A study on the transport of natural organic matter (NOM) and phosphorus in gypsum treated soils of the Mt Bold catchment and impacts on water quality.

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A thesis submitted for the degree of Doctor of Philosophy
August 2006

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Disclamer

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Acknowledgments

I would like to express my gratitude to my supervisors. Thank you to Prof. David Chittleborough and Dr. Jim Cox, you planted the seed that allowed this project to grow. A very special thank you to Dr. John Van Leeuwen for your tireless contribution throughout this study. I am most grateful John for your support during the thesis writing stage. Thankyou all for supporting this project and maintaining an interest in it until the end.

Many thanks also to the CRC for Water Quality and Treatment and inparticular to Prof. Don Bursill, Prof. Dennis Mulcahy and Dr Dennis Steffenson and for having the vision to include this project within your program and for your support throughout.

I would like to express further gratitude to the following people and organizations that supported this study:

- Mr Colin Rivers for all his field and laboratory expertise and moral support over the period of my study.
- All those who work in the water treatment laboratory at the Australian Water Quality Centre, thank you for your support and making me feel at home during my many visits.
- Dr Ron Smernik for his contribution to the ^{13}CNMR work presented in this thesis.
- Dr Darryl Stevens who instrumented the field sites and conducted the monitoring until the end of 1997.
- Dr Kaye Spark for her initial project supervision and early work on organic matter characterisation.
- The staff and students of the School of Earth and Environmental Sciences and CSIRO Land and Water for providing the warm and supportive environment within that this study was undertaken.
- My current employer, Environmental & Earth Sciences for allowing time to complete this, and their generous contribution towards printing and binding of this final copy.

Finally, a very special thank you to my family and friends. To my parents Maxine and Thomas for always having been and continuing to be there for me, and especially to my daughter Imogen Radbone Varcoe - this is for you.

Abstract

Losses of nutrient, specifically phosphorus and organic matter, from soil to water are thought to be primary agents of water quality decline in many South Australian (and Australian) drinking water reservoirs. Furthermore agricultural soils of southern Australia are generally nutrient deficient requiring supplementary additions of fertilizer to maintain fertility.

This study investigated the potential of an agriculturally viable soil amendment to enhance the soils' retention of these constituents. This study investigated the effect of gypsum on phosphorus and organic matter mobility in soils, including its effect on soil fertility and water quality. Gypsum was selected following a literature-based investigation of potential amendment alternatives and was selected based on its properties including: agricultural viability, availability, cost and physiochemical properties (including solubility and ease of application). While earlier investigations have found gypsum to be effective in reducing P solubility in soils of $pH > 6.5$, the soils of this investigation were of $pH < 6.5$.

Water quality was studied with reference to the Australian Drinking Water Guidelines (NHMRC and ARMCANZ, 1996) and the treatability of the water under simulated conventional water treatment (coagulation, sedimentation and filtration) conditions and specifically for removal of natural organic matter. Of particular focus was the effect of gypsum on the retention and transport of total and reactive P and on the concentration and character of soluble organic matter in leachate and soils.

In addition to studying the effect of gypsum on the distribution and characters of P and organic matter in soil, changes to physical and chemical properties were also assessed.

These investigations were conducted at a subcatchment scale at a site within the Mt Bold catchment of the Mt Lofty Ranges, South Australia, described in Chapters 2, 3 and 4. These trials were supported by laboratory based investigations utilizing core leaching and batch trials described in Chapters 5 and 6, respectively.

The subcatchment study investigated the application and effect of gypsum on a typical pasture of the Mt Bold catchment (Chapter 2), on its soil chemistry and fertility (Chapter 3) and on its surface and subsurface water quality (Chapter 4). The study was conducted over a four year period. In the first year, background water quality data for the site were obtained; in the second year, gypsum was applied and over yr 2, 3 and 4, surface and groundwater leachate monitoring and sampling were conducted. Parameters analysed included P content (total and dissolved reactive P), total and dissolved organic matter, total ion concentration, total dissolved solids and pH. Solution chemistry modeling was utilized to establish chemical phases and the organic content was characterized by techniques including pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) and ^{13}C-NMR.

Following 3 yr of leachate monitoring and study, the soils of the catchments were analysed for their physico-chemical properties including total exchangeable cations and the distribution of organic matter and P in silt and clay fractions.

Both physical and chemical properties of the soil were markedly different between treated and untreated soils. Increases in total exchangeable cations in the treated soil provided an increased sorption capacity for both P and NOM, and therefore potentially reducing the transfer of these constituents to surface and subsurface water.

Calcium ions released from gypsum at the surface exchanged with Al (and other cations) that subsequently were released into the soil solution, and were transferred deeper into the soil profile. The anion sorption capacity at depths >20 cm increased as a consequence of increased exchangeable cations, itself the result of adsorption of these released cations as well as Ca. The sorption capacity may have been further enhanced through the precipitation of new mineral phases (e.g. Al sulfates). The enhanced anion sorption capacity of the soils at depth (>20 cm) enabled the formation of micro-aggregates (size ≈ 50-100 μm) by the incorporation of organic matter, in a manner similar to podzolisation. These micro-aggregates appear to be significant repositories of NOM and P. Importantly the formation of these micro-aggregates (proportionally rich in P and NOM) would reduce the potential of their loss from soil via mobilisation by water and, if exposed, by wind.

The retention of these constituents combined with the higher exchangeable Ca, reduced exchangeable Al and with no reduction in exchangeable Mg (in the short term), suggests that gypsum had improved the chemical fertility of the pasture soils. Additional potential benefits to soil physical fertility, as found in this study, are: improved soil structure (particularly aggregate stability) and a small reduction in plant available water (PAW) leading to a complementary increase in air filled porosity (AFP).

The effect on the leachates from applying gypsum to field soils is analogous to the outcomes of conventional water treatment using coagulation (*viz.* reduced dissolved organic carbon (DOC), specific UV absorbance (SUVA), colour and P concentrations). The reduction in the high molecular weight hydrophobic component of natural organic matter (NOM) having a relatively high level of aromaticity (as indicated by SUVA and specific colour), was supported by both ^{13}C-NMR and Py-GC/MS.

Reductions in total P were accompanied with reduced proportions of molybdenum reactive phosphorus (MRP), (< 0.45 μm) compared with particulate P (>0.45 μm). These observations are further supported by the changes observed in organic matter and P distribution within the soil (Chapter 3).

Overall the results indicate that the mechanisms operating in soils accompanying gypsum treatment are similar to those that occur in conventional water treatment (i.e. coagulation and flocculation). Elevated ionic strength as well as the activity of polyvalent cations (Ca, Mg, Al, Mn and Fe) in the soil solution supports this analogy. In the case of the gypsum amended soils of this study, the final floc was composed not only of Al complexes (as in water treatment) but of high P and NOM- clay aggregates (see Chapter 3). Furthermore this treatment appears to have no deleterious effect on subsequent conventional water treatment of the soil leachates, based upon the jar tests conducted. The remaining, lower concentration of organics present in the leachate from the gypsum treated soil were found to be relatively more recalcitrant to removal with alum treatment under conventional water treatment conditions, as was expected.

The core leaching trials simulated the field environment under controlled laboratory conditions and were used to study the effects of varying gypsum application rates on leachate quality.

Comparison of the results of the core leaching study and the field investigation outlined above show very similar trends, i.e. reduced pH, P, DOC, SUVA, Specific Colour, Al and Fe and increases in Mn, Mg and Na. Furthermore, the results of this study indicated that a minimum application rate of gypsum required to effect a measurable reduction of P and DOC was between 3 and 10 t/ha for these soils.

Given that P is an important plant nutrient, understanding the precise mechanism of its adsorption in soils is significant for understanding soil fertility. Batch trials were also conducted to develop a greater theoretical understanding of the mechanism of its retention in soils associated with gypsum application.

This study showed that competition between NOM and P existed, however gypsum enhanced the retention of both constituents between pH 5 and pH 9. Defining the precise mechanism of enhancement of P sorption is complicated by the similarity in effect (i.e. inhibition) that both increasing ionic strength and the presence of NOM have on both cooperative adsorption and Ca-P precipitation. Observations in this study reinforce the concept of a continuum between adsorption and precipitation. The results indicate that below pH 7, cooperative adsorption mechanisms most likely dominate while above pH 7, precipitation of P as calcium phosphate most likely accounts for the removal P from suspension.

Gypsum has several established benefits in agricultural application and this study has demonstrated further potential benefits for agriculture, soils in general and in water quality. Results from this study show that gypsum can enhance the ability of soil to retain some of the primary agents of water quality decline, P and NOM. Potential benefits of using gypsum for this purpose were observed both on-site through improved nutrient retention and fertility in soils and off-site in water runoff (surface and subsurface) through improved water quality.

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1 Introduction and Literature Review

1.1 INTRODUCTION

Streams and water storages of southern Australia have relatively high levels of natural organic matter (NOM) compared to many other continents. The reasons for this are not entirely clear but may relate to the unusual nature of southern Australian soils (strong texture contrast) and peculiarity of climate (xeric - i.e. strong seasonal wetting and drying cycles). These physical characteristics may predispose the flux of high quantities of nutrient (especially P and N), fine clay and organic matter (Chittleborough *et al,*. 1992). These constituents are thought to be the primary agents of water quality decline in many South Australian (and Australian) reservoirs, adding significantly to the costs of water treatment for domestic consumption.

The aim of this study is to use soil management, specifically the addition of agriculturally viable amendments, to improve the quality of water at its first point of contact with the catchment, the soil. It is hoped that by being able to increase the soils ability to retain two of these constituents (specifically P and NOM), not only will the quality of the water entering these surface water bodies improve, but indeed the quality and fertility of the soils will also improve.

1.2 CHEMISTRY AND MOBILITY OF P IN SOILS

1.2.1 PHOSPHORUS AND WATER QUALITY

Phosphorus is an important nutrient in living things, contained in, for example, protein and ATP. Garrels *et al.* (1975) gives an approximate formula for algae or plant matter as being: $C_{280}H_{560}O_{280}N_{19}P_1$. As this formula indicates only small amounts of P are required to sustain life, and it is an essential requirement for all life. In streams, lakes and reservoirs, it is often the limiting factor in algal and plant growth. According to Tomson and Vignona (1984), algae require concentrations of P in the order of 0.001 to 0.01 mg/L for growth to take place, and when concentrations exceed approximately 0.5 mg/L, algal and plant growth is optimal. This can lead to eutrophication where the water body becomes choked with algae and other water plants that cause oxygen deficiencies and lead to plant and fish kills. Additionally the build up of organic matter in the water column and sediment results in an overall reduction in water quality. Some algal forms, such as blue-green algae, can also release toxins into the water.

Historically, P build up in surface water that can lead to eutrophication was believed to primarily be caused by point sources such as domestic waste water discharge. Tomson and Vignona (1984) noted that eutrophication appears to be a problem of local streams and lakes as these are the initial receiving bodies of point source input. The role of non point sources, specifically agriculture, and the ubiquitous use of P fertilisers has gained increasing recognition as an important contributor to eutrophication in recent decades. According to Sharpley *et al.* (2000) such P losses from agricultural soils are difficult to quantify due to their diffuse nature, and such losses are not as easily controlled as point sources.

1.2.2 FATE OF APPLIED PHOSPHATE

The fate of phosphate applied to soils as fertiliser is initially controlled by the type of compound applied (Table 1). The most common of the water soluble fertilisers are the single-, double-, and triple-superphosphate and mono- and di-ammonium phosphates (Nash and Halliwell, 1999).

In Australia, single superphosphate (monocalcium phosphate, MCP) is the most commonly used phosphatic fertiliser on pasture soils (from Pivot Ltd. Annual Report 1996-1997 in Nash and Halliwell, 1999).

The breakdown and release of P from a MCP granule begins as water moves into the granule from the surrounding soil as water vapour condensing on the inside of the granule. According to Lindsay (1979) the condensed water on the inside of the grain moves out of the granule into the surrounding soil by capillary action. This solution is then supersaturated with respect to $CaHPO_4.2H_2O$ (DCPD) and $CaHPO_4$ (DCP) resulting in the precipitation of these minerals at the granule site. The precipitation of DCPD gives a resultant localized pH of 1.5, and DCP precipitation results in a solution pH of 1.0.

Table 1 Phosphate compounds commonly used in fertilisers and compositions of their saturated solutions (Sample, Soper and Racz 1980)

Compound	Formula	Common name	Composition of saturated solution			
			pH	P M/L	Accompanying cation M/L	
Monocalcium phosphate	$Ca(H_2PO_4)_2.2H_2O$	Superphosphate (MCP)	1.0	4.5	Ca	1.3
		MTPS	1.5	4.0	Ca	1.5
Monoammonium phosphate	$NH_4H_2PO_4$	MAP	3.5	2.9	NH_4	2.9
Monopotassium phosphate	KH_2PO_4	MKP	4.0	1.7	K	1.7
Triammonium pyrophosphate	$(NH_4)_3HP_2O_7.H_2O$	TPP	6.0	6.8	NH_4	10.2
Diammonium phosphate	$(NH_4)_2HPO_4$	DAP	8.0	3.8	NH_4	7.6
Dipotassium phosphate	K_2HPO_4	DKP	10.1	6.1	K	12.2
Dicalcium phosphate	$CaHPO_4$	DCP	6.5	.002	Ca	.001
Hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$	HAP	6.6	10^{-5}	Ca	.001

Changes in solution composition would normally be expected to follow the congruent dissolution of MCP line (Figure 1) where 2 moles of P are released for every mole of Ca. Experimental evidence from Lindsay and Stephenson (1959a, b) found deviations from this line in the dissolution of MCP over a time period ranging from 15 s to 17 days. They found over the first 24 hr the solution composition was at the metastable triple point (MTPS) where MCP dissolves as DCPD precipitates (F1):

$$Ca(H_2PO_4)_2.H_2O + H_2O \leftrightarrow CaHPO_4.2H_2O + H_3PO_4 \qquad \text{(F1)}$$

It is the release of H_3PO_4 that causes the low pH (1.5) in the dissolution of MCP. Over 3 and 17 days the solution was found to shift from MTPS toward the final equilibrium with MCP and DCP at the TPS (stable triple point solution). Again the dissolution of DCPD and the precipitation of DCP that occurs as the dissolution of MCP reaches the final stage of equilibrium leads to a greater release of H_3PO_4 giving rise to even lower solution pH (1.0).

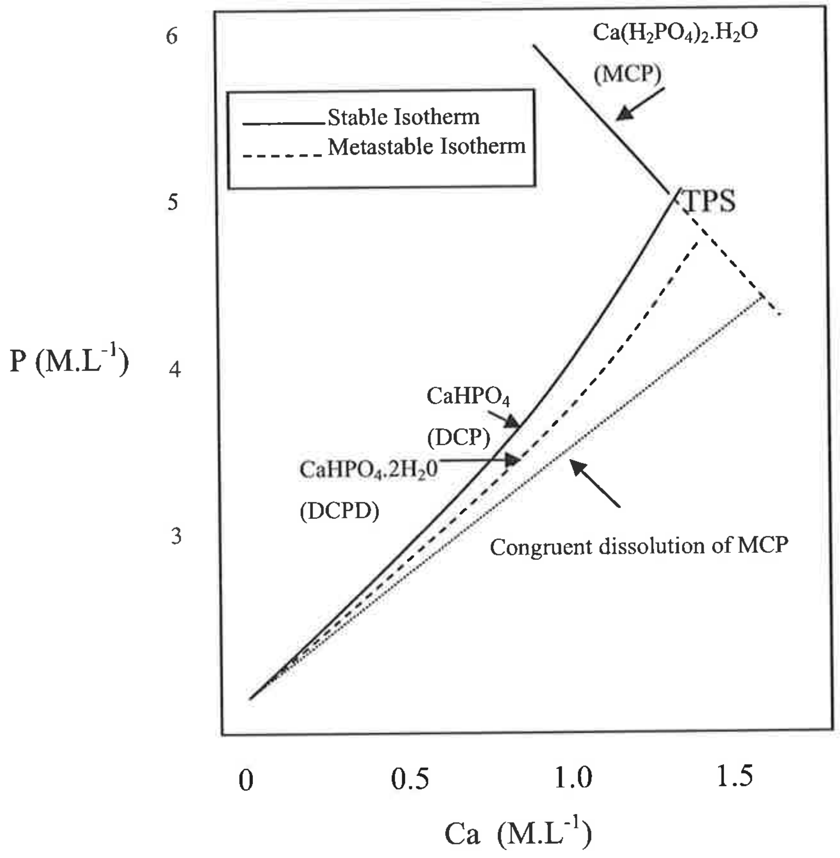

Figure 1 Solubility isotherms in the concentrated region of the CaO-P_2O_5-H_2O system at 25^{0}C, illustrating solution composition during the dissolution of MCP (redrawn from Lindsay 1979).

In soils the low pH attained at TPS causes cations such Fe, Al and Ca to be released from soil minerals into solution. According to Lindsay (1979) these reactions with soil bases cause pH to increase. Lindsay and Stephenson (1959b) found evidence that these cations can then be consumed in precipitation reactions forming a variety of phosphate minerals (Lindsay *et a,*. 1962). The inclusion of other cations such as NH_4^+, K^+, Ca^{2+} and Mg^{2+} in fertilisers can result in the formation of a variety of other initial reaction products.

1.2.3 PHOSPHATE REACTIONS IN SOILS

It has long been known that the key processes that affect the mobility of phosphate through soils are reactions involving either precipitation or adsorption. These basic mechanisms can be further expanded to include physical adsorption, chemisorption, anion exchange, surface precipitation and precipitation of separate solid phases (Sample, Soper and Racz, 1980). According to these researchers the process of P retention in soils can be considered a continuum encompassing precipitation, chemisorption and adsorption that occurs in the soil profile following P fertiliser application.

According to Barrow (1988) and He *et al.* (1991) the mechanism of phosphate retention dominates is broadly dependent on the concentration of phosphate in solution. Sorption reactions dominate at low concentrations whereas precipitation reactions dominate at high concentrations.

The interaction of dissolved phosphate and the soil at normal soil solution concentrations is summarised by as a series of chain reactions (from Mattingly and Talibudeen, 1967):

1. rapid formation of a surface adsorbed phosphate complex;
2. partial dissolution of the weathered and frayed edges of soil minerals (including soil carbonates) increasing the concentrations of phosphate-reactive metal ions in solution;
3. slow desorption of surface-adsorbed phosphate; and
4. slow nucleation, crystallisation and recrystallisation of metal phosphates, basic phosphates, and double phosphates of metals.

1.2.4 P RETENTION IN ACID SOILS

In acid soils, P fixation is closely associated with hydrous oxides of Fe and Al. Hydrous oxides and oxides of Fe and Al are common in soil environments. These groups are found on the edges of minerals; they can also occur as discrete compounds, as coatings on other particles or even as amorphous Al hydroxy compounds between expandable Al silicates (Sample, Soper and Racz, 1980). Swenson *et al. (*1949) found that the graphs for adsorbed P vs pH for geothite were very similar to that of Fe and kaolinite was similar to Al. This lead to the suggestion that the pattern of adsorption for soil minerals is similar to precipitation with their dominant metal cation (i.e. Fe or Al) (Hingston *et al,*. 1972; Muljadi, Posner and Quirk, 1966)

The study of Lopez-Herandez and Burnham (1974) concluded that there was a decrease in phosphate retention with increasing pH and that this corresponded with a large decrease in exchangeable (acetate extractable) Al. Murrmann and Peech (1969) found that the minimum solubility of phosphate in acid occurred in the pH range of 5-7. This is the range in that insoluble hydroxy-Al species precipitate (Haynes 1982). It is the presence these surface-active hydroxy-Al species that Lopez-Herandez and Burnham (1974) reported to be responsible for decreases in phosphate solubility observed in that pH range. Swenson *et al. (*1949) found that the maximum fixation of phosphate occurs at pH 2.5-3.5 for Fe and pH 3.5-4 for Al. These Figures agree with Bowden *et al. (*1980), Obihara and Russell (1972) and Parfitt (1978) for maximum adsorption by soil and soil components in the pH range 2-4. Similarly Lopez-Herandez and Burnham (1974) also found that maximum phosphate sorption occurred below pH 4. However Lopez-Herandez and Burnham (1974) found that in some soils P sorption still continued in at pH values where there was no exchangeable Al or Fe. At pH values greater than 5.5 phosphate can be removed from solution as Ca phosphates (Lopez-Herandez 1974 and White and Taylor 1977). There is some discrepancy in the literature regarding the optimal pH for phosphate retention. Nonetheless it appears that the fate of P in (acid) soils is dominated by the presece of Al, Fe and Ca ions and pH.

1.2.4.1 Ionic Strength, pH and P Adsorption

He *et al. (*1997) found that changes in the ionic strength of a solution alter the effects that pH has on P adsorption on γ-Al_2O_3 and kaolinite. This study found that at low pH (< 5) increasing the ionic strength led to a decrease in adsorption of phosphate, whereas at higher pH levels (> 6) increasing the ionic strength led to an increase in adsorption. Thus this study revealed a crossover point (pH ≈ 5.5) at that there was no effect of ionic strength on phosphate adsorption- the point of zero salt effect of the phosphate adsorption surface ($PZSE_P$). Similar results were observed by Barrow *et al* (1980) using goethite to model phosphate adsorption. This study revealed a $PZSE_P$ for goethite at approximately pH 4.5 compared to pH ≈ 8 for γ-Al_2O_3 and pH 5.5 for kaolinite (He *et al,*. 1997).

Bowden *et al.* (1980) and He *et al.* (1997) state that it is possible to distinguish between inner (specific) and outer sphere (non specific) anion surface complexation by studying the effects of ionic strength variation. Such a view is challenged by Manceau and Charlet (1994) who believe that binding mechanisms cannot be inferred by responses to variations in ionic strength. According to He *et al.* (1997), however if anion adsorption shows very little ionic dependence, it is believed to be an inner sphere complex, whereas a marked ionic effect indicated outer sphere complexation (Hayes *et al*,. 1988). He *et al.* (1997) concluded from their results that phosphate is adsorbed on the O-plane (by forming an innersphere complex) through ligand exchange and covalent bonding between the metal ions of the solid and phosphate ions.

Bowden *et al.* (1980) and He *et al.* (1997) describe a similar model for the effect of ionic strength on cation and anion adsorption. Consider a specifically adsorbing cation in a region of positive electrostatic potential (or alternatively an anion in a region of negative potential) on a variable charge surface (kaolinite and γ-Al_2O_3). The effect of increasing ionic strength is to reduce the potential (not the charge density), causing a reduction in repulsion and an increase in adsorption. He *et al.* (1997) specifically investigated ionic strength effects on phosphate adsorption. When the pH is < PZC (low pH) the potential of the O-plane is positive so that increasing ionic strength leads to decreasing the potential and thus decreasing the adsorption. At pH > PZC the O-plane potential is negative: increasing ionic strength makes this less negative (more positive) and increases phosphate adsorption. Alternatively ion adsorption in a region of opposite charge leads to the reverse situation: increases in ionic strength reduce net potential resulting in decreased net adsorption. In the case of minerals with permanent charge surfaces such as montmorillonite, Bowden *et al.* (1980) observed the reverse effect: increases in ionic strength at low pH (< 7.2) led to increased phosphate adsorption. At pH > 7.2, increasing ionic strength had very little effect, but did lead to a slight decrease in phosphate adsorption.

1.2.5 MECHANISMS OF ADSORPTION

Hingston *et al.* (1972) proposed a model of anion adsorption by goethite and gibbsite, that comprised 3 possible methods, separated into 2 broad classes (1) specific or ligand exchange and (2) non-specific adsorption.

1.2.5.1 Non Specific Adsorption:

In aqueous suspension, the terminal metal atoms on the surface of an oxide complete their coordination shells with OH groups and water molecules. At zero point of charge (ZPC), when an adsorption surface has an equal quantity of H^+ and OH^-, there is no spectator adsorption. At acid pH the surface gains a net positive charge as excess H^+ ions complete the coordination shell and result in anion adsorption (Figure 2).

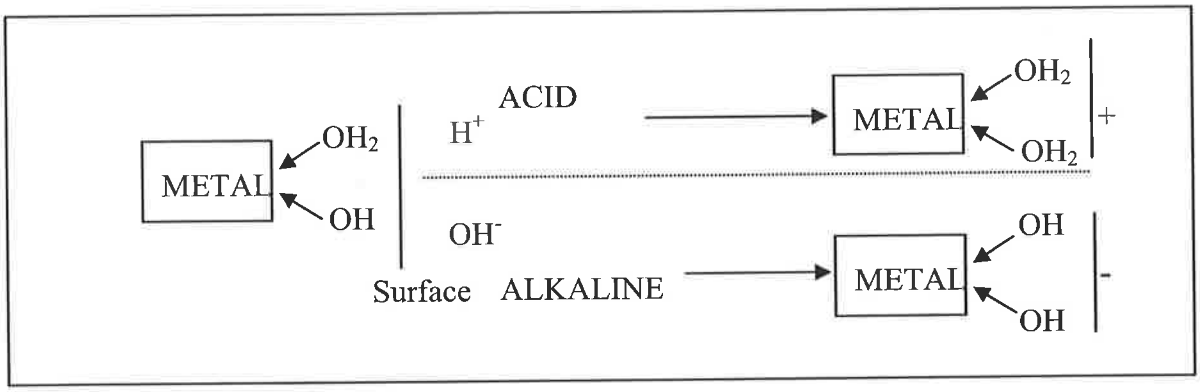

Figure 2 Model of pH effect on surface charge.

1.2.5.2 Specific Adsorption –ligand exchange

The mechanism that has been widely suggested (Parfitt 1978; He *et al*,. 1997) by that phosphate is adsorbed to hydrous oxides is via ligand exchange reaction. Figure 3 illustrates Parfitt's (1978) model of ligand exchange whereby phosphate is specifically adsorbed to goethite, by entering the coordination layer. In phosphate adsorption to goethite two surface-coordinated hydroxides ($Fe\text{-}OH^-$) exchange for each phosphate anion and form a binuclear bridging complex, Fe-OP(O)2O-Fe (Figure 3). The formation of this binuclear complex resulting from ligand exchange occurs relatively rapidly (hr) and is followed by a relatively slow phase of diffusion through the oxide surface or precipitation of the phosphates (months-yr) rendering much of the phosphate non labile (Parfitt 1978). Hingston *et al.* (1972) describe two models of ligand exchange, those that involve: a). anions of completely dissociated acids, or, b). anions of incompletely dissociated acids.

1.2.5.2.1 a). Anions of Completely Dissociated Acids

The anion of a fully dissociated acid is not absorbed unless the surface is positive, i.e. anion adsorption only occurs on the acid side of ZPC. The effect of ligand exchange is to neutralize positive sites, and in this instance exchange occurs because the anions have a specific affinity for a surface metal atom: the anions are absorbed out of proportion to their concentration or activity.

1.2.5.2.2 b). Anions of Incompletely Dissociated Acids

In this case anions of incompletely dissociated acids can be absorbed in excess of the positive charge or even a surface that has a net negative charge (ie, making a positively charged surface negative, or a negatively charged surface more negative). This may involve a process whereby the undissociated acid molecule can be absorbed as long as it is able to dissociate at the surface, thus providing a proton that reacts with the surface OH^-. It is believed that this can occur if the energy of adsorption is large enough to overcome the energy required to dissociate the acid at the surface.

$$H_3PO_4 + (M + OH^-) \rightarrow (H_2PO_4^- + M) + H_2O \qquad \text{(F2)}$$

Such a model (F2) is favoured by a pH value equal to the pK_{ai} of the acid H_3PO_4, that occurs at approximately a pH of 2. At this pH the phosphoric acid (H_3PO_4) is most susceptible to undergoing the deprotonation process that liberates a H^+ to form a water molecule with the OH^- on the mineral or hydroxide surface thus allowing $H_2PO_4^-$ to sorb onto the site OH^- vacated. Experimental evidence indicates that specific adsorption of anions by soil colloids is favoured most strongly near the pK value of the acid, because the proportion of negatively charged ions increases rapidly near the pKa values (Bowden *et al*,. 1980). As phosphoric acid is a polybasic acid it has several (3) stages of deprotonation in the series $H_3PO_4 \rightarrow H_2PO_4^- \rightarrow HPO_4^{2-} \rightarrow PO_4^{3-}$. Thus there are 3 pK_a values (pK_{ai}, pK_{aii} and pK_{aiii}) at pH approximately equal to 2, 7 and 12. Thus specific adsorption might also operate at a pH of 7.

White and Taylor (1977) and several other authors have all given results that somewhat disagree with the model put forward by Hingston *et al.* (1972). First the model mostly favours sorption at pH values near 2: very few studies have indicated that the strongest sorption rates occur at pH values as low as this. White and Taylor (1977) indicate that the Hingston *et al.* (1972) study used P concentrations far in excess of what occurs in nature.

1.2.5.3 Effect of Concentration- Adsorption v. Precipitation

The response of phosphate to pH in the soil environment is also controlled by the concentration of phosphate in the soil solution (White and Taylor, 1977). These authors compared adsorption at concentrations ranging from 1 to 1000 μM in the pH range of 4.2-6.8. At low concentration (< 100 μM) maximum adsorption was found to occur at pH 5.2-5.5. At this same pH the high concentration of phosphate (1000 μM) had a minimum solubility (approximately double the sorbed P at maximum sorbed P at 100 μM), that gradually increased as the pH rose. At these elevated concentrations and at pH 4.5, it would be expected that amorphous Al phosphate would precipitate. As the pH was raised the Al-phosphates began to dissolve, to a maximum solubility at approximately pH 5-5.5. Above pH 5.5, decreases in P solubility suggested a new phase was forming (Ca-phosphates), that remain stable above neutral pH values.

Similarly Lopez-Herandez (1974) found the dynamics of phosphate sorption is influenced by concentration. This work indicated that phosphate desorption increased as the concentration of phosphate in the final solution decreased. However, after a certain soil/solution P ratio is reached, phosphate desorption decreased as solution P decreased. This ratio is dependent on the phosphate sorption capacity of the soil (Table 2). In high P-retaining soils, this ratio was calculated at 1/20-1/40, i.e. at low soil/solution P ratios. For low P-retaining soils this ratio is much higher (1/6-1/10).

Clearly the pH at that adsorption or precipitation is most efficient will differ for the two mechanisms. That of these mechanisms dominates will largely be controlled by concentration of constituent components as well as pH (i.e. overcoming activation energy barriers). Both pH and concentration must be considered in studying retention mechanisms.

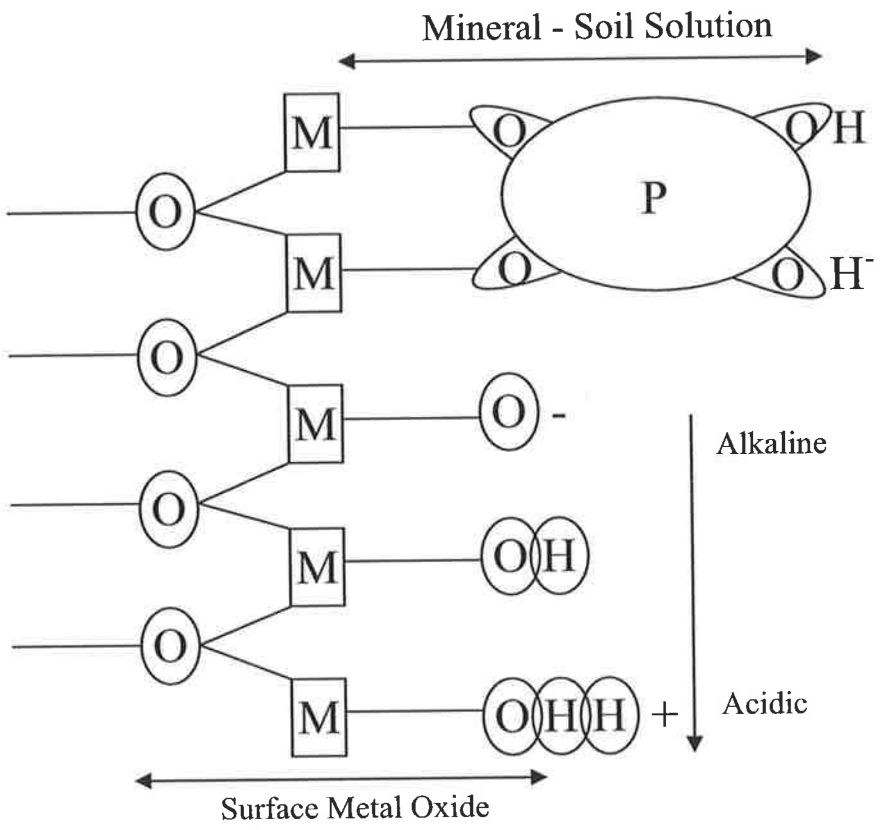

Figure 3 Model illustrating a specifically adsorbed phosphate ion (PO_4^{3-}) to a metal oxide surface (as shown in F2) and the effect that increasing H^+ concentration has on surface charge.

Table 2 Comparative effect of mineralogy on P sorption (Juo and Fox 1977)

Standard P Sorption (µg P/g Soil)	P Sorption Group	Typical Mineralogy
< 10	very low	quartz, organic material
10-100	low	2:1 clays, quartz-1:1 clays
100-500	medium	1:1 clays-oxides
500-1000	high	crystalline oxides, moderately weathered ash
>1000	very high	desilicated, poorly crystalline materials

1.2.5.4 Organometallic Complexes

Schnitzer and Skinner (1964) and Schnitzer (1969) found humic and fulvic acids can form complexes with Al and Fe ions (Parfitt, 1978). This complex could adsorb phosphate. Gerke (1992) concluded that orthophosphate levels in soil solutions at pH

< 4 are probably controlled by the formation of phosphate-(Fe/Al) complexes, whereas at pH > 5 levels are controlled by ligand exchange reactions on organically bound Al and Fe surfaces (Figure 4).

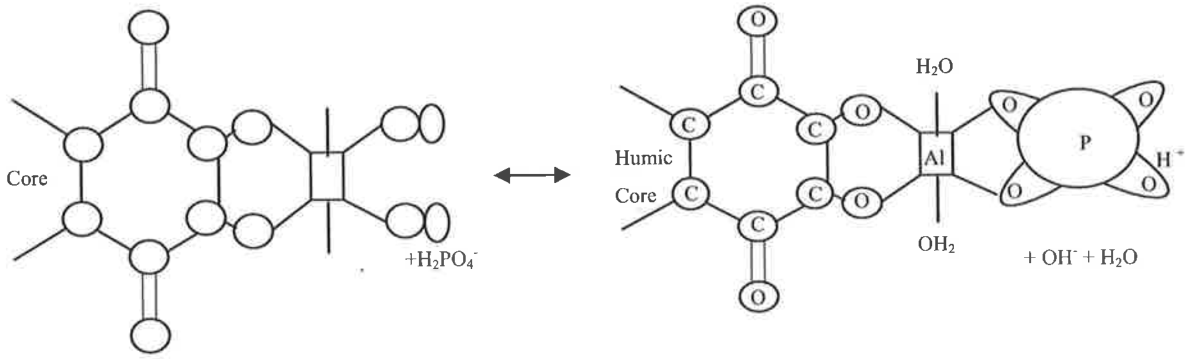

Figure 4 Reaction between humic Al complex surface and phosphate (Gerke 1992).

1.2.6 P RETENTION IN NEUTRAL / ALKALINE SOIL: CA-PHOSPHATE PRECIPITATION

The sorption reactions of P with Al and Fe, (adsorption or precipitation) reviewed in the previous section covered the dominant P retention mechanisms in acid soils. In slightly acidic to alkaline soils (pH > 5.5) Ca-phosphate precipitants have been found to control P solubility (Lopez-Herandez 1974; White and Taylor 1977). The following section reviews precipitation reactions with particular reference to Ca-P but the general theory also applies to Al and Fe phosphate precipitation.

1.2.6.1 Homogenous Precipitation

Homogeneous precipitation occurs in solutions that are highly supersaturated with respect to the mineral components, resulting from spontaneous nucleation (Stumm, 1992). Many investigators have studied the precipitation of calcium phosphates from supersaturated solutions not only in agriculture (soil fertility) and the water industry (softening and waste water treatment) but also in medicine (bone growth).

Hydroxyapatite (HAP) is structurally similar to bone (Feenstra and de Bruyn, 1979). HAP is also the most stable form of Ca-phosphate in soils.

HAP does not readily form despite supersaturation with respect to its constituents. It is generally believed that the precipitation of a precursor calcium phosphate is required before HAP can form. Eanes *et al.* (1965) demonstrated the formation of amorphous calcium phosphate (ACP) as a precursor to HAP formation. Feenstra and de Bruyn (1979) and Nancollas and Tomazic (1974) also concluded that octacalcium phosphate (OCP) is most probable as an intermediate phase either as a precursor to HAP or in the conversion of ACP to HAP. Importantly, OCP is less soluble than HAP (Table 3 and Figure 5). This can result in over estimations in the proportion of P removal by precipitation particularly when speciation models are used (House and Denison, 2000).

Nancollas and Tomazic (1974) demonstrated that, in neutral to alkaline solutions precursor ACP only formed in highly supersaturated solutions; in less supersaturated solutions HAP formed directly with no precursor phase. Boskey and Posner (1976) concurred that no precursor phase was required in HAP formation in solutions of low supersaturation with respect to the components.

Table 3 Equilibrium constants of reactions involving the precipitation of common soil calcium phosphates (Lindsay, 1979).

Mineral name	Equilibration Reaction			log *Ko*
MCP	$Ca(H_2PO_4)_2.2H_2O$	↔	$Ca^{2+} + 2H_2PO_4- + H_2O$	-1.15
Brushite	$CaHPO_4. 2H_2O + H^+$	↔	$Ca^{2+} + H_2PO_4^- + 2H_2O$	0.63
Monetite	$CaHPO_4 + H^+$	↔	$Ca^{2+} + H_2PO_4^-$	0.30
Octacalcium phosphate	$Ca_4H(PO_4) . 2.5H_2O + 5H^+$	↔	$4Ca^{2+} + 3H_2PO_4^- + 2.5H_2O$	11.76
	α- $Ca_3(PO_4)_2(c) + 4H^+$	↔	$3Ca^{2+} + 2H_2PO_4^-$	13.61
	β- $Ca_3(PO_4)2(c) + 4H^+$	↔	$3Ca^{2+} + 2H_2PO_4^-$	10.18
Hydroxyapatite	$Ca_5(PO_4)_3OH + 7H^+$	↔	$5Ca^{2+} + 3H_2PO_4^- + H_2O$	14.46
Fluorapatite	$Ca_5(PO_4)_3F + 6H^+$	↔	$5Ca^{2+} + 3H_2PO_4^- + F$	0.21

1.2.6.2 Heterogeneous Precipitation

Heterogeneous precipitation occurs in solutions supersaturated with respect to components, but at lower concentrations than where spontaneous nucleation can occur. In heterogeneous nucleation, the interfacial energy preventing crystal growth is reduced by the symmetry of surface molecules or ions of foreign bodies that closely match the configuration of the precipitating phase. Clearly the closer the configuration of the foreign body to that of the precipitating phases the more easily the interfacial energy can be overcome. Experiments investigating crystal growth of calcium phosphates, such as those by Nancollas and Tomazic (1974) and Grossi and Inskeep (1991), utilized heterogeneous precipitation principles by using calcium phosphate seed crystals (DCPD) upon that crystal growth was observed. Nancollas and Tomazic (1974) list a number of reasons for studying crystal growth in heterogeneous systems. These include reproducibility, and the "unlikeliness" that any medium can be free of foreign bodies: hence heterogeneous nucleation can never be truly discounted.

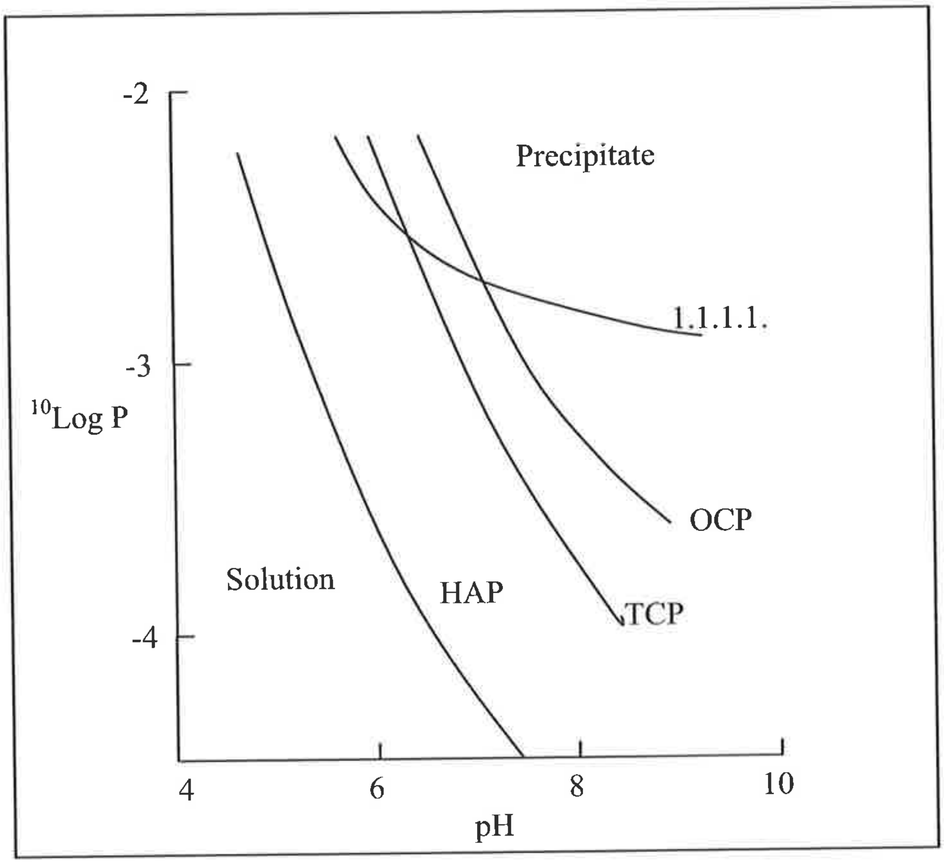

Figure 5 Comparison of precipitation boundaries with the solubility isotherms of HAP, TCP, OCP and DCPD at Ca:P ratio of 1.67 (redrawn from Feenstra and de Bruyn, 1979).

1.2.6.3 Inhibition of Calcium Phosphate Precipitation

P removal in supersaturated solutions, as well as being overestimated through the formation of less soluble precursor phases, also can be overestimated through the presence of inhibiting factors. The inhibition of HAP to form in over saturated solutions, particularly natural waters and soils, may be a consequence of the presence of inorganic ions or organic compounds. Inorganic anions that can possibly inhibit crystal growth of HAP are F^-, Cl^-, OH^- and SO_4^{2-} (Nancollas 1989). In terms of organic compounds, studies have investigated the inhibition of HAP precipitation initiated by both heterogeneous (Sharma *et al,*. 1992; Inskeep and Silvertooth, 1988) and homogeneous (van der Houwen and Valsami-Jones, 2001) nucleation.

Inskeep and Silvertooth (1988) found fulvic, humic and tannic acids were able to significantly impede the precipitation of HAP and Sharma *et al.* (1992) found that citrate could inhibit OCP precipitation. Both studies concluded the mechanism of inhibition to be the adsorption of the organic ligand onto the seed crystal. According to Sharma *et al.* (1992) citrate inhibited nucleation by forming phospho-citrate complexes on active growth sites of OCP seeding material. Inskeep and Silvertooth (1988) concluded that in addition, molecular size of the organic compound was an important factor. Based on experiments using lower molecular weight organic compounds (gallic, adipic and azelaic acids), they found these smaller compounds resulted in no inhibition of HAP. They postulated that these compounds are unable to provide sufficient surface coverage of the HAP seed, and additionally, that the adsorption of high molecular weight compounds may be energetically favoured. Van der Houwen and Valsami-Jones (2001) reported that citrate could also inhibit homogeneous precipitation, whereas acetate had a negligible effect. They postulated that citrate is bound to active growth sites of the nuclei. Clearly the mechanism of inhibition is similar for both heterogeneous and homogeneous nucleation, once a nucleus has formed.

1.2.7 CALCIUM SOIL AMENDMENTS AND P MOBILITY

1.2.7.1 Calcium Carbonate

Calcium, in the form of lime, is commonly used in agriculture to increase soil fertility: in particular for increasing pH in acid soils. Technically, lime is $Ca(OH)_2$, although the word is also applied to $CaCO_3$.

Apart from the study by Sova (1996) on the bioavaliability of P, very little work has been published into the effect that treating soils with lime (liming) has on the P content in runoff water. Many studies have been conducted into what effect liming of soils has on the availability of P to plants. Because plant available P is readily soluble (for plant uptake), these studies may give some indication on what effect liming would have on the P content of runoff water. However, even given the large number of studies, the effect of liming on phosphate availability is still unclear. Haynes (1982) and Sumner and Farina (1986) list several conflicting studies the conclusions of that range from increased availability to no difference to decreased availability. Holford *et al. (*1994) explain this apparent discrepancy by the differences encountered between field and laboratory conditions; in particular, the lack of free drainage encountered in the laboratory conditions of some experiments. Clearly there are a multitude of factors that can influence the effect of liming on P movement in the soil environment.

Two of the most important factors that must be considered when studying the effect that liming has on P solubility are the pH and bulk composition of the soil. Holford (1983) found that a variety of different effects were produced when highly acidic soils (pH < 5.2) were limed at different rates. Liming highly acid soils (pH < 4.5) to a pH of 4.8 decreased the sorption capacity and sorptivity[1], whereas liming to a pH of 4.8 to 5.8 increased the sorptivity and sorption capacity in soils. As the pH rose above 5.8 sorptivity decreased and sorption capacity remained steady or increased. These results agree with the findings of Amarastri and Olsen (1973), Mokwunye (1975) and Murrmann and Peech (1969) and indicate the minimum solubility of phosphate in many acid soils fell in the pH range of 5.5 to 6.5 (Figure 6). Haynes (1982) also agrees with these conclusions, that are consistent with phosphorus solubility being intimately linked with that of aluminium (Al) (and to a lesser extent Fe). The minimum solubility of Al falls into a similar range (between 5 and 7), at that insoluble hydroxy-Al (and Fe) species precipitate. Such precipitates have highly reactive surfaces that facilitate the absorption of P. As the pH rises beyond this the hydroxy-Al species become increasingly soluble, dissolving and releasing previously adsorbed phosphate. Holford (1983) agrees that the solubility of phosphate in some acid soils is influenced more by the dissolution of Al and Fe phosphates than by the desorption of exchangeable phosphate.

However, these findings apparently do not agree with those of White and Taylor (1977) who found that liming to pH values of 7 resulted in an increase in P fixation with relatively insoluble poorly crystalline Ca minerals. It is suggested that this result is a consequence of high phosphate concentrations (1000 uM) that result in the formation of calcium phosphate precipitates at pH values above 5.5.

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[1] Sorptivity is the maximum slope of the concentration sorption isotherm
[i.e. $mg.Kg^{-1}/mg.L^{-1}$] (Holford, 1983).

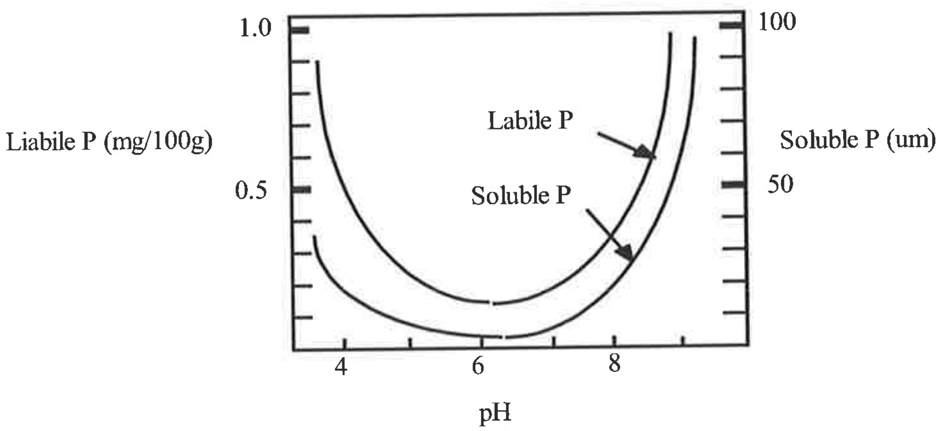

Figure 6 Effect of pH on the amount of phosphate in soil solution and on the amount of labile phosphate present in an illinous soil (redrawn from Mueemann and Peech, 1969).

1.2.7.2 Gypsum

Many studies have investigated the use of gypsum as a liming alternative to both alleviate soil acidity and reduce aluminium toxicity of soils (Oates and Cadwell, 1985; Sumner *et al*,. 1986; Smith *et al*,. 1994; Carr *et al*,. 1991; McLay and Ritchie, 1995). The mechanism by which it is proposed that gypsum reduces aluminium toxicity is poorly understood, although there is a clear link between increased gypsum additions and reduction in Al toxicity. Clearly any effect on Al in soils has implications for P solubility, and so the mechanism by which gypsum alleviates Al toxicity is important.

Oates and Cadwell (1985) suggest that the Ca ions from gypsum displace the Al ions from soil surfaces resulting in the loss of Al by leaching. However, Carr *et al. (*1991) found that in a low rainfall region (< 300 mm.yr^{-1}) leaching rates would be insufficient to prevent Al toxicity with gypsum addition. These findings lead to the suggestion that reduction in Al toxicity is a function of the increased Ca or SO_4 with no actual reduction in Al concentration (McLay and Ritchie 1995). McLay and Ritchie (1995) found that, following gypsum applications at varying rates, the concentration of Al was not effected. However, the amount of monomeric Al decreased and the amount of $AlSO_4^+$ increased. The possibility exits that the formation of $AlSO_4^+$ or possibly Al-SO_4 precipitates may limit the mobility of P following the addition of gypsum.

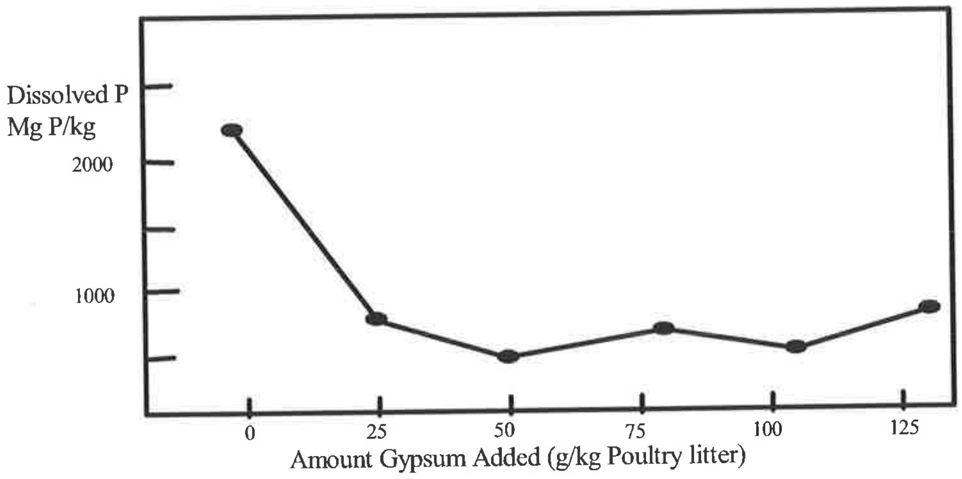

Figure 7 Effect of gypsum on P solubility of poultry litter (redrawn from Moore and Miller, 1994).

Indirectly it is known that gypsum reduces colloidal movement (from studies of sodic soils) and, as a consequence, P (as particulate P) loss may be reduced. Further in sodic soils gypsum increases infiltration: thus it may also increase leaching. Moore and Miller (1994) studied various amendments and their effect on P solubility in poultry litter. They concluded that gypsum application decreased P solubility by 50 to 60 percent. Solubility reductions resulted from application rates of 100 g of gypsum per kilogram of poultry litter (poultry litter contains approximately 1.8% P). This rate of reduction was reached with the minimum experimental application rate and remained constant (regardless of increases in the rate of application as shown in Figure 7). This finding lead Moore and Miller to conclude that the reduction in soluble P was a result of the formation of Ca phosphate minerals and through adsorption of P by gypsum. Similarly Coale *et al.* (1994) and Stout *et al.* (1997) observed reductions in P solubility when gypsum was applied to soils with pH > 7. At such a pH, it is also probable that this increase in retention capacity is a result of the precipitation of calcium phosphates. If so, such a mechanism is less likely in more acidic soil.

More recent studies such as Stout *et al.* (1998; 2000) and Callahan *et al.* (2002) found that using by-product gypsum on acid soils could enhance P retention. Stout *et al.* (1998) found that applying flue desulphurisation by-product gypsum (FGD) to soils of

$pH < 7$ (≈ 6.5-6.7) resulted in a conversion of resin and bicarbonate extractable P to NaOH extractable P. As this fraction (NaOH extractable) is indicative of Al and Fe bound P, they postulated the enhanced P adsorption resulted from the displacement of Fe^{3+} and acid organic groups into the soil solution by Ca^{2+}. This "mass action" as described by Stout *et al.* (2000) contributed to pH decline that favoured Fe and Al phosphate precipitation. Stout *et al.* (2000) similarly explained the action of FGD and agricultural gypsum as the mass action of Fe and Al release from cation exchange with Ca, and in turn the precipitation of Al and Fe phosphates. Callahan *et al.* (2002) also used the same mechanism to account for the reduction of water extractable P without lowering available P (Mehlich-3 P) with the addition of by-product gypsum to acid soils.

A significant drawback of FGD is that it is potentially toxic to the environment. Critical analysis provided by McDowell (2004) indicated the potential for a similar by-product, fly ash, obtained from the exhausts of coal fired power station to cause boron toxicity to plants when used as a soil amendment to reduce P mobility. Similar outcomes may be anticipated with other industrial by-products.

1.2.7.2.1 The Effect of Sulfate on P Mobility

In contrast to many of the studies listed in the previous section Arias and Fernandez (2001) found that the addition of gypsum to acid soils ($pH \approx 5$) did not increase phosphate adsorption. It was hypothesized this was result of competition between phosphate and sulfate ions for adsorption sites.

Harward and Reisenauer (1966) and Metson and Blakemore (1978) indicate that phosphate is preferentially retained in soils over sulfate. Metson and Blakemore (1978) demonstrated that phosphate adsorption was little affected by the presence of sulfate at concentrations up to 3 times that of phosphate (by weight). Bolan *et al.* (1988) found that incubation of soils with $Ca(H_2PO_4)_2$ resulted in a significant (2 to 5 fold) reduction in adsorption of sulfate. In a study that looked into the effect of phosphate on competitive adsorption between oxalate and sulfate to goethite, Liu *et al.* (1999) found that the addition of phosphate resulted in the almost complete desorption of sulfate over a large range of pH (> 3). However; studies of sulfate and phosphate adsorption in the lower soil pH range indicate competition for adsorption sites does exist. Geelhoed *et al.* (1997), in a study of both plant uptake of P and batch adsorption experiments demonstrated competitive adsorption between phosphate and sulfate on goethite. This competition increased with decreasing pH. In this study the critical pH for competitive adsorption between phosphate and sulfate was between 5 and 5.5, above which there was very little competition. The use of varying ionic strength in the study of anion adsorption (specifically phosphate) has been discussed in a previous section. In conducting such a study, Bolan, Syers and Tillman (1986) found that, whereas there was a characteristic pH (PZSE) above that increased ionic strength resulted in an increase in phosphate adsorption, there was no such PZSE for sulfate: increased ionic strength always lead to decreased adsorption. As such it was inferred that sulfate is adsorped only when the potential plane is positive, whereas phosphate is adsorped when the plane is positive or negative. This would account for the observation of competitive adsorption between phosphate and sulfate only at low pH (i.e. pH < PZSEp).

1.2.8 NATURAL ORGANIC MATTER (NOM) AND P

1.2.8.1 Organic P

Donald *et al. (*1993) found that the hydrophobic neutral fraction (HbN) accounted for approximately a 10 fold greater proportion of organic P than the hydrophobic and hydrophilic acid fractions (HbA and HlA respectively). Despite the fact that the HbN fraction was only 14% of the total (HbA and HlA totalled 72%) HbN accounted for 64% of the organic P.

As soil has a low sorption capacity for the HbN fraction, Donald *et al. (*1993) suggested that the leaching of this fraction might be an important mechanism for phosphate loss into surface waters.

1.2.8.2 Anion Competition: NOM and P

Violante and Gianfreda (1995) demonstrated a competitive relationship between phosphate and selected low molecular weight (LMW) organic ligands (oxalate and tannate) and reported that phosphate was able to partially remove oxalate, citrate and tartrate from Al precipitation products (formed with these organic ligands). The resultant precipitation product (P-Al(OH)) was able to absorb these organic ligands in different amounts. They also found that phosphate was very competitive with oxalate for sorption onto variable charge minerals (montmorillonite-pseudoboehmite). More phosphate was absorbed on all complexes, even when the concentration of oxalate was much greater than phosphate. This study also demonstrated that there are some specialised sorption sites for phosphate and organic ligands. Whereas phosphate has been shown to out-compete some organic ligands for sorption sites, Hue (1991) found that some organic acids were able to desorb phosphate. His study found that, of the three organic acids, malic was the most competitive, followed by tocatechuic, with acetic the least competitive.

1.3 NATURAL ORGANIC MATTER (NOM) MOBILITY IN SOILS

1.3.1 ORGANIC MATTER AND WATER QUALITY

Not only are agricultural soils important sources of diffuse P but they can also contribute to water quality decline as important sources of natural organic matter (NOM) and other organic contaminants (Chittleborough, 1992; Nelson *et al*,. 1993). Randkte (1988) grouped organic contaminants in water into three classes:

1. NOM: includes organic materials derived from flora and fauna (e.g,. humic substances and microbial exudates);
2. synthetic organic chemicals (SOC): includes synthetically derived chemicals such as pesticides or commercially generated waste products; and
3. chemical by-products formed in water treatment.

The aim of organic matter removal in water treatment prior to the 1960s was mainly focused on improving the aesthetic value of water by improving its clarity. In the 1970s it was discovered that some compounds in NOM reacted with free chlorine (used in water disinfection) to form potentially carcinogenic trihalomethanes (THMs) as well as other halogenated compounds that significantly altered the focus of NOM removal in water treatment (Randtke, 1988). In addition to reducing the risk of THM formation in drinking water, Randtke states other reasons for NOM removal are:

1. removal of associated hydrophobic SOC and toxic metals;
2. removal of biodegradable material that may act as a substrate for bacterial growth (within the distribution system);
3. control of naturally occurring taste- and odor-causing compounds,
4. corrosion control; and
5. reduction of organic load on downstream treatment processes (i.e. activated carbon adsorption).

1.3.2 ORGANIC MATTER IN SOILS

The study of natural organic matter (NOM) mobility through the soil environment is complicated by the diversity of NOM itself: it ranges from simple sugars to complex fulvic and humic acids (Moore *et al,.* 1992). Broadly, dissolved organic matter (DOM) can be divided into two fractions: hydrophilic and hydrophobic: these groups can then be subdivided into acids, weak acids and neutrals, as well as a small group of bases (Qualls and Haines 1991), see Table 4 (p. 44).

Whereas the concentration in all fractions of DOM is reduced in the soil solution with depth of soil (Qualls and Haines 1991), the percentage of hydrophilic DOM increases as hydrophobic DOM is preferentially adsorbed (Jardine *et al,.* , 1989; Qualls and Haines, 1991; Dunnivant *et al,.* , 1992).

The decline in DOM in the soil solution is widely accepted as being the result of abiotic processes including precipitation and sorption by Al and Fe oxides within the B horizon (Jardine *et al,.* , 1989; Qualls and Haines, 1991; Chittleborough *et al,.* , 1992; Guggenberger and Zech, 1993). Jardine *et al.* (1989) found that 50 to 70% of the total adsorbed DOM was retained by crystalline and non crystalline Fe oxides, the remainder adsorbed by some clay minerals with kaolinite in greater quantities than illite. This study found that, by using thermodynamic principles, the predominant mechanism of DOM sorption was found to be physical adsorption driven by favourable entropy changes. This idea is supported by the preferential adsorption of hydrophobic DOM in which weak positive sorbate-sorbent interactions overcome extremely weak solute solvent interactions in an entropy-driven process that results in the destruction of the highly structured water surrounding the DOM macromolecule giving rise to the adsorption of that molecule (Hassett *et al,*. 1981). The process of DOM adsorption was found to be pH-dependent with a maximum adsorption occurring at pH ≈ 4.5 (Jardine *et al,*. 1989) see Figure 8 below.

1.3.3 NOM ADSORPTION IN SOILS

It has been long known that organic matter and polyvalent cations are important components in soil structure (Edwards and Bremner, 1967; Oades, 1984). Podzolization, a process involving the coprecipitation of Fe (and Al) with DOM, was found to be an important mechanism in controlling the amount of dissolved organic carbon (DOC[2]) in surface streams (McDowell and Wood, 1984). Similarly Nelson *et al.* (1990) and Nelson *et al.* (1993) found that soil characteristics in a catchment exerted the dominant influence on the total organic content of streams. Nelson *et al.* (1993) reported that there was little or no preferential absorption of particular compounds within the DOC fraction, because comparison of leachate before and after soil contact was similar. This study indicated that it was most probably microbial modification that resulted in differences in DOC species between soil solution and stream waters. This finding contrasts with that of other studies. Dunnivant *et al.* (1992) concluded that hydrophobic constituents of DOC were preferentially absorbed over hydrophilic. Donald *et al.* (1993) found that hydrophobic and hydrophilic acid fractions were preferentially absorbed over the hydrophobic neutral fraction. This discrepancy may be an outcome of lack of agreement of the hydrophobic and hydrophilic classification (Nelson *et al,*. 1993).

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[2] DOC may be considered a quantifiable measure of DOM, and these terms are somewhat interchangeable.

Hydrophobicity is related to solubility (in water) and is governed by both molecular structure and molecular size. Water is a polar substance[3] and as a rule can only dissolve other polar substances. Alkanes are an example of a nonpolar organic compound, whereas alcohol is an example of a polar organic compound. However; even the longer chain alcohols, such as Decyl alchohol maybe only sparingly soluble in water. In general compounds with one to three carbon atoms are considered soluble, four or five are borderline and six or more are insoluble (Solomons 1984).

In the work of Dunnivant *et al. (*1992), the soil columns were saturated with organic C, and as such the high level of competition for a restricted number of sorption sites may have exploited the difference in chemical properties of these broad groups (hydrophobic, hydrophilic, HMW and LMW), compared with the lower competition that one would expect to encounter in a natural system. Differences between the studies may also be a consequence of different sorption properties of the soils that in turn are dependent on clay mineralogy.

Many studies have emphasised the importance of sesquioxides on the sorption of DOM by soils. Davis (1982) and Davis and Gloor (1981) related DOM sorption to the content of aluminum oxide, gibbsite, goethite and hematite. Dithionite-extractable Fe and amorphous Al and Si minerals on the surface of phyllosilicates were found to be important factors in the sorption of DOM (Jardine *et al,.* 1989). Studies have shown that free or HCl-extractable Fe (and to a lesser extent free Al) are important factors in the removal of DOM from soil solutions (McDowell and Wood, 1984 and Moore *et al,.* 1992). Another important factor appears to be the native organic content of the soil. Jardine *et al. (*1989) found a significant increase in the amount of DOM adsorption following the peroxide removal of organic matter from a subsurface horizon. A further factor to be considered is the removal of DOM from solution by microbial metabolism; although McDowell and Wood (1984) suggested that this mechanism may be of limited importance because the zone of maximum microbial activity was above the zone where most removal of DOM occurred. McDowell and

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[3] A polar molecule (such as water) possess a dipole moment in that the molecule has a shift in the electron density (or a charge separation across the molecule).

