement of P, however, once this critical point was reached the movement became significant. Therefore, the critical concentration of soil P needs to be evaluated in different soil types under different management systems to prevent or reduce the movement of P down the soil profile. However, improved understanding of the mechanisms involved is required.

1.8 Modelling

There are several approaches to soil P modelling, depending on the objective. First, models are required to predict fertiliser requirements for agricultural systems, and for this purpose two common techniques have been reviewed. Second, models focussed on P reactions and transport P in soil can lead to both predictions of fertiliser requirements in specific soils, or can generate tables of guidelines for specific crops.

1.8.1 Modelling Fertiliser Requirements

There has been a great deal of research has in this area over the last 40 years. In Australia farmers are often given the option of assuming that half a bag of superphosphate per acre is ‘close enough’ (~ 9 or 10 kg P per hectare), or the option of using sophisticated multinutrient response surface prediction methods (Bowden, 1989). The majority of fertiliser recommendations are simple single-figure advice, generally derived from biological levels of response to superphosphate

from regional trials on a soil type basis. Alternatively P recommendations have been done on a mass balance basis. All states have commercial soil testing laboratories that make fertiliser recommendations. Farmers usually apply fertiliser at a rate which they can afford using the recommendation as a guideline, if it is a good year they will apply more fertiliser. The recommendations are often imprecise, even those generated by specifically designed software. Many variables exist in a season-to-season response to fertiliser addition.

Response Surface Prediction Methods

The two ways of using this method are the direct regression approach and the mechanistic modelling approach. The latter method is less direct but more flexible. Direct regression is based on a number of trials carried out on farm conditions to try to trial for every variable. This approach has not been widely used in its original form in Australia. Some of the reasons for this are a lack of knowledge of the statistical and design errors in data sampling and analysis. The method is very demanding of resources, and is even more resource demanding if it has to be extended to a new crop or field, crop rotation or tillage conditions. It is impractical for such applications as grazing requirements because it would be necessary to trial different stocking rates and type and the potential yield is not given sufficient value using this approach.

Mechanistic modelling approach

This approach is more flexible and readily extendable across the wide range of environmental and management conditions which exist, and is normally applied with less statistical rigour. The smaller number of trials can lead to the ability to relate pasture responses to environmental variables, and can then be related to responses in animal products. This approach is more able to allow for variation in predicting the potential yield. Further research in this area is still necessary.

1.8.2 Modelling Phosphorus Behaviour

This area of modelling is used to predict responses for specific crops under certain soil conditions and is only useful for the current crop. These models often use the phosphate buffering capacity (PBC) of soil as this has been found to describe the relationship between solid phase phosphorus and P concentration in the soil solution. It can be referred to as a factor determining P flux by through the soil, influencing the movement of P to plant roots and the uptake of P by plants (Probert and Moody, 1998). However, PBC alone is not an adequate predictor of crop uptake, a soil with no P present will still have a PBC. The PBC is often used alongside the Quantity (Q) and the Intensity (I) of P in the soil. Q is the total measurable P in the soil and I is the amount of P in the soil solution. Therefore it is considered necessary to measure the intensity and quantity of the P in the soil solution and the PBC of the soil. From this it is possible to obtain a phosphate sorption curve.

Quantity is analysed using soil P tests that have a large soil / extractant ratio and a long extraction time using concentrated extractants and buffered pH, such as Colwell. Intensity soil tests will have a lower soil / extractant ratio, shorter extraction period and unbuffered low strength extractants, such as the calcium chloride method (Moody et al., 1983).

Recent research (Probert and Moody, 1998) has indicated that in principle it should be unnecessary to measure all three factors controlling P availability since they should be interrelated. Determination of the intensity factor is referred to as experimentally difficult it may be possible to obtain fertiliser requirements by measuring only quantity and PBC; as intensity and quantity have been found to be related to each other (Probert and Moody, 1998). This functional relationship between soil P and P uptake is important in crop growth models, as is the PBC. However, further work is still

required before it will be possible to produce a more transportable and practical model.

Other studies have tried to use modelling techniques to find the balance between P fertilisation requirements and the risk of leaching from over-fertilised land (Campillo et al., 1999). This is an area which will be of increasing interest as the risk of eutrophication of receiving waterways grows.

1.9 Discussion

Soil P fertilisation certainly still requires much more research in terms of land P needs and the risks to waterways. The reason for choosing this area of research was because of the lack of information in terms of fertiliser requirements in wetland soils and for wetland vegetation. Therefore, the discussion has been focused on fertilisers their production (Toy and Walsh, 1987), and interaction with upland (Barrow, 1983) and wetland soils (Kadlec and Knight, 1996), analysis of soil requirements (Tiessen and Moir, 1993), losses to water (Brookes et al, 1997) and modelling of P (Probert and Moody, 1998).

The next section of this study focuses on the fate of P in constructed wetland soils in both a chemically loaded and non-chemically loaded system, and what information can be obtained in trying to find the balance between P fertilisation and P losses to water in both situations. The third section reports and discusses the performance of the constructed Reed Bed Treatment System in treating ammonia, phenol and cyanide in the Coke Ovens ammoniacal liquor. The final section will involve using a model to predict fertiliser behaviour in the chemically loaded environment and comparing these results with those obtained through experimentation.

2. Investigation of Phosphorus Pools in a Constructed Reed Bed Treatment System.

Abstract

The aims of this investigation were to determine the fate of phosphorus (P) fertiliser when added to a constructed reed bed treatment system (RBTS) and to determine whether high chemical (ammonia, phenol and cyanide) loading changed the way P behaved.

Two RBTS trial cell containers were built, one as a control the other to be treated with a strong ammoniacal liquor solution. The cells were fertilised and batch fed. Tap water was used for the control, while a coke oven gas condensate liquor/water solution 1:9 with a high ammonia, phenol and cyanide content was used for the experimental trial cell.

Initial P analysis of the soil was carried out before fertiliser and liquor addition, using a modified version of the Hedley Fractionation. After fertilisation the same fractionation was performed to compare the size of the P pools, how they were affected by fertiliser addition and how these pools had changed over time. Phosphorus uptake by the plant was also determined along with run-off water to assess how much P was lost in the leaching fraction. It was found that a lesser amount of P was leached from the chemically loaded soil; however, the leaching levels were very low overall. The more labile inorganic P (Pi) fractions (Resin-Pi and $NaHCO_3$-Pi) increased in all samples after initial fertilisation and then decreased over time. Organic P (Po) ($NaHCO_3$-Po and NaOH-Po) was undetectable in the top 0-5 cm layer of soil after fertilisation and remained undetectable throughout the trial. However in the lower 10-15 cm layer of soil the $NaHCO_3$-Po levels was undetectable after fertilisation and then increased in the final sample with the largest increase being seen in the chemically loaded soil. In both control samples the NaOH-Pi pool showed an

overall increased in the final sample in both the topsoil and the root zone at the expense of the HCL-Pi pool, which could be related to changes in the iron binding sites. Soil used to build both the Control and the Trial systems had been previously exposed to high chemical loading by coke oven effluent. Therefore it is possible that the sulphate within this effluent could be responsible for preferential Fe binding but as the level of sulphate dropped in the control system the preference may have been for P to move into the pool associated with Fe and Al compounds. A reduction in the pH of the ground water from 8.3 to 7.6 during the course of the trial occurred in the Control system, which may have also influenced this movement.

2.1 Introduction

The Whyalla Steelworks uses a biological treatment system at its coke making facility for the treatment of a percentage of its effluent, allowing the water to be reused elsewhere in the process. The treated water from this 2 ha Reed Bed Treatment System (RBTS) does enter the on-site waste water treatment pond systems which have a tidal flow exchange with the local marine environment through a series of ponds. The 2 ha RBTS has been in operation since 1996 and fertilisation is required to ensure the continuing health of the plants in this system. As this is a unique system operating in a heavy industrial environment there are no similar systems that can be used to gauge how P behaves and at what application rates fertilisers should be applied. A key consideration is to ensure that over-fertilisation does not occur, which could lead to significant P runoff into the waste water treatment pond system.

The aims of this investigation were 1) to determine the fate of phosphorus (P) fertiliser when added to a constructed RBTS and, 2) to determine if high chemical (ammonia, phenol and cyanide) loading

changed the way P behaved and what influence this has on determining fertilisation rates for this type of system.

In this study the effects of fertilisation on the various P pools within control and chemically-loaded trial vertical-flow constructed wetlands, or Reed Bed Treatment Systems (RBTS) were studied, as well as P leaching fractions and plant uptake. Plant uptake was investigated to assess how much P was taken up by the plant during the trial. However this uptake fraction would be expected to return to the soil after plant senescence and the ensuing breakdown of dead matter, as plant material would not usually be removed in full scale versions of this kind of RBTS.

The flow rate of 45 L/m^2 per day used for this trial is about average for this type of treatment system, however hydraulic loading on constructed wetlands vary greatly, depending on chemical composition of the effluent.

2.1.2 Materials and Methods

Two trial cells were built for the purpose of this experiment. The dimensions of the plastic containers used were approximately 640 mm long by 350 mm wide and 295 mm deep. Collection pipes with drill holes along the length were laid in the base of the containers and gravel was used to cover the pipes. The containers were filled with 250 mm of soil taken from the 2 ha Reed Bed Treatment System (RBTS) at the Whyalla Steelworks containing healthy rhizomes of *Phragmites Australis*.

Figure 2.1 shows a sketch of the trial cells including the inlet-supply and outlet-collection systems with an inlay to show the layout of the outlet collection pipes. The level-control consisted of a flexible pipe

on an adjustable chain. During the trial the level was kept at 2-5 cm below soil level.

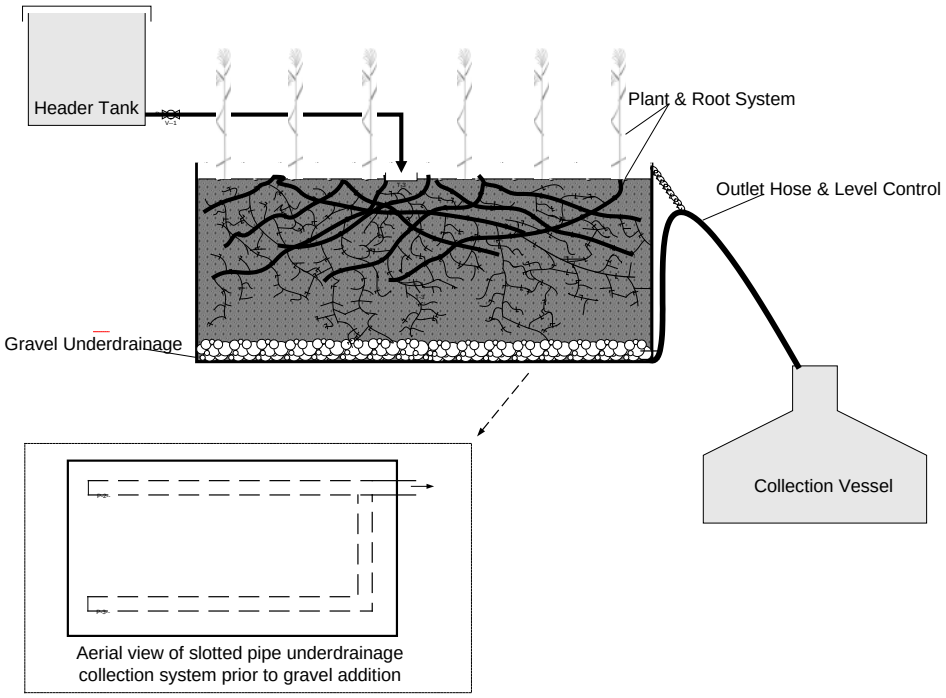


Figure 2.1: Sketch of the vertical flow RBTS containers used for the control and trial during the experiment. Inset shows perforated pipework for collection and drainage of effluent from the system.

The inset diagram is the top view of the pipe work located beneath the gravel base; the dotted lines represent the drilled collection pipe work. This is also pictured in plates 2.1a and 2.1b below. The inlet liquid was directed on to a plastic disc to prevent scouring of the soil surface and this also aided liquid distribution across the soil surface.

Plate 2.1a the outlet pipework (right) for drainage and collection of outflow from the system, gravel (right) used to protect drainage system from blockages in the RBTS cells.

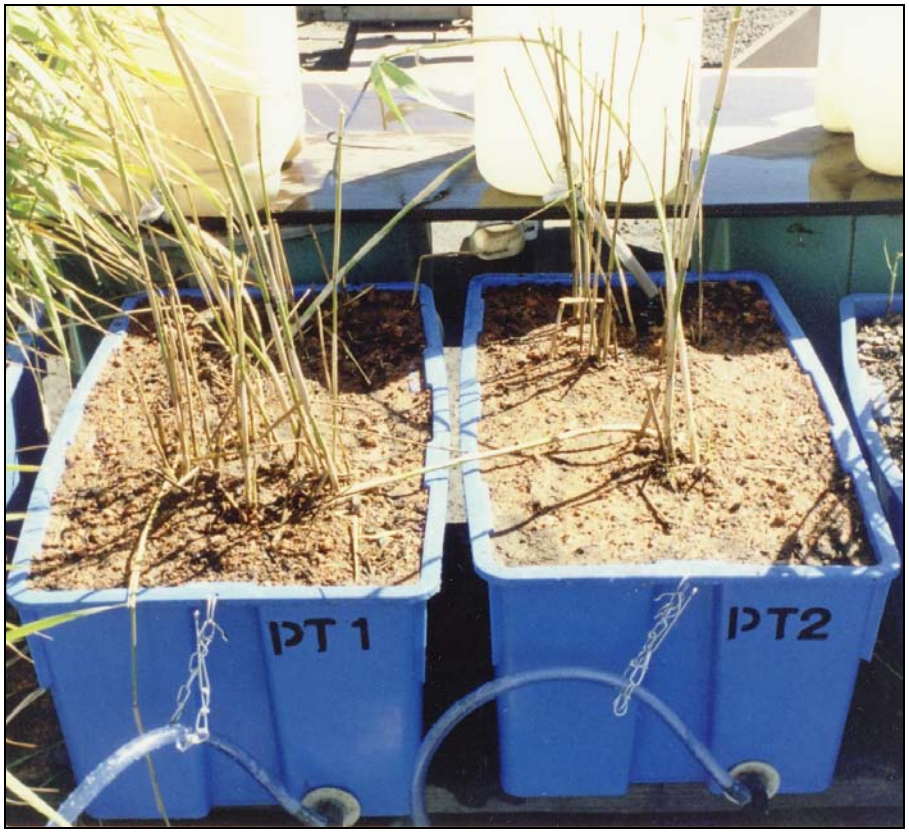


Plate 2.1b the completed RBTS cells prior to the start of the experiment.

Both trial cells were fed 10 litres of liquid per day for 27 weeks, this was drip fed in batches from the inlet supply container over a period of approx 10 hours per day, regulated by a tap. The control was fed mains tap water for the whole of the trial. The chemically loaded trial was fed water for one week in order to establish some initial plant growth and to allow the freshly excavated soil to settle. After the first week a 1:40 liquor:water solution was applied for one week to the chemically loaded trial. This was increased to 5% for one week. Finally the solution was increased to 10% for the balance of the experiment. Distribution across the surface of the cell was fairly even around the centre; however the edges of the container received less liquid. The depth of liquid was kept 2.5 cm below the surface; therefore the overall depth of the soil would have had a fairly even distribution of liquid. The outlet water was collected in a 25 L plastic container and sampled daily; analysis of a 7-day composite sample was carried out for P levels on a weekly basis. Solution P was determined using Standard Method 4500-P E, 1995 (Murphy and Riley, 1962). A calendar of application rates and fertiliser addition is included in Appendix 1.

Table 2.1 shows the main constituents of the chemical load added to the trial.

Constituent	Concentration	Units
Ammonia as N	200-250	mg/L
Total cyanide	4-10	mg/L
Sulphate	50-250	mg/L
Phenols	58-62	mg/L
Total PAH	1.3	mg/L
TPH	4.43	mg/L

Table 2.1 Approx composition of a 10% Coke Ovens liquor solution which was used to feed the trial RBTS. This liquor supply can be variable at times.

PAH – Poly aromatic hydrocarbons, TPH – Total petroleum hydrocarbons.

