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AN INVESTIGATION OF THE AGRONOMIC VALUE OF FINE GRINDING AND GRANULATING REACTIVE PHOSPHATE ROCKS.

A thesis presented in partial fulfilment
of the requirements for the degree of
Master of Horticultural Science
in Soil Science at Massey University
New Zealand.

Sally Jane Officer
1989

ERRATA

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194	equation 7		$-P^{32}c-$	Pc
194	equation 8		$-P^{32}c-$	Pc

ABSTRACT

The future trends in the use of reactive phosphate rocks in New Zealand may be dependent on improving the handling characteristics of these fine sand- and powder-like materials. Granulation of these materials has been suggested as one option. The effect of fine grinding and granulating reactive phosphate rocks on their agronomic performance was evaluated using a range of phosphate rocks, in laboratory studies and in field and glasshouse trials.

North Carolina, Arad, Sechura and White Youssafia phosphate rocks, in forms normally imported into New Zealand (sand sized material, majority <2mm particle size), were characterised in terms of origin, composition, particle size, and solubility in 2% formic acid. In a 30 minute formic acid extraction of the imported material, White Youssafia phosphate rock at 44% solubility was found to be less reactive than the other phosphate rocks, which ranged from 47% to 55% in formic solubility

In preliminary field trials a very finely ground North Carolina phosphate rock (100% <42μm particle size) was granulated with K_2SO_4. The ungranulated phosphate rock, and granules of 0.5-1mm, 1-2mm and 2-4mm diameter, were evaluated on permanent pasture on the Tokomaru silt loam, using an inverse isotopic dilution technique in which the field soil, at the 1.5-6cm depth, was uniformly labelled with P^{32} by a novel injection method. No plant yield response to fertiliser was observed but significant differences in herbage phosphate content and specific activity indicated a phosphate uptake response to fertiliser. Despite careful selection of areas of sward which had a similar plant content and vigour, the large variability in data from replicate treatments limited the amount of information which could be drawn from the results but the data indicated that the agronomic performance of the finely ground North Carolina phosphate rock was not limited by granulating to 0.5-1mm (mini-granules).

A further range of granulation agents, including neutral salts, organic and mineral acids, their salts, and tallow, were tested for their ability to form strong mini-granules from unground North Carolina phosphate rock. The best granulation agent was a 1:0.6 mixture of citric acid and magnesium sulphate, producing 0.5-1mm mini-granules which had an arbitrary crushing strength of 0.8kg/granule. The production of mini-granules involved pre-drying a phosphate rock/granulation agent slurry until it was just unsaturated, followed by cutting the wet mix through a 0.710mm seive, granulation at high speed for 30 seconds, and drying of the granules at 80°C for approximately 2 hours. This granulation process was then used to manufacture granules from unground Sechura and Arad phosphate rocks, as well as ground North Carolina and Arad phosphate rocks. Ground North Carolina phosphate rock was also granulated using tallow, by melting the fat and mixing in the phosphate rock, followed by setting the mix in a mould.

Granulated materials, including a commercially prepared product ("Hyphos"), and ungranulated phosphate rocks (including White Youssafia), were evaluated in a glasshouse pot trial. The fertiliser was applied to the surface of pots of established "Nui" perennial ryegrass, with 7 harvests over three and half months.

In general, at the common application rate of 60kgP/ha, the phosphate rock materials were never more than 70% as effective as mono calcium phosphate. The yeilds derived from unground, ungranlated Sechura, North Carolina, Arad and White Youssafia phosphate rocks were similar, the only significant difference being that the yield derived from Sechura phosphate rock was greater than the yield derived from North Carolina phosphate rock.

The effect of mini-granulation on agronomic performance varied with with the type and particle size of the phosphate rock used to make the granules. For example, mini-granulation of "as received" North Carolina and Sechura phosphate rocks caused no reduction in phosphate

availability from these materials, however, mini-granulated "as received" and works ground Arad phosphate rock caused a significant reduction in phosphate availability.

The agronomic performance of North Carolina phosphate rock was improved by grinding to less than 250µm in particle size but no further improvement occurred if the phosphate rock was more finely ground (<42µm particle size). The agronomic performance of Arad phosphate rock was not improved by grinding.

The sequential fractionation of soil phosphate (1MNaOH followed by 1MHCl) indicated that only approximately 8% of the works ground North Carolina phosphate rock fertiliser had dissolved in the soil at the 5th harvest (10 weeks). A comparison of yields derived from pots fertilised with different rates of K_2HPO_4 sprayed onto chromite (whch had a similar particle size distribution to the unground phosphate rocks) indicated that the dissolved phosphate in the soil from the phosphate rock had a similar agronomic value to the K_2PO_4. The low amount of phosphate rock dissolution and the absence of increased of yield response when works ground North Carolina phosphate rock was applied to soil at rates greater than 40 kgP/ha indicated that soil factors were limiting the dissolution of phosphate rock in this experiment. The extent of the limitation varied depending on the phosphate rock type and also the type of pot used (the black polythene bag used for the majority of treatments was enclosed in a galvanised steel cylind~~a~~er for an inverse isotopic dilution experiment). The variable effects of grinding and granulation were attributed to the limitation of the phosphate rock dissolution.

The type of granulation agent (including partial acidulation) had no significant effect on the agronomic performance of the granulated materials, except when tallow was used as a granulation agent and reduced the availability of works ground North Carolina phosphate rock. Unground White Youssafia phosphate rock requires further testing under more rigorous conditions before conclusions can be made about its agronomic availability.

Two isotopic techniques were utilised in the glasshouse experiment in an attempt to quantify the extent of phosphate rock dissolution in the soil. The surfaces of some phosphate rock treatments were sprayed with a carrier free solution of P^{32}, and the inverse isotopic dilution technique used in the field was used again on some treatments.

The use of labelled $K_2HP^{32}O_4$ as a control for the surface labelled experiment provided sufficient information to allow differentiation of phosphate in the plant which was derived from soil and the fertiliser but the model developed could not be directly applied to results from the phosphate rock treatments. The dissolution of different forms of phosphate rock could not be compared using this labelling technique.

The inverse isotopic dilution technique was re-evaluated in the glasshouse trial, by uniformly injecting the pots of ryegrass with a carrier free P^{32} solution. The fertiliser treatments unpredictably stimulated uptake of labelled soil phosphate, so that the changes in herbage specific activity provided little meaningful information.

These two unsuccessful attempts to derive quantitative information from the introduction of the P^{32} isotope into the phosphate rock-soil-plant system demonstrated the difficulties involved in using isotopic dilution techniques to examine phosphate rock dissolution in field soils.

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The Lord is my strength
and my shield;
My heart trusts in him, and
I am helped;
Therefore my heart exults

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CHAPTER 1: INTRODUCTION

Phosphate rock has become the general term for all rocks that contain approximately 2% (or more) phosphorus as orthophosphate (PO_4^{3-}) (Notholt, 1980). The fertilising value of these materials has been recognised for a long time (Morfit, 1873), but usually only in terms of their suitability as raw materials for superphosphate manufacture.

Recently reactive phosphate rocks have been recognised as a distinctive type of phosphate rock which can have a high agronomic performance when applied directly to the soil as fertiliser. These materials have been called "reactive" because they exhibit relatively high solubility in weak organic acid solutions, compared to other phosphate rocks.

The use of reactive phosphate rocks as fertilisers in New Zealand has been limited, but interest in these materials has increased as the cost of superphosphate has risen, and the ore deposits which have been traditionally used for superphosphate manufacture become depleted. There has also been interest generated in reactive phosphate rocks as slow release "natural" fertilisers, more suited to the "organic husbandry" philosophy.

Most reactive phosphate rocks are imported into New Zealand as light, dry, free flowing, sand-like products, which become fine powder when ground. The unground sand sized materials are proving difficult to handle efficiently in current transporting systems. In some cases considerable portions of loads have been lost as the material sifts through any small openings in the transport (Mr N. Charteris, Ravensdown, pers.comm. 1989). The unground phosphate rocks are also difficult to apply evenly to soil by aerial topdressing in anything but very calm conditions (Gillingham *et al.* 1987), although the small quantities at present being applied allow top-dressing operators to wait for optimum weather conditions (Mr. Bernie Haskill, Jet Spread. pers.comm. 1989). These problems will be accentuated if the phosphate rocks are ground, which is highly probable in view of the strong recommendation to grind these materials to improve their agronomic value. Several researchers have shown that the agronomic performance of these materials is significantly improved by grinding (Khasawneh and Doll, 1978; Rajan *et al.* 1987), and fertiliser regulations in the EEC already require that such materials be ground before application.

The solution to the handling and spreading problems of the reactive phosphate rocks is to granulate these materials, which would also allow the addition of other elements to the fertiliser. Conventional trials of granulated phosphate rocks have found that granulation reduces the amount of phosphate available from these materials (Buchan *et al.* 1970; Chien and Hammond, 1978a), but recent work suggests that on New Zealand pastures, where fertiliser is usually applied to the soil surface, the effects of granulation on agronomic performance may be negligible (Gillion *et al.* 1978; MacKay *et al.* 1981).

The objectives of this thesis are:

1. To examine research literature concerning reactive phosphate rocks, and their use as fertilisers directly applied to the soil (chapter 2), in such a way that a range of rocks can be selected and characterised (chapter 4) for the manufacture of granulated fertilser.

2. To evaluate methods for the granulation of unground and ground reactive phosphate rocks (chapter 6).

3. To evaluate the effects that grinding and granulation have on the agronomic performance of the selected reactive phosphate rocks (chapters 5 and 7).

CHAPTER 2: LITERATURE REVIEW

2.1 The Geology of Phosphate Rock

2.1.1 World deposits

In terms of gross tonnage produced and volume of international trade, the mining of rocks for phosphate ranks second in the world as a major mineral industry, after iron ore and excluding the hydrocarbon industry (Notholt, 1980). Phosphate rock deposits have been documented in almost every country of the world (Figure 2.1). Currently world production is dominated by the U.S.A, the U.S.S.R. and Morroco, and approximately 5% of mined rock is used as an untreated, directly applied fertiliser.

Mining is largely from deposits of sedimentary rock (84% of world production in 1978; Notholt, 1980) which form the bulk of world phosphate reserves. At present the U.S.A. is the biggest producer, with 39% of world production in 1980 (Willams and Zellars, 1989), largely from mines in Florida. The sedimentary deposits are largely marine in origin, occurring as a result of precipitation processes on the sea bed, although some significant deposits (Nauru and Christmas Island) are thought to have formed as a result of the accumulation of sea bird guano. The phosphate in these deposits is largely phosphorite ore, in the form of a calcium phosphate mineral called francolite.

Some igneous rock is also mined for phosphate, notably the U.S.S.R. deposits on the Kola peninsular. The usual source of phosphate in igneous rock is the calcium phosphate mineral, fluor-apatite. Fluor-apatite is a common accessory mineral in almost all igneous rocks, commonly 0.1 to 1% by volume (Deer *et al.* 1965), and reaching 65% by volume, and over, in mined deposits such as in the Khibiny igneous complex of the Kola peninsular (Emigh, 1973).

Metamorphic rocks are not generally a commercial source of phosphate although the shale phosphorite deposits of Idaho, U.S.A are mined.

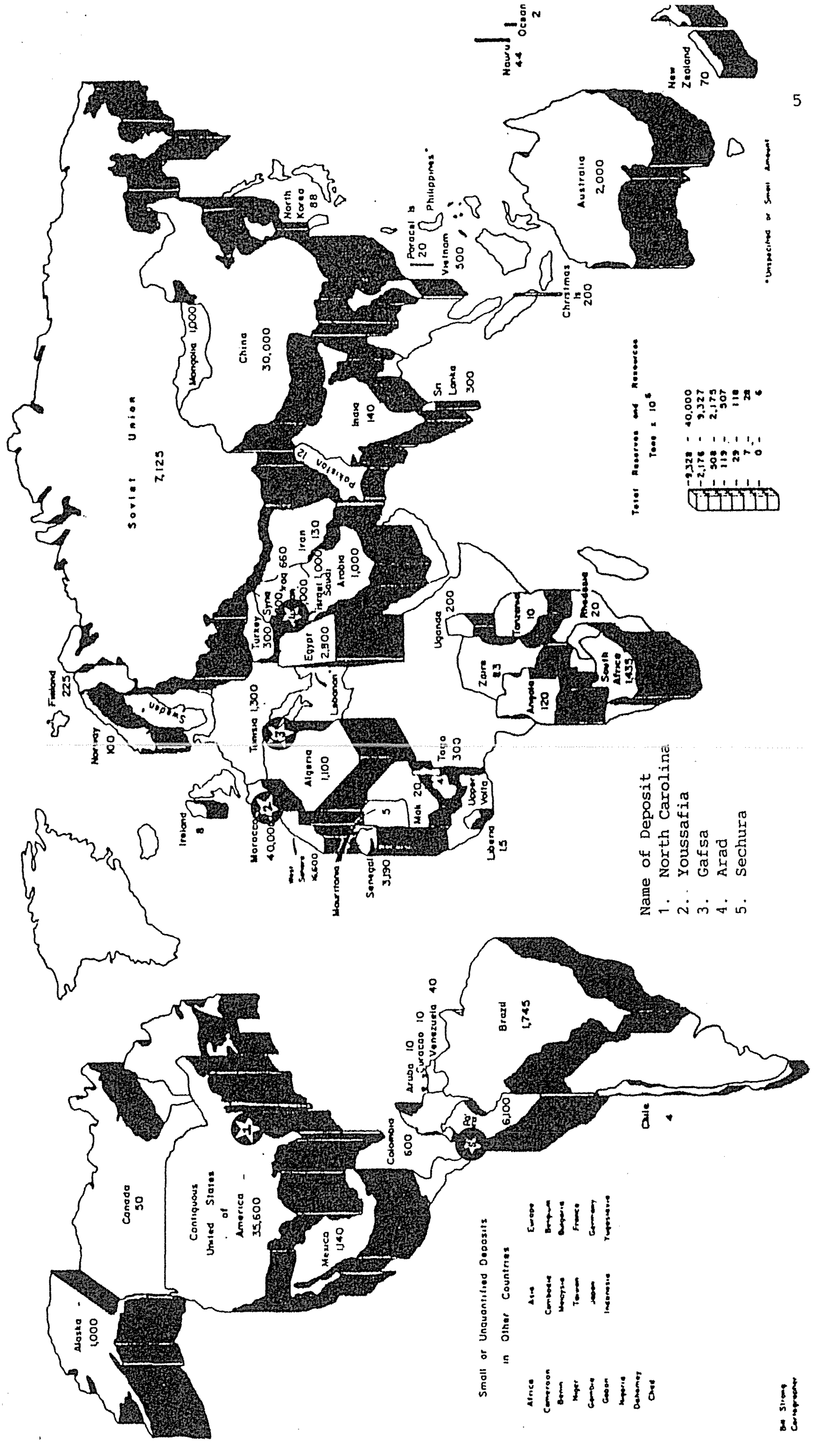


Figure 2.1: World phosphate reserves and resources, (Stangel, 1978) with the locations of some important deposits.

2.1.2 The formation of sedimentary phosphate rock deposits

Sedimentary phosphate rock deposits have been found to be associated with geological formations of specific historical time periods, generally denoted as "phosphate provinces". For example the miocene phosphate province, which occurred at about 20 million years B.P., included the formation of the Sechura, North Carolina, and Florida deposits.

It has also been noted that sedimentary deposits are largely associated with continental margins which have shallow ocean shelves or platforms. These are also typically on western coasts that are associated with an upwelling of deep ocean waters, or eastern coasts associated with the movement of warm currents or areas of frequent marine transgressions (Notholt, 1980). These deposits are also generally associated with a series of phosphatic and carbonaceous shales, clays, cherts and limestone in a typical sequence, the predictable pattern of which has been used to locate new phosphate rock deposits.

Such specific associations have given rise to the theory that very specific conditions are necessary for the precipitation of francolite but the exact processes which the deposits are still a matter of some debate. Early work proposed that all sedimentary phosphate deposits were detrital and directly derived from fossil deposits. It was thought that the high concentrations of phosphate in these deposits were achieved by the replacement of fossil calcium carbonates with calcium phosphate. Later fluorination of these calcium phosphates formed fluor-apatite (Deer *et al.* 1965).

Subsequent work noted that usually the deposits were composed of uniformly shaped peloids (or nodules) with little extraneous sediment, rather than fossil remains (Pettijohn, 1975). A typical peloid from a sedimentary phosphate deposit was generally composed of a central grain, such as quartz or calcite. This central grain was surrounded by a matrix of well sorted, unstructured material, which was largely composed of a cryptocrystalline (submicroscopic crystallite size) form of apatite named francolite (Pettijohn, 1975; Burnett, 1977).

It has been proposed that the central grain acted as a nuclei for the precipitation of francolite (Burnett, 1977). Where fossils did comprise a distinct central grain it was found that while both central grain and matrix were composed of apatitic compounds, the two compounds were usually quite different in their exact chemistry (Deer *et al.* 1965).

Soudry and Nathan (1980) found that where precipitation occurred around nucleus particles of an organic origin, in this case planktonic tests and bone fragments, the nuclei were subsequently altered by a process of recrystallisation until the material composing the nucleus was virtually indistinguishable from the surrounding precipitationary matrix. In some cases the test may form the outer perimeter of the peloid, such as has been recorded by Riggs (1980) in the Florida deposit, where many particles have the flattened discoid shape of a diatom but the typical inner cryptocrystalline francolite structure. Similar observations were made of the North Carolina deposit by Gibson (1967).

These observations have led to theories based on the direct precipitation of francolite crystals from solution, as opposed to the theory of substitution of fossil calcium carbonates by phosphate.

2.1.3 Specific conditions for the formation of francolite deposits

The general environment for the formation of francolite deposits is thought to be in basins on ocean shelves and platforms, in which there is intermittent turbulence. This provides a stable environment with periodic influxes of nutrient rich waters and may initiate an explosion of organic activity, which is commonly diatomaceous. The subsequent death of the organisms results in a high concentration of phosphate in the sediments of the basin, facilitating the precipitation of francolite (Berge and Jack, 1982).

At this point in the theory viewpoints diverge as to where the actual precipitation of the francolite occurs. Some support the view that precipitation occurs at the sediment water interface of the basin, but there is growing support for the theory that, in the majority of cases, precipitation occurs within the pore spaces of the basin bottom sediments.

Burnett (1977) proposed that the conditions necessary for the precipitation of francolite were:

1. A relatively high pH (above neutral).

2. High concentrations of phosphate in solution, enough to control the solubility of the calcium ion so that calcium phosphate is formed rather than calcium carbonate.

3. A high calcium to magnesium ratio in solution, to prevent the magnesium ion from competing with the calcium ion and inhibiting precipitation.

4. The presence of nucleus grains, e.g. quartz, feldspar, glauconite (a sedimentary marine silicate), calcite, siliceous skeletal material. (Soudry and Nathan (1980) also include chert, bone and peloid fragment.)

5. A relatively high temperature.

Burnett (1977) concluded, after a study of *in situ* sea phosphorite deposits off Peru and Chile, that francolite concretions had to be formed in the anoxic pore waters of sediments in order to meet the above stringent conditions necessary for precipitation.

Limited gaseous diffusion in the sediment pores allows the depletion of oxygen and the build up of carbon dioxide. Reducing conditions arise, consuming available protons, and causing a rise in pH. As a result the pH of pore waters may be considerably higher than at the sediment water interface. High phosphate concentrations in pore waters may be achieved during the decomposition of organic matter. Much phosphate is present in organic skeletal structures especially those of certain phosphatic brachiopods, crustaceans and bones and teeth of vertebrates (Pettijohn, 1975). The high concentration of phosphate would also be assisted by the reducing conditions which would inhibit the formation of hydrous ferric (and aluminium) oxides and subsequent sorption of phosphate.

Montmorillonite is a silicate clay mineral commonly associated with sedimentary calcium phosphate deposits (e.g. Notholt, 1980; Altschuler, 1973). This mineral forms a sink for magnesium and would facilitate a high calcium to magnesium ratio.

High pore water temperatures could result from local and global conditions, and degradational processes on a local land mass would largely determine the presence of nucleus grains.

Gibson (1967) studied the Pungo river geological formation, which is the source of North Carolina phosphate rock. This work found that fossil remains associated with the deposit indicated that the bottom waters of the basin in which the phosphate deposit had formed were aerobic and not stagnant. The above discussion suggests that in these conditions precipitation of francolite was unlikely to occur at the sediment water interface and supports a theory of formation in the sediment pores.

2.1.4 Post precipitation processes

After formation of francolite concretions in the sediments, a variety of processes may occur which will define the final form of the deposit. Simple burial in further layers of sediment may result in a massive consolidated deposit called microsphorite (Notholt, 1980). Turbulent conditions may `tear up' sections of phosphatic mud, producing irregularly shaped nodules or intraclasts. Less turbulent conditions may gently agitate the sediments in a winnowing and reworking process which causes the fine grained non-conretioary fraction to be eroded away and leaves a sand-like, well sorted, relatively pure deposit, often composed of very evenly sized peloids (Soudry and Nathan, 1980).

Geological uplift and subsequent exposure of the phosphorite deposit to weathering processes may further modify the deposits. Leaching may concentrate the deposits by removing associated calcite and dolomitic deposits. Further leaching may remove phosphate from the upper layers of the francolite deposit, often causing phosphatic enrichment of underlying rock, such as limestone. The leached phosphate is often replaced by aluminium and iron from overlying soils containing weathering silicate clays and eventually new minerals may be formed such as wavelitte ($Al_3(PO_4)OH_3.5H_2O$) which are unsuitable as a commercial source of phosphate (Emigh, 1973).

2.2 Chemical Characteristics of Phosphate Rock

2.2.1 Characteristics of the apatite group

Phosphate rock is a complex form of calcium phosphate. Pure calcium phosphate ($Ca_3(PO_4)_2$) is not stable at 25°C and does not occur as a mineral (Altschuler, 1973). The minerals that are found naturally are of the apatite group, with the general formula $Ca_{10}(PO_4)_6(F,OH,Cl)_2$, in which many other substitutions are possible (Lindsay and Vlek, 1977). Apatites are described as a six sided prismatic crystal, often thin and needlelike, commonly terminated by pyramids. The crystal colour is extremely variable, usually shades of green, blue-green, or brown, and it is generally colourless in thin section. The mineral is from transparent to opaque and often contains many small cracks, which give the crystal a shattered appearance (Vanders and Kerr, 1967).

The unit cell structure of the apatite is a hexagonal network of calcium and phosphate ions (Brown, 1973). The central void of the network is usually filled by either a fluoride, a hydroxyl, or a chloride ion, which may mutually one each other. Almost pure end-members of the isomorphous series can form, namely fluor-apatite, hydroxy-apatite and chlor-apatite. The apatitic structure is very stable, although the hydroxy apatite structure is a little expanded and relatively less stable (Deer *et al.* 1965).

2.2.2 Sedimentary apatite

Sedimentary apatites were originally assumed to be fluor-apatite but have been found to be in general more chemically reactive than pure fluor-apatite and to contain appreciable quantities of carbonate, and usually more fluorine and less phosphate than fluor-apatite.

The position of carbonate and the `excess' fluorine in sedimentary apatite has been a source of some controversy. It was initially proposed that the mineral was a simple mixture of calcium carbonate, calcium fluoride and fluor-apatite, but Deer *et al.* (1965) and McClellan and Lehr (1969) reported that x-ray patterns of the mineral showed no evidence of discrete crystalline carbonates or free calcium fluoride. When compared to pure fluor-, hydroxy- and chlor-apatites the sedimentary apatite had a distinctive x-ray pattern and distinctly different cell parameters.

Deer *et al.* (1965) also reported that a carbonate containing apatite could not be synthetically constructed except by the replacement of phosphate by carbonate. This was confirmed by Legeros *et al.* (1967), who also found that these synthetic fluor-apatite crystals containing carbonate were of a different shape compared to the other apatites. When compared to the typically needlelike shape of non-carbonate apatites, carbonate containing fluor-apatite was a more spherical particle with a length to thickness ratio approaching unity. It was proposed that this was because the carbonate substitution caused the formation of weaker bonds, which changed the crystal growth trends. Carbonate substitution therefore reduced the size and structural stability of the crystal, and increased the solubility of the crystal (Deer *et al.* 1965; Legeros *et al.* 1967). This work suggested that sedimentary phosphate rocks were composed of an independent mineral containing variable quantities of structural carbonate. The mineral was named carbonate-fluor-apatite, and the group named francolite.

Caro and Hill (1956) found that changes in the degree of carbonate substitution were also reflected in changes in particle density. When the particle weights of the 100 to 150 μm size fraction of selected phosphate rocks was compared a trend of decreasing particle weight with increasing carbonate substitution was found. This indicated that increasing carbonate substitution caused less uniform agglomeration of crystals within the peloid, as well as a smaller crystal size.

Khasawneh and Doll (1978) calculated theoretical surface areas of 75, 44 and 32.6 m_2/g for North Carolina, Central Florida and Idaho phosphate rocks respectively, estimated from the crystallite size determined by x-ray methods. Actual surface areas determined for ground samples of these phosphate rocks were, respectively, 48%, 20% and 11% of theoretical surface area, indicating the effect of crystallite packing.

2.2.3 The association of fluorine with carbonate

In 1966, Smith and Lehr reported that as the content of structural carbonate increased in carbonate-fluor-apatite, a general trend of a shortening "a" axis and a lengthening "c" axis had been found, but no completely satisfactory correlation had been made between the unit cell dimensions of carbonate-fluor-apatites and their carbonate content. Smith and Lehr considered carbonate-fluor-apatites, and the related group of carbonate-hydroxy-apatites (commonly found in fossil bone) and found that the carbonate *plus fluorine* content did correlate well to the length of the "a" axis. They suggested that because a divalent planar group was substituting for a trivalent tetrahedral phosphate group a packing void and a charge imbalance was created. The addition of a fluorine ion preserved the tetrahedral symmetry and countered the charge imbalance.

In 1969 McClellan and Lehr reviewed the various models which attempted to relate the unit cell dimensions to the carbonate and fluorine contents of francolites. The best model found (r=0.94) predicted the length of the "a" axis using the carbonate plus fluorine content, and also an interaction term where:

$$"a"(A^{\circ}) = a + bF + eCO_3 + f(F*CO_3) \qquad (1)$$

and a = 9.4436, b = -0.0332, e = -0.0899, f = 0.0238 and F and CO_3 are expressed in moles per formula weight and a_o is a minimum value for the "a" axis. The model suggested that a change in the level of carbonate substitution caused about twice as much change to the length of the "a" axis, compared to a change in the level of fluorine. The curvilinear shape of the model also indicated that a low level of carbonate substitution caused a relatively greater change in the "a" axis than did a high level of substitution.

McClellan and Lehr (1969) also found that the minimum observed value of the carbonate-fluor-apatite "a" axis was 9.322A°, which corresponded well to the minimum value of 9.321A° obtained from the above model. The maximum observed carbonate content was 1.347 moles per formula weight corresponding to 1.395 moles in the model. A selection of values of the "a" axis of a variety of apatites are presented in table 2.1.

Table 2.1 The length of the "a" axis dimension of various apatitic minerals .

Mineral	"a" (A°)	Reference
PURE END MEMBERS		
Fluor-apatite	9.35	Deer *et al.* 1965
Chlor-apatite	9.61	" "
Hydroxy-apatite	9.41	" "
Carbonate-apatite	9.34	" "
NATURALLY OCCURRING MINERALS		
Hydroxy-apatite,		
Hollysprings, U.S.A.	9.413	Deer *et al.* 1965
Flour-apatite,		
Durango, Mexico	9.386	" "
Carbonate-fluor-apatite,		
Tennessee, U.S.A.	9.357	Khasawneh and Doll, 1978
Idaho, U.S.A,	9.356	" "
Central Florida, U.S.A.	9.345	" "
Khouribga, Morocco	9.341	Cheney *et al.* 1979
Sechura, Peru	9.339	" "
Arad field, Israel	9.327	Axelrod, 1978
Gafsa, Tunisia	9.324	Smith and Lehr, 1966
North Carolina, U.S.A.	9.322	Smith and Lehr, 1966

Observations indicated that substitution reduced the number of unit cell repetitions possible before a misfit occurs preventing further growth of the crystallite. The carbonate and fluoride ions were not found to be coupled, so either may enter the packing void, but when carbonate ions entered the structure they blocked the subsequent entry of a fluorine ion. Only half to one third of the potential fluorine sites were occupied, and the charge imbalance was corrected by the replacement of divalent calcium ions with monovalent sodium ions.