Wood (1984) considered the volume of leaching water and contact time (because many of the absorption reactions are relatively slow) important factors in the amount of DOM adsorbed.

Table 4 Substances found in specific fractions of DOM (Qualls and Haines 1991).

Fraction	Example Compounds
Hydrophobic neutrals	Hydrocarbons Chlorophyll Carotenoids Phospholipids
Weak (phenolic) hydrophobic acids	Tannins Flavonoids Vanillin
Strong (carboxylic) hydrophobic acids	Fulvic acid and humic acid Humic bound amino acids and peptides Humic bound carbohydrates Long chain fatty acids Aromatic acids
Hydrophilic acids	Humic like substances with lower molecular size and higher COOH/C ratios Oxidised carbohydrates with COOH groups Small carboxylic acids Sugar phosphates
Hydrophilic neutrals	Simple neutral sugars Alcohols
Bases	Proteins Free amino acids and peptides

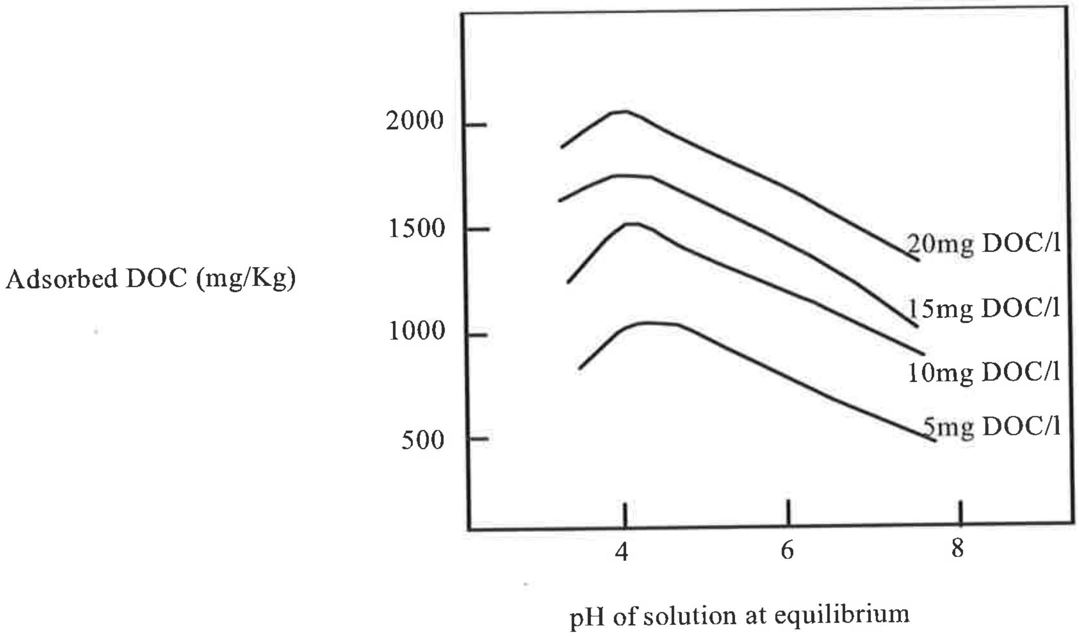

Figure 8 Adsorbed DOC as a function of equilibrium pH at a variety of equilibrium solution DOC concentrations (redrawn from Jardine *et al*,. 1989).

1.3.4 CALCIUM SOIL AMENDMENTS AND DOM MOBILITY

Leaching studies using lime such as by Karlik (1993) found that liming both cultivated and uncultivated soils ranging in pH from 4.5 to 7.0 increased the amount of leached DOM in each case. This study found that the effect was most pronounced in the most acidic soils (Table 5), suggesting that this is a response to unfavourable pH changes for NOM sorption or more favourable conditions for biologic activity and not directly related to Ca input.

Table 5 Soil type pH and comparison of total amounts of leached DOM from Karlik (1993).

Soil Type	pH (H_20)	Limed Soil	Non-Limed Soil	Relative Difference
		Total leached DOM (g)		(%)
Grey Brown podzol uncultivated	4.5	5.79	3.48	66
Black Earth uncultivated	7.0	0.87	0.63	38
Grey Brown podzol cultivated	6.7	0.42	0.30	40
Brown podzol cultivated	5.7	1.77	1.05	68
Brown podzol cultivated	5.6	2.13	1.50	42

1.3.4.1 Ca-NOM interaction in soils

Adesodun *et al.* (2005) found that organic matter amendments can potentially have a disaggregating effect on soil aggregates. It was concluded that the composition of the organic matter may be more important than the total amount available. In these experiments, the amendment of soil with organic matter was not supplemented with the addition of cations and this may indeed be more significant than the composition of the organic matter itself. Muneer (1987) and Muneer and Oades (1989a,b,c) describe a model wherein Ca behaves similarly to Fe by causing the aggregation of soil particles that range in size from individual clay particles and humic molecules to macroaggregates (> 250 μm).

It is believed that Ca binds OM in a manner similar to the manner in which Ca binds clays viz. the cross-linking of carboxyl and other functional groups, and the cross-linking of these organic functional groups to clay surfaces. The precise mechanisms involved are not clearly understood (Oades, 1995). Hering and Morel (1988) concluded that their findings were consistent with a discrete ligand site model of OM-polyvalent cation binding but they further concluded, in competitive sorption trials between Ca and Cu, that either a mechanism other than discrete ligand binding must be operating, or that different ligand sites must be involved, because there was no competition between Ca and Cu. Romkens and Dolfing (1998) suggested that the form of DOM in Ca stabilization was an important factor. They found that Ca is effective in flocculating only the high molecular weight (HMW) DOM fraction and that even at high Ca concentration, low molecular weight (LMW) DOM could not be flocculated.

The role of Ca in soil aggregation has never been considered as important as Fe and Al (McDowell and Wood 1984). However; Muneer (1987) and Muneer and Oades (1989a,b,c) postulate a model (described earlier) in that Ca can act as a fundamental unit in the removal of OM from soil water. This study further found that the addition of Ca^{2+} accompanied by organic matter increased aggregate stability beyond what can be achieved with the addition of organic matter alone. Muneer and Oades (1989c) found that the addition of Ca to soils reduced the NaOH extractability of organic matter, but pre-treatment with HCl eliminated the effect on NaOH extractable organic matter. They concluded that Ca acted as a cation bridge between humic acids and clays. Furthermore Muneer and Oades (1989b) found the effectiveness of Ca amendments on increasing retention of organic C was directly related to the supply of available Ca. Both gypsum and lime added to an acid soil (pH 5.6) were found to increase C retention, with gypsum being more effective than lime. The effectiveness of gypsum over lime was attributed to the higher solubility of the former. Additionally, lime soils may produce unfavourable pH changes for DOM sorption, similar to the findings of Karlick (1993).

Other studies that have demonstrated the potential for Ca to enhance DOM retention in soils come from the work of Romkens and Dolfing (1998) and Stuczynski *et al.* *(*1998). Romkens and Dolfing (1998) demonstrated that Ca added to DOM extracts was effective in flocculating much of the high molecular weight (HMW) component of the extract but had no effect on the low molecular weight (LMW) component. Stuczynski *et al.* *(*1998) also found that bed ash (containing Ca in the forms $CaSO_4$, CaO and $CaCO_3$) was successful in stabilising (flocculating) some forms of DOC.

1.4 ALTERNATIVE INDUSTRIAL BY-PRODUCT SOIL AMENDMENTS

Alternatives to Ca based soil amendments were considered as part of this investigation. The following section reviews industrial by-products that have been used in soils, in particular those that have shown potential in reducing nutrient loss from soils.

The two considered were a by-product of water treatment and a by-product of bauxite refinement to Al. Both have an apparent liming ability, that has recently been considered for agricultural applications. Further both of these are high in Al, and have been demonstrated to have a significant P fixing capacity. Given these properties these by-products are considered suitable for the purposes of this investigation.

1.4.1 WATER TREATMENT SLUDGE

Water treatment sludge is a by-product of the process of water purification that commonly occurs in the treatment of South Australian drinking water from reservoirs and the River Murray. This process involves the removal of suspended clays and DOM by flocculation typically using aluminium sulfate (alum) as well as other compounds such as lime. It is this flocculant that is referred to as the water treatment sludge. The processes involved in water treatment for domestic consumption, including alum dosing is covered in Chapter 4.

In Australia this sludge is currently treated as a form of industrial waste, a metal hydroxide (Ahmed *et al*,. 1998), and as such its disposal is difficult and expensive. The perceived hazard of such sludges is the inherent high Al content that when applied to soils has the potential to be toxic to plants. However, elsewhere in the world these sludges have been treated with less caution, with no apparent toxic effect from the high Al content. Because the initial process of flocculation includes added lime, these sludges have a liming quality, and have been used for such purposes in agricultural and forest soils in the United States for the last 40 to 50 yr (Elliot and Demsy 1991). Abdullah *et al. (*1995) reports that these sludges are commonly discharged into natural waterways in other parts of the world with no increase in soluble forms of Al. So clearly a less cautious and expensive approach to the disposal of this sludge in Australia should, and has been (Skene *et al,*. 1995; Ahmed *et al.* (1998) considered.

A study by Skene *et al. (*1995) found alum sludge to be a suitable plant growth medium. This study found the physical properties of the sludge (i.e. water holding capacity, drainage and structural stability) to be the biggest benefit of the sludge. More importantly, from an environmental point of view, there was no evidence of Al toxicity being a problem. The major problem of using this sludge was an apparent P deficiency in the plants. It is suggested that the high Al content of the sludge has a strong P fixing ability (Rengasamy *et al,*. 1980). Studies such as Ahmed *et al. (*1998) and Elliot and Singer (1988) have suggested that this P fixing ability of sludge has little effect on the growth rate of plants grown in the sludge. Ahmed *et al. (*1998) suggested that this may be a consequence of two possibilities. Either the relatively high N content of the sludge overcomes the P shortfall or there is a slow release of P with time. Data from the study of Ahmed *et al. (*1998) indicated that the latter maybe likely as P-uptake increased with time.

The P-fixing capacity of these sludges has been recently studied by Macks *et al. (*1998) as a potential tool for environmental remediation of contaminated waters and dairy effluent. Their study found that these sludges were capable of reducing the total P concentration, but only by removing the orthophosphate fraction, with little change in the organic P. However; they state that the conversion of organic P to orthophosphate is relatively easy under natural conditions. The process of repeatedly drying and rewetting sludges was found to be the best method of maximising P sorption.

1.4.2 BAUXITE RESIDUE (RED MUD)

Red mud is a by-product of the Al industry. It is a finely crushed alkaline residue rich in Fe and is produced in the process of bauxite digestion with caustic soda to remove the Fe (Summers *et al,*. 1996).

Over the last two decades red mud has been the subject of extensive study for its ability to remediate low fertility soils (Barrow 1982; Summers *et al,*. 1996). Barrow

(1982) found one of the major beneficial effects of red mud application was the increase in water retention of the treated soils, while Summers *et al.* (1996) also believed that the liming effect that the residue had also increased plant growth.

Red mud has also been the subject of many studies into its P retaining ability (Kayaalp *et al,*. 1988; Ho *et al,*. 1989; Vlahos *et al,*. 1989; Summers *et al* 1993; Sharpley *et al,*. 1994). There is general agreement that treating soils with the red mud reduces the amount of P leached from soils. Summers *et al.* (1993) found that in a large scale field trial red mud was able to retain up to 70% more P than untreated soil (at a application rate of 80 t/ha). At a higher rate (200 t/ha) Vlahos *et al.* (1989) found that red mud produced a 96% reduction in the P leached compared to an unamended soil for a period of 3 yr.

The major drawback of using red mud is the cost in transport, as no local sources are available in South Australia. The literature suggests minimal application rates of 20 t/ha. Such rates would make this a prohibitive product for non point source application as this study attempts to address. Other constraints are possible increases in groundwater salinity from leaching of major soluble constituents Na, Ca and SO_4 (Vlahos *et al,*. 1989). However; Summers *et al.* (1996) found the concentration of leachates (not including Na and Ca) were below maximum recommended limits for drinking water. Vlahos *et al.* (1989) suggests that red mud may have application for managing point source P hot spots such as piggery and intensive horticultural industries.

1.4.3 MISCELLANEOUS INDUSTRIAL BY-PRODUCTS

More recently McDowell (2004) tested a variety of industrial by-products. This investigation found industrial by-products melter slag and bottom ash were effective and ecologically viable soil amendments to mitigate P loss.

1.4.4 SUMMARY OF INDUSTRIAL BY-PRODUCT ALTERNATIVES

Water treatment sludge and red mud are limited in solubility and as such require some degree of incorporation into the upper soil. The additional soil tillage required is detrimental to soil structure and promotes soil erosion that may in itself promote further nutrient loss. Economic viability is an additional consideration of this investigation, and it is considered the cost associated with additional tillage is prohibitive to the consideration of low solubility amendments.

Although the products summarized above are considered effective in mitigating P mobility their local availability for broad scale use is questionable. Even if available in the long term the quality, given these are by-products of industry, is unpredictable. These factors also apply to the gypsum by-products reviewed in the preceeding sections.

1.5 CHOICE OF AMENDMENT

The earlier review clearly suggested the potential that Ca may have for reducing P and NOM mobility through soils. Additionally, Ca soil amendments have a strong history of agricultural applications, with multiple proven benefits. Lime and gypsum are the most common of these. Mineral gypsum was selected as the preferred amendment for this research is based on:

1. mineral gypsum of high purity is unlikely to be a source of toxicity to the environment;
2. a proven history of yield improvement when applied to some soils (see next section);
3. gypsum's relatively high solubility compared to liming agents;
4. gypsum has little effect on soil pH, that makes it favourable, as increases in pH due to liming has been demonstrated to reduce soil sorption of NOM. Additionally, if this amendment were to become widely adopted with a sole or

primary purpose of reducing P and NOM mobility in agricultural soils, then a neutral effect on soil pH would be favourable; and

5. local availability and cost of mineral gypsum (≈AD $30-40 T including transport to site).

The following discussion reviews the current uses and investigates the proven economic benefits (where available) of gypsum in agriculture. These aspects are considered paramount in the selection of gypsum as the selected amendment as they contribute to the amendments agricultural and economic sustainability.

1.6 GYPSUM AND AGRICULTURAL YIELD IMPROVEMENT

1.6.1 DISPERSIVE AND HARD-SETTING SOILS

According to Shainberg *et al.* (1989) the economics of gypsum usage on sodic soils are unquestionably positive. On marginally sodic to non-sodic dispersive soils in Western Australia gypsum used to improve soil structure has a significant to effect on improving grain yields (4-48%) (Table 6 - Jarvis, 1988; Howell 1987). For these studies average yield increases between 16 and 26 % were obtained depending on respectively on whether conservative tillage (e.g,. deep drilling) or conventional tillage methods were used. On such soils however, the economics of gypsum are uncertain, as the cost depends on both the source of gypsum and the distance that it has to be transported. Another cost to be considered is that of application. This cost may be further reduced if the type of fertiliser used is a by-product gypsum such as phosphogypsum that already contains significant quantities of P. However the economic viability is still highly dependent on the proximity of a plant producing this by-product. The other factor to be considered is the type of crop. Studies (particularly in Brazil, South Africa and the U.S.A.) indicate that many crop types respond well to gypsum, and in general, the higher the value of the crops the greater the economical viability.

Table 6. Effect of gypsum on grain yield, from Howell (1987) and Jarvis (1988)

Tillage method	No. Years Cropped	Grain Yield (t/ha)		% Response	Source
		No Gypsum	Gypsum		
Direct Drill	9	.90	.96	7	Howell (1987)
Conventional Drill	9	.62	.79	27	Howell (1987)
Direct Drill	2	.75	.78	4	Howell (1987)
Conventional Drill	2	.63	.75	19	Howell (1987)
Direct Drill	2	.95	1.1	16	Howell (1987)
Conventional Drill	2	.86	1.05	22	Howell (1987)
Direct Drill	2	.89	1.07	20	Howell (1987)
Conventional Drill	2	.66	0.91	38	Howell (1987)
Direct Drill	2	2.44	2.26	-7	Howell (1987)
Conventional Drill	2	2.3	2.28	-1	Howell (1987)
Triple disc drill	3	1.35	1.51	12	Jarvis (1988)
Scarifier/TDD	3	1.29	1.47	14	Jarvis (1988)
Direct Drill	3	1.47	1.53	4	Jarvis (1988)
District Practice	3	0.92	1.36	48	Jarvis (1988)

Gypsum at 5 t/ha for Howell (1987) and 4.7 t/ha for Jarvis (1988)

The final factor in determining gypsum economics is the rate of gypsum application. Results of these studies clearly indicated that a single application of gypsum at approximately 5 t/ha can continue to have an effect on yields for periods of 2 to 9 yr, and perhaps beyond for annual rainfalls ≈ 400 mm (Table 7). Greene and Ford (1985) concluded that gypsum is leached at a rate of 1 t/ha for approximately every 125 to 360 mm rainfall. These results suggest that the effect of gypsum at 5t/ha would last in the Adelaide Hills of South Australia (approx. 700 mm pa) from 2 to 5 yr. Whereas Howell (1987) states that there is no benefit in applying more than 2.5 t/ha in the first 4 yr, however higher rates do not harm the soil or crop, and may last longer. From the work summarised in Shainberg *et al.* (1989) it is apparent that an application of 5 t/ha continues to have positive effects for 3 to 4 yr. It is clear that there is evidence of long term yield increases in response to high levels of gypsum application (5-10 t/ha).

Note that the use of gypsum is not a panacea for arresting soil structure decline, but a valuable interventionist strategy that must be complemented with improved soil management strategies eg. reducing the initial causes of soil structure decline, through excessive tillage, over grazing etc.

There are other benefits, but they are not easily accounted for economically. First the increase in infiltration, and the resulting increase in plant growth will reduce the topsoil loss by erosion. Secondly, and as a consequence of the first, increased plant growth, and therefore increased plant uptake, should reduce fertiliser loss and reduce nutrient losses in runoff: an advantage to the farmer and the environment alike.

Table 7 Summary of McLay *et al.* (1994) Yield increases of various amendments over control (no amendment) on crops in different rainfall zones.

Site	Year	Treatment	Yield Increase (%)	Crop	Rainfall mm
Carrabin	1989	Gypsum 1,3,9 t/ha	45	Wheat	285
Carrabin	1989	Gypsum+Lime	77	Wheat	285
Carrabin	1989	Lime 2,4 t/ha	15	Wheat	285
Trayning	1989	3 above treatments	ns	Wheat	320
Carrabin	1990	Gypsum 1t/ha	12	Wheat	355
Carrabin	1990	Gypsum 3,9 t/ha	25	Wheat	355
Carrabin	1990	G+L	12-25	Wheat	355
Carrabin	1990	Lime 2,4 t/ha	15	Wheat	355
Trayning	1990	Gypsum 1t/ha	3	Wheat	344
Trayning	1990	Gypsum 3t/ha	10	Wheat	344
Trayning	1990	Gypsum 9t/ha	14	Wheat	344
Trayning	1990	Lime 2,4 t/ha	12-15%	Wheat	344
Trayning	1990	G+L	12-20	Wheat	344
Carrabin	1991	all amendments	reduced 0 to80%	Lupin	350

1.6.2 ACID SOILS

The economics of gypsum utilisation to alleviate the symptoms of soil acidity is more difficult to quantify than for sodic or dispersive soils because little study has been undertaken investigating yield responses, particularly in Australia. McLay *et al* (1994) found that surface-applied gypsum increased wheat yields by up to 55 % in the first 2 seasons in a Western Australian trial. In the same period lime increased yields by only 15 %. The longevity of the response to gypsum was significantly affected by application rate, with the effects of 1 t/ha lasting for 1 season. In this study the most significant increases occurred when gypsum and lime were applied together as with the study of McLay and Ritchie (1993). This study also showed that there were significant variations in yields between regions and climates. A pot study by McLay and Ritchie (1995) emphasised further the benefits of gypsum to increase wheat yields in acid soils.

It is difficult to predict a value by that gypsum may increase yields on acid soils because there appears to be significant variation between both soil type and plant species. Furthermore, to calculate the advantages of gypsum usage over lime, particularly in dealing with subsoil acidity, differences in application need to be considered. Because of its solubility, gypsum may be broadcast on the surface and effect the same change in subsoil acidity to a similar extent as lime that has been incorporated at depth by deep tillage. Such deep tillage may cause a loss of productivity as a result of a degradation of soil structure. The high yield responses particularly those reported McLay *et al.* (1994) (Table 7) are almost certainly the result of gypsum improving soil structure in addition to attenuating soil acidity. Quantifying the proportional yield response to the improvement in soil structure and reduction in acidic effects in acid soils as a result of the application of gypsum is not possible because of the paucity of studies on gypsum and acids soils.

1.7 AIMS AND SIGNIFICANCE OF THESIS STUDY

When catchments serve dual purposes as both a supplier of domestic water and as a major zone of agricultural industry, significant pressures are placed on this land. Generally the interests of the different land users (agriculturalists and water managers) are mutually exclusive. Compounding the difficulties for water managers is that they have little influence over soil, which is the primary source of water quality decline. Even with some control, the time and cost to water managers of providing measures to reduce diffuse P and NOM sources from catchments is generally prohibitive due to the area of land usally involved. The most practical approach would be to develop a solution whereby both parties can benefit, and the costs could be spread between both. Clearly agriculturalists would benefit from better water quality within their own dams, but the retention of important soil nutrients such as P and NOM has the potential to improve soil fertility. Such a solution can also reduce the scale of the problems associated with diffuse sources as it can be managed in partnership on a farm-by-farm basis.

Previous investigations into the impact that gypsum-like compounds have on water quality have focused on the mobility of phosphorus (Coale *et al,*. 1994; Stout *et al,*. 1997; 1998; 2000; Arias and Fernandez, 2001; Callahan *et al,*. 2002) with only limited attention given to NOM (Belkacem and Nys 1995; Nelson *et al,*. 1991). To the author's knowledge no work has been presented on both, particularly with a focus on water quality. Furthermore, studies of the impact of gypsum specifically on soil are generally limited to problematic soils such as dispersive or acid soils. Of these studies some have investigated impacts on leachate, but from a nutrient availability (to plants) perspective (O'Brien and Sumner, 1988; Pavan *et al,*. 1984).

This study aimed to take a holistic approach, investigating how gypsum amendment alters the chemical and physical condition of the soil, and the interrelation of these changes with P and NOM mobility. In addition these changes are examined in a context of sustainability, whereby the effect of gypsum on soil fertility and the suitability of soil leachate for potential domestic consumption (water quality and treat-ability) were investigated.

Soil fertility was investigated from both a physical and chemical perspective. Physical parameters included impact on soil stability and hydrologic characteristic. Chemical parameters included elemental toxicity, cation exchange capacity, pH, salinity and P availability.

The perspective from that water quality was addressed was with a focus on the impact on water required for domestic supply. As such this study investigates the effect of gypsum on the mobility of both P and NOM. In terms of water quality (particularly treatment for domestic supply), the impact of gypsum on NOM mobility is of most significance. Change in the character of the NOM resulting from gypsum amendment was studied, using both parameters and methodologies commonly used in the water treatment industry. This study expands the current knowledge base of the effect of Ca (and gypsum in particular) on NOM mobility through a detailed molecular chemical characterisation of changes in NOM in water, rather than the more general classification presented in the preceding review of literature (molecular weight or hydrophilic/phobicity). Such differences are compared with the corresponding changes in the SOM character. The mechanisms of P retention in soils is significant, not just from a water quality perspective but also in terms of plant availability and particular attention was given to this aspect through chemical (solution and sorption) modelling.

The study was based on three levels of investigation:

1. a field based sub-catchment scale investigation (Chapters 2, 3 and 4);
2. laboratory based core leaching (Chapter 5); and
3. batch experimentation / chemical modelling (Chapter 6).

The core of this study was based on a field study that utilised a paired *sub-catchments* approach to assess the effect of soil treatment on both soil and water. The paired sub-catchments were selected on the basis of similar physical characteristics (landform, geology, soils and vegetation). A detailed description of the field sites is presented in the following chapter.

2 Description of Field Sites

2.1 INTRODUCTION

The field area selected was the catchment of the Mt. Bold reservoir in the southern Mt Lofty Ranges in the southern portion of the Onkaparinga catchment (Figure 9). The Mt. Bold reservoir is a major source of the domestic water supplying the city of Adelaide 300,000 people or about 30 % of the population. The catchment area of the Mt. Bold reservoir is approximately 388 km^2, with a total holding capacity of 47,300 ML. The Mt. Bold reservoir suffers from relatively high levels of natural organic matter (NOM) (Dissolved organic carbon [DOC] ≈ 10 $mg.L^{-1}$, Page, 2001) that are typical of reservoirs of southern Australia. Additionally, the reservoir has a history of algal blooms. The factors that contribute to this are also typical of the region: xeric climate and texture contrast soils (Chittleborough *et al,*. 1992), with additional impacts resulting from the multiple land-uses within the catchment (*viz.* agricultural/ horticultural and native vegetation).

In selecting the sites, a number of criteria were considered. Firstly the soils had to be representative of the typical soils of Onkaparinga Catchment: texture contrast soils with acid soil over-lying metamorphosed sedimentary rocks. The experimental design required two sub-catchments (≈ 5 ha) that were proximal to one another, to ensure the weather regime was identical, and sampling of both could be conducted simultaneously (within min). Adjacent sub-catchments with similar physical characteristics (landform, geology, soils and vegetation) are hard to find. Apart from similar physical characteristics, access for frequent sampling in winter, some distance from main thoroughfares (to avoid vandalism of equipment), and the guarantee of a "stable" land use and land management regime over the course of this study were additional criteria.

2.2 SITE DESCRIPTION

The sub-catchments selected were located approximately 2 km north of the western end of the Mt Bold reservoir (Figures 9 and 10). The site is owned by the reservoir operator (SA Water) and is currently leased to a local farmer who grazes cattle over the entire experimental site.

The two sub-catchments selected were adjacent to one another and were hydrologically isolated from one another by a central valley. They were surveyed using a laser theodolite, with a 1 m resolution (Figure 11 and 12). The eastern sub-catchment was approximately 4.2 ha in size with the western approximately 3.6 ha. Both sub-catchments were similar in slope (≈ 20%) and the vegetation of both have a mix of a moderate cover of eucalypts on the upper slopes and open grazing pasture on the lower and bottom slopes. Average rainfall is approximately 600-700 mm per annum. Additionally the sub-catchments fulfilled the selection criteria with well-matched soils (see 2.2.2 Soil Description) and were under identical management regimes (see 2.2.1 Site Management Histroy).

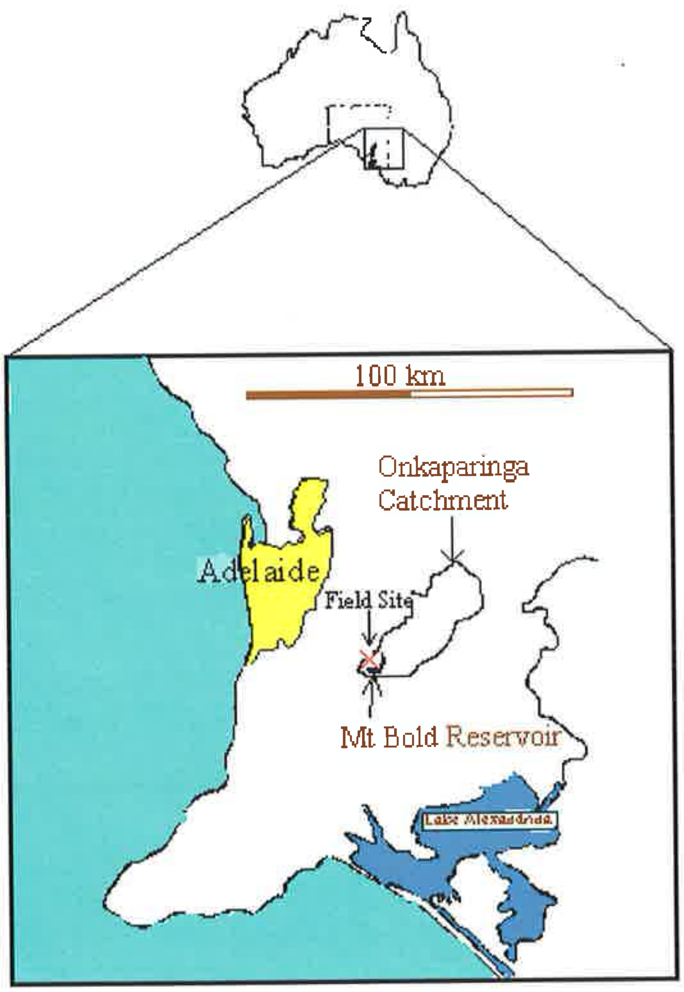

Figure 9 Field study area location (marked 'x') [for more detail see Figure 11].

Figure 10. A 3D photograph showing the location of the eastern and the western sub-catchments used in this study (BE and BW respectively) relative to the Mt. Bold Reservoir. The Eastern sub-catchment was treated with 15 T gypsum/ha (G15) [Figure 13] and western sub-catchment was untreated (G0) [Figure 14].

2.2.1 SITE MANAGEMENT HISTORY

Fertiliser was infrequently applied to both sub-catchments since clearing of native vegetation (Mark Quigley [lease holder] *pers. comm.* 1996). The current leaseholder applied single strength superphosphate at a rate of approximately 8 kg/ha P per from 1991 to 1996. There are no fences separating the two sub-catchments and cattle are free to graze both.

2.2.2 SOIL DESCRIPTION

A summary of soil classifications from the eastern and western sub-catchments is presented in Tables 8-12. These descriptions are representative of the major land forms in the lower-mid slopes of both of the catchments (sampling location see Figures 12 and 13). Table 13 and 14 give a more detailed chemical analysis of the soils prior to gypsum and fertiliser application (sampling location see Figures 11 and 12).

The soils of both sub-catchments had slight textural contrast with silty clay loam A horizons overlying clayey B horizons. The A horizons were of similar thickness in all soils presented with an approximate depth of 15 cm. The B horizon soils of G0 were generally higher in clay content with classifications ranging from medium to heavy clays, with the G15 soils ranging from light to medium heavy clays. Generally the soils are classified as dermosols (weak textural contrast) with some chromosols (strong textural contrast) present in the G0 horizon.

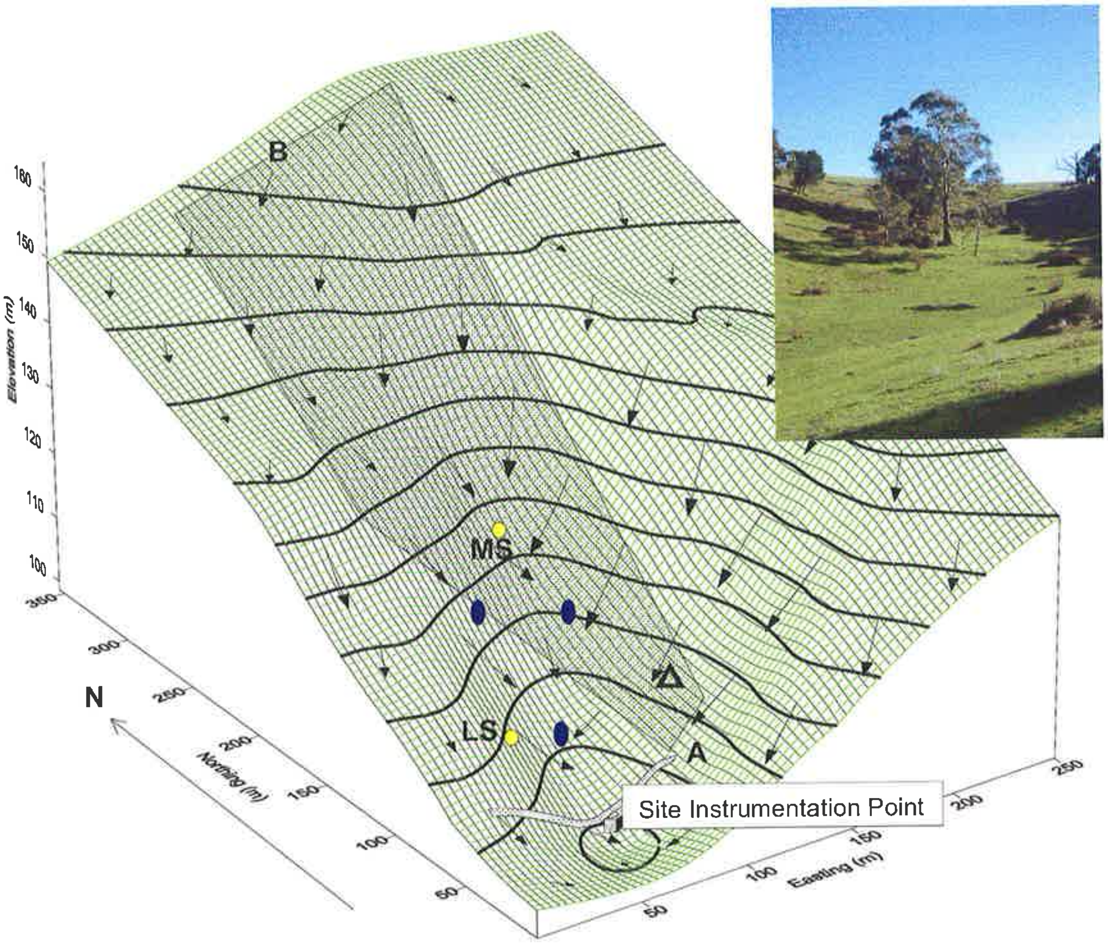

Figure 11. A 3D diagram showing the eastern (G15) sub-catchment, arrows indicate drainage. Inset is a photograph of the sub-catchment through A-B. Blue dots represent 2002 sampling locations, yellow dots represent pretreatment (1997) classification [Tables 10 and 12], and triangle pretreatment chemical analysis [Table 14]. Northings, eastings and elevation are all in meters (verticle exaggeration 3x).

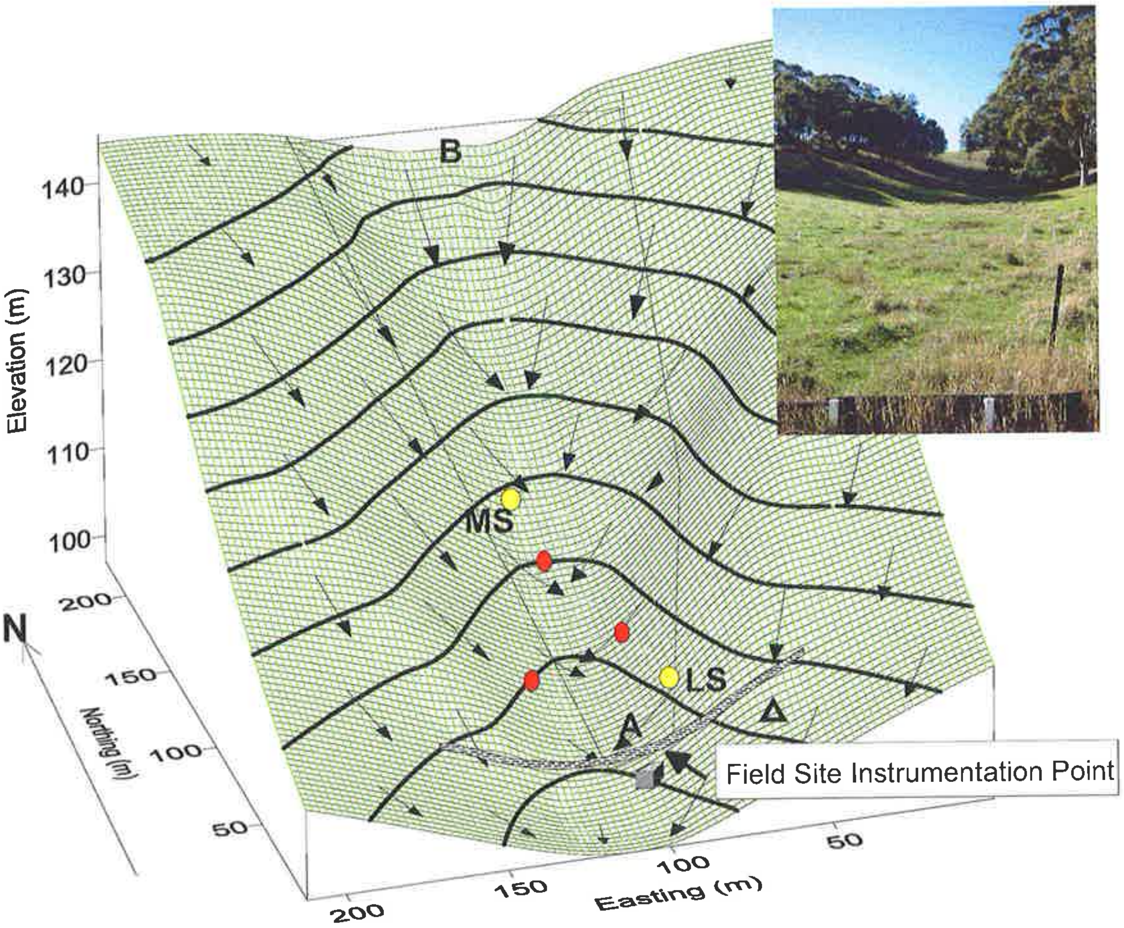

Figure 12. A 3D diagram showing the western (G0) sub-catchment, arrows indicate drainage. Inset is a photograph of the sub-catchment through A-B. Red dots represent 2002 sampling locations, yellow dots represent pretreatment (1997) sampling locations [Tables 11 and 13], and triangle pretreatment chemical analysis [Table 15]. Northings, eastings and elevation are all in meters (verticle exaggeration 3x).

Table 8 Lower slope (LS) soil properties of the eastern sub-catchment (G15).

Horizon	Depth (cm)	Particle Size (%) Clay	Silt	Sand	Texture	Colour (Munsell®)	pH 1:5 (soil:water)	EC (mS/cm)
Ap	0-12	21	36	43	Silty clay loam	10YR 3/2	5.5	0.115
B1	12-37	22	36	42	Light clay	7.5YR 5/3	5.8	0.055
B21	37-57	26	31	43	Medium clay	10YR 6/3	6.2	0.043
B22	57-90	53	16	31	Heavy clay	10R 4/6	5.8	0.071
C	90-120	23	33	45	Silt	2.5Y 7/4	5.8	0.106
C/BR	120-135	47	16	37	Medium clay	2.5Y 7/4	5.9	0.114

Table 9 Lower slope (LS) soil properties of the western sub-catchment (G0).

Horizon	Depth (cm)	Particle Size (%) Clay	Silt	Sand	Texture	Colour (Munsell®)	pH 1:5 (soil:water)	EC (mS/cm)
Ap	0-15	27	24	50	Silty clay loam	10YR 5/4	5.6	0.110
B21	15-50	39	29	32	Medium heavy clay	10YR 6/1	6.4	0.029
B22	50-75	50	23	28	Medium heavy clay	10YR 5/1	6.3	0.032
B23	75-133	55	18	27	Medium clay	10YR 5/8	6.0	0.048
B3	133-150	50	17	33	Medium heavy clay	10YR 6/2	6.2	0.043

Table 10 Mid slope (MS) soil properties of the eastern sub-catchment (G15).

Horizon	Depth (cm)	Particle Size (%)			Texture	Colour (Munsell®)	pH	EC (mS/cm)
		Clay	Silt	Sand			1:5 (soil:water)	
A	0-16	22	25	53	Silty clay loam	10YR 4/2	5.4	0.111
E	16-36	27	33	40	Light clay	10YR 6/2	5.8	0.017
B21	36-65	29	33	38	Medium heavy clay	7.5YR 6/2	5.8	0.015
B22	65-91	36	28	36	Medium heavy clay	10YR 5/3	6.5	0.015
B23	91-120	38	22	39	Medium clay	10YR 5/3	6.1	0.037

Table 11 Mid slope (MS) soil properties of the western sub-catchment (G0).

Horizon	Depth (cm)	Particle Size (%)			Texture	Colour (Munsell®)	pH	EC (mS/cm)
		Clay	Silt	Sand			1:5 (soil:water)	
Ap	0-15	29	34	37	Silty clay loam	10YR 3/2	5.9	0.079
B1	15-40	32	34	33	Medium heavy clay	10YR 7/2	6.2	0.031
B21	40-60	57	20	23	Heavy clay	10YR 5/8	6.4	0.033
B22	60-90	62	28	10	Heavy clay	10YR 5/8	6.1	0.035
B22	90-124	41	26	32	Heavy clay	2.5YR 6/3	6.3	0.031
B3	124-140	41	25	34	Medium heavy clay	2.5YR 6/3	6.5	0.039

Table 12 Chemical analyses of soils (1996) from the lower slope of the eastern sub-catchment (G15) (Stevens *et al*,. 1998).

Horizon	Depth (cm)	Particle size (%)			CEC (NH^{4+})	Available P $mg.kg^{-1}$	Organic C (%)	pH
		Clay	Silt	Sand				
A1	0-11	16	34	51	14.4	24	4.23	5.7
A3	11-28	20	34	46	6.4	8	0.87	5.8
B1	28-48	27	27	45	7.8	1	0.55	6.1
B2	48-68	44	23	33	11.6	0	0.51	5.8
B3/C	68-110	28	31	41	16.6	10	0.19	5.9

Table 13 Chemical analyses of soils (1996) from the lower slope of the western sub-catchment (G0) (Stevens *et al*,. 1998).

Horizon	Depth (cm)	Particle size (%)			CEC (NH^{4+})	Available P $mg.kg^{-1}$	Organic C (%)	pH
		Clay	Silt	Sand				
A1	0-19	12	32	56	10.9	30	4.45	5.2
A3	19-44	23	31	46	6.3	0	0.5	5.7
B1	44-87	53	23	24	16.4	11	0.48	6.0
B2	87-112	56	25	18	25.1	9	0.22	6.5
C	112-160	23	42	35	17.6	4	0.07	6.7

2.2.3 SITE INSTRUMENTATION

The Mt. Bold sub-catchments were first instrumented in May 1996, with a diversion barrier and flume, to measure and sample surface runoff, through a calibrated 150 mm

RBC flume (Clemmens *et al*,. 1984). Flow along the A/B and B/C horizons was intercepted and channelled into a sump consisting of 1.5 L tipping buckets via 10 cm slotted irrigation drain pipe (Stevens *et al*,. 1998) (Figure 14).

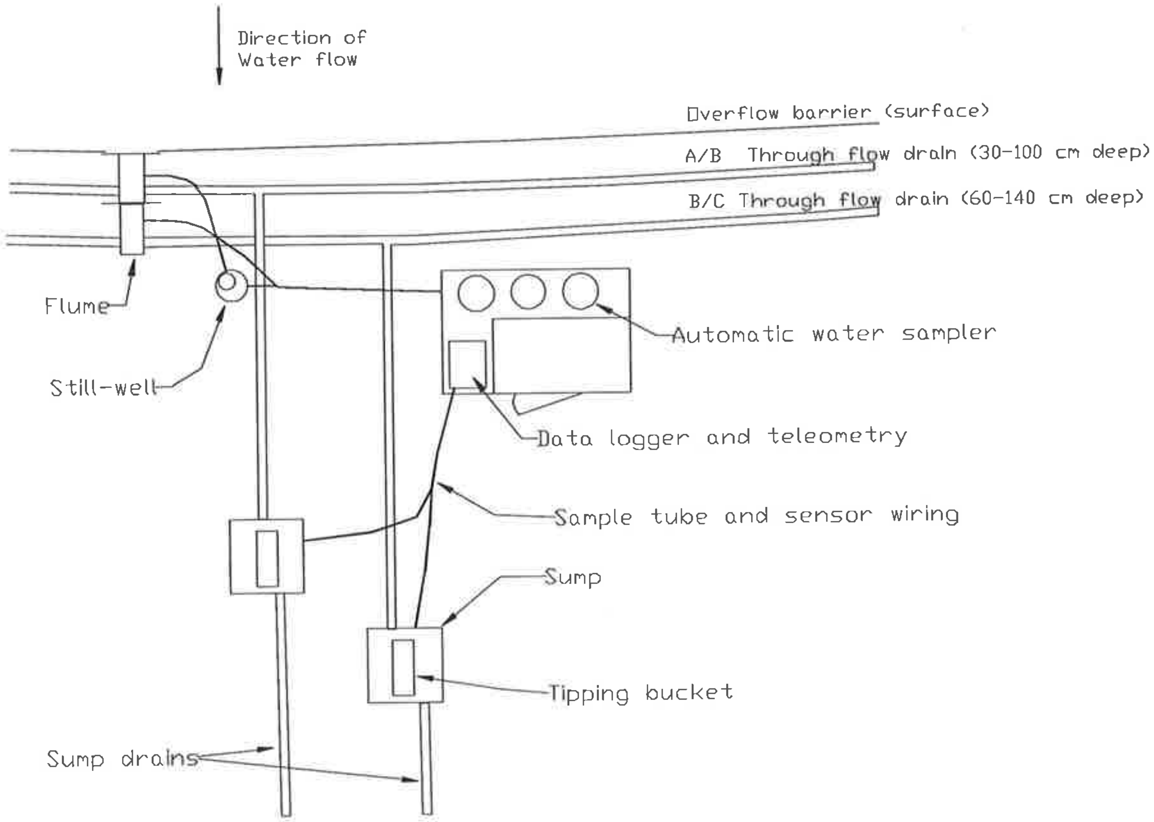

Figure 13. Site instrumentation overhead view (Stevens *et al*,. 1998).

2.3 EXPERIMENTAL SOIL TREATMENT

Each site was treated with single strength superphosphate at a rate of approximately 15 kg ha^{-1} P (full analysis presented in Table 14) in the first 3 yr after instrumentation was installed (i.e. 1996-1998). In late Autumn of 1998 the eastern sub-catchment was treated with approximately 15 T ha^{-1} of gypsum (full analysis presented in Table 15), western sub-catchment was left as an untreated control. Between 1999 and 2000 no P fertiliser was applied, then in 2001 a further 5 kg ha^{-1} P was applied to both sub-catchments at the start of winter (early June). The gypsum treated eastern sub-catchment is referred to as G15 and the untreated western as G0. Sampling and analysis of soils and water are detailed in chapters 3 and 4 respectively.

Table 14 Superphosphate composition (XRF).

SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	SO_3
					%					
7.48	0.77	0.44	0.01	0.96	28.77	0.27	0.07	0.07	20.24	9.44

Table 15 Gypsum composition (analysis by CSIRO Land and Water Laboratory, Adelaide)

Ca	S	Na	B	Al	Fe	K	Mg	Mn	P	Pb	Zn
% Total composition by wieght										Trace (mg/kg)	
21.7	17.1	0.04	< 0.01	0.1	0.17	0.05	0.07	< 0.01	< 0.01	< 100	< 10

3 Effect of Gypsum on Soil Properties and on P and NOM Retention

3.1 INTRODUCTION

In addition to reducing the mobility of P and natural organic matter (NOM), it was a fundamental requirement that the soil amendment selected also be agriculturally viable. In order to address the first aim, this chapter compares the distribution and form of NOM and P between the treated and untreated field soils. The second aim was addressed through assessing the effect on soil fertility, through comparison of selected soil chemical and physical properties.

Traditionally gypsum as a soil amendment is used to alleviated structural problems, to combat Al toxicity in acid sub-soils or to address specific nutrient deficiencies. The soils used in this field study show no sign of any of these conditions, such that notable improvements in soil fertility were not anticipated. In this case, to ensure agricultural viability, it was important that no reduction in soil fertility was observed. Any improvement would be significant in terms of economics as costs can be spread across both land and water managers. In many ways conducting this study on healthy soils is a worst-case scenario, as we would expect to see the least benefit to soil fertility.

This chapter presents a comparison of various chemical and physical properties of the treated (G15) and non-treated (G0) soils from the Mt. Bold field site 4 yr after the application gypsum amendment. Clearly changes that occur in NOM and P distribution are going to be intimately linked with the more general changes in the chemical and physical properties of the soil. A review of soil fertility issues particularly relevant to gypsum usage is presented below.

3.1.1 GYPSUM AS A SOIL AMENDMENT

Traditionally gypsum has been used as an amendment for the reclamation of sodic soils and as a nutrient supplying Ca or S. The reduction of surface and sub-surface crusting of low and non-sodic soils by gypsum amendment has been suggested. In more recent times, agricultural uses of gypsum have been expanded and it is now used as an alternative to liming for the amelioration of problems associated with Ca deficiency and Al toxicity in acid soils, particularly subsoils. Table 16 illustrates many studies throughout the world, including Australia (McLay *et al,*. 1992; Peoples *et al,*. 1992; Howell, 1987) have shown the agricultural benefits of gypsum, especially with respect to increases in crop yields (Sumner, 1994).

3.1.1.1 Use of Gypsum on Dispersive and Hard Setting Soils

3.1.1.1.1 Dispersive Soil Types

Clay dispersion is caused by the mutual repulsion of particles resulting from the presence of negative electric fields in the immediate environment of the particle. The strength of this field is enhanced by the presence of highly hydrated monovalent cations (e.g. Na^+), increasing pH that deprotonates hydroxyls on the clay surface, that increases the repulsive charge of neighbouring clay particles by increasing their negative charge. This is enhanced by low electrolyte concentrations in solution.

The primary effect of sodicity is the dispersion of clay resulting in reduced infiltration rates and increased runoff leading to increased erosion. Crop production may also be affected by other factors such as high osmotic pressure and the presence of toxic amounts of Na and Cl that interfere with the processes of nutrient uptake (Rubens, 1978).

Table 16. Examples of yield responses (%) in various crops to surface applications of gypsum (t/ha) (Sumner 1994).

Crop	Location	Soil Type	Gypsum Rate	Yield response (%)	Author
Corn	South Africa	Plinthic Paleudult	10	19	Farina and Channon (1988)
coffee	Brazil	Rhodic Hapludox	2.6	41	Guimaraes (1992)
sugar	Brazil	Typic Hapludox	6	7	Vitti *et al.* (1992)
sugar	Brazil	Arenoso Distrofico	2	16	Vitti *et al.* (1992)
sugar	Brazil	Typic Hapludox	6	8	Vitti *et al.* (1992)
corn	Brazil		8	9	Quaggio (1992)
corn	Brazil	Xanthic Hapludox	6	76	Souza *et al* (1992)
corn	Brazil	Rhodic Hapludox	4	47	Souza *et al* (1992)
wheat	Brazil	Xanthic Hapludox	6	72	Souza *et al* (1992)
leucena	Brazil	Xanthic Hapludox	6	81	Souza *et al* (1992)
sugar	Brazil	Udoxic Quartzipsamment	5.6	17	Dematte (1992)
sugar	Brazil	Udoxic Quartzipsamment	6	7	Dematte (1992)
corn	Brazil	Typic Hapludox	6	19	Ernani *et al* (1992)
barley	Brazil	Typic Hapludox	6	11	Ernani *et al* (1992)
beans	Brazil	Typic Hapludox	6	13	Ernani *et al* (1992)
oats	Brazil	Rhodic Kandiudult	1	32	Ernani *et al* (1992)
corn	Brazil	Typic Hapludox	6	82	Malavolta (1992)
corn	Brazil	Rhodic Kandiudult	6	77	Malavolta (1992)
coffee	Brazil	Oxisol	2.6	59	Malavolta (1992)
alfalfa	Georga	Typic Kanhapludult	10	18	Riley (1991)
sugar	South Africa	Humic Hapludox	5	13	Meyer *et al.* (1991)
wheat	Australia	Yellow Sandplain	9	55	McLay *et al.* (1992)
pasture	Australia		2.5	28	Peoples *et al.* (1992)
soybean	Kentucky	Typic Hapludult	3.5	40	Marsh and Grove (1992)

Rengasamy (1983) states that the critical value for percentage exchangeable sodium (ESP[4]) for which a soil can be defined as being sodic is approximately 6, however the exact value is somewhat controversial. How this value effects dispersivity of soils almost certainly varies with soil type. This study indicated that sodium absorption ratio (SAR[5]) was a better measure of sodicity, with the critical value being 3 or greater. The other factor controlling dispersivity was the total cation concentration. As this increases so too does the structural integrity of the soil (Figure 14). The classification scheme developed by Rengasamy (1983) suggests 3 broad classes.

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[4] ESP = (Exchangeable Na/Total Exchangeable Cations) x 100

[5] The ESP is approximately twice the SAR i.e. ESP = 1.95SAR + 1.8.

3.1.1.1.2 Class 1: Dispersive Soils

Spontaneously dispersive soils will have severe problems associated with crusting reduced porosity etc,. even when subject to no mechanical stress. These soils have an SAR greater than 3 and so are classified as sodic, they also have low total cation concentration (TCC) (0.6 to 2.5 m.e.L^{-1}). Because of the low TCC, it is important when ameliorating these soils with calcium compounds to maintain enough electrolyte to keep the clay flocculated.

3.1.1.1.3 Class 2a/2b: Potentially Dispersive

These soils are dispersive under mechanical shaking, and so would be subject to dispersion under cultivation or even raindrop impact. Class 2a soils have an SAR less than 3 and hence are low sodic soils. They are, however, dispersive due to low electrolyte concentration. In terms of managing these soils, increasing the electrolyte concentration (toward the ideal class 3c level) is the only effective method of combating the dispersion of these soils. Class 2b soils have similar electrolyte levels to 2a soils but elevated SAR (>3). The aim of managing these soils is to reduce the Na, while slightly elevating the TCC.

3.1.1.1.4 Class 3a/b/c: Flocculated soils

These are soils with sufficient electrolyte to maintain flocculation. In class 3a and 3b soils there are high electrolyte levels that may become problematic insofar as plant growth may be reduced. Class 3c is the ideal situation and should be the goal of soil management (Rengasamy, 1983).

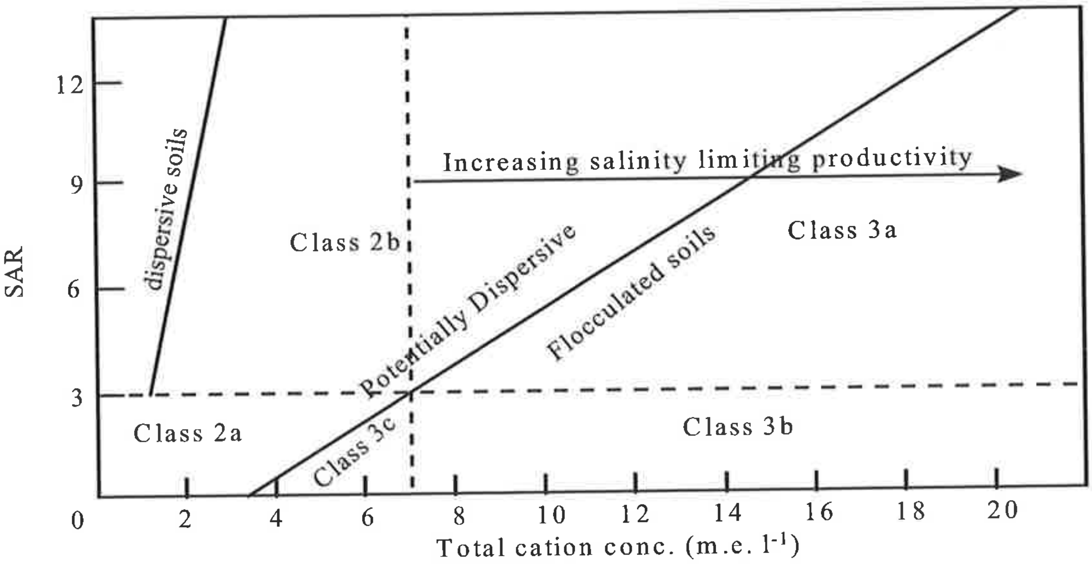

Figure 14 Classification scheme for the prediction of dispersive behavior of A-horizon Red-brown earths (xeralfs) (Redrawn from Rengasamy *et al,*. 1984)

3.1.1.2 Treatment of Dispersive Soils with Gypsum

3.1.1.2.1 Sodic Soils

Sodic soils (classes 1 and 2b) can be reclaimed by the addition of gypsum, Ca exchanges with the Na on the clay particles, driving Na into solution, Na is then leached out as Na_2SO_4.

3.1.1.2.2 Low Sodic Soils

Low sodic soils such as those in class 2a can also be reclaimed with the addition of gypsum (Rengasamy, 1983). In this case the gypsum acts as an electrolyte source increasing the TCC driving class 2a soils toward the ideal soil class 3c. The main problem that is presented by using gypsum to reclaim soils is to ensure that the electrolyte level isn't raised to a point where the water is too saline for plant growth.

3.1.1.3 Improved Sub-surface Structure

Radcliffe *et al,*. (1986) reported significant improvement in penetrometer measurements to 70 cm, in a soil that had 35 t/ha gypsum applied 4 yr previously. They concluded that at least some of the improvement was a result of the effects of deeper rooting caused by a reduction of the chemical barriers of subsurface soils to root growth. This it most likely directly attributable to the gypsum itself (see below- *Gypsum as a nutrient*).

3.1.1.4 Treatment of Acid Soil

In terms of soil fertility the main consequences of soil acidification are deficiencies in Ca, and toxic levels of Al. These shortcomings restrict root growth, the major manifestation of which is the appearance of drought stress when the upper soil dries out and roots do not penetrate the zones where water is present (Sumner, 1993). In a Mediterranean climate such as Adelaide (soils have a xeric moisture regime), this may be most noticeable in spring at which time rainfall intensity decreases, temperature increases, and the surface soil dries out at a point in time when the growth potential is probably the greatest.

3.1.1.5 Gypsum as an Ameliorant to Al Toxicity.

Generally the amelioration mechanisms limit the activity of the Al^{3+} ion, without significantly altering the pH of the soil, as is the case when soils are limed. These mechanisms are summarised in Sumner (1994) as: ion paring, self liming, precipitation and salt sorption.

3.1.1.5.1 Ion paring

As a consequence of the elevated levels of SO_4^{2-}, much of the soluble Al^{3+} becomes complexed as $AlSO_4^{+}$, that is non toxic. Furthermore, if phosphogypsum or flurogypsum that contain quantites of F^- are used, the formation of Al-F complexes further reduce the toxicity of Al^{3+}.

3.1.1.5.2 "Self-Liming"

Reeve and Sumner (1972) originally suggested this mechanism, as a process that involves the ligand exchange of SO_4^{2-} for the OH^- on the sesquioxide surface, producing an alkalinity that would *neutralise* soluble Al^{3+}.

3.1.1.5.3 Precipitation of Basic Al- SO_4 Minerals

Adams and Rawajfih (1977) suggest a mechanism whereby aluminium sulfate minerals are known to precipitate under acid conditions with elevated sulfate levels:

alunite	$KAl_3(OH)_6(SO_4)_2$
basaluminite	$Al_4(OH)_{10}SO_4$
jurbanite	$AlOHSO_4$

3.1.1.5.4 "Salt sorption"

Salt sorption is a process that is often exhibited by gypsum-treated soils. Cations and anions are absorbed by the subsoil in equivalent amounts (Alva *et al,*. 1991; Sumner, 1993). Through the co-immobolisation of Ca^{2+} and Al^{3+} together with SO_4^{2-} the level of Al^{3+} can be controlled.

3.1.1.6 Gypsum Usage as a Nutrient

In many crops Ca is required in solution at the point of root elongation to enable root growth to occur. As discussed earlier gypsum is a readily soluble source of Ca and S. The laboratory trial of Wendell and Ritchey (1996) used an equivalent of 22 t/ha raised the EC of the leachate to 2.54 dS/m (compared to 0.24 dS/m for the control). According to Ritchey *et al.* *(*1998), an EC in this range, as $CaSO_4$, would have no detrimental effect on most crops. Therefore gypsum is an ideal source of Ca as its solubility provides Ca in solution at relatively high concentrations making it readily available to plants without reaching levels that would be harmful to plants through causing excessively high osmotic pressure (or salt content) such as may result from more soluble forms like $Ca(NO_3)_2$ or $CaCl_2$ (Ritchey *et al,*. 1998). The alternative to surface-applied gypsum would be lime incorporated into the subsurface, so called deep-liming (Sumner, 1994), a costly exercise that has the potential to destroy the structure of the surface soil. Sumner (1994) suggests surface-applied gypsum as a mechanism for subsoil acidity amelioration with minimal soil disturbance. The work of Alcordo and Rechigl (1995) indicates that gypsum is also a readily available source of S, that is also essential for plant growth.

Another advantage of gypsum as a Ca source over the more commonly used lime is on crops and pastures that are adapted to acid soils. The increase in pH associated with using lime can decrease the availability of plant nutrients such as Zn, Cu, Mn, and Fe (Ritchey *et al,*. 1998.). This can be overcome by gypsum because it has very little effect on pH (Korack, 1992).

3.1.2 PROBLEMS ASSOCIATED WITH GYPSUM USAGE

Perhaps the major problem to soil fertility resulting from gypsum usage is the potential for exchange of Ca for Mg and K, and the loss of these nutrients from the soil through leaching (Shainberg *et al,*. 1989). The results of Pavan *et al.* (1984) are in agreement: they found that, following the application of gypsum to 100 cm soil cores containing a Brazilian Oxisol (at a rate of ≈ 4.3 to 26 t gypsum/ha) reduced exchangeable Mg throughout the soil core. Zaifnejad *et al.* (1996) found a slight reduction in exchangeable Mg to 90 cm when using a flue gas desulfurization by-product (FGD). Aitken *et al.* (1998), however, found that gypsum or phosphogypsum (at 2 t/ha) only significantly reduced exchangeable Mg at four, and K at three, of the 16 amended sites on acid soils of southeast Queensland. Other authors (Greene and Wilson, 1984; Greene and Ford, 1985) who have investigated the effects of gypsum on acid soils observed that the reduction in exchangeable Mg was limited to the upper 10 cm after 3 yr (5.4 t/ha) (Greene and Wilson, 1984) and the upper 15 cm after 5 yr (15 t/ha incorporated in the top 10 cm) (Greene and Ford, 1985).

Another potential problem of gypsum on soil fertility is associated with the risk of increasing the salt concentration beyond plant tolerance. Wendell and Ritchey (1996) suggest that the amount of gypsum required would have to be significant (>20 t/ha), to cause soil solution salinites of 2.5+ dS/m before plant growth would be effected.

3.1.3 SOIL PHYSICAL FERTILITY

The preceding review highlights gypsum as an ameliorant to soil structural problems. The following section highlights how such structural problems affect the physical fertility of soils, and the criteria by that physical fertility is assessed.

According to Cass (1999) the fundamental properties of soil physical fertility that should be optimized are:

1. infiltration rate of water into, and drainage of excess water out of the soil;
2. exchange of soil CO_2 for O_2 from the atmosphere;

3. storage of water and air within the soil;
4. movement of water and nutrient to the roots; and
5. ease of root growth.

3.1.3.1 Infiltration Rate

The infiltration rate, or ease of water movement into the soil, can be of importance not only for soil productivity *in situ*, but also for water quality off-site. A reduction of infiltration rate will increase the amount of water that flows across the soil surface, potentially increasing erosion rates that, in turn, may lead to increased loss of nutrients and increased turbidity of receiving waters.

3.1.3.2 Plant Available Water and Air Filled Porosity

Plant available water (PAW), the amount of water retained in the soil between its wettest drained content (field capacity (FC)) and the soil moisture condition at which plants are unable to extract water from the soil (wilting point (WP)) is an important property of soils with respect to plant growth. This property is related to the distribution of pore sizes within the soil, and the matrix suction that these pores provide. Field capacity is generally regarded as being that content of water remaining in the soil following application of a negative pressure of 10 kPa for 48 hr (Da Silva *et al*,. 1994). Wilting point is reached when the soil dries to the point that the soil pores still containing water are so small that the matrix (or capillary) suction provided by the soil pore exceeds what the plant is able provide (-1500 kPa). A large capacity to store PAW is not sufficient to sustain plant growth in a physical sense, unless there is a balance with air stored in the soil. Air stored in soil (air filled capacity (AFP)) is calculated by the difference between total porosity and the amount of water stored at FC. Figure 15 provides an interpretation of the physical fertility of soils with respect to their ability to store PAW and air within the soil pores (AFP).