Initial P levels in the soil were determined, including their corresponding pool sizes. Samples were taken from the top 0-5 cm soil layer, and also from the 10-15 cm soil layer which corresponded to the rhizome depth (root zone) for this trial. The 0-5 cm layer was predominantly the 2.5-5 cm layer as this was the layer considered to be reasonably uniform in terms of liquid application. Samples were taken from four locations in each container and mixed prior to analysis. Samples were taken by digging a hole using a small trowel and taking the sample from the wall of the hole at the appropriate depth using a spoon. The holes left from sampling were back filled using small amounts of the same soil type and the sample points marked to prevent further sampling at that point. The texture of the soil was clayey and smooth. Approximately 2.6 g P per container was applied on day 7 using liquifert$^{(T)}$ (12% N, 26% P, 10 g/L), distributed evenly across the surface.

The soil particle density was measured and was found to be 2.15 g/cm^3, which is much lower than normal soils. The soil bulk density was found to be 1.15 g/cm^3 (Plaster, 1997). Soil samples were taken 20 days after fertiliser application and again 24 weeks after fertiliser application for P analysis. Moist soil samples were used in the fractionation, and results were converted back to oven-dry measurements.

The procedure used to fractionate the soil P was a modified version of the Hedley Fractionation procedure (Hedley et al., 1982, Tiessen and Moir, 1993, Agbenin and Goladi, 1998). The procedure used is summarised in figure 2.2.

A modified Hedley Fractionation

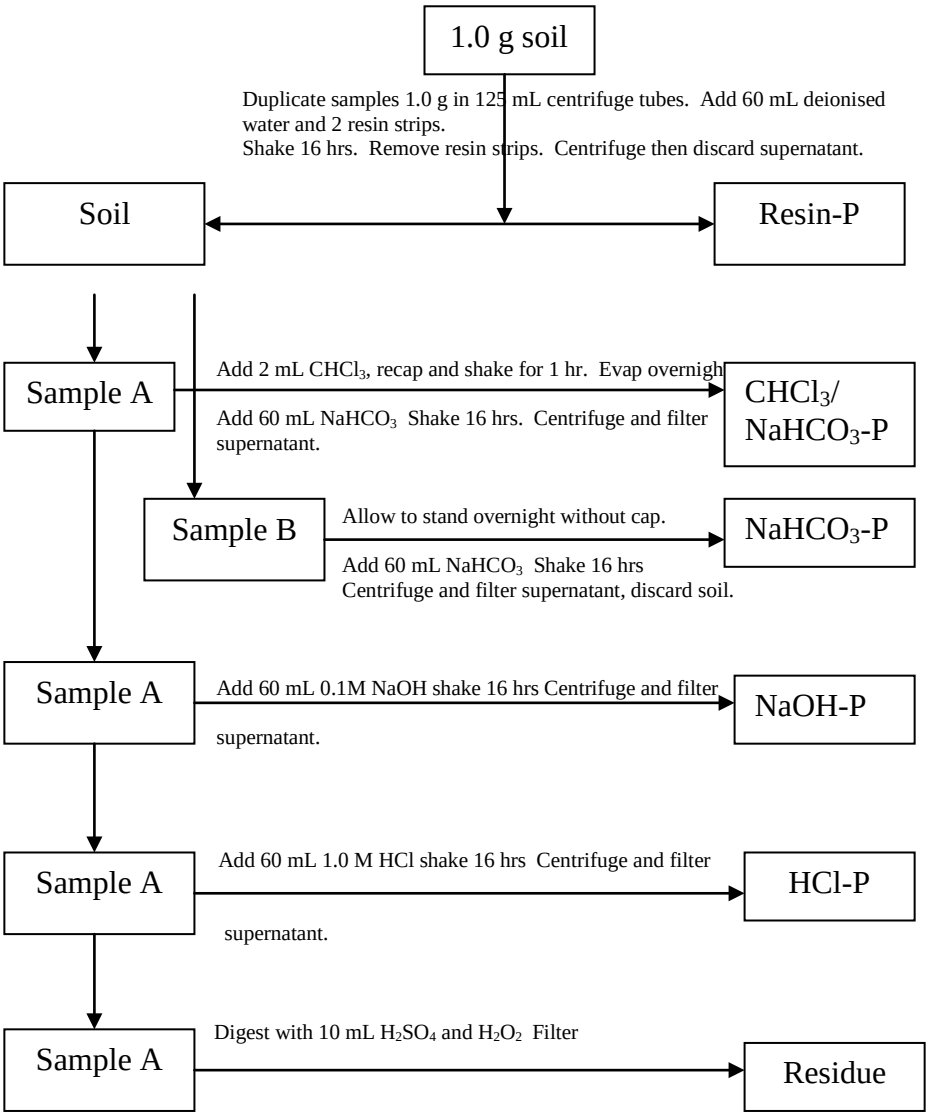


Figure 2.2 Flow chart for the fractionation of soil phosphorus into various fractions. Microbial-P estimates are calculated from the differences between $CHCl_3$/$NaHCO_3$-P (sample A) and $NaHCO_3$-P (sample B). Adapted from Hedley et al (1982).

A Berthold HermLe KG Gosheim Type 2364 centrifuge was used with 125 mL stoppered centrifuge tubes. Samples were shaken using a reciprocal shaker. A Perkin Elmer 552 UV/Vis spectrophotometer was used to analyse the P extracts.

The most biologically available P fraction was removed first using anion exchange resin (AER) strips (Myers et al 1999). The AER

strips were prepared as described by Myers et al. (1999). Soil corresponding to 1 g of oven-dry sample was extracted using two AER strips 2.08 cm x 4.15 cm and 60 mL of deionised water. After shaking for 16 hours the strips were removed and excess soil rinsed off. The AER strips were then extracted using 60 mL 0.5M HCl. The soil sample was then centrifuged, the supernatant discarded, and allowed to stand overnight.

The labile Pi and Po was removed by extracting with 60 mL of 0.5M $NaHCO_3$, shaken for 16 hours, centrifuged and the supernatant decanted. A duplicate resin extracted sample was treated with chloroform (2 mL) and shaken for one hour prior to being allowed to stand overnight. The samples were then extracted using $NaHCO_3$. The difference in P content between these samples was used as estimation of the P released from lysed microbial cells, although this would probably only constitute about 40% of the microbial P. A correction factor was not used here as P varies with composition of the microbial population and soil sorption of the lysed P (Selles et al., 1995), therefore the results listed are the actual differences between the two extractions.

The chloroform pre-treated NaHCO3 extracted soil sample was then further extracted using 60 mL 0.1M NaOH, shaken for 16 hours, centrifuged and the supernatant decanted. This was to remove Pi and Po compounds that are more tightly bound by chemisorption as in the case of Al and Fe bound P on the soil surfaces.

A further extraction was then carried out using 60 mL of 1M HCl, shaken for 16 hours, centrifuged and the supernatant decanted. This was to remove mainly apatite-type minerals but can also extract occluded P in highly weathered soils.

The final extract of the most chemically stable Po forms and the less soluble Pi forms was carried out using an oxidation and acid digestion

method using H_2O_2 and H_2SO_4. Concentrated H_2SO_4 (10 mL) was added to the soil sample and heated in a water bath, 10 mL of H_2O_2 was then added 1 mL at a time.

Inorganic phosphorus was determined by taking an aliquot of each extract using the Ascorbic Acid Standard Method 4500-P E, 1995 (Murphy and Riley, 1962). A further aliquot of the $NaHCO_3$ and NaOH extracts were taken and digested using an acidified ammonium persulphate oxidation (Standard Method 4500-P B, 1995). This was then analysed using the same method to give the total P content of the extract. The organic P was then estimated from the difference between the total P and the inorganic P.

P in plant tissue was determined using the extraction method described below. A dried tissue sample (0.1 g) was ashed at 500^oC for 4 hours. The ashed sample was dissolved in 10 mL of 1M HCl which was then diluted to 100 mL. Solution P was determined using Standard Method 4500-P E, 1995 (Murphy and Riley, 1962).

The P buffer capacity was determined by an external laboratory (Incitec pivot).

2.2 Results

2.2.1 Fractionation results

The data in Table 2.2 and Table 2.3 illustrate the changes in the P pools that occurred during this experiment. Duplicate determinations were performed (the data in the tables are the means of the duplicate samples, all duplicate samples were taken from a single composite sample). The maximum standard deviation between samples was 5.4 ug/g.

The main observations and trends were:

1) In both of the containers the Resin-P and $NaHCO_3$ Pi increased after fertilisation then decreased over time for the 10-15 cm depth and for the Trial container at the 0-5 cm depth, however for the Control 0-5cm depth there was a further increase in the $NaHCO_3$ Pi pool in the final sample. These pools are generally considered to be the most labile pools.

2) The $NaHCO_3$ Po was detected before fertilisation in all samples, after fertilisation it was undetectable in the Trial and Control 0-5 cm samples. In the Trial and Control 10-15 cm samples however it was undetectable after fertilisation, but in the final sample it was detected and had increased in both samples, more so in the Trial 10-15 cm sample.

3) The microbial Pi in the Trial and Control samples for 0-5cm depth showed a steady decrease over time. In the 10-15cm depth samples from the Trial there was an increase after the fertilisation, and then a decrease. The Control 10-15cm sample saw a decrease after the fertilisation and the final sample remained the same.

4) The microbial Po was only detected in the 10-15cm depth samples for both Trial and Control in the final sample. It is possible that not all microbial P was accounted for (Selles et al., 1995).

	0-5 cm						10-15 cm					
P fraction µg/g	Prior to fertilisation		20 days after fertilisation		24 weeks after fertilisation		Prior to fertilisation		20 days after fertilisation		24 weeks after fertilisation	
	Trial	Control	Trial	Control	Trial	Control	Trial	Control	Trial	Control	Trial	Control
Inorganic-P												
Resin-P	22.4	23.3	42.4	89.3	21.1	41.6	8.8	9.7	42.7	49.3	13.9	39.6
0.5M $NaHCO_3$-P	51.7	49.9	70.8	57.6	54.8	58.3	53.6	57.2	99.1	97.3	37.1	39.8
$CHCl_3$ released 0.5M $NaHCO_3$-P	14.3	12.4	12.6	8.3	4.2	4.2	18.1	16.5	22.5	3.9	13.8	4.0
0.1M NaOH-P	44.4	44.4	21.2	18.5	33.7	129.0	41.5	40.7	45.2	40.7	27.8	126.7
1.0M HCl-P	150.2	154.0	153.6	144.2	151.8	45.9	145.5	148.9	186.1	179.7	180.8	35.5
Total Pi fractions	283.0	284.0	300.6	317.9	265.6	279.0	267.5	273.0	395.6	370.9	273.4	245.6
Organic-P												
0.5M $NaHCO_3$-P	6.5	5.4	0.0	0.0	0.0	0.0	4.1	4.5	0.0	0.0	29.5	7.5
$CHCl_3$ released 0.5M $NaHCO_3$-P	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	30.7	4.5
0.1M NaOH-P	3.0	2.6	0.0	0.0	0.0	0.0	4.7	3.4	5.7	7.7	0.0	0.0
Total Po fractions	9.5	8.0	0.0	0.0	0.0	0.0	8.9	7.9	5.7	7.7	60.2	12.0
Residual-P												
H_2SO_4/H_2O_2-P	144.8	145.2	162.5	128.0	156.2	137.6	127.2	127.4	84.6	104.5	130.0	138.3
Total P												
Pi + Po + residual-P	437.3	437.2	463.1	445.9	421.8	416.6	403.6	408.3	485.9	483.1	463.6	395.9
H_2SO_4/H_2O_2-P of whole sample	445.4	438.2	471.4	454.8	433.3	426.5	421.2	413.9	494.3	487.4	479.5	402.4
% recovery	98.2	99.8	98.2	98.0	97.3	97.7	95.8	98.6	98.3	99.1	96.7	98.4

Table 2.2 Phosphorus removed by sequential extraction of soil samples from the chemically loaded soil and the control at 0-5 cm and 10-15 cm soil depths. Measurements in µg/g

	0-5cm						10-15cm					
P fraction %	Prior to fertilisation		20 days after fertilisation		24 weeks after fertilisation		Prior to fertilisation		20 days after fertilisation		24 weeks after fertilisation	
	Trial	Control	Trial	Control	Trial	Control	Trial	Control	Trial	Control	Trial	Control
Inorganic-P												
Resin-P	5.1	5.3	9.2	20.0	5.0	10.0	2.2	2.4	8.8	10.2	3.0	10.0
0.5M $NaHCO_3$-P	11.8	11.4	15.3	12.9	13.0	14.0	13.3	14.0	20.4	20.1	8.0	10.1
$CHCl_3$ released 0.5M $NaHCO_3$-P	3.3	2.8	2.7	1.9	1.0	1.0	4.5	4.0	4.6	0.8	3.0	1.0
0.1M NaOH-P	10.2	10.2	4.6	4.1	8.0	31.0	10.3	10.0	9.3	8.4	6.0	32.0
1.0M HCl-P	34.3	35.2	33.2	32.3	36.0	11.0	36.1	36.5	38.3	37.2	39.0	9.0
Total Pi fractions	64.7	65.0	64.9	71.3	63.0	67.0	66.3	66.9	81.4	76.8	59.0	62.0
Organic-P												
0.1M $NaHCO_3$-P	1.5	1.2	0.0	0.0	0.0	0.0	1.0	1.1	0.0	0.0	6.4	1.9
$CHCl_3$ released 0.5M $NaHCO_3$-P	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	6.6	1.1
1.0M NaOH-P	0.7	0.6	0.0	0.0	0.0	0.0	1.2	0.8	1.2	1.6	0.0	0.0
Total Po fractions	2.2	1.8	0.0	0.0	0.0	0.0	2.2	1.9	1.2	1.6	13.0	3.0
Residual-P												
H_2SO_4/H_2O_2-P	33.1	33.2	35.1	28.7	37.0	33.0	31.5	31.2	17.4	21.6	28.0	34.9
Total P												
Pi + Po + residual-P	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
H_2SO_4/H_2O_2-P of whole sample	101.8	100.2	101.8	102.0	102.7	102.4	104.4	101.4	101.7	100.9	103.4	101.6
% recovery	98.2	99.8	98.2	98.0	97.3	97.7	95.8	98.6	98.3	99.1	96.7	98.4

Table 2.3 Percentage phosphorus removed by sequential extraction of soil samples from the chemically loaded soil and the control at 0-5 cm and 10-15 cm soil depths.

5) NaOH Pi for both the Trial and Control samples at 0-5 cm decreased after fertilisation and then increased. The Trial samples at 10-15 cm depth increased after fertilisation and then decreased. The Control samples at 10-15cm depth remained constant after fertilisation then increased.

6) NaOH Po in the Trial and Control 0-5 cm depth samples was only detected prior to and not after fertilisation. For trial and Control 10-15 cm there was an increase in NaOH Po after fertilisation, however, it was undetectable in the final sample.

7) In both Trial samples and in the Control 10-15 cm depth the HCl P increased after fertilisation then decreased. The Control sample at 0-5 cm depth showed a decrease across all samples.

8) The Trial 0-5 cm sample residual P extracted using H_2SO_4/H_2O_2 increased after fertilisation and further increase in the final sample. The Trial 10-15 cm and the two Control samples residual P decreased after fertilisation and increased in the final sample.

There were a number of differences between the Trial and Control results the most significant difference being seen in the NaOH Pi pool. The final sample indicates that under normal conditions P was in a more available form than the Trial which was under high chemical loading and had more P in the HCl pool.

A further anomaly in the data is the behaviour of P in the organic fractions. Organic P may be rapidly mineralised into Pi and Residual P (Cross et al 1995). It is possible that under these circumstances that the Po is interchanging with these other fractions as a result of the flooding of this type of weathered soil. For the 0-5 cm region this pool in undetectable after the initial sample, but at the 10-15 cm depth we see an increase in this pool overall for both cells, however the

increase is greater for the chemical loaded soil which may be a consequence of more microbial activity following chemical loading.

These changes can be seen more clearly in figures 2.4a-d below.