2.2.4 Modelling the composition of Carbonate-fluor-apatite

McClellan and Lehr (1969) concluded that the main components of carbonate-fluor-apatite were calcium, phosphate, carbonate and fluorine, with lesser but significant amounts of sodium and magnesium. They presented the following model for the composition of the unit cell for carbonate-fluor-apatites.

$$Ca_{10-a-b}Na_aMg_b(PO_4)_{6-\beta}(CO_3)_\beta F_y F_2 \qquad (2)$$

with the following average values; $\beta = 0$ to 1.5, $y = 0.4\beta$, $b = 0.4a$. Electroneutrality was preserved when $a = \beta - y$.

Chien and Black (1976) proposed the following average values for the above model:

$$a = 0.3\beta$$
$$b = 0.12\beta$$

and also a theoretical limit of β where $\beta/6-\beta$ was not more than 0.3, which meant that β was always between zero and 1.385. This corresponded well to values from the model of McClellan and Lehr (equation 1) describing the "a" unit cell dimension, where the theoretical maximum value of β was 1.395 and the highest observed value was 1.347. Some specific compositions of unit cells are presented in table 2.2 (Chien and Hammond, 1978b).

Table 2.2 Unit cell compositions of a selection of carbonate-fluor-apatites (Chien and Hammond, 1978b).

Source of the material.	Empirical formula
North Carolina	$Ca_{9.53}Na_{0.34}Mg_{0.13}(PO_4)_{4.77}(CO_3)_{1.23}F_{2.49}$
Gafsa, Tunisia	$Ca_{9.56}Na_{0.32}Mg_{0.12}(PO_4)_{4.84}(CO_3)_{1.16}F_{2.46}$
Sechura, Peru	$Ca_{9.03}Na_{0.74}Mg_{0.13}(PO_4)_{4.88}(CO_3)_{1.12}F_{1.73}(OH)_{0.72}$
Central Florida	$Ca_{9.74}Na_{0.19}Mg_{0.07}(PO_4)_{5.26}(CO_3)_{0.74}F_{2.30}$
Tennessee	$Ca_{9.85}Na_{0.11}Mg_{0.04}(PO_4)_{5.54}(CO_3)_{0.46}F_{2.18}$

2.2.5 Further possible substitution into carbonate-fluor-apatite

Carbonate-fluor-apatites rarely occur as a pure compound. The most common substitutions are of magnesium and sodium for calcium, and hydroxyl and chlorine for fluorine (Khasawneh and Doll, 1978). A very wide variety of other elements have also been identified, including all the rare earth metals. Some reach economically significant levels, as in the case of the uranium content of some deposits (Notholt, 1980).

Altschuler (1973) reported that substitutions for Ca in the basic apatite structure of $Ca_{10}(PO_4)_6F_2$ that had so far been identified were: Sr, Mn, Pb, Mg, Ba, Zn, Cd, Fe, Cu, Na, K, Rb, Sc, Y, Rare earths, Bi, and U.

Substitutions found for PO_4 were: SiO_4, SO_4, AsO_4, VO_4, CrO_4, BeO_4, CO_4, F, OH, BO_4, GeO_4, AlO_4, FeO_4.

Substitutions found for F were: OH, Cl, Br, I, and possibly O.

These substitutions did not occur simultaneously, neither were they equally permissible, and often particular substitutions were coupled. The ion and the extent of substitution would determine how much structural change occurred, which in turn would determine whether the mineral was still classed as a francolite. McClellan and Lehr (1969) found potassium, rare earths, strontium, barium, silicate and sulphate to be the main substitutions in francolites, but that these were only present in small amounts. For instance, the largest amount of sulphate found in any francolite tested by McClellan and Lehr was 0.101 moles per formula weight (about 0.5% S).

2.2.6 The effect of carbonate substitution on reactivity

Chien (1977a) found that the standard free energy of dissolution (DGdo) was relatively constant among carbonate-fluor-apatites, and was 163.3 kcal/mole. This positive number indicated that a driving force was needed to dissolve carbonate-fluor-apatites and this was provided by the neutralisation of the anions by H+ where, at a pH range of 3.5 to 6.5, the major ionic species formed from PO43-, CO32- and F- would be H2PO4-, CO2 + H2O, and HF.

Chien (1977b) considered that the solubility of a carbonate-fluor-apatite will be dependent on the standard free energy of reaction (DGro) of the mineral. The standard free energy of reaction will be the sum of the standard free energies of dissolution and neutralisation. The standard free energy of neutralisation (DGno) was related to the extent of carbonate substitution by the following relationship (where b is the number of substitutions of carbonate for phosphate in a unit cell of apatite)

$$DGno = -(165.8 + 5.1b) \qquad (3)$$

And the standard free energy of reaction DGro will be:

$$DGro = DGdo + DGno \qquad (4)$$

$$\text{therefore} \quad DGro = -(2.5 + 5.1b) \qquad (5)$$

So that the reactivity of a carbonate-fluor-apatite is expected to increase linearly as b increases, disregarding other effects of substitution on the mineral, such as decreasing crystallite size.

Khasawneh and Dole (1978) examined the effect of carbonate substitution on the solubility of francolite. The francolite was in equilibrium with fluorite, in solutions of different levels of pH, differing activities of calcium and phosphate, and different total solution ionic strength. Based on pKa values for fluorapatite of 122, and 122.2 - 6.3b for carbonate-fluor-apatite, where $\overset{\beta}{b}$ is the number of moles of CO3 in the apatite structure, the relationship developed was:

$$pH2PO4 + 1/2pCa = a(pH - 1/2pCa) - bpCa - c \qquad (6)$$

where a, b, c, are dependent on b.

For example if b = 0, a = 2   if b = 1, a = 2.40
b = 0   b = 0.06
c = 0.82   c = 3.17

In this relationship as pH increased, differences in solubility between highly substituted (more soluble) and less substituted (less soluble) carbonate-fluor-apatites decreased until, at a certain pH, which seemed to be dependent on the activity of calcium, the lines of H2PO4- activity intersected. This theoretical intersection point was found to be between pH 7.18 and pH 8.42 for a range of calcium activities, and represents a point where solubility of the carbonate-fluor-apatites is the same regardless of the level of carbonate substitution. Above the common solubility pH the order of solubilities is reversed and carbonate-fluor-apatite is now thermodynamically more stable (lower free energy form) than fluorapatite, and as b increases the solubility decreases.

2.2.7 The composition of Francolite ore

Phosphate deposits are largely francolitic peloids mixed with siliceous material, principally quartz grains and silicate clays. Typically the ore is removed from an opencast mine as a slurry and put through a process of beneficiation which is largely aimed at removing siliceous sands and clays and concentrating the ore. Beneficiation may involve washing, screening, desliming and flotation, using a variety of reagents such as fuel oils and sulphuric acid (Williams and Zellars, 1989). The effect of the reagents on the francolite structure has not been examined.

Siliceous materials may also be present in the peloids. Rooney and Kerr (1967) found that a typical peloid from the North Carolina deposit was approximately ninety percent francolite and ten percent non-francolite. The francolite fraction was composed mainly of carbonate-fluor-apatite. The non-francolite fraction was composed of 3-5% quartz, 2% glauconite, 2% carbonaceous matter, 1-2% metallic minerals (mainly pyrite), and also feldspar, zircon, topaz, calcite and gypsum, all less than one percent. Some peloids were also found to have an outer coating of altered phosphate, which must be the result of a natural process, since the sample examined by Rooney and Kerr (1967) would not have undergone beneficiation. Table 2.3 catalogues the relative amounts of the major elements found in some purified apatite samples sorted from phosphate rock ore, and also the relative amounts of the major elements when the whole unsorted ore was analysed.

Table 2.3 Contents of the major elements in a selection of purified apatites and unpurified phosphate rock ores.

Mineral	Content of the major components (%)						
	P_2O_5	CaO	F	CO_2	Na_2O	MgO	Ref
A theoretical fluorapatite							
	42.2	55.6	3.77	0	0	0	1
Fluor-apatite sample from;							
South west Finland	41.87	55.16	3.63	0	0.09	-	2
Kola Peninsular, USSR	40.67	54.28	2.79	0	0.15	-	3
Carbonate-fluor-apatite sample from ore of:							
Central Florida, USA	37.1	55.5	4.6	3.95	0.72	0.36	1
Khouribga, Morocco	36.3	55.4	4.7	4.5	0.85	0.43	1
North Carolina, USA	35.3	55.3	4.8	5.4	1.04	0.52	1
Arad, Israel	34.8	52.8	4.0	3.9	-	-	4
Gafsa, Tunisia	34.7	55.2	4.9	5.7	1.20	0.60	1
A theoretical maximally substituted carbonate-fluor-apatite	34.0	55.1	5.04	6.3	1.4	0.7	1
Analysis of whole ore sample from:							
Central Florida, USA	33.4	48.9	3.9	3.0	0.53	0.29	1
Khouribga, Morocco	32.1	51.6	4.1	5.3	0.79	0.43	1
Sechura, Peru	30.2	46.5	2.9	4.4	1.85	0.50	1
North Carolina, USA	30.2	48.5	3.7	5.5	0.83	0.54	1
Gafsa, Tunisia	28.8	48.3	3.4	6.3	1.3	0.59	1

1. McClellan, 1978 2. Deer *et al.* 1965
3. Altschuler, 1973 4. Axelrod, 1978

When characterizing a phosphate rock a clear distinction must be made between an analysis of the elements in an unsorted ore sample and an analysis of a purified sample of carbonate-fluor-apatite extracted from the ore. Differences in any beneficiation undergone by the supposedly unsorted ore samples may also change the ore composition. Quite different conclusions about the phosphate rock may be reached depending on what type of sample has been analysed.

To illustrate the problem, North Carolina phosphate rock was taken as an example. Considering only calcium, phosphate, fluorine and carbonate as the major components, the percent content by weight composition (McClellan, 1978) of a purified North Carolina carbonate-fluor-apatite (table 2.2) was converted to moles per 100g, of Ca, P, C and F as follows; Ca: 0.98m, P: 0.49m, C: 0.12m, F: 0.25m. *This creates molar ratios of:*

P/C = 4, F/C = 2, P/F = 1.96 and Ca/P = 2.

This provided a β *value of 1.2, (indicating the extent of carbonate substitution for phosphate) from the structural model (section 2.2.4) for the purified francolite, which was generally confirmed by published data. For instance the* β *value of North Carolina carbonate-fluor-apatite from McClellan and Lehr (1969) was 1.23. The same value was found by Chien (1977b), while Khasawneh and Doll (1978) quoted 1.26, and Chien and Black (1976) reported a value of 1.20 for North Carolina carbonate-fluor-apatite which had been previously extracted with citrate.*

Using the Ca, P, C, and F content of a unpurified whole ore (McClellan (1978), table 2.3), and although the percent composition figures were lower, they were still in roughly the same proportions. However these mole ratios differed sufficiently from those of the purified carbonate-fluor-apatite to cause a major change in the theoretical unit cell structure. If the P/F ratio, now 2.26, which is regarded as the most stable of the molar ratios (Cheney et al. 1979) is accepted as indicating the extent of carbonate substitution, it was found that β *was now 0.77. This change represented a significant drop in substitution, from 1.2 to 0.77, and raises the question of which unit cell structure correctly represents the North Carolina ore.*

Chien and Black (1976) and McClellan and Lehr (1969) are of the opinion that a β *value of about 1.2 does represent the majority of the francolite in the North Carolina ore. The above composition of the unpurified ore however only provides sufficient carbon and fluorine for about 75% of the carbonate-fluor-apatite in the ore to be in the form* $b = 1.2$*. Similar problems occur when considering other phosphate rocks.* It would appear that detailed analysis of purified samples of carbonate-fluor-apatite from an ore sample may not characterise all the phosphate present in the ore.

One possible explanation is that the non-francolitic fraction of the ore contains significant quantities of calcium and phosphate compounds. Possible forms of these compounds are hydroxy-apatite, or crandallite type minerals ($CaAl_3(PO_4)_2OH_5.H_2O$), or combinations of separate calcium and phosphate minerals such as gypsum, calcite, and wavellite.

If it is accepted that the β value based on the analysis of purified samples of apatite does represent the form of the majority of the francolite present, it must be concluded that analysis of the composition of the whole unpurified ore cannot be used to predict the extent of substitution. It would also appear that significant quantities of non-carbonate-fluor-apatite phosphate minerals may be present in phosphate rock ore.

2.2.8 The effect of variable substitution on reactivity

In 1975 Olsen examined the rate of dissolution of various phosphate rocks in an EDTA solution system designed for a slow rate of dissolution and found a linear relationship with time over 24 hours. A general equation was fitted of:

$$x = 3Kt \qquad (7)$$

where x was the concentration of phosphate in solution at time t, and K was a rate constant which was roughly proportional to the extent of substitution. The time scale used was in hours, and the rocks used were not highly substituted. Olsen found that the rate of dissolution was very stable over 24 hours and concluded that a single extraction of 7 hours would have been sufficient to characterise the rate constant.

Chien (1977b) considered similar problems in more detail and utilised phosphate rocks of a wider range of substitution. Chien found that the dissolution of North Carolina, Florida, and Tennessee phosphate rocks in ammonium acetate at pH 4.8 was described by the equation:

$$x = Kt^{1/m} \qquad (8)$$

where x is the concentration of phosphate in solution at time t, K is a rate constant and m is an empirical constant. K was found to be dependent on the extent of substitution and on the solid:solution ratio. M was found to vary with extraction time, and K varied depending on whether a first or second extraction was being considered, indicating that the solubility characteristics of the phosphate rocks changed as the extent of dissolution increased. This range of solubility could generally be divided into a small portion (about 7%) of relatively more soluble phosphate rock and a greater portion with a lower solubility.

Chien and Black (1975 and 1976) proposed the following dissolution reaction for a carbonate-fluor-apatite (where x = β, the amount of carbonate substitution for phosphate per unit cell):

$$Ca_{10-0.42x}Na_{0.3x}Mg_{0.12x}(PO_4)_{6-x}(CO_3)_xF_{2+0.4x}$$
$$= (10-0.42x)Ca^{2+}+0.3xNa^{+}+0.12xMg^{2+}+(6-x)PO_4{}^{3-}+xCO_3{}^{2-}+(2+0.4x)F^{-} \qquad (9)$$

Chien and Black (1975 and 1976) noted that there was no direct relationship between the solubility product and the extent of substitution but predicted a linear relationship between the free energy of formation (ΔGf°) of a carbonate-fluor-apatite and β, the extent of carbonate substitution, because thermodynamic theory predicted that substitution would decrease the stability of a carbonate-fluor-apatite. Chien and Black proposed that a relationship between the free energy of formation and β might be used to find a general solubility product relationship for phosphate rocks. A theoretical relationship was found between the free energy of formation (ΔGf°), subtitution (β) and the solubility product (K_{CFA}):

$$\Delta Gf^{\circ} = -2924.6 + 1.37\log K_{CFA} + 116.1\beta \qquad (10)$$

Their theory was tested by extracting citrate and HCl insoluble fractions of francolites and equilibrating these fractions with dilute HCl. The relationship between the free energy of formation and the extent of substitution was linear within the fractions tested, but the axis intercepts and slopes varied with the fraction being tested. The relationships obtained were:

$$\Delta Gf^{\circ} = -3094.5 + 124.9\beta \qquad (11)$$

for the citrate extracted fraction and

$$\Delta Gf^{\circ} = -3104.4 + 130.2\beta \qquad (12)$$

for the HCl extracted fraction. These relationships could be substituted into the above relationship (9) to provide an estimate of K_{CFA} as β varied, but would be accurate only for the particular fraction of the phosphate rock tested.

2.3 The Availability of Phosphate Rocks in Agronomic Systems.

2.3.1 Formic solubility and agronomic availability

An approach to predicting phosphate rock performance has been to examine the extractability of the phosphate contained in phosphate rock. The usual aim of these extractions is to circumvent lengthy field trials of new phosphate rock fertilisers with a quick, cheap solubility test which can easily be preformed in a laboratory. The test is expected to provide an estimate of the phosphate availability of a material by ranking the solubility result against the solubility of other phosphate rocks which have previously been tested in the field. Solvents used have included 2% solutions of formic and citric acid (Chien and Hammond, 1978b; Mackay *et al.* 1984b), and solutions of neutral, alkaline (pH 9.35) (Mackay *et al.* 1984b) and acid (pH 3) (Chien and Hammond, 1978b) ammonium citrate.

The use of a solution of 2% formic acid as an extractant for phosphate rock was first tested by Hoffman and Mager (1953) and was preferred over other organic acid solutions, which included citric acid, because the greatest difference in the solubility of various phosphate rocks was found with this reagent. Since this finding a solution of 2% formic acid (w/v) has been extensively used to extract phosphate rock [e.g. Laske (1957), Doering (1958), Leon *et al.*(1986), Hagin *et al.*(1978), Chien (1978)]. The extraction has generally been at a 1:100, gsolid:mlsolvent ratio and the time period of the extraction has been either one hour [e.g. Mackay *et al.*(1984b), Chien and Hammond (1978b), Kucey & Bole (1984)] or half an hour [e.g. EEC reg. L213/8 (1977), Syers *et al.*(1986)].

A selection of results from Chien and Hammond (1978b) are presented in table 2.4. The phosphate rocks were ground (80% passing 100 mesh) and the extraction was carried out in 2% formic acid for 60 minutes.

Table 2.4 Solubility of the phosphate in a selection of phosphate rocks, using 2% w/w formic acid as an extractant for 60 minutes (Chien and Hammond, 1978b).

Phosphate rock	Solubility: % of rock[1].	% of total P.
North Carolina, U.S.A.	11.2	86.2
Gafsa, Tunsia	9.7	74.6
Sechura, Peru	9.5	73.1
Central Florida, U.S.A	3.6	25.4
Tennessee, U.S.A	3.0	22.9

[1] Weight basis.

Mackay *et al.*(1984b) compared the solubility of six phosphate rocks in a range of solvents against their agronomic effectiveness. The agronomic effectiveness was evaluated in a glass house trial in which pelletised phosphate rock was applied the surface of pots and either perennial ryegrass or white clover was grown for approximately six months. The phosphate rocks included North Carolina and Sechura phosphate rocks, and the soils included the Tokomaru silt loam (as was used later in thesis, chapters 5 and 7). The solvents used were solutions of 2% formic and citric acid, 5 and 15% citric acid, and also neutral and alkaline ammonium citrate, and up to four sequential extractions of 30 and 60 minute durations were made.

The conclusion of this work was that the solubility in 2% formic acid was best correlated with the agronomic results, whether single or multiple extractions were being considered. Shaking phosphate rock for one hour in a solution of 2% formic acid has also been a preferred solvent in other comparative studies which correlated the agronomic availability of various phosphate rocks against the solubility of the phosphate rock in various solutions (Kucey and Bole, 1984; Chien and Hammond, 1978b).

The prediction of agronomic performance from formic solubility

The EEC regulations expect that the total phosphate content of a phosphate rock which is suitable for direct application will be greater than or equal to 11%, that 95% of the fertiliser particle size will be below sixty three microns and that 55% of the phosphate in the fertiliser will be soluble in a solution of 2% formic acid when shaken at a 1:100 grock/vsolvent ratio for half an hour. (The New Zealand regulations only expect that 30% of the phosphate in the material is soluble in 2% citric acid and give no lower limit for phosphate content.)

Some phosphate rocks which qualify by the EEC standards for direct application are; Sechura, Gafsa and North Carolina (Syers *et al.* 1986). The solubility data presented in Table 2.4 indicate that, of the samples tested by Chien and Hammond (1978b), the expected order of decreasing agronomic availability of these three phosphate rocks will be North Carolina > Gafsa > Sechura.

Arad phosphate rock qualifies as a reactive phosphate rock, with a formic solubility of 55%, when the material was ground to a mean particle diameter of 48.8µm (Hedley, unpub.), but was marginally under the qualifying standard when 100% of the material was ground to less than 250µm (Syers *et al.* 1986). Arad phosphate rock would be expected to have less agronomic availability than the three previously mentioned phosphate rocks.

In order to assess the value of ranking phosphate rocks by means of a solubility test in formic acid, a review of published results of the agronomic performance of these materials was undertaken.

Mackay *et al.* (1984a) compared the agronomic effectiveness of five ground phosphate rock materials, using the dry matter response and phosphate uptake data of ryegrass obtained in a glass house trial using six New Zealand soils. The phosphate rock fertilisers were ground to less than 180µm, pelletised, and applied to the surface of the pots at two rates. Perennial ryegrass (cv. Grasslands Ruanui) was grown on the pots for approximately six months.

The phosphate rocks included North Carolina and Sechura samples, and the soils included the Tokomaru silt loam (as used in this thesis, chapters 5 and 7). After 22 weeks the total yield of ryegrass from pots fertilised with these two phosphate rocks at a rate equivalent to 75 kg/ha were similar to yields produced on superphosphate fertilised pots. The same result was also found at the higher rate of appplication (150 kgP/ha), and for three out of the six other soils used. On the two remaining soils the yield derived from the two phosphate rocks was lower than that from the superphosphate.

It was also found on these two soils that the yield derived from the Sechura phosphate rock was significantly lower than that derived from North Carolina phosphate rock at the higher rate of application, and for one of these soils the same effect also occurred at the lower rate of application.

Chien and Hammond (1978b) compared the performance of seven ground phosphate rocks (80% <150μm), including North Carolina and Sechura and Gafsa phosphate rocks, in glasshouse and field trials.

The glasshouse trial utilised an oxisol, with four rates of phosphate application and a crop of guinea grass was grown ninety days after the fertiliser had been incorporated. The accumulated yield derived from the Sechura phosphate rock was consistently higher than that derived from the North Carolina PR, although the difference in yield reduced as the rate of application increased. The yield derived from the Gafsa phosphate rock was intermediate at the two lowest application rates and lower than the other phosphate rocks for the two highest application rates.

In the field experiment the soil was limed 42 days before four rates of fertiliser were incorporated and three successive crops of beans grown. Yields from the three phosphate rocks were very similar, especially at the lower application rates. The best separation of the various yields occurred at the highest application rate but there was no consistent pattern as to which phosphate rock gave the highest yield for each crop.

Hagin *et al.* (1978) grew perrenial ryegrass on a limed soil in which the ground (-200mesh) phosphate rocks (Arad or North Carolina phosphate rocks amongst others) were incorporated at four different rates. Over the three month duration of the experiment the yield derived from the Arad phosphate rock was significantly lower than that from the North Carolina phosphate rock treatments at all four rates at the first harvest and at the higher two rates for remaining two harvests. At the lower rates for these remaining harvests the yields were not significantly different. Over the duration of the experiment the yield obtained from the North Carolina phosphate rock treatments was never different to that derived from superphosphate (SSP) incorporated at the same rates.

A general conclusion from the above work would be that the agronomic availability of Sechura, Gafsa and North Carolina phosphate rocks is very similar. There was no clear indication from the various trials considered of a consistent difference in the agronomic value of these three phosphate rocks, with the performance of the materials varying within the trials as well as between the trials. Ground Arad phosphate rock was not as effective as North Carolina phosphate rock, and would presumably also not be as effective as the Sechura phosphate rock. No direct comparisons were available for these phosphate rocks which had not been ground, except for a report from the national series of fertiliser trials undertaken in New Zealand from 1982 to 1986 (Sinclair and Dyson, 1988). These trials found that at twelve sites, over four years, on mown pasture, the average yield derived from "as received" North Carolina phosphate rock was the same as that derived from "as received" Sechura phosphate rock.

These results suggest that solubility tests of phosphate rock materials may only give a general indication of the agronomic availability of a material. Evidently factors other than the reactivity of the material influence plant availability.

2.3.2 Factors influencing the dissolution of phosphate rock in a natural soil environment: The Kirk and Nye mechanistic model

Much research has been carried out on the quantitative effects of applying phosphate rocks to soil systems but little work has been done on mechanistic modelling in order to predict and explain the effects that have been found.

Kirk and Nye initially developed a model based on the dissolution of particulate dicalcium phosphate dihydrate (DCPD) in a single dimensional soil system (1985 a & b). This model was extended to a three dimensional system (1986 a & b) and subsequently a simplified version of the model was adapted to predict the dissolution of carbonate-fluor-apatite (1986 c & d). The carbonate-fluor-apatite model has never been tested experimentally, although Bolland and Barrow (1988) demonstrated that that the model predicted the qualitative trends for North Carolina phosphate rock dissolution in a field trial.

Kirk and Nye (1985a) expected that the rate of dissolution of a carbonate-fluor-apatite would be controlled by the rate of diffusion of reaction products away from the particle surface, rather than being controlled by the rate of the dissolution reaction at the solid liquid interface.

Work on carbonate-fluor-apatite dissolution in solutions has already demonstrated that diffusion rather than the rate of reaction limits phosphate rock dissolution. Huffman *et al*. (1957) found that in studies of carbonate-fluor-apatite dissolution in phosphoric acid, solubility was controlled by the rate of diffusion of solute away from the reaction surface. The effective surface of a particle for this type of reaction was the apparent surface of a thin surrounding liquid layer, so that surface microscopic roughness and porosity are not important. Chien (1978) also tested the effect of stirring and found that agitation increased the dissolution of all phosphate rocks studied, indicating that the rate of dissolution was controlled by the diffusion of reaction products away from the particle surface, rather than by the actual kinetics of the surface reaction.

Kirk and Nye expected that this limitation would be accentuated in soil, where diffusion pathways are limited in volume and tortuous, and where the system is already plentiful in the solute ions which are dissolution products.

The DCPD dissolution system (Kirk and Nye 1985a, 1986a) was defined in terms of a continuity equation which assumed continuous diffusion of the dissolution products away from a spherical particle and a balanced ionic charge at the solute front. Congruent dissolution was expected with no precipitation of reaction products at the particle surface. A balanced flux of ions across the solid liquid interface and throughout the solute front was also expected, which would produce different concentration gradients for each of the solute ions. A first, more complex model (1986a) adjusted the rates of diffusion of base and phosphate as the solution concentrations changed with time and distance, but this degree of accuracy was found to be unnecessary and a second model (1986c) assumed constant rates of diffusion and this was not found to affect the model predictions significantly.

Kirk and Nye also predicted that close to the solid:liquid dissolution interface $H_2PO_4^-$ and Ca^{2+} would be the dominant ions, and that the HPO_4^{2-}-$H_2PO_4^-$ ion pair would be the major pH controlling ions, with lesser concentrations of HCO_3^- and $CaH_2PO_4^-$ in solution. Further away from the interface the concentration of H_3O^+ rises and H_3O^+-H_20 becomes the ion pair controlling pH as concentrations of the other solute ions drops. At the edge of the dissolution front $H_2PO_4^-$, Ca^{2+}, and H_3O^+ would be the main ions present with the concentration of $H_2PO_4^-$ expected to decline rather more sharply than the concentration of Ca^{2+}.