3.1.3.3 Soil Strength

Soil strength measured using a soil penetrometer, measures the cone penetration resistance (of the soil penetrometer): it is a surrogate for resistance to root penetration (Cass 1999). Cass (1999) cites the work of Taylor and Burnett (1964), Taylor and Gardiner (1963), Camp and Lund (1968) and Horben (1970), suggesting that critical values of penetration resistance are in the range 1-3 MPa (10-30 bar) measured at field capacity. As the water content falls below the field capacity the penetration resistance increases. Because of this, the water content at that penetration resistance is measured is an important factor, with the most appropriate water content for measurement being field capacity (Cass, 1999). Cass (1999) suggests the following critical values of resistance with respect to effective plant (root) growth.

1. at < 1 MPa roots and shoots can grow through with little difficulty (optimal);
2. at 1 – 2 MPa seedling emergence will be retarded (moderate soil physical fertility); and
3. at 2 – 3 MPa root growth will be impeded, with restricted capacity for water uptake (poor soil physical fertility).

3.1.3.4 Structural Stability

Soil structural (or aggregate) stability is a measure of the resistance to structural breakdown when exposed to external stresses that range from those induced by human activity (such as cultivation) to those caused by the impact and movement of water (precipitation or irrigation). Structural decline resulting from reduced aggregate stability can impede water infiltration and root penetration. Soil sodicity is a major cause of loss of aggregate stability.

Slaking and dispersion are the mechanisms of structural breakdown. Slaking is the rapid disintegration of large aggregates (2-5 mm) into smaller (often < 0.25 mm) aggregates when added to distilled water. Slaking results in a loss of large pores (macropores), and is caused largely by a lack of strong organic bonding between micro-aggregates (Cass, 1999). Dispersion is the breakdown of fine aggregates and clay associations, in that the complete breakdown of fine aggregates to particles (typically < 0.002 mm) occurs. Generally the cause of dispersion is excessive mechanical disturbance of wet soils or high levels of exchangeable sodium (Cass, 1999). Methods of aggregate stability measurement have been discussed by Marshall and Holmes (1988) and can be classified as wet-sieving (Kemper and Koch, 1966), permeability (Greenland *et al,*. 1962), or dispersion studies (Loveday and Pyle, 1973). Wet-sieving can be used to determine the stability during wetting of larger aggregates (>0.25 mm).

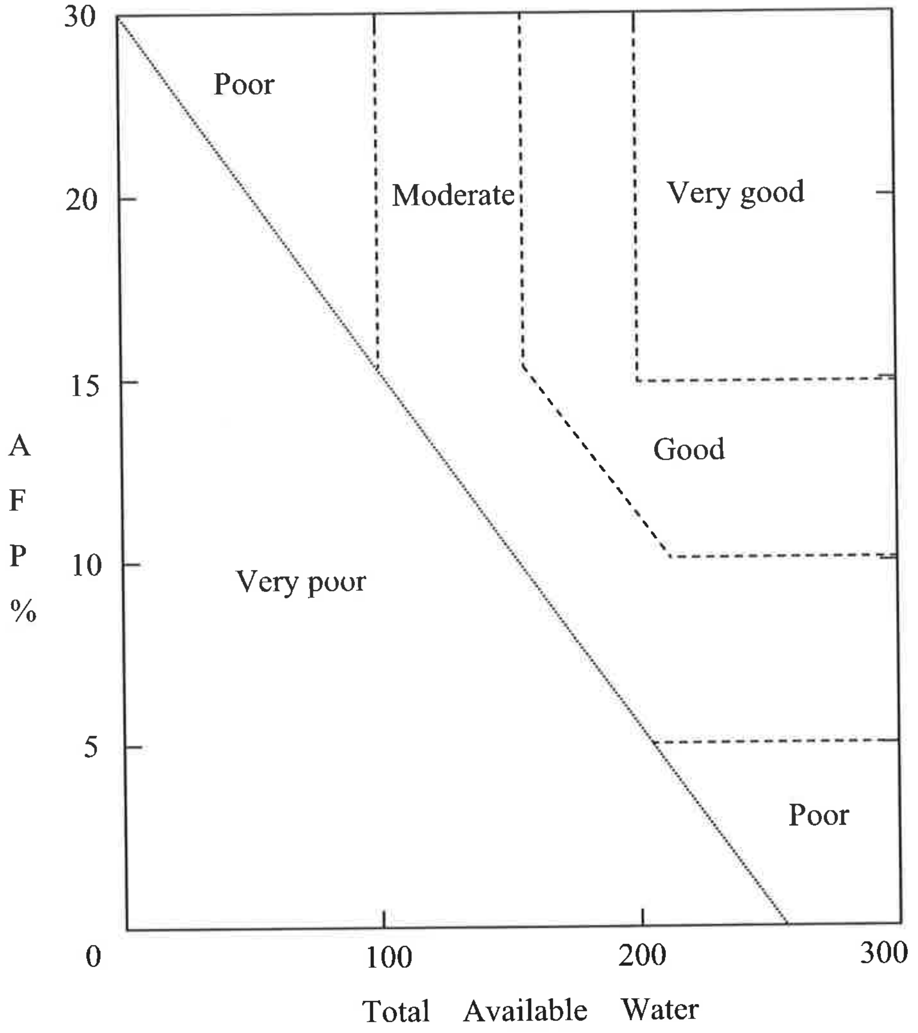

Figure 15 Interpretation of the physical status of soils based on their PAW and AFP (adapted from Hall *et al,*. 1977 by Cass, 1999).

3.2 MATERIALS AND METHODS

3.2.1 SOIL SAMPLING

In autumn 2002, four years after the gypsum application to G15, three soil cores were taken from each of the sub-catchments (G15 and G0). These cores were sampled from similar positions in the mid –lower slope of both sub-catchments (Figures 11 and 12 Chapter 2). The soil cores were air dried for two days and subdivided into depth intervals 0-5, 5-10, 10-20, 20-30, 30-40 and 40-50 cm. The subdivided soils were lightly ground with mortar and pestle and passed through a 1 mm sieve. The < 1 mm fraction was oven dried at 40 °C for 72 hr and stored in screw top polycarbonate jars until analysis.

3.2.2 SOIL CHEMICAL PROPERTIES

3.2.2.1 pH and Electrical Conductivity (EC)

pH and EC measurements were made of soil samples taken in autumn 2002 from G15 and G0 at depths 0-5, 5-10, 10-20, 20-30, 30-40 and 40-50 cm. Measurements were made using a 1:5 soil : solution in reverse osmosis (RO) water. Secondary pH measurements were made in 1:5 soil : 0.01 M $CaCl_2$ solution ratio. Suspensions were shaken for 60 min and allowed to settle for 45 min prior analysis. Measurements were made in triplicate using soils from three separate cores. $CaCl_2$ suspensions were retained for further analysis.

3.2.2.2 Common / Trace Element Distribution

The distribution of some common and trace elements were measured on soil samples taken from soil cores of both G15 and G0 sub-sampled at depths 0-5, 5-10, 10-20, 20-30, 30-40 and 40-50 cm. In order to gauge the variability between cores (replicates), a nitric-perchloric acid digest was conducted on soils from each core at all depths.

To confirm elemental abundances x-ray florescence spectroscopy (XRF) was also used. Composite samples for XRF were made by combining equal amounts of soil from each of the three cores from both sub-catchments.

3.2.2.2.1 Soil Digest

In the soil digest 100 mg of soil was combined with 10 ml of concentrated nitric acid and 1 ml of perchloric acid and the total volume raised to 25 ml with RO water, in long digestion tubes. The digestion was brought to 160 °C over 2 hr and held at that temperature for a further 16 hr. This released the bulk of elements of the soil into solution. The elemental composition of the soil was calculated from the concentrations in the digest solution measured by inductively coupled plasma atomic emission spectroscopy (ICPAES).

3.2.2.2.2 XRF- Major Elements

The samples were dried in an oven at 110°C for over two hr to remove the absorbed moisture, weighed into alumina crucibles and ignited overnight in a furnace at 960 °C, to yield the Loss on Ignition (LOI) values. Lost is organic material, CO_2 from carbonate minerals, H_20^+ (water in combination with the crystal structure), and possibly S, Cl and other volatiles, depending on the mineralogy of the samples. 1 g of the ignited material was then accurately weighed into Pt-Au crucibles with 4 g of flux (commercially available as type 12:22, comprising 35.3% lithium tetraborate and 64.7% lithium metaborate). The sample-flux mixture was fused using a propane-oxygen flame at a temperature of approx. 1150°C, and cast into a preheated mould to produce a glass disc suitable for analysis.

The samples were analysed in a Philips PW 1480 X-ray fluorescence spectrometer using an analysis program calibrated against several international and local Standard Reference Materials (SRM's) (J.Stanley- *pers. comm,*. 2003). A dual-anode (Sc-Mo) X-ray tube, operating at 40 kV, 75 mA was employed.

3.2.2.2.3 XRF- Trace Elements

About 5-10g of sample powder (depending on whether boric acid is used as a backing) was mixed with 1ml of poly vinyl alcohol binder solution, pressed to form a pellet, allowed to dry in air and heated in an oven for a further one to two hr at 60 °C to ensure that the pellet was completely dry before analysis.

Samples were analysed in a Philips PW 1480 XRF Spectrometer using several analysis prog covering suites of one to seven trace elements. Conditions were optimised for the elements being analysed. The prog were calibrated against many (30 or more in some cases) local and international SRM's. A dual-anode Sc-Mo tube (operated at sufficient voltage to excite the Mo) and an Au tube were employed. Matrix corrections were made using either the Compton Scatter peak, or mass absorption coefficients calculated from the concentration of the major elements.

3.2.2.3 Cation Exchange Capacity (CEC) and Exchangeable Bases

CEC and exchangeable bases were calculated using the method outlined by Rayment and Higginson (1992). Samples were measured on the triplicate samples on soils from both G15 and G0 at depths 5-10, 20-30 and 40-50 cm. Exchangeable bases were extracted by shaking a 1:10 soil-solution ratio using a 1 M NH_4Cl (pH 7) solution. The solution was then extracted by filtering the suspension through a Whatman no. 42 filter, leached by application of 1 M NH_4Cl to the filtered soil to bring the final soil:solution ratio to 1:20. CEC was determined by further leaching the soil with a solution containing 15% KNO_3 and 6% $Ca(NO_3)_2.4H_2O$ that displaced exchangeable NH_4^+. Exchangeable Na, K, Ca and Mg were measured by Atomic Absorption Spectroscopy. CEC was calculated by measurement of the N content of the 15% KNO_3 and 6% $Ca(NO_3)_2.4H_2O$ extracts. No pre-treatment for soluble salts was used as EC in the soils sampled did not exceed 300 $\mu s.cm^{-1}$.

3.2.2.4 Exchangeable Fe, Mn, Mg, Na, K and Al

Following pH measurements the 1:5 soil : 0.01 M $CaCl_2$ suspensions were centrifuged and passed through a 0.45 μm filter and the concentrations of elements in the filtrate measured by ICPAES. Exchangeable values were determined by subtracting the final from the initial solution concentrations.

3.2.2.5 Fractional P Distribution

Soil P was extracted using a sequential extraction procedure based on the method proposed by Hedley and Stewart (1982). Fractional P distribution was measured on soil from all depths sampled (i.e. 0-5, 5-10, 10-20, 20-30, 30-40 and 40-50 cm). The sub-samples were oven dried (at 105°C for 24 hr). Four additional soil samples were scraped from the surface to a depth of no more than two cm from both G15 and G0. Samples (2.5 g) of the oven-dried soil were placed into pre-weighed 50 cm^3 polythene centrifuge tubes.

The first stage in the sequential extraction sequence employed 0.5 M $NaHCO_3$ (pH 8.5). The resultant extract provided an estimate of *plant available* P. 50 ml of the $NaHCO_3$ solution was added to the centrifuge tube containing the soil. The tube was placed on an end over end shaker at 20 °C for 30 min, centrifuged at 4000 rpm for 10 min and the supernatant was then filtered through a Whatman no. 42 filter and stored at 4 °C until analysis. The remaining soil and bicarbonate was weighed in order to account for the bicarbonate not removed. In the second extraction procedure, 50 ml of 0.1 M NaOH was added to the centrifuge tube that was shaken for 16 hr on an end-over-end shaker at 20 °C. The solution was extracted as described for the first stage in the sequence. This extract provided an estimate of the *chemisorbed P bonded to Fe, Al and organic matter.* The third stage utilised 0.1 M NaOH; but, prior to shaking, the sample was sonicated in an ice bath for three min at an energy output of 105 J s^{-1}. This procedure broke open small soil aggregates and provided an estimate of the *physically-protected chemisorbed P bonded to Fe, Al and organic matter.* The samples were then shaken and treated as in the previous stages. The final stage in the extraction process was a 1.0 M HCl extraction that provided a estimate of the quantity of *inorganic Pas calcium phosphates and some occluded P.* Again 50 ml was added to the centrifuge tubes that were shaken, centrifuged and extracted as described for the previous stages.

3.2.2.6 Soil Organic Matter (SOM) Distribution

Samples from all depths (i.e. 0-5, 5-10, 10-20, 20-30, 30-40 and 40-50 cm) were analysed for SOM content. Samples were ground in a mortar and pestle and passed through a 1000 µm sieve and SOM measured by the total organic carbon (TOC) rapid titration method of Walkley and Black (in Rayment and Higginson, 1992). Repeat triplicate measurements were further analysed at depths 5-10, 20-30 and 40-50 cm on the cores from each sub-catchment.

3.2.2.7 SOM Characterisation- Carbon Isotope 13 Nuclear Magnetic Resonance (^{13}C-NMR)

^{13}C-NMR SOM characterisation was conducted for samples from two of the soil cores sampled in autumn 2002: sites G15 and G0. The samples were taken from 5-10, 20-30 and 40-50 cm.

Solid-state ^{13}C magic angle spinning (MAS) NMR spectra were obtained at a ^{13}C frequency of 50.3 MHz on a Varian Unity200 spectrometer. Samples were packed in a 7 mm diameter cylindrical zirconia rotor with Kel-F end-caps and spun at 5000±100 Hz in a Doty Scientific MAS probe. Free induction decays were acquired with a sweep width of 40 kHz; 1216 data points were collected over an acquisition time of 15 ms. All spectra were zero filled to 8192 data points and processed with a 50 Hz Lorentzian line broadening and a 0.01 s Gaussian broadening. Chemical shifts were externally referenced to the methyl resonance of hexamethylbenzene at 17.36 ppm.

Cross polarization (CP) spectra were acquired using a 1 ms contact time and a 1 s recycle delay. The number of transients collected for each CP spectrum ranged between 7,000 and 10,000 for the HF-treated soils, and between 10,000 and 55,000 for the NOM samples. Bloch decay (BD) spectra were acquired using a 7.0 ms (90°) ^{13}C pulse. A recycle delay of 90 s was used for all samples. The number of transients collected for each BD spectrum ranged between 660 and 2,500 for the HF-treated soils, and between 2,000 and 3,500 for the NOM samples. BD spectra were corrected for background signal (Smernik and Oades, 2001).

Spin counting experiments were performed using the method of Smernik and Oades (2000a,b). Organic C contents of the whole and HF-treated soil samples were determined using a LECO CR12 carbon analyser. Glycine (AR grade, Ajax Chemicals) was used as an external intensity standard (i.e. the glycine spectrum was acquired separately to those of the samples). For CP spin counting experiments, differences in spin dynamics between the sample and the glycine standard were accounted for using the method of Smernik and Oades (2000a), except that a variable spin lock (VSL) rather than a variable contact time (VCT) experiment was used to determine $T_{1\rho}H$. $T_{1\rho}H$ was determined explicitly for samples Nogyp1 40-50 ($T_{1\rho}H$ = 3.23 ms), Gyp1 20-30 ($T_{1\rho}H$ = 3.51 ms) and Gyp3 5-10 ($T_{1\rho}H$ = 3.17 ms) (Smernik *et al*,. 2002). An average $T_{1\rho}H$ value (3.30 ms) was assumed for all other samples. C_{obs} values are insensitive to differences in $T_{1\rho}H$ in this range; an error of ±0.5 ms in $T_{1\rho}H$ affects C_{obs} by less than 5%. Errors in carbon NMR observabilities (C_{obs} values) are estimated to be ±10% in C_{obs}-CP and ±15% in C_{obs}-BD (Smernik and Oades, 2000a).

3.2.2.7.1 Cross Polarisation (CP) vs Bloch Decay (BD)

The BD technique is much less sensitive than CP (Smernik and Oades, 2000a,b; Preston, 2001), mainly due to need for much longer recycle delays (times between acquisition of successive scans). This is evident in the signal-to-noise ratios, which are much lower for the BD than the CP spectra, despite the longer acquisition times for the BD spectra. However, BD spectra are more quantitatively reliable than CP spectra (Mao *et al*,. 2000; Smernik and Oades, 2000a,b). Thus differences in the distribution of signal between the CP and BD spectra can be attributed to structures whose NMR signal is under-estimated by the CP technique.

3.2.2.7.2 ^{13}C –NMR Spectra

A ^{13}C –NMR Spectra of a representative humic acid is presented in Figure 16. The broad bands observed can be divided into four principal regions, carbonyl, aromatic, O-alkyl and alkyl. Integration of the peaks of these spectral regions gives a semi-quantitative analysis of the major carbon structural units present within the DOM.

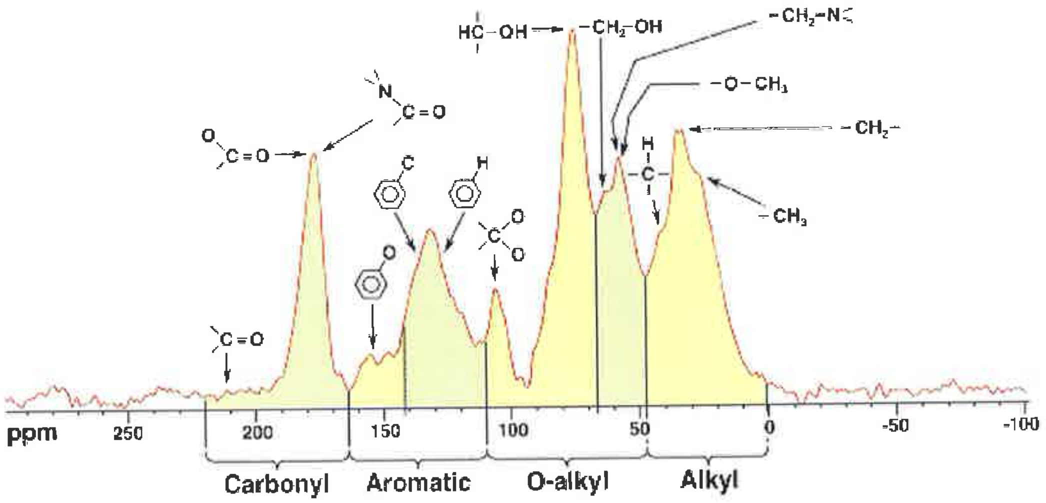

Figure 16. ^{13}C-NMR chemical shift assignments for a representative humic acid (source: Department of Soil and Water, University of Adelaide, www.waite.adelaide.edu.au/nmr/).

3.2.2.8 Soil Mineralogy

The mineralogical composition of soil (< 2 mm) at depths 5-10, 20-30 and 40-50 cm was identified by x-ray diffraction (XRD). Both oriented (suspension: 5-10 and 40-50cm and pressed powder: 5-10, 20-30 and 40-50 cm) and random powdered (5-10, 20-30 and 40-50 cm) XRD patterns were obtained. Oriented samples from suspensions were prepared by pipetting clay suspensions onto zero background silicon wafer XRD disks and dried at 40 °C. Oriented pressed powder disks were prepared using lightly ground, oven dried (24 hr at 105°C) soil sieved to < 500 µm and pressed (using a flat glass surface) into the XRD carrier disk. Random powder samples were prepared by sprinkling soil onto XRD carrier disks covered in a thin film of petroleum jelly, with excess removed. Oriented disks were used for the identification of layer silicate (clay) minerals that have a preferred orientation. Random powder mounts were used to distinguish dioctahedral and trioctahedral minerals.

Measurements were made using a Philips PW 1800 microprocessor-controlled diffractometer with Co Kα radiation, variable divergence slit and graphite monochromator. Diffraction patterns were acquired from 3 to 50° 2θ at 0.02° steps. Data were analysed using the software program X-Plot.

3.2.2.9 *Chemistry and Mineralogy of Fine Particles (< 63 µm)*

Fine particles (< 63 µm) were isolated from suspensions prepared for particle size distribution for both G0 and G15 at depths 0-10, 20-30 and 40-50 cm (see section 3.2.4 Soil Physical Properties). This suspension was prepared using calgon (sodium-hexametaphosphate) as a dispersing agent and had a final pH of 7.5. Under these conditions an unmeasured quantity of organic matter (OM) was desorbed and as the dispersant also contains Na and P, measurements of these three components are strictly comparative and not quantitative.

The < 63 µm fraction was isolated by wet sieving. The < 20 µm fraction was isolated from the < 63 µm suspension by settling under gravity for times calculated using Stokes formula (F3), i.e.:

$$T(\mathrm{sec}) = (18 \times \eta \times h \times 10^6) / (G \times d^2 \times \Delta p) \qquad (F3)$$

Where: h = settling height,
G = gravitation acceleration (980 cm.s^{-1}),
η = measured in c.p. and is dependent on temperature (1.0019 @ 20°C),
d = particle size diameter (µm), and
Δp = density difference (particle – solution = 1.6).

The particles were removed from suspension by centrifuging, with a centrifugal acceleration equal to approximately 50039 ms^{-2} for 2 hr. Using Stokes formula it was calculated that this settled particles to a minimum diameter of 0.06 µm. The supernatant was removed under suction and the upturned centrifuge containers were allowed to drain for 2 hr to ensure the solution was uniformly removed. This resulted in negligible loss of particulate material.

3.2.2.9.1 *Organic Matter Distribution within Fine Particles*

Organic carbon in the < 63 µm fraction of G0 and G15 soils at depths 0-10, 20-30 and 40-50 cm and the < 20 µm at 20-30 cm was measured using the rapid titration method of Walkley and Black (as modified in Rayment and Higginson (1992)). Repeat analysis of the OC in the 20 –30 cm samples confirmed that the initial analysis was accurate to (+/- 0.01% C).

3.2.2.9.2 Elemental Distribution within Fine Particles

The chemical composition of the < 63 µm fraction of G0 and G15 soils at depths 0-10 and 20-30cm and the < 20 µm at 20-30 cm was determined by XRF, using methodologies previously described.

3.2.2.9.3 Mineralogy of Fine Particles

Mineralogies of the < 63 µm and the < 20 µm fractions of G0 and G15 soils at 20-30 cm were determined by XRD. Oriented XRD disks were prepared by pipetting a suspension of clay onto silver filters of pore size < 0.4 µm, under suction. Clays were saturated with MgCl, excess electrolyte washed through with distilled water and the clays saturated with 10% glycerol. Measurements were made with a Philips PW 1800 diffractometer as detailed earlier.

3.2.3 FIELD SOIL BATCH EXPERIMENTS

Batch experiments were used to test the ability of gypsum to increase P sorption on the field soils under controlled laboratory conditions. Soil was sampled from the A horizon at Mt Bold at a site adjacent to the experimental sub-catchments. The soil was air dried for 14 days, gently ground in a mortar and pestle and passed through a 500 µm sieve.

3.2.3.1 Batch Experiment 1: Effect of Gypsum and Lime on P Mobility

RO water (50 ml) spiked with 4.14 mg/L dissolved P ($CaHPO_4$. $2H_20$) was added to samples (50 g) of ground (< 500 µm) soil from the A horizon in 250 ml polycarbonate jars. Treatments are listed in Table 17. Tonnes per hectare (T. ha^{-1}) equivalents were calculated based on 50 g of soil representing the upper 5 cm of the soil profile with a bulk density of 1 $g.cm^{-3}$; thus 50 g represents 1 cm^2 (10^{-8} ha). The volume of water applied was equivalent to 50 mm of precipitation. This would give rise to a slight over saturation of the upper 5cm. The suspensions were then mixed on an orbital shaker for 24 hr. These were placed in 50 ml tubes, centrifuged at 3500 rpm for 15 min, filtered through a < 0.45 µm filter and analysed for molybdate reactive phosphate (MRP) using a modified method of Murphy and Riley (1962). pH measurements were made on the unfiltered supernatant.

Table 17 Treatments used in Batch Experiment 1.

Treatment no.	Gypsum (mg)	Gypsum (t/ha)	Lime (mg)	Lime (t/ha)	Reps
1	100	10	0	0	3
2	100	10	10	1	3
3	100	10	30	3	3
4	100	10	90	9	3
5	0	0	0	0	3
6	0	0	30	3	3

3.2.3.2 Batch Experiment 2: Variable Gypsum Concentration.

Batch Experiment 2 was designed to determine the effect of variable gypsum rates on P sorption. The experimental design was the same as that used in the first trial, except that no lime was added and variable rates of gypsum where applied in triplicate (0, 50, 100, 200, 300, and 400 mg to 50 g of soil and 50 mls of solution). Similarly as in Experiment 1, the suspensions were shaken on an orbital shaker for 24 hr, centrifuged, passed through a 0.45 µm filter and analysed for MRP. pH measurements were made on the unfiltered supernatant.

3.2.4 SOIL PHYSICAL PROPERTIES

3.2.4.1 Particle Size Distribution

Particle size distribution of the < 2mm fraction was determined using the hydrometer method (Gee and Bauder, 1986). Composite samples from 0-10, 20-30 and 40-50 cm were combined in equal proportion from the three soil cores (as described earlier) for both G0 and G15. Approximately 20 g of the composite samples from each depth was weighed into separate 1 L bottles. The soil was dispersed in 50 ml of 10 % calgon (sodium-hexametaphosphate) solution with 0.5 ml 0.6 M NaOH, and 450 ml RO water. The suspension was shaken for 24 hr, and made to a final volume of 1L with

RO water for particle size determination. Measurements were made using a calibrated soil hydrometer (S and B Hillis Pty. Ltd. Sydney, Australia). Blank measurements were made using a solution of the same composition as the suspension.

3.2.4.2 Bulk Density (ρ_b)

Small undisturbed soil cores (radius = 48 mm, depth = 50 mm) were taken at depths 0-10, 20-30 and 40-50 cm from the internal wall of a soil pit (Figure 18). Soil cores were weighed prior to drying and oven dried at 105°C for 24 hr. The bulk density ($g.cm^{-3}$) of the soil was calculated by dividing the mass of the oven dried soil by the volume of the soil core. Porosity of the soil was estimated from bulk density using equation (F4).

$$f / 100 = 1 - (\rho_b / \rho_s) \qquad \text{(F4)}$$

Where: f = Porosity

ρ_b = Bulk Density ($g.cm^{-3}$)

ρ_s = Particle density (assumed 2.6 $g.cm^{-3}$)

3.2.4.3 Penetrometer

Soil resistance in the field was measured using a Bush penetrometer. The Bush penetrometer logs soil resistance (force required to penetrate) at 3.5 cm intervals to a maximum depth of approximately 50 cm. Nine penetrometer measurements were made on soils of each sub-catchment in a range of similar slope positions.

Soil moisture content (that may effect soil resistance) at the time the penetrometer measurements were taken, was estimated by subtracting the mass of the dry soil from the mass of the wet soil from the soil density cores (above).

3.2.4.4 *Aggregate Stability: Wet Seiving*

Soil aggregates used for stability measurements were sampled from the soil pit illustrated in Figure 18 at depths 0 - 10, 20 – 30 and 40 – 50 cm. Initial sampling was of large *fist-size* aggregates. Subsequently, these were gently broken into smaller aggregates of approx diameter 1 – 2 cm. Approximately 25 g of these aggregates (7 – 10 in total) were weighed and placed on a nest of sieves in order, (top to bottom) of mesh diameters 2 mm, 1mm, 500 μm and 250 μm. A separate sample of approx 25 g was weighed and oven dried at 105°C for 24 hr in order to calculate the approximate moisture content of the aggregates used in the stability assessment. The nest of sieves was placed on a mechanical oscillator within a cylinder (Figure 17). Water was added to the cylinder to a level that was seated at the base of the uppermost sieve containing the aggregates. The mechanical oscillator moved in a vertical plane within the water column with a stroke length of 2 cm and a frequency of 30 strokes per minute. Aggregates in the top sieve were completely immersed at the lowest point. The soil aggregates from the upper 10 cm of both soils were found to be extremely stable, and so the total agitation time was 1.5 hr. The less stable soil aggregates at 20 – 30 and 40 – 50 cm were agitated for 10 min. Following agitation, the sieves were allowed to drain for 10 min. The material collected in each of the sieves was carefully washed from each sieve into pre-weighed containers, oven dried at 105 °C for 3 days and reweighed.

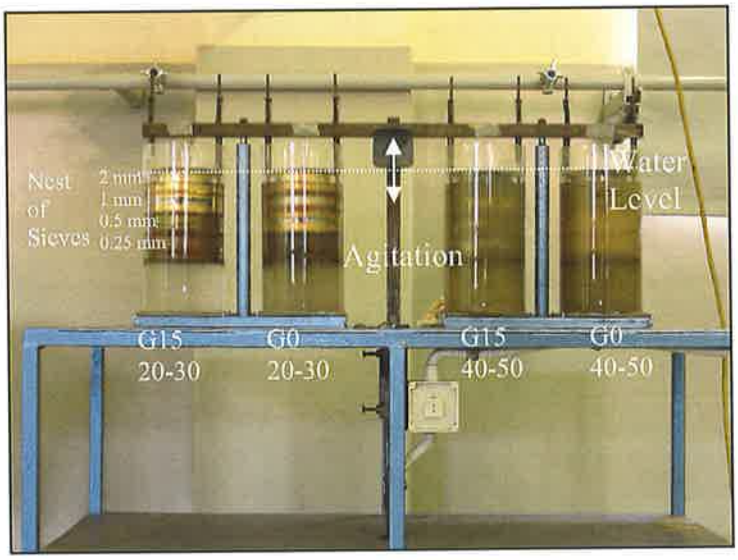

Figure 17. Mechanical agitator used in aggregate stability estimation.

3.2.4.5 Soil Water Retention Characteristics

Soil water retention characteristics were measured on samples taken in 2002 from the profile (at depths 0-10, 20-30, and 40-50 cm) illustrated in Figure 18. Soil samples were sieved to remove > 2 mm fraction. Sieved soils (< 2 mm) were placed in small PVC rings (2.5 mm diameter) and placed on ceramic pressure plates in triplicate. Soils were then re-saturated to exceed field capacity. Volumetric moisture contents of the soils were measured at 3 matric potentials (ψ_m = -10, -1000 and -1500 kPa).

A hanging water column was used to impose the higher matric potential (ψ_m = -10). To achieve a matric potential of –10 kPa the hanging water column was set at 100 cm (1 kPa ≈ 10 cm) below the mid point of the soil ring. The soils set at this potential were allowed to drain for 3 days.

Pressure chambers were used to enforce the lower matric potentials (ψ_m = -1000 and -1500 kPa). The soils subjected to these higher pressures were allowed to reach their equilibrium moisture contents over 14 days.

3.3 RESULTS

3.3.1 SOIL MORPHOLOGICAL CHANGES

The soils of both the sub-catchments in this study are characterised by a slight/moderate textural contrast between the A and B horizons. A horizons have a silty clay loam texture and are generally < 20 cm thick. They overlie a slightly acid, well-structured B horizon. The soils have formed in a micaceous siltstone parent rock. Profile depth in both catchments is about 1-1.5 m over the weathering bedrock but they are shallower on the upper slopes. Initial available phosphorus was reported by Stevens *et al.* (1998) as being in the 20-30 ppm range in the A1 horizon and negligible in the lower horizons.

Observations four yr following the application of gypsum indicate that the soils of G15 are clearly darker (10YR 3/1-4/1 moist (Munsell® soil colour classification system)) in comparison with the G0 profile (10YR 5/3-6/3 moist). The colour change occurred to a depth of at least 50 cm, or well into the B horizon (Figure 18). Photographs (Figure 18) were taken in comparable topographic positions (mid slope) adjacent to the soil core sampling locations (see Figures 11 and 12).

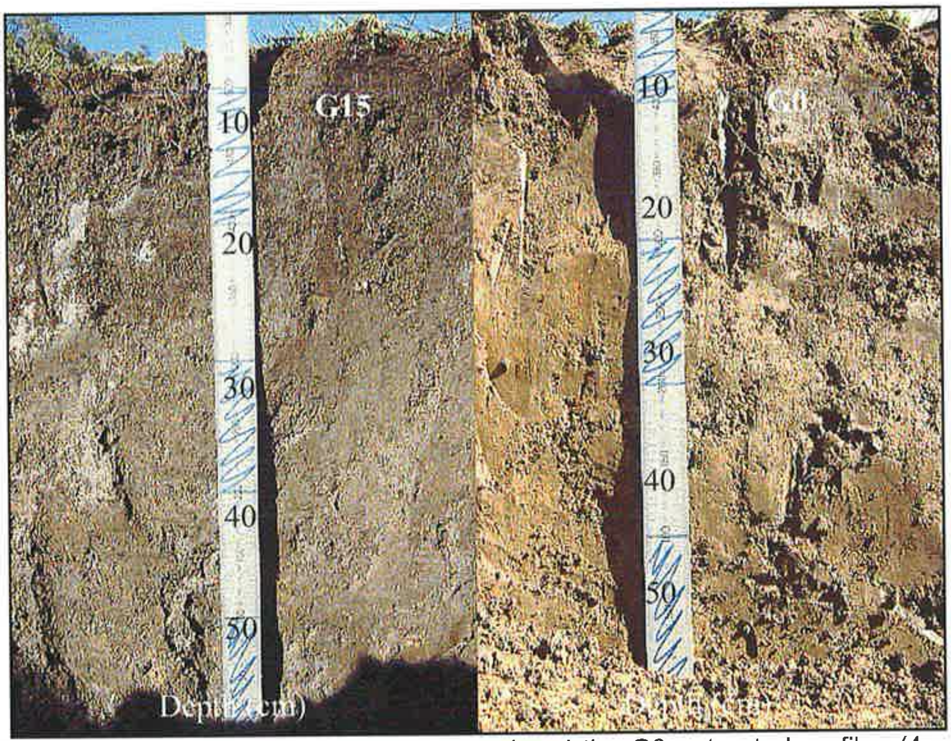

Figure 18. Photograph of the G15 gypsum treated and the G0 untreated profiles (4 yr after treatment).

3.3.2 SOIL CHEMICAL PROPERTIES

3.3.2.1 pH

The depth function of pH_w (1:5 water) and pH_{Ca} (1:5 $CaCl_2$) for the two representative profiles in both the G15 and G0 catchments (Figure 19) show that the gypsum treated soils have a lower pH_w (especially at depth) than the untreated soil. However, this effect is far less evident when pH was measured in $CaCl_2$ (pH_{Ca}). The pH_w profile of the non-gypsum treated site (G0) increased in a relatively linear fashion from approximately 4.9 in the upper 5 cm to 5.7 at 50 cm. Conversely, in the gypsum-treated G15 profile, the pH_w is higher in the surface 5cm than both the entire G15 profile and G0 at the same depth with a pH_w of 5.2. Below this depth it then decreased sharply at 10 cm to 4.7 and gradually rose to approximately 4.9 at 50 cm.

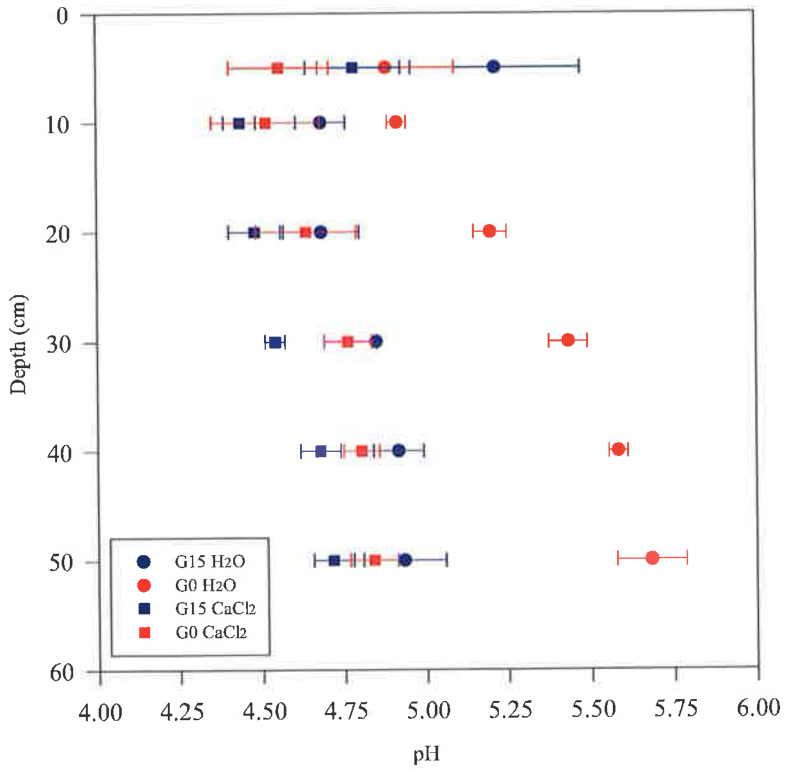

Figure 19. pH profiles for G0 and G15 measured in 1:5 0.01 M $CaCl_2$ and water.

3.3.2.2 Electrical Conductivity (EC)

The EC profiles (Figure 20) are very similar for the surface of both treated and untreated soils, the untreated marginally exceeds that of the treated soils (282 and 240 μ.s. cm^{-1} respectively). The trend below the surface horizon in the untreated soil was for a rapid reduction in soluble salts to a EC at a depth of 50 cm to result in an EC approximately equal to 23 μ.s. cm^{-1}. Below the surface the EC of the gypsum treated soil was markedly higher. This was most evident in the 5-10 cm horizon where a rise in EC to approximately 270 μ.s. cm^{-1} was observed. From 10 to 50 cm a gradual reduction in soluble salts was inferred from the slow decline in measured EC.

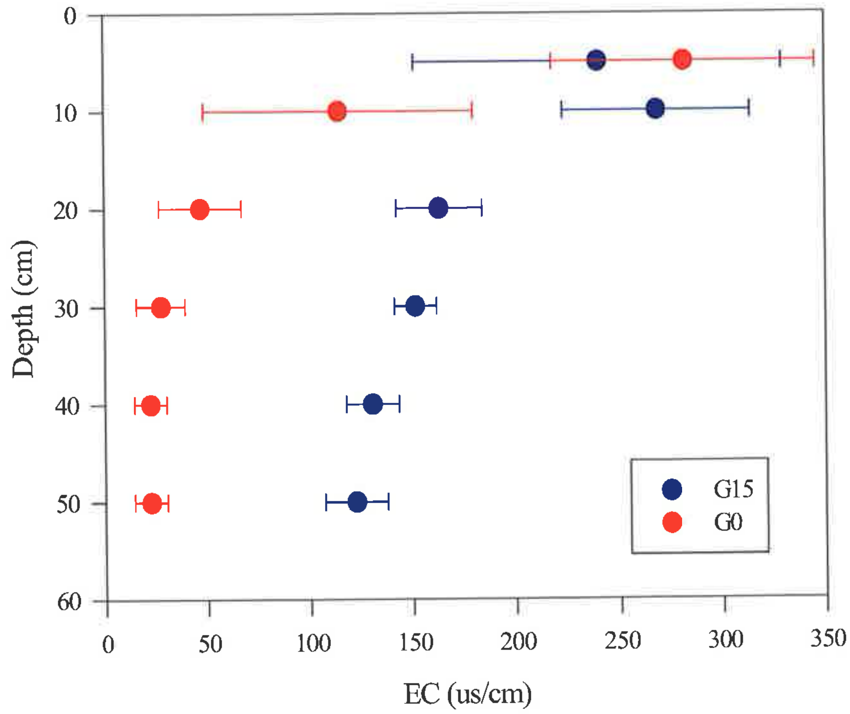

Figure 20. EC measured in 1:5 soil:water.

3.3.2.3 Mineralogy

The XRD traces for G15 and G0 are presented for both oriented specimens (silica wafer [Figure 21] and pressed powder [Figure 22]). Both soils have similar amounts of kaolinite, illite, quartz and some traces of smectite. Kaolinite is recognised by first order basal reflections at ≈ 7.1 Å (≈ 14.5°2θ) and second order reflections at ≈ 3.57Å (≈ 29°2θ). Identifiable basal reflections for illite are ≈ 10 Å (≈ 10°2θ) (primary) and ≈ 5 Å (≈ 21°2θ) (secondary). Quartz is identified by a strong primary reflection at ≈ 3.34 Å (≈ 31°2θ) and secondary reflections at ≈ 4.26 Å (≈ 24°2θ).

The surface 5 cm appears to be slightly richer in illite than kaolinite, however with depth the kaolinite increases and is the dominant phyllosilicate at 50 cm.

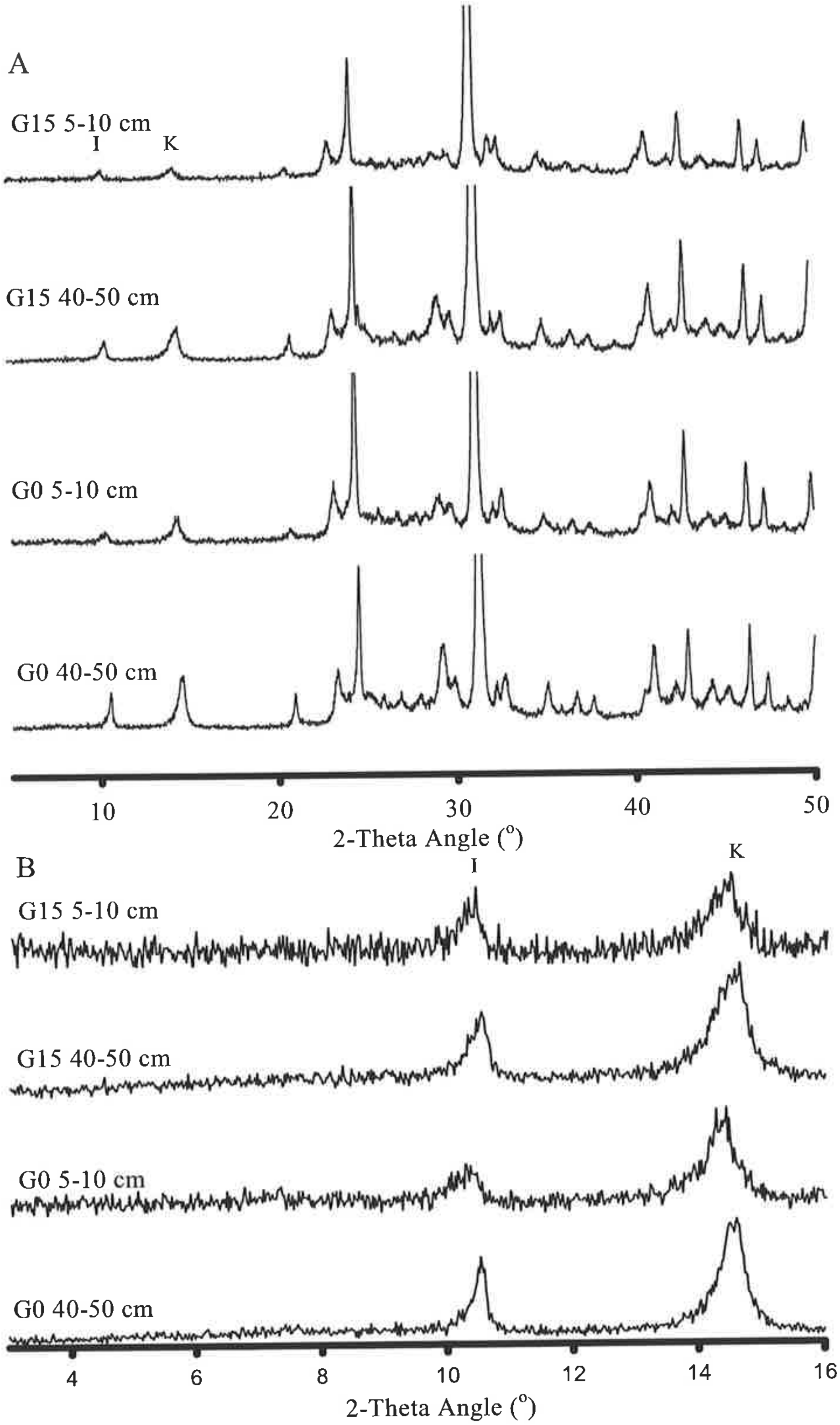

Figure 21. XRD traces of oriented whole soil (< 2 mm) at depths 5-10 cm and 40-50 cm for both treated and untreated soils. I = Illite, K = kaolinite.

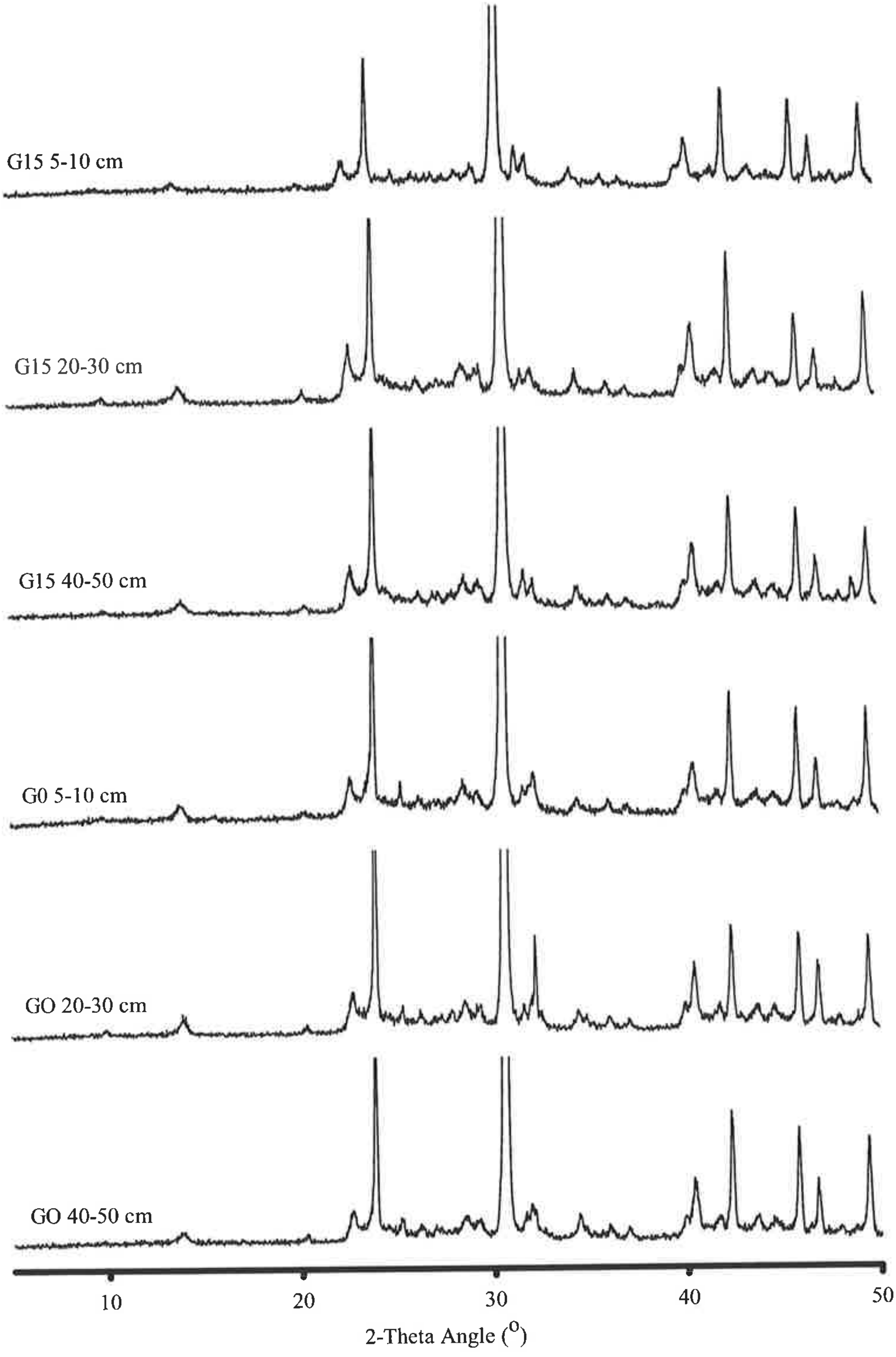

Figure 22. Randomly oriented powder XRD traces of treated and untreated whole soil (< 2mm) at depths 5-10, 20-30 and 40-50 cm.

3.3.2.4 Cation Exchange Capacity (CEC) and Exchangeable Bases

Table 18 presents the total exchangeable cations, and exchangeable Na, K, Mg and Ca values. The CEC of the treated soil is greater, throughout the profile, than the untreated. Exchange of Ca for both Mg and Na lead to an increase in the exchangeable Ca:Mg ratio and a decrease in the exchangeable Na percentage (ESP) in the gypsum-treated soil. Both of these outcomes have important implications for soil fertility (see discussion).

Table 18. Exchangeable cations following extraction from soil with 1 M NH_4Cl.

	Exchangeable cations									
Depth	Na		K		Mg		Ca		Ca:Mg	ESP
(cm)	cmol$_+$/kg	+/-	cmol$_+$/kg	+/-	cmol$_+$/kg	+/-	cmol$_+$/kg	+/-		
					Treated					
5-10	1.00	0.00	0.40	0.00	7.20	0.00	25.60	1.06	3.56	2.9
20-30	0.93	0.12	0.63	0.06	9.60	1.60	27.07	1.01	2.88	2.4
40-50	0.80	0.00	0.40	0.00	12.93	1.29	15.73	2.95	1.24	2.7
					Untreated					
5-10	1.27	0.31	0.83	0.32	10.80	2.23	18.93	7.81	1.83	4.0
20-30	1.13	0.12	1.30	0.62	10.27	2.01	15.07	2.81	1.49	4.1
40-50	1.13	0.12	0.67	0.21	10.27	2.95	10.13	2.89	0.99	5.1

3.3.2.5 Ca Exchangeable Fe, Mn, Mg, Na, K and Al

Exchangeable Fe, Mn, Mg, Na, K and Al were measured following extraction with 0.01 M $CaCl_2$ (Table 19). The dominant exchangeable cation was magnesium: values were > 200 mg/kg at all depths in the untreated soil and, with the exception of 5-20 cm, in the treated soil. The remaining exchangeable cations detected in order of ascendancy of exchangeability were Na, K, Mn, Al and Fe. With the exception of K (that had substantial variability) the amount of Ca-exchangeable ions in the upper 10 cm of the untreated soil was greater than in the treated soil. At 10 – 20 cm and below, exchangeable Mn and Al was greater in the treated soil, and below 20 – 30 cm exchangeable Mg was greater in G15. Exchangeable Na was always greater in the untreated profile.

Table 19. $CaCl_2$ (0.01 M) extractable Fe, Mn, Mg, Na, K and Al.

	Fe		Mn		Mg		Na		K		Al	
	mg/kg											
Depth (cm)	G15	G0	G15	G0	G15	G0	G15	G0	G15	G0	G15	G0
0-5	0.28	0.49	30.08	95.13	204.43	248.11	121.79	136.86	264.59	182.47	1.44	4.12
5-10	< 0.05	< 0.05	13.09	30.25	169.57	248.76	67.35	76.43	14.38	63.25	1.93	3.57
10-20	< 0.05	< 0.05	14.72	11.79	161.23	260.32	42.08	53.50	21.91	60.57	2.23	1.50
20-30	< 0.05	< 0.05	14.84	3.33	219.02	242.58	44.38	47.13	30.79	< 10	1.33	0.79
30-40	< 0.05	< 0.05	6.80	1.93	285.66	244.11	40.88	46.50	12.32	< 10	0.58	< 0.5
40-50	< 0.05	< 0.05	4.71	1.40	301.90	249.30	40.28	47.57	< 10	< 10	< 0.5	< 0.5
	Standard Deviation											
0-5	0.01	0.16	10.15	50.28	26.73	36.88	16.67	27.77	135.66	82.25	0.05	1.51
5-10			3.56	14.40	6.03	43.79	0.91	15.70	1.24	53.19	0.19	2.17
10-20			2.59	2.27	14.04	34.40	1.32	5.29	3.28	56.51	0.38	0.83
20-30			3.35	1.70	33.07	48.80	2.58	7.29	3.12		0.37	0.39
30-40			3.38	0.08	40.91	67.90	3.48	12.83	1.86		0.03	
40-50			1.99	0.36	40.30	61.66	2.20	14.94				

3.3.2.6 Common Trace-element Distribution

The results of the elemental composition of the G15 and G0 profiles are presented in Fgures 23-27. Elements measured in the soil digest (Fe, Mn, B, Cu, Zn, Ca, Mg, Na, K, P, S and Al) accounted for approximately 13.7% and 10.4% of the total mass of the treated and untreated profiles respectively (Table 20). The dominant elements were Al and Fe, was the next most common element observed. Si (not measured in soil digestion) was the most abundant element as measured by XRF. With the exception of slight deviations between values for Mg, Na and S both soil digest and XRF were similar. In all these cases XRF produced higher concentrations than soil digest.

Table 20. Total percentage of total soil mass of 12 analysed elements (soil digestion).

Depth (cm)	G15 % of total soil mass	G0 % of total soil mass
0-5	8.46	9.68
5-10	12.94	10.52
10-20	10.88	10.42
20-30	16.08	12.24
30-40	15.32	10.59
40-50	15.54	8.58
Profile ave:	13.70	10.39

3.3.2.6.1 Major Mineral Forming Elements (Si, Fe and Al)

The untreated soil has a marginally higher mean concentration of Fe and Al in the surface horizon than the treated, however there is a degree of deviational overlap (Figure 23). Between 5 cm and 20 cm (A horizon) there is very little difference between the soils for concentrations of both Fe and Al. Thereafter (to 50 cm) the treated soil has a higher concentration of both Fe and Al. The surface of the treated soils had a higher concentration of Si than the untreated; below this depth the reverse is true.

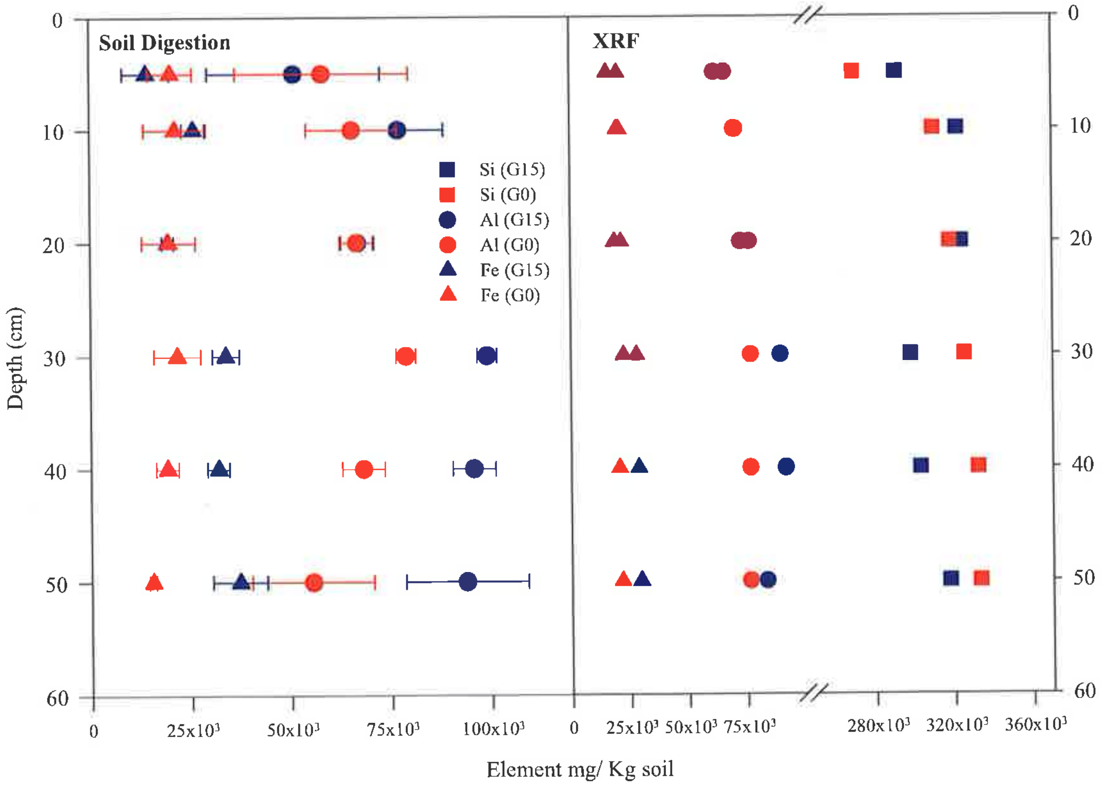

Figure 23. Fe and Al distribution as measure by nitric perchloric digestion (error bars = standard error) and Fe, Al and Si by XRF.

3.3.2.6.2 Major Cations (Mg and K)

With regard to Mg and K, soil digest results indicate there is no statistical difference between treatments in the upper 5 cm, although XRF indicated that K was considerably higher in concentration in G15 than G0 as well as indicated in soil digest (Figure 24). There is little effect of the treatment on Mg, but K is greater throughout the treated profile.

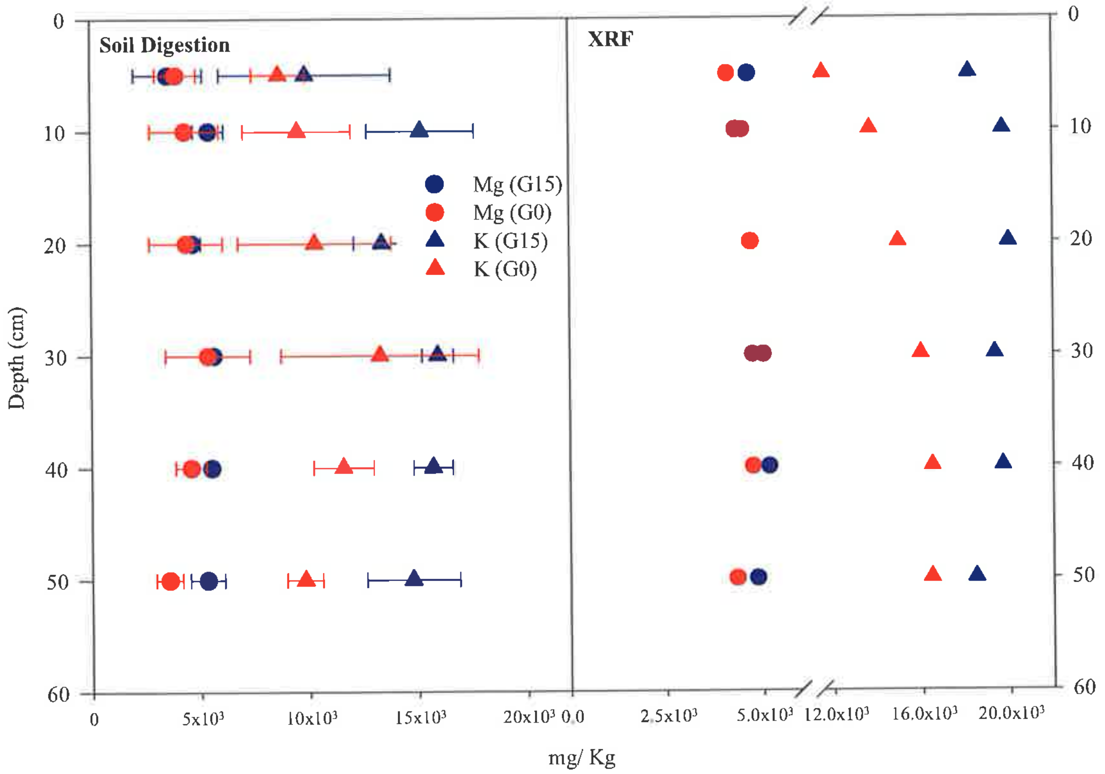

Figure 24 Mg and K distribution as measured by nitric perchloric acid digest (error bar = standard error) and XRF.

3.3.2.7 Major Cations (Ca, Mn, and Na)

Concentrations of Ca, Mn and Na were quite variable in the upper 10 cm of both profiles (Figure 25), although mean concentrations and XRF indicated they were in higher concentration in G15. The pattern of distribution for Mn is very similar to that of Fe and Al, with no observable difference between G15 and G0 to 20 cm. Below this depth there was marked increase in Mn in the G15 profile. Na was greater in the treated soils at depth (from 30 cm). Ca was in greater concentration throughout the gypsum treated profile.

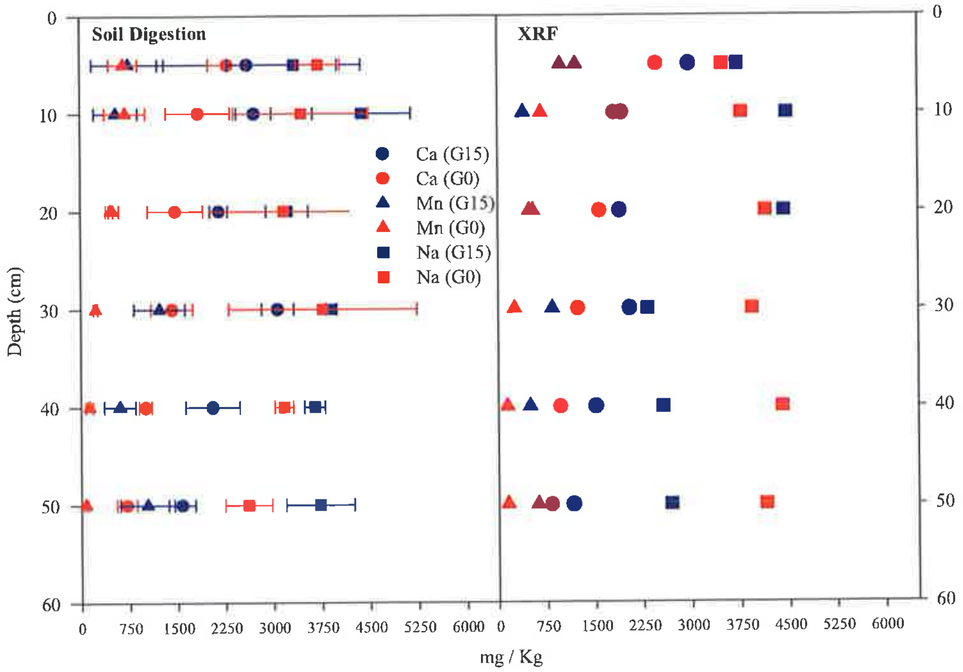

Figure 25. Ca, Mn and Na distribution as measured by nitric perchloric acid digest and XRF.

Trace Elements

Trace element distribution for G15 and G0 as measured by XRF are presented in Table 21. Zn, Sr, Rb, and Pb were notably greater in concentration throughout the G15 compared with the G0 profile, suggesting the applied gypsum as a possible source. If present these elements were below minimum detectable in the chemical analysis of gypsum (Chapter 2). Lower concentrations of Cu in the upper profile of the treated and higher concentrations below 20 cm are probably the result of exchange of Cu by Ca. In this respect Cu behavior is similar to Al. Other trace elements were in similar proportions in both soils.

Table 21 Trace element concentration in soil (ppm = mg/kg).