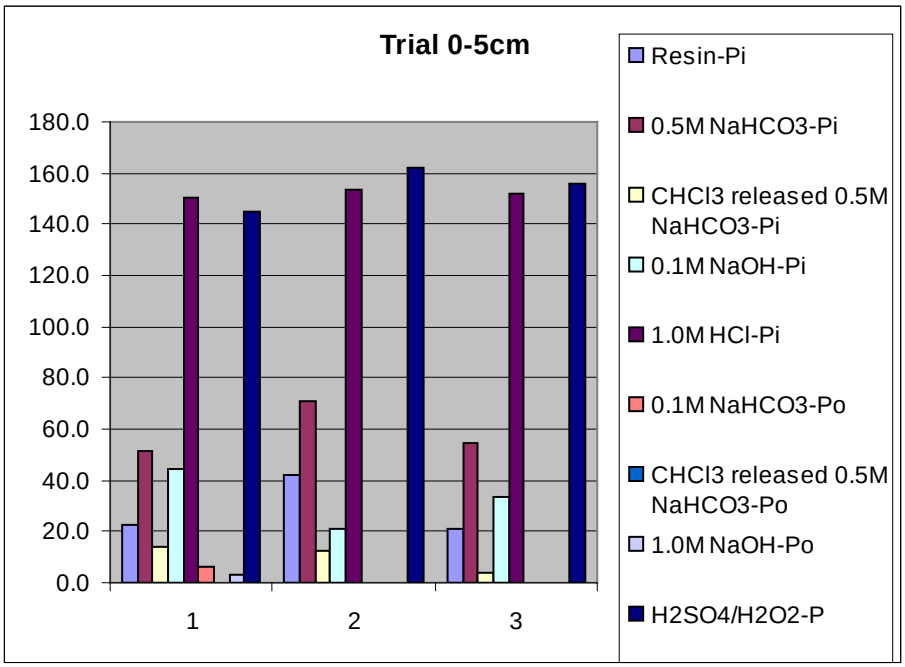


Figure 2.3a

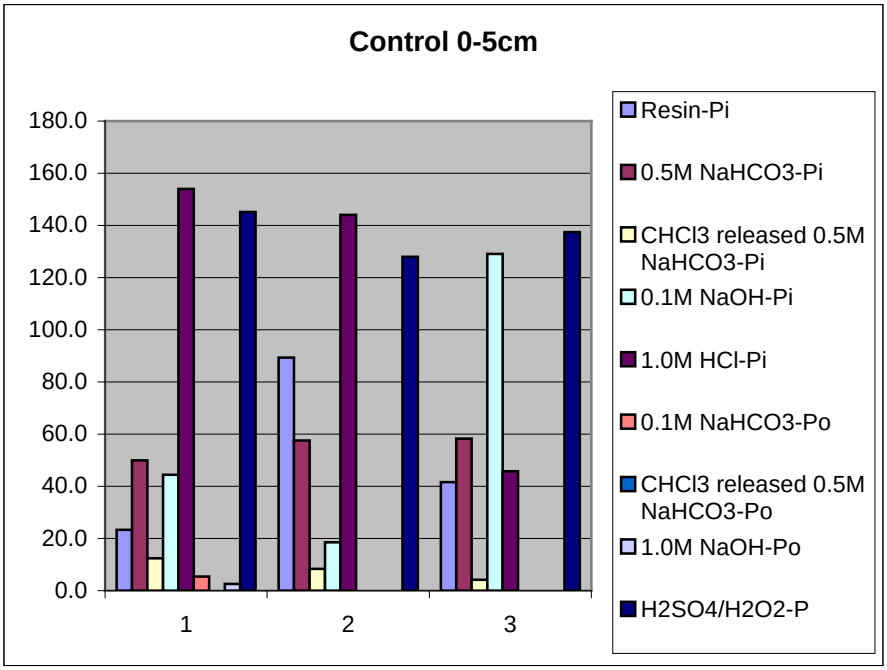


Figure 2.3b

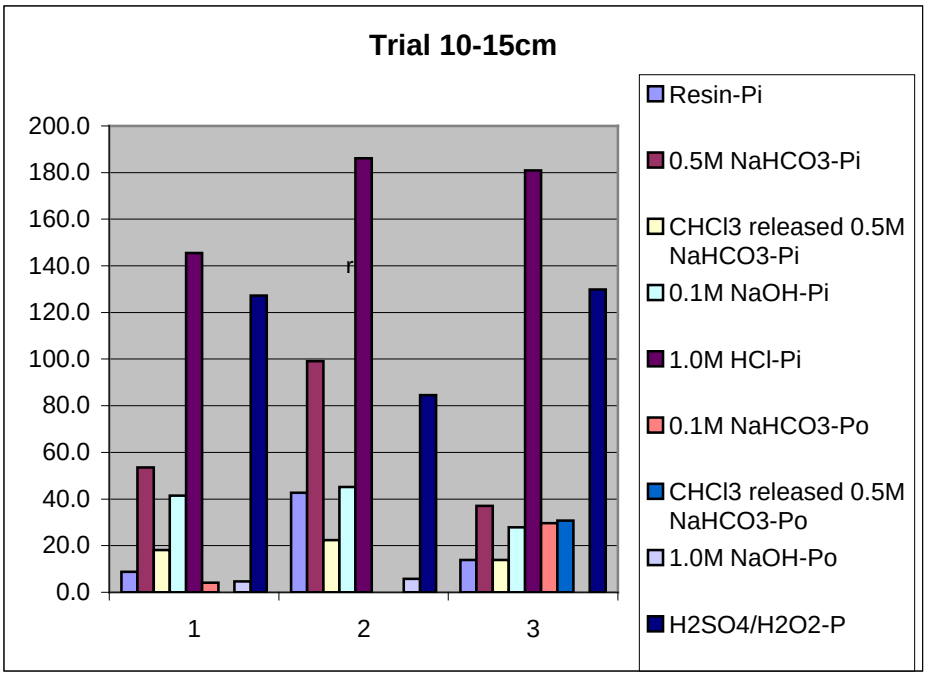


Figure2.3c

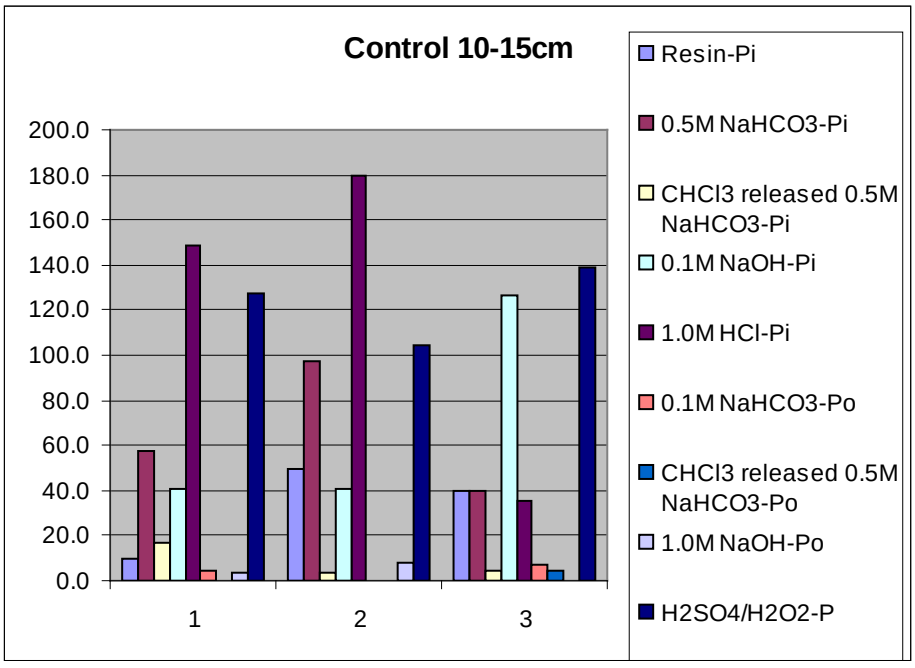


Figure 2.3d

Figures 2.3 a-d show how the P pools changed due to fertiliser inputs. The x axis represents the three different sample times, i.e. prior to fertilisation, 20 days after fertilisation and 24 weeks after fertilisation.

2.2.2 Phosphorus losses to water

The data in Table 2.4 illustrates the leaching data for both trials. As can be seen by the results the amount of leached P increased after the initial fertilisation and then decreased for the duration of the trial. This has been further illustrated in figure 2.4.

	Trial			Control		
Week No.	Pi conc µg/L	Po conc µg/L	P1 Total µg/L	Pi conc µg/L	Po conc µg/L	P2 Total µg/L
1	0.09	0.01	0.10	0.10	0.01	0.11
2	1.11	3.00	4.11	1.60	2.16	3.76
3	0.29	6.27	6.56	0.56	11.27	11.82
4	0.24	1.77	2.01	0.51	1.85	2.36
5	0.49	0.47	0.96	0.66	1.00	1.66
6	0.71	1.01	1.72	0.91	1.41	2.32
7	0.52	0.48	1.00	0.70	2.59	3.28
8	0.60	0.67	1.27	0.91	2.27	3.18
9	0.76	0.59	1.35	1.52	1.98	3.50
10	0.82	0.37	1.19	1.67	2.24	3.91
11	0.33	0.14	0.47	1.44	3.21	4.65
12	0.76	0.02	0.78	2.14	1.51	3.65
13	0.68	0.10	0.78	1.15	1.97	3.12
14	0.62	0.02	0.64	1.01	2.27	3.28
15	0.60	0.10	0.70	0.68	3.03	3.71
16	0.68	0.05	0.73	1.52	1.47	2.99
17	0.38	0.21	0.59	1.07	2.14	3.21
18	0.41	0.22	0.63	1.19	1.90	3.09
19	0.42	0.05	0.47	0.97	2.18	3.15
20	0.26	0.06	0.32	0.86	2.01	2.87
21	0.33	0.07	0.40	0.63	2.57	3.20
22	0.29	0.22	0.51	0.84	2.52	3.36
23	0.22	0.20	0.42	0.69	2.48	3.17
24	0.32	0.09	0.41	2.31	0.44	2.75
25	0.29	0.07	0.36	0.92	1.96	2.88
26	0.31	0.08	0.39	0.78	1.67	2.45
27	0.35	0.08	0.43	0.12	2.49	2.61

Table 2.4. Phosphorus leaching data from the Trial and Control cells

It was established through water balance measurements performed on the 2 Ha RBTS at Whyalla Steelworks that the evaporation + transpiration rate (ET) is approximately equal to the potential evaporation rate (E_{rate}) for the Whyalla area. Therefore the crop factor is assumed to be 1.0 using this factor and the evaporation data from the Bureau of Meteorology for Whyalla it is possible to estimate the total loss by leaching of P from the trial systems also located in Whyalla during the trial period.

P loss = (Total inlet water - (E_{rate} x surface area)) x P in outlet water

For the trial cell the total P loss was estimated to be 1.65 mg, and for the control cell the total P loss was estimated to be 5.32 mg.

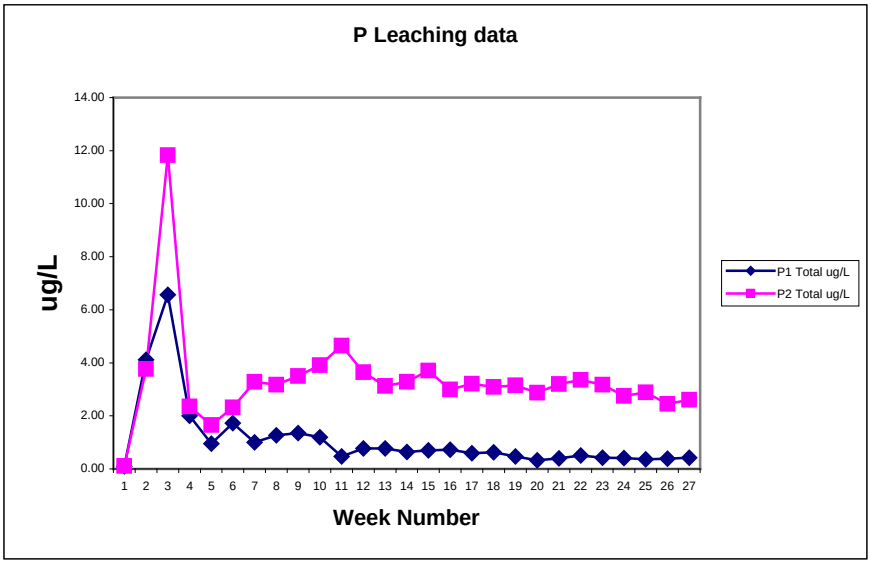


Figure 2.4 Time curve depicting the P Leaching pattern during the experiment

Outlet samples were taken daily. A seven-day composite sample was analysed giving the average P loss for the week. As can be seen from figure 2.4, both trials were losing negligible amounts of P prior to fertilisation. Once fertilisation took place both trials experienced an increase in the amount of P being lost, the control showed a higher

loss. The amount of P loss reduced with time, the reduction was slower in the control. Some variation was seen in the P2 samples between weeks 5 and 11 however due to the small values involved these are assumed not to be significant.

2.2.3 Plant Tissue

The plant tissue analysis gave P levels for the control plant to be 0.27% and for the trial plants 0.35% (on a dry weight basis). Plant growth in the containers was healthy for both cells with a similar number of plants in each cell. The plant growth is pictured below in plate 2.3.3.

Plate 2.3.3 Growth in the trial and control cells in week 18 of the trial period.

2.3 Discussion

2.3.1 Fertiliser Levels

The fractionation technique was chosen so as to separate the different P pools according to their lability. However any chemical extraction can only be at best an approximation of the biological functions happening in the soil at any one time. This is because of the many complex interactions continually taking place in the soil (Tiessen and Moir, 1993). For this reason it is difficult to obtain reproducible results. It was found that even a small loss of sample at any stage during analysis had a large impact on the final result and the extraction would have to be performed again. Great care was needed to get reliable results.

The modified Hedley fractionation process is a time consuming and difficult way of determining P for information about fertiliser needs. It is possible to use other techniques to determine fertiliser needs such as Quantity and Intensity (Q/I) relationships (Sui and Thompson, 2000). Q/I relationships are used to describe soil P equilibrium. This relationship allows the prediction of P retention and P release in soils. It involves the determination of P sorption isotherms. It was not possible during this experiment to determine this relationship.

For the application used here it is necessary to balance the needs of the plant with the risk of P loss through leaching. Therefore it may be possible to adapt the strategy used in the Netherlands (Sharpley, 1995). As discussed in section 1.7.3, the aim is to limit P entry into both surface water and groundwater. One of the approaches for accomplishing this goal is the identification of a soil P saturation level, above which P application rates should not exceed crop removal rates. The P saturation approach is based on the potential for soil P desorption to increase as sorbed P accumulates in soil. The degree of

accumulation in the soil is expressed in terms of the phosphate saturation (%), given by:

$$\text{P sorption saturation} = \frac{\text{Extractable soil P} \times 100}{\text{P sorption capacity}}$$

In the Netherlands, extractable soil P and P sorption capacity are determined from the content of oxalate-extractable P, Al and Fe of non-calcareous soils (Sharpley, 1995). For the purpose of this experiment it may be possible to use the Total extracted P and the P sorption capacity of the soil to determine P sorption saturation for this type of system. A P sorption of 25% has been established as the critical value above which the potential for P leaching becomes unacceptable. This however relates to upland soils, therefore the critical value is unlikely to be the same for a saturated soil.

The P buffer capacity for the soil used in this experiment is 4200 mg/kg, therefore the trial container P sorption saturation ranged from 10.6% prior to fertilisation, and 11.4% after fertilisation. The control container P sorption saturation ranged from 10.4% prior to fertilisation and 9.6% after fertilisation. The difficulty here is that not all P can be accounted for therefore this can only act as an approximate value for P sorption capacity. The Dutch regulations also have a critical limit of 0.1 mg/L as dissolved P in groundwater (Sibberson and Sharpley, 1997). If this is used in conjunction with the P sorption saturation it may be possible to estimate a critical level of P content.

For the chemical loaded soil at 11.4% P sorption saturation there is approx 0.4 µg/L in the groundwater, therefore this system is a long way from the critical P limit for this type of system. The control system contains approx 2.6 µg/L in the groundwater, again significantly below the critical P limit. The interesting point here is that the P levels in both systems are very similar and yet in the chemically loaded soil P is at less risk of being leached, which could

indicate that the change in soil conditions and pH resulting from the chemical loading increases the sorption of P taking place in the RBTS.