(a) The influence of phosphate rock composition on dissolution

Adapting the model to carbonate-fluor-apatite reduces the phosphate: base ratio and introduces F^-, Na^+ and Mg^{2+} into the ion balance and solubility product equations. Kirk and Nye based their dissolution predictions (for a maximally substituted carbonate-fluor-apatite) on a dissolution reaction as follows:

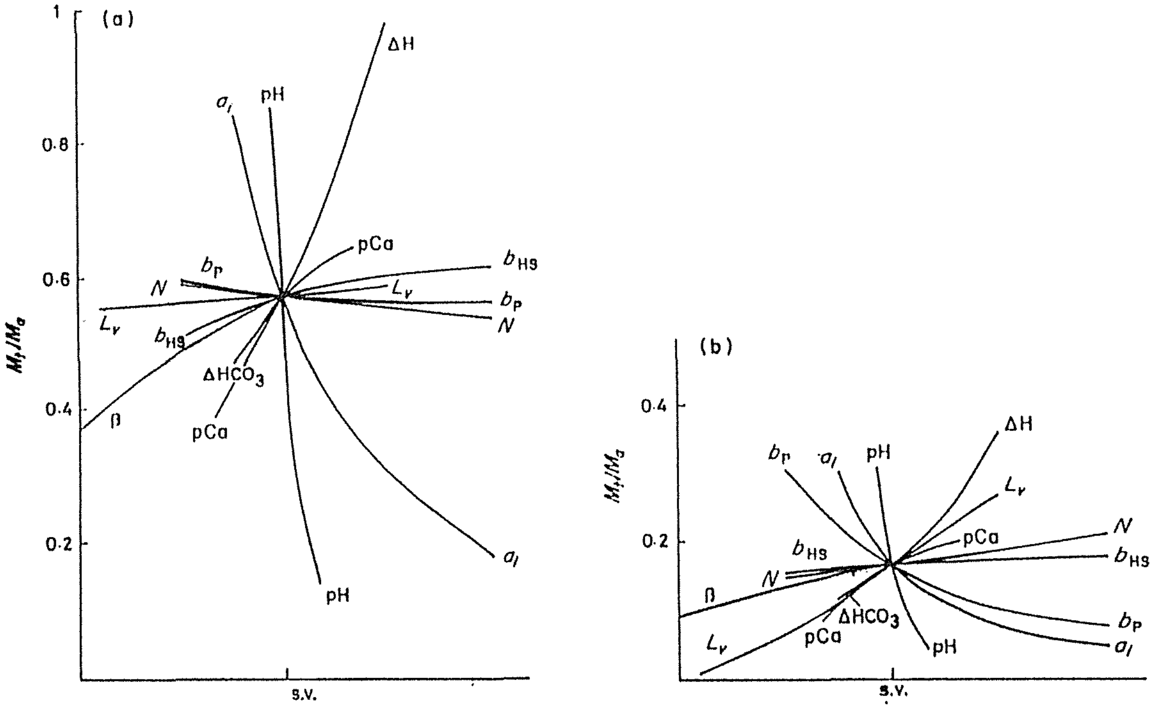
$$[Ca_{9.4}Na_{0.4}Mg_{0.2}(PO_4)_{4.5}(CO_3)_{1.5}F_{2.6}]^{0.5+} + 12H_2O \quad =$$

$$9.4Ca^{2+} + 0.4Na^+ + 0.2Mg^{2+} + 4.5H_2PO_4^- + 1.5H_2CO_3 + 2.6F^- + 12OH^- \qquad (13)$$

The solubility product for carbonate-fluor-apatite used was $pK_{CFA} = 122.2 - 6.3\beta$. This was based on work by Chien and Black (1977), who were careful to point out that β varies within a given sample of phosphate rock and meant that the Kirk and Nye model is based on the dissolution of pure carbonate-fluor-apatite with no gangue minerals rather than naturally occurring phosphate rock. This could introduce difficulties in applying the model to real systems because Kirk and Nye (1985a) found that the accuracy of the solubility product was vital to the correct functioning of the model. The problem is illustrated by the consistent finding that phosphate rock type is an important and dominating factor in tests of phosphate rock-soil dissolution systems (e.g. Bolan and Hedley (unpub), MacKay *et al.* (1986)), which is in contradiction to Kirk and Nye who predicted that changing β would have little effect on the extent of dissolution (figure 2.2). It was also assumed that the distribution of apatite would be constant over the reaction surface.

Kirk and Nye also suggested that the effect of F^- on the dissolution system would be negligible. Kirk and Nye expected that F^- would precipitate as CaF_2 (although Chien *et al.* (1975) found that phosphate rock dissolution solutions could remain supersaturated with fluorite for long periods of time), and that Na^+ and Mg^{2+} will behave as Ca^{2+}. The concentration of negative ions such as Cl^- is not expected to be affected at all by the dissolution but will determine the bulk soil solution concentration of Ca^{2+}.

The sensitivity of the model to various input parameters are shown in a diagram redrawn from Kirk and Nye, 1986d (Figure 2.2).



. The effects of the most important variables on the fraction of rock phosphate (a) that has dissolved, and (b) that has been taken up by roots, after 80 days. The standard values (s.v.) are as in Figs 4 and 7, and $L_v = 1000$ dm dm^{-3}. The ranges in values are:

P adsorption Freundlich a (αb_r)	0.07–0.28 mol dm^{-3} soil
b_{HS}	0.035–0.14 mol dm^{-3} soil pH^{-1}
pH	4.25–5.25
pCa	2–4
$w(\alpha N)$	0.08–0.32 kg P m^{-3} soil
a_l	0.05–0.2 mm
L_v	100–1500 dm dm^{-3}
ΔH	0–10^{-9} mol dm^{-3} soil s^{-1}
ΔHCO$_3$	0–5 × 10^{-10} mol dm^{-3} soil s^{-1}

β (degree of CO$_3$ substitution in

$$\mathrm{Ca_{10-\alpha}[NaMg]_\alpha(PO_4)_{6-\beta}(CO_3)_\beta F_\lambda};$$

see part I, equation (16)) 0–1.5

Figure 2.2: The theoretical effects of the most important variables on the dissolution of phosphate rock (carbonate-fluor-apatite) and the subsequent plant uptake of fertiliser phosphate (Kirk and Nye, 1986d).

(b) The influence of particle size and application rate on phosphate rock dissolution

Kirk and Nye (1986a-d) expected that the initial radius of the particle would be a dominant factor controlling the rate of dissolution, particularly in the early stages, where the rate is largely controlled by the advancement of the approximately spherical diffusion front surrounding the particle. Steep concentration gradients developed between the particle surface and the diffusion front, and as a small advance of the front necessitated a relatively large increase in the volume of solution involved in the diffusion front, Kirk and Nye (1986a) predicted that the rate of dissolution would be approximately proportional to the inverse square of the initial particle size. This assumption was expected to hold until the dissolution front met a similar dissolution front of an adjacent particle. At this time the "back reflection" or overlap effect was expected to change the reaction product concentration gradients, reducing the rate of dissolution, and causing the dissolution rate to be more responsive to any soil buffer terms which may influence the reaction product concentrations, such as soil solution phosphate concentration and the rate of phosphate diffusion through the soil.

Kirk and Nye (1986a) acknowledged that the initial particle size will be reduced as dissolution proceeds but did not expect that the rate of dissolution will be much affected. This was because the decrease in particle volume was relatively small compared to the increasing volume of solution in the dissolution front. Kirk and Nye also did not expect that unevenness of the particle surface would have a significant effect on the rate of dissolution. Cracks, or pits, would be filled with saturated solution so the "effective surface area" of the particle remained essentially spherical.

Introducing a range of particle sizes would not affect the early dissolution rate but would later reduce the rate of dissolution as smaller particles were exhausted and only larger particles remained (Kirk and Nye, 1986d).

When the effect of two dissolution fronts meeting was considered it became evident that the application rate ~~will~~ would be an important associated factor controlling the rate of dissolution. Particle size would interact with application rate to control the time taken to achieve a meeting of the dissolution fronts with a subsequent slowing of the dissolution rate. Associated factors will be the particle size distribution of the material and also the spatial distribution pattern of the particles in the soil.

An increase in the application rate would slightly decrease the amount of dissolution but would slightly increase the amount of phosphate taken up by a plant, as the extent of content with the roots increases. Kirk and Nye did not expect that changing the rate of application would have much effect plant availability. Their model predicted that the percentage dissolution will fall slightly as the application rate rises, but that phosphate uptake by plants will increase as the average distance between the roots and the fertiliser particles decreases.

(c) Soil and plant factors influencing phosphate rock dissolution

Kirk and Nye (1986d) evaluated various soil terms affecting the extent of phosphate rock dissolution and found that the main soil parameters expected to control dissolution were; the native soil solution pH and pCa, and the base and phosphate buffer capacities. The principal soil factor affecting dissolution was predicted to be the soil pH (1986d).

In the pH range considered by the authors soil solution pH would be largely controlled by the partial pressure of carbon dioxide in the soil atmosphere, unless the pH was below five in which case pH would be largely controlled by Al^{3+}. Kirk and Nye found that the model was sensitive to changes in the carbon dioxide partial pressure. This effect would be accentuated by the dissolution of highly substituted carbonate-fluor-apatite, which would cause the interface concentration of HCO_3^- to increase.

Changes in the other three factors (pCa, P and base buffer capacities) had relatively little effect (Figure 2.2). Solution concentrations of calcium were expected to be largely controlled by the total anion concentration of the bulk soil solution. The base buffer capacity was characterised by the titratable acidity, and the phosphate buffer capacity (twenty hours of phosphate sorption) characterized using a Freundlich isotherm. Associated factors were the diffusion coefficients of base and phosphate which were derived from the respective rates of diffusion in free solution and the soil buffer capacity, and also the soil water content and tortuosity. The effect of changing soil water content and tortuosity was not evaluated for carbonate-fluor-apatite dissolution although the complex DCPD model was highly sensitive to changes in these factors (1986a).

Kirk and Nye (1985a) did incorporate the interaction effect between Ca^{2+} and H^{+} concentrations on the cation exchange surfaces into the model. This effect would tend to buffer the rise in solution pH as dissolution proceeded. They chose not to include in their model the interaction effects of pH and phosphate adsorption, having determined experimentally that no interaction effects occurred for their test soil. The model also assumed that the "slow reaction" of phosphate adsorption (processes of continuous slow adsorption, and absorption) would not be a significant contributor to the phosphate buffer capacity.

The effects of changing the concentrations of negative ions in soil solution not directly involved in dissolution was also judged to be insignificant. These ions, such as Cl^{-} and NO_3^{-} were expected to control the solution concentrations of calcium ions but Kirk and Nye did not incorporate the effects of changing the concentrations of such ions into their model. This decision was made because the concentrations of Cl^{-} were low in the test soil and other ions were not expected to be significant because organic activity was inhibited. This situation is in contrast to the subsequent adaptation of the model to carbonate-fluor-apatite dissolution which included plant effects, although negative ion effects were still not included.

Kirk and Nye (1986d) suggested that the main effect of the presence of a plant in a carbonate-fluor-apatite and soil system would be the effect of rhizosphere acidification. The effect of rhizosphere acidification (or alkalinisation) was expected to occur largely in response to an imbalance in the cation to anion ratio of nutrient ions taken up by the plant. This is most commonly a release of H^+ from the roots in response to the uptake of NH_4^+ or excess cation over anion uptake in legumes. Kirk and Nye (1986d) predicted that a high level of H^+ release may significantly increase the amount of carbonate-fluor-apatite dissolution. The extent of this affect would be dependent on the species of plant, the soil nutrient balance (i.e. type of fertiliser), and also the soil buffer capacities for base and phosphate. The root density and the rate of application of the carbonate-fluor-apatite would also affect the extent of the effect, and would interact with time, if the root density increased in the proximity of the fertiliser.

Other processes such as the release of organic acids could also change the rhizosphere pH and any release of base by the plant was expected to reduce dissolution drastically, although this effect is not common, except when plants are fertilised with nitrogen solely in the nitrate form.

The effect of phosphate and calcium uptake by the plant roots was judged to be negligible because levels of base would tend to build up in the soil regardless of the rate of phosphate uptake. A higher root density was expected to allow simply a greater recovery of dissolved phosphate without significantly affecting the rate of dissolution.

2.3.3 The dissolution model and experimental measurements of phosphate rock dissolution

When the rate of solute diffusion was limiting phosphate rock dissolution Kirk and Nye predicted that the soil solution pH and pCa, and the soil phosphate and base buffer capacities would be the main soil factors controlling the amount of carbonate-fluor-apatite dissolution. Kirk and Nye tested their model for dissolution of particulate DCPD, but did not test their subsequent adaptation to carbonate-fluor-apatite. Some comments can be made on their model using the results of other workers.

(a) The diffusion assumption

The importance of the assumption that the rate of dissolution would be controlled by the rate of diffusion was shown by the work of Chien *et al.* (1980). This work found that in a shaken system of phosphate rock and soil very rapid dissolution occurred, quickly reaching a point of saturation equilibrium. Thereafter negligible dissolution of the phosphate rock occurred and there was a steady decline in the soil solution phosphate concentration, as characterised by a typical Elovich soil phosphate sorption relationship (Chien and Clayton, 1980). This work indicated that phosphate rock dissolution, being no longer limited by diffusion of solute away from the reaction surface was very rapid and quickly neutralised all the soil base, preventing any further dissolution.

(b) The soil chemical characteristics

Peaslee *et al.* (1962) tested phosphate rock dissolution in a variety of soils in an "exhaustive" style pot trial, where particle interaction effects would not be expected to be limiting. A highly significant linear relationship with soil pH was found. Bolan and Hedley (1988) and Kanabo and Gilkes (1987) found the same results in similar trials. Bolan and Hedley (1988) also demonstrated that the assumption of no change in phosphate adsorption with changing pH does not hold for all soils, indicating that the effect of a sharp rise in pH at the reaction interface may significantly decrease the rate of phosphate adsorption.

All the above trials utilised unamended soil or changed the pH using NaOH or HCl. Often in field work and in earlier pots trials the pH was changed using lime, or in the case of Ellis *et al.* (1955), $CaOH_2$. This added the effect of increasing pCa to an increase in the pH. Ellis *et al.* (1955) found that changing the pH and pCa of their growth medium maintained a strong relationship of increasing dissolution with decreasing pH, but the work of Mackay and Syers (1986) found that this effect may be almost entirely due to the change in pCa.

Hughes and Gilkes (1986b) incubated Sechura phosphate rock with thirty different soils at a range of application rates and found that the correlation of dissolution with various soil factors varied with the rate. Generally the effect of soil pH was more significant at the lower rates of application, while the significance of the buffer terms, in this case the reactive forms of iron and aluminium, increased with increasing application rate of the phosphate rock.

Mackay *et al.* (1986) incubated Sechura phosphate rock in soil at high application rates, and the extent of dissolution reached a static equilibrium condition after approximately 30 days. It was found that the soil factors best correlated to the extent of dissolution at "equilibrium" were the soil base and phosphate buffer capacities, and that soil pH had relatively little effect. In a subsequent paper using the same system (Mackay and Syers 1986), it was found that changing the soil solution concentration of phosphate had very little effect on the extent of dissolution and that pCa had a more significant effect than did soil pH.

It would appear reasonable to conclude from these studies, as was suggested by Kirk and Nye (1986a) that the effects of native soil pH, and also pCa, are more significant before there is an overlap between individual spheres of influence of the dissolving particle in the soil, while the soil base and buffer capacities are likely to be of increasing significance once the spheres of influence overlap and, as may be found in a closed soil-PR incubation system, when a saturation equilibrium can be achieved and can limit phosphate rock dissolution. Rate of application will evidently be an important interacting factor.

(c) Particle size

Chien (1978) partitioned various ground phosphate rocks into size fractions ranging from between 600μm and 250μm to less than 50μm and measured the solubility of the different fractions in a stirred system of ammonium acetate. Particle size had a significant effect on the rate of dissolution until the solution reached equilibrium (or saturation). As the particle size decreased the rate of dissolution was increased and consequently equilibrium was reached more rapidly. The rate of response varied with rock type. Data from McConnel and Evans (1981) tends to confirm the results of Chien (1978). Unground North Carolina phosphate rock was divided into six size fractions and dissolved, at two stirring speeds, in 2% citric acid. The rate of dissolution increased with decreasing particle size and increasing stirring speed.

Armiger and Fried (1958) partitioned a range of ground PR's (Gafsa, Curacao, South Carolina, Florida, Tennessee Brown, and Virginia) into three size ranges (150-106μm, 106-50μm, <50μm) and compared these with a composite mix of all sizes (-150μm). The phosphate rocks were incorporated into soil and cropped for approximately one year. A rough prediction, based on Kirk and Nye 1986d, that all of the <50μm size fraction would have dissolved within a month certainly was not substantiated. Part of the explanation may be perhaps found in the very high application rates of 640lbsP/acre, so that one year may not have been sufficient time for all the material to dissolve.

Also associated with the high application rate would be an expected "back reflection" effect of interacting dissolution fronts which should occur more quickly with decreasing particle size. Kirk and Nye predicted that "back reflection" would reduce the rate of dissolution, and increase the influence of the soil factors, presumably making the rate of dissolution fairly constant across the different particle size fractions. Armiger and Fried (1958) only presented comparisons within harvests so it is not known if the overall rate of dissolution changed. Certainly the relative differences between the size fractions appeared to be maintained throughout the trial. Possibly the effect of continuous phosphate uptake by the plants in the trial minimised the back reflection effect.

In the work of Armiger and Fried (1958) the general trend observed was that phosphate uptake and yield increased with decreasing particle size but this trend was subordinate to the effect of phosphate rock type. Within phosphate rock type this pattern of results is as would be predicted by the model of Kirk and Nye, particularly in the early stages of the experiment. However in contradiction of Kirk and Nye the effects of "back reflection", where the dissolution of the different size fractions would be expected to slow to a similar rate, as well as an "exhaustion" of the smaller particles, never appeared to occur within the duration of the experiment.

The above conclusions from Armiger and Fried were based on the assumption that a uniform chemical composition was maintained after partitioning the ground phosphate rock. Alston and Chin (1974) avoided this problem by differential grinding of individual samples of Florida and Christmas phosphate rocks. Hagin *et al.* (1978) also used the same technique on Arad phosphate rock. Both papers found a consistent increase in phosphate availability with decreasing fineness of particle size. Alston and Chin were also able to demonstrate, more clearly than Armiger and Fried, that while decreasing particle size gives the same general trend of increased rate of dissolution, the exact rate of change in the dissolution rate varies with rock type.

Alston and Chin (1974) felt that this effect of particle size may have been due to either an increased rate of "weathering" or from increased contact with root rhizospheres, as based on the theory of Moreno (1959). Moreno proposed that in an unconfined volume of soil, where the particles of an insoluble fertiliser were relatively large compared to the root radius, that the availability of nutrient would be directly proportional to the probability of a root finding the fertiliser particle, as well as being proportional to the concentration of the nutrient film around the particle. Kirk and Nye combined the effect of root density with that of particle size in modelling the rate of dissolution.

(d) Application rate

Chien and Hammond (1978b) tested a variety of phosphate rocks at a range of application rates. In a field experiment using successive crops it was found that at the first harvest the growth response was at first directly proportional and linear to increasing application rates, although the slopes varied with phosphate rock type and there was a strong difference between the types of phosphate rock. At the second highest and highest application rates all growth response to the different phosphate rocks appeared to reach a maximum, although the actual level of growth response varied with the rock type.

Similar work by Khasawneh and Sample (1978) found, by extractions of the soil solution phosphate, that the growth ceiling reached in spite of an increasing application rate was due to a lack of phosphate release by the phosphate rock, rather than attainment of a plant yield maximum. This pattern of phosphate availability is typical of trials of phosphate rocks applied at a range of rates as was also shown by; Hughes and Gilkes (1986b), Hagin *et al.* (1978), and Bolland and Barrow (1988). It would appear that increasing the level of application caused an extent of particle interaction sufficient to saturate the soil solution with respect to the phosphate rock, so that the soil solution phosphate concentration remained constant regardless of the application rate. The model of Kirk and Nye appeared to underestimate this effect, and this problem may be related to the initial assumption by Kirk and Nye that the soil conditions would allow a continuous, if slow, rate of dissolution, while phosphate rock dissolution in standard trial conditions often appears to reach a point of equilibrium saturation.

(e) Environmental factors

Lowe (1986) examined the processes affecting the weathering of *in situ* tephra and suggested that in natural systems the principal controlling factors would be environmental, with secondary factors of the primary composition of the material and time. This approach was similar to that of Kirk and Nye, but of the environmental factors the composition of the inorganic phase was subordinate to the principal effects of the moisture regime and the prevailing organic cycle. The moisture regime included the effect of the site drainage, rainfall, leaching, and the local wetting and drying cycles, acknowledging that in the long term the rainfall and leaching systems would be the basic source of protons for the dissolution reactions and that the processes of hydrolysis, precipitation and plant uptake of nutrients would be very dependent on the soil moisture levels.

The organic cycle included the effects of the local vegetation and the soil biomass on biological mixing, soil moisture levels, nutrient uptake and release, as well as the effects of nutrient complexing by organic acids and humus. The organic factors would largely be responsible for fluctuations in the soil solution levels of nutrients associated with the weathering reaction products, so having a major influence on the rate of weathering.

All these factors would interact with the application rate, placement and previous application history of the material to control the amount of weathering over time.

Lowe (1986) also suggested that rather than viewing the effects of time as a constant in the system, that time should be regarded in terms of the "effective period of weathering," acknowledging the variable rate of weathering of a material in a natural system. The time frame of the dissolution/weathering process of phosphate rocks in soil will probably be much shorter than the weathering of tephras (Lowe's work) but the concept of the effective period of weathering will still be relevant because the rate of weathering will be dependent on the changes in the environmental conditions. The time frame will also be an important consideration when applying experimental results to commercial agricultural systems. As pointed out by Elphick (1955) effects (due in this case to particle size differences) found in short experiments may be minimised when the effects of a fertiliser in a system for several years is considered.

With regard to the weathering approach the dissolution of the phosphate rock in an agricultural system is perhaps more appropriately regarded as a weathering reaction, subject to a system of delicate checks and balances imposed by the whole environment. In this sense the general trend of the phosphate rock to break down and release phosphate into the soil solution is recognised, but the weathering based approach acknowledges the difficulty of predicting at just what rate this breakdown will occur.

2.3.4 The question of granulation

Kirk and Nye (1985a and b, 1986 a-d) do not consider granulated materials. It appears that the dissolution of granules in soil could be regarded either as a conglomerate of particles behaving as a single large particle, i.e. the dissolution rate (until "back reflection") will be proportional to the inverse square of the granule radius, or it may be regarded as an extremely "clumped" distribution of the original material where the dissolution rate, until back reflection, is proportional to the inverse square of the radius of the particles of which the granule is composed.

Typical methods of fertiliser application were expected to produce a "clumped" spatial distribution of particles in the soil, as opposed to a random distribution or an absolutely regular distribution. Clumping would cause localised regions of increased solute concentration, resulting in a rapid "back reflection" effect within the clumps. Because a majority of the particles are within the clumps, the overall rate of dissolution will be reduced, so the rapidity and extent of this effect will be in proportion to the extent of clumping.

Buchan *et al.* (1970) compared granules of calcined Christmas Island phosphate rock mixed with soil with an even incorporation of the same material which had not been granulated, and also localised clumps of this material. Buchan *et al.* (1970) found that yields from clumping the ungranulated phosphate rock were significantly lower than an even mixing, and that yields from the granules were significantly lower than either of the ungranulated distributions.

Chien and Hammond (1978a) divided granulated North Carolina and Sechura phosphate rocks into a range of sizes (75µm to 2.8mm diameter). These were mixed with soil at various application rates and cropped with maize. It was found that the availability of the granules correlated well with their solubility in a sand H-resin mix. A plot of phosphate extracted by the resin against granule diameter gave a similar relationship as predicted by Kirk and Nye (1986a) for a single large particle.

Gillion *et al.* (1978) tested granules of North Carolina and Florida phosphate rocks in a similar size range as Chien and Hammond (1978a), but over a longer period of time. For granules which were incorporated into the soil they found the same general trend as Chien and Hammond in the early stages of the experiment, but it appeared that a saturation equilibrium was reached in the later stages reducing the differential effect of granule size. A stronger relationship was found when two sizes of Arad phosphate rock granules were compared using a lower application rates and different crop.

Using Arad phosphate rock a comparison was also made between granules incorporated into the soil and granules applied to the surface of the pots. Gillion *et al.* (1978) found that surface application increased the yield from the granules approximately seven-fold, so that the yield was more comparable to incorporated ungranulated Arad phosphate rock.

MacKay *et al.* (1981) confirmed the work of Gillion *et al.* (1978). Mackay *et al.* tested ungranulated and granulated Chatham Rise phosphate rock on the surface and incorporated into the soil. They found that surface application reduced the availability of the ungranulated material but increased the availability of the granulated material, so that the two forms when applied to the surface gave similar yields, especially when tested in the field.

In summary it would appear that when granules are incorporated into the soil they tend to behave as a single large particle. When granules are applied to the surface of the soil they tend to behave as a clumped distribution of the component material. These conclusions could hardly be said to have been exhaustively tested, and are based on the use of neutral salts as granulating agents.

2.4 Summary and conclusions

Reactive sedimentary phosphate rocks, containing francolite, are formed by a precipitation reaction which occurs in a very specific type of ocean shelf environment. The nature of phosphate in the francolite was found to differ from the fluor-apatite form of calcium phosphate found in igneous phosphate rocks because some of the phosphate in the mineral lattice underwent substitution with carbonate and/or fluorine. This characteristic substitution provided a model for the composition of a unit cell of the phosphate mineral in the francolite,

$$Ca_{10-a-b}Na_aMg_b(PO_4)_{6-\beta}(CO_3)_\beta F_y F_2$$

($\beta = 0$ to 1.5, $y = 0.4\beta$, $b = 0.4a$, $a = \beta - y$) which was named carbonate-fluor-apatite. The extent of substitution of the carbonate-fluor-apatite in a phosphate rock ore was found to be quite variable, and all the phosphate in the ore may not be in the carbonate-fluor-apatite form. Careful chemical characterisation of the material is required when drawing conclusions about a phosphate rock derived from purified samples of carbonate-fluor-apatite taken from an ore deposit.

The substitution for phosphate in carbonate-fluor-apatite caused characteristic changes in the lattice dimensions, crystallite size and packing, and the chemical reactivity of the mineral. In general as the extent of substitution increased the reactivity of the phosphate also increased. Attempts have been made to relate reactivity of phosphate rocks (as assessed by solubility in aqueous solutions) to the agronomic performance of these materials; however other environmental factors can have greater influence on performance.

A model of the dissolution of carbonate-fluor-apatites in soil systems has been developed, where the rate of dissolution was controlled by the rate of diffusion of the reaction products away from the particle surface. Information derived from the model indicated that the principle parameters controlling the initial rate of dissolution of particles of carbonate-fluor-apatite would be the particle size (the rate proportional to the inverse square of the initial particle size) and the soil solution pH (which was largely controlled by the soil atmosphere CO_2). The soil base and phosphaate buffer capacities (which are largely determined by the nature of the soil inorganic phase) are also important factors determining the rate of dissolution. When sufficient dissolution had occurred for the zones of reaction product of adjacent particles to overlap these buffer capacities become increasingly important. Other important factors are the soil solution pCa (which was largely controlled by the soil solution anion concentration), and also the solubility product, application rate and pattern of distribution of the carbonate-fluor-apatite in the soil. The principle plant factors expected to influence phosphate rock dissolution were rhizosphere acidification and ~~the extent of~~ root length.

The carbonate-fluor-apatie dissolution model had not been verified experimentally so the results from other research were drawn on in order to comment on the model. Other research confirmed the importance of the initial effects of soil pH and also the effects of phosphate rock particle size and the soil buffer capacities. Experimental evidence was also found that would support the fact that application rate and the type of phosphate rock (as represented in the model by the solubility product of the carbonate-fluor-apatite) will also effect the rate of dissolution, particularly when these two factors interacted with the other factors mentioned. The effect of application rate may be an artifact of the high rates of application of phosphate rock used in experimental trials and may not be relevant to the lower application rates in commerical agricultural systems. The importance of season climate changes and the effects of the wider environment also need to be considered when examining factors which will control dissolution in commercial systems.

An examination of the factors likely to affect the dissolution of granulated phosphate rocks suggested that the incorporation of granulated materials into soil would cause an effect similar to incorporating a single large particle of the same diameter as the granule. Therefore the rate of dissolution of the granulated material would be inversely proportional to the granule diameter radius. If the granulated phosphate rock was not incorporated and instead was applied to the soil surface then the effect on dissolution of the phosphate rock would be similar to the effects of a very uneven or "clumped" distribution of ungranulated phosphate rock on the soil surface. The extent of any reduction in the amount of dissolution of surface applied granules, compared to ungranulated materials, will be related to the extent of clumping, and therefore granule size, as well as other soil and phosphate rock factors which control the rate of dissolution of the phosphate rock.