Site	Zn	Cu	Sr	Zr	Ni	Rb	Ba	V	Cr	La	Ce	Pb	U	Th
depth (cm)							ppm							
G15 0-5	74	17	66	332	14	143	479	71	58	56	125	108	17	26
G15 5-10	64	14	60	362	11	158	539	78	60	45	118	80	13	25
G15 10-20	61	14	61	368	23	164	585	77	70	55	124	74	14	31
G15 20-30	72	30	60	314	21	161	637	94	94	48	108	155	14	38
G15 30-40	60	39	44	342	11	162	592	95	91	51	118	101	13	33
G15 40-50	52	41	40	376	13	143	541	89	82	47	137	92	14	36
G0 0-5	63	20	44	284	13	98	428	60	52	58	106	68	13	21
G0 5-10	49	17	41	356	15	114	471	65	63	72	118	74	14	31
G0 10-20	39	17	41	372	15	123	530	78	71	61	125	73	11	30
G0 20-30	32	18	37	385	14	122	531	79	77	66	119	69	9	27
G0 30-40	36	18	38	395	10	122	537	81	75	64	122	71	13	32
G0 40-50	40	17	36	409	12	116	538	83	77	59	126	69	11	33

3.3.2.7.2 Elements in Anionic Form in Soil (P and S)

The profile distribution of the anionic elements (i.e. those that exist dominantly in solution form as anions [i.e. PO_4^{3-} and SO_4^{2-}]) are presented in Figure 26. In the surface 5 cm, both were greater in the G0 soils; however, significant variation was observed in both the two upper horizons (to 10 cm) for both elements. Below 10 cm P and S are much higher in the treated soils. Variability in concentration notably decreased with depth in both treated and untreated soils.

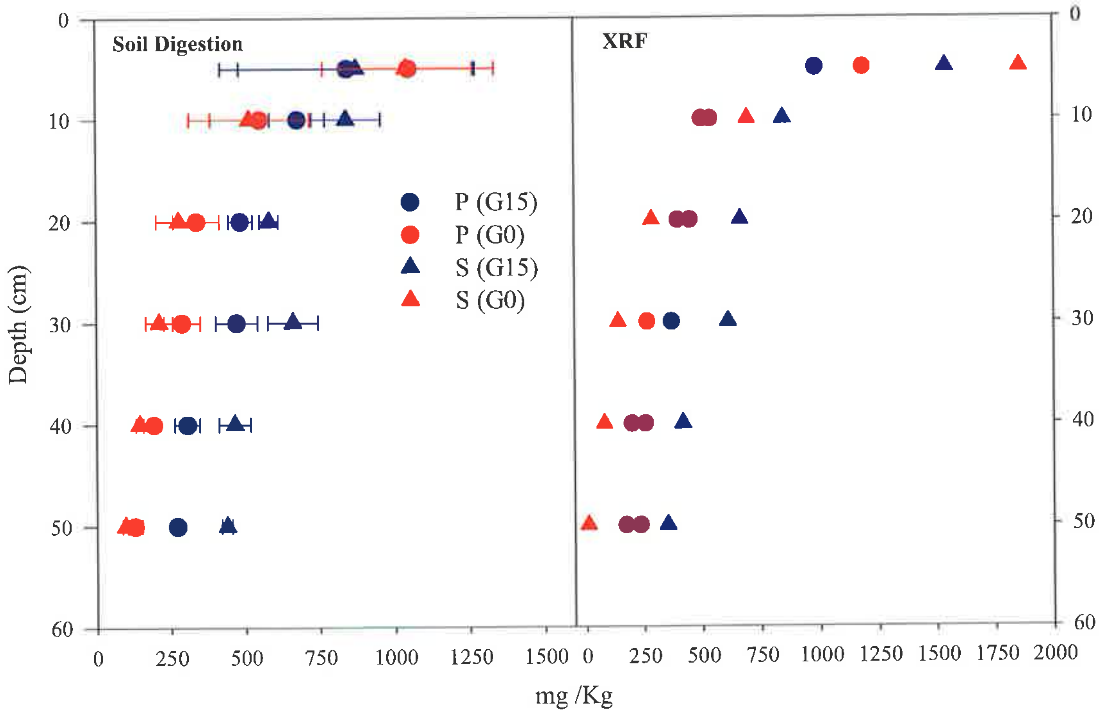

Figure 26. P and S distribution as measured by nitric perchloric acid digest and XRF.

3.3.3 FRACTIONAL P DISTRIBUTION

The distributions of $NaHCO_3$, NaOH, NaOH (sonicated) and HCl extractable P fractions are shown in Figures 27 and 28. With the exception of the upper 5 cm of G0, total extractable P (Figure 28) was greater in all horizons of the treated soils. All extractable fractions were greater in the top 5 cm of the untreated soils, with the NaOH extractable P being more in G0 to a depth of 10 cm. The $NaHCO_3$ extractable P was also greater in the G0 profile in the upper 5 cm and below 30 cm. The HCl extractable P was also marginally greater in the surface of G0, but below 10 cm was below detection limits, in the treated soils concentrations fell below detectable levels below 20 cm. At depths greater than 20 cm, all dectecable extractable P fractions were in greater concentration in the treated soils. Generally residual P (Figure 28) was greater throughout the G0 profile.

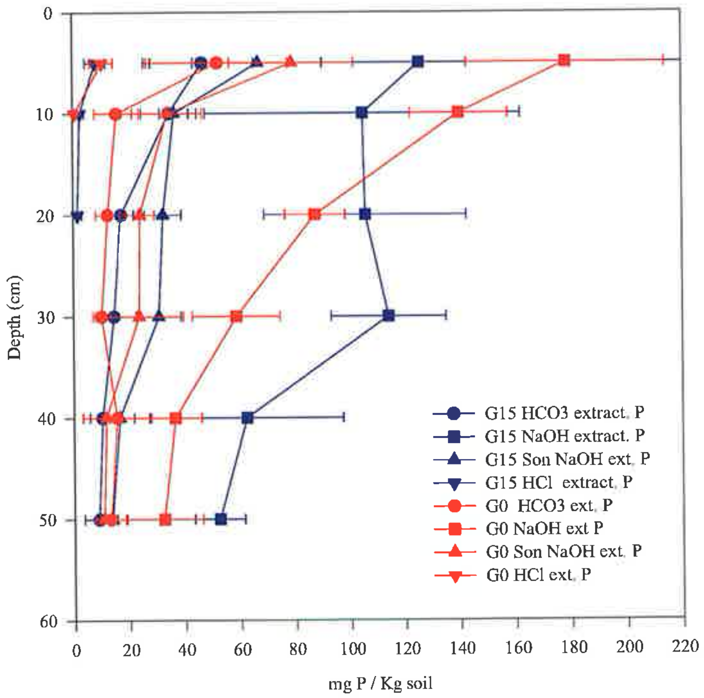

Figure 27. Extractable P fraction distribution.

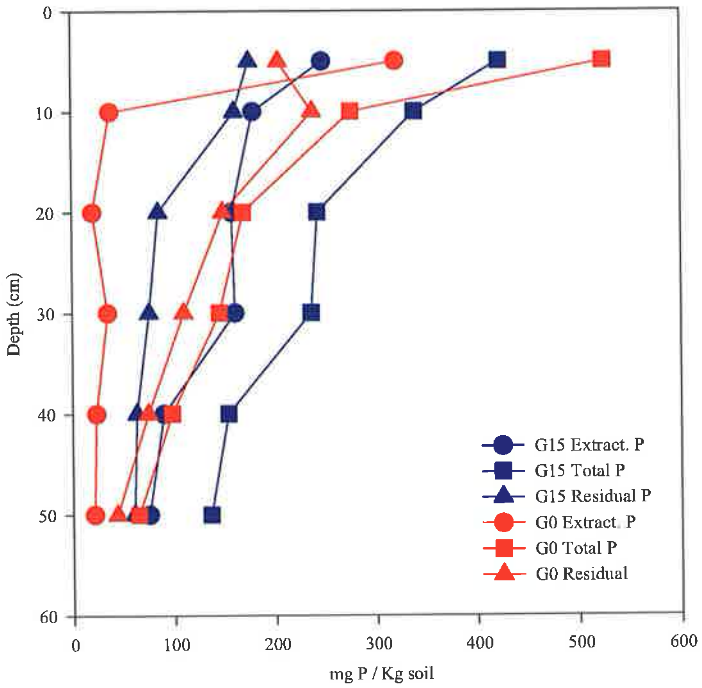

Figure 28. Total P, total extractable P and residual P.

3.3.4 SOIL ORGANIC MATTER (SOM) DISTRIBUTION

The results of the SOM distribution, as determined by the Walkley and Black method of organic carbon measurement show relatively high organic carbon concentrations in the upper 10 cm, particularly the upper 5 cm (7.1 and 5.4 % for G0 and G15 respectively) (Figure 29). The organic content of the upper 5 cm in both soils showed a large degree of variation. The results indicate the top 10 cm of the G0 soil had higher organic content. However, below 10 cm the G15 soils exceeded the organic content of G0, with a maximum differentiation at 30 cm: 2.2 % in G15 to 1.4 % in G0.

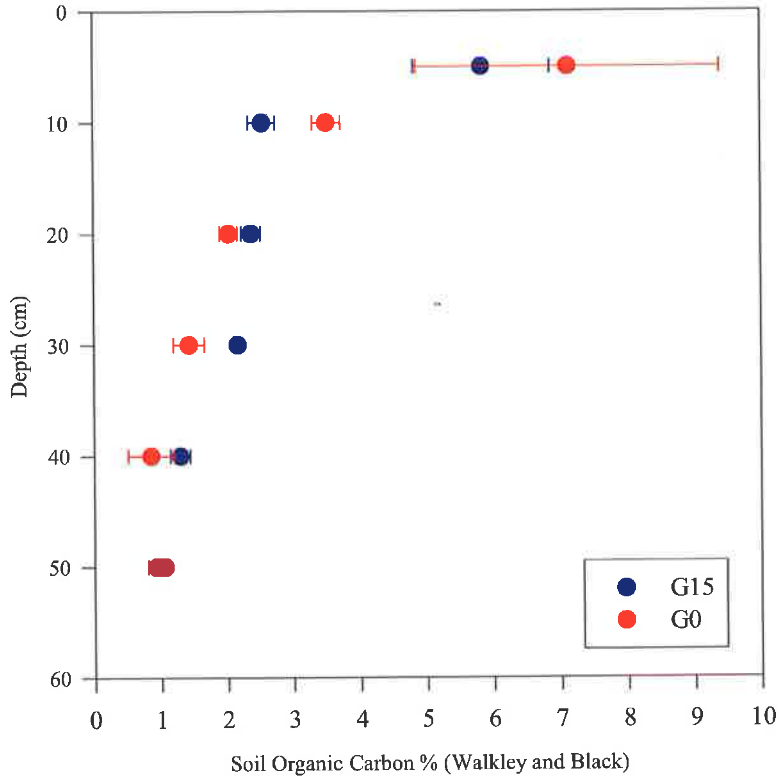

Figure 29. Concentration of SOM by Walkley and Black (%).

3.3.5 SOM CHARACTERISATION- ^{13}C-NMR

The cross polarisation (CP) and bloch decay (BD) ^{13}C-NMR spectra for G15 soil is presented in Figures 30 and 32, and for G0 in Figures 31 and 33. Similar spectra are observed between all the 5-10 cm soils analysed. Stronger differences are observed in the spectra between treatments, with depth. Generally higher peaks (relative to other peaks) are observed in the 120-130 ppm range of G0 soils. This indicates a more aromatic nature of this soil organic matter (G0), most likely due to a higher char (recalcitrant organic matter) component. This indicates a higher proportion of freshly deposited (less degraded) organic matter in the treated (G15) soils.

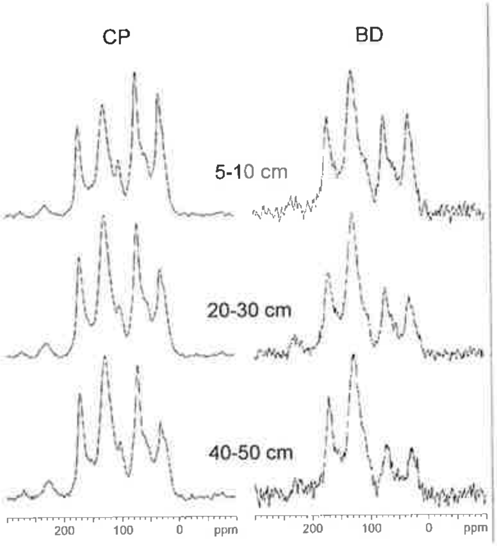

Figure 30 ^{13}C-NMR spectra of G15 (#1) soil.

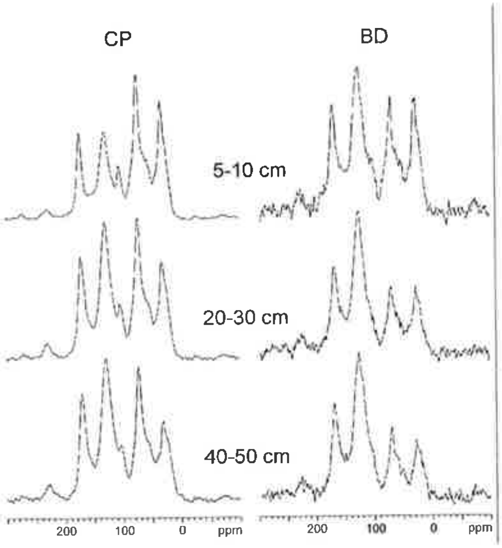

Figure 32 ^{13}C-NMR spectra of G15 (#2) soil.

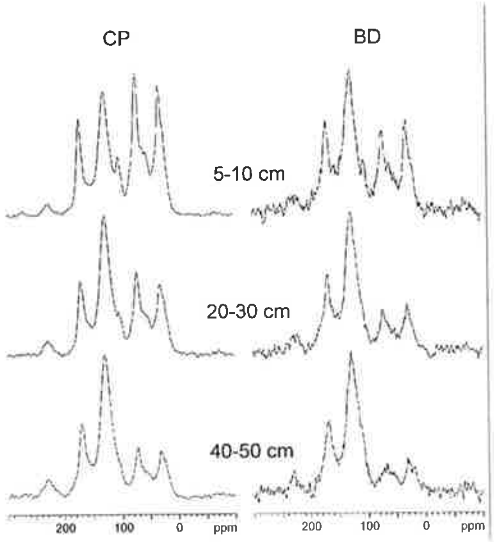

Figure 31 ^{13}C-NMR spectra of G0(#1) soil.

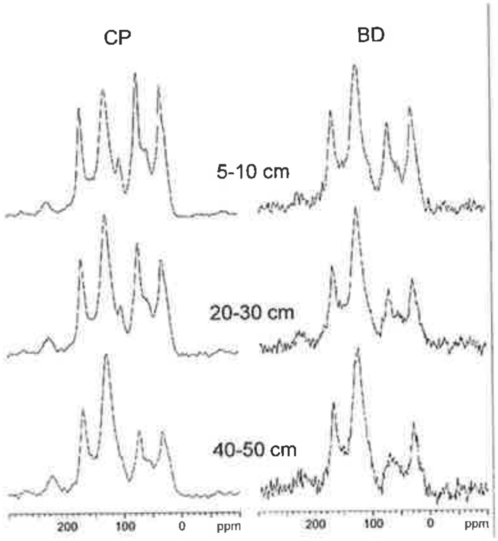

Figure 33 ^{13}C-NMR spectra of G0(#2) soil.

3.3.6 PARTICLE SIZE DISTRIBUTION

The distribution of particles (coarse and fine sands, silts and clays) within the soil analysed in this study are presented in Table 22. Generally the particle size distribution was similar between the treated and untreated sub-catchment soils. Both soils had much higher sand contents (particularly coarse sands) in the A1 (0-10 cm) horizons compared to horizons below. With the exception of the top 10 cm, where the treated soil contained approximately 20 – 25 % more (≈ 4 % more of total) coarse sand than G0, the distribution of coarse sands was very similar throughout both treated and untreated soils. Fine sands in G0 in all cases exceeded G15, whereas the silts were generally higher in G15. Distribution of clays was very similar between both G15 and G0, with the greatest difference occurring in the clay fraction in the upper B horizon. This analysis differs from the previous analysis (Chapter 2 and Stevens *et al*,. 1998), that indicated higher clay contents in the B horizon throughout the G0 profile.

Table 22. Particle size distribution of soil cores analysed.

	Sand				Silt		Clay	
	2000-63 μm		63 - 20 μm		20 -2 μm		< 2 μm	
Depth (cm)	G15	G0	G15	G0	G15	G0	G15	G0
0-10	20.7	16.6	9.7	12.6	37.1	36.7	32.5	34.1
20-30	7.9	7.7	7.1	10.5	45.3	45.7	39.7	36.1
40-50	9.5	9.0	7.7	14.1	42.8	38.7	40.0	38.2

3.3.7 ORGANIC MATTER (OM) DISTRIBUTION WITHIN FINE PARTICLES

The distribution of organic matter in the fine fraction (Table 23) reflected the distribution of organic matter in the whole soil, with OM in untreated soils exceeding treated soils in the surface horizons but the reverse in lower horizons. As expected, the organic content of the fraction < 20 μm (at 20 – 30 cm) in the G0 soil was greater than the fraction < 63 μm. It is normally assumed that the finer fraction (< 20 μm) would have a higher organic C content, as it would both contain a higher proportion of surface reactive minerals (i.e. a lower proportion of non reactive quartz) and a higher surface area to volume ratio. In contrast, with expectations and results from analysis of the untreated soils, the opposite was observed in the gypsum treated soils;

with the 63-20 μm fraction holding a greater proportion of organic matter than the finer < 20 μm fraction. The marginally higher clay content of G15 (i.e. < 2 μm - Table 22) does not solely account for the higher organic content in G15 (at 20-30 cm). Normalising the results to account for clay content indicated that the G15 < 20 μm fraction still contained approximately 44% more organic C per unit clay mass than G0 (rather than 50% without normalising).

Table 23. Organic C % for fine particles.

Depth (cm)	Particle Size (μm)	Organic carbon (%) G15	Organic carbon (%) G0
0-10	< 63	2.50	3.29
20-30	< 63	1.24	0.68
20-30	< 20	1.20	0.80
40-50	< 63	0.46	0.28

3.3.8 ELEMENTAL DISTRIBUTION WITHIN FINE PARTICLES

Elemental analysis of the fine particle fraction at depths of 1 – 10 cm and 20 – 30 cm for both treated and untreated soils are presented in Table 24. Chemical composition (particularly the major elements; Si, Al, Fe, Mg and K) of G15 < 63 μm and < 20 μm fractions at 20 –30 cm were very similar. Additionally the inorganic chemical properties of the < 20 μm fraction of both G15 and G0 (at 20 – 30 cm) were quite similar. The chemistry of the < 20 μm fraction for both treated and untreated soils at 20 –30 cm differed markedly from the < 63 μm fraction at 0 – 10 cm, indicative of very different mineralogy (i.e. higher quartz in the coarser fraction). Similar differences were observed between the < 20 μm and < 63 μm fractions at 20 – 30 cm of the untreated soils. In contrast, the inorganic chemical compositions of the two fractions at 20 – 30 cm were similar in the treated soils, suggesting these fractions have similar mineralogy. The chemical differences are highlighted when the oxide concentration of the < 20 μm fraction was subtracted from the < 63 μm fraction, most notably in comparison of SiO_2, Al_2O_3 and Fe_2O_3 (Table 24).

P followed a similar distribution pattern as described for organic carbon. P was greater in the < 20 μm fraction of G0 than the < 63 μm, however in the G15 soil the reverse was found.

Table 24. Chemical composition of fine fraction, as measured by XRF (< 2 mm reference only*)

Site (cm)	Particle Size	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	SO_3
							%					
G15 (0-10)	< 2 mm*	65.5	12.8	2.57	0.10	0.75	0.34	0.55	2.29	0.88	0.17	0.30
G15 (0-10)	< 63 μm	67.9	14.2	1.89	0.027	0.88	0.057	0.95	2.63	1.01	0.45	0.011
G15 (20-30)	< 2 mm*	63.8	16.9	4.04	0.11	0.83	0.29	0.31	2.33	0.98	0.09	0.15
G15 (20-30)	< 63 μm	55.9	23.3	3.63	0.042	1.27	0.028	0.72	3.24	1.22	0.54	0.004
G15 (20-30)	< 20 μm	57.4	22.0	3.54	0.042	1.21	0.023	0.67	3.13	1.23	0.45	0.004
G15 (20-30)	63 - 20	-1.5	1.3	0.09	0.000	0.05	0.005	0.05	0.11	-0.01	0.09	0.000
G0 (0-10)	< 2 mm*	61.9	12.5	2.96	0.11	0.72	0.299	0.49	1.52	0.85	0.20	0.319
G0 (0-10)	< 63 μm	66.2	14.4	2.19	0.023	0.85	0.056	1.10	1.90	1.02	0.48	0.009
G0 (20-30)	< 2 mm*	69.6	14.5	3.24	0.03	0.79	0.17	0.53	1.93	1.04	0.06	0.04
G0 (20-30)	< 63 μm	70.4	15.2	2.31	0.014	0.88	0.035	0.82	2.19	1.15	0.37	0.005
G0 (20-30)	< 20 μm	58.7	21.8	3.34	0.017	1.27	0.024	0.76	2.96	1.42	0.46	0.004
G0 (20-30)	63 - 20	11.6	-6.6	-1.03	-0.003	-0.39	0.011	0.06	-0.77	-0.27	-0.09	0.001

* The < 2 mm fraction was analysed on soil that had not been dispersed with calgon.

3.3.9 MINERALOGY OF FINE PARTICLES

XRD traces for the < 20 μm and < 63 μm fractions show that the mineralogy of the fine fractions is similar (Figures 34 and 35), being dominated by kaolinite and illite, with some quartz. Kaolinite is recognised by first order basal reflections at $\alpha \approx 7.1$ Å ($\approx 14.5°2\theta$) and second order reflections at ≈ 3.57Å ($\approx 29°2\theta$). Identifiable basal reflections for illite are $\alpha \approx 10$ Å ($\approx 10°2\theta$) (primary) and ≈ 5 Å ($\approx 21°2\theta$) (secondary). Quartz is identified by a strong primary reflection at ≈ 3.34 Å ($\approx 31°2\theta$) and secondary reflections at ≈ 4.26 Å ($\approx 24°2\theta$). The < 20 μm mineralogy is characterised by a higher kaolinite (primary) peak than illite peak. The kaolinite peak is approximately double the illite peak, indicating that they are in relatively equal proportions (Wilson, 1987). In the < 63 μm fraction of G0 (all depths) and G15 (5 – 10 cm) the illite peak is greater (7 – 50 %) than the kaolinite peak. For 20-30 and 40-

50 cm in G15 however, the kaolinite peak is 18 to 26 % larger than illite, suggesting that this fraction is of intermediate composition between the < 20 µm and < 63 µm of G0.

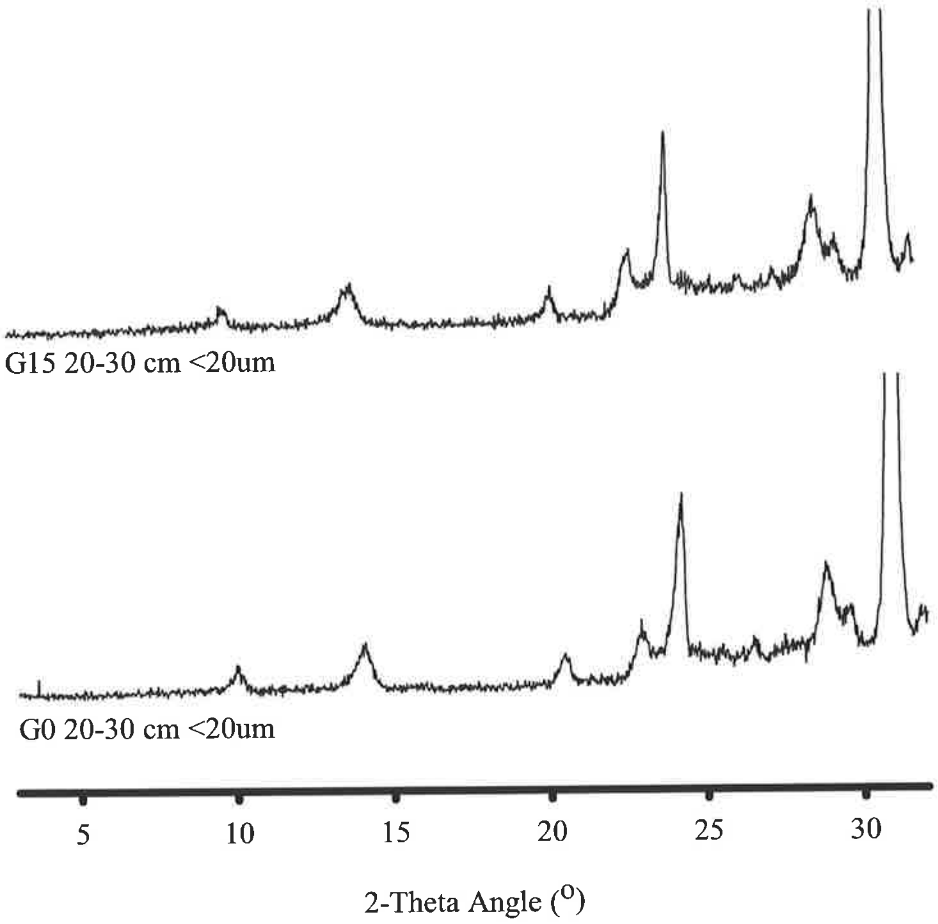

Figure 34. XRD traces of the < 20 µm fraction of G15 and G0 soils at 20 30 cm: Oriented (MgCl/Glycerol saturated)

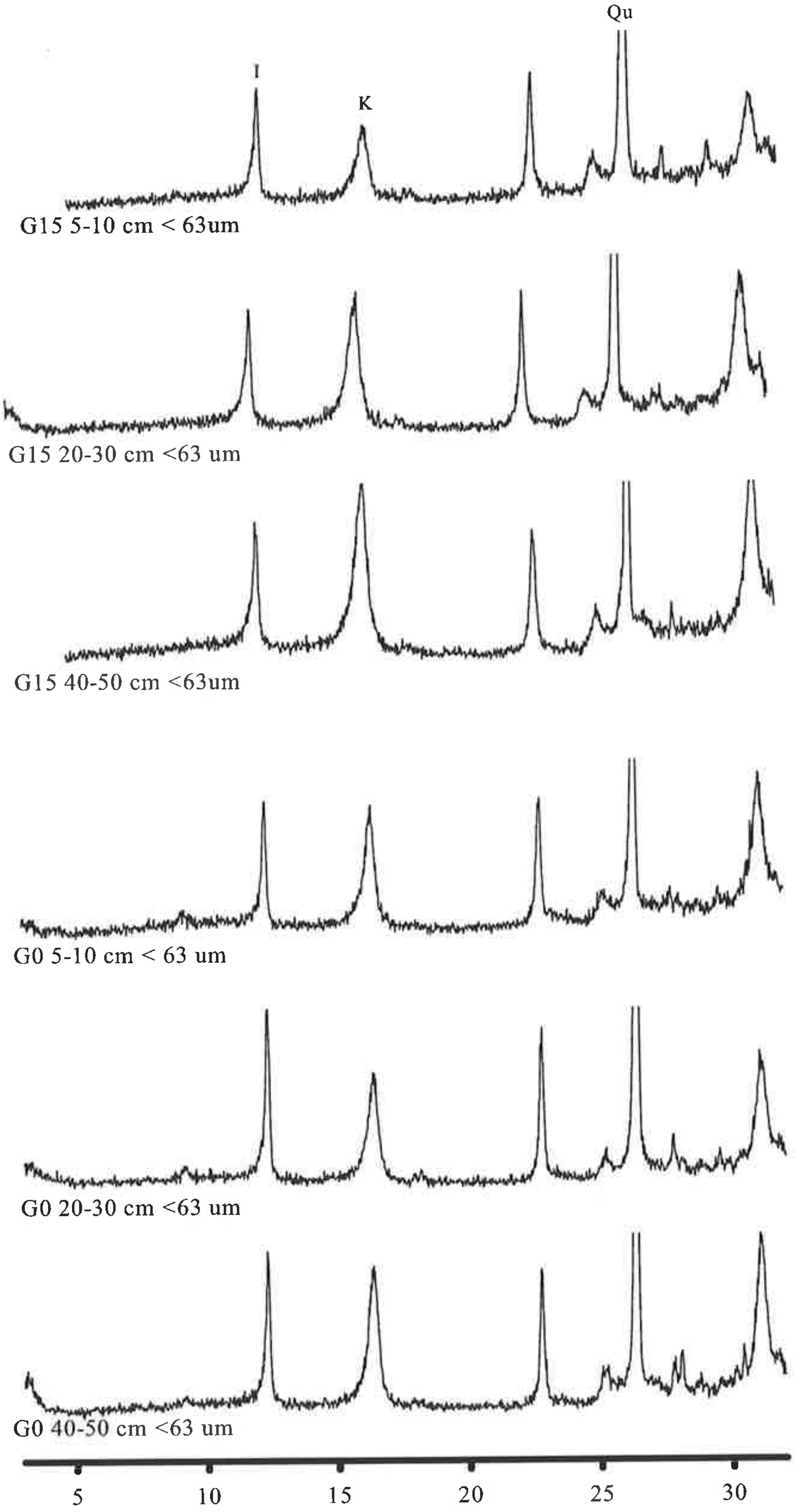

Figure 35 XRD traces of the < 63 µm fraction of G15 and G0 soils at 0 – 10, 20 – 30 and 40 - 50 cm: Oriented (MgCl/Glycerol saturated).

3.3.10 BATCH EXPERIMENTS WITH FIELD SOIL

3.3.10.1 Batch Experiment 1(field soil).

Increasing the liming rate in the field soil batch experiment led to increases in the pH of the suspension from approximately pH 5.0 with no lime to pH 7.0 at an equivalent experimental liming rate of 9 t/ha. The highest percentage of P removal from solution was achieved with gypsum and lime at the highest rate (99.3 %): P removal was 97.7 % with gypsum alone (Table 25). Gypsum with no lime, reduced the pH from 5.7 in the control (no lime, no gypsum) to 5.0, and retained P more effectively than with no gypsum both in the absence of lime or lime at 3 t/ha.

Table 25. Summary of results from batch trial 1. Standard deviations are calculated from 3 replicates. Gypsum and liming rates (t/ha*) calculated (see methods), initial P concentration 4.14 mg/L.

Gypsum t/ha*	Lime t/ha*	pH	S.D.	Final P concentration. mg/L	S.D.	Percentage P removed	S.D.	mg P removed per kg soil	S.D.
10	9	6.95	0.015	0.028	0.0036	99.3	9.0E-04	4.11	3.61E-03
10	3	5.79	0.026	0.050	0.0032	98.8	8.0E-04	4.09	3.21E-03
10	1	5.30	0.012	0.081	0.0017	98.0	4.0E-04	4.06	1.73E-03
10	0	5.03	0.015	0.096	0.0006	97.7	1.0E-04	4.04	5.77E-04
0	3	6.35	0.049	0.623	0.0208	84.9	5.0E-03	3.52	2.08E-02
0	0	5.70	0.025	0.923	0.0321	77.7	7.8E-03	3.22	3.21E-02

3.3.10.2 Batch Experiment 2 (field soil).

The results from the second field batch experiment are presented in a plot of gypsum application rate and equilibrium P concentration and pH (Figure 36). Suspension pH declined from pH 5.8 to 5.3 as the gypsum rate increased from 0 to 80 t*/ha. P removal was clearly higher in the gypsum treatment. There was very little difference in P removal (or equilibrium P) between the lowest and highest gypsum treatment.

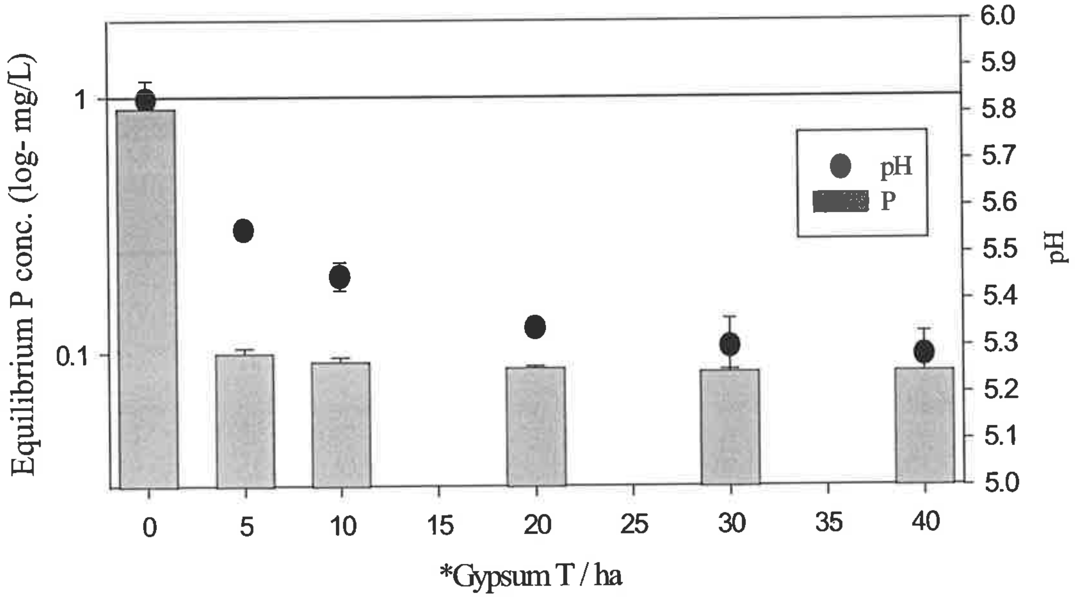

Figure 36. Effect of varying gypsum application rate on P removal from suspension.

3.3.11 SOIL PHYSICAL FERTILITY

3.3.11.1 Bulk Density and Porosity

From the bulk density measurements the porosity was calculated, with the results presented in Table 26. These results indicate a lower bulk density in the gypsum treated G15 soil, with a corresponding increase in porosity, compared to G0. This trend appears to run through the profile, but diminishes with depth.

3.3.11.2 Soil Water Retention Characteristic

The results of the soil water retention at field capacity (FC at 10 kPa), wilting point (WP at 1500 kPa) and an intermediate value (1000 kPa) for G15 and G0 at depths 0-10, 20-30 and 40-50 cm are presented in Table 26. This Table also presents the calculations of plant available water (PAW = FC-WP) and air filled porosity (AFP = Total Porosity – FC). This shows the water content at wilting point is higher in G15, indicative of a larger content of very fine pores. This higher proportion of very fine pores largely accounts for the greater total porosity in G15.

Table 26. Bulk density (ρb), porosity, air filled porosity (AFP), plant available water (PAW), and water content at field capacity (FC) and wilting point (WP).

Site	Depth (cm)	Water Content (%) (SD< 1%) FC	Intermediate	WP	PAW (mm/m)	AFP (%)	Porosity (%)	ρb (g/cm^3)
G15	0-10	51.6	39.7	20.4	31.2	14.5	66.08	0.88
G0		49.2	36.1	14.3	34.9	10.4	59.60	1.05
G15	20-30	31.7	26.8	19.1	12.6	15.4	47.05	1.38
G0		27.3	22.1	13.2	14.2	12.3	37.73	1.57
G15	40-50	32.4	27.6	20.7	11.8	12.4	44.80	1.44
G0		32.1	24.9	18.0	14.1	10.3	42.38	1.50

3.3.11.3 Aggregate Stability

Results of aggregate stability measurements as indicated by slaking are presented in Table 27. These results indicate that at the surface the aggregate stability is very similar between G15 and G0, with 98.3 and 97.1 % of the water stable aggregates respectively being greater than 2 mm and less than 1.5 % in both soils being smaller than 0.25 mm in diameter. As the depth increases (20-30 and 40-50 cm) there is a relative increase in the stability of aggregates from G15 compared with G0.

Table 27. Estimation of water stability of soil aggregates.

Site	Depth (cm)	Percentage (%) of water stable aggregates of different size fractions > 2 mm	1-2 mm	1-0.5 mm	0.5-0.25 mm	< 0.25 mm
G15	0-10	98.34	0.28	0.19	0.11	1.09
G0		97.12	0.78	0.33	0.33	1.44
G15	20-30	92.10	1.14	0.59	0.32	5.85
G0		52.54	5.50	2.76	4.07	35.13
G15	40-50	76.73	8.32	7.67	5.02	2.25
G0		32.06	4.29	9.74	11.31	42.60

3.3.11.4 Penetrometer Resistance

A plot of cone resistance (bar) versus depth for the soils of G15 and G0 is presented in Figure 37. With the possible exception of the top 3.5 cm, there appears to be no treatment effect of gypsum on soil strength, with a large degree of overlap in the standard deviation of triplicate samples between G15 and G0. Despite this there is a trend toward a reduction in mean soil strength with depth on the gypsum treated G15 soils.

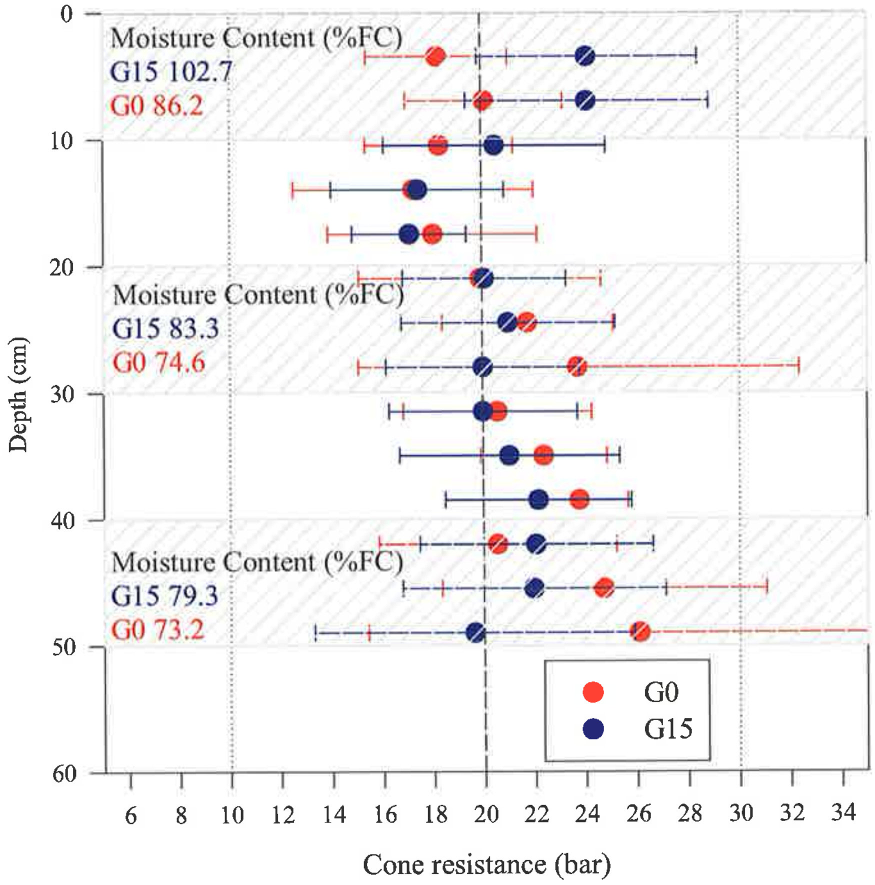

Figure 37. Cone penetrometer resistance.

3.4 DISCUSSION

3.4.1 SOILS: GENERAL

The darker profile of the gypsum treated soil may be a consequence of both inherited and treatment effects. Classification prior to gypsum application (Chapter 2) showed the natural condition of the soil of the upper 50 cm of G15 was slightly darker. Soil colour classification (using the Munsell® system) is broken into chroma (colour), value (lightness) and hue (strength). Prior to gypsum treatment the G15 soils had values up to 1 unit lower than G0: chroma and hue were similar. Although soil colour classification is somewhat subjective and differences between examiners are common, there were notable differences between soil colours 4 yr after gypsum application in so far as G15 soils have values and hues generally 2 units lower than G0. This darkening of G15 relative to G0 was attributed to a combination of the increase in SOM (particularly in the region 20 to 40 cm) along with enrichment of Fe (n.b. 30-50 cm).

The notably lower pH_w observed in the gypsum-treated soils was attributed to a salt effect. This was supported by the measurements of soil EC that are significantly greater in the gypsum treated soils, and by pH_{Ca} measurements that were not reduced to the same extent. A similar effect of gypsum on pH_w has been reported by Aitken *et al.* (1998). Gypsum treatment had little impact on pH_{Ca} in the upper 20 cm, below this depth however there was a slight pH reduction that may be attributed to gypsum. At 20-30 cm the pH_{Ca} was reduced by approximately 0.2 by gypsum: this difference is reduced to 0.1 from 30 to 50 cm. The order of magnitude and direction of this change, (either a decrease as observed here, or an increase as observed in other studies (Pavan *et al,*. 1984)) is within the range typically observed with gypsum treatments (Shainberg *et al,*. 1989). The pH reduction was most likely a result of H^+ released in exchange with Ca^{2+} sorption exceeding the OH^- released in exchange with SO_4^{3-}. The opposite mechanism occurs with observed pH increases (Pavan *et al,*. 1984). This may also account for the higher pH observed in the upper 5 cm of the gypsum treated soils. When there is no effect on pH this exchange mechanism is in equilibrium (Bolan *et al,*. 1993).

The increase in adsorbed cations throughout the profile following gypsum treatment is the most probable explaination for the observed reduction in soil pH (cations exchanging with and releasing adsorbed H^+ at the mineral surface). This was achieved through an overall increase in exchangeable Ca, which occurred in excess of the simple exchange of Ca for Na, K and Mg. This is confirmed by the results of Ca exchangeable cations, that in addition to these three (Na, K and Mg) cations, similar effects have been observed for Mn and Al.

Greene and Ford (1985) noted that the overall effect of gypsum on cation properties is progressive exchange of cations by Ca as gypsum is steadily leached down the profile. Similar processes were observed in the soils of this study. The effect of the Ca supplied in the gypsum treatment on Mn, K, Mg and Al appears to have been to simply displace these Ca-exchangeable cations from the upper 5 to 10 cm to lower in the profile (20 cm for Mn and Al, 30 cm for K, and 40 cm for Mg). Exchangeable Na is lower and less variable throughout the profile in treated than untreated soils, suggesting that Ca for Na exchange has taken place to at least 50 cm.

3.4.2 EFFECT OF GYPSUM ON P RETENTION

Results from the field trial and the batch experiments utilising similar soils show the potential of gypsum as an ameliorant for reducing P transfer from soil to water. The results of both indicate that P retention (or the P sorption capacity of the soils) was substantially enhanced by gypsum soil amendment.

In the field the distribution of P reflected the distribution of total and exchangeable Ca and Al, with the total and extractable P greater in the surface 5 cm of the untreated soils. The lower P content of the upper 5 cm of the treated soil is explained by a number of factors: a) differences in mineralogy (a much higher coarse sand content in the treated soils); b) exchange of Al^{3+} by Ca^{2+}, reducing net surface charge; and, c) competition between SO_4^{2-} and PO_4^{3-}. Given the pH of these soils the third factor (c) would only have very limited impact. Below 5 cm the soils of the treated soils had greater total and extractable P concentrations, with the only fraction greater in the untreated soils being the residual P. A common perception of increased P retention in the presence of high concentrations of Ca is via the precipitation of Ca phosphates. This would seem unlikely at the low pH of these soils, a prediction confirmed by relatively indifferent concentrations of HCl-extractable P in both soils. The differences between P content of treated and untreated soils is characterised by greater NaOH-extractable (or chemisorbed) P in treated soils. This suggests that the mechanism of P retention is through chemisorption of P on Fe and Al either through adsorption or surface enhanced heterogeneous precipitation (see Chapter 6: Precipitation). The increase in exchangeable Al below 10 cm (for example) is evidence that adsorption may be an important mechanism by that P is retained and this adsorption is promoted by increased surface charge. Additionally, the data support the mass exchange of Ca for Fe and Al model observed and described by Stout *et al,*. 1998; 2000 and Callahan *et al,*. 2002.

The importance of Mn is rarely thought of in studies of P mobility, but should be considered. Boyle and Lindsay (1986) found that, given the right pH and redox conditions (pH < 7.2; pe + pH = 13.5 to 17), $MnPO_4 \cdot 1.5H_20$ was more stable than hydroxyapatite and thus capable of controlling soil-solution P concentration. Strong support for the potential of such a mechanism is evident in the observation that the amount of Mn retained in treated soils below 30 cm exceeds the content in untreated soils (by 600 mg/kg). This amount could easily account for the entire excess of P (90 mg/kg) at the same depth in treated soils.

In addition to increasing P retention $NaHCO_3$-extractable (or plant-available) P was similar in both profiles indicating that gypsum treatment had no or only a minor effect on soil fertility in terms of P availability.

It is concluded that the addition of gypsum has increased the ability of the soils to retain P by the exchange of Ca for Al, Fe and Mn. The release of these cations into solution in the upper 10 cm of soil and their subsequent accumulation in lower horizons have increased the retention capacity of the soil at this depth. The reduction of P in the surface soil may also be important from an environmental point of view, in as much as high P levels in surface soils, regardless of the form of P (dissolved or particulate), will be more susceptible to loss through dissolution and erosion in surface flow.

3.4.3 EFFECT OF GYPSUM ON SOM RETENTION

The distribution of SOM between treated and untreated soil had a very similar pattern to that of P in that at the surface it was greater in the surface of G0 (to 10cm), and below this depth was in higher proportion in treated. Similar explanations for the lower P content of the surface soils can be used to explain the SOM distribution. Competition from SO_4^{2-} may be more important in the case of SOM (Belkacem and Nys 1995). As for P, this redistribution of SOM has important implications in terms of water quality as lower SOM in the surface leaves these soils less susceptible to contributing to high OM loads in runoff water. The total organic content of the top 50 cm of the treated profile exceeds untreated, suggesting that rather than simply a redistribution of SOM, the treated soils have a greater capacity for NOM retention. Importantly this results in reduced NOM contents of soil leachates and surface runoff (see Chapter 4). The lower proportion of residual (char) and thus higher proportion of freshly deposited SOM in the treated soils at 20-30 cm and 40-50 cm, as indicated by ^{13}C-NMR data, supports the concept that gypsum treatment increased the retention of organic matter. This is evidence that the application of gypsum has increased the soils capacity for SOM retention; the mechanism will be discussed in more detail in section 3.4.4.

3.4.4 ELEMENTAL AND OM DISTRIBUTION AMONGST FINES (< 63 µM)

The similarity of both chemistry and mineralogy of the < 63 µm of the treated soils (20-30 and 40-50 cm) to the < 20 µm of both treated and untreated soils suggests that this fraction is composed of micro-aggregates of flocculated clays (Figure 38). In contrast the same fraction in untreated soil (< 63 µm) is dominantly composed of coarser material of different mineralogy i.e. more silica based. The higher organic content of the coarser fraction (< 63 µm) compared with the fine fraction (treated < 20 µm), of the gypsum treated soils, whilst surprising, supports the model of Muneer and Oades (1989 a,b) for the formation of clay humic complexes with Ca^{2+} (or other polyvalent cations) acting as a cation bridge. Al, Fe and Mg are all in greater concentration in the coarser fraction, a fact that supports the argument that these may be important constituents in such aggregation, more so than Ca. The higher P content of the larger fraction (< 63 mm), whereas not definitive due to the use of a phosphatic dispersant, is indicative that in the process of aggregation phosphate was incorporated. This is supported by the higher content of NaOH physically protected (sonicated) extractable P fraction. The formation of these aggregates may also have important implications in the distribution of pores in the soil, and soil physical fertility.

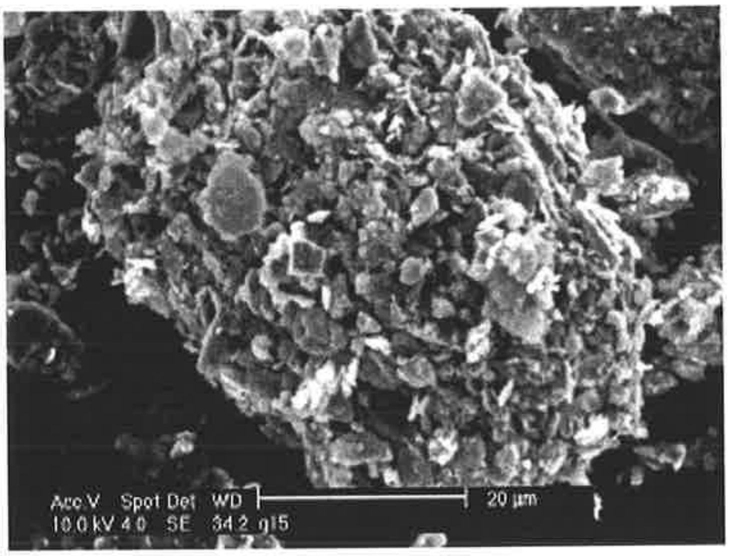

Figure 38. SEM micrograph of a soil aggregate (≈ 40-60 µm diameter) from gypsum treated soil.

3.4.5 SOIL FERTILITY

3.4.5.1 Soil Chemical Fertility

It would generally be considered that increasing the soil's retention of P would reduce the availability of this vital nutrient to plants. However in these soils plant availability of P has been unaffected by gypsum treatment; in fact through 10 to 30 cm slight increases in Olsen P ($NaHCO_3$ extractable) were measured in the G15 profile.

Compared to the untreated soils, significant reductions in exchangeable Mg and K were observed throughout the gypsum-treated soils, which were complemented by large increases in exchangeable Ca. This increased the Ca:Mg at 5-10 and 20-30 cm doubled from approximately 1.8 and 1.5 (untreated) to approximately 3.6 and 2.9 (treated) respectively. The difference in the Ca:Mg values at 40-50 cm was almost negligible at 1.0 (G0) and 1.24 (G15). Reid (1996) and Hailes *et al.* (1997) indicate that plant yields will be unaffected over a wide range of Ca:Mg ratios, provided there is sufficient exchangeable Mg is high enough. According to results of various studies summarised in Aitken and Scott (1999), the exchangeable Mg in both Mt. Bold soils are vastly in excess of critical minimum concentration (of the order 0.2 cmol/kg). Graley (1978) found, in glass house pot experiments, that the marginal concentration of exchangeable K for Perennial Ryegrass was 0.2 $cmol_+/kg$, with concentrations > 0.25 cmol/kg being adequate. Given these results, the reduction in exchangeable K with gypsum did not lead to exchangeable K deficiencies: reductions were in the range 0.67-1.30 to 0.40-0.63 $cmol_+/kg$.

With pH_w measured in the untreated soils at less than 5.5 (0-30 cm), Al toxicity may be a relevant property limiting growth in these soils. Depending on crop type a variety 0.01 M $CaCl_2$-extractable Al rates have been found to be toxic. Results published in Slattery *et al.* (1995) suggest that above 4-5 mg/kg 0.01 M $CaCl_2$-extractable Al may be considered limiting in crops such as Phalaris (Helyar and Conyers, 1994; Ridely, 1995), Cocksfoot (Helyar and Conyers, 1994) and Wheat (Geeves *et al,*. 1992). From these results, it appears that the untreated G0 soils have extractable Al levels in the upper 10 cm near 4 mg/kg, which is on the borderline of being limiting. Gypsum treatment had a significant impact on reducing this to < 2.2 mg/kg throughout the entire profile.

In addition to reduced Al toxicity, gypsum may improve soil chemical fertility through reducing Mn toxicity. Slattery *et al.* (1995) report levels of 0.01 M $CaCl_2$-extractable Mn of less than 10 mg/kg to be non toxic to a variety of crop types (barley, wheat or triticale). According to Uren (1999), Mn toxicity in canola with low pH ($pH_w < 5$) is associated with soils that have 0.01 M $CaCl_2$-extractable Mn > 20 mg/kg. Taking these estimates as toxicity levels, it appears that the soils of Mt Bold are at risk of plant yields being negatively affected by the high extractable Mn levels (≈ 60 mg/kg at 0-10 cm) in these soils. This was significantly reduced in the gypsum-treated soils to approximately 20 mg/kg in the upper 10 cm.

3.4.5.2 Soil Physical Fertility

According to Sumner (1993b), the exchangeable sodium percentage (ESP) of a soil that renders it sodic is in the range 5 to 6: whereas these soils both treated and untreated do not exceed this level, the untreated soils approach these values at 40-50 cm (5.1 %) and are slightly above values higher in the untreated profile (approx 4 % at 5-10 and 20-30 cm). The ESP in the G15 soils never exceeded 3 %.

According to Rengasamy and Churchman (1999) sodicity cannot be assessed by a single index such as the ESP: it is better defined by the dispersion and swelling behaviour of the soils. Both SOM and electrolyte concentration in the surface soils were high, as was the water stability of the aggregates in both untreated and treated soils. With depth, both values for these properties decreased more in the untreated than the treated soils, and it is concluded that the combination of increased electrolyte and SOM have contributed to significant changes in the physical character of the gypsum-amended soils. Improved stability is more a result of high ionic strength than gains in SOM, given the negligible gains in SOM in treated soils at 40-50 cm. At this depth, the stability of the aggregates is still notably greater in the treated soils than untreated soil.

The changes in the soil physical properties were not only limited to aggregate stability, but affected pore structure also. There was an overall increase in porosity and a corresponding reduction in bulk density throughout the treated profile. Gypsum treatment appears to have increased the number of very small pores, below what is accessible to plants. It is proposed that this increase in fine pores is a result of the flocculation of fine clay aggregates. This was discussed previously. As a result, and in spite of the overall increase in porosity, PAW was reduced, but the deleterious effects of this were offset by improvements in AFP (Figure 39) with the PAW:AFW ratio of the surface 10 cm improved from moderate-good to good-very good. There was no significant effect on soil strength as measured using the soil penetrometer.

Although the observed increase in soil EC in the gypsum-treated soils may have been a factor in improving soil structure, it is a concern in terms of soil fertility. According to Maas and Hoffman (1977), sensitive crops would suffer a 10 % yield reduction with $EC_{1:5}$ exceeding 90 $\mu S.cm^{-1}$. Some detrimental effects from the elevated soil salinity were likely. There would be less or no negative effects for more tolerant crops where $EC_{1:5}$ was generally less than 150 $\mu S.cm^{-1}$ at depths > 20 cm.

An additional benefit from a hydrologic perspective is the improved wettability of the surface soils with gypsum treatment (Figure 40). Observations illustrated in Figure 40 indicate that the water repellence of the non-gypsum treated soils is greater than that of the gypsum treated soils. As can be seen in Figure 40, the wetting front penetrated the G15 soil in 5 min, whereas the wetting front had penetrated approximately one third of the untreated soil. Chittleborough *et al.* (1992) explained surface hydrophobic conditions at the break of winter to be caused by hydrophobic components of organic matter. The lower organic content in the surface of gypsum-treated soil may explain the improved wettability of this soil.

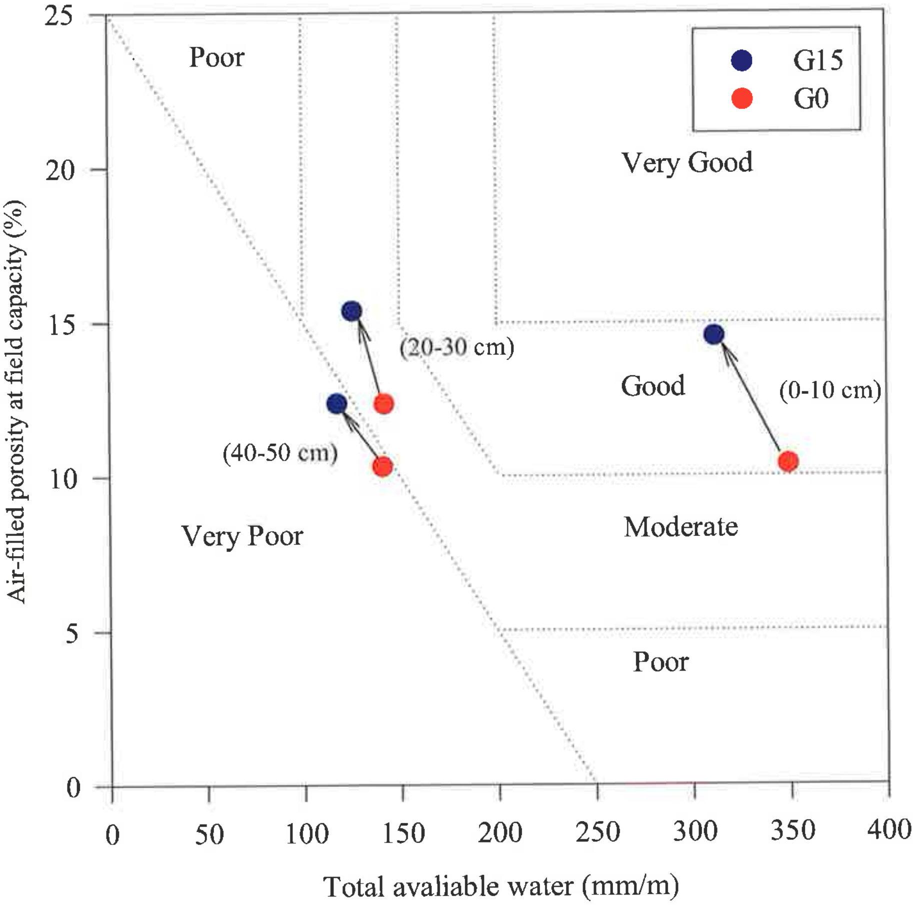

Figure 39. Relative differences in AFP:PAW resulting from gypsum treatment.

Figure 40. Illustration of the wettability of the gypsum treated and untreated surface soils.

3.5 CONCLUSIONS

Results from this study show benefits from gypsum application, not only for water quality- but also soil quality. Both physical and chemical properties of the soil were markedly different between treated and untreated soils. Increases in total exchangeable cations in the soil provided an increased sorption capacity for both P and NOM, and therefore potentially reducing the transfer of these constituents to water.

The release of Ca from gypsum at the surface have exchanged with Al (and other cations) that subsequently were released into the soil solution, and transferred deeper into the profile. The anion sorption capacity at depths >20 cm was increased as a consequence of increased exchangeable cations, itself the result of adsorption of these released cations as well as Ca. The sorption capacity may have been further enhanced through the precipitation of new mineral phases (i.e. Al sulfates). The enhanced anion sorption capacity of the soils at depth has enabled the formation of micro-aggregates (size ≈ 50 µm) by the incorporation of organic matter, in a manner similar to podzolisation. These micro-aggregates appear to be significant repositories of NOM and P. Importantly the formation of these micro-aggregates proportionally rich in P and NOM reduce the potential for loss of nutrient from the soil through mobilising by both water, and if exposed even wind.

The retention of these constituents combined with the higher exchangeable Ca, reduced exchangeable Al and no reduction in exchangeable Mg (in the short term), leads to the conclusion that gypsum has improved the chemical fertility of these soils. Additional potential benefits to soil physical fertility were:

1. improved soil structure (particularly aggregate stability); and
2. a small reduction in PAW lead to a complementary increase in AFP, that may have benefits for soil fertility.

In addition to the potential for long term reduction in exchangeable Mg, some caution is required when using such high rates of gypsum (15 t/ha) on the ionic concentration or EC of the soils. In the authors view this is the main risk to soil fertility associated with this method of amelioration.

The results of this study indicate that on these soils, the addition of large quantities of gypsum (15 t/ha) could be beneficial to both soil and water quality. The following chapter reports the impact gypsum had on the water quality of soil leachates and surface runoff at the Mt Bold field site.

4 Effect of Gypsum on Leachate Chemistry

4.1 INTRODUCTION

Some general effects of gypsum application to soils on the soil solution chemistry were summarised by Sumner (1993). These are (1) a slight increase in pH (2) an increase in total Al (usually as $AlSO_4^+$) with a decrease in Al^{3+} activity and (3) increases in the concentration and activity of Ca^{2+}. O'Brien and Sumner (1988) found that while exchangeable Al was reduced in soils following subsoil acidity amelioration with phosphogypsum, the leaching of Al could not account for this reduction. They accounted for reduced Al activity through the formation of alunite ($KAl_3(SO_4)_2(OH)_6$). The increase in pH following gypsum application is explained by the release of OH^- into solution following exchange with sulfate (Shainberg *et al,*. 1989). Increased leaching of Mg and K has also been noted as an effect of gypsum soil amendment (Shainberg *et al,*. 1989; O'Brien and Sumner, 1988; Pavan *et al,*. 1984). Increased leaching of Na may also be expected, particularly in soils with a high exchangeable Na content, i.e. sodic soils (Rengasamy *et al,*. 1984). O'Brien and Sumner (1988) noted increased leaching of Si in cores treated with phosphogypsum.

4.1.1 WATER QUALITY

4.1.1.1 Phosphorus (P)

Callahan *et al.* (2002) and Stout *et al.* (1998; 2000) found that industrial by-product gypsum (e.g,. flue desulphurisation by-product [FDG]) was effective in reducing the water extractable P (WEP) of soils, without affecting the plant availability of P. The mechanism appears to be pH dependent (Stout *et al,*. 1998 and Stout *et al,*. 2000). These authors concluded that the release of Fe and Al was from cation exchange with Ca in acid soils, that in turn form insoluble Fe- and Al- phosphates. In higher pH soils, the formation of Ca-phosphates is favoured. Stout *et al* (2000) found that this mechanism was only effective in limiting P loss in surface runoff when erosion was controlled.

4.1.1.2 Natural Organic Matter (NOM)

As has been previously discussed (Chapters 1 and 3) there is much conflicting evidence over the effect of Ca on NOM retention in soil. Some studies found when agricultural lime ($CaCO_3$) was used as a Ca source, NOM leaching increased (Karlik 1993; Belkacem and Nys 1995). When gypsum was trialled as a Ca source, Belkacem and Nys (1995) also found that NOM leaching was increased over their non-treated control soils. Various studies have found direct and indirect evidence for Ca decreasing NOM solubility (Nelson *et al,.* 1991, Romkens and Dolfing 1998 and Muneer and Oades 1987a,b). This conflicting evidence has been explained as a consequence of changes to pH (particularly with liming) promoting less favourable NOM adsorption conditions (Karlik 1993, Jardine *et al,.* 1989), or more favourable conditions for microbial activity, both leading to increased NOM leaching. Differences in results can also be a consequence of the nature of the organic matter. Romkens and Dolfing (1998) demonstrated the effectiveness of Ca in flocculating high molecular weight (HMW) organic compounds and found that there was little effect of Ca on low molecular weight (LMW) organic matter solubility. Clarification of the effect of Ca (hence gypsum) on NOM may come through a more in depth understanding of changes in character of NOM following gypsum treatment.

4.1.1.2.1 Characterisation of NOM in Water

Traditionally, the principal methods for characterisation of soluble humic substances in water were by non-specific parameters such as DOC concentration, absorbance of ultraviolet light (e.g,. at 254 nm- referred to as UV_{254}) and visible light (e.g. absorbance at 456 nm).

Absorbance at wavelengths longer than 200 nm is attributed to organic molecules that contain conjugated multiple bonds, such as aromatic compounds. Benzene is regarded has having maximum absorbance at wavelength near 255 nm (Solomons, 1984). Randtke (1988) found UV_{254} corresponds to the range of maximum absorbance for most phenols and carboxylic acids. Measurements of changes in colour and UV_{254}

were used by Hine and Bursill (1985) to demonstrate changes in the character of dissolved organic matter (DOM) in several South Australian reservoirs. In particular, they found increases in these parameters following heavy rain.