P saturation describes the effect of soil type on the differential release of soil P to surface run-off better than common soil P test measures. The added advantage of the P saturation approach is that it not only describes the potential for P release from soil but could also indicate how close the P sorption sites of a soil are to being saturated. There needs to be further work on saturated systems before a critical P limit could be proposed.

2.3.2 P Pools

It has been proposed (Guo and Yost, 1998) that P pools can be partitioned into three discrete pools of differing availability, namely labile P, reversibly available P and sparingly available P. Based on the results observed in this experiment even the sparingly available pools were subject to P movement under these saturated conditions. Therefore in this type of system the differing pools could be partitioned in to two discrete pools, labile P and reversibly available P. Tables 2.5 and 2.6 show the P-pools partitioned into labile P and reversibly labile P in terms of percentage contribution.

Trial	**0-5 cm**			**10-15 cm**		
P pool %	Prior to fertilisation	20 days after fertilisation	24 weeks after fertilisation	Prior to fertilisation	20 days after fertilisation	24 weeks after fertilisation
Labile	16.9	24.4	18.0	15.5	10.5	14.4
Reversibly available	83.1	75.6	82.0	84.5	89.5	85.6
Total P	100.0	100.0	100.0	100.0	100.0	100.0

Table 2.5 Percentage of P pools partitioned into labile and sparingly labile pools for the Trial cell.

Control	0-5 cm			10-15 cm		
P pool %	Prior to fertilisation	20 days after fertilisation	24 weeks after fertilisation	Prior to fertilisation	20 days after fertilisation	24 weeks after fertilisation
Labile	16.7	33.0	24.0	17.5	30.4	20.0
Reversibly available	83.3	67.0	76.0	82.5	69.6	80.0
Total P	100.0	100.0	100.0	100.0	100.0	100.0

Table 2.6 Percentage of P pools partitioned into labile and sparingly labile pools for the Control cell.

To group P into two discrete pools then Resin-P and the NaHCO3- Pi would be the most labile. This agrees with Guo and Yost's (1998) observations for slightly weathered soils, however the soils used in this experiment are likely to be highly weathered. The reversibly available pool would be the remaining P pools.

After fertilisation it was observed that the Resin-P, and NaHCO3-Pi pools increased in all samples suggesting that these pools are the initial destination of fertiliser P. The HCl-P pools in the Control and Trial 10-15 cm samples also increased, so this also could be classed as an initial destination. An interesting observation was the movement between the NaOH-Pi and HCl-P pools in the control container. In the 0-5 cm region there was increase of 20% in the NaOH-Pi pool and a decrease of 24% in the HCl-P pool. A similar shift occurred in the 10-15 cm region, with an increase of 22% in the NaOH-Pi pool and a decrease of 27% in the HCl-P pool. There was a decrease in the pH of the groundwater from 8.3 at the start of the experiment to 7.6 in the final sample this change in pH is unlikely to be able to account for the shift from apatite type minerals to Fe and Al compounds alone, as this would be expected to happen at lower pH values (Morgan, 1997). One explanation for this could be the reduced amount of chemical loading in the system causing a shift in the equilibrium between P pools (see Table 2.1).

The chemical loading on the trial container could be responsible for binding P in the HCl-P pool. This hypothesis is based from the following observations: at the start of this trial both the trial and control soils had been taken from the full scale RBTS that had already been exposed to a high chemical loading. Under these circumstances there was a preference for P to be stored in the HCl-P pool. The control container over the time scale of the experiment saw a shift from this HCl-P pool to the NaOH-P pool.

The preference of P under low chemical loading to move from the chemisorbed Fe and Al compounds to the apatite-type minerals could be due to the increased sulphate levels competing for the Fe binding sites. Lamers et al. (1998) suggested that sulphide produced in wetlands by sulphate reduction, interferes with Fe-phosphate binding in soils and sediments. However it would appear that in this system instead of this P being released into the more soluble forms and lost through leaching, it is potentially being readily converted into more fixed compounds. There are many other possible chemical interactions that could be contributing to this movement which are unable to be identified in this experiment.

Organic P behaviour was interesting in the cells. Po was detected in most pools except for CHCl3 released NaHCO3-P at the start of the study and then not detected again in the 0-5 cm samples. In the 10-15 cm samples there was considerable movement resulting in increased levels for all but the NaOH pool for both soils. This could be due to organic P fractions being rapidly mineralised into Pi fraction and Residual P (Cross et al. 1995) after fertilisation and then a new equilibrium being established towards the end of the trial where the 0-5 cm Po fractions were no longer detectable but at the 10-15 cm depth there were increased levels. This increase was significant for the chemically loaded soil which could be as a result of increased microbial activity in this region associated with the chemical interactions taking place at the root level of the system.

2.3.3 P Estimates

The amount of P lost through leaching is very small. Despite the fertilisation being extremely high the overall P content detected in the soil samples did not increase in line with the amount of P added. Some P was taken up by the plants but again this can only account for a small amount. One reason for this could be that P is not evenly distributed throughout the soil profile. Therefore it is not possible to assume that the samples taken were representative of the whole range of depths. Table 2.7 details the changes in the average total P levels in both the trial and the control containers. The total P in soil was calculated using the bulk density (Plaster, 1997), which for this soil is 1.15 g/cm^3.

Sample	Initial total P g	P added g	P leached g	P in plant tissue g*	Final total P g	Difference g
Trial	27.9	2.6	0.16	0.12	29.4	0.82
Control	27.4	2.6	0.52	0.09	26.7	-2.69

Table 2.7 Changes in the average total P levels in the Trial and Control cells.

* Assuming an average plant production of 15 tonnes/hectare

If the results from Tables 2.1 and 2.2 are used, there is an increase in both containers 20 days after fertilisation which then decreases by the 24 week sample. This is shown in Table 2.8.

	Prior to fertilisation (g)	**20 days after fertilisation (g)**	**24 weeks after fertilisation (g)**
Trial	27.9	31.1	29.4
Control	27.4	30.3	26.7

Table 2.8 Summary of total P measured at the three stages of the trial.

The trial container has an increase of 3.2 g followed by a decrease of 1.7 g, which represents an overall increase of 1.5 g P. The control container shows an increase of 2.9 g after fertilisation, and then a decrease of 3.6 g, resulting in an overall decrease of 0.7 g P. Again this supports the assumption that it is unlikely that an even distribution of P exists in the containers.

2.4 Conclusion

It is evident that a greater understanding of the behaviour of P in constructed RBTS requires further investigation. It would be useful to carry out a range of experiments on water-fed systems to discover typical behaviour. It may then be possible to better understand the observed changes in chemically loaded systems.

Further work needs to be carried out to find out the maximum P saturation value for saturated soils to prevent leaching of high levels of P. This value can then be used as a guide when determining the levels of P required for fertilisation and prevent over-fertilisation.

Using a fractionation scheme can give some very interesting and useful results, however it is extremely time consuming and difficult to perform. It would be very useful if a model could be developed to predict the behaviour of P in the different pools and how these pools would change with the addition of differing effluents. Due to the complex relationships and number of variables such a model may be a long way off, however it may be possible to predict the distribution of P into labile and reversibly available pools. This will be looked at in section 4.

A potential simple way of monitoring and predicting fertiliser requirements in a constructed RBTS would be to carry out regular P

tests on the outlet effluent, if the leaching remains below the Netherlands guidelines of 0.1 mg/L then an approximate application rate of 125 kg/ha of superphosphate could be used on an annual basis.

3.0 Investigation into the fate of ammonia, phenol and cyanide in a trial RBTS

Abstract

The aim of this investigation was to determine the treatment levels (the overall reduction in concentration of the key chemical constituents) and to discuss the likely dissipation mechanisms in the trial constructed Reed Bed Treatment System (RBTS).

Construction of the RBTS unit was described in section 2.1.2. Plate 3.0 shows the trial RBTS which was fed using ammoniacal solution from the coke ovens.

The trial RBTS achieved average treatment (concentration reduction) levels during the trial period (calculated by mass balance) of 76.7% for ammonia, 86.4% for phenol and 94.1% for cyanide. A slowing of treatment towards the end of the trial was observed as the Australis Phragmites moved into the winter senescence phase. The trial treatment levels were a good indicator of treatment levels within the full scale system at similar concentration levels.

Plate 3.0 Trial RBTS with established growth of Phragmitis Australis.

The most likely treatment (dissipation) mechanisms for ammonia are nitrification/denitrification with a limited amount of adsorption. Phenol treatment mechanism is likely to be predominantly via the catabolic conversion of phenol into the plant cellular tissue and metabolisation by soil based organisms. Cyanide treatment is most likely to occur through biological degradation within the soil matrix.

Oxygen transfer to the rhizosphere plays a critical role in many of the treatment mechanisms, be it directly in nitrification or indirectly by supporting the growth of aerobic microbial growth. There remains much debate about oxygen transfer rates to the rhizosphere (Sun et al 2004, Oceans 1999, Kadlec & Knight 2000). This is an area that could be investigated further by carrying out studies on high ammonia effluent concentration levels to determine if the concentration of the effluent influences the flow of oxygen into the rhizosphere. Investigations could also be carried out to determine if there are other treatment pathways under high ammonia loading conditions.

RBTS are becoming a cost effective alternative to conventional treatment methods, in Australia their use in the treatment of domestic effluents is quite wide spread (Davison et al 2005, Oceans 2005, Oceans 2005a) for both single houses and small communities. The RBTS at the Whyalla Steelworks has proven to be a robust system capable of coping with changing effluent qualities.

3.1 Introduction

A 2 hectare RBTS is in operation at the OneSteel Whyalla Steelworks in South Australia treating a portion of Coke Ovens effluent which is an ammoniacal liquor generated from the coke making process. Major wastewater streams are generated from the cooling of the coke oven gas and the processing of ammonia, tar, naphthalene, phenol, and

light oil. The components of this effluent of most interest to this project are ammonia, phenol and cyanide.

The aims of this investigation were to 1) to determine the fate of the ammonia, phenol and cyanide within a trial constructed Reed Bed Treatment System (RBTS) and, 2) to determine what treatment mechanisms could be involved.

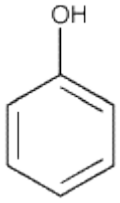
Two RBTS cells were built as described in section 2.1.2. For the purposes of this investigation only the trial cell was monitored as this was fed with a 10% solution of the Coke Ovens ammoniacal liquor solution. The flow rate of 45 L/m^2 used for this trial is consistent for a full-scale version of this type of treatment system treating an effluent of this type.

Ammonia is the principle form of nitrogen in Coke Ovens ammoniacal liquor. Ammonia nitrogen is made up of a single nitrogen atom (oxidation state 3^-), it has three or four hydrogen atoms associated with it depending on the temperature and the pH of the water:

$$NH_3 + H_2O = NH_4^+ + OH^-$$

Total ammonia is the sum of both ionised and un-ionised ammonia.

Phenol is an important component of the ammoniacal liquor from the coke ovens. Its transport and in wetland systems has been studied for many years (Kadlec & Knight 1996). The structure of phenol is shown below.



$C_6 H_6 O$

Cyanides can be in many forms; the free form is represented as

H-CN

In this study the inlet and outlet concentrations of ammonia, phenol and cyanide were monitored throughout the trial. Weekly monitoring of the full scale system took place which made it possible to determine if the results seen in the trial system were a good indicator of full scale performance at a concentration of 1:9 liquor/water solution.

3.2 Materials and Methods

Trial cells were set up as outlined in section 2.1.2. The trial cell received chemically loaded effluent from the coke-making facility during the trial period as described below.
The trial cell was fed 10 L liquid per day for 27 weeks, this was drip fed in batches from the inlet supply container over a period of approximately 10 hours per day, regulated by a tap. The chemically loaded trial was fed water for one week in order to establish some initial plant growth and to allow the freshly excavated soil to settle. After the first week a 1:39 liquor / water solution was applied for one week to the chemically loaded trial. This was increased to a 1:19 liquor / water solution for one week. Finally the solution was increased to a 1: 9 liquor / water solution after the third week for the balance of the experiment. Distribution across the surface of the bed was fairly even around the centre; however the edges of the box received less liquid. The depth of liquid was kept 2.5cm below the surface; therefore the overall depth of the soil would have had a fairly even distribution of liquid. A calendar of application rates and fertiliser addition is included in Appendix 1.

The inlet and outlet waters were sampled and analysed weekly for ammonia, phenol and cyanide concentrations. Samples were analysed

within four hours of the sample being taken. Sample techniques ensured that the bottles contained no air space at the top and that the lid of the sampling bottle was fitted securely to preserve the sample.

Table 3.2.1 shows the main constituents of the chemical load added to the trial.

Constituent	Approx Concentration (mg/L)
Ammonia as N	200-250
Free cyanide	4-10
Phenol	58-62

Table 3.2.1 Approx composition of 1:9 Coke Ovens liquor/water solution. The liquor quality can vary dependant on raw material and process variables.

3.3 Ammonia determination

The ammonia concentration was determined quantitatively by the use of an ammonia electrode (Orion 95-12) linked to a direct concentration readout specific ion meter (Orion 290A). The electrode utilises a hydrophobic gas permeable membrane to separate the sample solution from the electrode filling solution. Dissolved ammonia (NH_3) in the sample diffuses through the membrane until the partial pressure of NH_3 is equal. The partial pressure of ammonia is proportional to the concentration.

3.4 Phenol determination

Phenols and ortho- and meta- substituted phenols are determined by buffering the sample to a pH of 10.0 and adding 4- aminoantipyrene to produce a yellow or amber coloured complex in the presence of ferricyanide ion. The colour is intensified through extraction of the complex into chloroform. Measurement of this colour using a

DREL2010 uv/vis spectrophotometer can be used to quantitatively determine the concentration of phenol in the sample. The 4-aminoantipyrine method determines all ortho- and meta-substituted phenols but not para-substituted phenols.

3.5 Cyanide determination

The pHoenix Cyanide ion electrode consists of a solid membrane containing a mixture of inorganic silver compounds bonded into the tip of an epoxy electrode body. An electrode potential develops across the membrane when the electrode is in contact with a solution containing cyanide ions and is capable of measuring free cyanide ions. This potential is measured against a reference electrode, and using the Orion 290A hand held ion meter a direct reading can be obtained. All samples and standards containing cyanide ions have ionic strength adjuster added so that background ionic strength is high and constant relative to the variable concentrations of cyanide. The recommended ISA for the cyanide electrode is 10M NaOH.

3.6 Results

As detailed in Table 3.6.1 below, 76.4% removal of ammonia took place during the trial period, 86.2% removal of phenol and 94.1% removal of cyanide. These removal rates are similar to those observed in the full-scale system. By using soil that had previously been exposed to high chemical loading to build the trial box, it was possible to reduce the risk of losses as a result of adsorption mechanisms.

Mass Balance	Inlet vol (L)	Avg Inlet Conc (mg/L)	Inlet load (g)	Outlet Vol (L)*	Avg Outlet Conc(mg/L)	Outlet load (g)	Load Removed (g)	Overall Removal (%)
Ammonia	1,820	172.2	313.4	1,552	47.1	73.1	240.3	76.7
Phenol	1,820	46.6	84.8	1,552	7.5	11.6	73.3	86.4
Cyanide	1,820	7.5	20.3	1,552	0.8	1.2	19.1	94.1

* Outlet volume is estimated using Inlet volume plus rainfall minus ET

Table 3.6.1 Mass balance of ammonia, phenol and cyanide additions made to the trial cell during the trial period.

The outlet volumes were estimated using water balance measurements performed on the 2 Ha RBTS at Whyalla Steelworks demonstrating that the evaporation + transpiration rate (ET) is approximately equal to the pan evaporation rate (E_{rate}) for the Whyalla area. Therefore the crop factor is assumed to be 1.0. Using this factor and the daily evaporation data from the Bureau of Meteorology for Whyalla it is possible to estimate the outlet volumes from the trial system.

Graphical representation of treatment of ammonia, phenol and cyanide over the trial period are shown in figures 3.6.2 to 3.6.4 below.