Conclusions

Reactive phosphate rocks suitable for direct application to soil can be readily identified by rigorous chemical and x-ray analyses, or by simple extraction with organic acids.

The farming systems and soil conditons in which these reactive phosphate rocks will readily dissolve, and prove to be agronomically useful, can be determined from first principles, or by more lengthy trial work. Research has shown that reactive phosphate rocks are suitable for use on New Zealand acidic soils growing legume based pastures (Bolan *et al.* 1990; Rajan *et al.* 1987). However the aspects which may limit their wide spread use on New Zealand pastures are the poor handling and spreading characteristics of these sand-like materials. These problems could be avoided if the reactive phosphate rock materials were granulated. Fertilisers for New Zealand pasture are surface applied, not incorpoarted, so the limitation of application as granules would be the induction of a "clumping" effect which may reduce the agronomic performance of the phosphate rock.

It is apparent that more research is required, studying factors which determine the extent of the "clumping" effect, such as granule size, as well as efficient methods of preparing agronomically useful granular reactive phosphate rock fertilisers.

2.5 Objectives of the research programme.

1. To thoroughly characterise the phosphate rock materials used in these trials, with respect to their origin, particle size and chemical reactivity. This objective stems from the observation that the lack of standardized material preparation and description often makes it difficult to compare results from different publications on reactive phosphate rock research.

2. To evaluate various techniques for granulating "as received" and ground reactive phosphate rocks.

3 ~~4~~. To examine the effects of particle size and granulation on agronomic performance of a range of surface applied phosphate rock fertilisers.

4 ~~5~~. To evaluate two techniques using the radioisotope P^{32} which may provide more detailed information about the rate of reactive phosphate rock dissolution and the rate of fertiliser phosphate uptake by plants in the various agronomic trials.

CHAPTER 3: GENERAL EXPERIMENTAL TECHNIQUES AND METHODS

3.1 Characterisation of phosphate rocks

3.1.1 Sieving

A dry brushing method of sieving of a subsample obtained by riffling was followed for particle size analysis. A sample of between 20 and 100g of material was placed on a sieve stack, consisting of 1000, 500, 250, 150, 75 and 42µm sieves. The stack was sealed and shaken for approximately 2 minutes, then oversized material remaining on each sieve was sequentially brushed for at least 5 minutes. After brushing the material remaining on each sieve was weighed. The average sample recovery was 97%.

3.1.2 Grinding

Unground ("as received") phosphate rock materials were ground to obtain a particle size distribution which was similar to the commercially ground material. A sample of phosphate rock material was ground, using a ring grinder, for 2 seconds and sieved through a 75µm sieve. The oversize material was reground (2 seconds) and resieved. This process was repeated then all the ground material was recombined and mixed by sieving through a 500µm sieve.

3.1.3 Total phosphate content

Total fertiliser phosphate was measured by the triacid digestion method (Johnson and Ulrich, 1959). Concentrated nitric (HNO_3), hydrochloric (HCl) and perchloric acids ($HClO_4$) were mixed in the ratio 5:5:7 by volume, and left overnight. 1g of the sample was mixed with 20ml of the triacid mixture and left overnight, to preoxidise the organic matter (to overcome the explosion risk). The digest flask was covered and heated slowly to 260°C until white fumes had collected in the flask. Heating was then continued at this temperature for a further 20 minutes. The flask was then removed, cooled and 15ml of distilled water added. The digest was then reboiled for two minutes, cooled and filtered through Whatman no.41 filter paper. The digest was then analysed for phosphate using the method of Twine and Williams (1971).

3.1.4 Water soluble phosphate

A 0.4g sample of fertiliser was shaken end over end in 40mls of distilled water for 30 minutes in a 50ml screw capped centrifuge tube. The tube and contents were then centrifuged at 8000rpm for 10 minutes. The supernatent solution was filtered (Whatman no. 41) and collected after discarding the first portion of the filtrate. The concentration of phosphate in the solution was measured using either the method of Twine and Williams (1971), or the method of Murphy and Riley (1962).

3.1.5 Formic acid soluble phosphate

A 0.4g sample of fertiliser was shaken end over end in 40 mls of a 2% (w/w) solution of formic acid in a screw capped centrifuge tube. The standard shaking period is 30 minutes (EEC reg. L213/8, 1977). The effect of the shaking period on the amount of phosphate extracted by formic acid was also examined using two shaking periods (30 and 60 minutes). After shaking the sample was centrifuged for 10 minutes at 8000rpm and the supernatant solution filtered (Whatman no. 41) and collected, after discarding the first portion of the filtrate. The amount of phosphate in the solution was then measured using the method of Twine and Williams (1971).

3.1.6 pH

The pH of fertiliser samples was measured at a fertiliser:water ratio of 1:2.5. The pH of the solution was measured using a combined pH electrode and Radiometer PHM 82 pH meter.

3.1.7 Granule crush strength

Crushing strength was measured as the amount of weight required to crush or shatter a granule placed on a flat surface. This method was derived from the crushing strength test reported by the I.F.D.C. (1979).

The method involved placing a subsample of 0.5 to 1mm diameter granules on the pan of a Sartorius top pan balance. Ten granules were individually crushed, using the flattened head of a nail, and an average crushing strength found for the sample.

3.2 Dry matter analysis

3.2.1 Root extractions

All herbage above the soil surface was removed and the soil from the pot cut into sections at 1, 2, 5 cm from the surface. Each section was then washed through a nylon mesh sieve (mesh size approximately 1mm), collecting the root material in the sieve, until no roots remained in the washed soil. The roots were then collected, washed, and dried at 65°C.

3.2.2 Digestion of herbage for total phosphate analysis

The total herbage phosphate content was measured by nitric:perchloric digestion (Johnson and Ulrich, 1959). Dried herbage was weighed into digest flasks and mixed, with a 1:4 mix of concentrated $HClO_4$ and HNO_3, in an amount dependent on the amount of herbage (20ml acid for 0-0.9g dry matter, 25ml acid for 0.9-1.3g dry matter). The flasks were then left to digest overnight (to preoxidise the organic matter and minimise the explosion risk). The flasks were then covered and heated slowly until boiling (260°C). This temperature was maintained until white fumes collected in the flask. The flask was removed from the heat, cooled and 15-20ml of deionized water added. The diluted digest was reboiled, cooled and filtered through wet Whatman no.41 filter paper. The residue on the filter paper was rinsed three times with deionized water and then the combined filtrates were adjusted to 100ml.

3.2.3 Analysis of digest by auto analyser for phosphate

Dry matter digested in the 1:4 $HClO_4$ HNO_3 mixture was analysed for phosphate using a Technicon Autoanalyser II system, using the method of Twine and Williams (1971). Blanks were prepared from blank digests included in the above digestion (3.2.2), which underwent the same process as flasks containing dry matter, and were diluted to the same extent as the digests containing herbage.

3.3 Radioactive phosphate technique

3.3.1 Isotope preparation

The radioactive P^{32} isotope utilised in the glasshouse experiment (chapter 7) was initially in the form of 20mCi (370 MBq) of P^{32} as carrier free orthophosphate in dilute HCl.

The radioactive solution was diluted to 25mls, using a solution of 1ppmP to prevent adsorption of the phosphate (P^{32}) onto the surface of the utensils. This solution was then used in the surface labelling experiment (Chapter 6) and the remainder further diluted for use in the inverse isotopic dilution experiment undertaken in the glass house (Chapter 6).

Perspex was found to be an efficient shield for the xB particles emitted (no gamma radiation emmited, Tennent, 1979) by this radioisotope, so all handling of the isotope was done behind perspex screens, in association with full personal protective gear and regular Geiger counter checks for possible contamination.

All subsequent measurements of P^{32} activity were normalized for decay to a common date, using a half life for the P^{32} of 14.29 days.

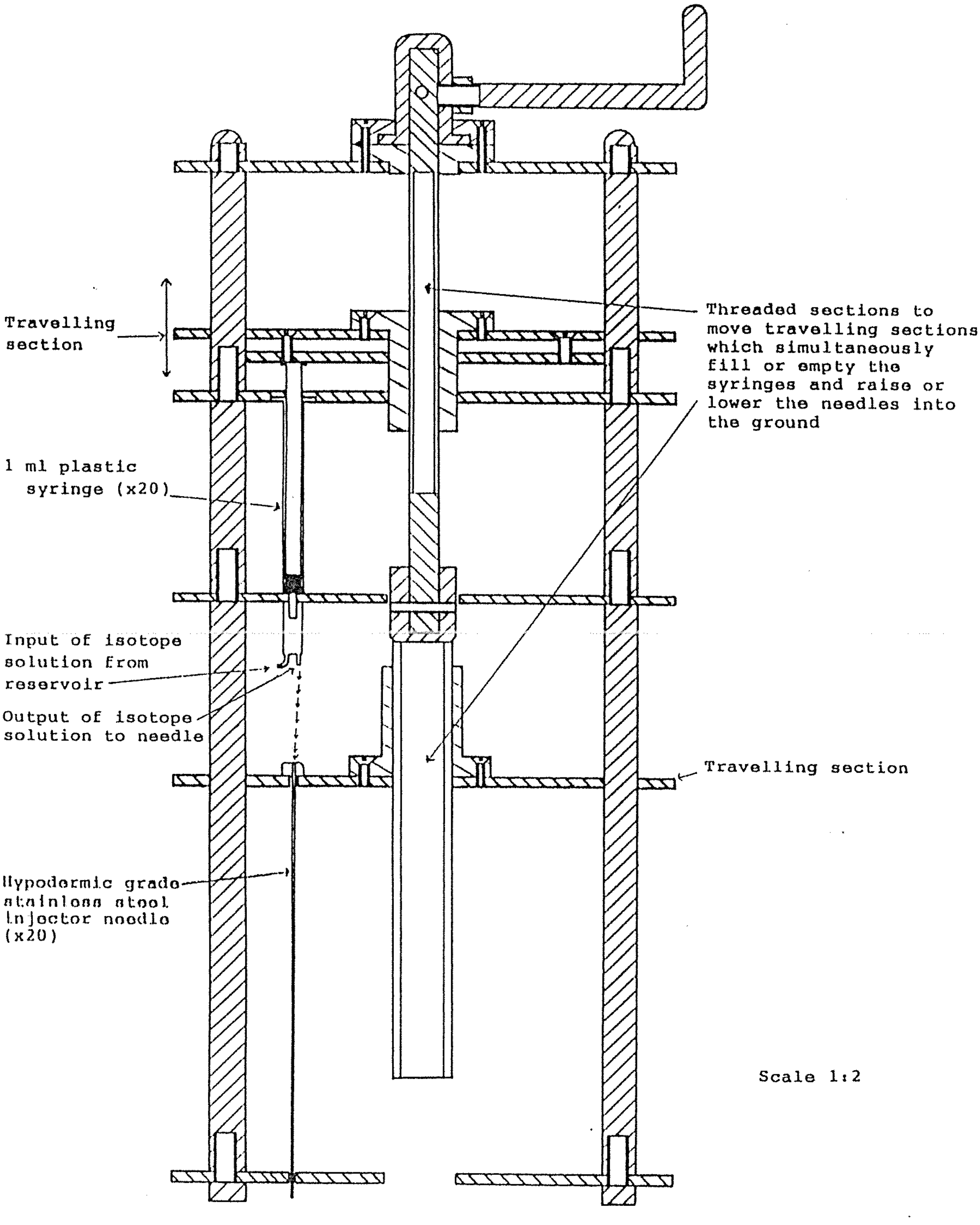


Figure 3.1: A cross sectional diagram of the injector system used to inject soil cores with radioisotope in the inverse isotopic dilution experiments.

3.3.2 Soil injection

The isotope injection system was developed for intact soil cores by Hedley and Tillman (unpub.). The system utilises 20 vertical fixed needles of 16 gauge stainless steel, 16 cm long, which are evenly arranged on a template of radius 7.5cm (Figure 3.1). Holes are first punched into the soil injection zone using a template of spikes of approximately 12µm diameter. After these holes are formed the injector needles are lowered into the soil. The labelled solution is drawn into a system of graduated syringes as the needles are lowered into the soil and then injected under low pressure into the soil from an opening on the side of each needle tip as they are withdrawn from the maximum injection depth. If the soil core used is *in situ* it is separated from the surrounding soil by means of a galvanised tin cylinder tamped into the soil. Horne and Hedley (unpub.) found that the labelled solution remained in the zone into which it was injected.

3.3.3 Cerenkov counting method

Aqueous solutions containing P^{32} are suitable for assessment by measuring their Cerenkov radiation (Lauchli, 1969). This system is based on the production of cerenkov radiation by charged particles travelling through a transparent medium at a speed greater than the speed of light in that medium. An aqueous solution containing P^{32} produces sufficient cerenkov radiation for the number of disintegrations to be assessed using a liquid scintillation counter.

Twenty milliliters of radioactive solution were placed in liquid scintillation vials and counted using a Beckman LS 3801 liquid scintillation counter. The number of light emmissions per minute was counted for time intervals of 2 to 20 minutes, to ensure that the count estimate was within 10% of the 95% confidence level. Estimates of the background radiation were made with each set of vials counted and for any change in the aqueous medium of the P^{32}, and was subtracted from all count estimates before correction for quenching (see following section) and decay.

3.3.4 Quench correction

Cerenkov counting was undertaken in a variety of aqueous media, including various dilutions of the acid digest described in 3.2.2, as well as solutions from soil extractions based on water, bicarbonate solutions, 1M NaOH and 1M HCl. The cerenkov system has a low efficiency so estimates were made of chemical and colour quench that occurred in the various media and all count estimates were subsequently corrected for quench.

Chemical quench estimates were made by digesting a range of known quantities of non-radiactive herbage and spiking the digest solutions with a common amount of P^{32}. No significant effects of chemical quench were found. Similar estimates were not necessary for the soil extractions because the ratio of soil to extractant remained the same for all extractions. A single internal P^{32} standard was used to calibrate counting efficiency.

Colour quench estimates were made by spiking solutions of the various media and comparing the actual counts registered with the theoretical number of counts in solution. The quench estimates were crosschecked by counting samples of spiked and non spiked solutions in the presences of scintillation cocktails (recipe: 1l cocktail contains 4g 2,5 Diphenyloxazole, 0.1g Dimethyl Popop, 670ml Toluene, 330ml TritonX. Paterson and Green, 1965).

3.4 Soil description

The soil used in this study was a Tokomaru silt loam. It is classed under the former New Zealand system as a moderately gleyed, originally forest melanized, central yellow-grey earth (Pollock, 1975) and under the American Taxonomy classification as a Typic fragiaqualf.

This soil is located on an elevated and dissected terrace mantled with loess (Ohakean loess of mainly greywacke origin) and has an established clover-perrenial ryegrass sheep pasture cover. The particular sites used for soil collection and the field experiment were not drained, although the surrounding pasture had been extensively mole drained. The mean rainfall at the site is approximately 1000mm/year and the driest month is February. The hottest month is also February, and the site experiences very few frosts.

The uppermost horizon of this soil has a silt loam texture and a friable, moderately developed, fine and medium crumb structure, with some mottling around the grass roots (Pollock, 1975). Mica and illite are the principal clays and no allophane has been found in this soil (Pollock, 1975).

The soil from this horizon is moderately acid (pH 5.7, 5.5) and has a low phosphate status (Olsen P estimates range from 6 to 12μgP/g). This soil has low P retention (approximately 16%) and medium status of cation exchange capacity (15.5 meq.%) and base saturation. The organic carbon and total nitrogen contents, and the exchangeable calcium, nitrogen, potassium, magnesium and sodium are rated as low to medium, (Based on results from Cowie (1978), Sorn-srivichai (1985), Mackay *et al.* (1984a) and L.D. Currie (pers.comm. 1989) and classified by the Soil Bureau ratings for New Zealand soils (Palmer *et al.* 1981).)

The remainder of the soil profile is characterised by a strongly developed, heavy textured, Btg horizon at 38-76 cm depth with a relatively high clay content, overlying a fragipan of coarse silt texture with a strongly developed, very coarse, polygonal structure. Between the polygons are distinctive vertical cracks which are filled with pale grey soil, rich in clay (Pollock 1975). The fragipan tends to control the moisture status of the upper horizons by becoming extremely hard and dry in summer, with cracks forming between the polygons facilitating rapid drainage of water through to the lower soil horizons. In winter as the fragipan becomes wet the cracks close and block the drainage so that the upper horizons become saturated.

3.5 Soil analysis

3.5.1 Water content

An estimate of the gravimetric water content of the soil was made by drying a known weight of field moist soil at 105°C for 12 hours and assuming that all weight loss was due to the evaporation of water. The proportion of water in the field moist soil was taken as soil water content.

3.5.2 Water extractable phosphate

A 1g sample of soil was shaken end over end in 40mls of distilled water for 60 minutes in a screw capped 50ml centrifuge tube. After centrifuging at 3200rpm for 10 minutes the supernatant solution was filtered through Whatman no. 41 paper, (Sorn-srivicai, 1985) The concentration of phosphate in the solution was measured using the method of Murphy and Riley (1962).

3.5.3 Bicarbonate extractable phosphate

A 1g sample of soil was shaken end over end for 30 minutes in 20mls of 0.5M $NaHCO_3$ adjusted to pH 8.5. After centrifuging for 2 minutes at 10000rpm, the supernatant solution was filtered through Whatman no. 42 filter paper (Olsen *et al.* 1954). The concentration of phosphate in the filtrate was measured using the method of Murphy and Riley (1962).

3.5.4 Soil phosphate fractionation

The phosphate in soil was fractionated by a sequential extraction using solutions of 1MNaOH and 1MHCl. A 1g sample of soil was shaken end over end in 40mls of 1M NaOH solution for 16 hours in a sealed 50ml polypropylene centrifuge tube. The tubes were centrifuged for 10 minutes at 8000 rpm and a 20ml sample taken from the supernatant solution, the rest of the liquid being discarded. 1M HCl (40ml) was then added to the soil residue in the tube which was then shaken for a further 16 hours and then centrifuged and sampled in the same manner (Apthorp *et al.* 1987). The inorganic phosphate concentration in the extracted solution was measured using the method of Murphy and Riley (1962).

3.6 Statistical methods

The basic experimental design employed in all experiments was a split plot in time design based on a random effects error model. Fertiliser treatment formed the main plots and time of harvest the subplot. Missing values were estimated (Gomez and Gomez 1984) and then the data was processed using the SAS or Genstat statistical packages to calculate the basic experimental mean squares and degrees of freedom. The degrees of freedom were adjusted to account for any missing values and then the mean square ratios tested against an "F" test. A 5% probability was utilised to judge the significance of the treatment, time, and treatment time interaction effects, with complex (Satherwaite) degrees of freedom calculations where appropriate. If an "F" test indicated a significant effect then means were separated using a least significant difference calcualted from a 5% two tailed "t" test (weighted when appropriate), with a standard error of the difference calculation adjusted for any missing values (Steel and Torrie, 1981). Because the reliability of the mean separation using the least significance difference test is reduced when many treatments were compared, all the analyses were broken into sets consisting of five treatments or less, before appropriate comparisons were made.

The plant uptake and phosphate uptake data were also examined on a cumulative basis. Data from each pot was accumulated over the desired number of harvests and then tested in randomised complete block design using the same procedures described above for the individual harvest data.

CHAPTER 4: THE ORIGINS AND CHARACTERISTICS OF FOUR PHOSPHATE ROCKS

4.1 Introduction

A criticism of much work on phosphate rocks is that often the origins of the samples being studied are not clearly characterised. The objective of the first section of this chapter was to characterise the phosphate rocks to be used in this study (North Carolina, Sechura, Arad and White Youssafia phosphate rocks), using existing literature, in terms of their origins, chemical composition and reactivity. The objective of the second section was to extend the characterisation of the phosphate rocks by examining the particle size distribution and formic solubility of the materials.

4.2 Information pertaining to the phosphate rocks in existing literature

4.2.1 North Carolina phosphate rock

The North Carolina phosphate rock deposit is located at Lee Creek on the south side of the Pamlico river, Beaufort County, in the state of North Carolina, U.S.A.. The deposit forms part of a belt of tertiary coastal phosphatic deposits extending from Florida to southern Virginia. These deposits are thought to have been formed during the Miocene phosphate province. Deposits in Florida, California, Baja (Mexico), Chatham Rise (New Zealand), Japan and Indonesia and also the Sechura phosphate rock deposit from Peru (Northolt, 1980) belong to this group.

Emigh (1973) reported that the North Carolina deposit covered many hundreds of square miles and was estimated to be in total about nine billion tonnes, approximately half of which is suitable for surface mining. The overburden varied from twelve to sixty meters in depth and consisted of the Miocene Yorktown formation, of unconsolidated quartz sand and clay, overlain by a thin layer of recent sediments.

Notholt (1980) found that over large areas the depths of overburden and the ore were relatively uniform, the ore being twelve to fifteen meters of dark grey to black, medium to fine phosphatic sands, which had as average content of 5% phosphate. Interspersed throughout the phosphatic sands were thin hard beds of phosphatic limestone, dolomite, and silty clay stones and coquinas. Emigh (1973) found that the phosphatic sands consisted mainly of unconsolidated quartz sand, small calcite shells and shell fragments, clay and phosphate peloids. The clays were reported by Notholt (1980) to be montmorillonite, illite and clinoptilolite, and the phosphatic peloids were largely of francolite and contained quartz grains, glauconite, carbonaceous matter and organic remains, and were usually structureless.

North Carolina deposit is mined by the Texasgulf company (Williams and Zellars, 1989). The overburden was removed in two stages and the phosphatic sands mined by electrical draglines. The ore was pumped as a slurry to a beneficiation plant where it was washed, screened and deslimed to remove 100 to 75µm particles. The ore was then put through a flotation process to remove quartz sand. The ore absorbed fatty acids, ammonia, and fuel oil reagents and was then floated and the sand removed. These reagents were then removed by scrubbing with sulphuric acid and refloating the ore with amine reagents, including kerosene for further concentration.

The length of the "a" axis of the unit cell, and the subsequently determined empirical formula of North Carolina phosphate rock were reported in table 2.1 and 2.2 of the literature review, respectively. The composition of the ore was reported in table 2.3 and the solubility in formic acid in table 2.4 of the literature review. All these results indicate that North Carolina phosphate rock is one of the most highly substituted phosphate rocks available at present for use as a fertiliser. The high extent of substitution results in a highly reactive material.

4.2.2 Sechura phosphate rock

Cheney *et al.* (1979) found that the deposits in the Sechura desert on the northern coast of Peru occurred in Marine sediments formed during the Miocene age, and consisted of phosphorite interbedded primarily with beds of aggregates of diatom particles composed of opaline silica, and also some sand and tuff beds. Three distinct beds of massive friable light brown to black phosphorite were continuous over a large area and were very regular in thickness and phosphate content.

Cheney *et al.* (1979) found that the phosphorite ore consisted largely of structureless oval shaped peloids, ranging from white to brown-black in colour. Impurities found in the phosphorite ore were, in decreasing order of abundance: fragments of diatoms, volcanic glass, soluble sodium, potassium and magnesium salts, feldspar, sponge spicules, gypsum, mica, and organic matter. In some sections of the beds mixing of the diatomite and phosphorite beds had occurred.

Individual peloids were usually found to contain less than 1-2% of impurities, consisting of much the same material as the impurities found in the bulk ore. The shape was usually subelliptical to ovoid, and often with an irregular pitted surface (Cheney *et al.* 1979). Some peloids were found to be oolitic, others were found to have the shape of fish teeth, scales, bones and casts. Some were also found to have the shape of internal moulds of forminifera, and a few had large cores of quartz or feldspar.

The dimensions of the "a" axis, the empirical unit cell composition, and the composition of the Sechura ore are presented in tables 2.1,2 and 3 of the literature review. This phosphate rock has been found to be an unusual rock with an anomolous composition. The level of carbonate substitution was similar to Florida rock but there was a significant content of OH replacing F (Cheney *et al.* 1979). McClellan and Lehr (1969) stated that the Sechura deposit formed in a fresh water lake. The formic solubility of this material was reported in table 2.4 of the literature review, and indicated that the reactivity of this material is closer to that of North Carolina phosphate rock, rather than the Florida phosphate rock. The results in table 2.4 indicate that Sechura phosphate rock is less reactive than North Carolina phosphate rock, but results from Syers *et al.* (1986) reverse this order of reactivity under slightly different test conditions.

4.2.3 Arad phosphate rocks

Another phosphatic province has been identified, called the Mediterranean province (Notholt, 1980). This was formed along the nothern edge of the African-Arabian platform in Upper Cretaceous and Eocene times (135 million years b.p.), forming deposits in such countries as Morocco, Israel and Tunisia (Gafsa and Kalaa Djerda mines). Typically, the Mediterranean phosphate province deposits are very rich in vertebrate remains and are capped with siliceous limestone. Up to twenty-three beds in sequence have been recorded but usually four distinct beds occur in the mined areas.

The phosphate rock deposits in Israel are located in the northern Negev desert, where thirty phosphate fields have been found and approximately four are being mined (Axelrod, 1978). Reserves are estimated at 200 million tonnes, (Emigh, 1973). Axelrod (1978) found, after investigation of four fields, that the ore from the lowest bed of the Arad field was most suitable for direct application, the upper beds containing more calcite which reduced the solubility of the phosphorite.

The length of "a" axis of the unit cell of the carbonate-fluor-apatite in the Arad phosphate rock was presented in table 2.1 of the literature review. The composition of the carbonate-fluor-apatite was presented in table 2.3 of the literature review and from these quantities an extent of substitution of carbonate for fluorine was calculated, where xB=0.91 in the unit cell model (equation 2 in the literature review). This level of substitution was supported by formic solubility results (reported in section 2.3.1) which were lower than those from the North Carolina and Gafsa phosphate rocks and intermediate between the Sechura and Central Florida phosphate rocks.

4.2.4 White Youssafia phosphate rock

The main mining area in Morocco is close to Khouribga, south east of Casablanca. Reserves were estimated to be 20 000 million tonnes of phosphate rock (Notholt, 1980). Deposits are also mined further south at Youssafia and at Ben Gaerin. The Moroccan deposits were initially underground mines because the deposits are typically capped by thick layers of siliceous limestone. These layers are now generally blasted to allow open cast mining where possible, which has lower costs and increases the ore recovery, but reduces the grade of the ore. Beneficiation processes tend to be limited by a lack of fresh water, sea water and air sorting may be used (Williams and Zellars, 1987).

The material used in this study was from the Youssafia mines, and called White Youssafia phosphate rock to distinguish it from the Black Youssafia phosphate rock which is a calcined product from the same mine.

No reports in the literature were found of the unit cell characteristics or the composition and reactivity of this material.

4.3 Physical and chemical characteristics

4.3.1 Introduction

It is clear from the review of literature section 2.3 that the particle size and chemical reactivity are two important phosphate rock characteristics controlling the agronomic value of a phosphate rock. For these reasons it is important that the physical and chemical characteristics of the samples to be used in this work be determined.

4.3.2 Source and appearance of the materials

(a) Material in the same form as it was when it arrived in New Zealand, ("as received" or AR).

1. North Carolina (NC); Imported by Ravensdown Fertiliser Co-op Ltd., in 1987.

The North Carolina phosphate rock used in this study was found to be the most variable in physical appearance of the four phosphate rocks considered. The ore consisted mainly of rounded peloids, varying from black to golden brown, to dirty white. The peloids varied from spherical to flying saucer in shape, with some looking like pieces of bone or shell. Also present were small pure white particles and clear angular particles.

2. Arad; Imported by Southland Fertiliser Co-op Ltd., in 1988.

It is not known which bed the Arad phosphate rock used in the present study came from, but the material had an unusually angular appearance as though it had been ground. There was very little typically rounded peloid material. Much of the material was white in colour with many small clear chips.

3. White Youssafia (Ysf); Imported by Ravensdown Fertilser Co-op Ltd., in 1988.

The White Youssafia material was found to consist mainly of relatively large white oval peloids, and also some of a smaller size which were golden brown. Some of the peloids had the appearance of being coated with dark brown material.