Page (2001) found that there was very little difference in the UV-vis spectra of reservoir waters in the southern Mt Lofty ranges, including Mt Bold. He concluded that specific ultra-violet absorbance (SUVA) was a more informative parameter than UV_{254}. SUVA is the ratio of UV_{254} to DOC multiplied by one hundred. The relationship between UV_{254} and aromatic compounds or molecules with conjugated double bonds means that SUVA gives a measure of the character of DOM with respect to these constituents (i.e. aromatcity). Likely sources of aromatic structures that result in high SUVA values in reservoir waters are terrestrially (allochthonous) derived DOM (i.e. lignins and tannins) (Hine and Bursill, 1985; Krasner *et al,*. 1996; Page, 2001)

The colour of water can be measured at 456 nm (Bennett and Drikas, 1993). This property is effected by the presence of compounds with a large number of conjugated multiple bonds. For example polyenes with eight or more conjugate double bonds adsorb light in the visible region of the spectrum. An example of such a molecule is β-carotene that has an absorption maximum at 497 nm (Solomons, 1984). Wavelengths at 497 nm correspond with the blue green region of the spectrum, meaning that substances that are rich in β-carotene, such as carrots, exhibit the complementary colour of red-orange. Colour is an important parameter in assessing water quality in water treatment as the Australian Drinking Water Guidelines (ADWG; NHandMRC and ARMCANZ) state finished water (post treatment) should have a maximum of 15 Hazen Units (HU). Colour measurements of natural waters may also be influenced by naturally occurring soluble iron (Hine and Bursill 1987). As, SUVA is a more useful parameter than UV_{254} , so too is specific colour a better characterisation parameter of DOM than true colour. Specific colour is a ratio of colour (HU) to DOC, which gives details of the character of DOM.

In addition to SUVA and specific colour, carbon : nitrogen ratios (C/N ratios) maybe useful indicators of the origin of organic matter. High C/N ratios are indicative of a high input of organic matter from allocthonous sources such as vascular or cellulosic plant debris (Ertel and Hedges, 1985; Meyers and Ishiwatari, 1993; Croue, 1999). Meyers and Ishiwatari (1993) demonstrated that the C/N ratio is fundamentally affected by the presence or absence of polysaccharides from plant sources of organic matter. In contrast to vascular plants, non vascular plants such as algae have typically low C/N ratios.

While SUVA and C/N ratios provide valuable information, particularly on the origin of DOM inputs, they provide little information of the molecular structure of the DOM. Common methods of molecular characterisation of organic material in waters are pyrolysis-GC/MS, C^{13} NMR and Fourier Transform Infrared (FTIR) spectroscopy.

Analytical pyrolysis techniques have been extensively used for the analysis of organic materials that are not amenable to chromatographic or analytical chemical techniques without additional degradation or fractionation steps (Page, 2001). Analytical pyrolysis was developed through the combination of pyrolysis with methods such as gas chromatography with mass spectrometry. In this study, this technique was used as the high ionic strength of the leachates derived from the gypsum treated soils precluded these samples from other characterisation techniques such as C^{13}NMR or FTIR, without pre-treatment to desalt the samples. Additionally only small sample sizes are required for pyrolysis-gas chromatography/ mass spectrometry (Py-GC/MS). Pyrolysis thermally degrades the DOM into smaller fragments that can be separated by gas chromatography and identified by mass spectrometry. This method generates a pyrogram that constitutes a fingerprint of the sample and gives information on the relative amounts of the pyrolysis by-products that may reflect the biopolymer composition.

C^{13} NMR is useful in determining relative quantities of carbonyl, aromatic o-alkyl and alkyls. This technique is the same as that described for soils and is covered in more detail in Chapter 3. FTIR is also commonly used for the characterisation of NOM in both water and soils. Some work by Spark *et al.* (1998) presents some results from FTIR analysis of leachates from the Mt Bold site (in this Chapter). This methodology suffers limitations in terms of high salt contents and as a result could not be applied to this study following gypsum application.

4.1.1.3 Importance of NOM in Water Quality: Implications for Treatment

Important water quality considerations for the water treatment industry include reducing or eliminating the potential for the formation of disinfection by-products (DBP) and bacterial regrowth in distribution systems in post treated water. Of the DBP formed, the focus has been on the potentially carcinogenic trihalomethanes (THMs) and other halogenated compounds (Simpson and Hayes, 1996). It was discovered in the 1970s that the reaction of some compounds comprising NOM reacted with free chlorine (used in water disinfection) to form THMs that significantly altered the focus to NOM removal in water treatment (Randtke, 1988). Additionally, of the DBPs, the THMs are produced in the highest concentration (Simpson and Hayes, 1996). In comparing different water sources Galapate *et al.* (1999) was not able to establish a strong relationship between total DOC concentration and THM formation potential (THMFP). From this it can be postulated that the chemical character of the DOM and other solutes, along with the chlorine dose, temperature, pH play an important role in THM formation (Chapra *et al,*. 1997; Rathburn, 1997; Galapate *et al,*. 1999). The remainder of this discussion relates specifically to the effect organic character on the formation of THMs.

According to Galapate *et al.* (1999) properties such as colour and UV_{254} give an insight into the chemical reactivity of DOM. Page (2002) found a positive correlation with THMFP and colour and UV_{254}. Page (2002) goes on to qualify the relationship between UV_{254} and THMFP as being due to the gross representation of phenolic substances (such as benzoic acids) in SUVA that are known THM precursors (Norwood *et al,*. 1987). Similarly, Marahaba and Pipada (2000) found that humic or aromatic compounds have generally a higher potential to form THMs than non-humic hydrophilic substances. From this it can be concluded that coagulation with alum, that is shown to be effective in removing these fractions, can reduce the potential for THM formation in subsequent disinfection. DBP's can also be removed following disinfection (i.e. using activated carbon) this is of considerable expense and the removal for NOM prior to disinfection remains the best option of control (Simpson and Hayes, 1996).

Coagulation of DOM with alum, preferentially removes the HMW aromatic compounds, leaving less aromatic LMW components that are more readily utilized by bacteria as a substrate for growth (Page, 2001). C/N ratios have been used by Findlay and Sinsabaugh (1999) and Hunt (2000) as an indicator of bacterial regrowth potential. Similarly Page (2001) found that samples with higher C/N ratios tended to have higher growth potentials. It is concluded that low C/N ratio represents highly degraded organic matter, that result in a low potential for a substrate of bacterial growth.

4.1.2 WATER TREATMENT

The removal of suspended matter (both organic and inorganic) is one of the major goals of water treatment, with only disinfection used more widely or considered more important (Ravina 1991). Coagulation, flocculation, settling and filtration are the process used in water treatment to achieve water clarification. As stated earlier there are a number of reasons why NOM removal from domestic water is essential in water treatment ranging from asthetic, taste and odour improvement to reducing health risks (such as THM formation and synthetic organic chemicals [SOC] contamination). Other reasons include reducing negative impacts on distribution systems such as corrosion or bacterial re-growth (to that P, as a nutrient, may also be a significant contributor). Another purpose of water treatment is to remove inorganic particulates.

4.1.2.1 Coagulation and Flocculation

Ravina (1991) defines coagulation taking place when the DLVO (named after Derjaguin, Landau, Verwery and Overbeek) energy barrier is effectively eliminated - (this is known as destabilization). The DLVO theory looks at the balance between the opposing forces of electrostatic repulsion and van der Waals attraction (Ravina, 1991). Repulsion occurs between particles when their electrical double layers overlap. The double layer of a particle includes the inner Stern layer (firmly attached layer of counter ions on the colloid surface), that is surrounded by an outer diffuse layer (a cloud of counter ions attracted by the colloid, but repelled by the Stern layer).

Flocculation has been defined by Ravina (1991) as what occurs following collisions between destabilized particles when particles are driven toward each other during rapid mixing. This leads to agglomeration of a few colloids in microflocs eventually leading to the formation of visible macroflocs.

Coagulation and flocculation occurs by double layer compression, charge neutralization, bridging or colloid entrapment (Ravina, 1991). Double layer compression is achieved by increasing the ionic strength by the addition of electrolyte, but this is not practical for water treatment for domestic supply, as the high salinity would compromise water quality (i.e. increased salinity). Charge neutralization is a commonly used method in water treatment, where inorganic coagulants like alum ($Al_2(SO_4)_3{:}18H_2O$) are used. Alum added to water results in the formation of aluminum hydrous oxides such as insoluble aluminum hydroxide and soluble hydroxides of aluminum such as $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$ (Ravina, 1991). The soluble cationic hydroxides of aluminum are adsorbed on the colloid surface, creating a charged surface coating that neutralizes the negative charge of the colloid, reducing the DLVO barrier. Bridging of particles utilizes inorganic primary coagulants (such as alum) and negatively charged organic polyelectrolytes. The organic polyelectrolytes are able to form threads of fibers that capture and bind multiple microflocs (formed following the addition of the inorganic coagulant together).

Flocculation is further enhanced by the presence of the aluminum hydroxide precipitates. The addition of these particles increases the chances of collisions occurring in flocculation, and the precipitant growth also aids in the process of colloid entrapment (*sweep floc)*. Sweep floc involves high doses of coagulants, greater than required for charge neutralisation, that precipitate as hydrous metal oxides. The colloids are removed from the water as they are trapped by the settling precipitant (floc) (Ravina, 1991).

4.1.2.2 NOM Removal in Water Treatment

In waters of high NOM concentration the first stage of water treatment is generally NOM removal by coagulation. As well as reducing the risk of THM formation with disinfection by chlorination, this may also improve the efficiency, and potentially reduce the cost of water treatment by reducing the load on filtration, activated carbon adsorption, or ion exchange mediums.

The removal of particulate NOM is most likely maximized in the same conditions that maximize turbidity reduction, particularly as most of the particles in water would at least be partially coated with organic matter (Randtke, 1988).

Dissolved NOM is generally defined as that fraction that passes through a 0.45 μm filter. As such, the dissolved NOM fraction includes two different materials, soluble NOM and fine colloidal NOM. The removal of soluble NOM provides difficulties as NOM cannot be precipitated or co-precipitated and colloidal destabilization has no impact on dissolved substances (Randkte, 1988). According to Randkte (1988) removal rates of dissolved NOM by coagulation ranges between 10 and 90%, with averages of around 30%. Removal rates will depend on both the operating conditions and the characteristics of organic matter. Although the removal of NOM by coagulation is only partially effective, Randkte (1988) reports that studies have found it to be effective in removing the fractions that are the precursors to THM formation and that cause colouration, as well as the hydrophobic SOCs. These higher MW compounds are also the fraction that present the greatest resistance to removal by activated carbon (i.e. granulated activated carbon (GAC)), and as such coagulation presents an excellent pretreatment stage in water purification. Additionally, removal of any NOM in pretreatment will generally improve the removal of SOC (and other fractions) in subsequent treatment by activated carbon, by reducing competition for adsorption sites (Randtke 1988).

4.1.2.3 P Removal in Water Ttreatment

Precipitation of P using Ca^{2+}, Fe^{2+}, Fe^{3+}, or Al^{3+} salts is the primary method of P removal from domestic waste waters (Tomson and Vignona, 1984). Salts typically used are alum, sodium aluminate ($NaAl(OH)_4$), ferric chloride ($FeCl_3$), *pickle liquor* (a steel industry by-product) ($FeCl_2/HCl$) or lime ($Ca(OH)_2$). Of these methods the precipitation of calcium phosphates using lime at pH > 9.5 is regarded as the most effective in P removal. In the pH range 7 – 10, precipitation by Fe^{2+} (pickle liquor) salts to form minerals such as vivinite ($Fe_3(PO_4)_2.H_20$ is a strongly favoured mechanism of P removal. This mechanism may also be favoured if Fe^{3+} comes into contact with organic matter under anaerobic conditions and is reduced to Fe^{2+}. In more acid conditions salts of Fe^{3+} and Al^{3+} (ferric chloride, alum, or sodium aluminate) favour the precipitation of $FePO_4$ and $AlPO_4$ in the pH range 3-7.

4.2 MATERIALS AND METHODS

4.2.1 GENERAL WATER SAMPLING PROCEDURE

The samples analysed were obtained from the surface flow and from the B/C interface leachate at Mt. Bold. Sample collection was via automatic samplers (Figure 13), programmed to sample at given changes in flow rates. The changes in flow rates used to trigger sample collection had been customised for each of the sites given their individual hydrologic characteristics, calculated from the previous and current monitored seasons.

Samples were collected within 24 hr of a flow event. A sub-sample of these was then filtered through a 0.45 μm Whatman cellulose nitrate membrane filter to isolate the dissolved fraction. Unfiltered samples and filtered samples were stored at 1-4°C (for NOM characterisation). Filtered samples for molybdate-reactive P (MRP) analysis were stored at -15°C.

Bulk elemental composition of surface runoff and soil leachates from the G15 and G0 sub-catchments was determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICPOES) on the < 0.45 μm fraction. Comparison of the compositions of the < 0.45 μm fraction with the whole unfiltered water was carried out on the final samples collected in the study (September 2002) from the B/C horizon interface flow. The whole-water sample analysed was decanted from the field-collected sample after a 7 day settling period (at < 4°C) to allow large particulate material to fall out of suspension. These were analysed by ICPOES with no further treatment. Total phosphorus (TP) in 1999 to 2001 was also measured on decanted field samples prepared in a similar fashion to the whole-water sample in 2002.

4.2.2 GENERAL ANALYTIC METHODS

4.2.2.1 Inductively Coupled Plasma Optical Emission Spectrometry (ICPOES)

ICPOES analysis was conducted at the Plant Science Department (University of Adelaide) using a ARL Inductively Coupled Plasma Optical Emission Spectrometer (ARL 3580 B, ARL Switzerland 1985). The instrument is a combination simultaneous/sequential system that was set up to simultaneously analyse all the elements in the standard "plant matrix suite". The instrument has radial view plasma. The detection system uses an array of photo-multipliers that are set in fixed positions to detect the particular wavelengths required for the standard "plant matrix suite" of 16 elements (Al, B, Cd, Ca, Cu, Fe, Pb, Mn, Mg, Mo, Ni, P, K, Se, Na, S and Zn).

4.2.2.2 Reactive Phosphate (RP)

Reactive phosphate (or molybdate reactive-P, MRP) was analysed by an automated modification of the colorimetric molybdenum blue method (Murphy and Riley, 1962) on the dissolved ($< 0.45\ \mu m$) fraction. Total P in 1998 was measured by MRP of samples neutralized following nitric perchloric acid digestion of whole water samples. This was done as the minimum detection limit of the ICPOES in 1998 was 0.34 mg/L, that was higher than many TP concentrations from surface runoff and leachates.

4.2.2.3 Chemical Speciation- Saturation Indices

Saturation indices (SI) have been used to study solution – mineral interactions in soils (Karathansis, 1991; Biddle, 1995). SI is related to the Gibbs free energy change for crystallisation, and is a measure of the thermodynamic driving force for the crystal nucleation reaction. SI is the log of the degree of saturation (Ω), that is the ratio of the ion activity product (IAP) to the thermodynamic solubility product (K_{sp}) (F5):

$$\mathrm{SI} = \log(\Omega) = \log(\mathrm{IAP}/K_{sp}) \qquad \text{(F5)}$$

$$\mathrm{IAP} = i^x \times j^y \times k^z$$

where i, j, k = activities of the species common, and

x, y, z = number of moles of each species.

When SI is negative, the solution is undersaturated with respect to the mineral components, when SI is equal to 0, there is equilibrium between the solution and mineral phase. If the SI is just greater than 0 (Si $\geq$ 0), then the mineral is metastable but unlikely to precipitate. Moderate increases in the component concentration (SI > 0) result in heterogeneous nucleation, that is aided by the symmetry of surface molecules or ions of a foreign body (Stumm 1992). Homogeneous nucleation occurs with further increases of the SI (>> 0). The specific SI(s) at that the transition from metastable mineralisation to heterogeneous and then to homogeneous nucleation take place are dependent on the nature of the precipitating phase (i.e. ion activities) and the foreign bodies present. Computer prog such as PHREEC (Pankhurst 1995), have been used by van der Houwen and Valsami-Jones (2001) to calculate the SI of hydroxyapatite (HAP) and House and Denison (2000) to calculate the activities of iron hydroxides. Similar equilibrium prog such as GEOCHEM (Sposito and Mattigod 1979) have been used by Inskeep and Silvertooth (1988) and Grossi and Inskeep (1991).

PHREEQC Interactive RCI (PHREEQC$_{RCI}$) was used in this study to calculate SI for a wide range of common minerals in aqueous systems of selected leachates. PHREEQC$_{RCI}$ is available on the world wide web (at http://water.usgs.gov/software/). It is based on PHREEQC version 2 a computer program written in the C programming language that is designed to perform a wide variety of low-temperature aqueous geochemical calculations (Pankhurst, 1995). PHREEQC is based on an ion-association aqueous model and has capabilities for speciation and saturation-index calculations. Input thermodynamic data used in these calculations were derived from a database included with PHREEQC$_{RCI}$ using the aqueous model defined by the input data file *Wateq4f.dat*. The *Wateq4f.dat* file contains thermodynamic data for the aqueous species and gas and mineral phases, that are essentially the same as WATEQ4F (Ball and Nordstrom, 1991). The SI of hydroxyapaptite was calculated using the LogK$_{sp}$ value supplied by the *Wateq4f.dat* database (-40.46) and also using LogK$_{sp}$ = -57.74 a value used by Nancollas and Tomazic (1974) and van der Houwen and Valsami-Jones (2001).

Solution compositions used in these calculations were averages of the 1998-99 soil leachates measured by ICPOES (Table 28). Input to PHREEQC$_{RCI}$ allows for direct input from a common spreadsheet compatible with ICPOES result files, using the standard units presented (mg/L).

4.2.3 NOM CHARACTERISATION

4.2.3.1 Dissolved Organic Carbon (DOC)

DOC concentrations in water samples were measured using either a Skalar Model SK-12 TOC Analyser or a Sievers Model 820 TOC Analyser. Using the Skalar Model SK-12 TOC analyser, DOC is oxidised by persulfate UV irradiation, and the carbon dioxide formed is reduced to methane with hydrogen using a nickel catalyst at 400°C. The methane was then measured with a flame ionization detector. The Sievers Model 820 TOC analyser incorporates UV / persulfate oxidation. The organic derived CO_2 was measured by conductivity.

Comparisons were made between the DOC methods to determine if the high salt concentrations of the leachates from the gypsum-treated site affected DOC measurements. The Sievers instrument measures DOC as CO_2 in a conductivity cell and it was considered that the high salts in the gypsum-treated soil leachates might impair DOC measurement by this method. No effect on DOC measurement from gypsum was detected.

4.2.3.2 Colour and UV_{254}

For colour and UV_{254}, measurements were made on the < 0.45 μm fraction. Absorbance at 254 nm (UV_{254}) of the filtered sample was measured using a Perkin-Elmer Lambda 2 UV/Vis spectrometer (Perkin-Elmer GmbH, Dusseldorf, Germany). Specific ultra violet absorbance (SUVA) was calculated as the ratio of UV_{254} to DOC multiplied by one hundred. Colour, in Hazen units (HU) was determined from absorbance at 456 nm (Bennet and Drikas, 1993). Specific colour was calculated as the ratio of colour (in HU units) and to DOC.

4.2.3.3 Total Kjeldhal Nitrogen (TKN)

Total Kjeldhal nitrogen (TKN) (organic nitrogen) was determined using automated flow colourimetry. Organic nitrogen was converted to ammonium sulfate by digestion with sulphuric acid and potassium sulfate. The ammonia reacts with dichloroisocyanate to form monochloroamine that then undergoes oxidative coupling with salicylate to form an indophenol dye, the concentration of that was determined by measuring the optical density at 630 nm.

4.2.3.4 Pyrolysis Gas Chromatography Mass Spectrometry (Py-GC/MS)

NOM isolated from soil leachates from key flow events at Mt Bold in 1999 and 2001 was characterised by Py-GC/MS. In order to have sufficient sample quantity for analysis, samples from various events were combined. The 1999 samples included samples grouped from events of: (a) May; (b) July; (c) June, August, September and October. The 2001 samples came from bulk (≈ 2-3 L) *grab* samples taken at the same time from G15 and G0 A/B leachate.

NOM was freeze-dried and then analysed without further preparation. A flash pyrolysis Pyroprobe 2000 system (CDS, Analytical Inc.) interfaced to a Hewlett Packard (HP) 5890 gas chromatograph and a VG Tritech TS-250 mass spectrometer was used. For application of this technique, a solid freeze-dried sample (about 0.5 to 15 mg) was placed into a quartz tube, each end plugged with quartz wool and inserted into the platinum coil of the probe. The probe was then placed into the interface unit that enabled pyrolysis products to be transferred from the probe, after flash heating to the injection port of gas chromatograph. Compounds were separated using capillary columns and controlled temperature conditions, and were identified by mass spectrometry. Mass spectrometry was performed with electron impact ionization at 70 eV and the scan speed was 1 scan s^{-1}. Mass scans were performed from 50 to 600 amu with a resolution setting of 600. Total ion current chromatog were obtained for each sample.

Absolute quantification of pyrolysis products is difficult because of the wide range of pyrolysis products obtained, and integration of peak areas is unreliable because of the different weights and relative amounts of organic carbon pyrolyzed (Page, 2001). The qualitative comparison of pyrolysis approach data was based on the method of Page (2001), where relative abundances of pyrolysis products were compared (by ratio) to abundance of a common product, for example relative to phenol.

4.2.3.5 C^{13} NMR Sample Preparation: Desalting by Ultra Filtration

Further organic matter characterisation was conducted using ^{13}C-NMR. Characterisation was conducted on freeze-dried combined samples from the events of 2001. The high ionic strength (measured by EC) of the G15 sample meant that they could not be used directly for characterisation by these techniques, and required desalting prior to freeze drying. Samples were desalted by ultra filtration using a 1000 MW membrane filter with only the retentate retained for characterisation. The ultrafiltration procedure was conducted on both the G15 and G0 soil leachates, ensuring comparisons could easily be drawn between the treatments.

Samples were pre-concentrated by rotary-evaporation at 40°C. Samples for ultra filtration were concentrated from an initial volume of 2-3 L to a final volume of 200 ml with a DOC concentration of approximately 175–225 mg/L (a total DOC content of approximately 35-45 mg).

Ultrafiltration was performed using an Amicon cell (Figure 41) and Diaflo YM1 (nominal 1,000 MW) ultrafiltration membranes. Practical flow rates through the membrane were achieved by application of positive pressure to the headspace of solutions by means of pressurised nitrogen gas (approximately 60 psi). To ensure constant mixing of the sample, and to prevent blockage of the membrane by settling material, samples were constantly mixed with a magnetic stirrer. Ultrafiltration was performed at ambient temperature (approx. 20°C).

To ensure that the majority of material less than the nominal 1000 MW was removed, a number of Milli-Q water rinses (100 ml) were performed. The first rinse was performed after 100 ml of permeate was collected, with 100 ml of Milli-Q water being added to the retentate in the ultrafiltration cell. Rinses (100 ml aliquots) were then repeated. To assess when the majority of material less than the nominal 1000

MW was rinsed through the membrane, colour and UV_{254} measurements were made on the permeate. Rinses were conducted until there was no or only negligible changes in these measurements. A total of 9 rinses were conducted on the samples collected from surface flow and 11 on the samples collected on subsurface (B/C horizon interface) flow. The final values for UV_{254} and colour for G15 and G0 permeates were 0.114, 11.25 HU and 0.084, 9.75 HU for the surface and 0.090, 9 HU and 0.097, 10.5 HU for the subsurface interface flow respectively.

4.2.3.6 Characterisation: Solid State ^{13}C NMR

^{13}C NMR characterisation was conducted on the freeze-dried retentate from ultrafiltration. Instrument settings used to gather the solid-state ^{13}C magic angle spinning (MAS) NMR spectra were as described for characterisation of soil organic matter (see Chapter 3). As with soil organic matter characterisation, spectra were gathered using both the bloch decay (BD) and cross polarisation (CP) techniques.

4.2.4 LEACHATE TREATABILITY- JAR TESTING

The treatability of organics in leachates from the G15 (gypsum-treated sub-catchment) and G0 (non-treated sub-catchment) was assessed through a simulated water treatment procedure known as a *Jar Test*. The Jar Test is a common and routine procedure used for the determination of coagulant dosing of reservoir waters. When applied to simulate a water treatment process, it enables the determination of a wide range of treated water parameters such as residual coagulant, dissolved organic carbon (DOC), pH, and turbidity. The Jar Test was carried out in this study to assess if the changes to water quality resulting from gypsum amendment would affect water treatment. It also offers a comparative assessment of the effect on water quality of gypsum amendment of soils to standard water treatment practices.

The leachates assessed in this study were collected as bulk grab samples on 13/6/01 from subsurface (A/B horizon interface) flow at G0 and G15.

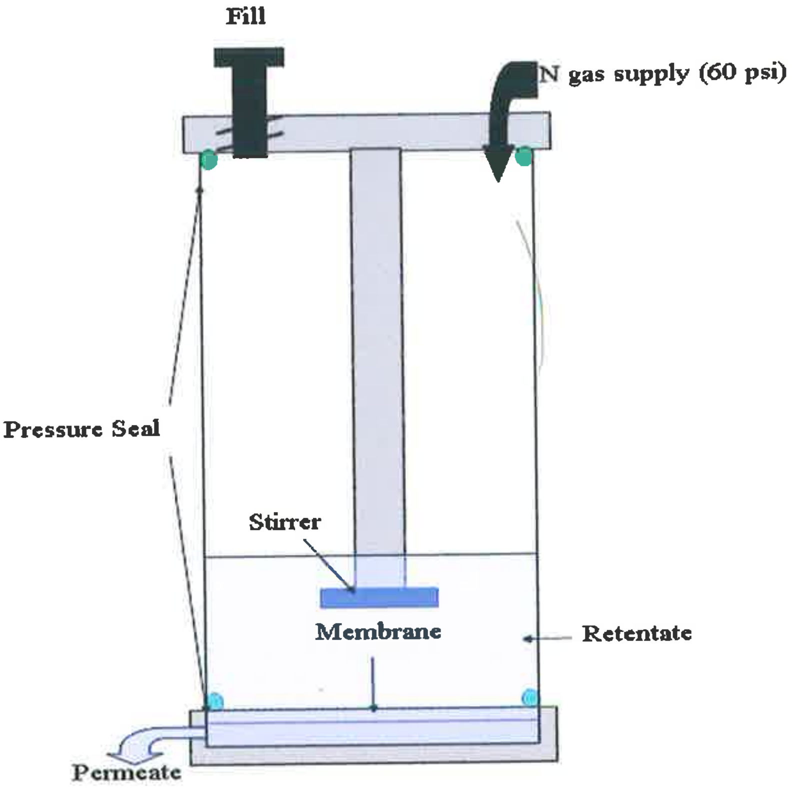

Figure 41. Amicon ultrafiltration cell.

Using the Jar Test procedure flocculation was performed with aluminium sulfate (alum) [$Al_2(SO_4)_3.18H_2O$] as the coagulant. Based on initial colour and UV_{254} measurements, the G0 leachates were diluted 1 part solution to 2 parts Milli-Q water to reduce them to comparable levels with the G15 leachate. Water samples (1L) were flash-mixed at 200 r.p.m. for 1 min. and slow mixing was performed at 20 r.p.m for 14 min. Flocs were allowed to settle for 30 min. Water samples were tested at adjusted pH (with the addition of bicarbonate) and at ambient temperature (approximately 20°C). Alum doses used in the Jar Test were determined using a computer based model (van Leeuwen *et al*,. 2001a, 2005), based on titration with alum of the untreated waters to a pH of 5.5, together with measurements of turbidity, colour and UV_{254}. As the alkalinity of the raw samples used was not sufficient, with alum dosing, for the coagulation pH to remain at or above 5.5, bicarbonate (as sodium bicarbonate) was added to the raw waters (73 mg /L for G0 and 79 mg /L for G15 HCO_3).

4.3 RESULTS AND DISCUSSION

4.3.1 SUB-CATCHMENT HYDROLOGY 1996-1999

Figures 42-45 show the rainfall, surface and subsurface (A/B and B/C) flow rates for the G0 and G15 catchments from 1996 to 1999. The flow (and rainfall) data are presented as total flow (or precipitation) per day through the flow season (autumn to spring) following installation of instrumentation in August-September 1996.

The flow characteristics between the sub-catchments through the period 1996 to 1999 were very similar, and there appears to be no treatment effect following gypsum application in 1998.

Flow in both sub-catchments was dominated by surface flow, with B/C flow generally exceeding A/B flow (particularly in the G15 sub-catchment). Seasonal flow first began in the G0 sub-catchment, through all monitored horizons. These early (generally autumn- early winter) flows were dominated in volume by G0 (i.e. G0 > G15). By mid winter (generally 4-6 weeks following initial flow) G15 flow volumes exceeded G0, in total, surface and B/C flow, with G0 A/B flow generally greater than G15 A/B flow.

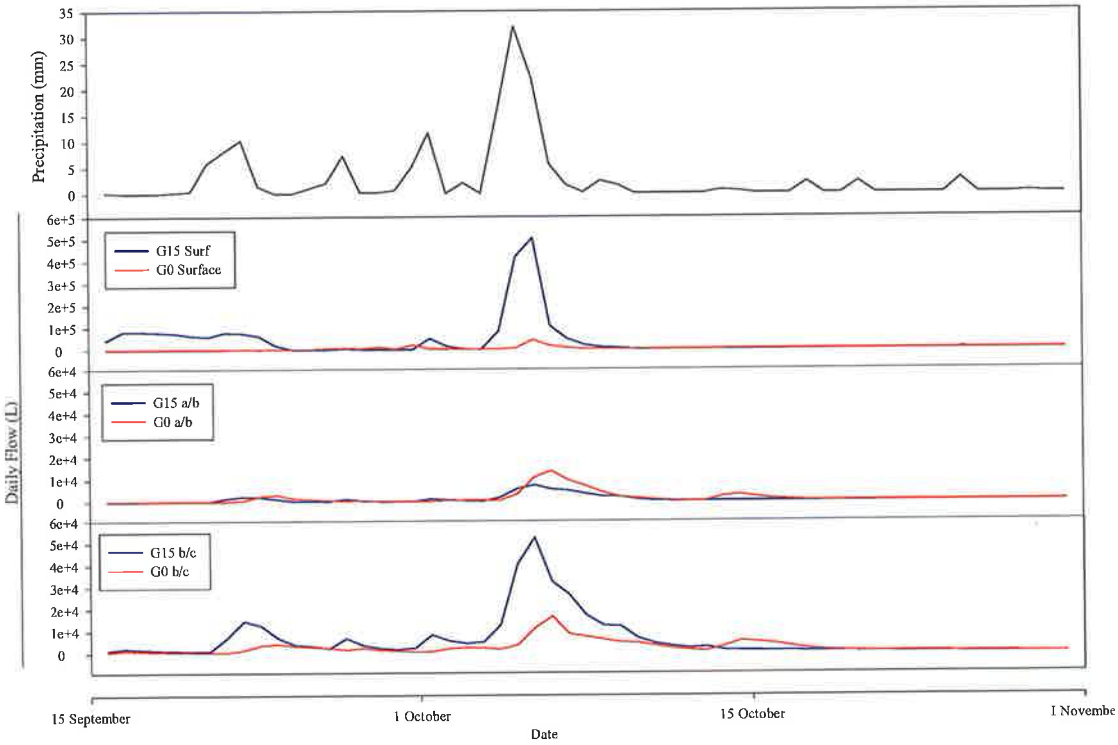

Figure 42. Flow data 1996 for G15 and G0 sub-catchments.

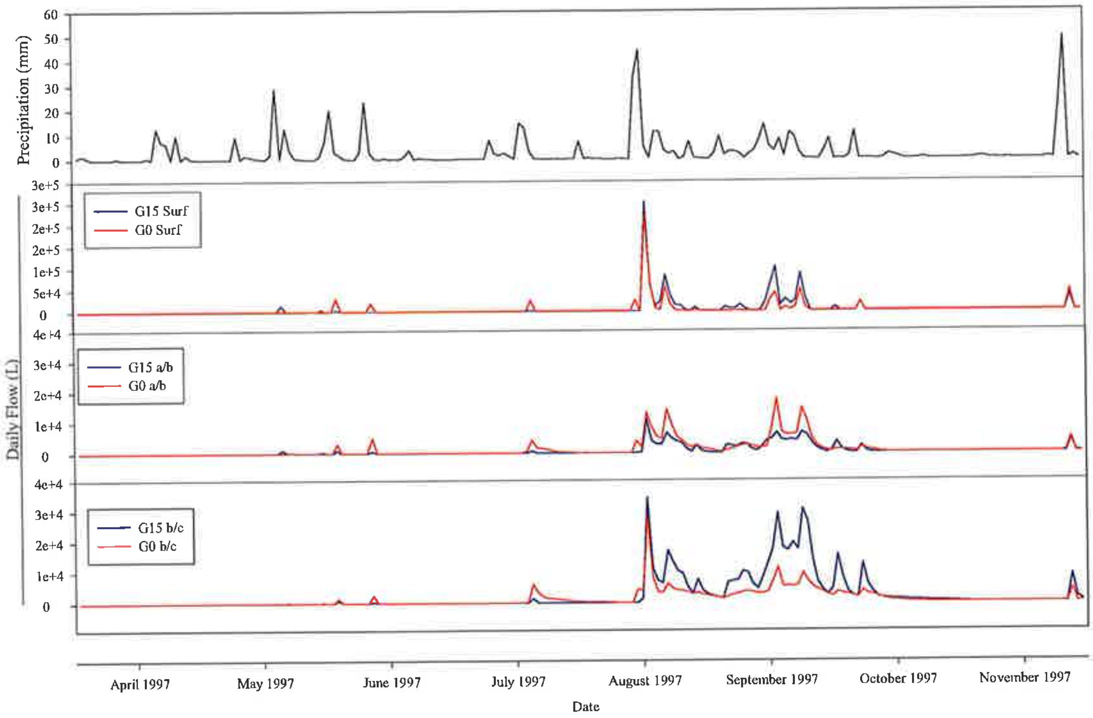

Figure 43. Flow data 1997 for G15 and G0 sub-catchments.

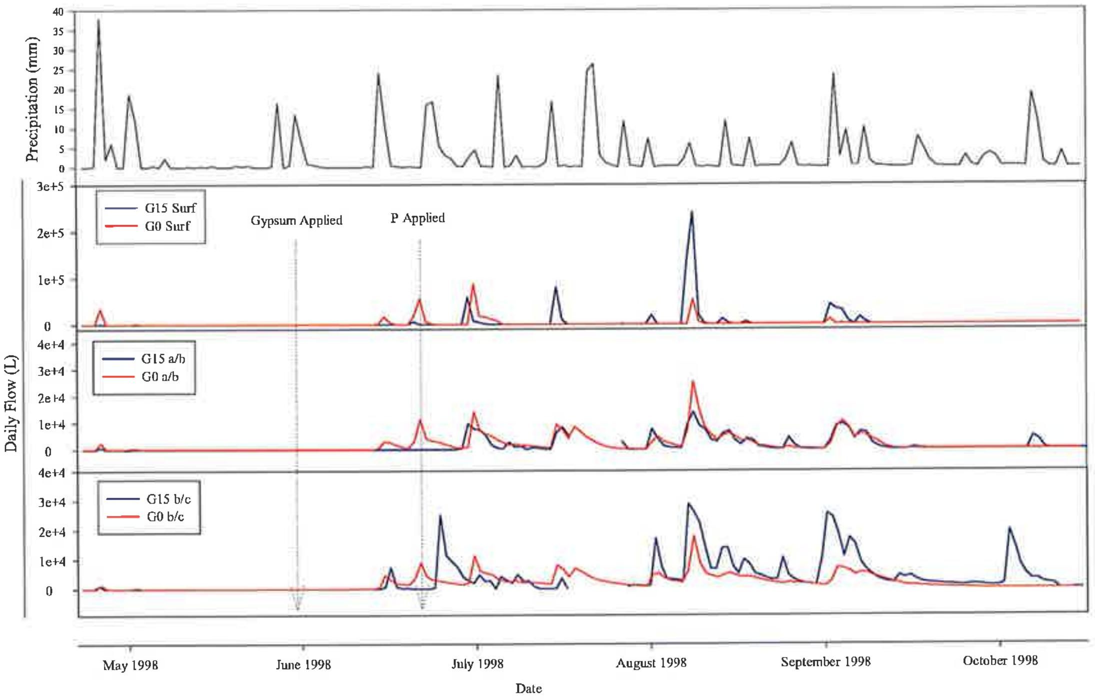

Figure 44. Flow data 1998 for G15 and G0 sub-catchments.

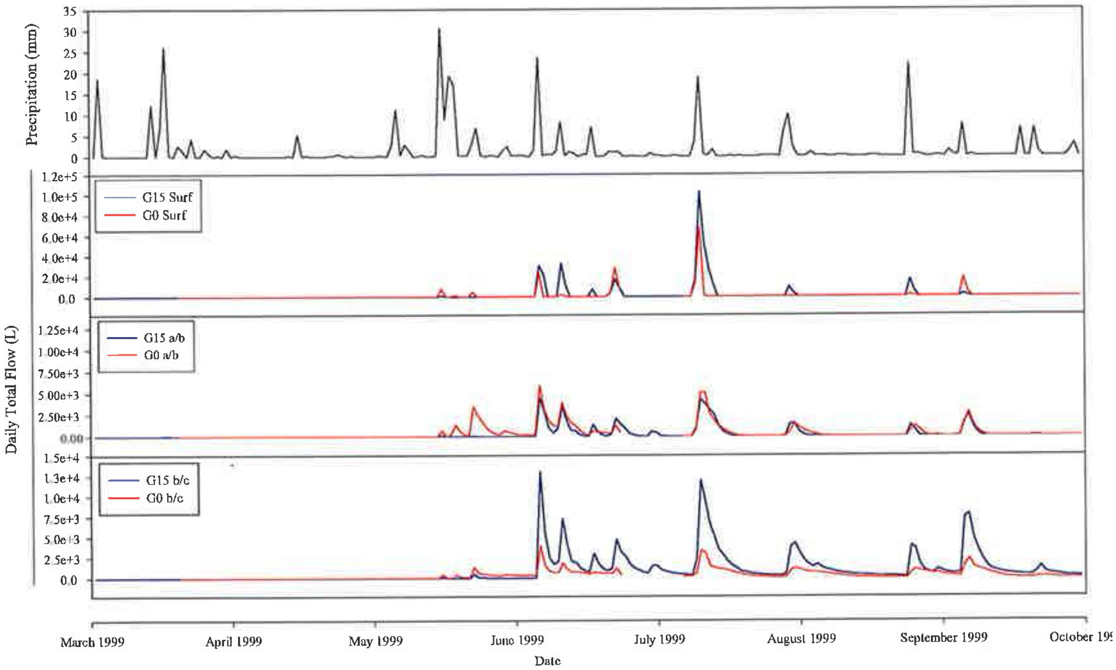

Figure 45. Flow data 1999 for G15 and G0 sub-catchments.

4.3.2 WATER CHEMICAL CHARACTERISITCS- PRIOR TO GYPSUM TREATMENT

4.3.2.1 Inorganic Chemistry

A summary of the average monthly leachate composition (< 0.45 µm) (i.e. P, Ca, Fe and Al) and pH in 1996 is presented in Figure 46 (data from Stevens *et al,*. 1998). This provides a comparison between the chemical compositions of sub-catchments prior to gypsum treatment. Leachate compositions for 1997 are not presented as only the G0 sub-catchment was sampled.

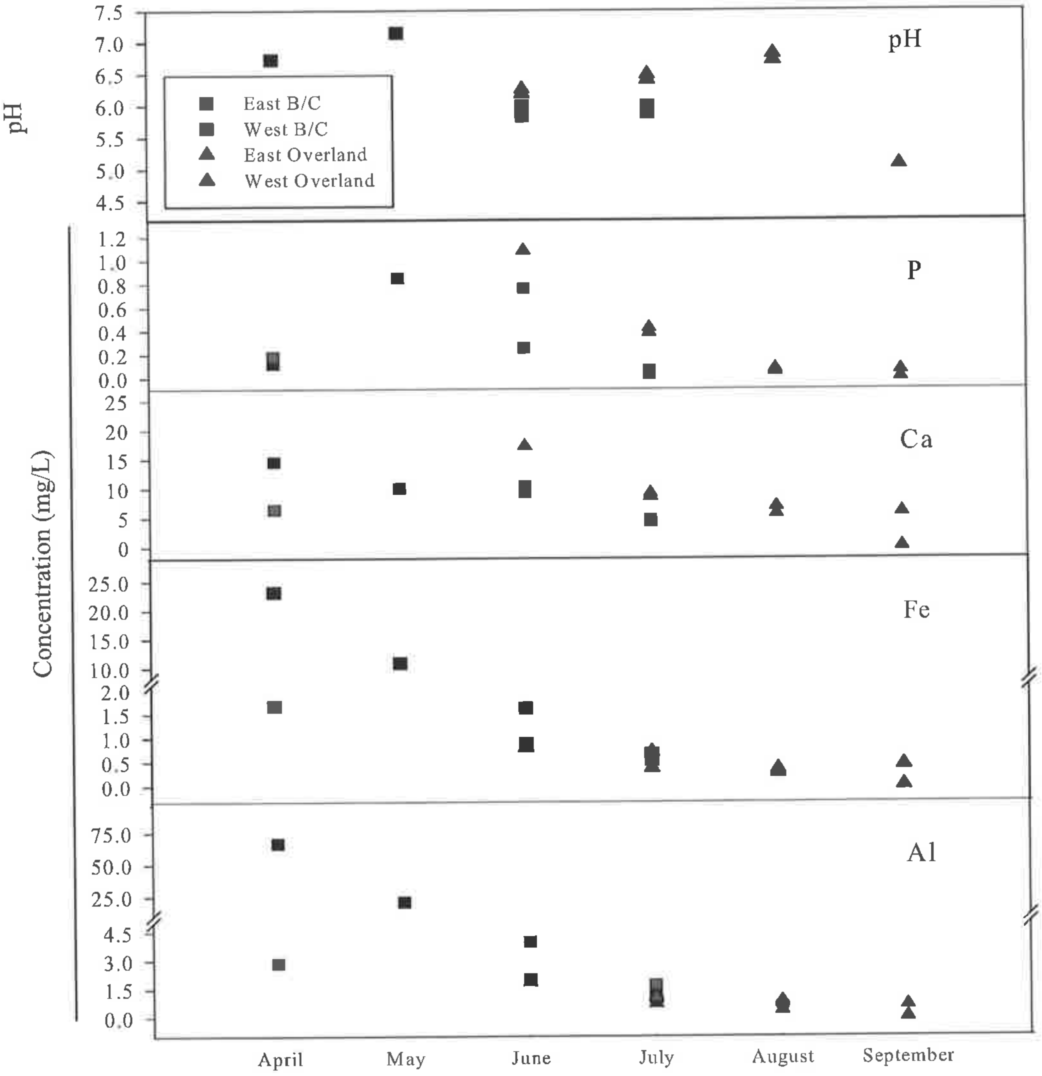

Figure 46. Average monthly leachate dissolved inorganic composition and pH 1996

In 1996, the average monthly pH levels of the surface flow water and subsurface leachates were similar in the east and west catchments, ranging between 5.9 and 7.

Maximum average monthly dissolved P (DP) concentrations were observed in the June surface flows of the eastern sub-catchment (G15) (≈ 1 mg/L). Apart from June when the DP concentration in the subsurface flows were greater in the western (G0) sub-catchment (≈ 0.7 compared with ≈ 0.2 mg/L), the DP in all other flow events were very similar in both sub-catchments. Ca concentration inflows from both sub-catchments were very similar throughout 1996, averaging approx 10 mg/L. Al and Fe concentrations were significantly higher in B/C flows of the eastern sub-catchment in autumn (April) flows compared to the concentrations of the western sub-catchment leachate. The most likely source of this would be fluxes of clay minerals. At other times, all leachates and surface flows of G0 and G15 averaged much less than 5 mg/L, generally < 1.5 mg/L Al and Fe.

From the inorganic leachate and surface flow water chemistry, it was concluded that there was generally negligible difference between the two sub-catchments prior to gypsum treatment.

4.3.2.2 Organic Chemistry

Figure 47 presents the total DOC and SUVA of waters sampled in 1996, for both the surface and B/C horizon flows. Linear regressions of these measurements are also presented for comparison of seasonal trend. Generally, the subsurface (B/C) flows were very similar, both in terms of DOC concentration and organic character (as indicated by SUVA). In addition, the seasonal trend for organic composition in flow from both sub-catchments along the B/C interface was very similar. Slight differences in seasonal trends were observed for surface flow, although average DOC contents were still quite similar over the monitored time period.

As with the inorganic chemical characteristics, the data from 1996 indicates that differences in the organic character of the leachates and surface flow were negligible between sub-catchments.

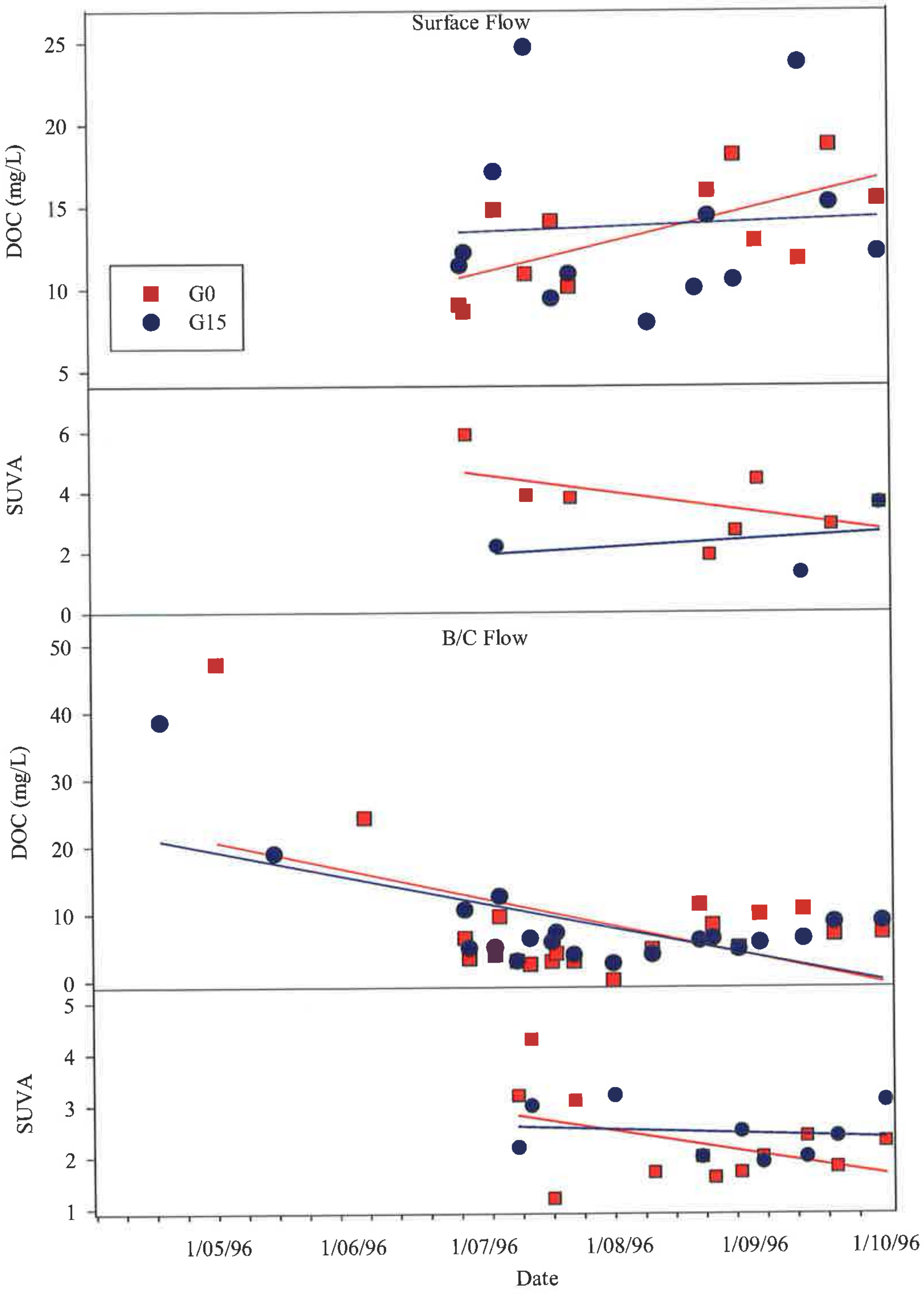

Figure 47. DOC and SUVA values of leachates in 1996, prior to gypsum treatment.

4.3.2.3 *Organic Matter Characteristics- Prior to Gypsum Treatment*

Diffuse Fourier Transform Infrared (DRIFT) spectroscopy was applied to characterise the dissolved fraction of the NOM (DOM) from leachates collected from the eastern sub-catchment G15 prior to gypsum application by Spark *et al.* (1998). The spectra are presented in Figure 48.

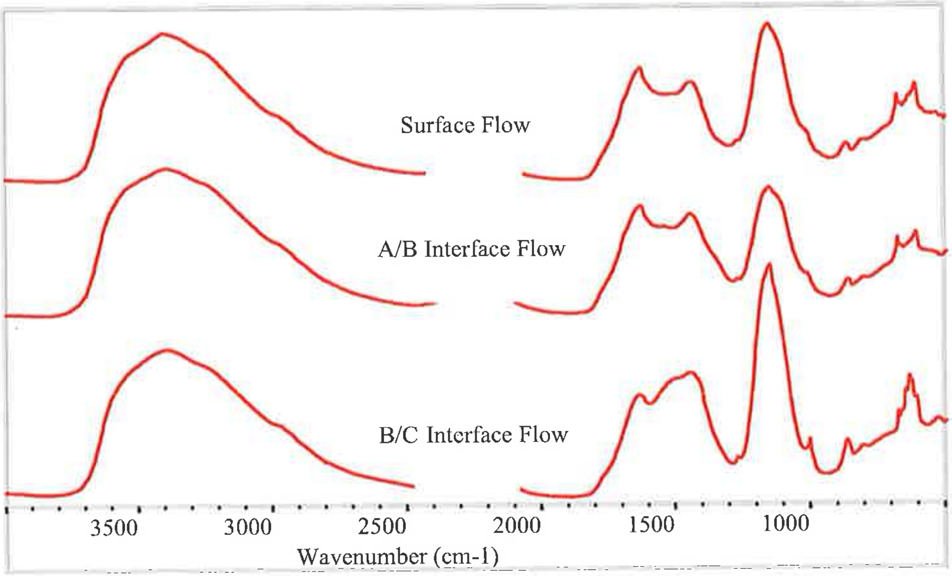

Figure 48 Drift spectra of DOM isolated from leachates from surface runoff and A/B and B/C interface flow 8/8/96 (Spark *et al* 1998).

The spectra of the samples collected from the Mt Bold site indicate the presence of aliphatic oxygen groups (1100 cm^{-1}), amide/amine type functional groups (1400-1550 cm^{-1}) and phenolic groups (3400, 3200, 1640 cm^{-1}) (Spark *et al,*. 1998). The drift spectra indicate similar DOM character between surface runoff and A/B interface flow. Between A/B interface and B/C interface flow the spectra indicate a greater proportion of amide/amine and aliphatic alcohol/ether was observed. These groups are polar and soluble, therefore likely to be transported with the mobile soil solution (Spark *et al.,* 1998). To further account for the differences Spark *et al.* (1998) goes on to state that amide/amines and aliphatic alcohol/ethers are not charged at moderate pH and so would be less likely to be adsorbed by electrostatic interactions with charged soil particles. Differences were found between DRIFT spectra of DOM isolated from the runoff and subsurface leachate from soils of a lighter (more sandy) texture near to the Myponga Reservoir, 50 km south of Mt Bold, (Spark *et al,*. 1998). It was found that Mt Bold East (G15) pre-gypsum treatment samples had a lower proportion of carboxylates. This was attributed to carboxylate groups being more easily adsorbed by soil minerals such as iron and aluminium oxides and clays (Fabris and Spark 1998) that are in higher proportion at Mt Bold (compared with Myponga). Characterisation of DOM by DRIFT over the period July to September 1996 in the pre gypsum-treated eastern sub-catchment found that time had little effect on DOM (Spark *et al,*. 1998).

4.3.2.4 Conclusions Drawn from Water Chemistry- Pre-Gypsum Treatment

From analysis of 1996 chemical characteristics of the water from G15 and G0, it was concluded that there was negligible difference between the two sub-catchments, prior to gypsum treatment. From this it was assumed that differences observed in the inorganic and organic water chemistry between the two sub-catchment, following gypsum application to G15, could be attributed to the gypsum, and not as a result of inherent differences between the sub-catchments themselves.

4.3.3 LEACHATE INORGANIC CHEMISTRY- POST GYPSUM TREATMENT

4.3.3.1 General

A summary of the average monthly concentrations of Fe, P, Al, Mn, Ca, Mg, Na, S and K (< 0.45 μm fraction) in leachates collected from surface and B/C horizon flow is shown in Table 28. Concentrations of samples from events were averaged on a monthly basis. The results from 2001-02 are of individual samples. Consistent trends in leachate composition of the above elements are evident between treated and untreated sub-catchments. These trends where consistent from the first flow following gypsum treatment (June 1998), and have continued through to July 2001.

Table 28. Mt. Bold average monthly leachate composition 1998, 1999, 2001 and '02.

			Fe	Mn	Ca	Mg	Na	K	P	S	Al	pH	EC
						ave$^+$ concentration mg/L							us.cm^{-1}
Surface	G15	Jun-98	< 0.017	0.112	385.0	67.57	36.08	9.36	0.29	395.0	< 0.22		
		Jul-98	< 0.017	0.814	425.5	42.48	20.87	5.22	0.70	388.2	< 0.22		
		Aug-98	< 0.017	0.942	357.5	31.56	16.31	3.12	0.24	322.5	< 0.22		
		Sep-98	< 0.017	1.103	360.0	71.61	38.75	4.00	0.25	420.0	< 0.22		
	G0	Jun-98	0.09	< 0.002	2.83	1.47	6.75	4.90	0.32	1.91	< 0.22		
		Jul-98	0.12	0.005	7.00	4.19	17.45	4.31	0.53	7.66	< 0.22		
		Aug-98	0.17	0.007	12.03	5.11	17.08	4.44	0.73	12.80	< 0.22		
B/C	G15	Jun-98	0.03	0.041	185.3	25.19	22.42	4.97	0.29	186.6	< 0.22		
		Jul-98	0.03	0.585	255.7	44.79	31.77	2.66	0.19	271.9	< 0.22		
		Aug-98	0.03	0.463	172.4	57.33	41.33	< 2.5	0.23	225.2	< 0.22		
		Sep-98	< 0.017	0.210	144.6	61.75	47.39	< 2.5	0.25	215.0	< 0.22		
	G0	Jun-98	0.07	0.005	4.29	4.58	22.13	< 2.5	0.17	6.08	< 0.22		
		Jul-98	0.06	0.043	12.57	8.31	22.95	3.77	0.50	20.65	< 0.22		
		Aug-98	0.07	0.008	4.95	5.38	22.40	2.99	0.23	8.08	< 0.22		
		Sep-98	< 0.017	0.005	3.45	4.70	24.23	< 2.5	0.25	5.79	< 0.22		
Surface	G15	Jun-99	0.04	0.756	250.00	31.09	18.09	6.52	0.16	250.0	0.16	5.9	1173
	G0	May-99	0.35	0.198	2.98	1.62	7.87	15.73	1.45	1.59	0.57	6.53	68
		Jun-99	0.13	0.005	2.19	1.17	5.25	9.96	0.68	0.83	0.18	7.33	110
		Jul-99	0.37	0.138	4.06	1.74	6.63	11.18	1.31	2.10	0.32	7.48	105
		Oct-99	0.25	0.071	5.15	2.76	13.11	3.86	0.16	2.04	< 0.15	6.95	121
B/C	G15	May-99	0.09	0.235	153.9	24.70	16.84	5.86	0.18	161.5	0.25	6.7	825
		Jun-99	0.03	0.130	236.5	44.80	24.98	4.05	< 0.11	258.3	0.17	6.5	1139
		Jul-99	0.07	0.223	232.7	57.77	34.14	2.94	< 0.11	278.6	0.20	6.57	1297
		Oct-99	< 0.014	0.018	82.58	71.09	62.90	< 1.7	< 0.11	190.8	< 0.15	6.9	1049
	G0	May-99	0.24	0.015	2.57	2.18	7.97	5.80	0.34	1.47	0.81	6.4	76.3
		Jun-99	0.29	0.034	3.77	3.96	18.33	9.47	1.38	3.92	1.79	6.9	135.7
		Jul-99	0.07	0.017	3.05	4.33	24.68	< 1.7	< 0.11	5.89	0.21	6.31	146
		Oct-99	0.06	0.015	3.15	4.38	24.19	< 1.7	< 0.11	5.57	0.16	8	151.3
Ave*	**G15**	**98-99**	0.05	0.433	249.4	48.59	31.68	4.87	0.28	274.1	0.20	6.51 +/-0.38	1096
Ave*	**G0**	**98-99**	0.17	0.040	4.94	3.73	16.07	6.95	0.62	5.76	0.58	6.99 +/-0.59	114
Surface$^+$	G15	Jul-01	0.05	0.030	97.12	24.71	18.70	2.47	< 0.1	116.1	0.15		
B/C$^+$	G15	Jul-01	0.05	0.056	105.4	21.91	18.31	2.57	< 0.1	119.5	0.17	5.6	650
B/C$^+$	G0	Jul-01	0.68	0.005	2.67	3.16	15.71	< 2	< 0.1	3.15	1.36	6.3	130
B/C	G15	Sep-02	< 0.01	0.022	96	69	48	< 2	< 0.1	186	< 0.1		
B/C^t	G15	Sep-02	< 0.01	0.023	96	70	48	< 2	< 0.1	186	< 0.1	6.15	900
B/C	G0	Sep-02	0.37	0.005	2.9	4.3	27	4.9	< 0.1	5.6	0.56		
B/C^t	G0	Sep-02	1.9	0.007	3.0	4.4	27	8.1	< 0.1	5.7	6.2	5.9	150

Averages$^+$ based on average monthly concentration; average* calculated only on samples with concentration greater than minimum detectable by ICPOES; pH, EC ave of 1999 only. P concentrations in 1998 determined by MRP of total digested leachates. B/C^t: total concentration.

The flows from the gypsum treated (G15) sub-catchment were consistently higher in Ca, S, Mn, Mg, and Na, and were lower in Fe, Al, and P with no notable difference in K compared to the untreated G0 sub-catchment. The EC of G15 samples were also consistently higher albeit with a slight reduction over time. The pH of the G15 leachates was also consistently 0.25-1.5 units lower than G0 and, over 1998-1999, the average pH was 0.5 units lower in G15. In contrast to this trend, the pH of the G15 sample taken in September 2002 was approximately 0.25 pH units higher than that of G0. This is potentially indicative of both a degree of natural variation in pH, and a declining effect of gypsum on pH with time.

4.3.3.2 Chemical Speciation Calculations

The relationships between the magnitude of SI and the saturation state of the solutions with minerals are summarised in Table 29. Results of the chemical speciation calculations using $\text{PHREEQC}_{\text{RCI}}$ for the average leachate compositions in 1998 and 1999 from both sub-catchments are presented in Tables 30 (G15) and 31 (G0). Differentiation between minerals that are metastable or likely to precipitate is difficult to interpret, as it is extremely case specific. It has been shown that for hydroxyapatite (HAP) precipitation at pH 7, a $SI \approx 11$ is required (van der Houwen and Valsami-Jones, 2001) whereas, at pH of 7.4, a $SI \approx 2$ is sufficient (Boskey and Posner 1976). For the purposes of this study, SI ranging from 0 to 2 is assumed to be metastable. Such SI may, at the very least, indicate a tendency for ion pairing, and hence reduced ion activity.

Table 29. Relationships between SI and mineral stability.

Value of SI	Saturation state	Stability response
$SI < 0$	under-saturated	dissolution
$SI = 0$	equilibrium	no response (to possible dissolution)
$SI > 0$*	over saturated	metastable (similar as above)
$SI >> 0$*	over saturated	stable (precipitation)

* dependent on factors such as mineral phase, solution pH and presence of foreign bodies that may act as template in heterogeneous nucleation.

Stable mineral phases ($SI > 2$) common to both solutions are the basaluminite ($KAl_3(SO_4)_2(OH)_6$), gibbsite ($Al(OH)_3$), boehmite ($AlOOH$), cupric-ferrite ($CuFe_2O_4$), cuprous-ferrite ($CuFeO_2$), goethite ($FeOOH$), hematite (Fe_2O_3) and magnetite (Fe_3O_4). In the G15 solutions alunite ($KAl_3(SO_4)_2(OH)_6$ had a SI > 2 and was only metastable ($0 < SI < 2$) in the G0 solutions. Alternatively magehemite (Fe_2O_3) was stable in G0 and metastable in G15. The only phase metastable in both solutions was $MnHPO_4$. Additionally, strengthite ($FePO_4.2H_2O$), and the iron and aluminium hydroxides $Al(OH)_3(a)$, $Fe(OH)_3(a)$ and $Fe_3(OH)_8$ were metastable in G0 and undersaturated in G15. Generally, the higher stability of Al and Fe minerals, particularly the hydroxides can be attributed to both the high solution concentrations of Fe and Al as well as the higher pH of the G0 solution modelled. Conversely, the stability of alunite is a result of the high S content of the G15 solution. The SI of HAP calculated using the $LogK_{sp}$ value from the *Wateq4f.dat* database (-40.46) gave negative SI for HAP, however using $LogK_{sp} = -57.74$ (Nancollas and Tomazic, 1974; van der Houwen and Valsami-Jones, 2001) resulted in positive SI of 6.97 for the G15 solution and 4.28 for the G0 solution. Although these are positive values, they are still lower than the SI value van der Houwen and Valsami-Jones (2001) suggest spontaneous (homogeneous) precipitation would occur at pH 7 (SI = 10.93). Heterogenous precipitation is still possible, but extremely questionable without the presence of pre-existing calcium phosphates to act as a seeding crystal.

Table 30 Chemical speciation modelling of G15 leachate using Phreeqc RCI. Leachate Composition; Fe 0.0478, Mn 0.433, Cu 0.050, Ca 294.4, Mg 48.6, Na 31.7, K 4.87, P 0.28, S 274.1 and Al 0.196 and pH 6.5.

Phase	SI	log IAP	log KT	Formula
$Al(OH)_3(a)$	-0.02	10.78	10.80	$Al(OH)_3$
Alunite	4.36	2.96	-1.40	$KAl_3(SO_4)_2(OH)_6$
Basaluminite	4.47	27.17	22.70	$Al_4(OH)_{10}SO_4$
Boehmite	2.20	10.78	8.58	$AlOOH$
CupricFerrite	8.91	40.83	31.92	$CuFe_2O_4$
CuprousFerrite	11.81	13.19	1.38	$CuFeO_2$
Diaspore	3.90	10.78	6.88	$AlOOH$
$Fe(OH)_3(a)$	-0.77	17.14	17.91	$Fe(OH)_3$
$Fe_3(OH)_8$	-5.34	40.92	46.26	$Fe_3(OH)_8$
Gibbsite	2.67	10.78	8.11	$Al(OH)_3$
Goethite	5.12	17.14	12.02	$FeOOH$
Gypsum	-0.86	-5.44	-4.58	$CaSO_4{:}2H_2O$
Hematite	12.25	34.28	22.03	Fe_2O_3
Hydroxyapatite	-1.24	-41.26	-40.46	$Ca_5(PO_4)_3OH$
Hydroxyapatite*	6.97	-50.768	-57.74	$Ca_5(PO_4)_3OH$
Maghemite	1.86	34.28	32.43	Fe_2O_3
Magnetite	11.15	40.92	29.78	Fe_3O_4
Manganite	-7.22	18.12	25.34	$MnOOH$
$Mn_3(PO_4)_2$	-16.17	-39.71	-23.83	$Mn_3(PO_4)_2$
$MnHPO_4$	1.48	-23.66	-25.29	$MnHPO_4$
$MnSO_4$	-11.01	-8.34	2.67	$MnSO_4$
Strengite	-0.90	-14.14	-13.38	$FePO_4{:}2H_2O$
Vivianite	-6.92	-42.64	-36.00	$Fe_3(PO_4)_2{:}8H_2O$

Table 31. Chemical speciation modelling of G0 leachate using Phreeqc RCI. Leachate Composition; Fe 0.17, Mn 0.040, Cu 0.042, Ca 4.94, Mg 3.73, Na 16.07, K 6.95, P 0.62, S 5.76 and Al 0.58 and pH 7.00.