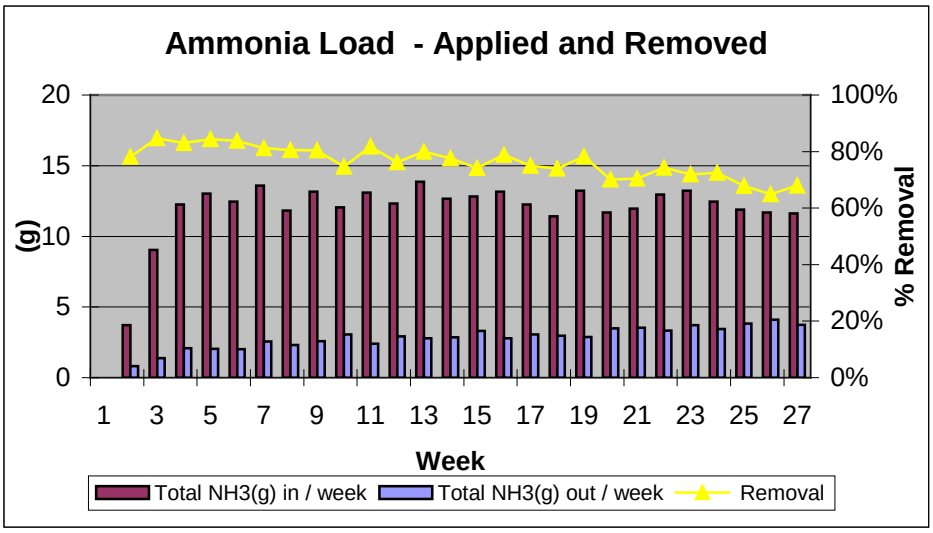


Figure 3.6.2 Trial cell ammonia load application and load removed.

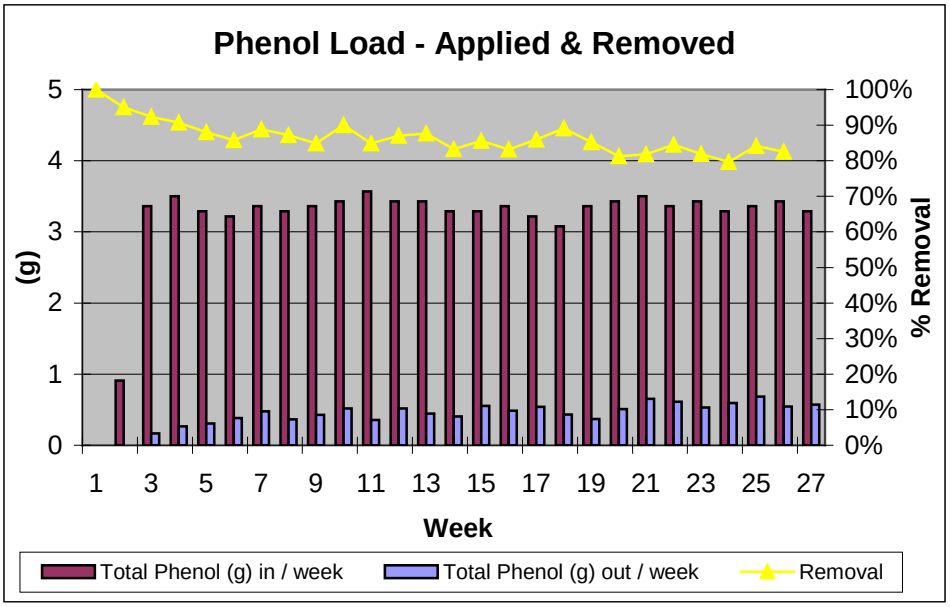


Figure 3.6.3 Trial cell phenol load application and load removed

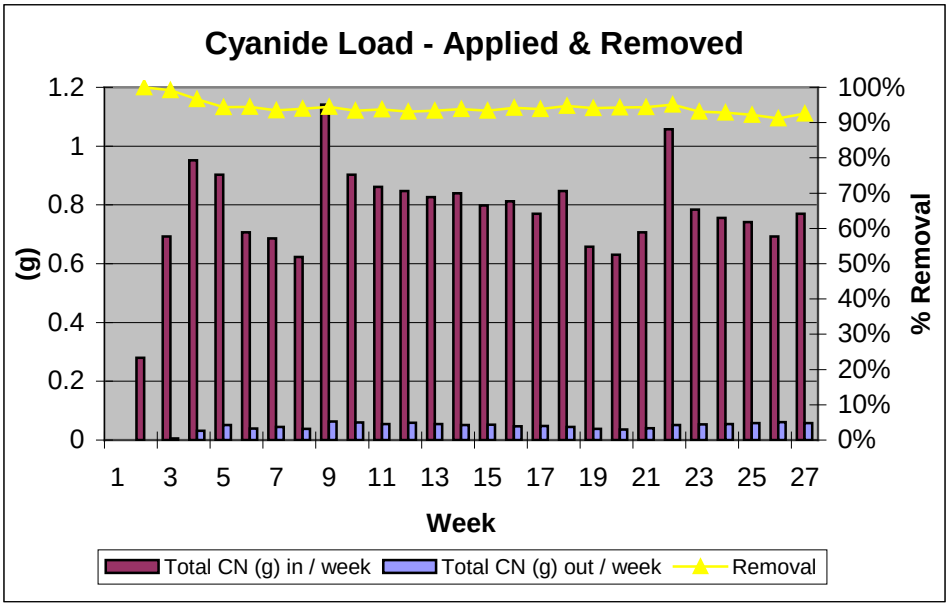


Figure 3.6.4 Trial cell cyanide load application and load removed

Fluctuations in the average concentration of ammonia, phenol and cyanide in the ammoniacal liquor feed occurred throughout the trial, owing to raw material and process variation. The greatest fluctuations were in the cyanide concentrations.

For all three chemical species monitored there was a reduction in treatment levels over the trial period as outlined in table 3.6.5. The final treatment levels are indicative of those observed in the full scale system.

Date	Ammonia Removal	Phenol Removal	Cyanide Removal
15/12/2000			
22/12/2000	78.18%	100.00%	100.00%
29/12/2000	84.73%	95.07%	99.20%
5/01/2001	82.96%	92.36%	96.63%
12/01/2001	84.40%	90.74%	94.38%
19/01/2001	83.80%	88.06%	94.50%
26/01/2001	81.18%	85.74%	93.48%
2/02/2001	80.56%	88.88%	93.88%
9/02/2001	80.45%	87.24%	94.50%
16/02/2001	74.61%	84.87%	93.42%
23/02/2001	81.72%	90.02%	93.73%
2/03/2001	76.20%	84.91%	93.08%
9/03/2001	79.97%	87.05%	93.41%
16/03/2001	77.54%	87.64%	93.85%
23/03/2001	74.16%	83.23%	93.40%
30/03/2001	78.84%	85.58%	94.18%
6/04/2001	74.96%	83.19%	93.83%
13/04/2001	73.98%	85.94%	94.74%
20/04/2001	78.25%	89.07%	94.14%
27/04/2001	70.15%	85.20%	94.26%
4/05/2001	70.46%	81.29%	94.35%
11/05/2001	74.31%	81.81%	95.12%
18/05/2001	71.92%	84.53%	93.15%
25/05/2001	72.46%	81.95%	92.84%
1/06/2001	67.82%	79.65%	92.17%
8/06/2001	64.86%	84.18%	91.16%
15/06/2001	67.93%	82.58%	92.56%

Table 3.6.5 Percentage removal rates of ammonia, phenol and cyanide over the trial period.

3.7 Discussion

Treatment levels show reduction in ammonia, phenol and cyanide throughout the trial period. There was however a reduction in the percentage removal efficiency of all three chemical species over time. The likely treatment mechanisms and trends are discussed below.

3.8 Ammonia dissipation mechanisms

The major removal mechanism of ammonia in RBTS is nitrification/denitrification. Ammonia is oxidised to nitrate by nitrifying bacteria in aerobic zones (Kadlec & Knight 2000). Nitrates are converted to dinitrogen gas (N_2) and nitrous oxide (N_2O) by denitrifying bacteria in anoxic and anaerobic zones. The oxygen supplied for nitrification is supplied by leakage from the root system of the plants, diffusion from the atmosphere, and by carriage within the diluted feed effluent.

Nitrogen is also taken up by plants, incorporated in to the biomass and released back as organic nitrogen after decomposition (Kadlec & Knight 2000). For a short trial period such as this it was not expected that any nitrogen taken up by the plant would be returned to the system. Other removal mechanisms include volatilisation and adsorption, however, as there was very little surface water during the trial period volatilisation is unlikely to have played a major role in ammonia removal. By using soil that had been pre-exposed to high ammonia levels this would have reduced but not removed the role that ammonia adsorption would have played in this system.

As can be seen by the results in Table 3.6 there was a gradual decrease in dissipation levels over time which may potentially indicate that adsorption could have been responsible for this observation, however

the dominant reason for the decline would have been the decreasing temperatures going into the winter period which reduces biological activity.

Oxygen supply is potentially a limiting factor for the nitrification process; this will be discussed further in section 3.11.

3.9 Phenol treatment mechanisms

Phenol treatment in a constructed wetland can take place via a number of methods: metabolisation by soil based organisms, catabolic conversion into plant cellular tissue, and volatilisation. Volatilisation is likely to be relatively low in this system as there was very little surface water during the trial period; however the water levels were only 2.5cm below the soil surface. As the plants were growing during the trial period it is possible that the catabolic conversion of the phenol into the plant cellular tissue was responsible for a significant portion of the losses of phenol, as growth slowed down for winter this uptake would have dropped off. Along with a slowing of biological activity during winter due to temperature this could be responsible for the trend observed in table 3.6 of the treatment levels reducing slightly over the trial period.

3.10 Cyanide treatment mechanisms

Cyanide is dissipated through biological removal within the soil matrix (Akcil et al 2003) or volatilisation. Again as discussed above volatilisation is not likely to be significant in this instance.

3.11 Oxygen transfer mechanisms

The ability of *Phragmites Australis* to transfer oxygen from its leaves and stem structure into the rhizosphere is an adaptation to living in marshy environments where the available oxygen for the health of the root systems and the support of symbiotic bacteria is limited due to water saturation. There have been a number of studies in relation to oxygen supply and consumption rates in constructed wetlands planted with *Phragmites Australis*. For example, Sun et al. (2004) estimated that the roots of *Phragmites Australis* are capable of supplying between 0.02 and 20 g O_2/m^2/day (although he does suggest these figures are debatable). He also lists several other functions of the species of plants that help wastewater treatment, such as providing a suitable environment for microbial growth and for opening up hydraulic pathways to assist wastewater flow.

However, there is still uncertainty about the exact mechanisms involved, especially with respect to the breakdown of ammonia in RBTS. It appears ammonia breakdown continues to occur, even when calculated oxygen supplies are potentially inadequate for nitrification, however, low oxygen would favour denitrification. It has been demonstrated (Oceans, 1999) that RBTS can treat ammonia at levels above predictions based on estimates of oxygen supplies to support nitrification/denitrification processes. It may be possible that the inundation with ammonia-rich effluent could accelerate the diffusion of oxygen into the rhizosphere as the available oxygen is absorbed.

As discussed above, *Phragmites Australis* is capable of developing a substantial root system with primary, secondary and tertiary root systems capable of supplying oxygen to the root zone. It has been proposed that oxygen supplied to the root zone system which creates the rhizosphere can support bacteria up to 50cm away from the roots (Munch et al. 2005). This could indicate that nitrification is also possible in the wider root surroundings. Given this information and

the extensive nature of the *Phragmites Australis* root system (see plate 3.11.1) it is possible that significant amounts of oxygen are being delivered to the aerobic zones of the RBTS, and that these aerobic zones could be larger than initially expected.

Plate 3.11.1 Cross section of a reed bed showing rhizome density.

Oxygen transfer to the rhizosphere plays a critical role in many of the treatment mechanisms, be it directly in nitrification or indirectly by supporting the growth of aerobic microbial growth. There remains much debate about oxygen transfer rates to the rhizosphere (Sun et al 2004, Oceans 1999, Kadlec & Knight 2000). There is evidence that consistent treatment of ammonia, phenol and cyanide takes place within the full scale RBTS at Whyalla and the same was observed at British Steel RBTS in Llanwern (Oceans 1999). If the only significant mechanism available for the reduction of ammonia was through nitrification/denitrification then there has to be oxygen entering into the system at higher rates then those normally accepted (Sun et al 2004), this could be by the inundation of ammonia rich effluent accelerating the diffusion of oxygen into the rhizosphere as the available oxygen is absorbed, or there may be alternative treatment pathways available. This is an area that could be investigated further by carrying out studies on high ammonia effluent levels to determine if the strength of the effluent influences the flow of oxygen into the rhizosphere. Further investigations could be carried out to determine if there are alternative treatment pathways such as the existence of a

"short way removal" of ammonium nitrogen taking place in heavy ammonia dosing conditions as follows:

$$NH_4 + NO_2 \rightarrow H_2N\text{-}NO + H_2O \quad (1)$$

$$H_2N\text{-}NO \rightarrow N_2 + H_2O \quad (2)$$

This is a second order reaction, which is reported to have been confirmed by experiments undertaken at the University of Bielefeld in the late 80's and early 90's (Oceans 1999). If these findings can be confirmed they could be of great importance in estimating nitrogen removal in heavy load ranges.

3.12 Investigation improvements

The investigation did show significant treatment was taking place during the trial period within the RBTS cell, however, the monitoring was limited and was unable to sufficiently identify the potential treatment pathways.

Future investigations could be improved by monitoring the redox of the system and in particular measuring the dissolved oxygen levels in the rhizome to determine if sufficient oxygen is entering the system by this route to account for some of the treatment levels being observed. Further improvements could be made by measuring the forms of nitrogen in the influent and effluent. Nitrates and nitrates were not monitored during this investigation and this is another area that could be used to gain a greater understanding of the ammonia treatment pathways.

Temperature will also play an important role in potential treatment processes including volatilisation, a comparison of treatment levels

plotted against temperature could assist in identifying treatment patterns.

3.13 Conclusion

The trial RBTS achieved average treatment levels (calculated by mass balance) of 76.4% ammonia, 86.2% Phenol and 94.1% cyanide. A slowing of treatment was observed as the *Phragmites Australis* moved into the winter senescence phase at the end of the trial.

The trial treatment levels were a good indicator of treatment levels within the full scale system at similar concentration levels.

The most likely treatment mechanisms for ammonia are nitrification/denitrification with a limited amount of adsorption. Phenol treatment mechanisms are likely to be predominantly via the catabolic conversion of the phenol into the plant cellular tissue and metabolisation by soil based organisms. The cyanide treatment is most likely to occur through biological removal within the soil matrix.

Reed beds are becoming a cost effective alternative to conventional treatment methods (Davison et al 2005). Soil-based RBTS have been in operation in Australia for a number of years, treating effluents ranging from from coke-oven ammoniacal liquor to domestic sewage. These systems are generally low maintenance with low running costs. They are also a form of wetland habitat providing an example of synergy between potentially polluting processes and habitat creation.

4.0 Simulating Phosphorus Behaviour in a Constructed Reed Bed Treatment System.

Abstract

Using a research model LEACHN developed by John L Hutson (Hutson, 2003), it was possible to simulate some of the P movement in the chemically loaded Reed Bed Treatment System (RBTS) used in section 2 of this paper, using some of the parameters measured in that section.

The results showed similar trends in terms of leaching. The rate at which the leaching occurred however was off-set by a number of weeks. Levels of leaching were lower in the Trial RBTS than in the simulated model, part of this difference could be down to differing rate constants and the influence of the P sorption capacity. There was no facility to include the P sorption capacity of the soil in the model other than the percentage contribution from clay, silt and organic matter; however this is a developing model which could be expanded to take this into account in future versions.

The labile P pools values that had been simulated could not be closely compared to those obtained by measurement of the chemically loaded RBTS because of too few data points in the actual trial. However, the incremental leaching data obtained from measurements followed a very similar trend to that of the simulated labile pools. It would be expected that more leaching would occur whilst the labile pool was not yet fully equilibrated.

The model was not designed with permanently saturated soils in mind; however with more experimental work it could be possible to expand LEACHN to be able to closer model the behaviour of P in wetland or RBTS soils.

4.1 Introduction

Modelling of various processes within soil is a very useful way of predicting the fate of certain elements. There are many models available each varying in how they model soil interactions. A further differing feature of many models is the number of parameters required to simulate a system.