4. Sechura (S); Imported by Challenge Fertiliser Ltd., in 1988.

The material used in this study was found to be very uniform and consisted mainly of smooth golden brown to opaque white peloids of an oval shape.

(b) *Factory ground materials (works ground or WG).*

North Carolina; Imported by Ravensdown Fertiliser Co-op Ltd., in 1987 and ground at the Napier works in a factory roller grinder, using air separation to continuously remove material as it reached the correct particle size.

4.3.3 Particle size analysis

The phosphate rock materials detailed in section 4.4.2 were assessed for particle size distribution (NCAR, AradAR, YsfAR, SAR, NCWG). Two extra ground materials were prepared from Arad and North Carolina phosphate rocks. "As received" Arad phosphate rock was ground to achieve a size distribution similar to the works ground North Carolina phosphate rock (designated AradWG). Works ground North Carolina phosphate rock had been further ground for a previous study (Hedley *et al.* 1987) so that all the material passed a 32μm mesh, (designated NCFG).

The particle size of the materials was assessed by a dry brush sieving method (see chapter 3.1.1) and the results are presented in table 4.1.

Table 4.1 Particle size analysis of the materials used. The results are the amount of material collected on each sieve, expressed as a percentage of the total amount of material recovered from all the sieves. The methods used was a dry brushing method.

	"As received" phosphate rocks				Ground phosphate rock	
Seive size (μm)	North Carolina (NCAR)	Sechura (SAR)	Arad (AradAR)	White Youssafia (YsfAR)	North Carolina (NCWG)*[1]	Arad (AradWG)
>1000	0	0	6.3	4.3	0	0
1000-500	0	0.5	8.2	3.9	0	0
500-250	25.7	11.2	20.7	33.1	0.02	0
250-150	58.9	57.4	32.8	40.5	2.3	7.3
150-75	14.7	29.4	23.1	11.9	23.5	20.9
75-42	0.6	1.4	5.6	(6.3)*[2]	31.0	29.5
<42	0.2	0.1	3.3		43.2	42.3

*[1] The very finely ground North Carolina phosphate rock (NCFG) was sieved and found to be 100% <42μm.

*[2] <75μm fraction, very small amount estimated to be in the <42μm fraction.

Of the four "as received" (AR) materials, the AradAR was found to have the greatest amount of coarse material, and also the greatest range of particle size. It was noted in section 4.4.2 that this phosphate rock had the appearance of being very angular and chipped which suggested that this material had been previously ground, compared to the typical smooth rounded peloid shape of the majority of the materials in the other three "as received" phosphate rocks. The wide range of particle sizes and evenness of the spread of the particle size would seem to confirm this.

The particle size range of the YsfAR was similar to the AradAR, but with a greater predominance of particles between 500µm and 150µms. This material did not appear to have been ground. The predominant particle size of the NCAR was also between 500µm and 150µms, but the range of particle size was less than the YsfAR. The particle size distribution of the SAR was similar to the NCAR, but with a slightly wider range, and a predominance of the smaller 250µm to 75µm particle size. These materials also had no appearance of having been ground.

The particle size ranges of two forms of ground North Carolina phosphate rock were assessed. The commercially ground material (NCWG) was coarsest in particle size. The majority of this material was below 150µm in size, with the largest fraction being less than 42µm. The other sample of ground North Carolina phosphate rock was an extremely fine material, NCFG. It was found that all of a sample of this material passed a 42µm mesh.

The ground Arad phosphate rock (AradAR) was found to have a very similar particle size distribution to the NCWG, with a slightly higher amount of material in the 150µm to 250µm size fraction.

4.3.4 Solubility of phosphate rock in dilute formic acid

The solubility of phosphate rocks in formic acid has become an accepted method of assessing the relative reactivity of different phosphate rock materials. This is discussed in section 2.3.1 of the literature review.

It is difficult to compare results between results between extractions carried out by various authors because the rock grind, extraction time and solid solution ratios have not been standardised. However, a tentative ranking of these results (section 2.3.1 of the literature review) indicates that the relative ranking is North Carolina> Sechura> Arad.

Table 4.2 Solubility in formic acid of the phosphate rock materials used in this work. The results were found by the standard method (see section 3.1.5). Extractions were carried out for both one hour and half an hour.

		Duration of extraction:			
	Total P[1]	30minutes		60 minutes	
Phosphate rock	% w/w	gP/grock	%totalP	gP/rock	%totalP
North Carolina;	13.1				
"as received"(NCAR)		0.069	52.5	0.081	61.8.
works ground(NCWG)		0.092	70.2	0.098	74.8
fine ground(NCFG)		0.113	86.3	0.112	85.5
Arad;	14.6				
"as received"(AradAR)		0.069	47.3	0.079	54.1
"works" ground(AradWG)		0.087	59.6	0.084	57.5
Sechura;	13.3				
"as received"(SAR)		0.073	54.9	0.085	63.9
White Youssafia;	13.8				
"as received"(YsfAR)		0.058	43.6	0.070	52.6

[1] Total phosphate results from P. Phommasone, FLRC.

No information appears to be available on the reactivity of the White Youssafia phosphate rock. For this reason, a series of formic acid extractions were performed in order to evaluate the reactivity of the materials used in this study against published results, and to evaluate the White Youssafia phosphate rock. The effect of rock grind on the chemical reactivity of the North Carolina and Arad phosphate rocks was also evaluated.

The solubility results of North Carolina phosphate rock was utilised as a standard with which to compare these results with other work. Chien and Hammond (1978b) found that the phosphate solubility of a finely ground sample extracted for one hour in formic acid was 85.5%, Mackay, Syers and Gregg (1984b) found that the solubility of a similarly ground sample was 88%. Unpublished results from the FLRC

(P. Phommasone) found that the phosphate solubility of works ground material when extracted for 30min was 70.1%, and an "as received" sample was 54.6% (as also tested in this work). These results suggest that the results in the present work are in good accord with previously published work.

Of the "as received" materials, Sechura phosphate rock (SAR) had the highest percentage of the total phosphate soluble in formic acid, followed by North Carolina (NCAR), Arad (AradAR), then White Youssafia (YsfAR) phosphate rocks, in that general order. This ranking, excluding YsfAR, was the same as was found by Syers *et al* (1986) when rocks ground 100% <250μm were extracted for 30 minutes. Results for the White Youssafia phosphate rock have not been presented before, and indicated that the White Youssafia phosphate rock had the lowest solubility ("reactivity ") of the four phosphate rocks tested.

Grinding the phosphate rock caused an increase in the quantity of phosphate dissolved but this was not a consistent effect. The general trend of a higher solubility of North Carolina phosphate rock compared to Arad phosphate rock did not change when these materials were ground, although the details of the ranking changed depending on whether the 30 or 60 minute solubility was being considered and whether the amount of phosphate in solution was being looked at, or the ratio of phosphate released to total phosphate content in the rock.

Finely ground North Carolina phosphate rock (NCFG) and works ground Arad phosphate rock (AradWG) appeared to reach a saturation point, where enough phosphate had been released into solution within 30 minutes to saturate the solution and prevent further dissolution during the extended 60 minute extraction. This effect evidently did not occur for the works ground North Carolina material (NCWG), which indicates that this effect is not wholly particle size dependent.

4.4 Conclusions

North Carolina and Sechura phosphate rocks are materials of relatively high reactivity and the samples examined in this study were of similar particle size. Although North Carolina phosphate rock is more highly substituted than the Sechura phosphate rock, the formic solubility test of the "as received" materials found that Sechura phosphate rock released more phosphate into solution.

Arad and White Youssafia phosphate rocks had similar origins and had wider particle size distributions and lower formic solubilities than the North Carolina and Sechura phosphate rocks. When particle size was no longer limiting the amount of phosphate dissolution in formic acid, the Arad phosphate rock supported less phosphate in solution than North Carolina phosphate rock. The formic solubility of the White Youssafia phosphate rock was lower than the Arad phosphate rock and, considering the very marginal qualification of the Arad phosphate rock as suitable for direct application (EEC standards), the White Youssafia phosphate rock would probably not qualify as being suitable for direct application.

CHAPTER 5: FIELD EXPERIMENT

5.1 Introduction

The main objective of this experiment was to evaluate the agronomic effectiveness of various forms of ground and granulated North Carolina phosphate rock (NCPR) fertiliser. A review of current literature (section 2.3) found that particle size and granule diameter were likely to significantly affect the rate of dissolution of phosphate rocks and therefore their agronomic performance. The literature review also indicated that the performance of granulated phosphate rocks would vary depending on the whether the material was applied to the surface or incorporated into the soil.

The objective of this trial was to evaluate the fertiliser materials under conditions which were as close as possible to the usual surface application techniques for established pasture.

A range of granule sizes was manufactured from a very fine grind of North Carolina phosphate rock (<42μm) (NCFG), to compare the agronomic performance of minigranules (0.5-1mm) with two larger granule sizes (1-2mm and 2-4mm). The finely ground material was also compared with a coarser commercial grind and the performances of the phosphate rock fertilisers were compared with a standard fertiliser, mono-calcium phosphate (MCP).

A secondary objective of this experiment was to test an inverse isotopic dilution technique for evaluating the fertiliser. This technique involved labelling a zone of the soil with radioactive phosphate to enable calculation of the amount of phosphate released from a fertiliser. This was based on the "A" value concept of Fried and Dean (1952), and adapted to phosphate rock evaluation by Kucey and Bole (1984). The aim of this trial was to compare the use of an "A" value for evaluation of fertiliser effectiveness and the more usual dry matter production and phosphate uptake in a field trial on established pasture.

5.2 Materials and Methods

5.2.1 Phosphate rock

North Carolina phosphate rock was previously identified as a highly reactive phosphate rock with a relatively high agronomic effectiveness (Chapter 2). Works ground and finely ground North Carolina phosphate rocks were used in this experiment. The source of the material and an analysis of particle size are in chapter 4, section 4.3.

5.2.2 Granulation method

Finely ground North Carolina phosphate rock (<42µm), was granulated using solid potassium sulphate (K_2SO_4), as a binding agent. K_2SO_4 was mixed with the phosphate rock (10% w/w) and blended in a coffee grinder, with water added until the mixture was moist.

The K_2SO_4-rock mixture was then granulated in a rotating drum, where it was sprayed with water until granulating freely. The granules were subsequently oven dried (65°C), and sieved into 3 size classes: 0.5 to 1mm, 1 to 2mm, and 2 to 4mm. The granules were firm to the touch and it was noted that the water content of the mix was an important factor affecting the strength of the granules.

5.2.3 Field trial design

A site was chosen on Massey dairy unit No.4, on the Tokomaru silt loam, where no fertiliser had recently been applied and variation in pasture growth was expected to be minimal. (Details of the soil characteristics are in chapter 3.4.)

The pasture cover on site was mown closely, and metal cylinders (diameter 15cm, length 10cm), were driven into the soil. The soil between the depth of 1.5 to 6cm in each cylinder, was injected with carrier free P^{32}, at a rate of $1.68*10^8$dpm per soil core. (Details of the injection system are in the methods chapter, 3.3.2.)

Figure 5.1: The site of the field experiment, showing the three caged groups of *in situ* pasture cores which formed the three treatment replicates.

Fertiliser samples were then distributed over the surface of the soil core in amounts calculated to provide 60 kg/ha of P. Quantities of K_2SO_4 equal to that present in the granulated fertilisers were added to all soil cores not receiving the K_2SO_4 bound granules.

The site was then caged and cut uniformly to 1.5cm whenever the pasture reached 8 to 10 cm in height. No clippings were returned. The trial was laid down on 19/2/87 and completed on 30/6/87 (late summer to early winter), during which time 7 harvests were made at approximately 20 day intervals.

A split plot design was used, with main plots consisting of the treatments and a "sub plot" of the harvests. (The details of the methods used for statistical analyses are presented in the methods chapter 3.6.)

5.2.4 Herbage analysis

Herbage samples were dried at 65°C, weighed and the dry matter yield recorded. The samples were then digested using an acid digest mixture of 4:1 HNO_3:$HClO_4$. The digest was diluted and analysed for total phosphate and P^{32} content. Total phosphate was measured by auto analyser. P^{32} was measured using the Cherenkov counting system on a liquid scintillation counter. (The details of the methods are in chapter 3.2.)

5.2.5 Theoretical and methodological background of the "A" value concept

The purpose of using the inverse isotopic dilution method in this experiment was to implement the "A" value concept. Fried and Dean (1952) defined the "A" value concept as measuring the availability of a nutrient to a plant with reference to a standard source. The objective of the technique was to present the two sources of the nutrient (standard and test source) to the plant in such a way that the plant would take nutrient from each of these sources in proportion to the amounts of nutrient "available". If the amount of nutrient in the standard source was known then the amount of nutrient in the second source could be inferred by equation 1.

$$\frac{\text{Amount of the nutrient "available" in the soil}}{\text{Amount of the nutrient "available" in the standard source}} = \frac{\text{Uptake of the nutrient from the soil}}{\text{Uptake of the nutrient from the standard source}} \qquad (1)$$

This concept was inititally employed to measure the availability of nutrient in the soil, using a fertiliser as the standard. The nutrient from the standard source was radioactively labelled and the specific activity of the standard was known. Any differences between the specific activity of the standard and the specific activity of the nutrient in the plant was attributed to uptake by the plant of the nutrient from the soil. The amount of nutrient available in the soil could then be calculated by equation 2;

$$A = \frac{B(1-y)}{y} \qquad (2)$$

where A was the amount of the nutrient available in the soil, B was the amount of the nutrient in the standard, and y the proportion of the nutrient in the plant derived from the standard.

Fried (1964) proposed that ideally, the experiment would be of short enough duration to ensure that there was no interaction between the two sources, but of sufficient duration to minimise errors due to the presence of the nutrient in the plant seed.

Fried and Dean (1952) summarised a number of experiments and found that while the "A" value was affected by the nature of the standard and the method of placement, this did not invalidate the values found, but did necessitate careful interpretation of the results.

Venkat Reddy *et al.* (1982) employed the "A" value concept in an experiment where a small amount of labelled phosphorus fertiliser was applied to pots of soil and a variety of plants grown from seed for thirty days. They found that while the "A" value was empirical and varied with type and growth stage of the plant grown, it was still a reliable index of the amount of phosphate available in the soil. Nearpass *et al.* (1961) employed labelled sulphate fertiliser in an "A" value experiment and found that although there was a small interaction between soil and fertiliser sulphate, the "A" value did correlate well with the sulphur content of the plant, until the plant yield reached the yield ceiling. In a similar experiment Harward *et al.* (1962), found that the "A" value provided a better measure of available soil sulphate than did conventional soil extractions.

These experiments sucessfully utilised a labelled fertiliser to evaluate the "A" value of the nutrient in the soil. This technique can be reversed to evaluate the "A" value of a fertiliser, usually by labelling the plant growth medium in some fashion that is common to all treatments.

Kucey and Bole (1984) sprayed soil with P^{32} in a carrier solution and applied unlabelled fertiliser in a band in the middle of the pot. The "A" values correlated well with the dry matter production derived from the fertilisers, although some interaction between the labelled soil phosphate and the fertiliser phosphate appeared to occur and may have artificially lowered the "A" value of some fertiliser. Kucey and Bole (1984) concluded that the calculation of "A" value under these experimental conditions led to the same results as availability calculations based on a simple isotopic dilution concept, although the availability values based on the latter concept had a slightly better correlation with the dry matter production. Neither method correlated as well as the simple relationship between phosphate content and dry matter yeild.

A better implementation of the "A" value concept may have been achieved if the there had been no interaction between the labelled soil phosphate and the fertilser. A method that could place P^{32} in a specific zone, with no contact with the fertiliser would be desirable. The results would also be of increased relevance to agricultural systems if such a study could be carried out on undisturbed pasture.

To enable field studies of undisturbed soil using radioactive labels, an injection system was developed by Hedley and Tillman (1984, pers.comm.), to place P^{32} evenly in a soil core with minimal disturbance of pasture or soil. The injection system had previously been successfully utilised in an isotopic dilution study in the field (Rowarth 1987).

To implement the "A" value concept the P^{32} would be injected between 1.5 and 6 cm depth from the soil surface, while the fertiliser would be applied to the pasture surface. This would ensure that the two phosphate sources would be kept separate. The *in situ* pasture was assumed to effectively sample the system, and more than one harvest would be taken after injection, to minimise the effect of phosphate originally present in the plant upon isotope injection. The specific activity of the plant available pool could not be obtained directly with accuracy. Instead, a standard amount of P^{32} was applied to each core and the specific activity of pasture herbage (using the plant to sample the soil solution), where no fertiliser has been applied, became the standard against which the other treatments were measured. The "A" value of the fertiliser was estimated using the difference in specific activity between herbage from the fertilised and unfertilised cores. Further details are in section 5.4.1.

5.3 RESULTS

5.3.1 Herbage yield

The fertiliser treatments had no significant effect on the pasture growth rate or final cumulative yields (table 5.1), so no difference was found between the herbage yields of pasture cores fertilised with phosphate rock, MCP, or the unfertilised controls. It was concluded that phosphate availability was not limiting growth at this site.

Time did have a significant effect on the pasture growth rate. The average pasture yield (data not shown) followed a seasonal growth trend, with an increase in growth rate and yield in late summer to early autumn, followed by a steady decline in growth rate in late autumn and early winter. This is a typical trend on a clover-ryegrass pasture, caused largely by changes in temperature and daylength (Broughham, 1959) and accentuated by cutting the pasture every two to three weeks while still in the constant growth phase (Brougham, 1956), as was done in this experiment.

5.3.2 Uptake of Phosphate by Pasture

An analysis of variance found that at each harvest the phosphate content of the collected herbage (mgP/core) was significantly affected both by time and treatment, ($P<0.05$). It was also found that the coefficient of variation of the data was high (average:21%) which did not allow separation of some treatment means.

The amount of phosphate taken up by the herbage was accumulated for all harvests taken over the 131 days, and the data is presented in table 5.1.

Table 5.1 Accumulated plant yield and herbage phosphate 131 days after fertiliser was applied to pasture. (Granule size in parenthesis.)

Treatment	Yield (g dry matter/core)	Phosphate (mgP/core)
Mono-calcium phosphate	4.69a	25.6 a *
Granulated finely ground PR,(0.5-1mm)	5.05a	21.5 a
Finely ground PR	4.87a	20.9 ab
Granulated finely ground PR,(1-2mm)	4.65a	19.8 ab
Granlated finely ground PR,(2-4mm)	4.43a	19.5 b
Works ground PR	4.40a	19.1 b
No fertiliser	4.07a	14.8 b

*Common letter postscript indicates results were statistically the same, ($P<0.05$).

There was significantly more phosphate in the pasture fertilised with MCP and the smallest granule size of the finely ground NCPR, compared to phosphate uptake derived from; the unfertilised control, the works ground NCPR and the largest granule size of the finely ground NCPR. No other significant differences were found between the treatments.

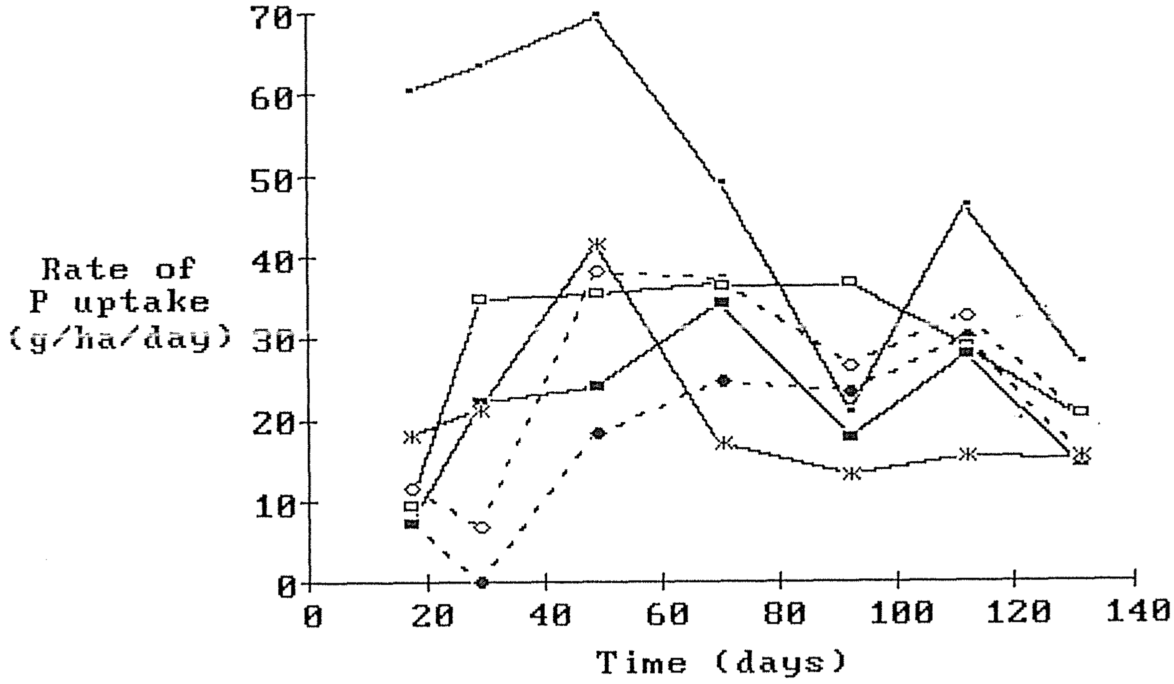


Figure 5.2: The uptake of phosphate by fertilised pasture over the duration of the field experiment. Presented as the increase in phosphate taken up per hectare per day above the unfertilised control (◆ NCWG, ◇ NCFG, □ NCFG 0.5-1mm granules, ▨ NCFG 1-2mm granules, ⋇ NCFG 2-4mm granules, ▪ MCP).

The phosphate content of the herbage was also examined in terms of changes in the rate of phosphate uptake (gP/ha/day) of the pasture. The the total phosphate content of the pasture at each harvest is presented in table 1 of appendix 3. The trends are presented in figure 5.2 and summarised as follows.

At the first and second harvests (17 and 29 days from the commencement of the experiment) only the pasture fertilised with MCP had a rate of phosphate uptake which was significantly greater than phosphate uptake from the unfertilised pasture. The rate of phosphate uptake from the MCP treatment remained significantly greater than that of the control for the rest of the experiment, except at the fifth and the seventh harvests, (92 and 131 days).

The rate of phosphate uptake by pasture fertilised with the smallest granule size (0.5-1mm granules from finely ground phosphate rock) was significantly greater than that of the unfertilised pasture only between the third to the sixth harvests (49-112 days). Finely ground phosphate rock which was not granulated had a very similar pattern of phosphate uptake. The rate of phosphate uptake from the medium granule size (1-2mm) was significantly greater than the unfertilised pasture only at the fourth harvest, and phosphate uptake from the large granules (2-4mm) was significantly greater only at the third harvest. The rate of phosphate uptake from the coarser works ground phosphate rock was never significantly greater than that of the unfertilised pasture.

The rate of phophate uptake data also showed that there was a lag of approximately 4 weeks before any of the phosphate rock treatments began to release significant amounts of phosphate, compared to the MCP fertiliser which had a rapid initial availability.

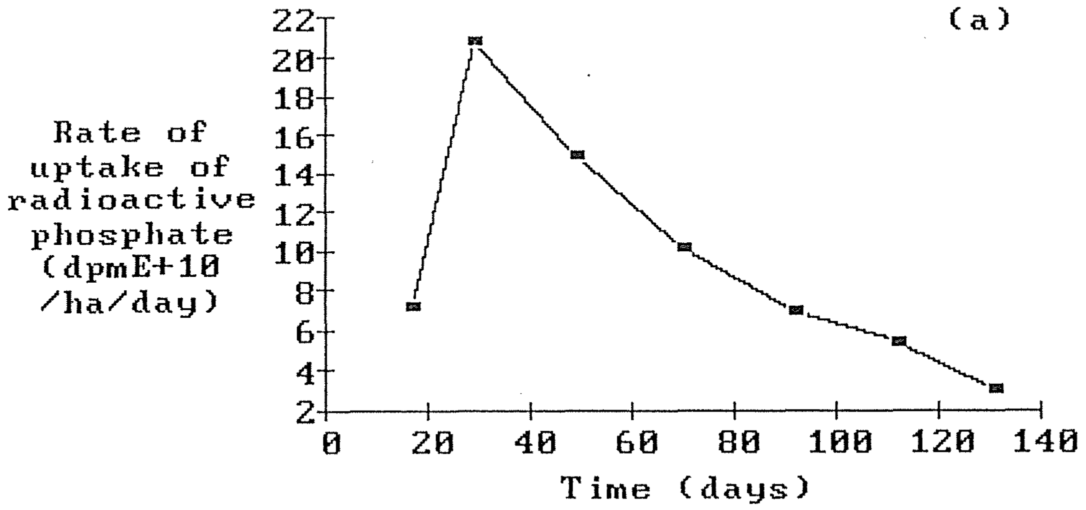
Similar results were obtained by Rajan *et al.* (1987), using ground and granulated (80% of the granules were between 1 and 3.35mm) North Carolina, Sechura and Chatham rise phosphate rocks on eight field sites. On a yearly basis the yield derived from the phosphate rocks was not significantly different to that derived from superphosphate, although the the response from the phosphate rocks lagged three to six months behind the superphosphate after each annual application.

5.3.3 Uptake of labelled phosphate

The uptake of labelled P^{32} by pasture was not affected by the application of fertiliser over the whole experimental period of 19 weeks. Time only had a significant effect ($P<0.01$) indicating that changes did occur in the rate of P^{32} uptake by pasture, but that these changes were the same regardless of treatment.

The general pattern of P^{32} uptake is presented as an average of all the treatments in figure 5.3, demonstrating that there was an increase P^{32} uptake by the pasture between the first and second harvests, followed by a steady decline in the amount of P^{32} taken up over subsequent harvests. A model ($y=a+b[1-\exp[-0.018x])$) was fitted to the cumulative uptake of P^{32} by the herbage (y) at each harvest, where x was the number of days since the commencement of the experiment. The model predicted that there would be no further uptake of P^{32} approximately 500 days after the commencement of the experiment. This decrease in P^{32} uptake indicated that the "availability" of the P^{32} injected into the soil decreased with time. This may have occurred for the following reasons.

Uyo (1974) suggested that in dry conditions, which did occur at the start of this experiment, that pasture, very similar in location to that tested here, took up little phosphate from the surface soil and recovered 30% of the herbage phosphate from below a soil depth of 5cm. Under wetter spring conditions only 2% of the herbage phosphate was taken up from soil greater than this depth. In this experiment the soil moisture content increased until the third harvest but then remained constant until the final harvest. During the initial dry period a greater proportion of the plant phosphate could have been derived from the injected zone. After rainfall, however, the top soil wetted up and more plant phosphate could have been derived from the non-injected top 1.5 cm of soil. This change in the relative uptake of soil phosphate from different depths does not however explain why the amount of P^{32} taken up from depth should decrease.