Phase	SI	log IAP	log KT	Formula
$Al(OH)_3$(a)	0.14	10.94	10.80	$Al(OH)_3$
Alunite	0.84	-0.56	-1.40	$KAl_3(SO_4)_2(OH)_6$
Basaluminite	2.76	25.46	22.70	$Al_4(OH)10SO_4$
Boehmite	2.36	10.94	8.58	AlOOH
Brucite	-6.73	10.11	16.84	$Mg(OH)_2$
CupricFerrite	13.86	45.78	31.92	$CuFe_2O_4$
CuprousFerrite	14.15	15.53	1.38	$CuFeO_2$
Diaspore	4.06	10.94	6.88	AlOOH
$Fe(OH)_3$(a)	1.34	19.25	17.91	$Fe(OH)_3$
$Fe_3(OH)_8$	0.49	46.75	46.26	$Fe_3(OH)_8$
Gibbsite	2.83	10.94	8.11	$Al(OH)_3$
Goethite	7.23	19.25	12.02	FeOOH
Gypsum	-3.71	-8.29	-4.58	$CaSO_4{:}2H_2O$
Hematite	16.47	38.50	22.03	Fe_2O_3
Hydroxyapatite	-3.93	-44.39	-40.46	$Ca_5(PO_4)_3OH$
Hydroxyapatite*	4.28	-53.46	-57.74	$Ca_5(PO_4)_3OH$
Maghemite	6.08	38.50	32.43	Fe_2O_3
Magnetite	16.98	46.75	29.78	Fe_3O_4
MnHPO4	1.59	-23.70	-25.29	$MnHPO_4$
Strengite	1.13	-12.25	-13.38	$FePO_4{:}2H_2O$
Vivianite	-2.24	-38.24	-36.00	$Fe_3(PO_4)_2{:}8H_2O$

4.3.3.3 P Transfer

The mean concentration of P, as total P (TP) and molybdate reactive P (MRP) for flow events in G15 and G0 (following gypsum application to G15) from 1998 to 2000 are presented in Table 32. The average TP and MRP over that period are also shown for the same period (average TP was calculated only when concentrations exceeded 0.1 mg/L, the minimum detectable by ICPOES). Average TP (> 0.1 mg/L) was 35.3 % lower in the surface flow and 11.4% lower in the B/C leachates derived from the G15 sub-catchment.

The ratio of MRP to TP in both surface and B/C flow was lower in G15 (0.71 and 0.41 for surface and B/C respectively) compared with G0 (0.80 and 0.59 respectively). Additionally, the ratio was always lower for both sub-catchments in the B/C leachates than the surface flow. Low MRP:TP ratios are indicative of relatively high particulate P (PP).

Following P fertiliser application in mid June 1998, P concentrations were initially greatest in the G15 leachates and surface flow in the period immediately following application (25 June- 8 July). This would appear to be a consequence of hydrologic factors rather than gypsum treatment, as the volumes and flow rates were notably higher, particularly over the period June 25 to 30, in the G15 sub-catchment B/C flow. Succeeding these events, concentrations of both MRP and TP were largely greater in the G0 B/C leachates and surface flows (mid July 1998 – Oct 2000). Differences were most evident in the early flow events of 1999 (May – July) when P concentrations in G0 were between five and ten fold greater.

By 2000 only trace concentrations of P were observed in both sub-catchments, indicating the pool of water soluble P had been largely depleted in both sub-catchments. Although only trace concentrations were detected, concentrations of MRP in 2000 were still marginally lower in G15 than G0 (≈ 0.03 compared with ≈ 0.05 mg/L).

Table 32. P concentrations (mg/L) in G15 and G0 flows from 1998 to 2000.

	G15				G0			
	Surface		B/C		Surface		B/C	
Date	MRP mg/L	TP mg/L	MRP mg/L	TP mg/L	MRP mg/L	TP mg/L	MRP mg/L	TP mg/L
17-Jun-98			0.19	0.24	0.32	0.43	0.24	0.27
25-Jun-98	0.29	0.51	0.56	1.18			0.20	0.20
30-Jun-98			0.29	0.56			0.14	0.20
8-Jul-98	1.28	1.74					0.80	0.87
15-Jul-98							0.49	0.53
24-Jul-98			0.17	0.35			0.28	0.28
28-Jul-98	0.39	0.57	0.20	0.28				
31-Jul-98	0.29	0.27			0.53	0.64	0.33	0.36
7-Aug-98			0.22	0.28				
13-Aug-98			0.19	0.29			0.25	0.27
17-Aug-98			0.23	0.27			0.19	0.23
24-Aug-98	0.24	0.30	0.29	0.31	0.73	0.81		
2-Sep-98	0.25	0.45					0.25	0.34
11-Sep-98			0.25	0.33				
25-May-99			0.14	0.18	0.95	1.62	0.28	0.34
2-Jun-99					0.5	1.16	0.03	< 0.1
16-Jun-99			0.04	< 0.1				
1-Jul-99			0.03	< 0.1				
21-Jul-99	0.15	0.16	0.02	< 0.1	1.24	1.31	1.01	1.4
17-Sep-99						0.16	0.03	< 0.1
6-Oct-99			0.03	< 0.1				
23-Jun-00			0.03	< 0.1			0.04	< 0.1
29-Jun-00			0.03	< 0.1			0.04	< 0.1
23-Aug-00			0.03	< 0.1			0.05	< 0.1
19-Oct-00			0.03	< 0.1			0.05	< 0.1
AVE*	0.41	0.57	0.16	0.39	0.71	0.88	0.26	0.44

TP in 1999-2000 measured by ICPOES (min detectable 0.1mg/L) average* calculated only on samples > 0.1mg/L

4.3.3.4 Discussion: Inorganic Chemistry

Increased pH of leachates following gypsum application has been commonly observed (Sumner, 1993), and explained as the exchange of SO_4^{2-} for OH^- (Shainberg *et al,*. 1989). The reduced pH of the leachate from the G15 observed in this study indicates that exchange of SO_4^{2-} for OH^- was exceeded by the exchange of Ca^{2+} for H^+ (Shainberg *et al,*. 1989). The higher pH of the G15 leachates, compared with that collected from G0 in September 2002, may be a result of the exchange of SO_4^{2-} for OH^- occurring in equilibrium or in excess of exchange Ca^{2+} for H^+. Alternatively, it may simply represent natural variation of the system (i.e. G0), as mentioned earlier.

Increased leaching of Ca and S was observed, and would be expected, given the dissolution of applied gypsum. There was a steady decline in the concentration in the < 0.45 μm fraction of the constituents of gypsum over the 5 seasons, from Ca ≈ 400 mg/L and S ≈ 400 mg/L in 1998 to Ca ≈ 100 mg/L and S ≈ 120-180 mg/L in 2001-02. This is indicative of a reduced pool of available gypsum for leaching. The ratio of Ca:S in gypsum by weight is approximately 1.25. The ratios observed in solution were considerably less than this (average 0.9 for 1998-99), with the highest Ca:S ratio in 1998 surface flows of July and August at approximately 1.1, the lowest 0.5 observed in October 1999 and September 2002. There appears to have been a seasonal effect of time, as this ratio was observed to reduce over the period of the autumn break to the end of seasonal flow in both 1998 and 1999.

The high proportional loss of S indicates it was preferentially leached through the profile compared with Ca. This indicates significant adsorption or exchange of Ca, that would account for the increased leaching of Na, Mg and Mn and would confirm the observed pH reduction. Other studies have reported increased leaching of K (Shainberg *et al,*. 1989; O'Brien and Sumner, 1988; Pavan *et al,*. 1984) that was not clear in this study. From the results presented in Chapter 3 however, increased exchangeable Ca accompanied decreased exchangeable K throughout the profile, supports the findng of Shainberg *et al.* (1989) Additionally, in the G15 profile, Ca exchangeable (using 0.01 M $CaCl_2$) Fe and Al was reduced in the upper profile compared to G0 (Fe 0-5 cm and Al 0-10cm), with Ca exchangeable Al increasing down profile in G15. The reduced exchangeable Al, Fe and K accompanied by reduced leachate concentration of these cations suggested they might be consumed in precipitation of solid phases. O'Brien and Sumner (1988) gave similar explanations for reduced Al concentration through the precipitation of alunite ($KAl_3(SO_4)_2(OH)_6$). Chemical speciation calculations (Table 27) confirm that this is possible, along with the precipitation of basaluminite ($Al_4(OH)_{10}SO_4$). This may further account for the reduction in K concentration (i.e, alunite precipitation). The overall reduction of exchangeable Al and Fe, particularly in the upper 10 to 20 cm results, indicate that the concentration of these constituents in the soil solution at that depth would have been higher than that indicated by the concentration in the leachate collected. So it is possible that the precipitation of Al and Fe hydroxides and oxides (and phosphates i.e.

strengthite $FePO_4:2H_2O$) may have been more significant in G15 than indicated in modelling (Table 30).

Gypsum appears to have reduced P transfer. As in the study of Stout *et al.* (2000), this appears to be a result of increasing the particulate proportion of P. This may have been enhanced by the net increase in anion exchange capacity of the soil (from increased Ca throughout the profile, and displaced cations Al and Mg lower in the profile). Additionally, this may be enhanced through the direct precipitation of phosphate minerals, namely Fe phosphates such as strengite and Mn phosphates (e.g,. $MnHPO_4$). Futhermore, the precipitation of other mineral phases, most significantly the Al- sulfates, alunite and basaluminite may provide additional reactive surfaces for phosphate adsorption.

4.3.4 LEACHATE ORGANIC CHEMISTRY – POST GYPSUM TREATMENT

4.3.4.1 General

Yearly averages of UV_{254} absorbance, colour (HU), organic nitrogen (TKN), DOC and SUVA from 1998 to 2001 for G15 and G0 are shown in Table 33. With the exception of TKN, there appears to be a treatment effect on each of these parameters, with the yearly averages of each lower in the G15 leachates.

Table 33. Summary of early averages of organic characterisation criteria for leachates.

	Site	UV_{254um}	Colour (HU)	TKN (mg/L)	DOC (mg/L)	SUVA	Specific Colour
Ave 1998	G0				14.9		
Ave 1998	G15				11.2		
Ave 1999	G0	0.77	200	1.97	19.4	3.95	10.28
Ave 1999	G15	0.13	16	1.17	5.9	2.22	2.74
Ave 2000	G0	0.54	112	1.15	12.5	4.32	8.91
Ave 2000	G15	0.27	43	1.26	8.2	3.26	5.20
Ave 2001	G0	0.80	121		18.5	4.31	6.55
Ave 2001	G15	0.31	55		9.6	3.21	5.71

4.3.4.2 Dissolved Organic Carbon (DOC) Transfer

Average DOC concentrations in leachates of G15 and G0 from 1998 to 2001 are shown in Figure 49 (surface) and Figure 50 (B/C). With the exception of isolated events on 23 March 2000 (surface) and 23 June 1998 (B/C), the DOC concentration in the G15 leachates was consistently lower over the 3-4 year monitoring period. Over this period, DOC concentrations in the G15 surface runoff and B/C leachate rarely exceeded 10 mg/L. In contrast, the DOC concentration of G0 surface runoff was consistently greater than 15 mg/L, regularly exceeding 20 – 30 mg/L. Gypsum treatment appears to have limited DOC transfer, essentially by maintaining consistently low DOC concentrations throughout the flow period, eliminating the high fluctuations to the peak concentrations in individual events particularly prevalent in G0 B/C leachates. Linear regressions of DOC concentrations over the monitored period (Figures 49 and 50) further emphasize the long term (3-4 yr) effect of gypsum on both surface and subsurface DOM movement. The near parallel linear regressions in the surface indicate that the suppression of DOM movement in G15 is only moderately reduced over the monitored time period. More significantly a divergent trend in the DOC concentrations in the B/C interface flows of G15 and G0 indicates the treatment effect is becoming more pronounced with time.

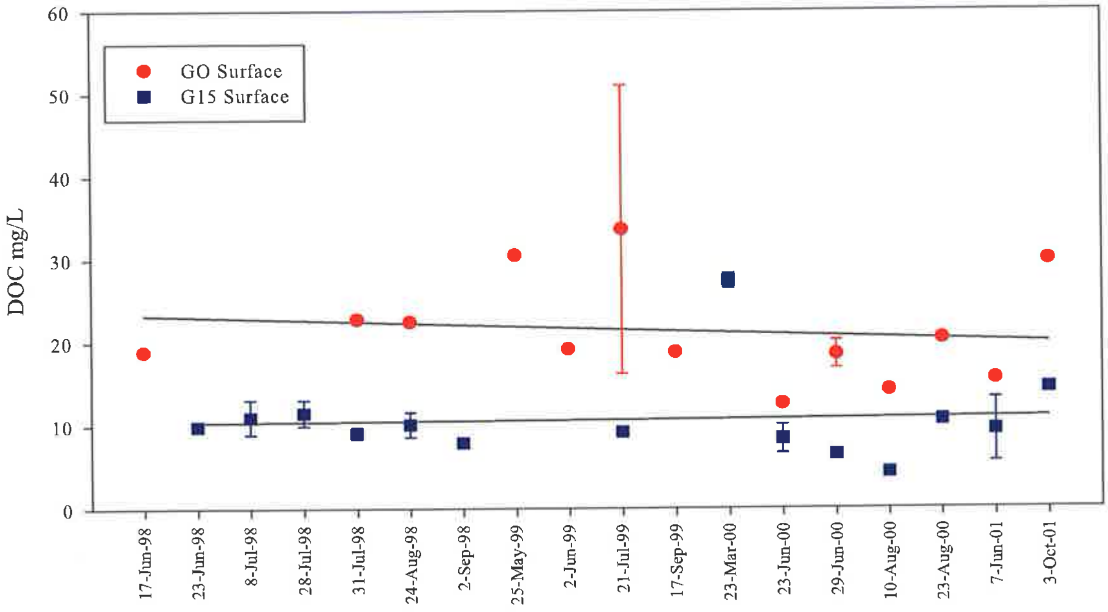

Figure 49. Average DOC concentrations in surface flow per event from June 1998 to October 2001

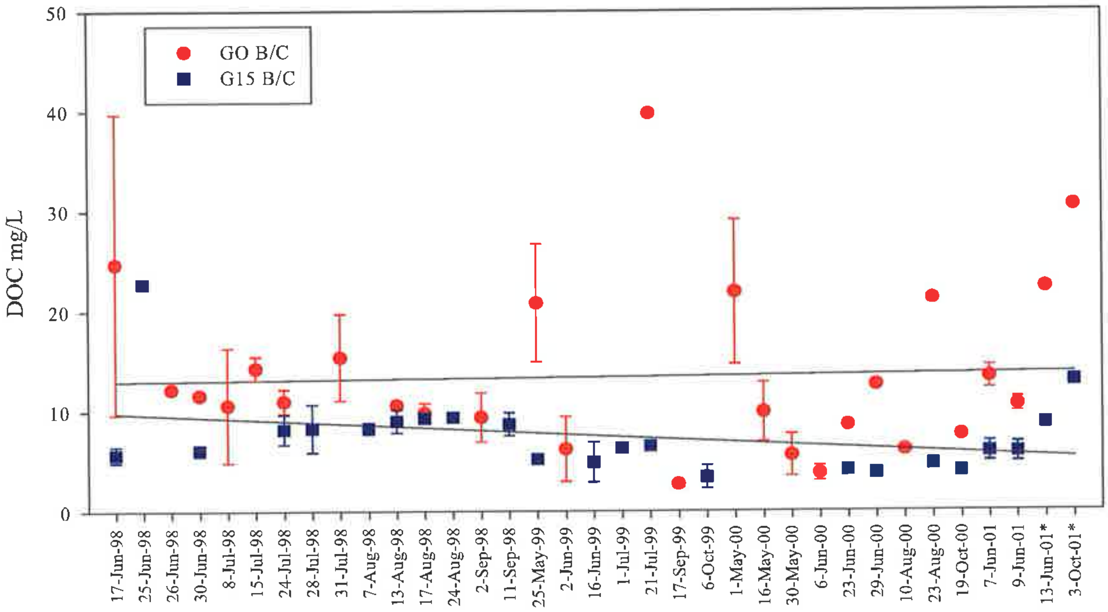

Figure 50. Average DOC concentrations in B/C interface flow per event from June 1998 to October 2001.

4.3.4.3 Non Molecular Organic Matter Characterisation

4.3.4.3.1 SUVA

The average event values of SUVA calculated for both surface and B/C interface flows for 1999 to 2001 are presented in Figures 51 and 52. Over the monitored period, an increasing trend of SUVA values in both sub-catchments was observed. This trend was strongest in the gypsum treated surface flows; however, average SUVA was consistently lower with treatment in both surface and B/C flow.

The trend over time in surface flow is a gradual reduction in effectiveness of gypsum as indicated by the convergent course of the linear regressions. In subsurface flows, the linear regression trend lines are virtually parallel, indicating that at depth the gypsum treatment continued to maintain a consistent effect on DOM character over the monitoring period.

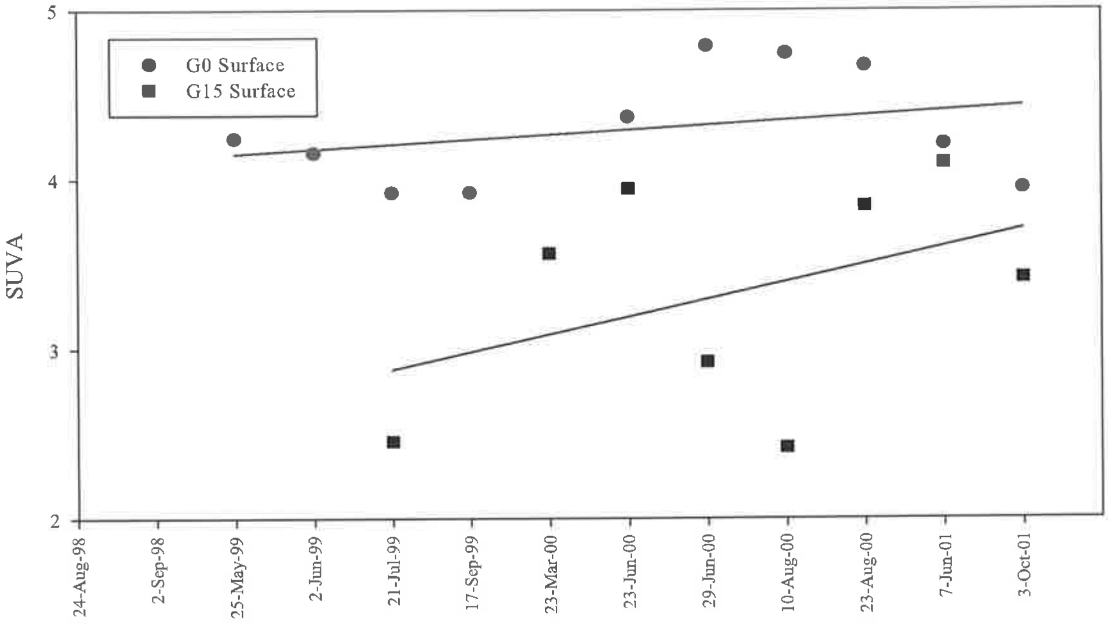

Figure 51. Average SUVA of waters in surface flow for events from May 1999 to October 2001.

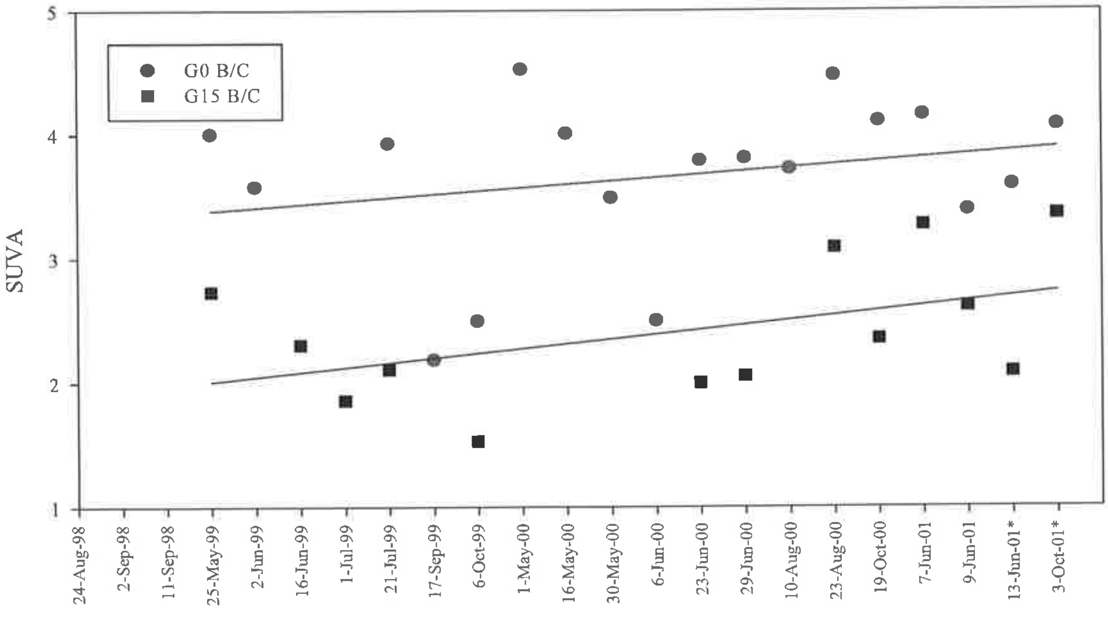

Figure 52. Average SUVA of waters from the B/C interface for events from May 1999 to October 2001.

4.3.4.3.2 Specific Colour

The average event values of specific colour calculated for both surface and B/C interface flows from 1998 to 2001 are presented in Figures 53 and 54. In flows from both horizons, average specific colour values are consistently lower in the treated soil, most notably in early flows up to August 2000. Beyond this date differences become negligible. This is illustrated in the trends (linear regressions) of both surface and subsurface flows. Again the treatment effect is stronger in the subsurface. One data point for the G0 surface flow water (3 October 2001) is considerably lower than the overall average. This has a significant impact on the linear regression, and it does not appear representative of the trend of earlier values. Further measurements would have aided in the assessment of whether this data point is an error or part of the actual trend. Further sampling, particularly of surface runoff, was unable to be conducted due to drought conditions in 2003 that lead to no measured surface runoff.

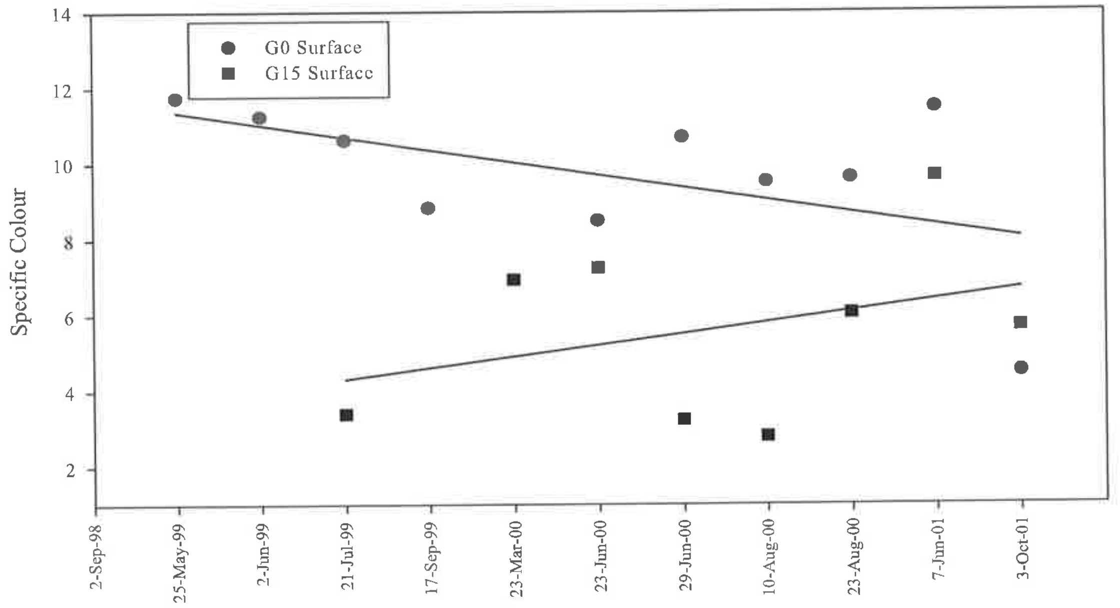

Figure 53. Average Specific Colour in surface flow for events from May 1999 to October 2001.

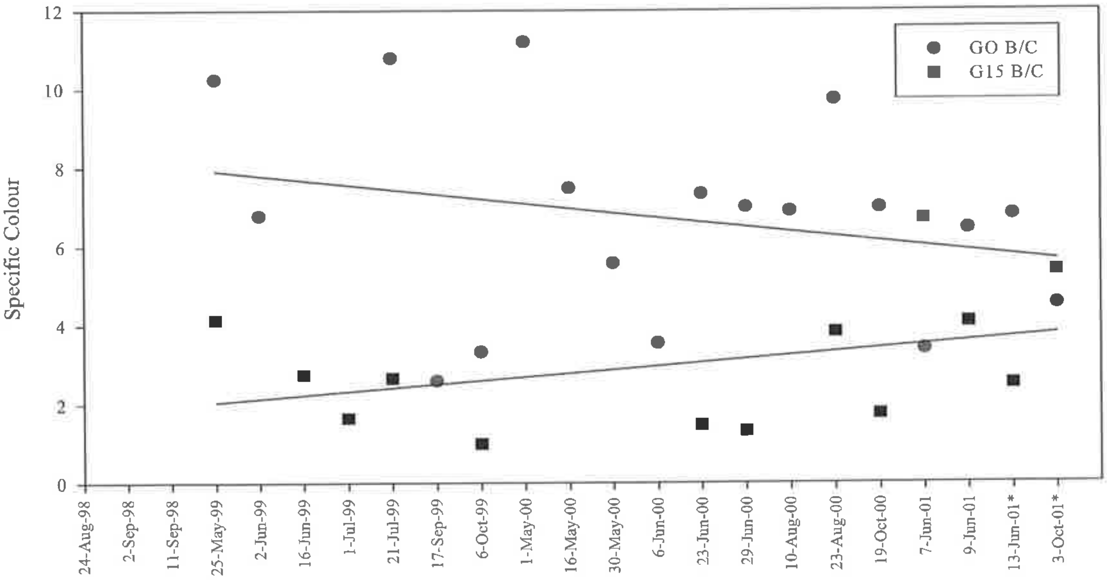

Figure 54. Average Specific Colour in B/C interface flow for events from May 1999 to October 2001.

4.3.4.3.3 C:N

The average event C/N ratios calculated for both surface and B/C interface flows for 1999 to 2001 are shown in Figures 55 and 56. The trend in C/N ratios was similar to the observations for specific colour. Initially, there was a notable treatment effect, with reduced C/N ratios in G15 waters. However, this is minimal beyond July 2000.

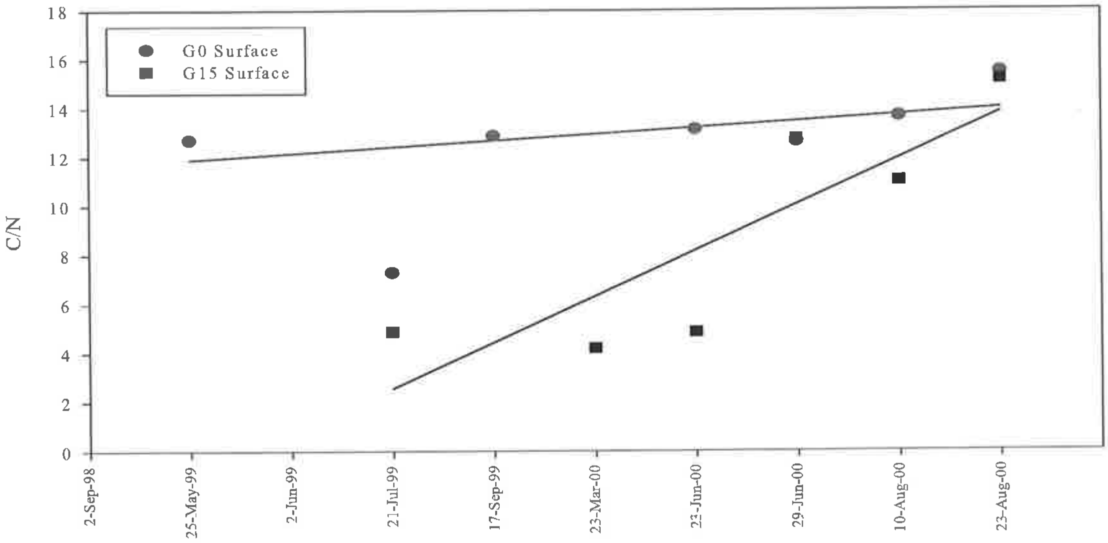

Figure 55. Average C/N ratios in surface flow waters for events from May 1999 to August 2000.

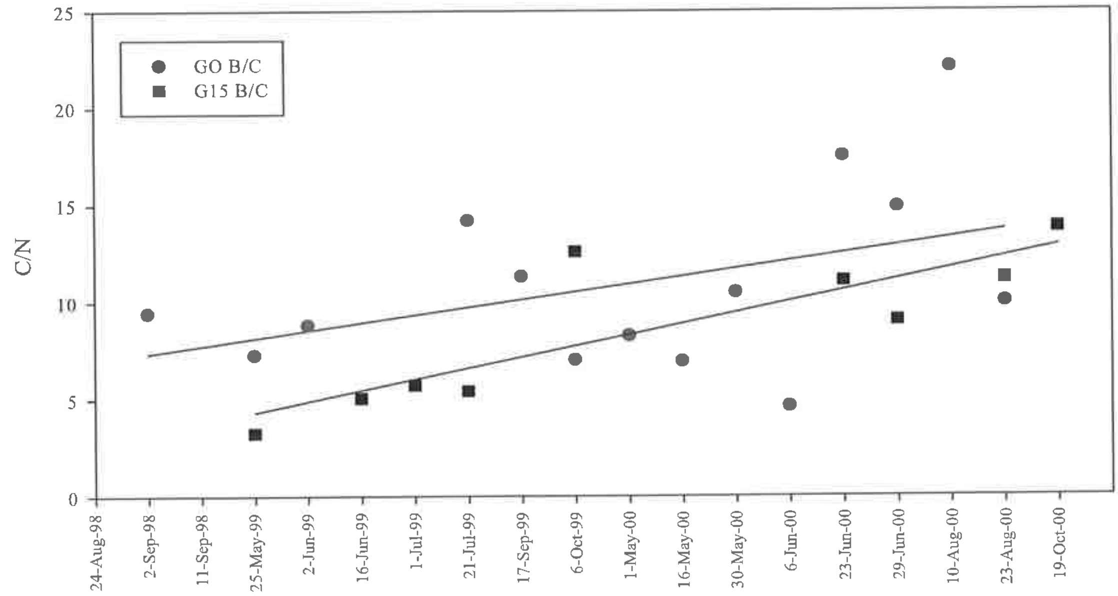

Figure 56. Average C/N ratios of waters from B/C interface flow for events from May 1999 to August 2001.

4.3.4.3.4 Summary: Non-molecular Characteristics of Organics

Large reductions in DOC concentrations, attributable to gypsum amendment, were observed over the period 1998 – 2001. Ratios of light adsorption at wavelengths 456 nm and UV_{254} to DOC (known as Specific Colour and SUVA respectively) indicated that the gypsum treatment reduced total DOM movement by the preferential removal of particular fractions (n.b. larger aromatic molecules). This conclusion is further supported by reduced C/N ratios. These parameters, particularly DOC concentration, specific colour and SUVA were consistently lower over the monitored period, that indicates the addition of gypsum has a prolonged effect (at least 3 to 4 yr) following the application of gypsum. The reduction in these parameters are consistent with the goals of organic matter removal in water treatment, i.e. to reduce both trihalomethane formation potential (THMFP) and bacterial regrowth potential (BRP).

4.3.4.4 *Molecular Organic Matter Characterisation*

4.3.4.4.1 *^{13}C-NMR*

The NMR spectra can be divided into four regions, corresponding approximately to aliphatic (alkyl C, 10-48 ppm), carbohydrate (O-alkyl C, 48-110 ppm), aromatic (aryl C, 110-165 ppm) and carbonyl regions (165-190 ppm). Spectra for the Mt Bold leachates are shown in Figure 57 (CP) and Figure 58 (BD). The relative percentage integrals for the corresponding spectra are presented in Tables 34 and 35. The spectra all show a strong presence of carbonyl (≈ 175 ppm) and O-alkyl (≈ 70-80 ppm) groups in both surface flow and subsurface leachates of both sub-catchments. There are also strong similarities between the spectra of the surface water of G0 and the surface water and subsurface leachate of G15. All have a less well defined peak at ≈ 130 ppm than the G0 A/B spectra, indicating the stronger presence of aromatic compounds in the latter. Page (2001) found that DOM extracted from the soils of the Mt Bold catchment had a significant aromatic component, hypothesizing the source was lignin from remnant and cleared eucalypt vegetation. The increased aromaticity of DOM in water that has passed through the soil, as observed by comparison with the G0 spectra, is consistent with his findings. The lower aromaticity of the G15 leachate is also consistent with the lower SUVA observed over the 4 yr since gypsum application. The sharp peaks in the G15 A/B leachate spectra (< 40 ppm) are most likely to be from contaminants.

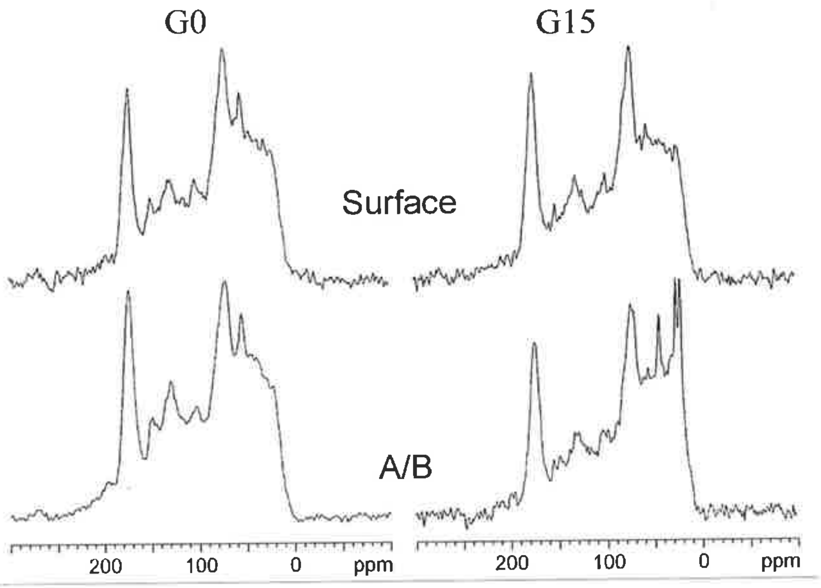

Figure 57. C^{13} NMR CP spectra of the surface runoff water and subsurface leachate from G0 and G15 of Mt Bold.

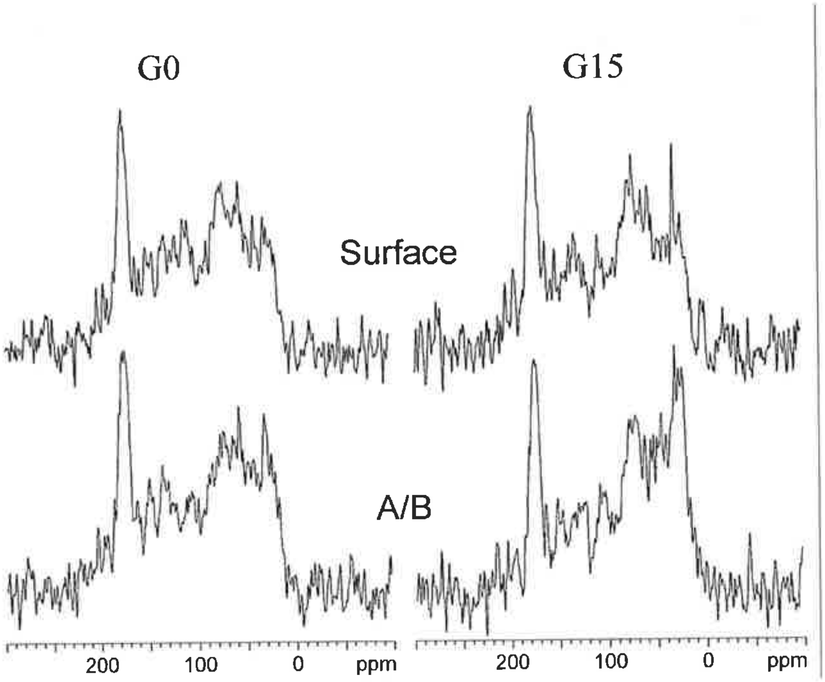

Figure 58. ^{13}C-NMR BD spectra of the surface runoff water and subsurface leachate from G0 and G15 of Mt Bold.

Table 34. Characterisation of organic matter by ^{13}C-NMR using the cross polarization (CP) method.

Leachate (Horizon)	190-165 ppm carbonyl	165-145 ppm O-aryl	145-110 ppm aryl	110-45 ppm O-alkyl	45-0 ppm alkyl	190-0 ppm total
G15 surf	14.5	6.0	14.0	44.4	21.1	100.0
G15 A/B	12.2	4.9	12.1	42.5	28.2	99.9
G0 surf	12.5	6.2	14.4	45.1	21.8	100.0
G0 A/B	14.1	6.8	16.2	43.7	19.3	100.1

Table 35. Characterisation of organic matter by ^{13}C-NMR using the bloc decay (BD) method.

Leachate (Horizon)	190-165 ppm carbonyl	165-145 ppm O-aryl	145-110 ppm aryl	110-45 ppm O-alkyl	45-0 ppm alkyl	190-0 ppm total
G15 surf	18.7	7.3	14.1	40.7	19.2	100.0
G15 A/B	15.8	6.0	11.1	39.4	27.6	99.9
G0 surf	17.4	8.1	17.3	40.3	16.8	99.9
G0 A/B	18.3	8.1	15.1	38.5	20.1	100.1

4.3.4.4.2 Py-GC/MS

Lists of the pyrolysis products, detected by Py-GC/MS of organics in leachates from the Mt Bold sub-catchments (G15 and G0) from various flow events in 1999, are presented in Tables 36, 37, 39, 40, 42, 43, 45 and 46. These Tables include (where known) the corresponding compounds from that these pyrolysis products are derived. Examples of pyrog are shown in Figures 59 and 60. Tables 36 and 37 correspond to waters collected from flow events in the B/C subsurface in May 1999 for G15 and G0 respectively; Tables 39 and 40 from subsurface B/C leachate in July 1999; Tables 42 and 43 from composite of samples from B/C events June to October; and, Tables 45 and 46 from composite samples of surface flow events in 1999.

The relative abundance of each pyrolysis product was measured as its ratio of total ion current (TIC) to commonly detected (in comparative samples) compounds (i.e. phenol for B/C events [May, July and June – October] and benzonitrile for surface flow samples collected over 1999). Tables 38, 41, 44 and 47 list the products detected and their corresponding ratios.

Generally there were fewer pyrolysis products detected in G15 waters compared with the corresponding samples from G0. This may not necessarily mean a smaller range of organic compounds are dervived from the treated soils. For example comparison of ratios to phenols and benzonitrile between G15 and G0 indicates that in G15 compounds with relatively high ratios (and thus concentration) were detected compared with G0. As such this may be indicative of a matrix effect (i.e. higher salt content) reducing the sensitivity of detection of compounds in G15.

Rather than a direct comparison of compounds detected to compare treatments, another approach, that may reduce the impact of matrix effects, is to compare the relative abundances of compounds common to both G15 and G0 (Tables 38, 41, 44 and 47).

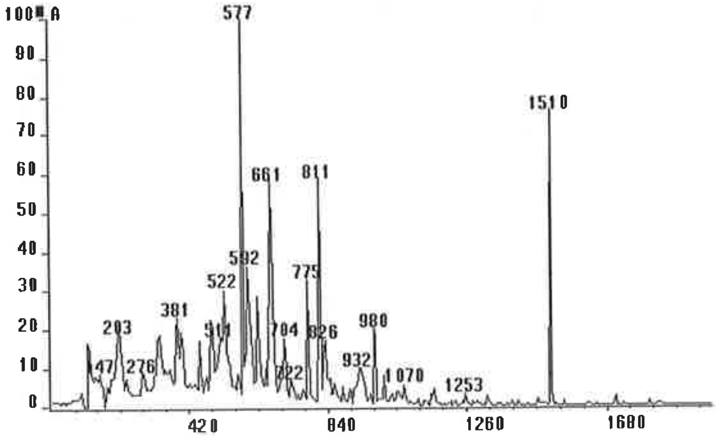

Figure 59 Pyrogram of B/C leachates collected from G15 in May 1999 (x axis = retention time [RT] and y axis = relative intensity [%] total ion current).

Table 36. Pyrolysis products detected by Py-GC/MS of B/C samples collected from G15, in May 1999.

R.T.	Pyrolysis Product	Possible Origin	Reference	Ratios to phenol
393	Benzene, chloro-			1.494
448	Benzene, ethenyl-	PH	1	1.311
533	Cyclobutane-tetramethyl-, -cis-			0.476
577	Benzene, dichloro-			5.872
587	Benzaldehyde	Lg	2	0.555
592	Benzene, dichloro-			1.519
599	Pyrrole, ethyl-methyl-	PR	1	1.606
602	Phenol	PH, PR, Lg , Ps	1,2	1.000
624	Benzonitrile	PR	1	1.625
704	Benzene, (dichloromethyl)-			0.828
722	Benzene, isocyano-methyl-	PH	1	0.448
775	Benzaldehyde, chloro- oxime (Z)-			2.118

FA fatty acid; PR protein; Ps polysaccharide; PH polyhydroxyaromatic; Lg lignin

Reference:

1. Bruchet, *et al.* (1990)
2. van Leeuwen *et al.* (2001b)

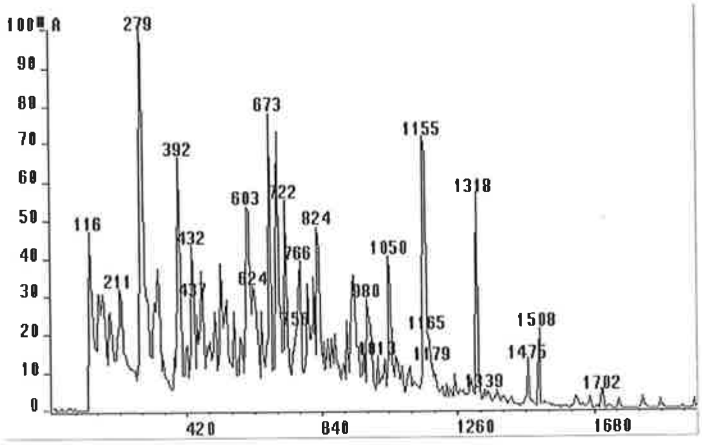

Figure 60 Pyrogram of B/C leachales collected from G15 in May 1999 (x axis = retention time [RT] and y axis = relative intensity [%] Total ion current).

Table 37 Pyrolysis products detected by Py-GC/MS of B/C samples collected from G0, in May 1999.

R.T.	Pyrolysis Product	Possible Origin	Reference	Ratios to phenol
116	Propenoic acid, (dimethylamino) ethyl ester			0.448
157	Propanenitrile			0.283
179	Benzene	PH	1	0.219
275	Benzene, methyl-	PH, FA, AR	1	0.089
282	Benzene, (butoxymethyl)	PH	1	0.872
294	Pyrrole, methyl	PR	1	0.106
319	Pyridinemethanol -pyridinyl-			0.072
378	Penten			0.079
392	Benzene, dimethyl-	FA, AR, Lg, Ps	2	0.621
437	Pyrrole, methyl-	PR	1	0.133
448	Benzene, ethenyl-	FA, AR		0.159
455	Aniline			0.105
462	Pyrazole, methyl-			0.077
488	Benzenemethanamine			0.096
501	Benzene, ethyl--methyl-	FA, AR		0.109
506	Benzene, methoxy-	PH, Lg	2	0.039
524	Cyclopenten-methyl-	Ps	2	0.246
537	Benzene, trimethyl-	FA, AR		0.095
549	Pyrrole, ethyl-	PR	1	0.061
561	Benzene, methyl (methylethyl)-	FA, AR		0.130
583	Benzene, ethyl-methyl-	FA, AR		0.062
586	Benzaldehyde			0.049
602	Phenol	PH, PR, Lg, Ps	1, 2	1.000
624	Benzonitrile	PR	1	0.092
649	1H-Indene			0.057
673	Phenol, methyl-	PH, PR, Lg	1, 2	0.624
697	Phenol, methyl-	PH, PR, Lg	1, 2	0.449
704	Benzeneacetonitrile, alpha-oxo-	PR		0.118
756	Phenol, ethyl-	PH, PR, Lg	1, 2	0.050
766	Phenol, dimethyl-	PH, PR, Lg	1, 2	0.286
793	Phenol, ethyl-	PH, PR, Lg	1, 2	0.247
877	Benzofuran-dihydro-	Ps		0.142
890	Phenol, propyl-	PH, PR	1	0.059
936	Eicosene			0.161
990	Ethanone -hydroxy-methylphenyl	FA, AR, Lg	2	0.062
1050	Indole			0.382

FA fatty acid; PR protein; Ps polysaccharide; PH polyhydroxyaromatic; Lg lignin

Reference:

1. Bruchet *et al* (1990)
2. van Leeuwen *et al.* (2001b)

Benzonitrile, a pyrolysis by-product indicative of protein (Bruchet *et al,*. 1990), was present in leachate from both sub-catchments in May 1999 (Table 38). Its vastly higher concentration (relative to phenol) in G15 suggests a higher proportion of proteinaceous compounds in the gypsum treated leachates. Given the high N content of protein, the low C/N ratio in G15 leachate (relative to G0) for the same sample (and generally over time- Figure 56) supports this conclusion.

Table 38 Pyrolysis products detected by Py-GC/MS of B/C samples common to both G15 and G0 collected in May 1999, and relative abundance to phenol.

Site	RT	Pyrolysis Product	Possible Origin	Reference	phenol
G15	624	Benzonitrile	PR	1	1.625
G0	624	Benzonitrile	PR	1	0.092

FA fatty acid; PR protein; Ps polysaccaride; PH polyhydroxide-romatic; Lg lignin
Reference:

1. Bruchet *et al.* (1990)

Table 39. Pyrolysis products detected by Py-GC/MS of B/C samples collected from G15 in July 1999

RT	Pyrolysis Product d	Possible Origin	Reference	Ratios to phenol
278	Benzene, methyl-	FA, AR		0.92
298	Carbon oxide sulphide			1.67
418	Pyrrole,dimethyl-	PR	1	0.30
448	Benzene, ethenyl-	PH, FA, AR	1	1.20
450	Imidazol, ethanamine, beta-methyl-			0.36
468	Pyrrazole, methyl-			0.46
500	Benzene, trimethyl-	FA, AR		0.49
525	Cyclopenten-methyl-	Ps	1, 2	0.51
533	Cyclobutene-tetramethyl-, -cis-			0.11
537	Benzene, trimethyl-	FA, AR		0.85
561	Benzene, methyl(methylethyl)-	FA, AR		0.39
577	Benzene, dichloro-			1.60
582	Benzene, trimethyl-	FA, AR		0.47
599	Pyrrole, ethyl-methyl-	PR	1	2.35
604	Phenol	PH, Lg , Ps	1, 2	1.00
619	Cyclopenten-methyl-	Ps	1, 2	0.59
691	Phenol, methyl-	PH, Lg	1, 2	0.96
704	Benzeneacetonitrile, alpha-oxo-	PR	1	0.28

FA fatty acid; PR protein; Ps polysaccharide; PH polyhydroxyaromatic; Lg lignin
Reference:

1. Bruchet *et al* (1990)
2. van Leeuwen *et al.* (2001b)

Table 40. Pyrolysis products detected by Py-GC/MS of B/C samples collected from G0 in July 1999.

RT	Pyrolysis Product	Possible Origin		Ratios to phenol
116	Propenoic acid-(dimethylamino)ethyl ester			0.88
178	Benzene	PH	1	1.10
273	Benzene, methyl-	FA, AR		2.52
282	Benzene, (butoxymethyl)-	FA, AR		2.18
294	Pyrrole, methyl-	PR	1	0.37
391	Benzene-dimethyl-	FA, AR, Lg	2	2.47
415	Imidazole, ethanamine, beta-methyl-			0.27
446	Furancarboxaldehyde	Ps	1, 2	0.51
462	Pyrazole, methyl-			0.65
488	Benzenemethanamine	PH	1	0.18
500	Benzene, ethyl-methyl-	FA, AR		0.45
506	Benzene, methoxy-	PH	1	0.12
524	Cyclopenten-methyl-	Ps	1, 2	0.44
529	Pyrrole, dimethyl-	PR	1	0.33
561	Benzene, ethyl-dimethyl-	FA, AR		0.18
582	Benzene, ethyl-methyl-	FA, AR		0.20
605	Phenol	PH, Lg , Ps	1, 2	1.00
610	Benzene, ethoxy-	PH, Lg	1, 2	1.93
624	Benzonitrile	PR	1	0.38
628	Benzenamine, hydrochloride			0.22
649	Benzene, propynyl	PH	1	0.13
673	Phenol, methyl-	FA, AR Lg , Ps	2	1.82
700	Phenol, methyl-	FA, AR Lg , Ps	2	2.14
722	Cyclopenten-trimethyl-	Ps	2	0.73
768	Phenol, dimethyl-	Lg	2	0.64
794	Phenol, ethyl-	Lg	2	0.52
869	Phenol-(-methylethyl)-	FA, AR, Lg	2	0.16
946	Naphthalene, methyl-			0.13
990	Ethanone, (hydroxy-methylphenyl)-	PH, Lg	1, 2	0.35
1050	Indole	PR	1	0.47

FA fatty acid; PR protein; Ps polysaccharide; PH polyhydroxyaromatic; Lg lignin
Reference:

1. Bruchet *et al* (1990)
2. van Leeuwen *et al.* (2001b)

Table 41. Pyrolysis products detected by Py-GC/MS of B/C samples common to both G15 and G0 collected in July 1999, and relative abundance to phenol.

Site	RT	Pyrolysis Product	Possible Origin	Reference	phenol
G15	278	Benzene, methyl-	FA, AR		0.92
G0	273	Benzene, methyl-	FA, AR		2.52
G15	525	Cyclopenten-methyl-	Ps	1, 2	0.51
G0	524	Cyclopenten-methyl-	Ps	1, 2	0.44

FA fatty acid; PR protein; Ps polysaccharide; PH polyhydroxyaromatic; Lg lignin
Reference:

1. Bruchet *et al* (1990)
2. van Leeuwen *et al.* (2001b)

Table 42 Pyrolysis products detected by Py-GC/MS of B/C samples collected from G15, in June, August, September and October 1999.

RT	Pyrolysis Product	Possible Origin	References	Ratios to phenol
110	Hepten-one-hydroxy-methyl-	PH	1	2.86
433	cyclopentadiene-(-methylethylidene)-	Ps	2	0.17
447	Benzene, ethenyl-	FA, AR		0.27
449	Furancarboxaldehyde	Ps	1, 2	0.31
467	Pyrazole, methyl-			0.17
537	Benzene, trimethyl-	FA, AR		0.43
561	Benzene, methy-(methylethyl)-	FA, AR		0.25
577	Benzene, dichloro-			0.94
582	Benzene, trimethyl-	FA, AR		0.27
600	Phenol	PH, PR, Ps, Lg	1, 2	1.00
693	Phenol, methyl-	PH, PR, Ps, Lg	1, 2	0.25
713	Benzofuran-methyl-	Ps	1	0.11

FA fatty acid; PR protein; Ps polysaccharide; PH polyhydroxyaromatic; Lg lignin
Reference:

1. Bruchet *et al.* (1990)
2. van Leeuwen *et al.* (2001b)

Table 43. Pyrolysis products detected by Py-GC/MS of B/C samples collected from G0 in June, August, September and October 1999.

RT	Pyrolysis Product	Possible Origin	Reference	Ratios to phenol
179	Benzene	PH	1	3.94
279	Benzene, (butoxymethyl)-	FA, AR		3.26
392	Hydroxylamine, o-(phenylmethyl)-	PH	1	1.62
416	Furancarboxaldehyde	PS, Ps	1,2	0.30
448	Benzene, ethenyl-	FA, AR		0.92
537	Benzene, trimethyl-	FA, AR		0.74
577	Benzene-dichloro-			1.56
587	Benzaldehyde			0.31
596	Phenol	PH, PR, Ps, Lg	1, 2	1.00
612	Cyclopenten-methyl-	PS, Ps	1, 2	0.59
623	Benzonitrile	PR	1, 2	1.82
691	Phenol, methyl-	PH, PR, Ps, Lg	1, 2	0.81
721	Benzonitrile, methyl-	PR	1, 2	0.40
741	Benzene-isocyano-methyl-	FA, AR		0.17

FA fatty acid; PR protein; Ps polysaccharide; PH polyhydroxyaromatic; Lg lignin
Reference:

1. Bruchet, *et al.* (1990)
2. van Leeuwen *et al.* (2001b)

Table 44 Pyrolysis products detected by Py-GC/MS of B/C samples common to both G15 and G0 collected in June, August, September and October 1999, and relative abundance to phenol.

Site	RT	Pyrolysis Product	Possible Origin	Reference	phenol
G15	447	Benzene, ethenyl-	FA, AR		0.27
G0	448	Benzene, ethenyl-	FA, AR		0.92
G15	537	Benzene, trimethyl-	FA, AR		0.43
G0	537	Benzene, trimethyl-	FA, AR		0.74
G15	577	Benzene, dichloro-			0.94
G0	577	Benzene, dichloro-			1.56

FA fatty acid; PR protein; Ps polysaccharide; PH polyhydroxyaromatic; Lg lignin
Reference:

1. Bruchet, *et al.* (1990)
2. van Leeuwen *et al.* (2001b)

The methyl- and ethyl- benzene compounds commonly detected in both G15 and G0 B/C leachates of July and the composite of June to October in 1999 (Tables 42 and 43 respectively) are indicative of fatty acids or aromatic precursor compounds (Saiz-Jimenez, 1994). In both cases these compounds appeared to be notably lower in concentration in G15. This is consistent with the observations of both SUVA and ^{13}C-NMR, that also strongly suggest a less aromatic nature of the G15 leachate. The cyclopentenes detected in both B/C leachates in July (Table 41) are indicative of polysaccharide precursor compounds, that were in relatively equal proportions in both G15 and G0.

Table 45. Pyrolysis products detected by Py-GC/MS of surface flow samples collected from G15 in 1999.

RT	Pyrolysis Product	Possible Origin		Ratios to benzonitrile
179	Benzene	PH	1	1.77
279	Benzene, (butoxymethyl)-	FA, AR		3.52
444	Thiadiazol-amine, (dimethylethyl)-			3.48
448	Benzene, ethenyl-	FA, AR		2.67
537	Benzene, trimethyl-	FA, AR		1.23
597	Furancarboxaldehyde, -methyl-	Ps	1, 2	5.98
615	Cyclopenten-methyl	Ps	1, 2	0.92
623	Benzonitrile	PR	1	1.00
649	Indene, chloro, dihydro-			0.43
689	Phenol, methyl	PH, PR, Ps, Lg	1, 2	1.55
704	Benzeneacetonitrile, alpha-oxo-	PR	1, 2	0.79

FA fatty acid; PR protein; Ps polysaccharide; PH polyhydroxyaromatic; Lg lignin
Reference:

1. Bruchet *et al.* (1990)
2. van Leeuwen *et al.* (2001b)

The results from Py-GC/MS analysis of surface runoff water from combined samples from all runoff events sampled in 1999 are presented in Tables 45 and 46. Compared with subsurface flow, differences between treatments indicated by composition were less notable in the surface flow water (Table 47). This is consistent with other parameters presented (SUVA, specific colour, C/N and ^{13}C-NMR), and is clear evidence that interaction with soil is critical in the retention mechanism.

Table 46. Pyrolysis products detected by Py-GC-MS of surface flow samples collected from G0 in 1999.

RT	Pyrolysis Product	Possible Origin	Reference	Ratios to benzonitrile
146	Cyclopentadiene, methyl			3.15
179	Benzene	PH, Ps	1, 2	2.79
279	Benzene, methyl	FA, AR		14.38
294	Pyrrole, methyl	PR	1	0.32
320	Pyridinemethanol, pyridinyl-			1.72
391	Benzene, dimethyl-	FA, AR		9.02
416	Furancarboxaldehyde-	Ps	1, 2	0.59
437	Pyrole, methyl	PR	1	0.78
447	Benzene, ethenyl	FA, AR		0.94
457	Aniline			1.36
462	Pyrazole, methyl			2.19
501	Benzene, ethyl, methyl	FA, AR		1.56
506	Benzene, methoxy-	PH	1	0.61
523	Cyclopenten, methyl-	Ps	1, 2	1.82
537	Benzene, trimethyl-	FA, AR		1.13
561	Benzene, methyl (methylethyl)-	FA, AR		0.60
582	Benzene, ethyl-methyl-	FA, AR		0.50
598	Phenol	PH, PR, Ps, Lg	1, 2	8.25
610	Benzene, methoxy-methyl-	FA, AR		0.55
617	Cyclopenten, methyl-	Ps	1, 2	0.97
628	Benzonitrile	PR	1	1.00
636	Benzene, ethyl, dimethyl-	FA, AR		0.12
649	1H-Indene			0.55
670	Phenol, methyl-	PH, PR, Lg	1, 2	5.26
691	Phenol, methyl-	PH, PR, Lg	1, 2	4.39
704	Benzeneacetonitrile, alpha-oxo-	PR	1, 2	0.72
721	Benzene, (dimethylethoxy)-methoxy-	PH	1	2.32
752	Phenol, ethyl-	PH, PR, Lg	1, 2	0.63
762	Phenol, dimethyl-	PH, PR, Lg	1, 2	1.61
788	Phenol, ethyl-	PH, PR, Lg	1, 2	1.25
947	Naphthalene, methyl-			0.73
1048	Indole	PR	1	1.29
1065	Phenol, -bis(dimethylethyl)-	PH, PR, Lg	1, 2	0.58
1111	Naphthalene, dimethyl-			0.67
1701	Benzenedicarboxylic acid, butyl-methylpropyl-			0.51

FA fatty acid; PR protein; Ps polysaccharide; PH polyhydroxyaromatic; Lg lignin

Reference:

1. Bruchet *et al.* (1990)
2. van Leeuwen *et al.* (2001b)

Table 47 Pyrolysis products detected by Py-GC-MS of surface flow samples common to both G15 and G0 collected in 1999, and relative abundance ratioed to benzonitrile.

Site	RT	Pyrolysis Product	Possible Origin	Reference	benzonitrile
G15	179	Benzene	PH, Ps	1, 2	1.77
G0	179	Benzene	PH, Ps	1, 2	2.79
G15	448	Benzene, ethenyl-	FA, AR		2.67
G0	447	Benzene, ethenyl-	FA, AR		0.94
G15	537	Benzene, trimethyl-	FA, AR		1.23
G0	537	Benzene, trimethyl-	FA, AR		1.13
G15	615	Cyclopenten-methyl-	Ps	1, 2	0.92
G0	617	Cyclopenten-methyl-	Ps	1, 2	0.97
G15	704	Benzeneacetonitrile, alpha-oxo-	PR	1, 2	0.79
G0	704	Benzeneacetonitrile, alpha-oxo-	PR	1, 2	0.72

FA fatty acid; PR protein; Ps polysaccharide; PH polyhydroxyaromatic; Lg lignin
Reference:

1. Bruchet *et al.* (1990)
2. van Leeuwen *et al.* (2001b)

4.3.4.5 Jar Testing

The parameters used to assess water quality following treatment using the Jar Test procedure were SUVA, colour, DOC and UV_{254} and are presented in Table 48. Percentage reductions (indicative of treatability) for these parameters were greater in the non-treated leachates. This appears to be reflective of the lower initial values of the raw waters from the gypsum treated leachates, and not due to the presence of gypsum itself. Actual values following water treatment for these parameters were all lower for the gypsum treated leachates.

The similarity in values for the measured water quality parameters in the gypsum treated raw water, and non-treated water, following the Jar tests may be significant. This is indicative that analogous mechanisms are operating in the removal of DOC with alum water treatment to the processes in the soil as a response to gypsum treatment.

Table 48. Water quality data of G0§ (diluted ~ 3 x) and G15‡ (diluted ~ 2 x) and % removals with alum in jar tests. (Dilution was performed to ensure sufficient volume for jar testing).

Sample		SUVA		DOC		Colour		UV_{254}	
Site	Alum Dose.		% Rem.	mg/L	% Removed	HU	% Reduced	ABS	% Removed
G15 initial		2.08		8.8		22		0.182	
G0 initial		3.53		22.3		54		0.786	
G15‡	Model* Predicted	2.02	2.9	4.9	43.6	10.5	52.3	0.10	45
G15‡	Alum to pH 5.5‡	1.97	5.6	4.6	47.7	10.5	52.3	0.09	50
G0§	Model* Predicted	2.21	37.4	6.5	70.8	9.75	82.0	0.144	81.7
G0§	Alum to pH 5.5	2.11	40.2	6.1	72.5	9.75	82.0	0.129	83.6
G0§	Model* Predicted	2.46	30.3	7.1	68.2	4.5	91.7	0.174	77.9
G0§	Model* Predicted + gypsum	1.38	60.9	8.4	62.2	7.5	86.2	0.117	85.1

* using the method of van Leeuwan *et al.* (2001a, 2005) for dose determination.

‡ alum dose applied to lower the coagulation pH to 5.5

4.3.4.6 Water Treatment v Gypsum Soil Amendment: Outcomes for Water Quality

As discussed in the literature review (this Chapter), the aim of water treatment is to bring raw water to a potable condition through both clarification and disinfection. The removal of organic matter both dissolved and particulate is a key objective of this process, as this improves clarity, taste and odor as well as reducing the potential for carcinogenic disinfection by-products and bacterial re-growth. In water treatment, the removal of suspended material (both inorganic and organic) and dissolved organic matter is achieved through coagulation-flocculation followed by settling and filtration. Utilising inorganic coagulants such as alum, coagulation and flocculation are key to removing organic matter in water. Alum added to water leads in the formation of soluble and insoluble aluminum hydroxide species. The soluble species are adsorbed onto colloid surfaces, neutralizing the negative surface charge, and creating sorption bridges between colloids and organic matter and between organic compounds. The insoluble species provide further absorption surfaces, and precipitant growth (*sweep floc*) can also incorporate organic matter. The similarity between these processes and observations made in this study as to the process observed in this study to be occurring within the soil as a response to gypsum amendment is striking. Most pointed are the changes to organic character, and the role of aluminum, that was released into solution following a mass exchange with Ca in the upper A profile and the accumulation within the B horizon. Chemical modeling suggests the accumulation may involve aluminium sulfate precipitation; and increases in exchangeable Al (Chapter 3) suggests the soluble Al species are being adsorbed to mineral surfaces, as occurs with coagulation and flocculation with alum. NOM removal within the soil solution would be further enhanced by the presence of other cations in the soil solution such as Ca and other ions released in mass exchange (e.g,. Mn, Mg, Na and K)

4.4 CONCLUSIONS

Conventional water treatment with inorganic coagulants not only reduces DOC concentrations in treated water, but also influences the character of the residual organic matter. Typically lower SUVA and specific colour values occur. Such changes improve not only the aesthetic value of water, but also reduce the potential for the formation of halogenated organic compounds (i.e. THM's) resulting from disinfection, that may be of health concerns. Additional goals of water treatment are to reduce the potential for bacterial regrowth (BRP) in distribution systems. It is thought that by lowering the C/N ratios and P concentrations, water treatment may achieve this objective.