Kadlec described wetland models in his paper "An autobiotic wetland phosphorus model" (Kadlec,1997), here both a single parameter model and a multi parameter model were described however the focus of this model was the removal of P from the inlet waters. Other models have looked at P leaching predictions to reduce the risk of eutrophication in surface waters (Campillo et al., 1999, Mansell et al., 1992). There are many other models described in the literature, the details of which will not be described here.

For this exercise the element of interest was phosphorus (P). The aim was to model P behaviour in chemically loaded soil in a constructed Reed Bed Treatment System (RBTS) and to compare the results against the analytical results obtained in Section 2 of this paper.

The model used in this investigation is named LEACHM which is an acronym for Leaching Estimation And Chemistry Model. There are a number of versions of this simulation model which describe the water regime and the chemistry and transport of solutes in unsaturated or partially saturated soils to a depth of about 2 metres (Hutson, 2003). The version used here is LEACHN which is a nutrient version of the model. Version 4 was chosen so as to model phosphorus transport and transformations, prior to this version this function was not available. A full explanation of the background and development of the model is given in the LEACHM manual (Hutson, 2003). This

model allowed the soil to be saturated without causing run off even after large rain events.

4.2 Method

The input data for LEACHN is contained in a single ASCII data file; this can be edited or viewed in any ASCII text editor. Output files are assigned the same name as the input file. This is useful in terms of reducing any confusion as to which output file belongs to which input file. Files extending over a large number of days can be quite cumbersome because of their size. This is made easier however by having the rainfall and evaporation data, which is the largest component of the file, at the end of the input file.

The model parameters were kept as close as possible to the chemically loaded RBTS used in section 2 of this paper. Where values were not known certain assumptions were made.

A copy of the input data used in this run with a brief explanation of why certain parameters were chosen is below.

Time periods, profile depths and node spacing:

"angie004 < DOS Filename, 8 characters with no extension. Used in batch runs (started as LEACHF<filename)."

LEACHN NITROGEN AND PHOSPHORUS DATA FILE.
"Unless defined as 'not read' a value must be present for each item, although it"
may not be used. Free format with blank delimiters. Preserve division and
heading records. Number of depth segments may be changed.
****
********** ****
"2 <Date format (1: month/day/year; 2: day/month/year). Dates must be 6 digits, 2 each for day, mo,"
yr.
081200 <Starting date. No date in the input data should precede this date.
150601 <Ending date or day number. The starting date is day 1. (A value <010101 is treated as a day
number).
0.05 <Largest time interval within a day (0.1 day or less).

"1 <Number of repetitions of rainfall, crop and chemical application data."
"250 <Profile depth (mm), preferably a multiple of the segment thickness."
25 <Segment thickness (mm). (The number of segments should be between about 8 and 30.
"1 <Lower boundary condition: 1:fixed depth water table; 2:free drainage, 3:zero flux 4:lysimeter."

25 <If the lower boundary is 1 or 4: initial water table depth (mm).

The start and end date of the trial were the same as those in the actual experiment in section 2 (see Appendix 1). The largest time interval in a day chosen was 0.05, which means 20 intervals per day, this is usual for this type of modelling. The number of repetitions of rainfall, crop and chemical application was set to 1 as this was modelling actual applications rather than simulating a number of events. Segment thickness was chosen to be 25mm, the profile depth as described in section 2 was 251mm for the purposes of this model this was assumed to be 250mm therefore the profile was split into 10 segments. The lower boundary condition was a fixed depth of 25mm which means 25mm from the surface of the soil.

Water flow options:

The steady-state flow option uses constant water fluxes during the application
"periods specified in the rainfall data table, and a uniform water content"
"specified here. Steady-state flow implies a lab column, and crop and evaporation data are ignored."
---

1 < Water flow: 1: Richards; 2: Addiscott tipping bucket; 3: steady-state.
0.4 < Steady-state flow water content (theta); 999: saturated column.

The water flow option chosen was the Richard's equation a mobile/immobile capacity model adapted from Addiscott's simple computer model for leaching in structured soils (Hutson, 2003).

Output file specifications:

3 <Number of output files: 1: OUT + .P only; 2: OUT + SUM; 3: OUT + SUM + BTC

```
----------------------------------------
--- For the *.OUT file :
"1     <Units for depth data: 1: mg/kg, 2: mg/m2 per segment, 3: g/m2, 4: kg/ha"
"1     <Node print frequency (print data for every node (1), alternate nodes (2)."
1      <Print option: Select one of the following two (enter 1 or 2)
7     <Option 1: Print at fixed time intervals (days between prints). 999 for monthly print.
1      <Option 2: No. of prints (the times for which are specified below)
3      <Tables printed: 1: mass balance; 2: + depth data; 3: + crop data
"0     <Reset cumulative values in .OUT after each print? 0: No, 1: Yes"
----------------------------------------
--- For the * .SUM file :
.05   <Summary print interval (d) (for calendar months use 999)
50    <Surface to [depth 1?] mm     ( Three depth segments for the
150    <Depth 1 to [depth 2?] mm      summary file. Zero defaults to nodes
250    <Depth 2 to [depth 3?] mm      closest to thirds of the profile)
2    <4th segment: Root zone (1); profile (2); Depth 3 to lower boundary (3); Surface to shallowest of
              lower boundary or water table (4)
----------------------------------------
--- For the *.BTC (breakthrough) file :
2.0    <Incremental depth of drainage water per output (mm)
---------------------------------------------------------------------------
-- List here the times at which the *.OUT file is desired for print option 2.
-- The number of records must match the 'No. of prints' under option 2 above.
"Date or    Time of day          (At least one must be specified,"
Day no.  (to nearest tenth)      even if print option is 1)
--------  ----------------
9999        .2       (These dates can be past the last day)
```

It is possible to choose the number of output files required. Here 3 was chosen, the *.OUT file contains a detailed mass balance along side concentrations at each node depth, the *.SUM file contains a mass balance summary and data for 4 macro segments, and the *.BTC file produces leaching (or breakthrough) data.

*.OUT - units for depth data used was mg/kg, node print frequency was every node, printing at a fixed time interval of 7 days was chosen, tables chosen for printing were mass balance, depth data and crop data. There was no resetting of cumulative values.

*.SUM - this allows you to set the print intervals which here was chosen to be 0.05 (20 intervals/day). It is also possible to set data for the 4 macro-segments you want the profile to be separated into. The

first three are incremental depths, 0-50mm, depth 1, 50-150mm depth 2 and 150-250mm depth 3. The fourth macro-segment was chosen as the complete profile.

*.BTC - prints to this file will occur as soon as the depth of drainage exceeds the depth of that specified, in this case 2mm. These will be irregular as they will take into account rainfall in addition to the irrigation added per day.

Print option 1 in the *.OUT file was chosen therefore the final section doesn't apply, however a value must be entered therefore 9999 was chosen, this will be ignored.

Soil Physical properties:

SOIL PHYSICAL PROPERTIES

"-- Retentivity model 0 uses listed Campbell's retention parameters, otherwise"

#NAME?

Soil layer no.	Clay %	Silt %	Organic carbon %	Retention model (one is used)	Starting theta or potl kPa	Roots (for no growth) (relative)	Starting temperature (C) (not read in LEACHC)
1	15.	10.	5.9	0	.000	-10.0	.00	15.
2	15.	10.	5.9	0	.000	-10.0	.00	15.
3	15.	10.	5.9	0	.000	-10.0	.00	15.
4	15.	10.	5.9	0	.000	-10.0	.00	15.
5	15.	10.	5.9	0	.000	-10.0	.00	15.
6	15.	10.	5.9	0	.000	-10.0	.00	15.
7	15.	10.	5.9	0	.000	-10.0	.00	15.
8	15.	10.	5.9	0	.000	-10.0	.00	15.
9	15.	10.	5.9	0	.000	-10.0	.00	15.
10	15.	10.	5.9	0	.000	-10.0	.00	15.

"2 < Use water contents (1), potentials (2)"

Particle density: Clay Silt and sand Organic matter

2.1 2.1 2.1

****

For a uniform profile: Any non-zero value here will override those in the table below.

1.3 2.1 <Soil bulk density and particle density (kg/dm3) .

-1.0 <'Air-entry value' (AEV) (kPa).

6.0 <Exponent (BCAM) in Campbell's water retention equation.
1.0 -20.0 <Conductivity (mm/day) and corresponding matric potential (kPa) (for potential-based version of eq. 2.5).
1.0 <Pore interaction parameter (P) in Campbell's conductivity equation.
25.0 <Dispersivity (mm).
0.0 <For Addiscott flow: Matric potential (kPa) at field capacity
0.0 < : Division between mobile and immobile water (kPa)
****
***
Soil | Soil retentivity | Bulk | Match K(h) curve at: | Dispersivity | For Addiscott flow option:
segment parameters | density | K Matric using | | Field Mobile/immobile
no. | AEV BCAM | | potl P | | capacity threshold
| kPa | kg/dm3 | mm/d kPa | mm | kPa kPa

1	-4.89	5.54	1.33	1.	-20.	1.	100.	-5.0	-200.
2	-1.69	4.50	1.39	1.	-20.	1.	100.	-5.0	-200.
3	-1.69	4.50	1.39	1.	-20.	1.	100.	-5.0	-200.
4	-1.69	4.50	1.39	1.	-20.	1.	100.	-5.0	-200.
5	-1.28	4.34	1.54	1.	-20.	1.	100.	-5.0	-200.
6	-1.28	4.34	1.54	1.	-20.	1.	100.	-5.0	-200.
7	-2.02	4.76	1.93	1.	-20.	1.	100.	-5.0	-200.
8	-2.02	4.76	1.93	1.	-20.	1.	100.	-5.0	-200.
9	-2.02	4.76	1.93	1.	-20.	1.	100.	-5.0	-200.
10	-2.02	4.76	1.93	5.	-00.	1.	100.	-5.0	-200.

****
***
Runoff according to the SCS curve number approach. Curve number listed here will be
"adjusted by slope. During periods of crop growth, CN2 replaced by value for crop."
(Procedure according to J.R. Williams (1991). Runoff and Water Erosion.
"Chap 18, Modelling Plant and Soil Systems, Agronomy 31.)"

"75 <Curve number (CN2). In LEACHM, water content use to adjust CN2 based on top 20 cm."
"0 <Slope, %. Used to adjust CN2 according to equation of Williams (1991)."
** (Set slope to 0 to bypass the runoff routine. Runoff owing to profile saturation will still be accumulated)
****

The soil layer was divided into 10 segments, estimations of the percentage of clay, silt and organic carbon were made. The retention model uses Campbell's retention parameters (Campbell, 1974). The matric potential was set at -10.0 kPa and the starting temperature was set at 15^{o}C. The root growth was set at 0 which means the root distribution was assumed to be constant with time.

Soil bulk density was set at 1.3 and the particle density set at 2.1kg/dm^3. (The actual bulk density was 1.2kg/dm^3). Air entry value was set at 1.0kPa. A value of 6 was given to the exponent in Campbell's water retention equation. Conductivity was rated at 1 mm/day and the matric potential at -20.0kPa. Pore interaction parameter in Campbell's conductivity equation was 1. The dispersivity was assumed to be 25mm. The Adiscott flow and division between mobile and immobile water were both set to 0. Parameters relating to each depth are then automatically calculated.

Crop data:

CROP DATA

"Data for at least one crop must be specified, even if no crop desired."

"For fallow soil, set flag below to 0, or germination past the simulation end date."

"1 <Plants present: 1 yes, 0 no."

1 <No. of crops (>0)

#NAME?

-3000 <Min.root water potl(kpa).

1.1 <Maximum ratio of actual to potential T.

1.05 <Root resistance.

Growth	Perennial	N_uptake	Date or day of					Rel.	Crop	Pan	Crop	Min	Harvested
1: No	1: Yes	1:to maturity	Maturity					root	cover	factor	uptake	N	fraction
2: Yes	2: No	2:to harvest	Germ.	Emerg.	Root	Cover	Harv.	depth	fraction		N	P	fixed
											kg/ha		
2	2	2	1	2	2	14	190	.15	.9	1.00	100.	20.	0.	.8	A1

Plants of one type were present. The minimum root water potential was set at -3000 this limits transpiration. The maximum ratio of actual to potential transpiration was set to 1.1. This ratio is the factor by which actual transpiration can be increased to compensate for reduced evaporation from a dry surface. A ratio of 1 would be equivalent to no change whereas a ratio of 1.2 would represent a potential 20% increase. The root resistance is based on water flow through the xylem system of the plants an average value being 1.05.

Growth was assumed to take place, and the plants used in the actual trial are perennial, however for the purposes of this run they were modelled as not being perennial. Nitrogen uptake was assumed up to maturity, this also set Phosphorus uptake using the Watts and Hanks uptake function (Watts and Hanks, 1978).

The planting, emergence, plant and root maturity and crop cover fraction at maturity are only used if plant growth is to be simulated.

A pan factor of 1 is used, this is in line with observed behaviour at the Whyalla Steelworks RBTS.
Potential nutrient uptake values in terms of N and P are also given in this section.

Chemical Applications:

"INITIAL NITROGEN, PHOSPHORUS AND CARBON POOLS (excluding soil humus)"
---------- ----
"| NITROGEN POOLS | CARBON POOLS | PHOSPHORUS POOLS | (Humus C, N, & P calculat" ed from org.C)
SOIL |UREA NH4 NO3 Residue Manure| Residue Manure | Labile Residue Manure | (Fertilizer P absent at s tart)
LAYER | ----mg N/kg dry soil---- | -- mg C/kg -- | mg P/kg dry soil | (Bound P pool in equilibrium with labile P.
---------- ----
1 100. 0. 0. 50. 0. 1000. 0. 050. 10. 000.
2 100. 0. 0. 50. 0. 1000. 0. 050. 10. 000.
3 100. 0. 0. 50. 0. 1000. 0. 050. 10. 000.
4 100. 0. 0. 50. 0. 1000. 0. 050. 10. 000.
5 100. 0. 0. 50. 0. 1000. 0. 050. 10. 000.
6 100. 0. 0. 50. 0. 1000. 0. 050. 10. 000.
7 100. 0. 0. 50. 0. 1000. 0. 050. 10. 000.
8 100. 0. 0. 50. 0. 1000. 0. 050. 10. 000.
9 100. 0. 0. 50. 0. 1000. 0. 050. 10. 000.
10 100. 0. 0. 50. 0. 1000. 0. 050. 10. 00.

"Concentration (mg/l) below profile, used with lower boundary 1."
"0 0 0 (NH4, NO3 and P)"
0 < Depth (mm) of water in mixing cell. Enter 0 for no mixing cell.

Initial urea, nitrogen, carbon and phosphorus levels are given in this section. LEACHN is set up to assume three organic pools: plant residue, manure and soil humus. Each is defined in terms of C:N:P ratios. Inorganic N pools include urea, nitrate and ammonium; if a non interacting tracer is required the urea pool can be used by setting all the urea rate constants and sorption coefficients to zero. Inorganic P pools are divided into labile and bound; the labile pool is in equilibrium with the solution and sorbed phases, the bound inorganic P pool is in a kinetically-controlled equilibrium with solution P. P sorption can be described using Freundlich or Langmuir isotherms.

For this run an initial level of 50mg/kg of N and 1000mg/kg of C has been assumed. Labile P is assumed to be 50mg/kg which is an estimation of what would be expected in the system being modelled.

Chemical Properties:

```
CHEMICAL PROPERTIES
-------------------
Kd
Name     L/kg
---------- --------
'   Urea-N'    0
'    NH4-N'    3
'    NO3-N'    0
'Residue-N'        (Plant 'residues' and 'manure' pools representing
'"  Humus-N'          added organic sources of N, P and C.  They"
' Manure-N'          differ in that the plant residue pool is supplied
'"Residue-C'          by the non-harvested portion of annual crops,"
'"  Humus-C'          and the non-harvested, non-perrenial portion of"
' Manure-C'          perennial crops)
'    CO2-C'
'   Fert-P' 10000  69.3         <Solubility; Dissolution rate (d**-1)
' Labile-P'     1   10  .9     <1: Freundlich or 2: Langmuir; [Freundlich Kd; Exponent  OR  Langmuir    Qm;
k]
'Residue-P'
'  Humus-P'
' Manure-P'
'  Bound-P' 2000 0.65  .5  .0050  <Freundlich sorption: Kd; Exponent; Phase transfer: Dissolution ra  "te,
precipitation rate, (days^-1)"
```

This is where the C:N and C:P ratios are specified, the initial concentrations of bound P are calculated from the initial labile P with the assumption that these pools will be in equilibrium. No provision can be made for the initial fertiliser addition of P that occurred in the actual trial.