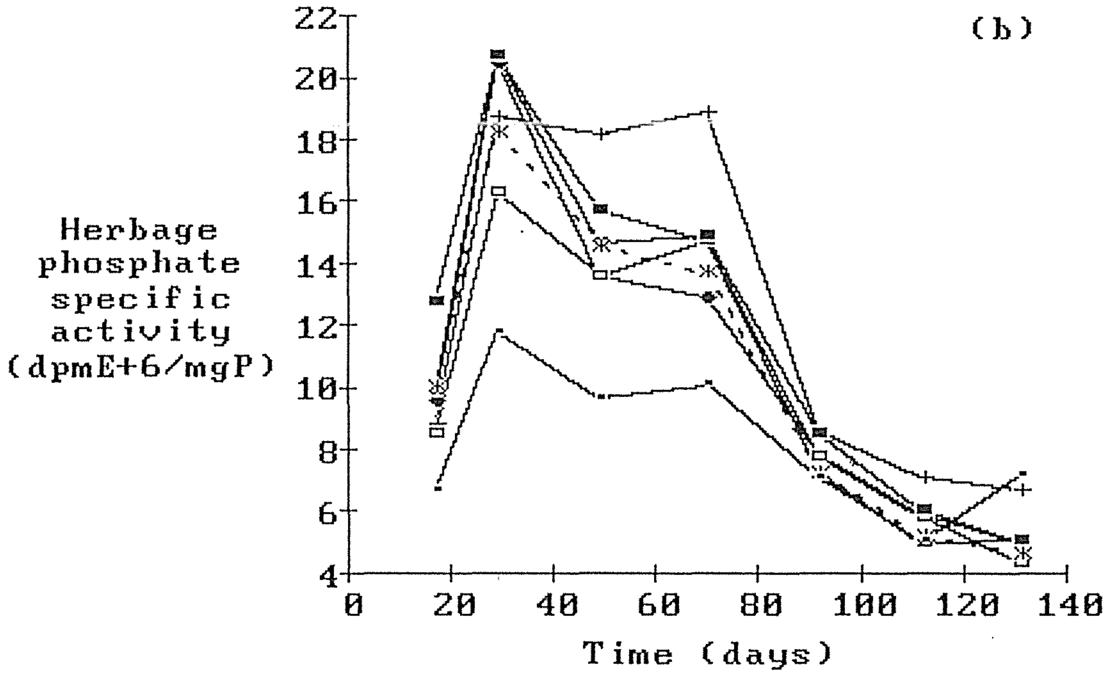


Figure 5.3: The P^{32} uptake by pasture from injected soil cores (average for treatments) in the field experiment (a), and the resulting herbage specific activity in different treatments over the duration of the experiment (b). (◆ NCWG, ◇ NCFG, □ NCFG 0.5-1mm granules, ▨ NCFG 1-2mm granules, ✳ NCFG 2-4mm granules, ▪ MCP, + unfertilised control).

Of the total P^{32} applied to the soil 12% was recovered in the cut herbage from each injected core. Some P^{32} would also be expected to have been immobilised in the plant tissue which was not harvested, especially the roots. This quantity was not measured but was liable to be a static quantity which did not change much over the duration of the experiment, in view of the lack of plant yield response to the fertiliser.

The initial rise in P^{32} uptake may possibly be attributed to the growth of root hairs into the holes left by the injector and this effect may also explain the decline in P^{32} uptake after the second harvest. Only a very small proportion of the soil was labelled with P^{32} so the speed of diffusion of the P^{32} into, and exchange with, the wider soil pool would determine the specific activity the phosphate in the injected zones. If the plant uniformly sampled the whole soil phosphate pool the P^{32} uptake and the herbage specific activity may not change, but if plant uptake shifted into the injected zone, as was possibly indicated by the increase in uptake between the first and second harvests, the P^{32} uptake and herbage P^{32} specific activity may drop as the specific activity of the injector hole zones drops.

The specific activity of the plant available pool in the injected zone may also drop as P^{32} moves into the non-labile pool. Larsen and Sutton (1963) found that an application of carrier free P^{32} to a soil took ten weeks to attain equilibrium with the non-labile pool of a sandy loam. The non-labile pool may be inorganic phosphate strongly sorbed or precipitated onto soil surfaces, or organic immobilised phosphate. P^{32} attaining equilibrium with this pool will drop the specific activity of the labile pool. Although this soil has a moderate to low phosphate retention (methods 3.4) the low phosphate status (Olsen P 6-12µgP/g) indicates a capacity for irreversible sorption of phosphate.

Such uniform and steady decline may also indicate that the P^{32} was being removed from the soil labile phosphate pool by immobilisation of P^{32} into soil biomass. A process of net immobilisation of soil phosphate into organic matter is expected to occur over the autumn period (During, 1984).

Shedley, Till and Blair (1979) injected the surface soil of pots of established plants with radioactive sulphate and found that the tracer initially remained in the plant available pool, rather than being directly adsorbed by the soil. Boswell (1983) used the same system and found that that the ^{35}S was rapidly immobilised into the soil organic matter and generally was not mineralised back into the labile pool over the 100 day duration of the experiment. These studies indicated that a radioactive label added to the soil labile pool, rather than becoming evenly distributed throughout the various soil nutrient pools, initially tended to enter the prevailing soil cycle and only label the pool which was currently being incremented. In the case of phosphate either immobilisation or absorption processes may occur, removing the label from solution. Subsequent mineralization of material in which the phosphate has not exchanged with the added P^{32} label would cause a reduction in the specific activity of the labile pool and a drop in the total amount of P^{32} uptake.

It seems possible that a combination of root growth in the injector holes, accompanied by processes of sorption and immobilisation, combined to produce the observed pattern of P^{32} uptake.

5.3.4 Specific activity

Specific activity is the ratio of the pasture content of P^{32} to the pasture content of total P. As in Kucey and Bole (1984) it was found that, relative to the specific activity of pasture to which no fertiliser had been applied, the specific activity dropped when fertiliser was applied to the pasture. This indicated that there was uptake of unlabelled fertiliser phosphate which had `diluted' the concentration of P^{32} in the pasture.

The specific activity data was tested using an analysis of variance procedure. In this experiment the specific activity of the treatments at each harvest was significantly affected ($P<0.05$) by both treatment and time. There was also a significant time-treatment interaction. The average c.v. of the data was 15%.

Because there was ~~a~~ no significant effect of ~~time~~ treatment on the total P^{32} content of the pasture during the experiment, and ~~no~~ or significant effect of ~~time~~ treatment on the total phosphate (P^{31}) content of the pasture, it was concluded that the ~~time~~ treatment effect found in the specific activity results was caused by the changing pattern of $P^{3\cancel{2}}$ 31 uptake alone.

As shown in figure 5.3, at the third (49 days) and fourth (70 days) harvests the pasture of all the phosphate rock treatments, except the coarsely ground rock, had specific activities which were significantly lower than the unfertilised pasture. The specific activity of the MCP treatment was significantly lower than all other treatments.

There was no statistical differentiation between any specific activities in the other harvests, (first, fifth, sixth and seventh).

These results indicate that while the specific activities of the pasture were reduced by fertiliser application due to isotopic dilution within the plant, the two sources of error (P^{32} content and P^{31} content) in the specific activity calculation were large, so it was not possible to attribute any significance to the difference between treatment means. Calculating the specific activities of the cumulative total phosphate and P^{32} content of the pasture also encountered the same problem, with no significant difference found between the mean P^{32} specific activities from the different phosphate rock treatments.

5.4 Discussion; Agronomic evaluation.

5.4.1 Evaluation of the "A" value inverse isotopic dilution technique

The "A" value concept, as based on the work by Kucey and Bole (1984) utilises a labelled zone of soil as a standard against which to compare the availability of a fertiliser. The method uses a plant to sample the system, which in this case was established pasture. The soil phosphate was labelled using an injection system. The "A" value is calculated in terms of an increase in the size of the plant available pool, which was estimated (equation 3) by assuming that all the P^{32} injected remained in the plant available pool and that specific activity of the plant available pool in the soil and the specific activity of phosphate in the herbage which was derived from this pool were the same.

$$\text{Amount of phosphate the soil available pool (Psoil)} = \frac{P^{32}\text{ remaining in the soil at a harvest}}{\text{specific activity of herbage at a harvest}} \qquad (3)$$

A third assumption made, that the addition of fertiliser to the soil would not alter the efficiency of phosphate uptake from the soil, and therefore, the proportion of phosphate taken up from the available pool (as found for the unfertilised pasture) would be the same when fertiliser was added to the soil pool. This assumption agrees with the similar P^{32} uptake pattern observed for all treatments and enabled the increase in the soil available phosphate pool due to the dissolving of the fertiliser to be calculated (fertiliser "A" value) at each harvest (equation 4).

$$\text{Increase in the soil available pool due to fertiliser ("A")} = \left(\text{ratio of plant available pool to herbage P in the control cores} * \text{amount of herbage P from fertilised cores}\right) - \text{Psoil} \qquad (4)$$

The "A" value of the various fertilisers used in this experiment was calculated for each harvest interval (except the first) and presented in table 5.2. The above assumptions were not expected to hold for the first harvest because some of the phosphate in the herbage would probably have been taken up from the soil before the available pool was labelled. This contribution from the original plant phosphate was expected to be similar for each treatment.

An examination of the derived values found that the "A" values were somewhat higher than would be expected. Some of the "A" values derived for the various fertilisers were higher then the amount of fertiliser applied, the most obvious example being the "A" value for the MCP treatment at the 6th and 7th harvests. The amount of increase in the soil available phosphate pool due to the fertiliser was found to be 153 and 145 mgP respectively, but only 106 mgP was intially applied. This would indicate that the "A" values were overestimated and therefore some of the assumptions underlying the equations were incorrect.

Table 5.2 Estimates of the size of the labile pool in each pot (mgP/pot) and the "A" values derived for fertilisers, at each harvest (mgP/pot).[1]

TREATMENT HARVEST;	2	3	4	5	6	7
Size of the soil available pool(mgP)	89	92	84	189	216	225
"A" values for fertilised pots						
MCP	55	85	89	56	153	145
small granules	30	41	64	98	99	113
finely ground PR	4	44	69	77	108	113
med. granules	17	28	64	49	90	80
large granules.	17	51	74	35	54	80
works ground PR	0	20	44	63	99	80

[1] The average c.v. of the soil available pool size was 13%. The significance of the "A" values would be much the same as those of the herbage phosphate data (table 1, appendix 3).

The first assumption was that all the injected P^{32} (which was not taken up into the herbage) remained in the plant available soil phosphate pool. This was unlikely to be correct because there appeared to be considerable removal of P^{32} from the available pool by absorbtion or immobilisation (as discussed in section 5.3.3), probably coupled with the release of unlabelled P^{31} into the available pool. This process would have caused an apparent increase in the calculated size of the available pool.

The assumption that the specific activity of the available pool equalled the specific activity of the herbage of the control cores was not validated in this experiment, but subsequent work (Chapter 7, soil fractionation section) did tend to uphold it.

The third assumption, that the plant would additively sample any increment to the soil pool may also have been incorrect. The fertiliser was applied to the soil surface and the P^{32} injected between 1.5 and 6cm depth. If the plant root density increased in the surface of the fertilised cores, the ratio of plant uptake to soil pool size in these zones would also probably be different in the fertilised cores. (The majority of pasture roots were found to be in the top 10cm of the soil and the highest densities in the top 5cm, Barker *et al.* 1988). The expected effect (a priming effect) would be that phosphate uptake from the top 1.5 cm of the soil would be very efficient as this is the zone of highest root density. This would narrow the plant uptake to soil pool ratio in this zone and, in the above calculation, inflate the "A" value.

Fertiliser dissolution and agronomic performance

The final assumption implicit in the "A" value calculation was that any change in the size of the plant available pool was due solely to the presence of the fertiliser. In this experiment there was no difference between the accumulated P^{32} content of the unfertilised pasture and the accumulated P^{32} content of the fertilised pasture, so that all differences in specific activity were only caused by changes in total phosphate content of the pasture. These changes in the phosphate content of the pasture may have been caused by differences in phosphate uptake from the different fertilisers, or by changes in soil phosphate uptake from the unlabelled zone in fertilised cores.

A distinction must be made between assessing the agronomic performance of a fertiliser, and assessing the actual amount of nutrient released by dissolution from a fertiliser. If only actual dissolution is to be considered, any effects that the presence of the fertiliser may have on the availability of a nutrient from the soil, or on the rate of nutrient uptake, must be partitioned from the total amount of a nutrient taken up. This cannot be done completely using this technique. Changes in phosphate uptake in the labelled zone can be accounted for (ie increased uptake due to an increase in root length in this zone) using the equations derived in appendix 4, but any effects that the presence of the fertiliser may have on phosphate uptake in the top 1.5 cm of the soil cannot be separated from the phosphate taken up from the fertiliser. Therefore, agronomic performance of a fertiliser rather than absolute dissolution is assessed by this technique.

In summary, the assumptions necessary for the calculation of "A" values could not be upheld in this experiment, so no direct estimate of the amount of phosphate available from the fertiliser sources could be made. To find the amount of fertiliser dissolution only, the variations caused by changing phosphate uptake in the top 1.5cm could only be accounted for by labelling the whole soil volume. This in turn would create problems of P^{32} exchanging with the fertiliser phosphate and artificially increasing specific activity, which was thought to be a problem in the Kucey and Bole experiment (1984). In fact, labelling the whole soil volume creates an assessment of "L" value (Larsen, 1952), which would normally require a uniform distribution of fertiliser within the soil.

5.4.2 Agronomic evaluation

Kucey and Bole (1984) proposed that an estimate of relative agronomic value could be obtained by calculating the PUD (relative phosphate uptake difference) of different fertiliser treatments. Kucey and Bole also introduced RAID values (relative availability as determined by isotopic dilution), which utilised the specific activity results rather than the phosphate uptake to evaluate the fertiliser sources, calculating the amount of phosphate in the herbage which is derived from the fertiliser. This would provide a ranking of the availability of the fertiliser sources, although no estimate of the total amount of phosphate available from the fertiliser.

The PUD values were found using equation 5, where P(z) stands for the herbage phosphate (mgP/core) of the treatment z, and z stands for the following treatments of: PR = phosphate rock, C = unfertilised control, MCP = Mono calcium phosphate.

$$\mathrm{PUD} = \frac{\mathrm{PPR-PC}}{\mathrm{PMCP-PC}} * 100 \qquad (5)$$

RAID values were found using equation ~~6~~ 7, the amount of phosphate derived from the phosphate rock (PdfPR) and the MCP (PdfM) being first calculated by equation ~~4~~.6

$$\mathrm{Pdf.RP} = 1 - \frac{\text{specific activity PR}}{\text{specific activity C}} * 100 \qquad (6)$$

$$\mathrm{RAID} = \frac{\mathrm{PdfPR}}{\mathrm{PdfMCP}} * 100 \qquad (7)$$

Table 5.3 PUD and RAID values calculated using accumulated phosphate content of herbage.

Harvest		1	2	3	4	5	6	7
finely	PUD	20	30	32	43	51	38	53
gr. PR	RAID	0	0	21	35	36	41	39
0.5-1mm	PUD	15	32	40	48	61	61	65
gran.	RAID	3	23	40	39	43	43	43
1-2mm	PUD	12	38	27	38	42	45	46
gran.	RAID	0	0	3	17	15	17	17
2-4mm	PUD	30	55	44	41	44	42	43
gran.	RAID	0	0	19	29	32	32	39
works gr.	PUD	10	12	16	24	33	38	38
PR	RAID	0	0	0	9	17	26	23

Kucey and Bole (1984) found that RAID values were poor indicators of available fertiliser phosphate in soils where phosphate status was not very growth limiting. The basis of these calculations is the ratio of the herbage specific activities of the unfertilised to the fertilised treatments. Mathematical analysis of this ratio (Appendix 4, part 1.) proved that under the conditions of this experiment, i.e. no growth response and consequently no effect on P^{32} uptake, that utilizing this ratio was the same as simply finding the difference between the amount of herbage phosphate in unfertilised pasture and the amount in the fertilised pasture. If there had been a growth response, and as a consequence the uptake of P^{32} had varied between treatments, then the only way to estimate the amount of herbage phosphate which was derived from fertiliser would be through the specific activity ratio, as an estimate of fertiliser phosphate in herbage would be confounded by the uptake of extra phosphate from the soil.

In the present situation of no growth response to applied phosphate, the "A" value and inverse isotopic dilution approaches provided no more information than simply measuring the phosphate uptake response of the pasture, except that the calculations using specific activity have an extra source of error, ie P^{32} content of the pasture. Therefore, the PUD values are expected to give the best relative indication of available phosphate in this experiment, although these values only give a relative value of phosphate supplied by the fertiliser, rather than the traditional agronomic ranking based on relative yield differences.

The assessment of agronomic value usually includes some standard source of phosphate against which the fertiliser is measured. In this experiment MCP was used, which is classed as moderately water soluble (1.8g soluble in 100cc cold water; Stecher, 1968). Phosphate was released into the soil very rapidly from this source, so that the rate of phosphate uptake from the MCP was significantly above that of the unfertilised pasture at the first harvest (17 days), and remained so until the fifth harvest at 92 days after fertiliser application, after which time the rate of phosphate uptake dropped. In contrast, the phosphate rock treatments had a slow initial release rate and in this experiment were not releasing significant amounts of phosphate until the third harvest (49 days), after which time a relatively steady release rate was maintained.

This brings into question the validity of evaluating phosphate rock in terms of water soluble fertilisers. The effect of the different release rates was to cause the relative agronomic value to increase steadily with time, but this was because the amount of phosphate taken up from the MCP treatment dropped, not because the amount of phosphate available from the phosphate rock increased.

5.5 Conclusions

The application of soluble (MCP) and sparingly soluble (North Carolina phosphate rock) sources of phosphate fertiliser caused no pasture growth response on the permanent pasture field site. Phosphorus was not the key factor limiting pasture growth.

Although the information was limited by high experimental variability, the accumulated phosphate uptake and also the rate of phosphate uptake of pasture fertilised with MCP and phosphate rock did increase. It was concluded that the availability of the phosphate rock was marginally increased by fine grinding. The availability of the phosphate rock was reduced by granulation, except when the smallest granule size of material was used, when there was no effect on pasture phosphate uptake.

These conclusions need to be confirmed in more rigorous conditions, preferably where dry matter responses to applied phosphate can be obtained, in order to gain a more complete view of the effects of these fertilisers on plant growth.

Use of an isotope injection technique provided little additional information, except that, through observing the pattern of P^{32} uptake, it was possible to confirm the that all the cores provided replicate plant growth units. An attempt to gain more information through the use of an "A" value technique was unsuccessful, because of the lack of significant treatment effects caused, in part, by the large errors associated with spatial variability in the field. The isotope injection technique may be more successful under more controlled conditions, where the spatial variability of P^{31} and P^{32} uptake between replicates can be reduced. The technique may also be more successful under conditions of a plant growth response to fertiliser. Theory suggested, based on isotopic dilution principles, that this technique would provide a means of separating soil and fertiliser phosphate in the herbage, providing information on the extent of a priming effect.

The relative agronomic value of the phosphate rock fertilisers was evaluated in terms of an MCP standard fertiliser source. The RAID and PUD values did not provide a realistic assessment of the agronomic performance of the phosphate rock fertilisers in this short term experiment.

CHAPTER 6: MINI-GRANULATION OF PHOSPHATE ROCK

6.1 Introduction

A field experiment (Chapter 5) established that mini-granulation (0.5-1mm granule diameter) of finely ground North Carolina phosphate rock did not reduce the agronomic performance of the phosphate rock. In this chapter the advantages of granulating phosphate rock, and previous granulation agents and methods are reviewed. This chapter describes a series of trials which were undertaken to evaluate a variety of granulation agents and the development of an efficient method of producing strong mini-granules.

6.2 Literature review

6.2.1 The advantages of granulating phosphate rock

Phosphate rocks are dry free-running materials of fine particle size, particularly when ground. The fine particle size has posed problems in bulk transport where current systems are designed for granular products. Bulk transport operators have found it necessary to tape up all openings in the vehicles or lose considerable portions of the load (Mr N. Charteris, Ravensdown, pers.comm. 1989).

Much of the fertiliser application in New Zealand is done by topdressing aircraft. Phosphate rock is easy to handle when loading and spreading from an aerial topdressing plane but maintaining an even spread is difficult in anything except calm conditions. At present, since very little phosphate rock is being applied to pasture by topdresser, operators are able to wait for suitable conditions for spreading. If the phosphate rock material can be granulated this may overcome some of these problems. The product should, ideally, be free-running, dry, light, and of as high an analysis as possible (Mr. Bernie Haskill, Jet Spread. pers.comm. 1989)

The difficulty of spreading phosphate rock has also been pointed out by Gillingham *et al.* (1987). A series of test flights and ground spreading trials demonstrated that moderate cross winds had a significant effect on the distribution of North Carolina phosphate rock (which had not been ground). The distribution pattern of the phosphate rock (once on the ground) was shifted down wind, widened and flattened, and in fact could not be fully covered by the area of the collector system used. Extrapolation of the data given suggested that the phosphate rock moved 80 to 100m away from the point of release. Whereas a sideways shift and an evening out of the distribution pattern may provide a more even application, these figures, and a consideration of the particle size difference between ground and unground phosphate rock, lend some credence to the tale of watching ones fertiliser land solely on the neighbours' property, or possibly not land in sight at all.

At present a partial commercial solution to the particle size problem has been the introduction of the current Ravensdown product "Hyphos". This product consists of ground North Carolina phosphate rock (65% >75µm) acidulated to 20 or 30% with H_3PO_4 and mixed with molten sulphur. After denning the product is stockpiled for 24 hours and then drum granulated and partially dried. A variety of other acidulated products (eg. 70:30 SSP:RPR mixtures, "longlife" supers) have also been modified to include significant proportions of non acidulated phosphate rock. It has yet to be demonstrated that the value of these types of product in a commercial farming system extends beyond the fertiliser content of water soluble phosphate.

The "Hyphos" manufacture process is very suitable for a superphosphate plant but unless these facilities are available the machinery is specialised and expensive. The "Hyphos" type of fertiliser, incorporating a mineral acid, is also unacceptable to the biological husbandry disciplines of organic production. It is therefore desirable to consider granulation of phosphate rock with the so called natural salts and organic acids, which would also provide a simpler and cheaper granulation process.

6.2.2 Suitable granulating agents

A wide variety of granulation agents have been used with phosphate rock. Livingston (1978) employed a pin mixer, which consisted of pin-like rods arranged on a horizontal shaft in a circular staircase design, to successfully mini-granulate (75-250 µm diam.) finely ground phosphate rock sprayed with solutions of urea, KCl, $MgSO_4$, H_3PO_4, and H_2SO_4.

Laing (1981) reported that weak granules were obtained using cellulose wall paper paste, 3% KCl or 20-50% H_2SO_4. Use of 10% and 20% Urea and 10%, 20%, and 40% $(NH_4)_2SO_4$ for granulation caused some problems with the release of NH_3 gas.

Gillion *et al.* (1978) granulated four phosphate rocks with: 5% and 10% KCl, 5% $MgSO_4$, 5% $(NH_4)_2SO_4$, 5% and 10% $MgCl_2$, and 14% H_2SO_4. From a glasshouse experiment they concluded that the type of granulation agent had no significant effect on the yield obtained when the granules were applied as fertiliser, with the exception of granules made with H_2SO_4, where partial acidulation improved the phosphate availability of these granules.

Carmon (1978), using a pan granulation system, granulated (2-4mm) a finely ground phosphate rock using a dilute solution of $MgCl_2$. Important factors controlling the size distribution and porosity were associated with the mixing and granulation stages and were; the moisture content, the degree of mixing, the residence time of the mix in the granulation pan, the speed and angle of the pan, and also the ratio of new material to recycled undersized granules.

Important factors controlling the strength of the granules were associated with the drying step. This step can be divided into three stages. In the first stage, the wet granule shell saturated a diffusion boundary layer around the granule, so that the rate of drying was constant. The second step commenced when the granule surface began to dry and water began moving from the interior of the granule by capillary action, resulting in a constant decrease in the drying rate. In this second stage the salt in the granule began to move towards the surface of the granule. The third drying stage occurred when the granule surface was completely dry and moisture was lost from the interior of the granule by gaseous diffusion. This third stage was the period when the salt crystals formed in the granule.

Increasing the drying temperature shortened stage two and lengthened stage three, reducing the movement of the salt solution to the granule surface and accelerated the salt crystal nucleation. A greater number of smaller crystals were formed as well as a more even distribution of the salt cystals within the granule, which will increase the number of intragranular bonds and so increase the granule strength.

Carmon (1978) also found that granule strength increased with the fineness of the granulated material, and that the hygroscopicity of the granulation agent was not much of a problem because bulk storage stock piles developed an outer moist layer of about 25mm thickness which protected the rest of the material.

6.3 Materials and methods

6.3.1 Phosphate Rocks

The materials granulated were "as received" North Carolina, Sechura and Arad phosphate rocks, as well as ground forms of the North Carolina and Arad phosphate rocks. The particle size of the materials was assessed by sieving (see chapter 3.1.1) and the results were presented in table 4.1.

6.3.2 Granulation apparatus

This consisted of the following pieces of equipment;

A Kenwood food mixer with a "K" beater.

A Watvic fan oven, set to 80°C.

A granulation unit consisting of a plastic drum (dimensions; length=22.5cm, base diameter=18cm, mouth diameter=20cm) bolted to the rotating shaft of a Zeromax 400 variable speed motor. The angle of the drum was adjustable and set so that the drum was approximately horizontal.

A Millipore air pump.

Endecott sieves with stainless steel mesh.

6.3.3 Granulation method

This is the final granulation method, used to generate the results in tables 6.3, 6.4 and 6.5. The method is discussed in section 6.4.3.

1. Preparation of the granulation agent

4.00 ± 0.01g of $MgSO_4$ or 3.08 ± 0.01g Citric acid with 1.92 ± 0.01g $MgSO_4$ was dissolved in distilled water, the amount of water being dependent on the type of phosphate rock to be granulated, as follows;

North Carolina phosphate rock	9ml
Arad phosphate rock	12ml
Sechura phosphate rock	10ml

2. Addition of phosphate rock

36.00 ± 0.02g of phosphate rock was mixed with the dissolved granulation agent, using a food mixer, for three to four minutes. The slurry was then transferred to an metal dish for pre-drying.

3. Pre-drying

The slurry was dried for approximately fifteen minutes between 75°C and 85°C, until water did not move to the surface of the slurry when the surface of the mixture was pressed down.

4. Granulating

The slurry mixture was cut through a 0.710mm sieve and the resulting "strings" of mix were placed in a drum which was rotating at approximately 120rpm. The particles in the drum were kept separate and rotating using a stream of air generated by a millipore pump. After approximately thirty seconds of rotation the granules formed were tipped out onto a 1mm sieve and shaken. Those granules not passing through the sieve were pushed through the 0.710mm sieve again and regranulated.

5. Drying

The granules were transferred to a metal plate and dried at between 75°C and 85°C for between 1.75 and 2 hours.

6. Granule strength evaluation and storage

Once cooled granules made using citric acid were sieved to separate out the 0.5-1mm diamter fraction and the strength of the granules evaluated (method chapter 3.1.7). These granules were than stored in a sealed container. Granules made using only magnesium sulphate were sieved and left unsealed overnight before the granule strength was evaluated because it was found that the strength of the granules increased 20-40g via this method. These granules were then evaluated and stored in a sealed container.

6.4 Evaluation of granulation agents and granulation method

6.4.1 Evaluation of granulation agents, using NCAR

Very finely ground North Carolina phosphate rock was granulated using 10% K_2SO_4, and divided into granule size fractions of 0.5-1mm, 1-2mm and 2-4mm. The agronomic performance of the granules was evaluated in a field trial (Chapter 5) and it was concluded that the 0.5-1mm diameter granules were the optimum granule size.

Having found the optimum granule size testing was begun to evaluate new granulating agents, using "as received North Carolina phosphate rock (NCAR). The "as received" material was used on the principle the large particle size would be the most difficult to form into the small granules with any strength.

The method used to manufacture the granules was the same as that detailed in chapter 5.2, except that the mix was moistened to a greater degree, and mixed in a Sunbeam mixer rather than a coffee grinder. In addition the mixture was usually cut through a 0.710mm aperture sieve rather than being put directly into the granulating drum after mixing.

A wide variety of granulation agents were tested with NCAR and the results are summarised in the following table (6.1). The criteria upon which the granulation agents were evaluated were the efficiency, yield and strength of mini-granules formed from the mix.

Table 6.1 Summary of granulation agents tried with "as received" North Carolina phosphate rock. The proportion of granules in the 0.5-1mm diameter size range is given as an estimated percent of the total yield of granules. The average crushing strength of individual granules and comments are also given where relevant.