The effect (on the leachates) of applying gypsum to field soils is analogous to the outcomes of alum water treatment (*viz.* reduced SUVA, colour, C/N ratios and P concentrations). The reduction in the high molecular weight hydrophobic component of NOM having a relatively high level of aromaticity (as indicated by SUVA and specific colour), was supported by both ^{13}C-NMR and Py-GC/MS.

Reductions in total P were accompanied with reduced proportions of MRP (< 0.45 µm) compared with particulate P (>0.45 µm). These observations are further supported by the changes observed in organic matter and P distribution within the soil (Chapter 3).

Overall the results indicate that the mechanisms operating in soils accompanying gypsum treatment may be similar to those that occur in water treatment (i.e. coagulation and flocculation). Elevated ionic strength as well as the activity of polyvalent cations (Ca, Mg, Al, Mn and Fe) in the soil solution supports this analogy. In the case of the gypsum amended soils of this study, the final floc was composed not only of Al complexes (as in water treatment) but of high ([P and NOM- clay]) aggregates (see Chapter 3). Furthermore this treatment appears to have no deleterious effect on subsequent conventional water treatment of the soil leachates, based upon the jar tests conducted.

Problems to be addressed that have arisen from this study are associated with enhanced Mg and Mn mobility and increased ionic strengths.

Mg is essential to plant growth and elevated ionic strength can have detrimental effects on fertility. The enhanced leaching of Mg and increase in ionic strength of the soil solution might be considered limiting factors to the application of high doses of gypsum. However, the investigation into the effect on soil fertility indicating that the changes observed in this study may not be significant for these soils.

Additionally, the ionic strength in the leachates of the gypsum treated soil indicates the concentrations of total dissolved solids exceed Australian Drinking Water Guidelines (ADWG) that would contribute to unsatisfactory taste and excessive scaling and corrosion (NHRMC 2004). Ionic strength of leachate from the gypsum treated leachate declined over the period of this study, indicating this to be a short term consequence of the initial relatively high concentration of gypsum applied.

Concentrations of Mn greater than 0.5 mg/L exceeds the ADWG for health, and above 0.1 mg/L exceeds the ADWG for aesthetic value (taste and staining) (NHRMC 2004). Such concentrations were commonly exceeded in the gypsum treated leachates. Reductions in both exchangeable Mn in upper soils, and declining concentrations in leachates over the period of the study indicate this is possibly a transient problem, specific to the soils investigated in this study. Further investigation is therefore recommended.

5 Soil Core Leaching

5.1 INTRODUCTION

Differences in hydrologic characteristics between sub-catchments as well as variations in climatic regimes (from season to season) are typical of the complicating factors involved in subcatchment scale studies. Laboratory controlled conditions would be preferred; however, such conditions may reduce relevance to the natural environment. One of the most difficult conditions to simulate in the laboratory is also the most relevant to this study, the soil. Soil is not structurally homogenic (such as the presence of macropores) and these irregularites control how water moves through and interacts with the soil. This difficulty was addressed by using intact soil cores, that maintain natural soil structure, and presumably hydrologic character.

5.2 MATERIALS AND METHODS

5.2.1 SOIL CORES

The core leaching study presented in this Chapter used intact soil cores extracted from a site neighbouring the Mt Bold field study sub-catchments (Chapter 2). The soils had similar physical and chemical properties to the field soils described in Chapter 2. Twenty soil cores were extracted by pressing a PVC pipe (15 cm diameter by 50 cm length), with a detachable sharpened steel cutting edge, to the required depth (≈ 45 cm) in the soil profile (Figure 61a). This method retains the natural soil structure (Figure 61a and b).

Following removal from the field, the soil cores were air dried for 4 weeks. After air drying the soil, the cores contracted within the PVC piping, creating a 1 – 2 mm gap between the soil core and pipe edge. Warmed petroleum jelly was poured into the gap between the soil and pipe to produce a water tight seal to prevent preferential water flow along this interface.

Capillary resistance at the base of the core was overcome by replacement of the bottom 2.5 cm of soil, with acid washed sand. A nylon mesh was placed across the base cap to that the drainage pipe was attached, to prevent the loss of sand during leaching.

All the soil cores were initially leached with 1750 ml of RO water (equivalent to 100 mm precipitation given the core had a 15 cm diameter) in order to select cores of similar drainage rates for treatment and experimental leaching. The water was applied through a gravity feed rainfall simulator (Figure 61b), in that the reservoir was filled with the volume of water to be leached. The water was applied to the core surface as artificial *raindrops* generated by syringe needles at the base of the reservoir. This delivered a simulated rainfall at a rate of approximately 50 mm/hr, a similar rate as high intensity storm events observed in the Mt Bold region. From the original 20 cores, only 9 cores were found to drain after a 72 hour period (presumabley the remaining 11 cores contain no hydraulically continuous macropores through the core).

5.2.2 SOIL CORE TREATMENTS

With 9 serviceable cores 2 gypsum treatments were selected: 3 t/ha and 10 t/ha (3 replicates of each) and 3 controls (no gypsum). Based on a core surface area ≈ 176.7 cm^2, 5.3 g and 17.7 g of reagent grade gypsum were applied to the surface through a 500 μm sieve to the 3 and 10 t/ha gypsum treatments respectively. To each of the soil cores P fertiliser (single superphosphate- SSP) was surface applied at a rate ≈ 20 kg P/ ha (400 mg SSP/ core). To ensure uniform P release from the fertiliser granules, they were sieved to a minimum diameter of 1.5 mm and a maximum of 2 mm

Two concurrent experiments were run on the 9 soil cores. Experiment 1 used the cores as prepared with the treatments described above. Experiment 2 incorporated the treatments above with the addition of lime ($CaCO_3$) to cores that were found to have leachate pH < 6. Both the experimental conditions are detailed in the following section.

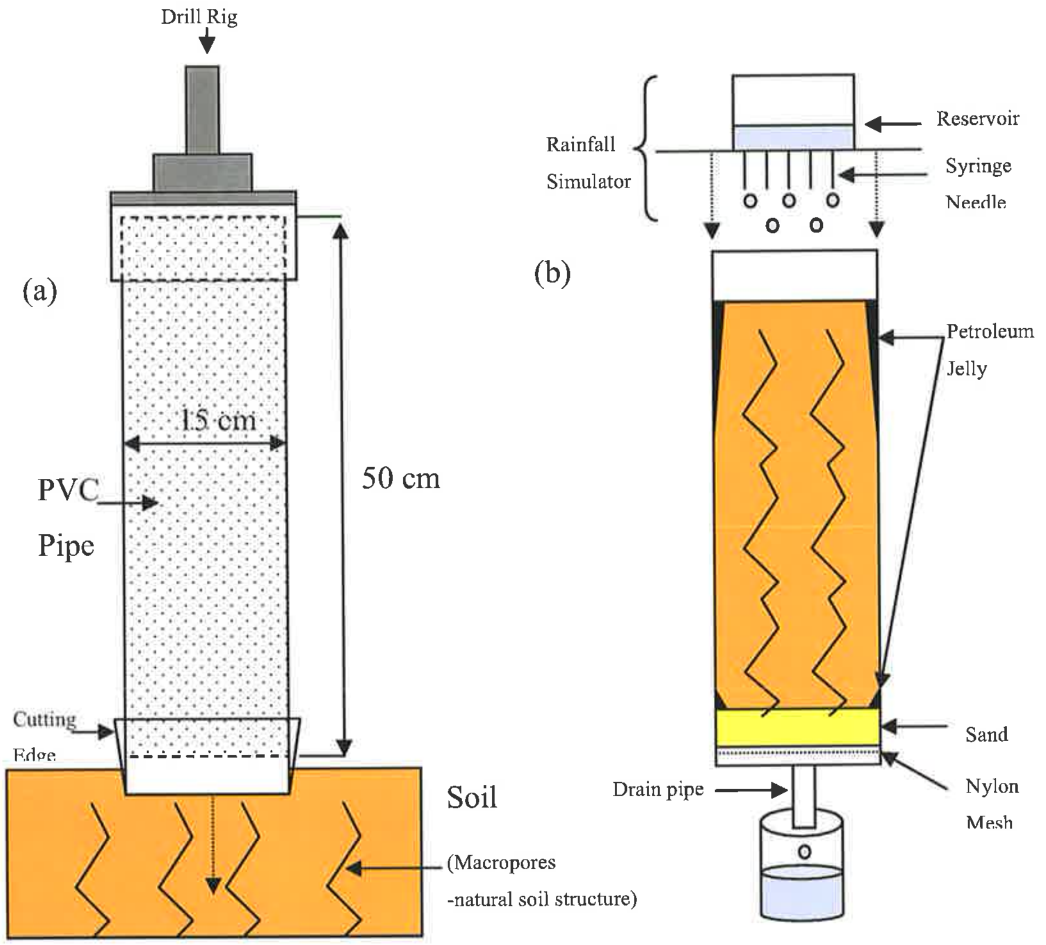

Figure 61 a. Soil core recovery; b. Soil core leaching set up.

5.2.3 EXPERIMENT 1

5.2.3.1 Leaching Regime

Experiment 1 consisted of 5 leaching cycles (L1 to L5), the cores were oven dried (45°C) for 7 days between L2 and L3, with all other leaching runs separated by 48 hour drainage periods. The extended oven drying was designed to simulate an extended drying period, such as happens naturally at the field site in summer.

The leaching regime in Experiment 1 consisted of five separate irrigations each of 1250 ml (equivalent to 71 mm). Between each leaching there were 4 drying cycles summarised in Table 49.

Table 49 Drying cycles used in Experiment 1.

Drying Cycle	1	2	3	4
Leaching Interval	L1-L2	L2-L3	L3-L4	L4-L5
Method	Air	Oven (45°C)	Air	Air
Drying Time	48hrs	7days	48hrs	48hrs

5.2.3.2 *Sampling Regime*

The time and exact volume of each sample collected was recorded, from that the average flow rate of each core was determined.

5.2.3.3 *Analysis*

Immediately upon collection, a sub-sample of the leachate was filtered through 0.45 μm filter, and the filtrate stored at < 4°C prior to analysis. The pH was measured within 6 hr of collection. The concentration of total phosphorus (TP) and other cations was measured on whole water samples by ICPOES (for method see Chapter 3). MRP was measured in the < 0.45 μm fraction of all samples from each leaching using a modified method of Murphy and Riley (1962) (see Chapter 3). In the subsequent leachings TP was measured on solutions using the MRP method on neutralised whole water samples digested using nitric-perchloric acid.

Turbidity measurements were made using a Hatch Turbidity Meter.

5.2.4 EXPERIMENT 2

5.2.4.1 *Soil Treatment*

Experiment 2 used the same cores as in Experiment 1. From Experiment 1, it was found that some cores (Core 1 [0 t/ha] and all gypsum treated cores) had leachates with pH values considerably more acidic than the other 2 non-gypsum treated cores (see Results: Figure 62). To account for these differences in pH, lime was added to the more acidic cores at a rate of 3 T $CaCO_3$/ha. The lime was incorporated into the upper 2 cm of the core soil.

5.2.4.2 *Leaching Regime*

The soil cores were allowed to air dry for 8 weeks between experiments 1 and 2. The $CaCO_3$ was applied 24 hr prior to the first leaching of Experiment 2. The upper 2 cm of soil, including the lime was overturned to incorporate the lime into the soil. Experiment 2 consisted of 5 leachings, some of that had been spiked by the addition to the irrigation water of organic extract (below) or phosphate, either separately or combined (Table 50). Leachings in this experiment were separated by periods of air-drying (Table 50).

The concentrations of gypsum ($CaSO_4.2H_2O$) (100 mg Ca L^{-1}) and NOM (35 mg DOC L^{-1}) were chosen from concentrations observed in previous field work (Chapter 4). The NOM was extracted from surface litter (SL) obtained from the Mt Bold field site (Chapter 2). The SL was combined with RO water in a ratio of 5 parts water to 1 part SL by weight and the suspension left for 24 hr with occasional stirring. The solution was extracted by filtration, initially through silica wool and then through a Whatman 42 filter paper. This made a solution of approximately 1800 mg/L DOC.

Table 50. Leaching regime for Experiment 2. Dry = drying period from last leaching (w=weeks, d=days). OM = organic matter spiking, P = phosphorus spiking.

	L1	L2	L3	L4	L5
Leaching Vol (ml)	1500	1000	1000	1000	1000
Eqiv. Precip (mm)	85	57	57	57	57
OM mg/L (Spiking)	0	35	35	0	35
P mg/L (Spiking)	0	0	0	5	5
Drying (Time)	8 w	7 d	2 d	4 d	4 d

5.2.4.3 *Sampling and Analysis*

Single bulk samples of leachates were collected from each leaching cycle. Measurements (pH, EC and MRP) were made immediately following collection (within 48 hr of initiation of irrigation). Total concentrations of elements Fe, Al, Mn, Zn, Ca, Mg, Na, K, S and P were measured by ICPOES of nitric-perchloric acid digests of whole water samples. PP was calculated by the difference between TP and

MRP. Samples were stored at < 4°C prior to further organic analysis (DOC, UV-vis and colour).

DOC, absorbance at 254 nm (UV_{254}) and colour measurements were made on the < 0.45 μm fraction of leachates from L1, L4 and L5. DOC of the leachates was measured using a Skalar Model SK-12 TOC analyser (Chapter 3). Colour and UV_{254} measurements were made on < 0.45 μm fraction. UV_{254} of the filtered sample was measured using a Perkin-Elmer Lambda 2 UV/Vis spectrometer (see Chapter 3). Specific ultra violet absorbance (SUVA) was calculated as the ratio of UV_{254} to DOC multiplied by one hundred. Colour, in Hazen units (HU) was determined from absorbance at 456 nm (Bennet and Drikas, 1993). Specific colour was calculated as the ratio of colour (in HU units) to DOC concentration.

5.3 RESULTS AND DISCUSSION

5.3.1 FLOW RATES

Table 51 Flow rates for each core calculated from the first 60 mls collected in leaching 1.

Treatment (Gypsum t/ha)	Core #	Flow Rate (ml/min)	Ave For 3 Core
0 (0)	1	2.0	
	2	2.0	
	3	0.2	1.4
L (3)	1	0.8	
	2	1.8	
	3	2.3	1.6
H (10)	1	1.3	
	2	0.9	
	3	1.6	1.3

5.3.2 P TRANSFER

5.3.2.1 Experiment 1.

Figure 62 shows the average P concentrations (MRP and PP) in L1 and L2 along with and the pH of leachates.

No obvious treatment effect can be attributed to gypsum on P concentration in leachates of Experiment 1, although a distinct trend was evident (Figure 62). Consistently through each leaching the H gypsum treatment was lower in MRP concentration than the 0 treatment. Such a difference was not clearly evident between the L and O or the L and H treatments. There was no apparent trend between pH and P concentration.

Generally, the P concentration in leachates decreased in consecutive events with all treatments. The average P concentration in the leaching event following the extended oven-drying period however was slightly higher in the L and O treatments, with no difference (on average) in the H treatment. The average in the O treatment was substantially affected by the high flux of Core 2. Such a trend is consistent with field observations (Chapter 4), with the most significant differences between the P concentration in leachates noted between the gypsum treated and non treated soils.

The average turbidity of leachates 1-5 is presented in Figure 63. This illustrates a clear trend in that both the gypsum treated cores, the turbid load was considerably less on average. The variability (as indicated by standard deviation error bars) was also inversely proportional to the treatment, i.e. variability increased in the order 10 t/ha < 3 t/ha < 0 t/ha.

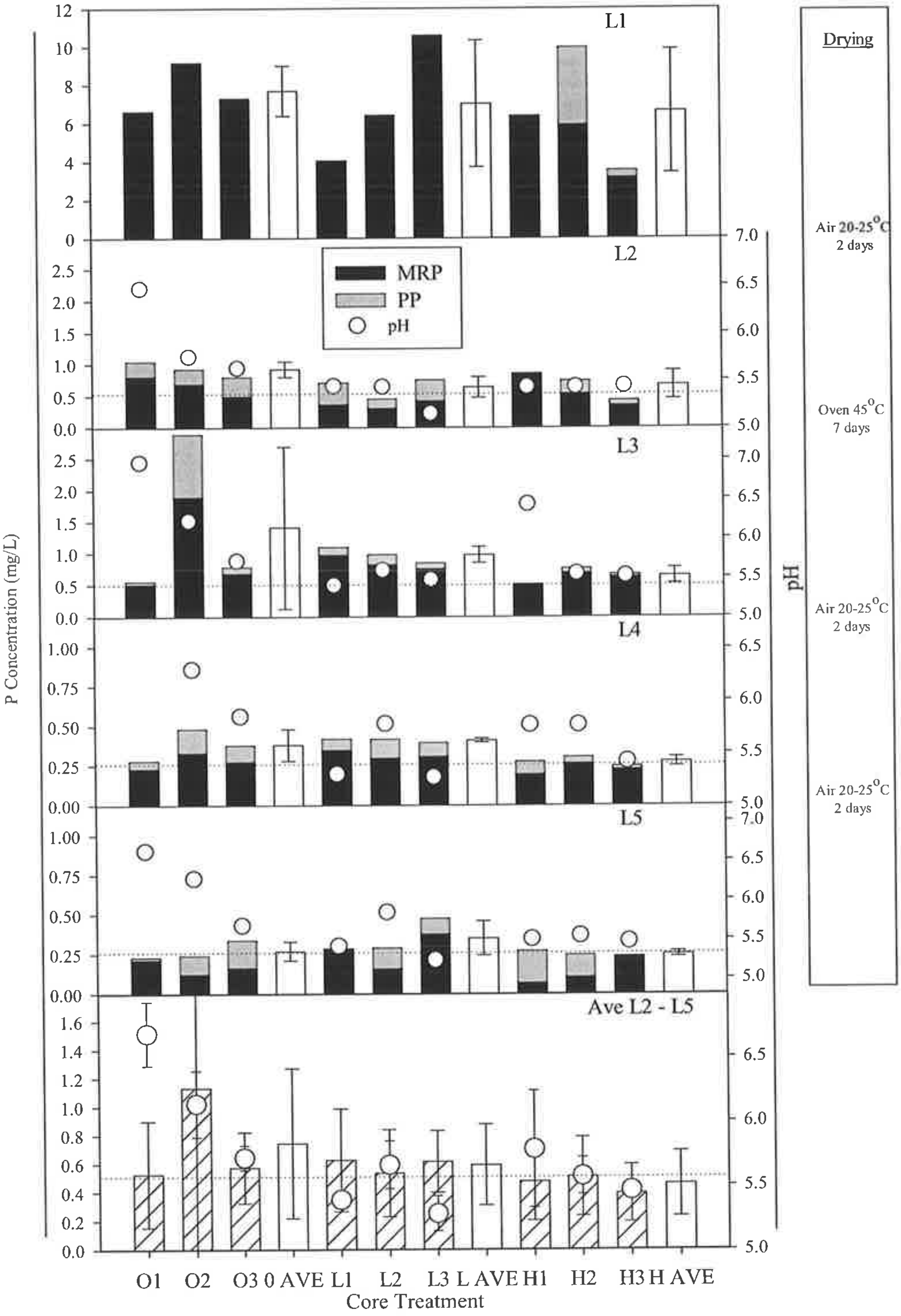

Figure 62 Average P concentration (as MRP and PP) and average pH of leachates from Experiment 1 with corresponding drying cycles. L1 was not included in the average due to the very high concentration of P that would bias the subsequent data. The dotted line in L2 to Ave L2-L5 is a reference line. 01-3, L1-3 and H1-3 represent each of the 3 repetitions of the gypsum treatments (0, 3 and 10 t/ha).

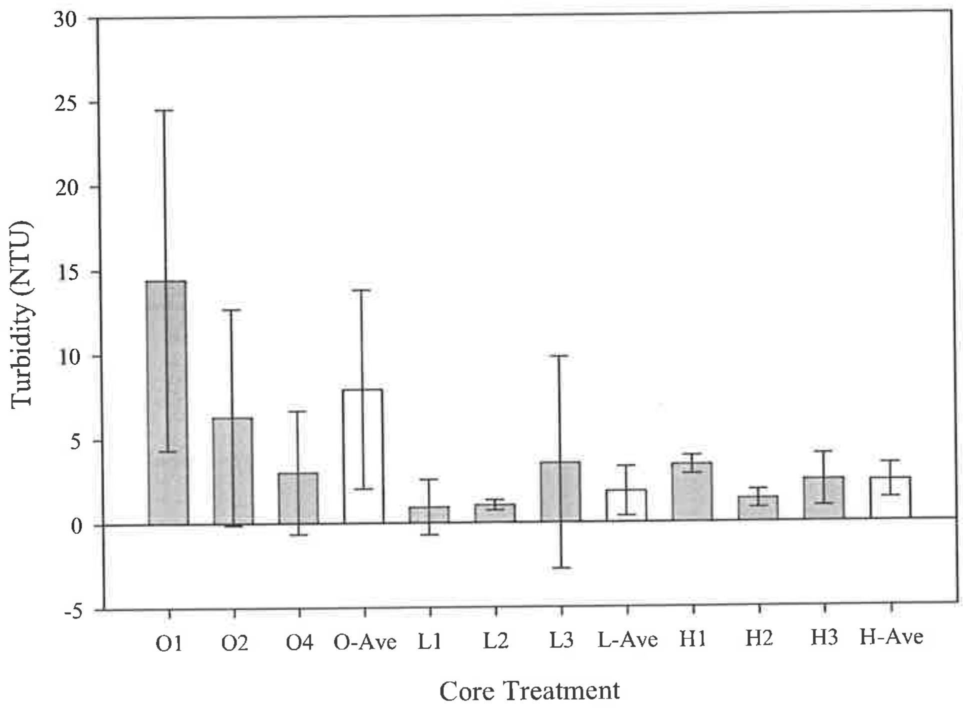

Figure 63. Average turbidity of leachates (1-5) from Experiment 1 and average for each treatment. 01-3, L1-3 and H1-3 represent each of the 3 repetitions of the gypsum treatments (0, 3 and 10 t/ha).

5.3.2.2 *Experiment 2*

Figure 64 presents TP (as PP and MRP) in leachate solutions collected from the 5 leachings (L1 – L5) in Experiment 2. A much stronger treatment effect was evident in Experiment 2, most notability in the P spike leachates of L4 and L5.

5.3.2.2.1 *L1 (1000 ml H_2O)*

TP concentrations in L1 were less than ~0.1 mg/L, that are lower but of a similar magnitude to the concentrations in the final leachate collected in the experiment. The MRP was marginally lower in all gypsum treated cores.

5.3.2.2.2 *L2 and L3 (1000 ml H_2O + 35 mg DOC)*

The trend of L1 from Experiment 1 to Experiment 2 continued through leachings L2 and L3 with a continued decline in P leaching. Solutions from the gypsum treated cores contained negligible MRP with only 1 core in the 3 t/ha treatment eluting PP (approximately 0.1 mg/L). In L3, the only cores to release any MRP were the untreated cores (1 and 2) that had solution concentrations less than 0.05 mg/L.

5.3.2.2.3 L4 (1000 ml H_2O + 5 mg P)

Spiking the irrigation solution with 5 mg/L P increased the total P (both MRP and PP) concentrations in the leachate. All leachates had concentrations lower than 5 mg/L indicating P was still being adsorbed in all the cores. Clear treatment effects were observed between the 10 t/ha gypsum and 3 and 0 t/ha treatments, with little observable difference between the latter two. The leachates collected from all 3 cores treated with 10 t/ha contained lower TP (both PP and MRP) than all other cores.

5.3.2.2.4 L5 (1000 ml H_2O + 5 mg P + 35 mg DOC)

Solution concentrations of both MRP and PP exceeded those observed in L4 in all leachates, but were still less than the 5 mg/L of applied P, indicating the cores still had a capacity for P retention. As with L4, the concentrations of both P fractions were significantly less in the high gypsum treatment, again with little difference between the low and 0 gypsum treatments.

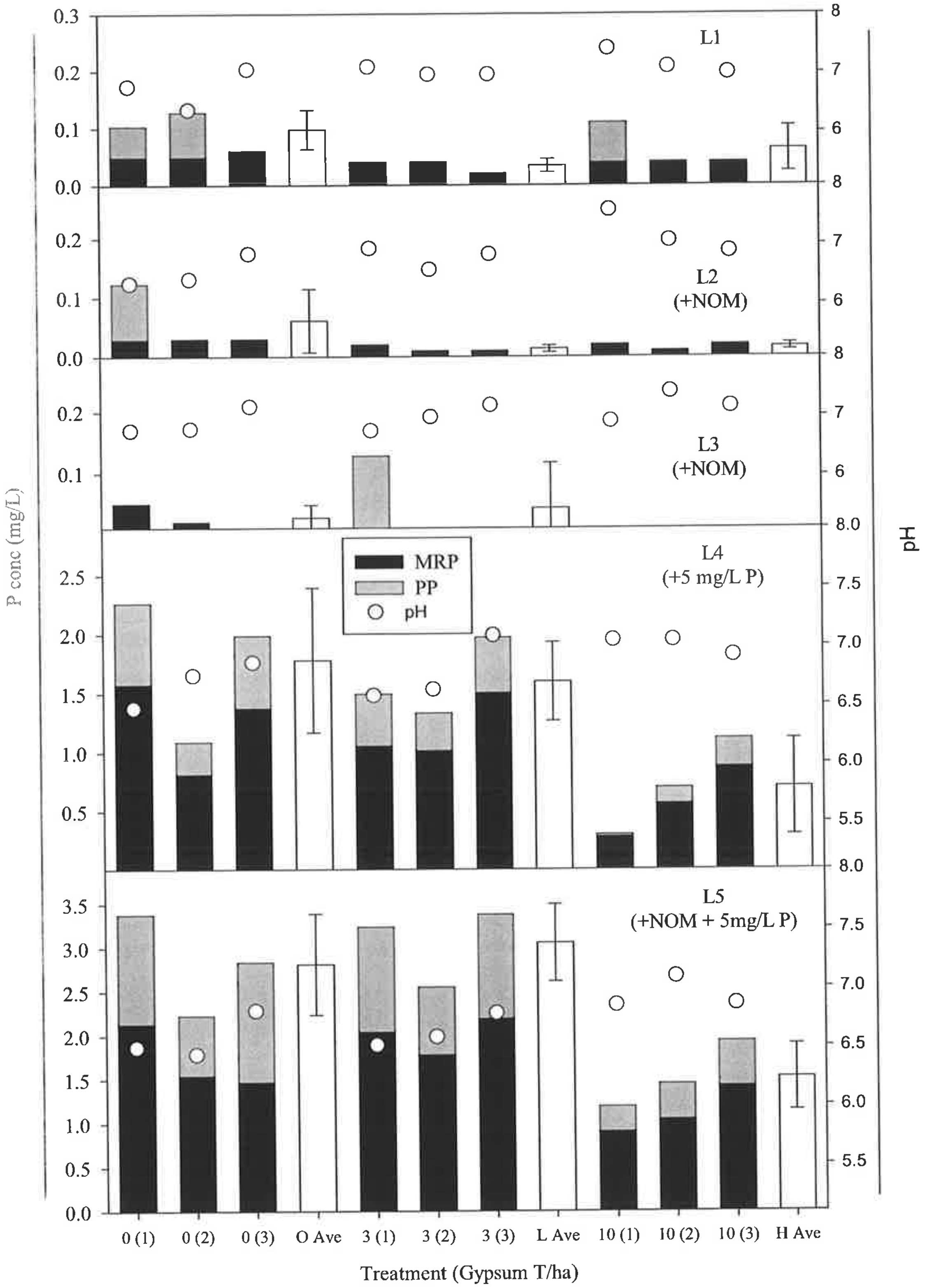

Figure 64. P concentration and pH of leachates collected from leachings1-5 of Experiment 2. 01-3, L1-3 and H1-3 represent each of the 3 repetitions of the gypsum treatments (0, 3 and 10 $T.ha^{-1}$).

5.3.3 DOM TRANSFER: EXPERIMENT 2

Little treatment effect on DOC movement through the soil cores was evident in the initial leachate (L1), although average DOC was slightly lower in the H treatment compared with the O and L treatments (Figure 65). There was however substantial change in the character of the DOM, with reduced SUVA and Specific Colour in gypsum treated cores, most notably the H treatment (Figures 66 and 67). These latter two parameters indicate a preferential removal of HMW hydrophobic organic compounds in both gypsum treatments, a trend consistent with field observations (Chapter 4).

The irrigation water of L4 was spiked with approximately 35 mg/L of organic extract, and the leachates of the gypsum treated cores in this and the subsequent L5 leaching had significant reductions in DOC concentrations. There was no observable difference between L and H treatments in L4, however in L5, the DOC concentration was clearly lower in the H treatment. Similar to L1, the gypsum treatments also affect changes in the character of the DOM with reduced SUVA and Specific Colour. An interesting trend, that was evident in the gypsum treated cores, was that the greater the reduction in DOC the higher were the SUVA and Specific Colour values. Such a trend is indicative that the higher DOC removal in these cores was through the preferential removal of LMW organic matter. This observation contrasts with the general observations and conclusion from the field leachate study (Chapter 3). This appears to be a result of spiking the solution with organic matter, that results in a net desorption of organic matter as the DOC content of the leachates was greater than the leaching solution applied (Figure 65). From this observation it is concluded that the LMW organic material was more strongly retained in the gypsum treated cores, whereas it was more easily dislodged by preferential adsorption of HMW compounds in the untreated cores. This would be a result of a generally higher sorption capacity (hence reduced competition) in the gypsum treated cores.

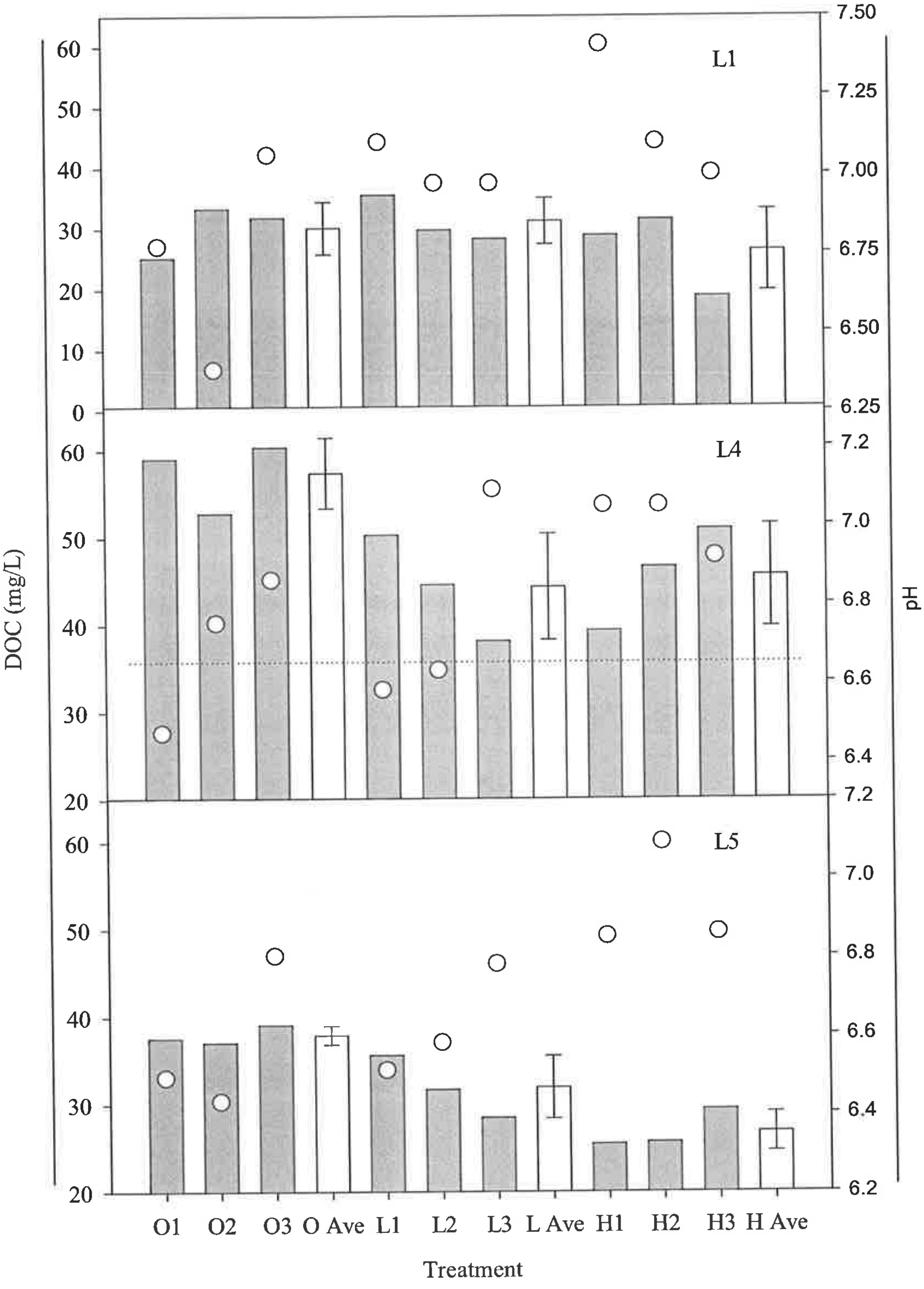

Figure 65 DOC concentration and pH of leachates from L1, L4 and L5 in Experiment 2. 01-3, L1-3 and H1-3 represent each of the 3 repetitions of the gypsum treatments (0, 3 and 10 T.ha^{-1}).

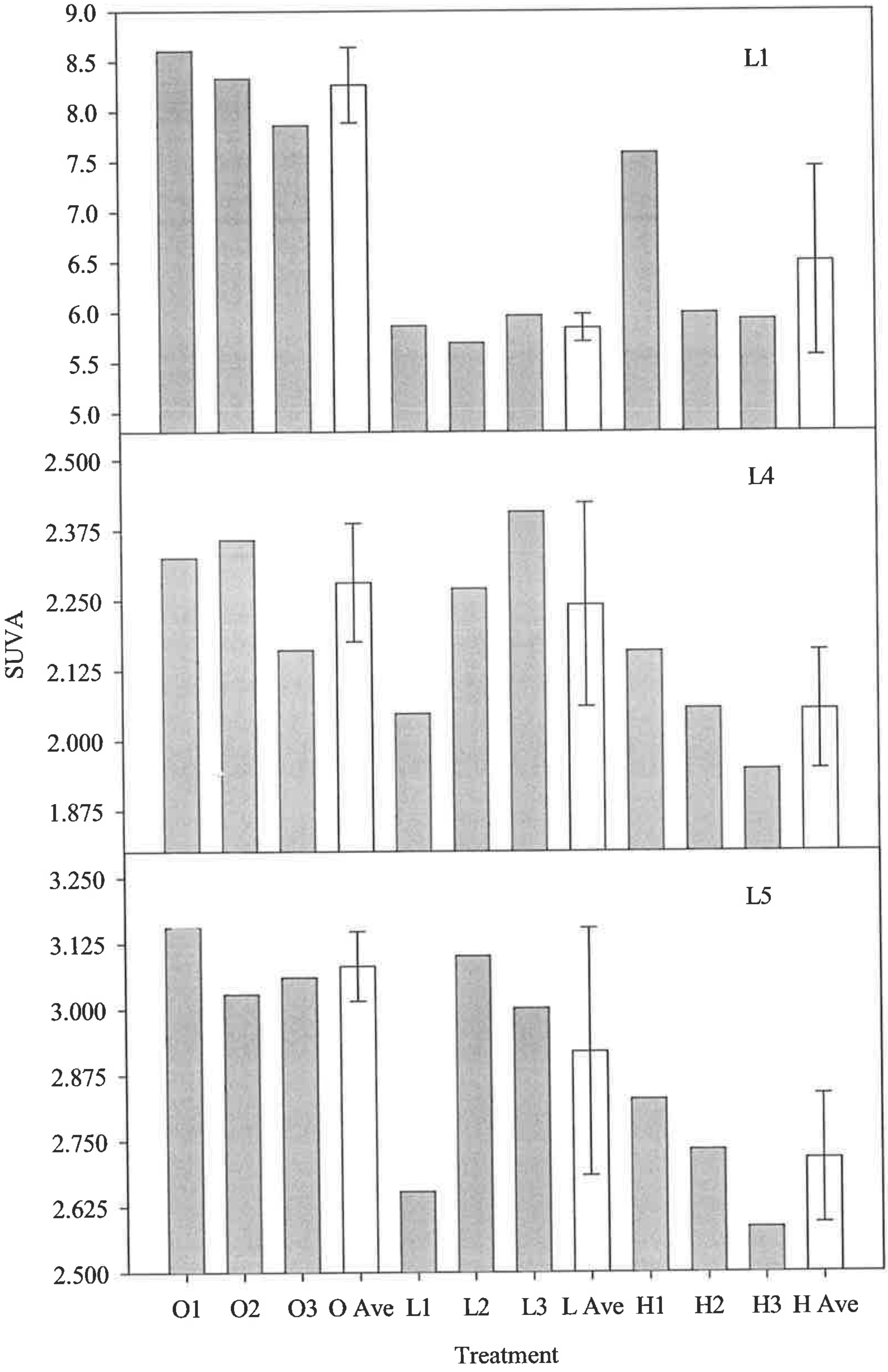

Figure 66 SUVA in leachates from L1, L4 and L5 in Experiment 2. 01-3, L1-3 and H1-3 represent each of the 3 repetitions of the gypsum treatments (0, 3 and 10 T.ha^{-1}).

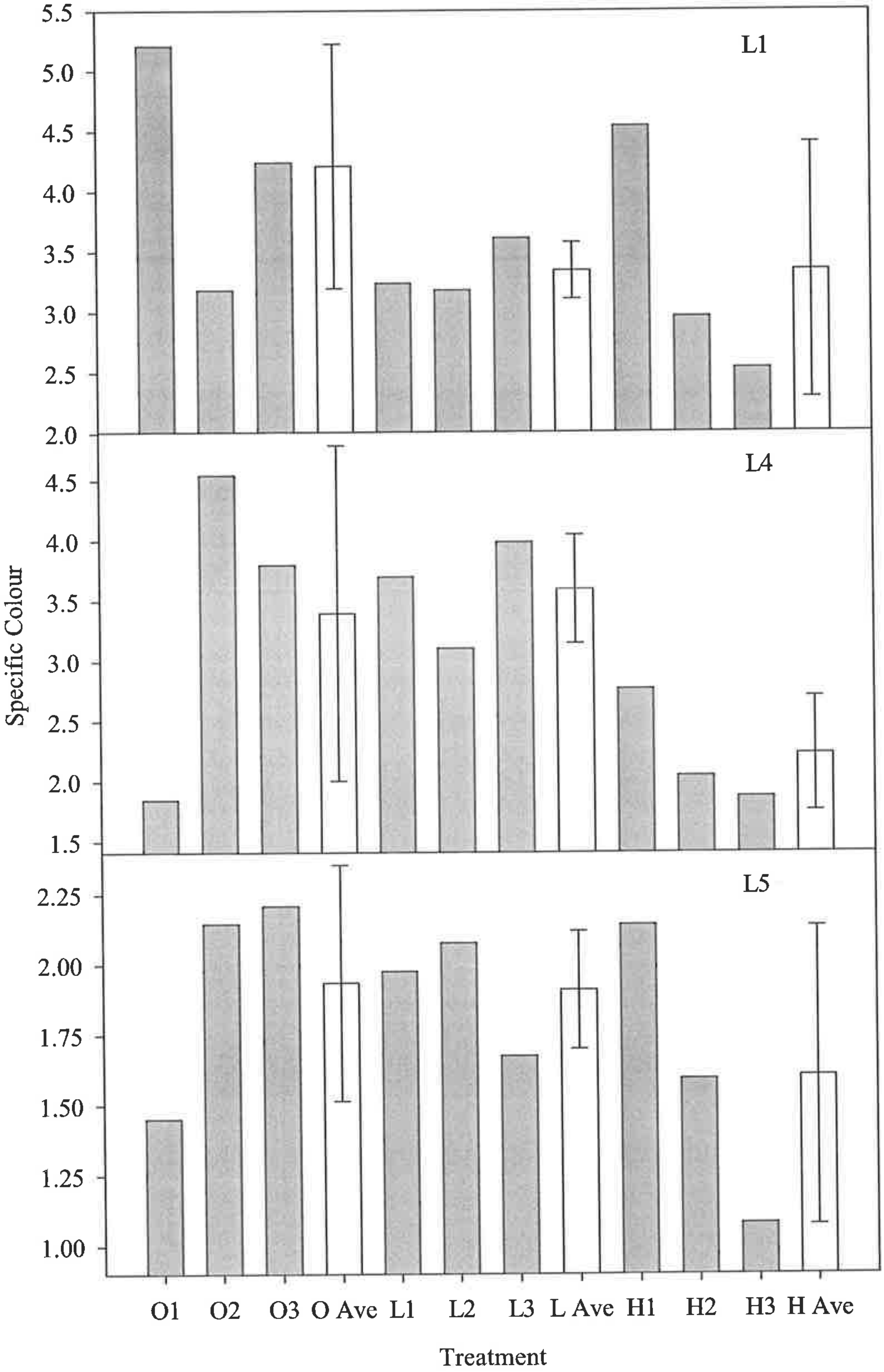

Figure 67 Specific Colour in leachates from L1, L4 and L5 in Experiment 2. 01-3, L1-3 and H1-3 represent each of the 3 repetitions of the gypsum treatments (0, 3 and 10 T.ha^{-1} respectively).

5.3.4 LEACHATE INORGANIC CHEMISTRY

5.3.4.1 Experiment 1

Elemental compositions and pH of leachate collected from L1 are presented in Table 52. Solutions from the two gypsum treatments were higher in Ca and S as expected, but also had elevated concentrations of Mn, Zn, Mg and Na compared with the non-gypsum treated cores. The leachates from the 0 t/ha cores had higher pH levels and solution concentrations of Fe and Al. These observations were consistent with field measurements presented in Chapter 4.

The losses of Mn, Mg and Na (in addition to Ca and S) in the leachate was proportional to gypsum application, i.e. the concentration of these elements increased with increasing gypsum application (0 < 3 < 10 t/ha gypsum). There was no clear difference between the 3 and 10 t/ha treatments on Fe, Al or Zn concentrations. As reagent grade gypsum was used in these experiments, this result clearly indicates mass exchange, similar to that hypothesised in the preceding chapter is indeed occurring.

Table 52 Elemental Composition first Leaching (L1)

		Fe	Mn	Zn	Ca	Mg	Na	P	S	Al	pH
Treatment	Core					mg/L					
0t/ha Gypsum	1	0.053	0.04	0.015	21.0	2.82	4.89	6.56	6.60	0.063	6.7
	2	0.112	0.09	0.027	17.8	2.77	2.09	13.35	5.30	0.270	6.3
	3	0.088	0.14	0.057	12.1	2.92	4.53	7.30	3.94	0.185	5.7
	ave	0.084	0.093	0.033	16.98	2.84	3.84	9.07	5.28	0.173	6.233
3t/ha Gypsum	1	0.016	0.56	0.068	102.5	8.78	12.54	3.27	88.7	< 0.05	5.4
	2	0.014	0.31	0.144	103.6	3.95	2.64	8.38	81.0	< 0.05	5.8
	3	0.028	0.35	0.079	148.2	6.94	3.20	18.81	115.2	< 0.05	5.25
	ave	0.019	0.409	0.097	118.10	6.56	6.13	10.15	94.95	< 0.05	5.483
10t/ha Gypsum	1	0.019	0.71	0.088	374.5	15.67	19.30	6.96	314.2	< 0.05	5.6
	2	0.027	0.65	0.091	303.3	10.68	12.40	7.93	250.2	< 0.05	5.5
	3	< 0.01	0.24	0.060	230.1	9.42	12.96	5.16	189.6	< 0.05	5.5
	ave	0.023	0.536	0.080	302.70	11.90	14.89	6.68	251.30	< 0.05	5.533

5.3.4.2 Experiment 2

Similar trends with respect to Mn, Zn, Mg, Ca, S and Na were observed in Experiment 2 (Table 53) and Experiment 1 (Table 52). Again the losses of Mn, Mg and Na were proportional to gypsum treatment (0 < 3 < 10 T gypsum/ ha). Generally the concentrations of most constituents, particularly Mn, Mg and Na were higher in Experiment 2. The liming of the gypsum treated cores and core 3 of the non treated cores resulted in pH increases of the leachate in the order of approximately 1.5 units. Despite liming of Core 3 (0t/ha), the Ca content of the leachate from this core was still similar to the magnitude of the un-limed control (0 t/ha) cores.

Table 53. Elemental composition of leachates from L1-L5 of Experiment 2.

Leaching		Core Treatment	Fe	Mn	Zn	Ca	Mg	Na	K	P	S	Al	MRP	PP	pH
							mg/L								
1		0 t/ha (1)	0.030	0.14	< 0.009	52	7.6	53	3.2	0.10	7.6	< 0.1	0.05	0.053	6.77
		0 t/ha (2)	0.18	0.30	0.020	45	10.0	51	3.2	0.13	9.6	0.16	0.05	0.078	6.38
		0 T/ ha (3)	0.044	0.63	< 0.009	67	10.0	65	4.6	< 0.1	11.5	< 0.1	0.06		7.06
		3 T/ ha (1)	0.032	1.9	0.035	220	30	68	6.1	< 0.1	153	< 0.1	0.04		7.1
		3 t/ha (2)	0.030	0.81	0.024	240	23	70	3.8	< 0.1	172	< 0.1	0.04		6.97
		3 t/ha (3)	0.032	0.57	< 0.009	143	13.9	81	5.2	< 0.1	107	< 0.1	0.02		6.97
		9 t/ha (1)	0.053	3.6	0.045	440	34	75	25	0.11	350	< 0.1	0.04	0.069	7.41
		9 t/ha (2)	0.028	1.1	0.033	350	34	68	5.6	< 0.1	290	< 0.1	0.04		7.1
		9 t/ha (3)	0.015	0.79	0.016	280	32	71	3.4	< 0.1	230	< 0.1	0.04		7
2	+ NOM	0 t/ha (1)	0.11	0.32	0.017	46	6.4	30	3.7	0.12	6.0	< 0.1	0.03	0.093	6.34
		0 t/ha (2)	1.0	0.23	0.018	27	5.7	29	2.3	< 0.1	4.2	0.17	0.03		6.41
		0 T/ ha (3)	0.15	0.47	0.013	45	6.6	32	3.4	< 0.1	5.5	< 0.1	0.03		6.84
		3 T/ ha (1)	0.17	1.7	0.057	140	20	38	7.1	< 0.1	101	< 0.1	0.02		6.93
		3 t/ha (2)	0.11	0.90	0.024	106	11.8	34	3.3	< 0.1	75	< 0.1	0.01		6.57
		3 t/ha (3)	0.039	0.35	0.011	84	10.3	27	3.1	< 0.1	49	< 0.1	0.01		6.83
		9 t/ha (1)	0.66	3.5	0.032	390	36	56	22	< 0.1	310	< 0.1	0.02		7.58
		9 t/ha (2)	0.083	1.3	0.034	260	23	36	4.2	< 0.1	210	< 0.1	0.01		7.06
		9 t/ha (3)	0.045	0.71	0.020	181	24	32	2.6	< 0.1	145	< 0.1	0.02		6.88
3	+ NOM	0 t/ha (1)	0.099	0.28	< 0.009	38	6.1	23	2.5	< 0.1	4.2	< 0.1	0.05		6.75
		0 t/ha (2)	0.63	0.25	0.014	29	6.3	24	< 2	< 0.1	4.3	< 0.1	0.02		6.78
		0 T/ ha (3)	0.17	0.25	0.014	37	6.1	25	2.1	< 0.1	3.7	< 0.1	0.01		7.16
		3 T/ ha (1)	0.10	1.5	0.042	102	14.2	31	5.5	0.13	74	< 0.1	0.00	0.128	6.75
		3 t/ha (2)	0.16	0.58	0.021	95	13.1	28	2.3	< 0.1	69	< 0.1	0.00		6.98
		3 t/ha (3)	0.050	0.28	< 0.009	78	11.1	23	2.4	< 0.1	44	< 0.1	0.00		7.18
		9 t/ha (1)	0.19	2.5	0.032	220	14.5	32	17.3	< 0.1	171	< 0.1	0.00		6.91
		9 t/ha (2)	0.10	1.1	0.032	220	23	30	3.2	< 0.1	175	< 0.1	0.00		7.41
		9 t/ha (3)	0.052	0.78	0.022	171	27	29	2.3	< 0.1	145	< 0.1	0.00		7.16
4	+ 5 mg/L P	0 t/ha (1)	0.034	0.13	< 0.009	30	4.6	11.8	< 2	2.3	3.7	< 0.1	1.58	0.685	6.47
		0 t/ha (2)	0.16	0.14	< 0.009	17.6	4.0	13.3	< 2	1.1	2.8	< 0.1	0.82	0.271	6.75
		0 T/ ha (3)	0.053	0.22	< 0.009	27	4.3	13.3	< 2	2.0	2.8	< 0.1	1.38	0.608	6.86
		3 T/ ha (1)	0.041	0.61	0.022	50	8.0	11.4	2.2	1.5	36	< 0.1	1.06	0.434	6.58
		3 t/ha (2)	0.042	0.33	0.014	67	8.2	12.3	< 2	1.3	50	< 0.1	1.02	0.313	6.63
		3 t/ha (3)	0.018	0.15	< 0.009	58	7.5	9.1	< 2	2.0	33	< 0.1	1.51	0.464	7.09
		9 t/ha (1)	0.072	1.7	0.013	170	14.0	19.2	13.4	0.30	135	< 0.1	0.29	0.013	7.05
		9 t/ha (2)	0.044	1.0	0.024	200	16.3	15.6	3.0	0.70	161	< 0.1	0.57	0.129	7.05
		9 t/ha (3)	0.019	0.59	0.021	145	20	14.2	< 2	1.1	121	< 0.1	0.88	0.237	6.92
5	+ NOM + 5 mg/L P	0 t/ha (1)	0.13	0.21	< 0.009	30	4.5	9.9	2.1	3.4	3.3	< 0.1	2.14	1.241	6.49
		0 t/ha (2)	0.92	0.16	< 0.009	17.7	4.0	11.0	< 2	2.2	2.5	0.20	1.55	0.679	6.43
		0 T/ ha (3)	0.22	0.25	0.016	28	4.6	11.7	2.3	2.8	2.5	< 0.1	1.48	1.358	6.8
		3 T/ ha (1)	0.15	0.54	0.019	43	6.8	9.0	3.0	3.2	28	< 0.1	2.05	1.190	6.51
		3 t/ha (2)	0.19	0.39	0.014	63	7.5	11.0	< 2	2.6	44	< 0.1	1.79	0.766	6.58
		3 t/ha (3)	0.069	0.14	< 0.009	58	7.4	8.3	2.9	3.4	31	< 0.1	2.20	1.181	6.78
		9 t/ha (1)	0.32	1.5	0.017	140	11.4	13.8	11.7	1.2	110	< 0.1	0.91	0.281	6.85
		9 t/ha (2)	0.16	1.2	0.034	199	15.7	12.6	3.3	1.5	158	< 0.1	1.05	0.401	7.09
		9 t/ha (3)	0.046	0.56	0.022	138	20	12.9	< 2	1.9	115	< 0.1	1.43	0.506	6.86

5.4 CONCLUSIONS

Comparison of the leachate compositions, between the control (0 t/ha) and the H treatment (10 t/ha) and those from the field (see Chapter 4) show very similar trends, i.e. reduced pH, P, DOC, SUVA, Specific Colour, Al and Fe and increases in Mn, Mg and Na. P retention was substantially enhanced when the soils of the H cores were limed. Little difference was observed in leachate composition in the L cores (with the exception of elevated Mg and Mn concentrations and reduced pH) compared to the control cores. This indicates that a minimum dose of gypsum is required to effect a measurable change on P and DOC removal, that is between 3 and 10 t/ha for these soils.

6 Kaolinite Batch Experiments

6.1 INTRODUCTION

The purpose of the work described in this chapter was to investigate the mechanisms of P and NOM adsorption in a pure system. In order to predict adsorption behaviour in variable charged soils, Bowden *et al.* (1980) suggest the following factors that should be considered; concentration of adsorbing ions pH; ionic strength; competing ions; cooperating ions; and nature of the adsorbent. Thus these were the factors considered in this study of the effect of gypsum on the retention of phosphate (PO_4^{3-}) and natural organic matter (NOM) on a model soil mineral (kaolinite). The list of variables considered in experiments presented in this chapter are: concentration of adsorbing ions (PO_4^{3-} and organic anions); pH; ionic strength; competing ions (organic anions and sulfate-SO_4^{2-}); cooperating ions (Ca^{2+}); and nature of the adsorbent (kaolinite). As redox conditions are an important consideration, all experiments carried out in this study were under oxic (atomspheric) conditions.

The concentrations of various ions, including PO_4^{3-}, SO_4^{2-}, Ca^{2+} and NOM (organic anions), and the pH and ionic strengths used in this study are commonly measured, all drawn from results in the leachates from the catchments (Chapter 4). Kaolinite is used as the soil mineral because it is the dominant clay mineral in the soils of the Mt Bold catchments.

6.2 REVIEW OF THEORY

The following discussion details the interactive nature of the factors listed above, and indicates how studying these interactions can give insight into potential mechanisms by that PO_4^{3-} retention may be enhanced by the addition of gypsum. Additionally, the effect on NOM retention was also investigated.

6.2.1 ADSORBING ION CONCENTRATION AND PH

At a constant pH the surface activity of an adsorbing ion increases as its concentration in solution increases. This increase is not in proportion to the increase in ion concentration because: (1) there is a reduced probability of the ion finding a vacant site, and (2) the surface becomes increasingly like-charged (and thus resistant) to adsorption as adsorption proceeds (Bowden *et al,*. 1980).

Variations in pH at constant adsorbing ion concentration can also affect the rate of ion adsorption, by changing either the activity (or valency) of the adsorbing ion or the surface activity of the adsorbent. The effect of variations in pH on ion activity is well illustrated with the polybasic anion, phosphoric acid (H_3PO_4). As pH increases phosphoric acid undergoes a series of deprotonations $H_3PO_4 \leftrightarrow H_2PO_4^- \leftrightarrow HPO_4^{2-} \leftrightarrow PO_4^{3-}$; ($pK_{a1} \approx 2.1$, $pK_{a2} \approx 7.2$, $pK_{a3} \approx 12.3$). At pH 4, when maximum phosphate adsorption occurs (Bowden *et al,*. 1980), $H_2PO_4^-$ is the dominant phosphate species. However, phosphate adsorption at this pH is dominated by the less concentrated divalent HPO_4^{2-} ion, such that HPO_4^{2-} is adsorbed to an extent greater than its concentration would suggest.

6.2.2 IONIC STRENGTH

According to McBride (1994), ionic strength is a measure of the *nonideality* that the solution imposes on any dissociated electrolyte. As solutions increase in ionic strength, the interaction between ions of opposite charge increases such that this electrostatic attraction lowers the effective activity of the ions of interest. Bowden *et al. (*1980) illustrates the effect that increasing ionic strength has on adsorption with two examples. Where an ion that is specifically adsorbed in a region of like-electrostatic potential, increasing ionic strength reduces this potential near the adsorbent surface and allows for increased adsorption. The second case is where an ion is adsorbed in a region of opposite charge. Increasing ionic strength in this situation reduces the attractive forces and, as a consequence, adsorption is diminished. Although disputed by Manceau and Charlet (1994) several authors including Bowden *et al.* (1980), Hayes *et al.* (1988) and He *et al.* (1997) suggest that by studying the effects of ionic strength on adsorption, the mechanism of surface complexation (i.e. specific or non-specfic) can be inferred. For this reason variable ionic strength was a factor considered in this study.

6.2.3 COMPETING IONS

Competitive ions are ions of like charge to the ions of interest that either directly compete for the same adsorption sites (direct competition), or increase the net like charge in a region where the competing ion is adsorbed (electrostatic competition).

6.2.4 COMPETING IONS, IONIC STRENGTH AND PH: Ca^{2+} AND SO_4^{2-}

Variations in pH not only effect the properties of the adsorbing ion of interest and the adsorbent surface, but also effect the activities of other ions (both competitive and cooperative). As SO_4^{2-} is a significant component of gypsum, it is important to consider the competitive relationship between PO_4^{3-} and SO_4^{2-}. The competitive relationship of adsorption between PO_4^{3-} with SO_4^{2-} has previously been studied by Metson and Blakemore (1978), Bolan *et al.* (1986), Geelhoed *et al.* (1997), He *et al.* (1997) and Liu *et al.* (1999). Geelhoed *et al.* (1997) found SO_4^{2-} increasingly competitive with PO_4^{3-} for adsorption on goethite with decreasing pH. These studies found that while increasing ionic strength in all cases lead to reduced SO_4^{2-} adsorption, increased ionic strength increased PO_4^{3-} adsorption above a characteristic pH level. The pH at that this occurs is a characteristic of the adsorbent and is related to the point of zero charge (PZC) and the point of zero salt effect (PZSE). This suggests that phosphate can be adsorbed whether the plane of adsorption is positive or negative, whereas SO_4^{2-} can only be adsorbed when the potential is positive (Bolan *et al*,. 1986). He *et al.* (1997) modelled adsorption of these anions on the triple layer model (TLM), suggesting that SO_4^{2-} better fitted the outer sphere (or non-specific) adsorption, whereas PO_4^{3-} better fitted an inner sphere (specific) model of adsorption. It also explains the competitive relationship between SO_4^{2-} and PO_4^{3-} at low pH (<PZC), at that the adsorption plane is positively charged and where electrostatic attraction (outersphere or non-specific) is the dominant adsorption mechanism. Alternatively at higher pH (>PZC), when the adsorption plane is negatively charged, PO_4^{3-}, can out compete SO_4^{2-} because it is specifically adsorbed.

6.2.5 PO4 AND ORGANIC ANIONS

Additionally, this study considered the effect of competition between PO_4^{3-} and organic anions. Violante and Gianfreda (1995) have demonstrated that PO_4^{3-} can out-compete selected LMW (low molecular weight) organic ligands (oxalate and tannate) and this study demonstrated that there are some specialised sorption sites for both PO_4^{3-} and organic ligands. Conversely, Hue (1991) found that some organic acids were effective in desorbing PO_4^{3-} in the order: malic > tocatechuic > acetic.

6.2.6 COOPERATIVE ADSORPTION

Cooperative ions are ions of opposite charge to the ion of interest. Cooperative effects are observed when ions of opposite charge are specifically adsorbed at a common point. In this situation, favourable electrostatic effects are caused by adsorption of oppositely charge ions in the same region as the ion of interest. The cooperative ions of particular interest in this study is Ca^{2+}.

Helyar *et al.* (1976 a,b) found that, whereas Mg^{2+}, K^+ and Na^+ had no effect on PO_4^{3-} adsorption, adsorption was enhanced by Ca^{2+}. Based on this observation Helyar *et al.* (1976a,b) proposed a specific association between Ca^{2+} and adsorbed PO_4^{3-}. This study postulated that Ca^{2+} increased PO_4^{3-} adsorption because the Ca^{2+} complexes to an adjacent adsorbed phosphate ion, reducing the repulsive forces between them (co-operative adsorption). This model involves the coordination of 2 PO_4^{3-} to 1 Ca^{2+}, the same ratio of moncalcium phosphate (MCP). The precipitation of more soluble di or octo-calcium phosphates (DCP or OCP) was considered unlikely as the solubility product was not exceeded even in the most concentrated solutions. This mechanism fails to account for changes in surface charge with anion adsorption (Bolan *et al,.* 1993). Bolan *et al.* (1993) accounted for increased SO_4^{2-} adsorption in the presence of Ca^{2+} by two main mechanisms. At low Ca^{2+} concentration (< 0.003 mol L^{-1}) adsorption of Ca^{2+} increases the positive charge inducing further SO_4^{2-} adsorption. As concentration increased toward 0.015 mol·L^{-1}, increases in positive charge has progressively less effect and the remaining increase in SO_4^{2-} adsorption was attributed to the co-adsorption of the two ions as a $CaSO_4^0$ ion pair, similar to the model of Alva *et al.* (1991) and Macrano-Martinez and McBride (1989).

6.2.7 PRECIPITATION

Homogeneous precipitation occurs when a critical supersaturation of the mineral components is exceeded, thus overcoming an energy activation barrier. The presence of a foreign body may induce precipitation at concentrations lower than that required for homogeneous nucleation, such a mechanism is referred to as heterogenous nucleation (Stumm, 1992). Energy barriers preventing precipitation are overcome when the foreign body has an adsorptive surface that, in effect, acts as a template or nucleation point for crystal growth. The presence of this foreign body can help reduce interfacial energy promoting crystal growth. The presence of clays and other minerals means heterogeneous nucleation is the dominant crystal forming mechanism in natural waters (Stumm, 1992). Based on the work of Stumm and Leckie (1971) and Griffin and Jurinak (1973 and 1974), Parfitt (1978) describes a chain of events in the formation of calcium phosphates in a heterogeneous nucleation model:

1. chemisorption of phosphate accompanied by heterogeneous formation of a nuclei of amorphous calcium phosphate;
2. a slow transformation of these nuclei into crystalline calcium phosphate; and
3. crystal growth of calcium phosphate.

6.2.8 SATURATION INDICES AND CALCIUM PHOSPHATE PRECIPITATION

Saturation indices (SI - see Chapter 4) have been used extensively in studying the kinetics of calcium phosphate growth. Such studies have investigated or identified critical SI associated with homogeneous (Boskey and Posner, 1976; van der Houwen and Valsami-Jones, 2001) and heterogenous (Nancollas and Tomazic, 1974) precipitation, as well as the effect of precipitation inhibitors (van der Houwen and Valsami-Jones, 2001).

Boskey and Posner (1976) studied homogeneous precipitation of calcium in supersaturated (Ca –P) solutions (SI of 5 and 9) at pH 7.4, an ionic strength of 0.15 M at 25°C. This study found that no precursor phases were formed at these SI in contrast to many other studies at higher SI (Feenstra and de Bruyn, 1979; Nancollas and Tomazic, 1974). Boskey and Posner (1976) further predicted, on the basis of their results, that nucleation of hydroxyapatite (HAP) would not take place at SI < 2. Under similar conditions (ionic strength 0.1 M at 25°C) but at pH 7, van der Houwen and Valsami-Jones (2001) found the critical SI for spontaneous (homogeneous) nucleation to be with a solution supersaturation of SI = 10.93. This same study found that the addition of acetate had a negligible effect on this (SI = 10.94), whereas the addition of citrate increased this to 11.73, i.e. indicating that some organic anions can significantly inhibit precipitation. As with the study of Boskey and Posner (1976), no precursor phase to HAP was observed in this study.

The seeded or heterogeneous precipitation studies, using crystalline calcium phosphate seeds, by Nancollas and Tomazic (1974) and Koutsoukos *et al.* (1980), also found similar results, in terms of direct HAP precipitation. These studies found that at low supersaturations (SI = 7) and at pH 7.4 no precursor phase formed, whereas at the same pH and more saturated solutions (SI = 11), Nancollas and Tomazic (1974) found a precursor amorphous calcium phosphate (ACP) did form. From these results it is difficult to interpret to what degree seeding reduces the required SI at that precipitation will occur.