Diffusion

---

120 <Molecular diffusion coefficient

****

NITROGEN TRANSFORMATIONS

.5 <Synthesis efficiency factor.

.2 <Humification fraction.

10.0 <C/N ratio:biomass and humus.

50.0 <C/P ratio:biomass and humus.

------Temperature and water content adjustments------

"1 <Temperature subroutine? yes(1), no(0). If no, base temperature used."

"20 <Base temperature, degrees C"

2 <Q10: rate constant adjustment factor per 10C temperature change.

".08 <High end of optimum water content range, air-filled porosity."

#NAME?

#NAME?

"0.6 <Relative transformation rate at saturation (except denitrification), days^(-1)"

The conceptual basis of the organic N and P transformations are dealt with in more detail in the LEACHN manual (Hutson, 2003). 'The synthesis efficiency factor (FE) determines the relative production of CO_2, and humus + biomass. The humification factor (FH) determines the split between humus and biomass. These factors are used in conjunction with the overall mineralisation rate (adjusted for temperature and water content) and C:N ratios to determine the production of CO2, humus and biomass C, N and P. The relative rates are:

CO2	1-FE
Biomass + humus	FE
Humus:	FE x FH
Biomass:	FE x (1 – FE)'

Rate Constants:

RATE CONSTANTS [days^(-1)]

Layer	Urea hydrolysis	NH4->NO3	NO3->N	Mineralization Residue	Manure	Humus
1	.0000e-0	.200E-0	2.00e-00	.020e-0	.020e-0	.100e-4
2	.0000e-0	.200E-0	2.00e-00	.020e-0	.020e-0	.100e-4
3	.0000e-0	.200E-0	2.00e-00	.020e-0	.020e-0	.100e-4
4	.0000e-0	.200E-0	2.00e-00	.020e-0	.020e-0	.100e-4

5 .0000e-0 .200E-0 2.00e-00 .020e-0 .020e-0 .100e-4
6 .0000e-0 .200E-0 2.00e-00 .020e-0 .020e-0 .100e-4
7 .0000e-0 .200E-0 2.00e-00 .020e-0 .020e-0 .100e-4
8 .0000e-0 .200E-0 2.00e-00 .020e-0 .020e-0 .100e-4
9 .0000e-0 .200E-0 2.00e-00 .020e-0 .020e-0 .100e-4
10 .0000e-0 .200E-0 2.00e-00 .020e-0 .020e-0 .100e-4

Additional rates and constants used for calculating N transformations:
".10 <Ammonia volatilization from the surface, days^(-1)"
10 <Denitrification half-saturation constant (mg/l).
8 <Limiting NO3/NH4 ratio in solution for nitrification

No changes were made to the rate constants, it should be noted however that the rate constants for urea are set to zero, this allows urea to be used as a non-interacting tracer.

Additional applications:

"NITROGEN, PHOSPHORUS AND CARBON APPLICATIONS (kg/ha)"

---

1 < No. of nutrient applications

Date or	Incorp n	NITROGEN					CARBON		PHOSPHORUS		
day no.	segments	Urea	NH4	NO3	Residue	Manure	Residue	Manure	Fertilizer	Residue	Manure
9999	1	0	0	0	0	00	0	0000	000.0	0	00

No N, P or C applications were included. The only actual addition in the system to be modelled was P fertiliser.

Cultivations:

CULTIVATIONS

---

1 < Number of cultivations. At least one must be specified. Can be past last day.

Date or	Depth of cultivation
day no.	mm
9999	200

No cultivations were made during the trial.

Rain and Irrigation:

RAIN/IRRIGATION AND WATER COMPOSITION

---

42 < Number of water applications. Some or all can be past last day. (See manual on setting automated i rrigation thresholds)

"1 < For sensor-triggered irrigation, set to 1, edit and rename NITRTEST.SCH."

Start	Amount	Surface flux	Dissolved in water (can be 0)			
Date/day	Time	density	Urea-N	NH4-N	NO3-N	P
	--day-	--mm--	---mm/d----	----------	mg/l	---------
151200	0.3	4.46	446.0	0.000	0.000	0.000	4600
221200	0.3	4.0	20.0	0.000	0.000	0.000	0.000
271200	0.3	1.0	5.0	0.000	0.000	0.000	0.000
250101	0.3	0.4	2.0	0.000	0.000	0.000	0.000
260101	0.3	5.6	28.0	0.000	0.000	0.000	0.000

100201 0.3 3.0 15.0 0.000 0.000 0.000 0.000
130201 0.3 4.0 20.0 0.000 0.000 0.000 0.000
140201 0.3 0.2 1.0 0.000 0.000 0.000 0.000
250201 0.3 0.2 1.0 0.000 0.000 0.000 0.000
260201 0.3 1.0 5.0 0.000 0.000 0.000 0.000
160301 0.3 4.6 23.0 0.000 0.000 0.000 0.000
170301 0.3 0.8 4.0 0.000 0.000 0.000 0.000
210301 0.3 0.4 2.0 0.000 0.000 0.000 0.000
220301 0.3 2.0 10.0 0.000 0.000 0.000 0.000
230301 0.3 0.1 0.5 0.000 0.000 0.000 0.000
270301 0.3 0.8 4.0 0.000 0.000 0.000 0.000
080401 0.3 5.4 27.0 0.000 0.000 0.000 0.000
230401 0.3 1.2 6.0 0.000 0.000 0.000 0.000
240401 0.3 0.1 0.5 0.000 0.000 0.000 0.000
280401 0.3 2.2 11.0 0.000 0.000 0.000 0.000
030501 0.3 1.4 7.0 0.000 0.000 0.000 0.000
040501 0.3 2.4 12.0 0.000 0.000 0.000 0.000
050501 0.3 0.2 1.0 0.000 0.000 0.000 0.000
100501 0.3 16.2 81.0 0.000 0.000 0.000 0.000
150501 0.3 1.8 9.0 0.000 0.000 0.000 0.000
160501 0.3 0.1 0.5 0.000 0.000 0.000 0.000
170501 0.3 0.8 4.0 0.000 0.000 0.000 0.000
180501 0.3 8.2 41.0 0.000 0.000 0.000 0.000
190501 0.3 0.1 0.5 0.000 0.000 0.000 0.000
260501 0.3 6.8 34.0 0.000 0.000 0.000 0.000
270501 0.3 2.6 13.0 0.000 0.000 0.000 0.000
280501 0.3 2.6 13.0 0.000 0.000 0.000 0.000
050601 0.3 1.2 6.0 0.000 0.000 0.000 0.000
060601 0.3 40.0 200.0 0.000 0.000 0.000 0.000
070601 0.3 11.6 58.0 0.000 0.000 0.000 0.000
080601 0.3 0.3 1.5 0.000 0.000 0.000 0.000
090601 0.3 0.8 4.0 0.000 0.000 0.000 0.000
110601 0.3 11.0 55.0 0.000 0.000 0.000 0.000
120601 0.3 0.2 1.0 0.000 0.000 0.000 0.000
130601 0.3 5.6 28.0 0.000 0.000 0.000 0.000
140601 0.3 0.4 2.0 0.000 0.000 0.000 0.000
150601 0.3 0.4 2.0 0.000 0.000 0.000 0.000

Data for rainfall was obtained from the Bureau of Meteorology specifically for the Whyalla area. A separate irrigation file was used, this has been included on an attached data disc due to its size.

"POTENTIAL ET (WEEKLY TOTALS, mm), DEPTH TO WATER TABLE (mm)"
MEAN WEEKLY TEMPERATURES AND MEAN WEEKLY AMPLITUDE (degrees C)

Week	ET	Water table	Mean temp	Amplitude
111200	34.4	0.	23.9	7.0

181200	31.4	0.	23.4	5.6
251200	32.7	0.	24.0	5.7
010101	31.9	0.	22.6	6.5
080101	39.6	0.	27.4	6.9
150101	47.0	0.	30.5	8.4
220101	42.3	0.	27.7	8.3
290101	38.0	0.	27.4	5.9
050201	38.5	0.	26.9	6.8
120201	39.5	0.	28.6	5.8
190201	35.6	0.	25.7	5.9
260201	34.0	0.	25.1	5.7
050301	29.4	0.	22.6	5.0
120301	35.4	0.	24.5	7.0
190301	27.1	0.	19.7	6.2
260301	25.6	0.	18.4	6.4
020401	27.5	0.	18.9	7.3
090401	29.6	0.	19.8	7.7
160401	26.4	0.	17.6	7.8
230401	22.4	0.	17.3	5.0
300401	22.7	0.	16.2	6.4
070501	20.3	0.	15.6	5.3
140501	25.5	0.	17.8	6.8
210501	16.1	0.	12.7	4.6
280501	18.1	0.	13.1	5.8
040601	17.8	0.	12.9	5.8
110601	16.4	0.	14.3	3.5
180601	13.2	0.	10.7	4.2
250601	17.8	0.	12.8	5.9
020701	17.3	0.	11.1	7.1
090701	16.2	0.	11.5	5.8
160701	14.7	0.	11.9	4.3
230701	13.4	0.	10.2	4.8
300701	15.6	0.	9.9	6.8
060801	17.1	0.	12.8	5.4
130801	18.2	0.	12.8	6.3
200801	20.3	0.	14.6	6.2
270801	16.3	0.	11.5	5.9
030901	15.7	0.	12.4	4.7
100901	19.4	0.	13.6	6.4
170901	20.6	0.	15.3	5.7
240901	27.3	0.	18.8	7.1
011001	24.1	0.	17.1	6.4
71001	16.5	0.	80.3	39.0

This section contains the potential evaporation in weekly totals.

3.3 Results

The output data files for this run were imported into an excel spreadsheet which is included in attached data disc. Although these files are easily transferred into excel spreadsheets, often the columns do not line up due to the space delimiting factor and manual manipulation of the columns is required. The output files give a weekly mass balance. P which is the main focus of this investigation is given in the second output file.

The output data is written to the summary file which is easily imported into an excel spreadsheet or any other graphics or spreadsheet package. The summary file does import correctly without any manipulation. This file is very large and has been included in the data disc file. The summary file is useful for producing time series plots. It also includes all of the P data in a very useful format.

The summary file contains one record per print time. The results are divided into the 4 macro segments which were defined in the input file. Each record contains cumulative time, cumulative rain and irrigation, actual transpiration and evaporation, depth to water table, water and chemical contents of the 4 macro-segments and water and chemical fluxes across the soil surface and across the lower boundaries of the macro-segments. Figure 3.3.1 is a diagrammatical representation of the macro-segments and the fluxes and concentrations.

The .SUM file produced in this run contained 132 columns of information; an explanation of these data columns is given in table 4.3.1.

Columns Listing parameters in the summary file			
Variable	Unit	Definition	Period
Days		Elapsed time since start of simulation	

Year		Calendar year (single digit)	
Month		Calendar month (up to 2 digits)	
Rain	mm	Rain events	a
Irrigation	mm	Planned irrigation	a
Runoff	mm	Run off	a
ActEvap	mm	Actual evaporation	a
PotEvap	mm	Potential evaporation	a
ActTran	mm	Actual transpiration	a
PotTran	mm	Potential transpiration	a
Drainage	mm	Drainage below profile	a
WaterTbl	mm	Depth to water table	b
WatFlux	mm	Net flux of water across the soil surface	a
mmWater Tn	mm	Equivalent depth of water in macro-segment n	b
Theta Tn	Volume fraction	Water content at the lower boundary of macro-segment n	b
Matric Tn	kPa	Matric potential at the lower boundary of macro-segment n	b
UptNH4	kg/ha	Plant uptake of NH4-N	
VolNH4	kg/ha	Volatilisation of NH3-N	
LeachNH4	kg/ha	NH4-N leached	
UptNO3	kg/ha	Plant uptake of NO3-N	
AtmFxN		Atmospheric fixed N	
VolNO3	kg/ha	Denitrification of NO3-N	
LeachNO3	kg/ha	NO3-N leached	
UptP	kg/ha	Uptake of P	
LeachP	kg/ha	P leached	
FlxnUrea	kg/ha	Flux of urea-N across the lower boundary of macro-segment n	a
TnUrea	kg/ha	Urea-N content in macro-segment n	b
FlxnNH4	kg/ha	NH3-N	a
TnNH4	kg/ha	NH4 content in macro-segment n	b
FlxnNO3	kg/ha	NO3-N	a
TnNO3	kg/ha	NO3 content in macro-segment n	b
TnResN	kg/ha	Plant residue-N	b
TnHumN	kg/ha	Soil humus-N	b
TnManN	kg/ha	Manure-N	b
TnResC	kg/ha	Plant residue-C	b
TnHumC	kg/ha	Soil humus-C	b
TnManC	kg/ha	Manure-C	b
TnFerP	kg/ha	Fertiliser-P	b
FlxnLabP	kg/ha	Labile-P (solution and sorbed phases in this pool always in local equilibrium)	b
TnLabP	kg/ha		b
TnResP	kg/ha	Plant residue-P	b
TnHumP	kg/ha	Soil humus-P	b
TnManP	kg/ha	Manure-P	b
TnBndP	kg/ha	Bound-P	b
SurUrea	kg/ha	Surface Urea-N	

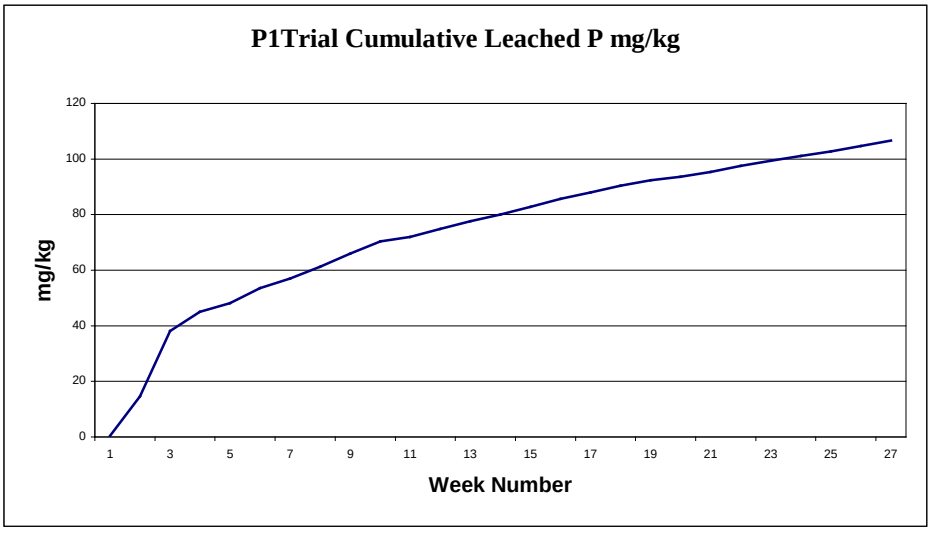
SurNH4	kg/ha	Surface NH4-N	
SurNO3	kg/ha	Surface NO3-N	
SurResN	kg/ha	Surface plant residue-N	
SurHumN	kg/ha	Surface humus-N	
SurManN	kg/ha	Surface manure-N	
SurResC	kg/ha	Surface plant residue-C	
SurHumC	kg/ha	Surface humus-C	
SurManC	kg/ha	Surface manure-C	
SurFerP	kg/ha	Surface fertiliser-P	
SurLabP	kg/ha	Surface labile-P	
SurResP	kg/ha	Surface plant residue-P	
SurHumP	kg/ha	Surface humus-P	
SurManP	kg/ha	Surface manure-P	
SurBndP	kg/ha	Surface bound-P	
TotSurP	kg/ha	Surface-P	
RunUrea	kg/ha	These columns list the quantity of each chemical species estimated to have been lost in run off water. The LEACHM manual states that this is an arbitrary assessment in LEACHM, is subject to change in the way it is calculated and should be regarded as a relative index of runoff hazard.	
RunNH4	kg/ha		
RunNO3	kg/ha		
RunResN	kg/ha		
RunHumN	kg/ha		
RunManN	kg/ha		
RunResC	kg/ha		
RunHumC	kg/ha		
RunManC	kg/ha		
RunFerP	kg/ha		
RunLabP	kg/ha		
RunResP	kg/ha		
RunHumP	kg/ha		
RunManP	kg/ha		
RunBndP	kg/ha		
FertUrea	kg/ha	Urea-N fertiliser	a
FertNH4	kg/ha	NH4-N fertiliser	a
FertNO3	kg/ha	NO3-N fertiliser	a
FertResN	kg/ha	Plant residue-N	a
FertManN	kg/ha	Manure-N	a
FertP	kg/ha	Fertiliser-P	a
FertResP	kg/ha	Plant Residue-P	a
FertManP	kg/ha	Manure-P	a
Celcius Tn	^{o}C	Temperature at the lower boundary of macro-segment n	b

Table 4.3.1. Definitions of the different parameters displayed in the LEACHN .SUM file.