Granulation agent (%w/w)	Yeild %	Strength (g)	Comments
5% K_2SO_4	-	-	Mix would not granulate.
10% K_2SO_4	-	-	Three runs attempted, oversize granules produced if at all.
20% K_2SO_4	30%	215	Mix easier to granulate, some granules formed.
10% $MgSO_4$(hyd)	70%	267	High yield of mini-granules .
10% $MgSO_4$ (anhyd)	-	105	Difficult to granulate, quite soft.
10% KCL	0	-	Large granules only, difficult to granulate.
10% $NaH_2PO_4.2H_2O$	5%	148	Easy granulation but mainly oversize granules
10% K_2HPO_4	0	-	Oversize granules only, went soggy overnight.
5% K_2HPO_4	20%	-	Mix difficult to granulate.
5% K_2HPO_4+5%K_2SO_4	20%	-	Mix difficult to granulate.
10% Citric acid ($HOC(CH_2CO_2H)CO_2H$)	60%	459	Dried in sun for 1/2 an hour before granulating, mix easy to granulate and good yield of mini-granules.
10% $(NH_4)_2SO_4$	-	133	Mix difficult to granulate but hard granules.
10% KH_2PO_4	-	-	Mix did not granulate
5ml 50% H_2SO_4	-	28	Very soft granules.

Table 6.1 continued;

Granulation agent (%w/w)	Yeild %	Strength (g)	Comments
10ml 50% H_2SO_4	-	94	Granules soft and oversize.
10% CH_3OOK	-	-	Quite soft granules.
10% NH_3NO_3	-	-	Quite soft granules.
10% L-Ascorbic acid		179	Mix difficult to granulate but granules fairly hard.
10% Oxalic acid	-	-	Mix easy to granulate but granules oversize and soft.
Concentrated apple juice		102	Granules very soft, and little improvement with a second addition of juice.
11ml Acetic acid, glacial			Granules had no strength.

6.4.2 Evaluation of granulation agents using NCWG

Some of the more successful granulation agents (table 6.1) were also tested with works ground North Carolina phosphate rock (NCWG). An assessment of the particle size distribution of this material is found in table 4.1. A summary of granulation results is presented in table 6.2.

The highest yields of hard 0.5-1mm diameter granules were obtained when 10% citric acid was used as the granulation agent. Magnesium sulphate was found to give the best results of the neutral salts. It was subsequently decided to use citric acid and magnesium sulphate as the two granulation agents to test a range of granulated phosphate rocks (diameter 0.5-1mm) in a glasshouse experiment.

Table 6.2 The proportion of granules in the 0.5-1mm diameter size range is given as an estimated percentage of the total yield of granules. The average crushing strength of individual granules and comments are also given where relevant.

Granulation agent (%w/w)	Yeild %	Strength (g)	Comments
10% K_2SO_4	40%	44	Mix would not granulate without pushing mixture through a seive, granules soft.
10% K_2SO_4	50%	-	Less water used in the mix and no cutting, produced very powdery granules.
10% K_2SO_4	60%	56	Longer granulation drum time, producing harder granules.
5% Citric acid	-	116	Quite soft granules and hard to keep small.
10% $MgSO_4$(hyd)	65%	166	Fairly soft granules.
10% Citric acid	-	297	Good granulation, but needed to resieve mix and repeat drum granulation to acheive correct granule size.

6.4.3 Refining the granulation method

Manufacture of a larger amount of the granules for use in a pot trial was commenced, but duplicating the results found during the intial testing proved unexpectedly difficult. The granules produced were very weak (20g) compared to the first run which had produced an average granule crushing strength of 459g per granule (eleventh agent trialed in table 6.1). A series of mixing and granulation trials were undertaken, gradually improving the method until the original results were duplicated. The final method used to achieve maximum granule strength and yield is summarised in the section 6.3.3, while relevant points are discussed in this section.

(a) Granulation agent

A 10% content of granulation agent was chosen as a compromise between achieving a good granule strength and diluting the phosphate content of the product parent material.

Dissolving the ($MgSO_4$) granulation agent in water before mixing with the phosphate rock appeared to result in an increase in granule strength, as the highest $MgSO_4$ granule strength attained (207g) was achieved when this aspect was incorporated into the method. Dissolving the agent also reduced error in judging the mix water content and achieved a maximum concentration of the granulation agent in the liquid phase of the mix.

(b) Effect of moisture content

Sufficient water was added to obtain a thick slurry, the amount being dependent on the phosphate rock. The slurry was thick enough to flow but was not completly saturated, although this amount of water necessitated a drying step before granulation. Less water than this amount in the mix appeared to consistently reduce the final strength of the granules. For instance the strength of both types of granules decreased by 60g when the amount of water added to a North Carolina mix was decreased from 9mls to 7mls.

(c) Effect of pre-drying

The effect of drying the mix before granulation was found to be based primarily on the effect of the water content of the mix. The mix could be dried by leaving it in the granulation drum for an extended period or by oven drying. Changing the temperature of the pre-granulation drying did not appear to affect the final granule strength, for example, a run which compared pre-drying a MgSO4 mix in an oven at 80oC while leaving the mix in the granulation drum for an extended period, caused no difference in granule strength. However, differences in granule strength were found when both citric acid and MgSO4 mixes were dried for different periods of time. In general, no pre-drying or a very short (e.g. 2 min) pre-drying resulted in little or no granulation because the mix would not form granules and could not a hold shape when cut through a sieve. A moderate amount of drying (10 to 30 min) was found to produce a manageable mix and no loss of granule strength, but the exact time necessary varied with the amount of water in the original mix, and the drying temperature. Extended drying severely reduced the final granule strength, even when the mix was rewetted during granulation.

The best measure of the correct amount of pre-drying was found to be a physical assessment of the amount of water remaining in the mix, where the surface of the slurried mix was pressed down after drying to see if any water moved to the surface. When there was no longer free water in the mix the water content was optimal for granulation.

(d) Cutting out

After pre-drying the mix was "stiff" enough to hold a shape when pressed through a sieve. A sieve aperture of 0.710mm was found to give a higher yield of 0.5-1mm granules than a sieve aperture of 1mm. Cutting through 0.5mm mesh could not produce the discrete "strings" of material suitable for granulation which were formed by the larger sieve sizes. Transferring intact "strings" into the granulation drum proved quite difficult and waste of mix on the sieve was high, but cutting the mix was found to be the only way to separate the mix after pre-drying into clumps of particles small enough to form the mini-granules, especially if the phosphate rock used in the mix had been ground. Mixes of ground phosphate rocks were often recut and regranulated after an initial cut and granulation in order to attain the required granule size.

(e) Granulation

A short period of granulation (30 sec.) at high speed proved the most efficient. Longer periods in the drum (2-5 min) dried out the granules and lowered the final strength by 30 to 100g. The granlation speed was the fastest which could be acheived and still allow the granules to fall instead of circulating around the perimeter of the drum. The cut mix was kept from adhering to the sides of the drum and the granules kept in motion using a stream of compressed air. This was found to be more efficient than using a spatula, which tended to compress the mix and create larger granules. The drum speed was dependent on the mix being granulated, with the minimum speed being for NCAR granulated with citric acid (102rpm) and the maximum for AradWG granulated with the citric acid:$MgSO_4$ mix (150rpm).

After granulation the granules were shaken through a 1mm sieve and transferred to an oven for drying. Oversize granules could be recut and regranulated but this was found to lower granule strength, for example from 173g to 65g in one MgSO4 run.

(f) Effect of final drying

The temperature for the final drying of the granules was found to have an important effect on the final granule strength. Drying the granules at room temperature reduced granule strength considerably (about 100g) and the granules became powdery. Extended drying at 105°C was found make the citric acid granules brittle and of low strength, while MgSO4 granules often developed a salt-ike coating which was associated with a loss of strength. Drying at between 75°C and 85°C for approximately 45 min was found to provide the best compromise.

6.4.4 Secondary trials using citric acid as a granulation agent

After refining a successful method of granulating the phosphate rock, the source of citric acid which had been in use as a granulation agent ran out. When a new source of citric acid was used as a granulation agent it was found that the mix was uncharacteristically sticky and very difficult to handle. The granules which were made were found to be weak and went soft when exposed to the air after the final drying. At this point several other brands of citric acid were tried out, all with similar results and it was surmised that the original source of citric acid, which was evidently fairly old, had been contaminated in some fashion.

A variety of other citric salts (eg. ammonium and sodium citrates) were then trialed as granulation agents (Table 6.3). It was found that while the stickiness of the mix was reduced, the granules still went soft after drying. Finally, various mixtures of critic acid and neutral salts were tested (Table 6.3), giving results which were closer to those from the original citric acid (results for the original are repeated at the start of table 6.3). Eventually a granulation agent was found which gave even better results than the original citric acid, although the granules still tended to soften somewhat after drying.

Table 6.3 Granulation results using "as received" North Carolina phosphate rock and the full granulation method as stated in section 6.3.3. The average crushing strength of individual granules and comments are given where relevant.

Granulation agent (%w/w)	Strength (g)	Comments
10% Citric acid :	459	Mix easy to granulate and a good yield of mini-granules.
10% Citric acid : [New source, May & Baker brand]		Mix very sticky after pre-drying, very difficult to granulate.
7.8% Citric acid: M&B	151	No improvement with slightly less acid.
5% Citric acid: M&B	296	Granule strength very variable.
10% Citric acid: Sigma	36	Very sticky mix so difficult to granulate.
10% Citric acid: Empire [Old household type]	319	Mix not so sticky.
10% Citric acid: BDH	108	Easiest to granulate of new citric acid sources. Strength up to 241g in second batch.
10% Diammonium citrate	392	Good small granule formation. Mix did not go sticky after pre-drying but granules went soft after drying.
10% Triammonium citrate	332	Same effects as diammonium citrate.
10% Trisodium citrate	477	Granules alternated between soft and hard.
13% mix of 1:0.2 Citric acid & KCL	226	Mix sticky but not too bad. Granules went sticky when exposed to air but hardened when redried.

Table 6.3 continued;

Granulation agent (%w/w)	Strength (g)	Comments
18% mix of 1:0.6 Citric acid & $MgSO_4$	595	Mix not sticky. After drying granules exposed to air were no longer brittle but were still strong (approx. 300g). Granules kept in sealed containers did not lose any strength.
17% mix of 1:0.5 Citric acid & $MgSO_4$	-	Granules rather sticky at granulation and went soft very quickly after drying.
19% mix of 1:0.75 Citric acid & $MgSO_4$	658	Granules still went soft but a lot slower than 40% mix. Strength down to 400g and softer over three days.
22% mix of 1:1 Citric acid & $MgSO_4$	443	Granules did not go soft.
10% mix of 1:1 Citric acid & $MgSO_4$	483	Granules did not go soft.
10% mix of 1:0.6 Citric acid & $MgSO_4$	798	Mix easy to granulate, Granules very hard and did not go soft if not sealed.

The final granulation agent of a 1:0.6 w/w mixture of citric acid and magnesium sulphate, using a 10% w/w mixture of granulation agent and phosphate rock was chosen, to produce mini-granules for a glasshouse experiment.

6.5 Characterization of the granulated materials

6.5.1 Effect of citric acid as a granulation agent

It was suggested that the presence of the citric acid in granules of phosphate rock might have some advantageous influence on the dissolution of the phosphate rock. The phosphate solubilising properties of citric acid on di- and tricalcium phosphates have been demonstrated by Johnston (1952).

The content of water soluble phosphate was tested for granules of works ground and "as received" North Carolina phosphate rock, where the granulation agent was the original older citric acid, without additives. A small amount of water soluble phosphate in the granules was found (Table 6.4).

Table 6.4 Extraction of water soluble phosphate from fertilisers granulated with 10% 1:0.6 mix of citric acid and $MgSO_4$.[1] (Average coefficient of variation 2.3%)

Granulated material	%Pw/w	%P,of total P
North Carolina AR	0.19	1.57
North Carolina WG	0.15	1.15
Sechura AR	0.18	1.49

[1] Analysis by P. Phommasone, FLRC.

The pH of a 2/5 w/v mixture of fertiliser and water was found to be 3.28 for citric acid granules as compared to 7.5 for plain phosphate rock and 3.2 for a sample of superphosphate. The water soluble phosphate content of these same citric acid granules was found to be approximately 4% of the total phosphate, as compared with 0.02% in the parent material.

These results suggest that some acidulation of the phosphate rock occurred either during granulation or when water was added to the granules during the tests. The acidulation effect may enhance the dissolution of the granules and improve their agronomic performance.

6.5.2 Stability to water

The stability to water of "as received" North Carolina PR granulated with either $MgSO_4$ or the citric acid/$MgSO_4$ mix was examined by spraying a small sample of the granules with water. The citric acid-$MgSO_4$ granules were found to collapse immediately upon the addition of water. The $MgSO_4$ granules began breaking down as soon as water was added, but took some minutes to collapse completely.

6.5.3 Effect on granulation of different phosphate rocks

"As received" North Carolina, Sechura and Arad phosphate rocks and works ground North Carolina and Arad phosphate rocks were mini-granulated with either $MgSO_4$ or the citric acid/$MgSO_4$ mix (Table 6.5). Particle size analysis of the parent materials is presented in table 4.1, and formic solubility in table 4.2.

The granulation method developed was found to be specific to NCAR, so that the strength of granules made using other materials was considerably lower. The binder content of the granules was found to be quite variable. The average binder content of the granules was 12%, which may indicate that the content of binder tended to be slightly concentrated by the granulation process, or that extra water was taken up by the granules after granulation. The formic solubility of the materials was increased, in proportion to the amount of binder in the granules, although this was probably an artifact of the weight for volume basis of the test, which would not compensate for the diluting effects of the binder.

Table 6.5 Analysis of the strength, total phosphate content, binder content (derived from the total phosphate content) and solubilty in formic acid (30 minutes) of a range of granulated materials.

Granulated Material	Strength (g)	Total P[1] %w/w	binder %w/w	Formic acid[1] % of total P
NCAR + 10% $MgSO_4$.	109	10.58	19.2	67.1
NCWG + 10% $MgSO_4$.	203	10.70	18.3	85.1
AradAR + 10% $MgSO_4$.	102	13.80	5.5	45.14
AradWG + 10% $MgSO_4$.	114	12.74	12.7	54.1
SAR + 10% $MgSO_4$	43	11.56	13.8	64.01
1:0.6 mix of citric acid and				
$MgSO_4$ granulating:NCAR	798	12.08	7.8	56.7
NCWG	380	10.93	16.6	80.3
SAR	86	12.10	9.0	60.8
Average coefficient of variation		2.9%		1.4%

[1] Analysis by P. Phommasone, FLRC.

6.6 Conclusions

The granulation of reactive phosphate rocks is a desirable method of overcoming handling and spreading problems but will reduce the w/w phosphate content of the fertiliser. Desirable granulation agents will increase the agronomic performance of the phosphate rock to compensate for the reduced analysis.

From testing a wide range of neutral salt and organic and mineral acid granulation agents the best granulation agent for the efficient production of strong mini-granules (0.5-1mm diameter) was found to be a mixture of citric acid and magnesium sulphate. The use of an organic acid in association with the reactive phosphate rock may increase the dissolution of the phosphate rock in soil. In order to provide a comparison with the effects on agronomic availability of granulating with an organic acid, magnesium sulphate was also extensively tested as a granulation agent.

A technique of mini-granulation using these two granulation agents was refined and it was found that the small granule size requirement necessitated two drying steps and also a cutting step which reduced the yield and the speed of the process, compared to more conventional methods of spraying water on a dry mix of rock and granulation agent whilst granulating.

The temperature and moisture content of the granules at the commencement of the final drying step were found to be important factors controlling the strength of the granules confirmimg the work of Carmon (1978). The strength and yield of the mini-granules was also influenced by the type and particle size distribution of the phosphate rock used for granulation.

CHAPTER 7: GLASSHOUSE EXPERIMENT

7.1 Introduction

In this experiment the agronomic performance of the phosphate rock materials characterised in Chapter 4 were evaluated in a glasshouse pot trial. The effects of grinding and granulation on the agronomic performance of phosphate rocks was further examined after a preliminary experiment (Chapter 5) established that very finely grinding caused no increase in the agronomic performance of commercially ground North Carolina phosphate rock and that mini-granulation (granule diameter 0.5-1mm) caused no reduction in the agronomic performance of very finely ground North Carolina phosphate rock. The isotopic technique utilised in the field experiment was re-evaluated and as well as a new isotopic technique.

The specific objectives of this experiment were:

1. To further evaluate the effects of grinding on the agronomic performance of phosphate rock.

2. To test the agronomic performance of mini-granulated phosphate rock under conditions of a yield uptake response to phosphate fertiliser, using a variety of phosphate rock materials.

3. To examine any effects that granulation agent might have on the agronomic performance of mini-granules.

4. To examine the agronomic performance of "as received" White Youssafia phosphate rock, which has not previously been evaluated, relative to "as received" North Carolina, Sechura, and Arad phosphate rocks.

5. To re-evaluate the inverse isotopic dilution technique, as utilised in the field experiment (Chapter 5), under conditions of a plant yield response to fertiliser.

6. To investigate what information might be obtainable from the technique of labelling the surface of phosphate rock materials with a phosphate radioisotope.

7.2 Materials and methods

7.2.1 Glasshouse trial preparation and maintenance

The soil used in these experiments was collected from a position adjacent to the field site described in section 3.4 of chapter 3. After removal of the pasture turf, the top ten to fifteen cm of soil was transferred to a drying room, and dried to 7.4% gravimetric water content. The soil was sieved to less than 7mm particle size to remove concretions and roots etc. and mix the soil.

After further drying the soil was potted into black polythene bags (size PB5) with 2.00kg soil per bag and 400mls of distilled water was applied to all pots. Seeds (100 to 120) of "Nui" perennial ryegrass were mixed with 10g of soil (seived to <2mm), which was spread over the surface of the pots, and then covered with a further 30g of <2mm soil.

Two weeks after sowing, the plants were thinned to twenty one plants per pot. Three weeks after sowing a weekly application of 50mls of nutrient solution was commenced, to supply 0.026g K, 0.0023g S and 0.019g N as KNO_3, NH_4NO_3 and $MgSO_4$, plus trace elements to each pot. Most applications of nutrient solution were made using a mist spray. Four weeks after sowing 1mg of phosphate as KH_2PO_4 was applied to each pot to prevent a phosphate deficiency hindering plant establishment. Applications of fungicide ("Benlate") were made at approximately monthly intervals once the plants were established and fortnightly applications of pestcide ("Vapona") were commenced when some plants were found to be infected with thrips at about 10 weeks after fertiliser application.

All pots were maintained at a target water content of 75 to 80% of field capacity. "Field capacity" was measured by saturating two pots and leaving them to drain overnight on newspaper. The difference between the saturated weight and the approximate oven dry weight of the soil was taken as a measure of the field capacity. This calculated water content was confirmed in the later stages of the experiment by oven drying soil from a pot. Water applications were made to the pots in approximately three day cycles and were made by placing the pots on a balance and spraying the pots with distilled water until the target weight was reached. The surface of the pot was allowed to dry between watering events. Surface spraying was felt to be a better approximation of field conditions than maintaining a constant source of water in the tray under each pot.

Optimum growth of perennial ryegrass plants is maintained by irradiance levels of over 100W/m^2 (approximately the photosynthetic radiation level expected near Palmerston North on a late winter/early spring day) and temperatures of 20°C. Approximately 35°C is the highest temperature tolerated by perennial ryegrass (Hunt and Field, 1979). In this trial the minimum temperature was 0°C and the maximum was 30°C. The usual diurnal temperature range was between 5 and 25°C. During the winter months of the trial, before fertiliser was applied, the natural light was supplemented by 2 hours of extra light in the evening. Shade paint was applied to the glasshouse in the very latter stages of the trial. The trolleys on which the pots stood were regularly moved around the glasshouse, and the position of the pots on the trolleys was changed at every harvest and when the water content was checked.

During the experiment the herbage on the pots was harvested three times before fertiliser was applied, at approximately two months, three and a half months, and four months after the seed was sown. Over the three harvests 1.2g to 1.7g was removed from each pot and the average coefficient of variation of dry matter yield from all pots at each harvest was 17.5%. Fertiliser was applied after the third harvest.

7.2.2 Fertiliser treatments

A comprehensive list of all treatments applied to pots in the glasshouse experiment may be found in appendix 1. In all forty three treatments (trts) were applied, with four replicates of each treatment.

(a) Phosphate rock treatments

North Carolina, Sechura, Arad and White Youssafia phosphate rocks were used in this experiment. All the phosphate rocks were applied in the "as received" form (trts: 20, 26, 31, 34) and ground forms of the Arad and North Carolina PRs were also applied (trts: 3, 6, 25, 26). Most of these materials were also applied as mini-granules (0.5-1mm diameter), using $MgSO_4$ (trts: 7, 10, 12, 21, 22, 23, 27, 29, 30, 32, 33) or a 1:0.6 mix of citric acid and $MgSO_4$. Details of the physical and chemical characteristics of these materials may be found in Chapters 4 and 6.

Works ground North Carolina phosphate rock was also applied in two further forms.

One form was (trt. 14) a factory granulated partially acidulated material called "Hyphos", which was obtained from the Ravensdown fertiliser co-op ltd. This material contained 14.2% total phosphate (w/w), 5.65% water soluble phosphate (w/w), and 8.79% citric soluble phosphate, (Analysis by P Phommasone, FLRC).

The second form was works ground North Carolina phosphate rock granulated with tallow. An 80:20 w/w mixture of works ground NCPR and food grade dripping was melted together until boiling and then pushed into a mould and cooled until hard. The resulting granules were pill shaped, approximately 4mm in diameter and 1.5mm thick.

All the fertilisers were applied to the pots at the same rate as used in the field experiment, 60 kgP/ha (106 mgP/pot). Works ground NCPR was also applied at four different rates of 10, 20, 40, and 80 kgP/ha (trts: 16, 17, 18, 19). A treatment of mono-calcium-phosphate (MCP) was also included, applied at a rate of 60kgP/ha (trt. 43).

(b) Labelling phosphate rock with P^{32}

Phosphate rocks were surface labelled by spraying a solution of labelled phosphate over the surface of the material before granulation or direct application to the pots. The solution contained 0.0012µgP per microcurie of P^{32}, so was regarded as carrier free. A 1ml syringe with a crimped needle, was used to apply the fine mist spray. The phosphate rock was turned after each milliliter of solution had been applied. When all the solution had been applied the fertiliser was sealed into a canister and shaken overnight and then oven dried. Labelled phosphate rock, which was to be applied as granules, was granulated after the phosphate rock had been labelled. The amount of solution sprayed over the phosphate rock was calculated to provide 18.11 µCi of P^{32} per pot (0.17 μCiP^{32} /mgP^{31}). The only treatments where 18.11 µCi/pot was not applied was when NCWG was applied at rates other than 60 kgP/ha. These treatments were all labelled so that the NCWG had the same specific activity as the NCWG applied at 60kgP/ha, so that the amount of P^{32} applied per pot was proportional to the amount of phosphate rock applied.

Labelled (P^{32}) and unlabelled phosphate rock treatments are shown in appendix 1. Treatments 21 and 22 were used to provide a comparison of the effects of surface labelling on the agronomic value of the fertilisers.

(c) Controls for the surface labelling technique

Several rates (0, 5, 10 and 20 mgP per pot) of water soluble phosphate (K_2HPO_4) were also applied (trts: 35 to 42). These were expected to provide a response curve relating yield, or phosphate uptake to the amount of water soluble phosphate derived from the fertiliser. The relative agronomic values of the phosphate rocks could be assessed using this curve.

Each amount of K_2HPO_4 was labelled with the same amount of P^{32} per pot as was applied to the phosphate rock treatments. The objective was to estimate the size of the plant available pool and the specific activity of the plant when the pool was incremented by a known amount of water soluble phosphate. The specific activity of herbage from these pots could then be compared with the results obtained from the phosphate rock treatments, in attempt to gauge the amount of phosphate rock dissolution.

The K_2HPO_4 treatments were applied using 1.92g of chromite per pot. The chromite was employed as a relatively inert carrier, the amount used having roughly the same surface area as the amount of North Carolina phosphate rock applied to each pot. The particle size of the chromite was very similar to that of the NCAR (table 7.1). The P^{32} was sprayed over the surface of the chromite in the same way used for labelling the phosphate rocks with P^{32}. The labelled material was then shaken overnight and then the appropriate amount of K_2HPO_4 was sprayed over different subsamples before drying.

Table 7.1 Particle size analysis of the chromite.The results are expressed as a percentage of the total amount of material recovered from the sieves by a dry brushing method (see methods section 3.1.1).

PARTICLE SIZE (μm)	% not passing sieve
>1000	-
>500	2.5
>250	42
>150	39
>75	16
>42	0.4
<42	-

All pots (except treatment 39) received $MgSO_4$ in amounts equivalent to that contained in the $MgSO_4$ granulated treatments (no.s 10, 11, 12 etc.). In order to check the effects of the $MgSO_4$ on the plant growth response, no $MgSO_4$ was added to treatment 39, which was an extra 5mgP K_2HPO_4 treatment. Another K_2HPO_4 treatment (also 5mgP) with the same objective was also included, where the same amount of the citric acid /$MgSO_4$ was applied as found in the phosphate rock treatments granulated with this mix (treatment 40).

(d) Inverse isotopic dilution

The inverse isotopic dilution technique was repeated using glass house studies because the earlier field trial (Chapter 5) did not provide unequivocal evidence that this was a useful technique for studying phosphate rock dissolution in field soils. The advantages of the glass house trial over the field trial were expected to be a reduced variability between the replicates and to facilitate conditions which would result in a dry matter response to the presence of phosphate fertiliser. It was predicted that the inverse isotopic method might only provide useful information under conditions of a growth response to the phosphate fertiliser (Appendix 4).

The pots used in this experiment received the same preparatory treatment as that outlined above for pots used in the main experiment (7.2.1), except that galvinised tin cylinders were placed around pots when the soil was bagged. These cylinders were the same as those used in the field trial (Chapter 5), and the pots were of sufficient depth to fill the cylinders with soil, giving an approximation of the volume of the *in situ* field cores.

On the same day that fertiliser was applied to all other experimental pots the pots used in the inverse isotopic dilution technique were injected between 1 and 5cm depth (see methods 3.3.2 for details), with approximately 5mls of solution, containing 250.5µCi of P^{32} and 3.99µg of P^{31}. After injection fertiliser was applied.

Five different fertiliser treatments were applied to the injected pots. Finely ground (NCFG) and works ground (NCWG) North Carolina phosphate rocks were applied (trts. 25 and 6) and granules of the works ground material, made with 10% $MgSO_4$ (trt. 13) were the main fertiliser treatments. The other two treatments were an unfertilised control (trt. 1) and granules of "as received" North Carolina phosphate rock (trt. 24) made using the original contaminated source of citric acid (see chapter 6, section 6.4.4).

7.2.3 Harvesting of herbage and soil sampling

After the fertiliser was applied seven further herbage harvests were taken (see table 7.2 for details) at approximately two week intervals. At each harvest herbage was trimmed to one cm above the top leaf axil, using scissors.

Table 7.2 Dates and intervals of harvesting pot herbage, after the fertiliser application on 25/8/88.

Harvest No.	Date	Time since fertiliser was applied: days	approximate weeks
1	4/9/88	11	1.5
2	15/9/88	21	3
3	30/9/88	37	5
4	14/10/88	50	7
5	2/11/88	69	10
6	18/11/88	85	12
7	5/12/88	102	14.5

After cutting, the herbage was bagged and dried overnight at 65°C. The entire sample was then removed from the bag and weighed, and then digested (see methods chapter 3.2.2) in preparation for the analysis of P^{32} and P^{31} (see methods chapter 3.2.3 and 3.3.3).