6.2.9 SURFACE PRECIPITATION

In surface precipitation, the adsorbing ion at high concentrations may form a precipitate with the constituent ions of the mineral (Farley *et al,*. 1985). In this case, the solubility of a constituent is greatly reduced, and thus a solid species such as a metal $(OH)_2$ can precipitate at lower pH values in the presence of a hydrous oxide than in its absence (Stumm, 1992).

6.2.10 SORPTION: ADSORPTION V PRECIPITATION

Stumm (1992) defines the term sorption as ion incorporation, and may include the mechanisms of both adsorption and precipitation, with a continuum existing between the two (possibly involving surface precipitation). After reviewing the literature, it is difficult to identify precise sorption mechanisms, because, in batch studies, adsorption is generally measured by changes in solution concentration of the ion of interest. Helyar (1976a,b) attempted to distinguish precise mechanisms by investigating adsorption ratios of key components (i.e. Ca:P) in order to discriminate between adsorption and precipitation. However, according to Nancollas and Tomazic (1974) it is doubtful that such ratios are useful indicators of the types of calcium phosphate phases formed. The reason they give for this is that, under the conditions that such experiments (i.e. calcium phosphate growth studies) are performed, not only is there formation of different calcium phosphate phases but also the concomitant dissolution of thermodynamically unstable phase(s) formed rapidly in the initial stages of the reaction.

6.3 AIMS

In addressing the main objective of this study, to reduced C (in the form of NOM) mobility, the precise mechanism of P retention may not be important. However, given that P is an important plant nutrient, understanding the precise mechanism may be significant for soil fertility. Historically, batch studies of the type adopted here have been used to study extensively the interactive relationships in (ad)sorption. In the experiments described in this chapter the aims were twofold:

1. assess the potential of gypsum to enhance P and DOM retention in a model system; and
2. to postulate possible mechanisms by that retention is enhanced.

Parameters were chosen such that they related as closely as possible to the field conditions (reported in previous chapters).

6.4 MATERIALS AND METHODS

6.4.1 KAOLINITE CHEMISTRY

The kaolinite used in this study was identified using XRD (Soil Mineralogy - see Chapter 3). Exchangeable cations were measured using a 1:5 kaolinite to 0.01 M $CaCl_2$ suspension. Suspensions were shaken on an end-over-end shaker for 1 hour, centrifuged and passed through a 0.45 µm filter. Elemental composition of the filtrate supernate was analysed by ICPOES. Ions adsorbed or released were calculated by subtracting the final solution concentration from the initial ($CaCl_2$) solution concentration (Chapter 3). Plant available (Olsen P) was extracted from the kaolinite using 0.5 M $NaHCO_3$ (pH 8.5). The amount of chemisorbed P attached to the kaolinite was measured following extraction with 0.1 M NaOH (Chapter 3).

6.4.2 EFFECT OF VARIABLE P AND CA ON ZETA POTENTIAL (ζ)

Zeta potential (ζ) is calculated from the electrophoretic mobility and is a consequence of the surface charge of the particles. ζ was measured on a Malvern Zetasizer at 20°C and a field strength of 80 $V.cm^{-1}$. Measurements were conducted with a run-time of 30 s, and final values were an average of five runs.

Suspensions (25 $mg.L^{-1}$ kaolinite) were shaken and allowed to equilibrate for 16 hr prior to measurement of ζ. All suspensions were measured at their naturally buffered pH: all pH's were between 6.3 and 6.5.

Two experiments were conducted to assess the effect of differing Ca concentrations on ζ and the effect of differing P concentrations on ζ. Details of both experimental conditions are presented below.

6.4.2.1 Variable Ca

In order to investigate the effect of changes in Ca concentration on ζ, variable concentrations of Ca were used. With gypsum as the Ca source, it is difficult to interpret the effect on PO_4^{3-} adsorption because of competion from the adsorption of SO_4^{2-}. Hence both $CaCl_2.2H_2O$ and $CaSO_4.2H_2O$ (gypsum) were used as Ca sources. The Ca concentrations were ($mg \cdot L^{-1}$): 0.05, 0.1, 0.25, 0.5, 1, 2.5, 5, 10, 25 and 50.

6.4.2.2 Variable P

In this experiment sodium phosphate was added to a suspension containing 36.7 $mg \cdot L^{-1}$ $CaCl_2.2H_2O$ or 10 mg/L Ca to generate a series of solutions to 0.77, 1.5, 3.1, 7.7, 15, 23 and 31 $mg \cdot L^{-1}$ PO_4.

6.4.3 BATCH EXPERIMENT 1- EFFECT OF IONIC STRENGTH AND PH

6.4.3.1 Experimental Conditions

The effect of Ca (in the form of gypsum) on P adsorption was studied under conditions of varying ionic strength and pH, in the presence and absence of natural organic matter (NOM). The reagents used in this study were all AR grade. The ranges in pH (5 - 9) and ionic strength (0.001 – 0.05 M) are common in soils. pH adjustments were made using HCl and NaOH; ionic strengths were adjusted with NaCl. The concentrations of gypsum ($CaSO_4.2H_2O$) (100 mg Ca L^{-1}) and NOM (18 mg DOC L^{-1}) were selected based on concentrations observed in previous field work (Chapter 4). The NOM was extracted from surface litter (SL) obtained from the Mt Bold field site (Chapter 5).

In order to study the effect of Ca on P adsorption, a non gypsum control of sodium sulfate (Na_2SO_4) was employed. In the control, SO_4^{2-} was added at approximately 47 % of the concentration of the gypsum treatments. Because this experiment was designed to assess the potential of gypsum to increase P retention, the impact of increased competition from SO_4^{2-} had to be considered. The Na_2SO_4 added matched for much of the increase in ionic strength (measured by electrical conductivity [EC]) that occurred with the addition of gypsum while maintaining increased competition for adsorption from SO_4^{2-}.

Batch Experiment Variables:

1. Phosphate concentration	(1 mg/l)
2. Ionic Strength	(0.001, 0.01 and 0.05 M NaCl)
3. pH	(5 - 9)
4. Organic Matter	(0 and 18 mg/l)
5. $CaSO_4.2H_2O$	(0 and 467 mg/l)
6. Na_2SO_4	(233 and 0 mg/L)
7. Mineral	(kaolinite)

The study was conducted using a batch method. An initial solution of 1 mg P /L (in the form of KH_2PO_4) was divided into 3 sub-solutions made up to the 3 different ionic strengths. NOM was added to the solution at this point in the appropriate trial. 150 ml of these solutions were added to 250 ml polycarbonate jars that contained 500 mg of kaolinite and either 70 mg of gypsum or 35 mg of Na_2SO_4. pH of the suspensions (that had initial pH ≈ 6.0 - 6.5) were adjusted to the desired pH with NaOH or HCl. Following an initial pH adjustment, suspensions were placed on a orbital shaker and pH adjustments were made every 90 min for the first 6 hr. Final pH measurements were made after 24 hr, at that time suspensions were centrifuged (20 min @ 3000 rpm) and MRP measured on the supernatant. Because of increased buffering capacity suspensions with NOM, pH was adjusted after 18 – 24 hr and final measurements made after 48 hr. MRP concentration was measured using an automated modification of the molybdenum blue method of Murphy and Riley (1962). P adsorbed (or P retained) was measured as the difference between initial and final MRP. Batches were in triplicate, and MRP measured in duplicate.

The effects of gypsum and variable ionic strength and pH on dissolved organic matter (DOM) adsorption (or retention) were measured by UV adsorbance at 254 nm (UV_{254}), as a surrogate for DOM concentration. UV_{254} was measured on the fraction < 0.45 µm of selected samples (in triplicate) using a Perkin-Elmer Lambda 2 UV/Vis spectrometer (Perkin-Elmer GmbH, Dusseldorf, Germany)- (Chapter 4).

6.4.4 CA-PHOSPHATE SATURATION CALCULATION

The solubility of Ca-phosphates hydroxyapatite (HAP) and octocalcium phosphate (OCP) was calculated from the saturation indices using the formula (F5):

$$SI = \log (IAP/K_{sp}) \qquad (F5)$$

where:

K_{sp} = solubility constant (for either HAP or OCP).

IAP = ionic activity product, and,

= $i^x \times j^y \times k^z$

where

i, j, k = activities of the species common, and

x, y, z = number of moles of each species.

The IAP for HAP and OCP was calculated manually (equations F6 and F7) using constituent species activities calculated by the computer program PHREEQC$_{RCI}$ (Pankhurst, 1995) (Chapter 4). The thermodynamic data was provided by the supplied data file *Minteq.dat,* that is derived from the database files of MINTEQA2 (Allison *et al,*. 1990).

$$\mathrm{LogIAP_{OCP}} = 4\log(\mathrm{Ca}^{2+}) + 3\log(\mathrm{PO_4}^{3-}) + \log(\mathrm{H}^{+}) \quad \text{(F6)}$$

$$\mathrm{LogIAP_{HAP}} = 5\log(\mathrm{Ca}^{2+}) + 3\log(\mathrm{PO_4}^{3-}) + \log(\mathrm{OH}^{-}) \quad \text{(F7)}$$

The solubility constant used for OCP was $\log K_{sp}$ = -46.19 (Moreno, Brown and Osborn, 1960) and for HAP, $\log K_{sp}$ = -57.74 (Nancollas and Tomazic, 1974; van der Houwen and Valsami-Jones, 2001). The K_{sp} used for HAP was markedly different from that in both of the supplied databases in PHREEQC$_{RCI}$, *Wateq4f.dat* (-40.46) and *Minteq.dat.* (-44.20). Neither of these databases contained thermodynamic data specific to OCP. Both of these values reduce the calculated SI significantly compared with the value used in this study.

The model compositions were calculated from the $CaCl_2$ exchangeable ions (see 6.4.1: Kaolinite Chemistry). Concentrations were adjusted to account for the lower Ca concentration in the batch experiment (107 mg·L^{-1}) compared with the $CaCl_2$ extract solution (440 mg·L^{-1}) and the lower solution: kaolinite ratio (300:1 versus 5:1). It was assumed that the cation exchange was proportional to the concentration of the Ca and kaolinite in suspension. Solutions were calculated at 1/247 (concentration = (0.01 M $CaCl_2$ ext) × 107/440 × 5/300)) of the extract solution concentration, i.e. Mn= 0.00036, Mg = 0.266, K = 0.636 mg·L^{-1} respectively. Ca concentrations were calculated by assuming that Ca was adsorbed in the same proportion as in the $CaCl_2$ exchangeable, given the different initial concentrations (i.e. 27.2 % Ca adsorbed giving a final concentration of 77.8 mg/L). A pilot study indicated that the proportion of S adsorbed on the model kaolinite was approximately 50 % of Ca adsorbed. S concentrations were therefore calculated assuming 13.6 % of the applied S was adsorbed (final concentration 74.9 mg/L). Na and Cl concentrations were based on the 0.01 M NaCl solutions (i.e. 229.9 and 354.5 mg/L respectively) and P was 1 mg/L.

6.4.5 BATCH EXPERIMENT 2- EFFECT OF CLAY CONCENTRATION ON P REMOVAL

In order to measure the effect of varying amounts of clay on P removal in the presence of gypsum, 25 ml suspensions containing 400 mg/L gypsum and 1.5 mg/L P ($CaHPO_4.2H_2O$) were made up with kaolinite contents of 0.1, 0.25, 0.5, 1, 2.5, and 5g.

Following a pilot study in that it was observed that the addition of gypsum reduced the final suspension pH by approximately 0.5 – 0.8 units (depending on the kaolinite content), a second batch of suspensions was prepared containing gypsum plus NaOH in varying amounts depending on kaolinite content (Table 54).

Table 54 Amount and concentration of NaOH added to kaolinite suspensions

Kaolinite (g)	M NaOH	ml NaOH
0.10	0.05	0.100
0.25	0.05	0.125
0.50	0.05	0.150
1.00	0.05	0.175
2.50	0.10	0.100
5.00	0.10	0.150

The suspensions were placed on an end-over-end shaker for 24 hr, centrifuged at 3000 rpm for 20 min and the final pH measured. The final and initial MRP contents were measured and the amount of P removed calculated by the difference between these values.

6.5 RESULTS AND DISCUSSION

6.5.1 KAOLINITE MINERALOGY AND CHEMISTRY

The purity of the kaolinite used in this batch experiment was confirmed by XRD. Strong first order basal reflections at 7.1 Å and second order reflections at 3.57 Å revealed a highly crystalline kaolinite. Trace levels of illite (basal reflections at 10 and 5 Å) and quartz (at 3.34 Å and 4.25 Å) were present. Other properties, such as total

$CaCl_2$ exchangeable ions per kg of kaolinite and $NaHCO_3$ and NaOH extractable P, are presented in Table 55.

Table 55 $CaCl_2$ exchangeable elements and exchangeable P.

	Ca	Mn	Mg	Na	K	S	P			
	Ads	CaCl₂ Exchangeable					CaCl₂	HCO₃	NaOH	Chemisorbed
mg/kg	600.0	0.45	332.3	39.9	79.4	45.5	0.92	33.8	37.8	4
(+/-)	0.00	0.001	2.91	0.86	0.83	0.81	0.07			

6.5.2 EFFECT OF VARIABLE P, CA AND S ON ZETA POTENTIAL (ζ)

6.5.2.1 Effect of the form of calcium on ζ ($CaSO_4.2H_2O$ v $CaCl_2.2H_2O$)

Figure 68a compares the effect of two differing Ca sources, $CaSO_4.2H_2O$ and $CaCl_2.2H_2O$, on ζ. The ζ of kaolinite reached a maximum at a gypsum concentration where Ca was near 0.05 mg·L^{-1}, and the ζ did not change with Ca between 10 - 25 mg·L^{-1}. The trend over a Ca range 25 to 50 mg·L^{-1} was for a slight reduction (more negative) in ζ-potential. When Ca was supplied as $CaCl_2$, there was no observable inflection point, i.e. increased concentration led to a reduction in ζ for all concentrations used, suggesting a proportionate increase in Ca adsorption. Near the inflection point for $CaSO_4.2H_2O$ (concentration ≈ 5-10 mg·L^{-1}), there is a cross over, above that calcium chloride becomes more effective in increasing ζ. The differences in ζ-potential ($CaCl_2$ < $CaSO_4$) measured at the lowest Ca concentration are most likely due to a more rapid equilibration time (or sorption rate) of Cl^- over SO_4^{2-} (Kolics *et al*,. 1998). In the experiment presented here equilibration time was 16 hr, that may not have been long enough for complete SO_4^{2-} adsorption (Marcano-Martinez and McBride, 1989). This may be further enhanced by the relatively rapid adsorption of Ca (Marcano-Martinez and McBride 1989), the combined effect causing a higher (less negative) ζ than would be expected with a longer equilibration time.

The negligible change in ζ-potential with $CaSO_4.2H_2O$ between 0.5 and 25 mg/L may indicate that the adsorption of Ca is being electrostatically compensated by SO_4^{2-} adsorption as an ion pair (Marcano-Martinez and McBride, 1989; Bolan *et al*,. 1993). Similar ion pairs may result in enhanced PO_4^{3-} adsorption. The decrease in ζ-potential at Ca = 50 mg/L may be the result of specific adsorption of SO_4^{2-} through ligand exchange with OH^-, occurring in excess of Ca adsorption. A slight increase in pH (0.4 over the concentration range) supports this interpretation.

6.5.2.2 Effect of PO_4^{3-} on ζ-potential

The effect of variation of PO_4^{3-} on ζ-potential of Ca-kaolinite is illustrated in Figure 68 (B). The line drawn at a ζ of 16 is equal to the ζ of kaolinite in a 10 mg/L Ca (in the form of $CaCl_2$) solution, as used in this experiment. The reduction in ζ indicates that adsorption of PO_4^{3-} is occurring.

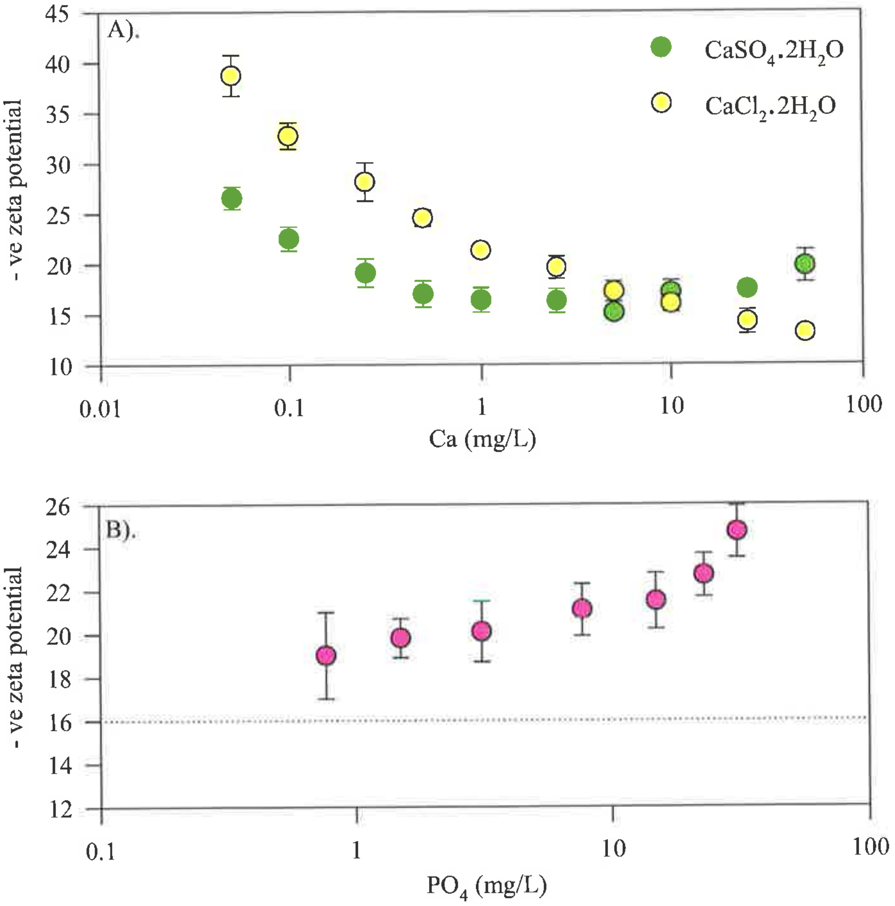

Figure 68. A). Effect of variable gypsum ($CaSO_4.2H_2O$) and calcium chloride ($CaCl_2$) on ζ of kaolinite. B). Effect of variable PO_4^{3-} on ζ on Ca saturated kaolinite.

6.5.3 BATCH EXPERIMENT 1: EFFECT OF IONIC STRENGTH AND PH

Figure 69 shows the amount of phosphate sorbed per unit mass of kaolinite (mg/kg) in suspension for the three ionic strengths, with and without gypsum added [G (+) and G (-) respectively] as a function of pH. In the absence of gypsum, the dominant trend with increasing pH is for the release of pre-adsorbed PO_4^{3-} (PO_4^{3-} desorption), the degree of that was inversely proportion to ionic strength. The source of this P is most likely from a dispersing agent used in the preparation of the kaolinite. The kaolinite used contained approximately 38 mg/ kg NaOH extractable P (Table 55). In high ionic strength [I = 0.05 M G(-)] suspension no net PO_4^{3-} sorption or desorption was observed between pH 5.5 and 8 with some sorption observed at pH 5 to5.5. At medium ionic strength [I = 0.01 M G(-)] there was no net sorption/desorption at pH < 8 and at the lowest ionic strength [I = 0.001 M G(-)] desorption of PO_4^{3-} occurred at pH > 5.1. The effect of ionic strength is consistent with observations of He *et al.* (1997) with kaolinite and Ryden and Syers (1975) and Bolan *et al.* (1986) with soils generally. According to Sposito (1989), the PZSE of pure kaolinite is in the range 4.5-5, so that in the pH range of this study (≈5.1 – 8.5), the PZSE (and PZC) of kaolinite is exceeded. These observations are consistent with a model of specific adsorption of PO_4^{3-} (He *et al,*. 1997; Hayes *et al,*. 1988). This model suggests that in the absence of Ca^{2+}, increasing the ionic strength increases the o-plane potential, making surfaces less negative and thereby increasing affinity for PO_4^{3-} adsorption (Barrow *et al,*. 1980).

In the presence of gypsum, there was no observed P release, indeed the retention (or sorption) of P was enhanced at all pHs > 5.1. This trend increased with increasing pH. The effect of ionic strength on PO_4^{3-} sorption was the opposite to that observed when gypsum was not present, thus giving a strong indication that a different mechanism is operating. This trend is what one would expect to observe with cation adsorption at pH > PZSE (Bowden *et al,*. 1980). This infers a cooperative adsorption mechanism is probably controlling PO_4 sorption. There are two distinct zones of phosphate removal in the presence of gypsum, separated by an apparent PZSE at pH near 7. Reduction in PZSE has been attributed to anion adsorption (Bolan *et al,*. 1986, 1993), and this result may reflect the adsorption of Ca^{2+}, thus increasing the PZSE. At pH near 5 however, there is also very little difference in ionic effect, indicating that the PZSE is near 5 for this kaolinite. The apparent PZSE near pH 7 may be attributable to a shift in the dominant PO_4^{3-} sorption mechanism. Adams and Rawajfih (1977) and Freeman and Rowell (1981) attributed increased PO_4^{3-} sorption at high levels of Ca and at pH > 7 to a precipitation reaction (i.e. formation of calcium phosphates). Such a mechanism would account for the rapid increase in P removal with increasing pH, a process that begins near pH 7. Such a mechanism may also explain the apparent PZSE near the same pH. If this pH is near the point at that calcium phosphate precipitates, PO_4^{3-} concentrations in the suspension would be very sensitive to changes in pH, that could override the ionic effect with slight variations, giving rise to an only apparent PZSE. It is postulated that below this critical pH PO_4^{3-} sorption is dominated by cooperative adsorption mechanisms.

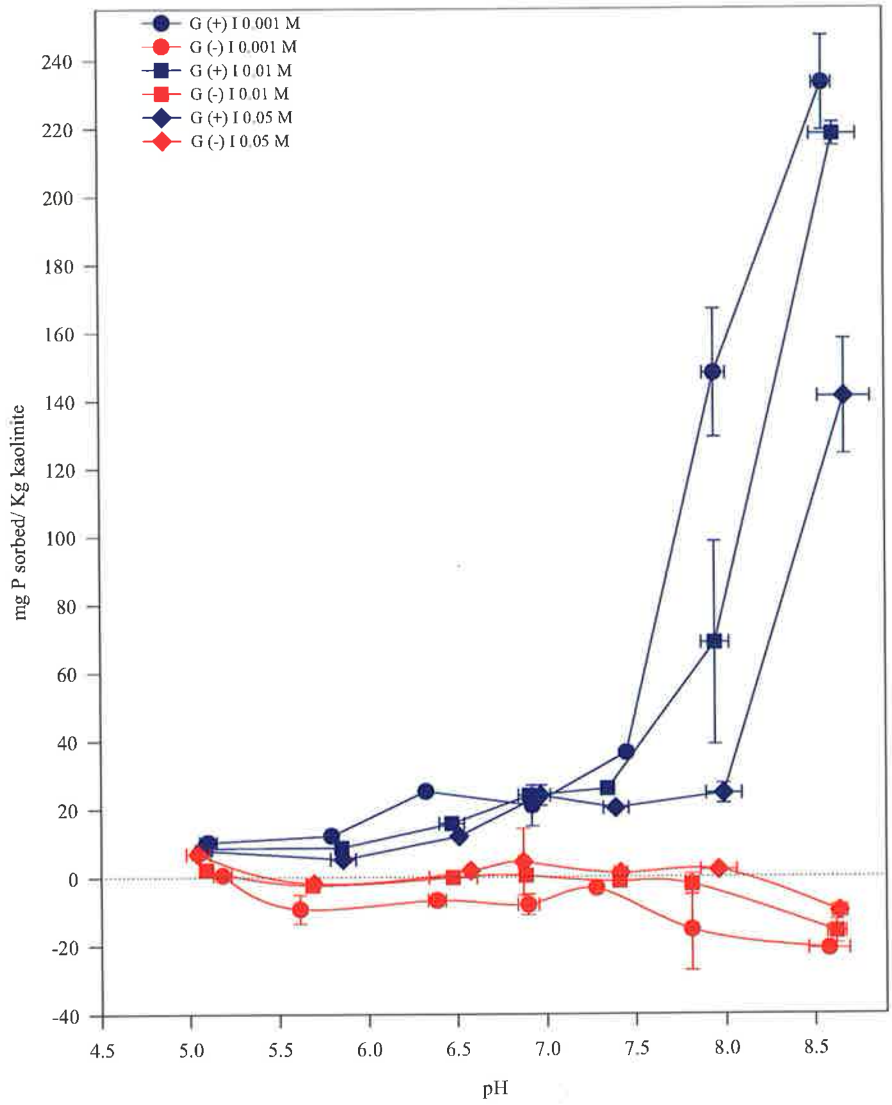

Figure 69. Effect of gypsum on PO_4 sorption under variable pH and ionic conditions.

The effect of OM on PO_4^{3-} sorption is illustrated by comparing Figures 69 and 70. The trend in ionic strength impact is the same as for the suspension with no added OM. However, from this data it is clearly shown that PO_4^{3-} remaining in solution is increased when OM is added. For the gypsum treatment, PO_4^{3-} removal is diminished, whereas in the non-gypsum suspension desorption of PO_4^{3-} is enhanced. The general shape of the curves between OM + and OM - is similar, however, the critical pH at that the exponential increase in PO_4^{3-} removal for G (+) has increased from approximately 7 to 7.8. Similarly, the linear increase in PO_4^{3-} release from G (-) has also shifted toward a pH of 7.8. The level of PO_4^{3-} released at the highest pH (8.8-9) accounts for the total NaOH extractable P of the kaolinite (previous section).

In a manner similar to that observed by Hue (1991) and Violante and Gianfreda (1995) the effect of OM on PO_4^{3-} sorption in the absence of gypsum and in the presence of gypsum can be accounted for through competitive adsorption. In the gypsum-treated suspension at pH > 7, organic matter such as fulvic, humic and tannic acids (Inskeep and Silvertooth, 1988) and citrate (van der Houwen and Valsami-Jones, 2001) have also been shown to inhibit calcium phosphate precipitation.

6.5.3.1 Calcium Phosphate Solubility

Figure 71 illustrates the calculated SI over the pH range 5 - 8.5 for the calcium phosphates HAP and OCP modelled for the batch experiments discussed in the previous section. These modelled solutions suggest that positive SI for HAP occurred at approximately pH 5.5, with positive SI for OCP at pH 7. The points (A) and (B) represent the SI and corresponding pH at that van der Houwen and Valsami-Jones (2001) (A) and Boskey and Posner (1976) (B) found to be the minimum values at that spontaneous (or homogeneous) precipitation of HAP occurs. The line drawn through them represents a postulated precipitation isotherm, for that values to the right favour spontaneous HAP precipitation. The point at that HAP precipitation is postulated immediately precedes the pH at that there is an observed dramatic increase in P sorption in Figure 69 (see Figure 72). Such coincidence is strongly suggestive that the significant increase in P sorption that begins at pH 7.2 –7.5 is a result of direct HAP precipitation. Clearly this postulated isotherm represents conditions in that HAP precipitation is strongly favoured where it may be precipitating directly from solution, or onto pre-existing surfaces (i.e. kaolinite). HAP was not observed in XRD analysis, probably because the quantity precipitated, the size of crystals, or indeed the poorly crystalline structure of the precipitate may have rendered it unobservable by XRD.

Alternatively this may support the hypothesis of surface precipitation rendering its presence non identifiable by XRD.

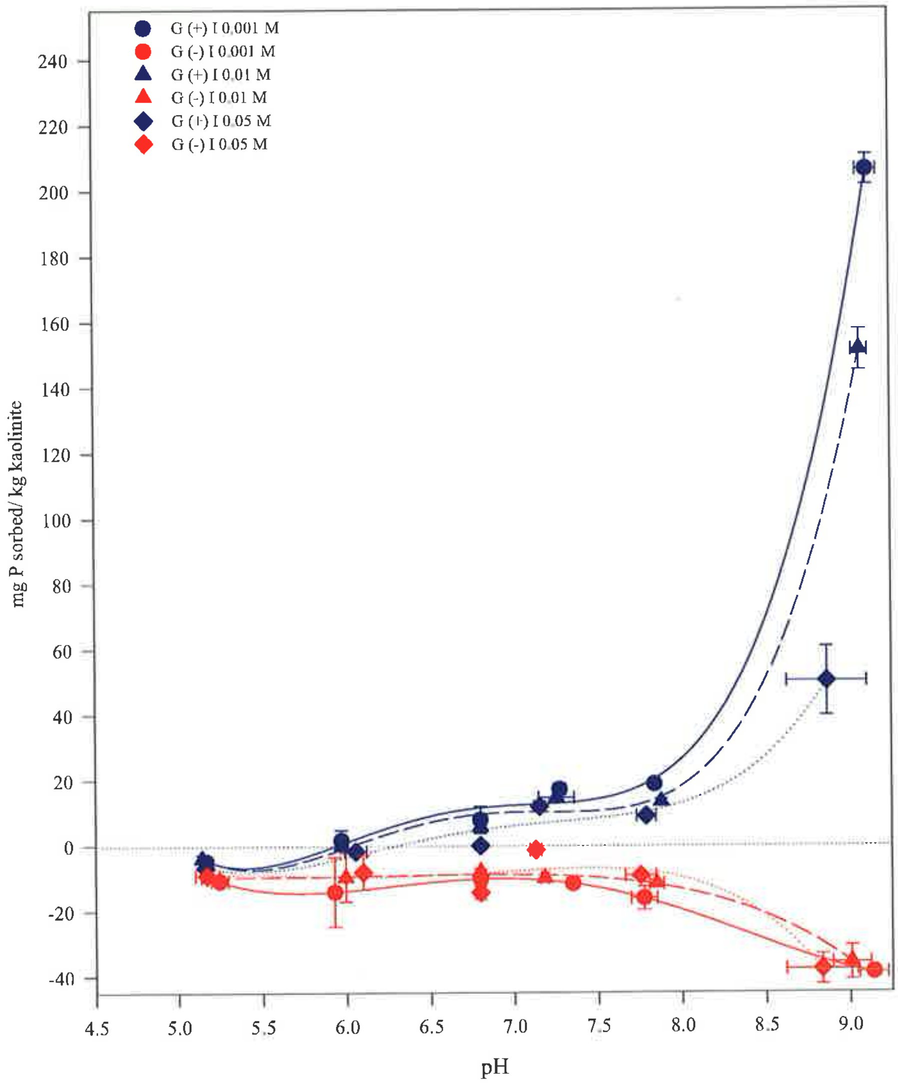

Figure 70. Effect of Gypsum on PO_4^{3-} sorption under variable pH and ionic conditions with NOM.

Although these results indicate the mechanism of gypsum enhancement of P sorption above pH 7 (viz,. HAP precipitation), they give little information as to the mechanisms below. Clearly heterogeneous precipitation may explain much of this enhancement below pH 7; however, there appears to be little information in the literature of the possible role of kaolinite in heterogenous HAP precipitation. Seeds for HAP heterogeneous precipitation are other calcium phosphate nuclei - commonly HAP itself - suggesting that there must be a strong match between the symmetry of the seeding material (or foreign body) and the crystal precipitating in order to overcome interfacial energy. The results presented in Figures 69 and 72 suggest that P sorption is enhanced below the pH at that the SI of HAP in these experiments was < 0 (pH < 5.5) and are strongly indicative that precipitation (both homogeneous and heterogenous) is not solely responsible for gypsum enhancement of P sorption.

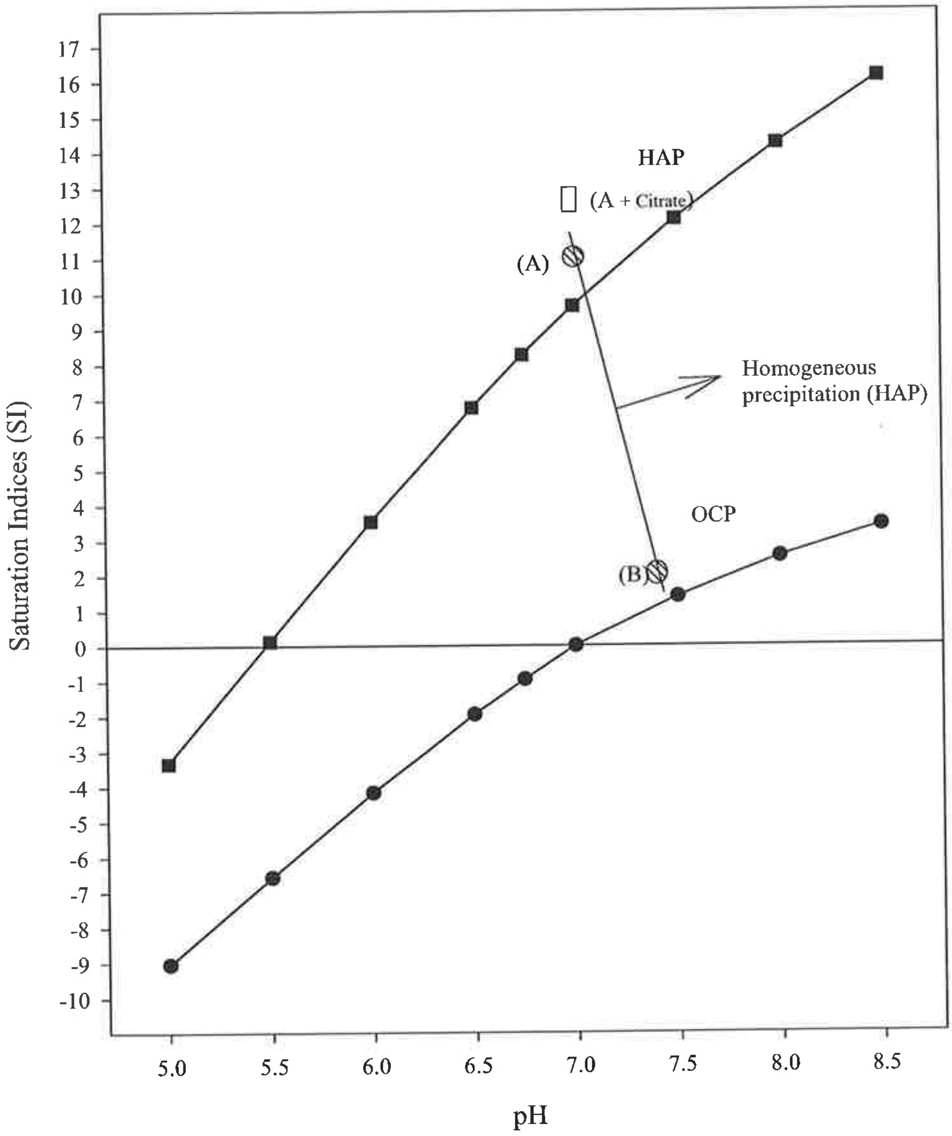

Figure 71 HAP (square) and OCP(circle) saturation indices. The line drawn through A (van der Houwen and Valsami-Jones, 2001) and B (Boskey and Posner, 1976) represents a theoretical isotherm to the right of that homogeneous or spontaneous precipitation of HAP proceeds. The point A (+ citrate) also originates from van der Houwen and Valsami-Jones (2001) and represents the effect of citrate addition on HAP precipitation, corresponding with the conditions for (A).

6.5.3.2 DOM Retention

Relative differences in DOM UV_{254} absorbance for the batch solutions containing NOM are presented in Table 56. In order to account for the effects of pH and ionic strength, results are presented as ratios of UV_{254} for gypsum treated [G(+)] to non-gypsum [G(-)] for each of the conditions. In all cases, UV_{254} was reduced in the G(+) indicating that DOM retention was enhanced by gypsum treatment. The effect was greatest at the highest pH, and at ionic strengths below 0.01 M. Differences were negligible at the most acidic pH at the highest ionic strength. The greater reduction in DOM (or, more correctly the components of DOM measured by UV_{254}) at the higher pH may be indicative of the specific removal of high molecular weight (HMW) aromatics in the process of inhibiting calcium phosphate precipitation. Inskeep and Silvertooth (1988) found that adsorption of HMW compounds by this mechanism were favoured.

Table 56. Ratio of UV_{254} for gypsum treated batches to control.

pH (ave)	+/-	$G(+)UV_{254}/G(-)UV_{254}$		
		0.001 M	0.01 M	0.05 M
5.27	0.02	0.71	0.67	0.96
6.63	0.03	0.58	0.58	0.79
8.50	0.12	0.52	0.45	0.50

6.5.4 BATCH EXPERIMENT 2: EFFECT OF CLAY CONCENTRATION ON P REMOVAL

As the amount of kaolinite in suspension increased, the amount of P removed also increased. However, this was disproportionate to the amount of kaolinite added (Table 57). With 4 g kaolinite L^{-1}, 13 mg of P were removed per kg of kaolinite compared to only 1.9 mg of P per kg of kaolinite when the suspension concentration was 200 g kaolinite /L. This may be a likely result of increased competition between sorption sites for limited PO_4^{3-} (and Ca^{2+}), and/or surface-surface interactions between clay particles; indicating a strong surface effect associated with the mechanism of PO_4^{3-} removal.

Table 57. pH, Total P and P sorbed mg/ kg kaolinite in the variable kaolinite experiment.

Kaolinite g/L	pH	P Removed Total (mg)	P Removed mg P/kg kaolinite
4	6.51	0.0013	13.0
10	6.53	0.0022	8.8
20	6.64	0.0037	7.4
40	6.68	0.0058	5.8
100	6.71	0.0085	3.4
200	6.77	0.0093	1.9

6.6 GENERAL DISCUSSION

The batch experimentation presented in this chapter indicates that over a broad range of pH (5 to 8.5) gypsum enhanced the removal of PO_4^{3-} in a kaolinite suspension. Further it appears to suppress the release of pre-adsorbed PO_4^{3-}. Through utilising batch experimentation with variable ionic strength and pH, combined with chemical modelling and surface charge studies, mechanisms of increased PO_4^{3-} retention can be inferred. Three distinct pH dependant retention mechanisms appear to operate and can be observed in reference to Figure 72.

At pH < 5.5 chemical modelling of the solution used indicated the SI of hydroxyapatite (HAP) would be less than zero, such that precipitation of calcium phosphate would be unlikely. Surface charge measurements indicate that Ca^{2+} adsorption is occurring, suggesting that the enhancement of PO_4^{3-} at this pH is a consequence of co-operative adsorption, i.e. the coupled adsorption of PO_4^{3-} and Ca^{2+}.

At pH > 7.0, to the right of the intersection of the line through A and B (Figure 72) and the calculated SI for HAP, is where homogeneous precipitation of HAP is predicted as the dominant PO_4^{3-} retention mechanism. Apart from solution modelling, further lines of evidence for this is the rapid increase in the efficiency of PO_4^{3-} retention as pH increases over 7, and the apparent PZSE that occurs at 7, that marks a point where a significant change point in mechanisms must occur.

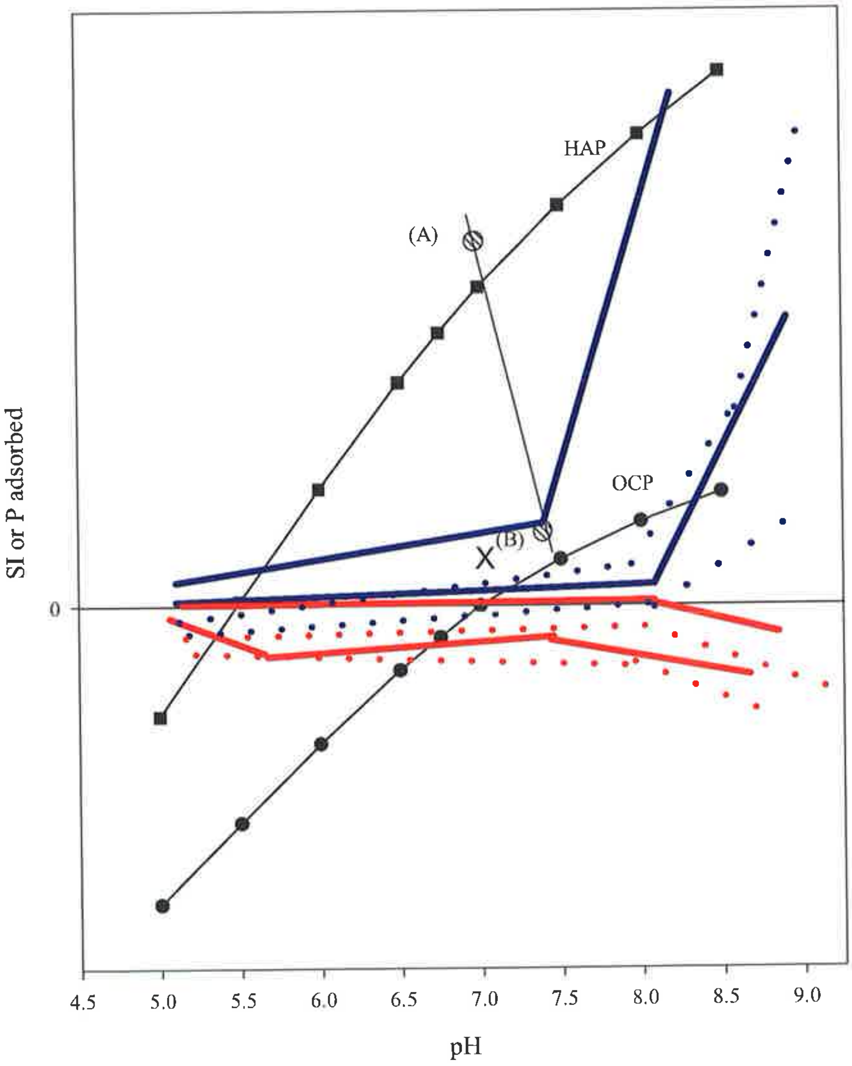

Figure 72 Figures 69 (solid line) and 70 (dotted line) over laying Figure 71, showing relative position of P adsorbed (to pH) to SI of HAP and OCP and the homogenous precipitation point (black line A-B) from Figure 4. X marks *apparent* PZSE (Figure 69)

Between pH 5.5 and 7.0, heterogeneous precipitation is predicted as the dominant mechanism of PO_4^{3-} retention. This process appears to be a continuum between co-operative adsorption and homogeneous precipitation, a region dominated by heterogeneous precipitation. In this pH range, the modelled SI of HAP is greater than zero, suggesting precipitation can occur, but below the SI where it will occur spontaneously. Here it is predicted that the co-operative adsorption mechanism acts to promote surface precipitation of HAP (or a HAP like amorphous calcium phosphate), i.e. the kaolinite surface acts as a seed for calcium phosphate growth.

6.7 CONCLUSIONS

Although competition between NOM and P existed, gypsum enhanced the retention of both constituents across the pH range and ionic strengths examined in this study. Defining the precise mechanism of enhancement of P sorption is complicated by the similarity in effect (i.e. inhibition) that both increasing ionic strength and the presence of NOM have on both cooperative adsorption and Ca-P precipitation. Modelling sorption ratios of Ca and P will improve the understanding of this mechanism. Models of heterogeneous nucleation (precipitation) are initially driven by co-adsorption of the required components in a manner that cannot be discriminated from cooperative adsorption. Observations in this study reinforce the reality of a continuum between these mechanisms.

7 Final Discussion and Conclusions

7.1 DISCUSSION

7.1.1 HYDROLOGIC EFFECTS ON WATER QUALITY

Figure 73 shows a generalisation of the pathways of water movement through the upper reaches of a catchment. "A" represents direct overland flow, with negligible interaction with the soil. The greatest potential for loss of organic matter and P is through surface flow, particularly in a xeric climate when long dry periods allow the build up of decaying organic matter, through the breakdown of plant material built up through the preceding winter growth period. The surface hydrophobic conditions resulting from high surface organic matter and the application of phosphatic fertiliser prior to winter exacerbate the problem. "B" (1 and 2) represent *return flow* where water fluctuates between surface and subsurface. Water flowing along this path would be expected to emerge at the surface in the lower slopes or in topographic depressions in mid and upper-slopes. Surface collected water (i.e. collected along the surface interception barrier) is a combination of both A and B. This was the dominant pathway of water movement in the soils of the Mt. Bold reservoir catchment presented in this study. The relative ratios are highly dependent on catchment soil characteristics (i.e. surface hydrophobic and permeability). Thus the hydrologic character is likely to change over an individual season (i.e. becoming less hydrophobic) and changes in the relative contribution from these sources over a season would be expected.

"C" represents subsurface flow along a textural interface, where the lower horizon is of a lower permeability (due to a heavier clay content) and water flow is directed preferentially along the horizon interface. This is considered an important sub-surface flow path in a texture contrast soil, such as the soils used in this study. "D" illustrates flow that moves within a horizon either as matrix flow, or through macropores contained within a single textural horizon. Due to the heterogeneity of soils, a similar process to return flow can operate in the subsurface, waters collected from "C" may carry some proportion of both "D" and "B" (and visa versa). The potential for loss of organic matter and P in subsurface flow comes from organic matter and P incorporated into the soil, including that retained on soil particles.

The model by that gypsum enhances P and NOM retention as hypothesised in this study requires the interaction of the soil solution with soil particles, particularly the clays. Without soil contact, only direct coagulation or precipitation with Ca can be expected, and at the pH of the soils in this study, precipitation of P is unlikely. Three factors can explain why interaction with soil is essential: 1. Movement through the soils limits the size of the material that can be mobilised (i.e. no bigger than the smallest pore through that the water moves); 2. The speed of water movement through soils (mm to cm h^{-1}) is considerably slower than across the surface (m to dm h^{-1}); this increased retention time allows longer periods for sorption (adsorption, precipitation or flocculation) to operate; 3. Movement through soils allows interactions with soil constituents, i.e. more surface area contact.

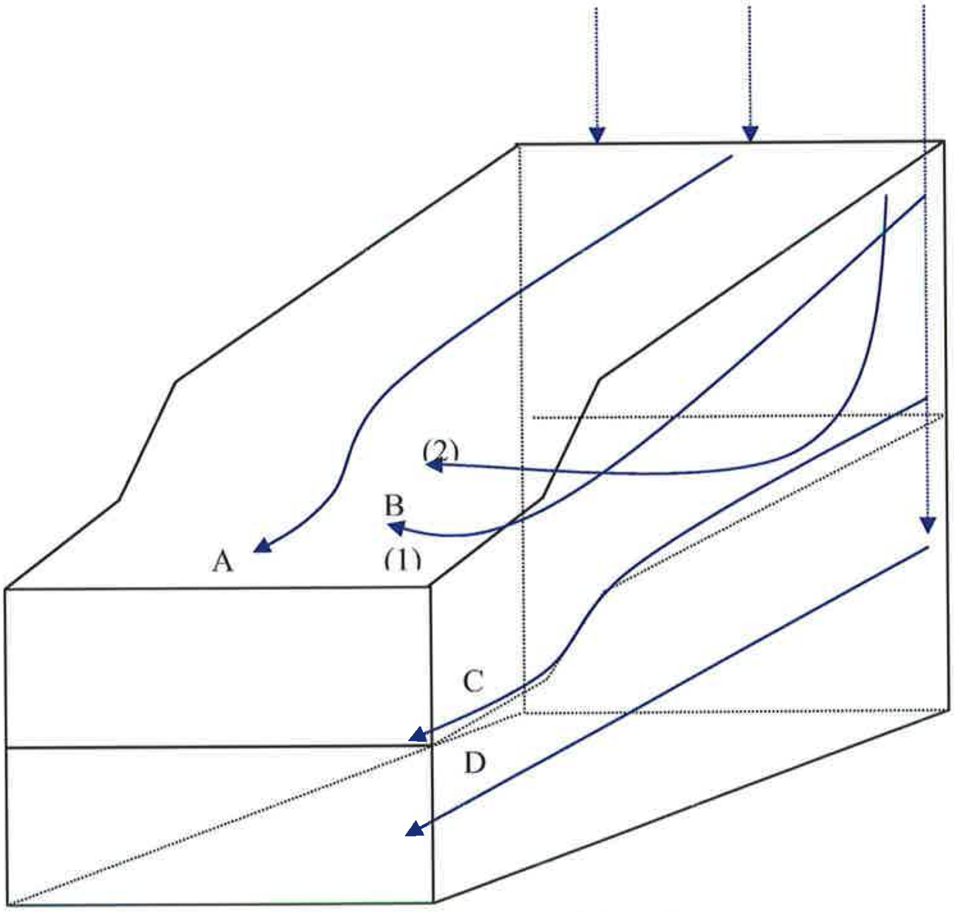

Figure 73 Pathways of water movement through a catchment.

From this it can be understood that improving the quality of surface runoff water (A) is the most difficult to target. Increasing infiltration, in combination with increasing adsorptive capacity, would clearly achieve the best outcomes for water quality. It appears that gypsum may have aided in achieving the former (increased infiltration), through reducing the hydrophobicity of the surface soils (Figure 40 – Chapter 3). Lower total SOC at the surface (possibly from competition with SO_4^{2-}), and Ca interaction with hydrophobic components of OM may have contributed to this. The reduction of organic matter and soluble P in the upper cms of the soil, both observed in this study, is a further benefit to reducing the loss of these constituents into surface flow i.e. reduced source material. Benefits in terms of increased infiltration would be expected to be even more evident on problematic soils (i.e. sodic).

7.1.2 MECHANISMS RESPONSIBLE FOR INCREASED SORPTION CAPACITIES

Following gypsum application, early winter rainfalls readily dissolve gypsum releasing Ca and S in concentrations initially $\approx$ 400 mg/L. This high flux of ions results in changes in the chemistry of the soil throughout the profile, particularly exchange of Mg, Al, Na, and Mn for Ca cations in the upper 10 cm of the soil (Figure 74). These cations are then released into the soil solution, percolating down the profile. The exchange of the trivalent cations (Al) for the divalent Ca, and increased anion competition from SO_4^{2-}, results in the upper 10 cm having a lower capacity for adsorption of PO_4^{3-} and organic anions (Figure 75). As the water percolates down the profile, the increase in the clay content at approximately 20-30 cm retards the flow rate of water. It is speculated that this retarded flow allows a greater solute interaction time with the soil particles that allows both the sorption of cations released in the upper profile (increasing CEC) and the precipitation of new mineral phases, particularly Al sulfates. Both these processes increase the anion sorption capacity at this depth.

Subsequent to the application of gypsum, fluxes of NOM and P occur (Figure 75), particularly in break-of-season (autumn and early winter) flows. In the gypsum-treated soils less adsorption of these constituents occur in the surface soils as a result of their reduced anion adsorption capacity, compared with the non treated soils. These anions are intercepted as the water percolates through the deeper soils, attracted to clays with increased anion adsorption capacity. Here PO_4^{3-} and organic anions, largely HMW aromatic compounds, are adsorbed by the clay minerals, and additional dissolved cations lead to strong associations between clay-cations and anions (PO_4^{3-} and organic). The net result of this is the formation of clay microaggreates (Figure 76). Formation of such aggregates has important consequences in terms of both aggregate stability and the pore size distribution.

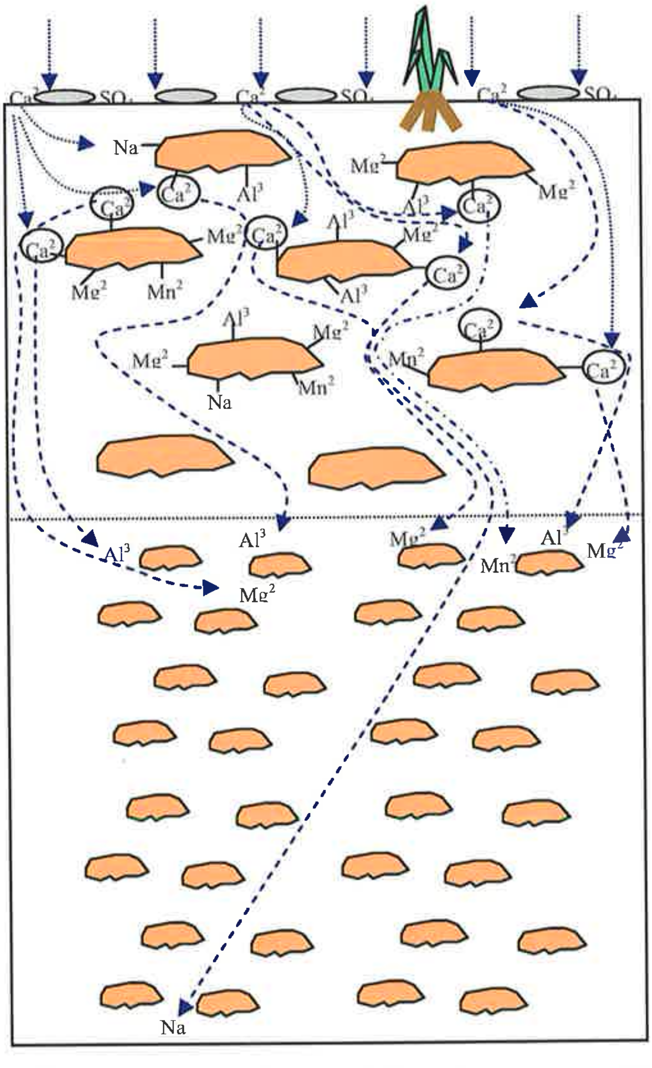

Figure 74. Dissolution of gypsum and exchange of Ca with exchangeable cations that are displaced deeper into the profile.

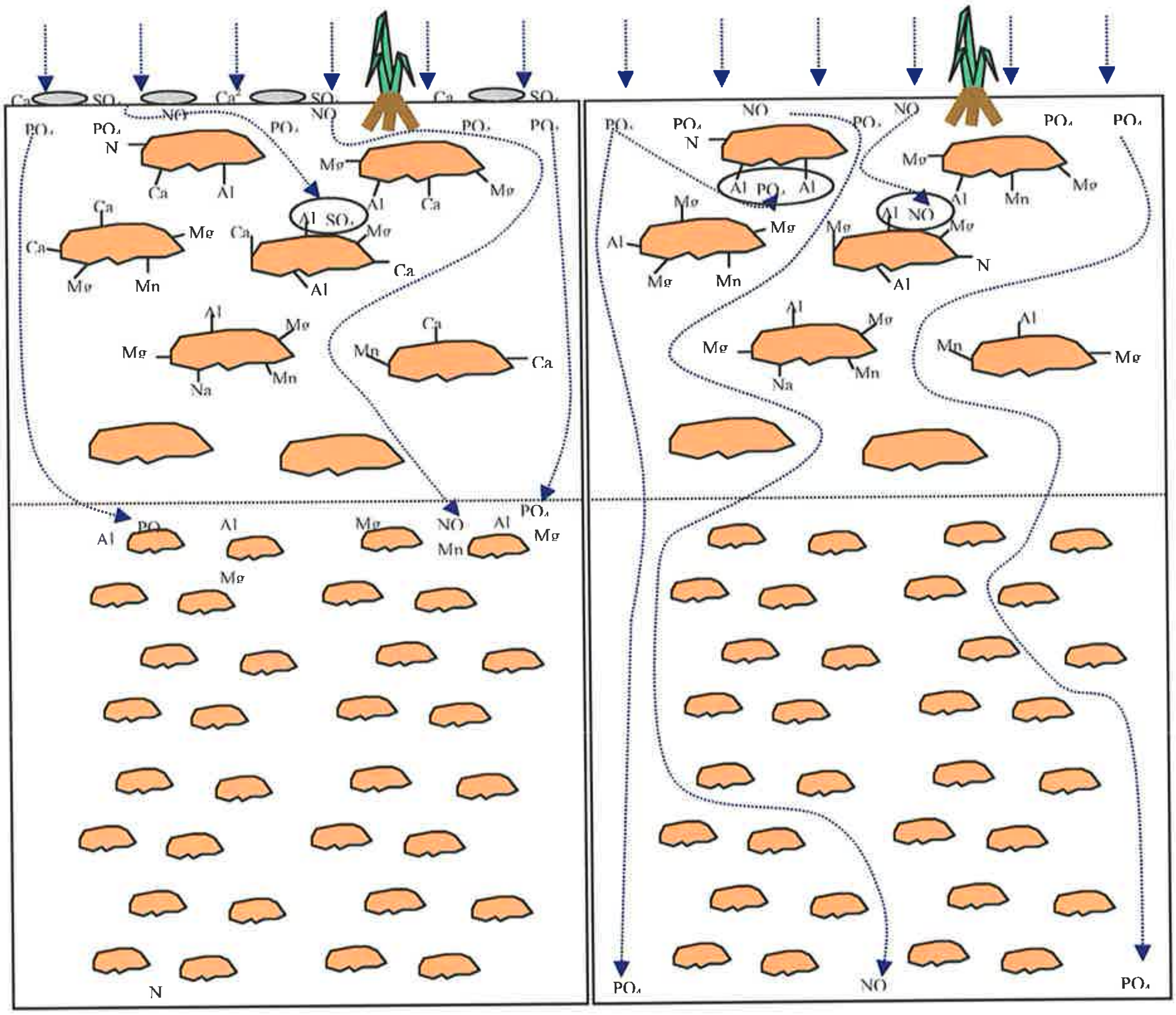

Figure 75. Showing differences between anion movement in gypsum treated (left) and non - reated (right) soils.

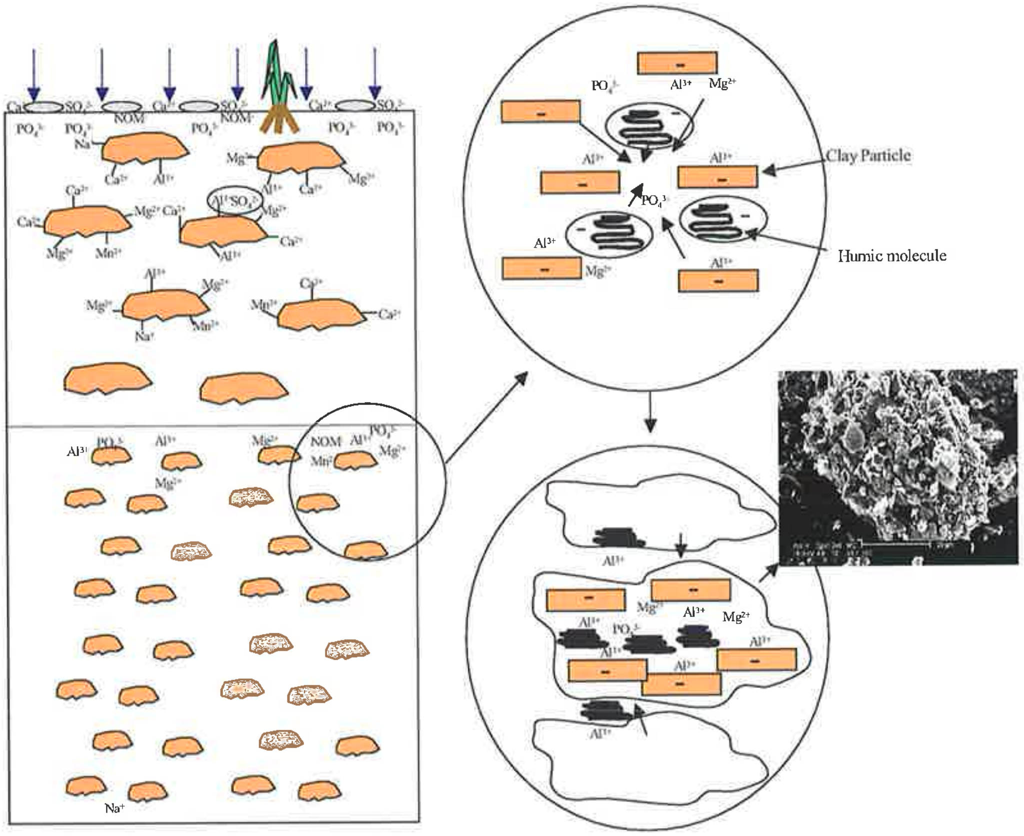

Figure 76 Model of clay aggregation through interaction of solution and adsorbed cations, causing flocculation of clay-organic complexes, that also incorporate phosphate.

7.2 CONCLUSIONS

Gypsum is a valuable agronomic product with a wide range of agricultural applications. The ability of gypsum to improve soil structure (particularly in sodic soils) is well documented. The higher solubility of gypsum over agricultural lime has seen the use of gypsum more recently in amelioration of subsurface soil acidity.

In addition to these uses the benefits of gypsum application to both soil and water quality have been demonstrated in this study. The application of gypsum to the soils used in the field component of this study, significantly altered the ion balance of these soils. Changes observed were a reduction in anion adsorption capacity in the upper 10 cm, with a significant increase in anion adsorption capacity below 10 cm. This increase below 10 cm significantly enhanced the overall anion adsorption capacity of through the gypsum treated soil profile. This change had a major impact on the soil leachate composition, with reductions in both NOM and P concentrations. Parallels between water treatment and the changes in water chemistry as a response to gypsum treatment can be drawn, further the treatability of the leachate was not diminshed by these changes. This has lead to overall increases in soil organic matter retention, with higher proportions of freshly deposited organic matter that has enhanced both the stability and potential fertility of the soils. Total P in the soils has also been increased, without impacting available P. Confirmation of these field observations came through both core leaching and batch studies

Core leaching studies, using the same soils, showed liming to increase soil pH increased effectiveness of gypsum in reducing P concentration of leachate. This was most likely achieved through more favourable conditions for Ca-P precipitation. At this elevated pH, gypsum was still effective in reducing NOM mobility and effected similar changes in character. The core leaching also indicated that relatively high doses of gypsum were required (≈ 10 t/ha) to effect these changes. Such quantities will certainly impact on the cost effectiveness of using such an amendment. Further, the effects from a single large application are potentially long term, five or more years and additional economic benefits to be considered are reductions in water treatment costs and increases in soil fertility.

Batch experiments indicated that gypsum can be used to reduce P and NOM solubility in kaolinite suspensions over a wide range of pH and ionic conditions. When batch experimental results were combined with chemical modelling and measurements of surface charge, mechanisms of P retention could be inferred. This experimentation established a continuum of mechanisms ranging from cooperative adsorption of Ca^{2+} and PO_4^{3-} in acidic conditions, through surface seeded heterogeneous precipitation at intermediate pH, through to potential homogeneous precipitation under alkaline conditions.

7.3 FUTURE RESEARCH DIRECTION

Results of this study strongly favor using gypsum as an ameliorant for reducing losses of NOM and P from soils to water. Benefits were observed in both water quality and agricultural viability.

The mechanism by that gypsum enhances P retention was inferred from the batch trials presented in this study. Further work is recommended to refine this model. Investigative tools such as ^{31}P NMR (McDowell *et al,.* 2003) may aid in further identifying the nature of the surface complex. In addition modelling of anion:cation adsorption ratios (similar to the earlier studies of Helyar *et al,.* 1976 a,b) could be further used to enhance mechanistic understanding.

Improvements to soil fertility were identified in this study from a theoretical standpoint. Pot testing or assessing changes to soil biologic activity (i.e. direct measures of soil fertility) as a response to gypsum treatment are recommended to further assess changes to soil fertility.

Economic viability most likely remains the largest obstacle and before this method can be widely employed as a mitigation tool this critical area needs to be addressed. Suggested areas to be investigated in terms of economics are:

- Cost benefit analysis to both land holders and water managers.
- Long term research into the period of time a single large application remains effective. Evidence from this study suggests that 15 t/ha remained effective for at least 4 yr, clearly the longer the period of time costs can be spread the more viable this management option becomes.
- Further refinement of the minimum dosage required, that may vary between soil types.
- Research into the effectiveness on other soil types, and even climatic regimes.

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