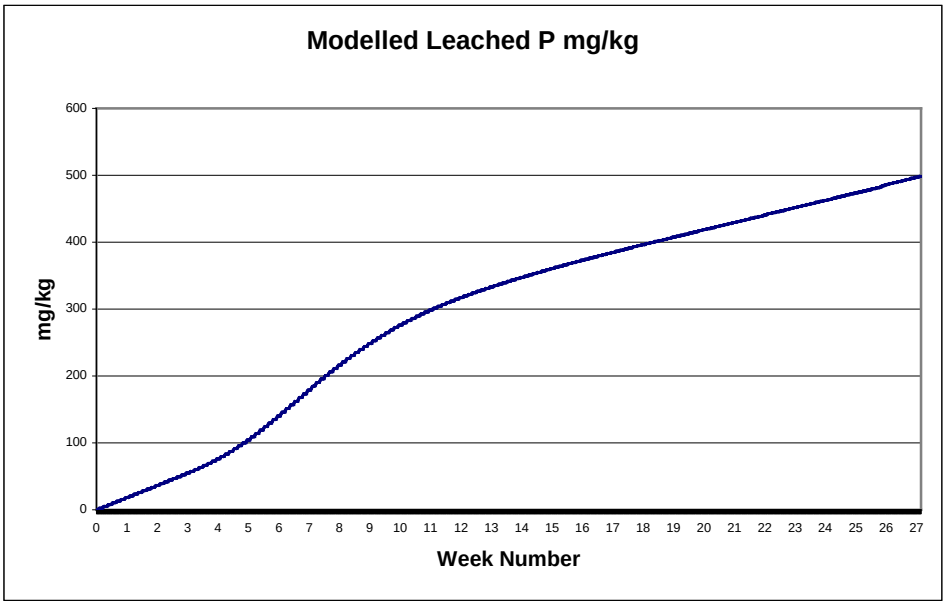
Below are four graphs displaying the behaviour of both measured P and simulated P. Graphs 4.3.1 and 4.3.2 both show cumulative

leached P. Graph 4.3.1 is the actual measurements made during the trial described in section 2 and Graph 4.3.2 is the simulated leaching behaviour. As can be seen from the graphs the measured leached P peaked in the first four weeks, whereas the model showed the peak occurring between weeks 5-10. The trends although delayed were similar. Another difference between the measured leaching and the simulated leaching is the P values. The amount of P leaching is much higher in the model than in the actual trial, this could be due to the higher P sorption value of the soil used in the trial or differing rate constants.

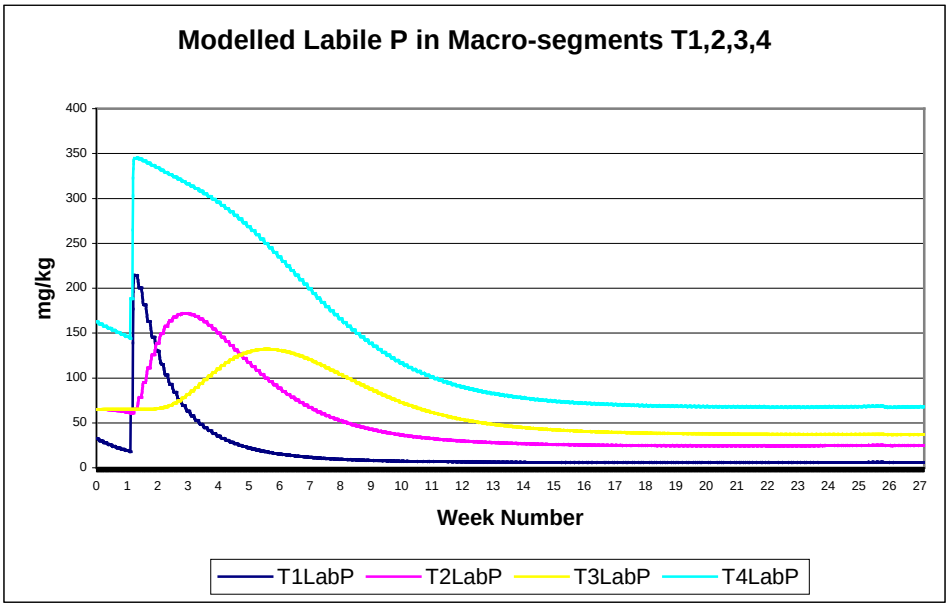
Graph 4.3.3, shows the simulated changes in the labile pool in the four macro-segments. The fertiliser addition was put in at the start of the run, the graph shows a delay of a week before the effect of this is seen. The trend displayed here is very similar to the trend displayed in graph 4.3.4. This graph shows the measured non-cumulative P leaching data. In the trial the fertiliser was added after the first week in a soluble form. The higher P levels were observed immediately and continued to reduce until week 10 which coincides with the time taken for the labile and bound pools to equilibrate in the model.



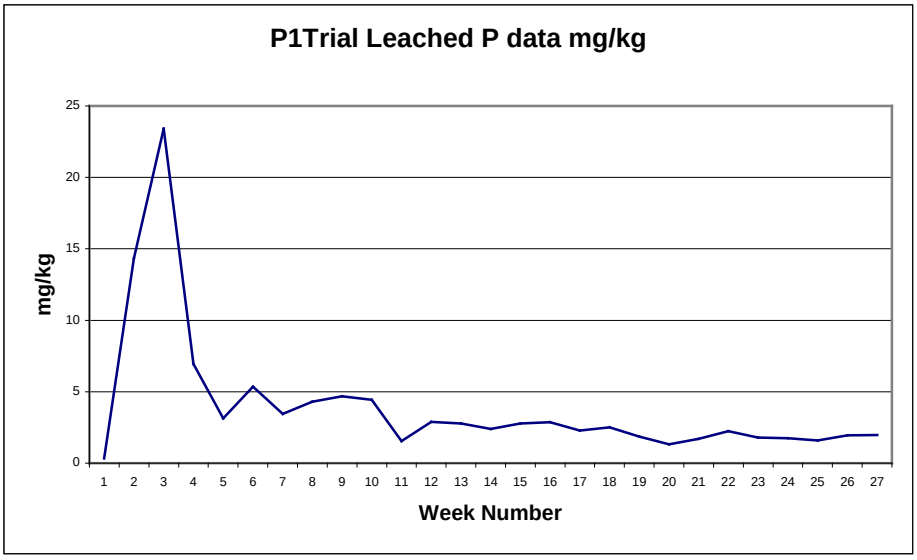
Graph 4.3.1. Actual cumulative leached P as measured for the P1 trial in section 2, mg/kg.



Graph 4.3.2. Modelled cumulative leached P, mg/kg.

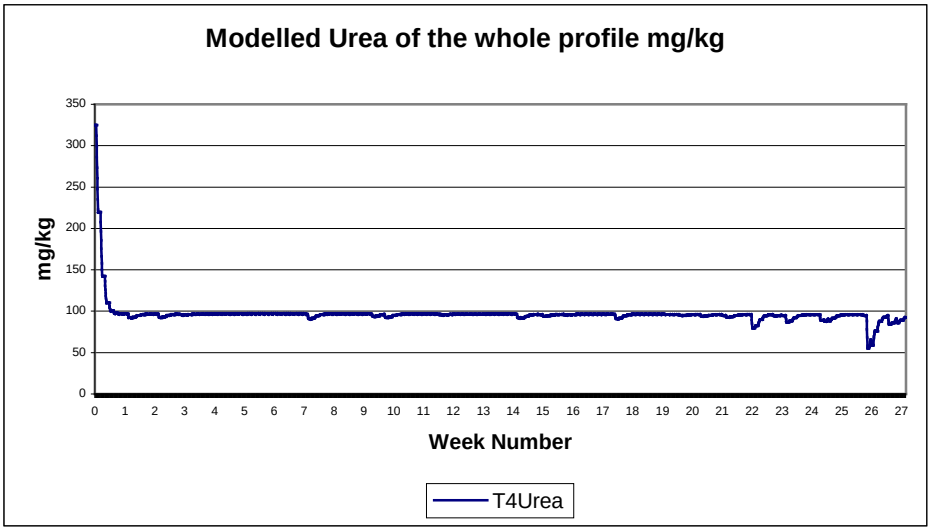


Graph 4.3.3. Modelled labile P in the four macro-segments, T1, T2, T3 and T4, mg/kg.



Graph 4.3.4. Actual leached P from the P1 trial, mg/kg.

The rate constants for urea were set at zero so that urea could be used as a non interactive tracer. As you can see in graph 4.3.5, the urea level dropped within the first week from over 320 mg/kg to between 90 and 100 mg/kg. It hovered around this level for most of the simulated period with just a few dips.



Graph 4.3.5. Modelled urea for the whole profile, mg/kg.

3.4 Discussion

The LEACHN model, showed reasonably good correlation between the movement in the labile P pools and the observed leaching in the actual trial in terms of trends, but not in terms of values. There was a difference between the rate at which the labile pools peaked and the rate at which the actual leaching peaked. It could be that the rate constant is different in the actual trial compared to the model and further work could be carried out to attempt to close the gap between them.

In the actual trial the fertiliser addition took place on the 15th December which was week 1 of the model. The model doesn't allow for fertiliser additions to be included after the start of the trial, there was a difference of about a week until the effects of fertilisation was seen, this is probably due to the dissolution rate chosen for the fertiliser. The model assumes a solid fertiliser addition and not a solution fertiliser which could have an effect on the rate at which the P fertiliser would enter the soil solution due it being in a soluble state.

The cumulative leaching observed in the actual trial measurements were again similar in trends but not values to those predicted by the model but again there was a greater delay in the model than in the actual results. This could be related to the rate constants used and the fertiliser addition in the actual trial. Leaching is also impacted by the P sorption capacity of the soil which was not directly taken into account in the model.

The model has some very useful characteristics. Even though this model is not specifically designed for use in constructed wetland soils, the results showed that there is the potential for further development. The model is flexible enough to allow for many parameter adjustments. A useful addition in the LEACHN section would be P

sorption capacity, which would then take into account the effect of this parameter when modelling P retention.

There was not enough data from section 2 to be able to explore the equilibrium between labile and bound P in the actual trial and the simulated trial. If this were to be investigated further an alternative strategy would be to measure just the labile and bound pool in the constructed wetland soils. This would allow more samples to be taken and a better spread of data points following the addition of fertiliser P.

Further simulation could then be run to find out more about how the rate constants change between upland and wetland soils.

5. Concluding Discussion

5.1 Introduction

The primary aim of this research project was to investigate the behaviour of P in soils that were subjected to flooding with a high ammoniacal liquor solution. Improved understanding of P in these soils will enable better management of plant health in the constructed Reed Bed Treatment System at the Whyalla Steelworks in South Australia. The initial literature reviews were extensive however there was a lack of information relating to fertiliser application rates and management of P for plant health for similar wetlands, as available literature was focussed preferentially on nutrient removal and leaching by such systems.

The aim of the literature review was to collate and examine as much information about P behaviour in soils as was practicable. This was done by focusing on a number of key areas such as P chemistry in soil, P fertilisers, P analytical techniques and P requirements in wetland plants.

To assist with understanding of likely P behaviour and P pools in this type of system it was important to understand the typical behaviour of P in soils in general, including binding mechanisms, pH influences etc. There was a need to understand fertiliser types and associated soil reactions, long-term impacts, and prediction of application rates. This led further to assessment of analytical techniques, including tests available for the prediction of P application rates, and tests to understand the fate of P within in the soil system. Given that most wetland systems discharge into waterways it was also critical to understand the potential environmental impacts resulting from over-application of P. The use of a model to compare actual behaviours with predicted behaviours was a useful way to understand the benefits

and weaknesses of modelling and the differences between predicted behaviour in a flooded dry land soil and those observed in a flooded dry land soil subjected to heavy chemical loading.

Due to the nature of this unique system it was important to gain a good understanding of how P applied to these systems are likely to behave. A review of analytical techniques and published information resulted in the identification of the Hedley Fractionation process as the technique most likely to portray a complete picture of P behaviour. The Hedley Fractionation process was capable of providing a complete overview of the pools preferred by P in these types of systems and potentially some guidance as to which pools could be used as indicators of future P requirements.

As this wetland system was such a unique situation it was appropriate to cover as many facets of the large scale project as was practicable. In particular the inclusion of a chapter on the fate of the three key components of the ammoniacal solution, namely ammonia, phenol and cyanide, gave a more complete picture of the chemical loading the system was under.

5.2 Experimental Design

Significant effort was expended in designing the experiment. It was important to set up a trial system that as far as practicable could mimic the larger scale system. The establishment of RBTS cells was of particular importance as these formed the basis of the entire investigation.

The Hedley Fractionation procedure experiment presented some challenges; the laboratory facilities at the Whyalla Steelworks are designed for the steelmaking industry and not for soil analysis. It was

critical therefore before making the final decision to use this approach, to ensure access to appropriate equipment was possible.
The study of the changes in effluent composition occurring in the cells was already established and the samples obtained in the trials were added to the routine analyses carried out on the main system.

The model used was a research model LEACHN developed by Dr John L Hutson (Hutson, 2003). It was possible to simulate some of the P movement in the chemically loaded Reed Bed Treatment System (RBTS) used in section 2 of this paper, using some of the parameters measured in that section. This enabled comparisons to be made between actual and predicted data.

5.3 Discussion

The outcomes from this study have been significant. Although there was a large amount of material available in the scientific literature the difficulty lay in interpreting and adapting this information to the area of interest, so it was important to keep the aim and objectives of the study in perspective at all times.

An improvement on the experiment design would have been to have a replication of the cells; however due to restrictions in access to equipment both for the cell construction and for the additional analysis it was not possible for this study at this location. A further improvement would have been to operate the system for a longer period, and to continue the P analysis for a full year to determine the changes in P through a plant senescence cycle and concurrent cooler temperatures.

The study of chemical treatment within the cells was useful as this showed a similar treatment pattern as that obtained the 2Ha system, which gave confidence that using smaller systems could be reliably

used for further investigations on chemical treatment. Improvements in this area could have been a closer investigation of the fate of all nitrogen products to re-affirm that the exact breakdown mechanisms in the cells were the same as those for the larger system.

The LEACHN model was not designed with permanently saturated soils in mind; with more experimental work it could have been possible to expand LEACHN to be able to closer model the behaviour of P in wetland or RBTS soils, but this is outside the scope and objectives of this project.

5.4 Conclusion

This study was a valuable learning experience combining the development of research skills, experimental design, understanding the possibilities of using modelling and the limitations of modelling, and provided increased understanding of the complex soil chemistry of P within a specific and unique soil environment.

Appendix 1 Trial Additions

Calendar of changes and applications for the Trial RBTS box.

MONTH/DAY	S	M	T	W	T	F	S	S	M	T	W	T	F	S	S	M	T	W	T	F	S	S	M	T	W	T	F	S	S	M	T	W	T	F	S	S
Dec-00						1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
Jan-01		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31				
Feb-01					1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28				
Mar-01					1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	
Apr-01	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30						
May-01			1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31			
Jun-01						1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	

Set up trial
Fertiliser addition
Water application
2.5% liquor/water
5.0% liquor/water
10% liquor/water

The control box was set up and fertilised as above, water addition was at a rate of 10litres per day for the duration of the experiment.

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