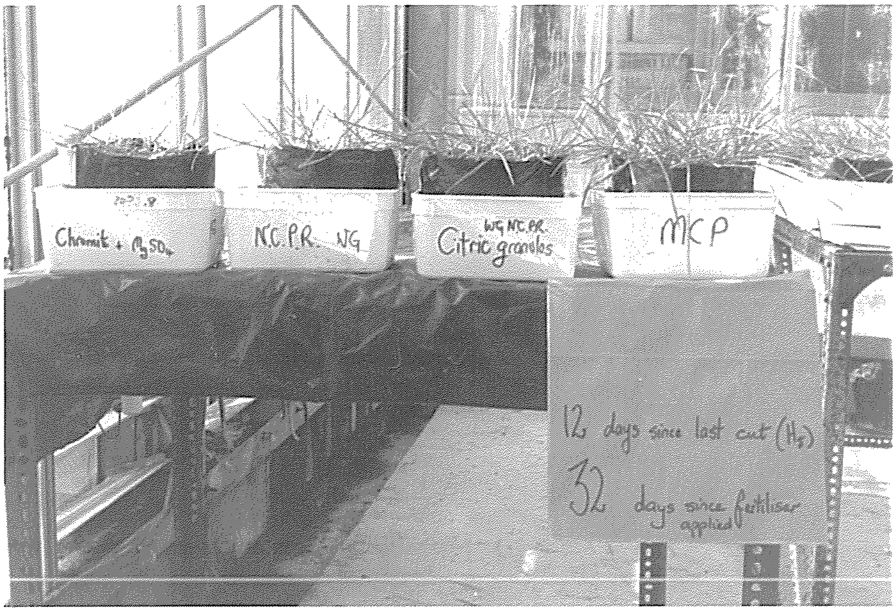


Figure 7.1: Selected experimental pots from the glass house experiment demonstrating the plant response after 12 days growth to various fertilisers. The fertiliser treatments applied the pots 32 days previously were (left to right); no phosphate fertiliser, works ground North Carolina phosphate rock, works ground North Carolina phosphate rock mini-granulated with a mixture of citric acid and $MgSO_4$, and monocalcium phosphate. The pot type for these treatments was "surface labelled" and the surface of the fertilisers applied to these pots (except MCP) was labelled with P^{32}.

Figure 7.2: Selected experimental pots from the glasshouse experiment which were used for the inverse isotopic dilution technique. Note the galvinised metal cylinders around the pots. The fertiliser treatments applied to these pots (left to right) were; no fertiliser, work ground North Carolina phosphate rock, and finely ground North Carolina phosphate rock, and had been applied 7 weeks previously. The most recent harvest from these pots had been taken 14 days previously.

In order to follow the fate of the applied fertiliser a selection of treatments were replicated and the soil destructively sampled at four and ten weeks after the fertiliser was applied. The treatments which were sampled were surface labelled NCWG (ungranulated and two granulated forms) and 5 mgP as labelled K_2HPO_4 (trts: 2, 4, 5, 8, 9, 11, 12, 37, 38). The top 1cm of soil, containing the applied fertiliser, was cut off the pot and air dried. The dried soil was pushed through a 1mm sieve to remove roots and concretions and then weighed. Samples of the soil were then sequentially extracted with solutions of 1M NaOH and 1M HCL (details of extraction in the methods chapter, 3.5.4).

Evaluation of the seqential phosphate fractionation procedure

The efficiency of the soil extractions was tested by mixing known quantities of air dry soil (sieved <1mm) and samples of two labelled fertilisers (which were applied to pots in the glasshouse experiment) in similar proportions to soil samples taken from the top 1cm of the experimental pots. The two fertilisers were 5mgP as K_2HPO_4 mixed with chromite, and NCWG granulated with $MgSO_4$. These fertilisers were mixed (by coffee grinder) with soil in proportions of 0.424 g fertiliser /100g soil and 0.402g fertiliser /100g soil respectively. Samples of these mixtures were then extracted in the same manner as the samples taken from the experimental pots (details of extraction in methods chapter, 3.5.4).

7.3 Results and discussion

7.3.1 Dry matter yields produced by the "as received" phosphate rock fertilisers

All pots fertilised with "as received" phosphate rocks (PRs) produced accumulated dry matter yields which were significantly greater than the yield of the unfertilised pots. The accumulated yields from pots fertilised with "as received" Sechura (SAR) and Arad (AradAR) phosphate rocks were similar to one another (2.84-2.81 gdm/pot) and significantly greater ($P<0.05$) than the accumulated yield derived from "as received" North Carolina phosphate rock (NCAR) (2.47g/pot). The yield from pots fertilised with White Youssoufia phosphate rock (YsfAR) (2.62g/pot) was intermediate (accumulated data and least significant differences summarized in Figure 7.3). In general the differences between the accumulated yields produced by these different fertiliser treatments were small. This was a consequence of the similar growth rates of ryegrass over the duration of the experiment on the pots fertilised with the different phosphate rocks (Appendix 2, table 1).

The results are contradictory to the findings of the MAFtech National series of field trials (see literature review, section 2.3.1) which found that generally the performance of NCAR was similar to that of SAR. Formic acid extractions (section 4.3.4), which generally correlate well with agronomic performance, suggested that the expected response from the phosphate rocks would follow the order SAR > NCAR > AradAR > YsfAR. The AradAR performed rather better than might have been predicted and the NCAR not as well as might have been predicted.

Work by Chien (1977b) and Chien and Black (1975 and 1976) found that the extent of substitution of a particular phosphate rock sample was quite variable and that there was usually a small proportion of highly substituted material which was more reactive than the remaining material. The early dissolution of this more soluble material may create an environment which limits the dissolution of the less substituted material. An effect of this nature may also account for the fact that the order of agronomic performance of the "as received" phosphate rocks did not follow the reactivity as found in formic acid.

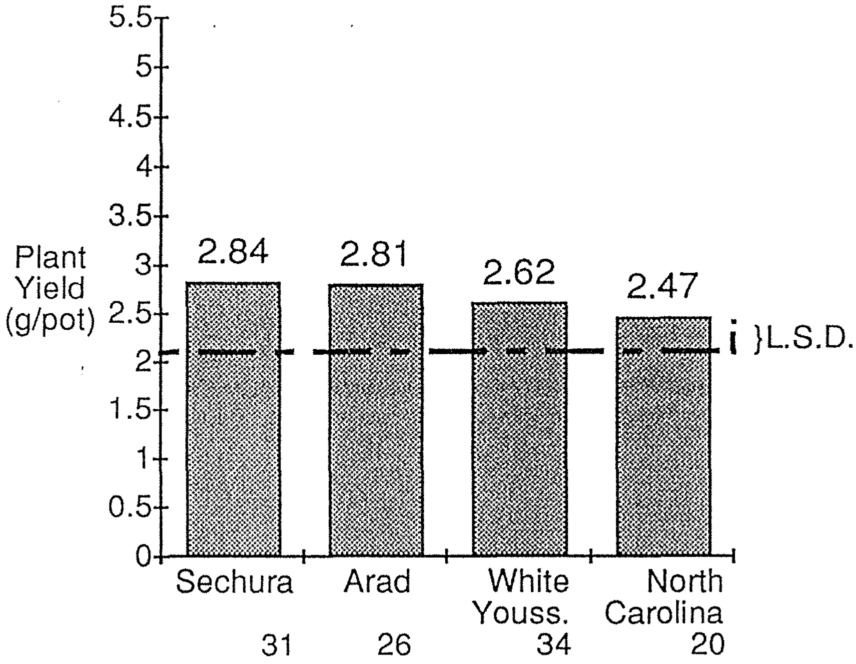


Figure 7.3: The accumulated plant yield (102 days) of ryegrass growing in pots fertilised with various "as received" phosphate rock fertilisers (respectively Sechura, Arad, White Youssafia, North Carolina). The broken line represents the yield of the unfertilised control pots. The number at the base of the chart is the treatment number, referring to appendix 1. L.S.D.=0.31

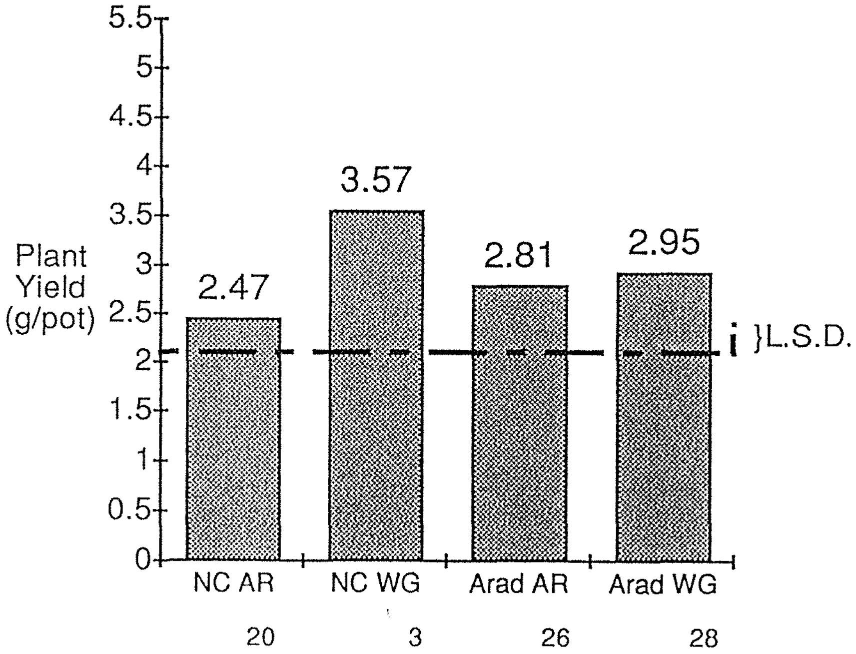


Figure 7.4: The effect of grinding "as received" (AR) North Carolina (NC) and Arad phosphate rock fertilisers to a "works" particle size (WG) on the accumulated yield (102 days) of ryegrass. The broken line represents the yield of the unfertilised control pots. The number at the base of the chart is the treatment number, referring to appendix 1. L.S.D.=0.31

7.3.2 Dry matter yields produced by phosphate rock fertilisers of different particle size

The total accumulated yield from pots fertilised at 60kgP/ha with works ground North Carolina (NCWG) phosphate rock (3.57g/pot) was significantly greater than the yield derived from the NCAR (figure 7.4). This effect was reflected in the significantly higher plant growth rates of pots fertilised with NCWG from five weeks after fertiliser application (Appendix 2, tables 1 and 2).

The accumulated yield from AradAR was 2.81g/pot and that of "works" ground Arad phosphate rock (AradWG) 2.95g/pot, therefore grinding the Arad phosphate rock resulted in no significant change in the plant yield (Figure 7.4). This was despite the fact that the AradWG was ground to achieve a particle size distribution that was similar to the NCWG (see section 4.3.3 for particle size analysis) and that grinding increased the formic solubility of the Arad phosphate rock.

In their ground state, the sequence of agronomic performance of the phosphate rocks was different to that produced by the "as received" materials, where the performance of the AradAR was better than the NCAR. The NCWG performed significantly better than the AradWG and this was the same result as found in the work of Hagin *et al.* (1978), (see section 2.3.1 for details). Unlike the "as received" material, the dry matter production from the works ground materials followed the formic solubility trend (section 4.3.4), where the NCWG was found have a greater solubility than the AradWG.

Although there was an increase in yield between NCAR and NCWG when applied in the surface labelling experiment, in the inverse isotopic dilution experiment the application of a finer grinding of North Carolina phosphate rock (NCFG) compared with NCWG did not increase yield further. No significant differences in plant yield were found between the accumulated yields or the plant growth rates derived from NCWG and NCFG. This was a similar to the result found when the same particle sizes of North Carolina phosphate rock were compared in the field experiment (Chapter 5).

From the discussion in section 2.3 of the literature review, it is clear that provided the rate of application does not cause the zones of dissolution around a phosphate rock particles to overlap very quickly, decreasing the particle size of a phosphate rock should increase plant availability and yield. Whereas grinding the NCAR to NCWG confirmed this effect, there was no increase in yield when AradAR was compared with AradWG or when NCWG was compared with NCFG. The reasons for these contradictory effects are not clear.

7.3.3 Dry matter yields produced by granulated and ungranulated phosphate rocks

The effect of granulating phosphate rocks on plant dry matter yield was variable. Accumulated yield results are presented in figure 7.5-8 and growth rate results for the same treatments are found in Appendix 2.

(a) Granulated "as received" phosphate rocks

There was no significant change in the plant yield produced when SAR was applied as mini-granules (made with $MgSO_4$ or the $MgSO_4$/citric acid mix), or when NCAR was similarly applied in the two granulated forms. All yields from these treatments were significantly greater than yields derived from the unfertilised control. A lower accumulated yield was produced when "as received" Arad phosphate rock was applied as granules bound with $MgSO_4$. The yield from the granulated AradAR was not significantly greater than the yield derived from the unfertilised control pots.

(b) Ground phosphate rocks granulated with $MgSO_4$ and citric acid/$MgSO_4$

NCWG was granulated with either $MgSO_4$ or the citric acid/$MgSO_4$. Both treatments were applied as part of the P^{32} surface labelling experiment and no significant differences were found between accumulated plant yields (Figure 7.7) or plant growth rates (Table 2, Appendix 2) derived from the ungranulated NCWG and the granulated forms.

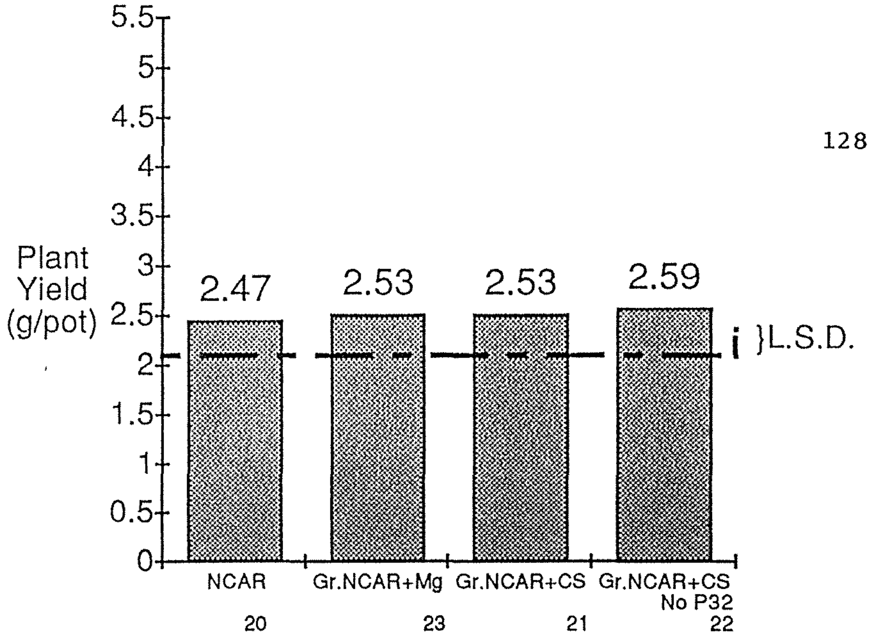


Figure 7.5: The effect of mini-granulating (Gr) "as received" North Carolina phosphate rock (NCAR), with either $MgSO_4$ (Mg) or a citric acid/$MgSO_4$ mixture (CS), on the accumulated yield (102 days) of ryegrass. All treatments were labelled with P^{32} except where stated. The broken line represents the yield of the unfertilised control pots. The number at the base of the chart is the treatment number, referring to appendix 1. L.S.D.=0.27

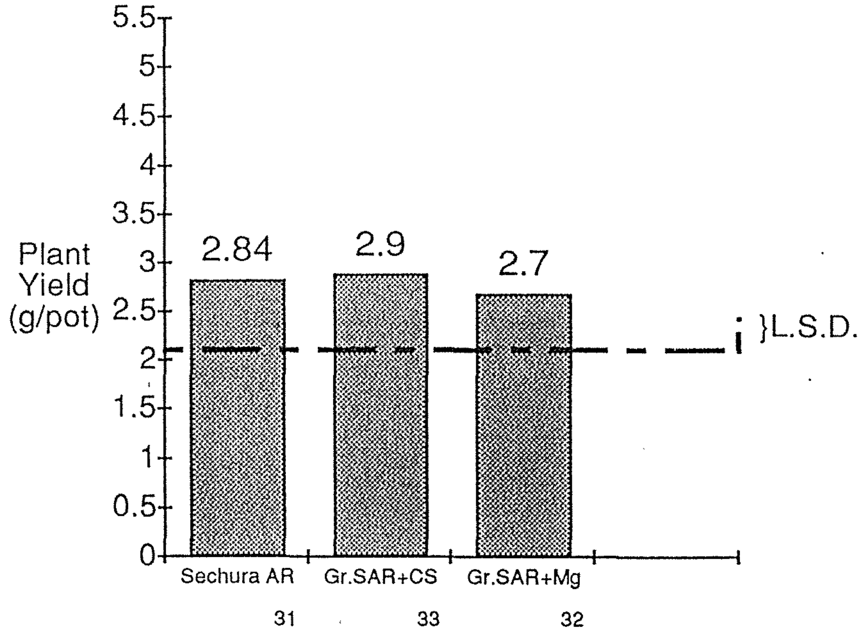


Figure 7.6: The effect of mini-granulating (Gr) "as received" Sechura phosphate rock (SAR), with either a citric acid/$MgSO_4$ mixture (CS), or $MgSO_4$ (Mg), on the accumulated yield (102 days) of ryegrass. The broken line represents the yield of the unfertilised control pots. The number at the base of the chart is the treatment number, referring to appendix 1. L.S.D.=0.33

By contrast, when pots in the inverse isotopic dilution experiment were fertilised with NCWG granulated with $MgSO_4$ the accumulated plant yield was significantly lower than that of the ungranulated material (Figure 7.10). This finding was supported by a significantly lower growth rate (from seven weeks onwards) from pots fertilised with the granulated material (Table 7, Appendix 2). No citric acid/$MgSO_4$ granulated treatment was included in the inverse isotopic dilution experiment.

Plant yield decreases were also observed when AradWG was granulated, with either $MgSO_4$ or a 1:0.6, citric acid:$MgSO_4$ mix. The significant decrease in accumulated yields (Figure 7.8) resulted from lower plant growth rates at the third, fourth and fifth harvests in pots fertilised with either of the granulated materials (Table 4, Appendix 2).

Granulation of the ground materials reduced yields in three of the four treatments. Reasons for the differences in treatment effect when NCWG granulated with $MgSO_4$ was applied on the surface labelled experiment (no reduction in availability) and in the inverse isotopic dilution experiment (a significant reduction in availability) appear to be related to the increased yields obtained from the inverse isotopic dilution pots. Plant yield and phosphate uptake from the ungranulated NCWG was 24% higher in the inverse dilution experiment compared to the same treatment applied to surface labelled pots (Figure 7.11). This provided a significantly greater relative response to the NCWG. Under these conditions the clumped distribution of the granulated material may have limited the availability of the phosphate rock.

Why yields were higher on the injected inverse isotopic dilution pots is unclear but there were physical differences between the pots in the two experiments. Apart from the 20 fine vertical injection holes in the inverse dilution pots, the main physical difference between pots used for the two different isotope treatments, was that galvinised tin cylinders were placed around the inverse isotopic dilution pots. It is suggested that the presence of the cylinders,

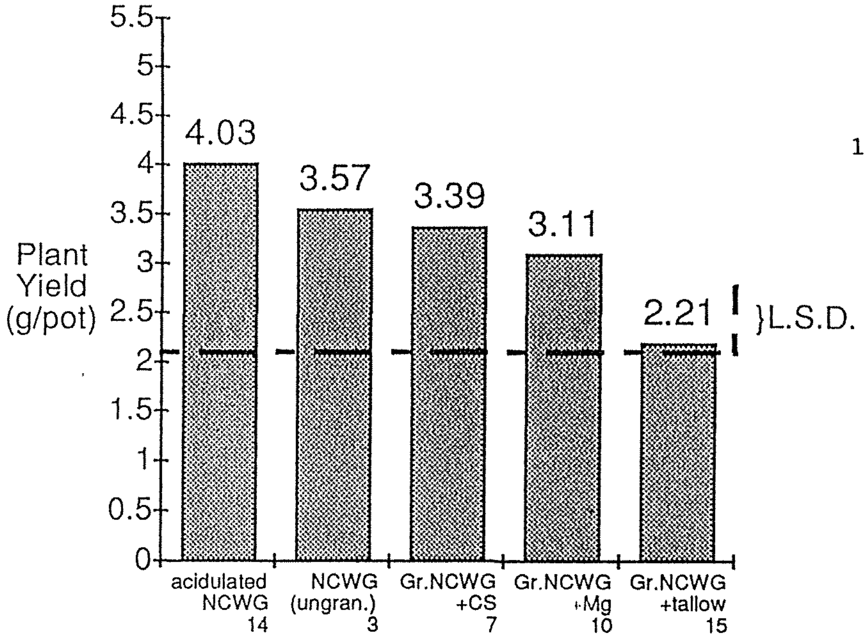


Figure 7.7: The accumulated yield (102 days) of ryegrass grown on pots fertilised with works ground North Carolina phosphate rock (NCWG ungran.), compared with NCWG that had either been partially acidulated, or granulated with either a citric acid/$MgSO_4$ mixture (CS), or $MgSO_4$ (Mg), or tallow. The broken line represents the yield of the unfertilised control pots. The number at the base of the chart is the treatment number, referring to appendix 1. L.S.D.=0.67

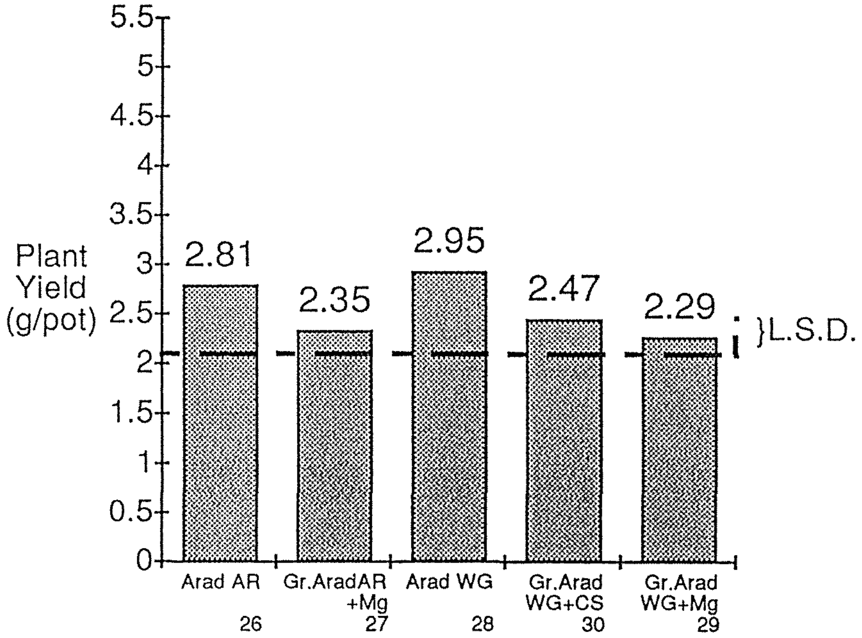


Figure 7.8: The effect of mini-granulating "as received" (AR) and "works" ground (WG) Arad phosphate rock, with either a citric acid/$MgSO_4$ mixture (CS) or $MgSO_4$ (Mg), on the accumulated yield (102 days) of ryegrass. The broken line represents the yield of the unfertilised control pots. The number at the base of the chart is the treatment number, referring to appendix 1. L.S.D.=0.37

covering up the black polythene potting bags, lowered the soil temperatures. Lower soil temperatures during the day, especially during the later stages of the experiment (early summer) probably caused the increased plant growth rate (Hunt and Field, 1979) as well as reducing evapotranspiration rates (pot surfaces were dry for shorter periods of time) and possibly reduced the effects of the root knot nematode infection (see appendix 5). Higher yields also imply a greater root mass and an increased efficiency of phosphate recovery from the soil and the fertiliser.

The increased rate of plant growth was associated with increased phosphate availability from phosphate rock fertiliser. This increase may have been due solely to a more efficient recovery of of the dissolved fertiliser, however an increase in the amount of dissolution may also have occurred. Under these conditions the granulated material was unable to release as much phosphate as the ungranulated material, inter particle interactions apparently limiting the rate of phosphate release.

If the same conclusion is applied to the results from the surface labelled experiment, the clumping effect of granulation was sufficient to limit the availability of the granulated AradWG materials, but did not limit the availability of the granulated NCWG materials. Evidence from treatments where the application rate of NCWG was varied tended to suggest that the availability of the NCWG was depressed to a level which could be sustained by both the granulated and ungranulated materials, but does not explain why this effect occurred only in some treatments.

(c) Ground NCPR granulated with H_2SO_4 and tallow

NCWG was applied as a granulated partially acidulated commercial preparation ("Hyphos"). Yields from pots with this treatment were found to be similar to yields produced from the ungranulated parent material (NCWG) (Figure 7.7).

NCWG was also granulated using tallow and yields from this treatment were lower than the yields derived from the ungranulated NCWG and not significantly different from the unfertilised control pots. These results are presented in figure 7.7 and appendix 2, table 2. The lack of phosphate availability from the tallow granules was surprising in view of results from laboratory incubation of tallow granules on soil. These showed that after 3 days at 28°C that fungus colonies were visible on the surface of the granules, and that after 12 days the tallow was visibly breaking down with hyphae distributed throughout the granule. It was thought that the fatty acid content of the tallow (Liquid Fuels Trust Board, 1982) and additional compounds produced from the degradation of the tallow by fungi and bacteria would possibly assist phosphate rock dissolution. Evidently applying the tallow granules to the surface of the soil provided an environment which was too dry for much fat breakdown to occur since the tallow granules remained visible on the soil surface for the duration of the experiment. It is also possible that any phosphate which was released from the phosphate rock was immediately immobilised by the bacteria and fungi.

Under the conditions of this glasshouse experiment granulation of NCWG by partial acidulation did not reduce agronomic performance of this, but also did not enhance it. More extensive trialing of this material is recommended, under field conditions. Granulation of NCWG with tallow resulted in a reduced agronomic performance and cannot be recommended as a suitable granulation agent.

7.3.4 The effect of granulation agent on dry matter yield

The majority of the granules tested were manufactured using either 10% w/w $MgSO_4$ or a 10% w/w mix of 1:0.6 citric acid and $MgSO_4$ as a granulating agent. Applications to pots of the appropriate amount of the two salts, in the presence of 5mg of water soluble phosphate, resulted in similar plant yields (Figure 7.9). There was also no significant difference between yields of pots fertilised with any one phosphate rock granulated with either of these two granulation agents; although treatments where the citric acid/$MgSO_4$ mix was used as a granulation agent consistently performed better relative to other treatments than plain $MgSO_4$ granulation.

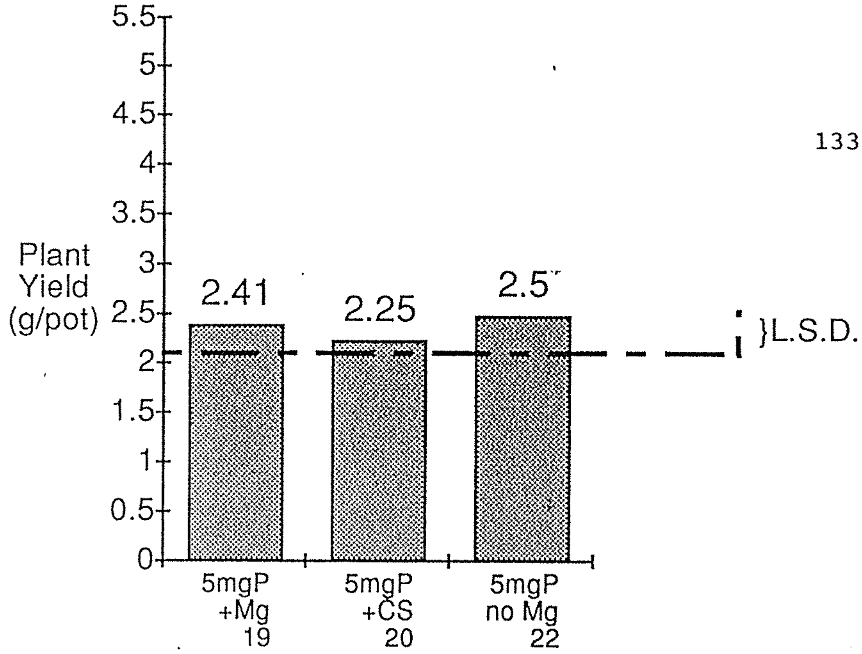


Figure 7.9: The effect of the granulation agents, $MgSO_4$ (Mg) and a citric acid/$MgSO_4$ mixture (CS), on the accumulated yield (102 days) of pots of ryegrass fertilised with K_2HPO_4 (5mg P per pot). The broken line represents the yield of the unfertilised control pots. The number at the base of the chart is the treatment number, referring to appendix 1. L.S.D.=0.40

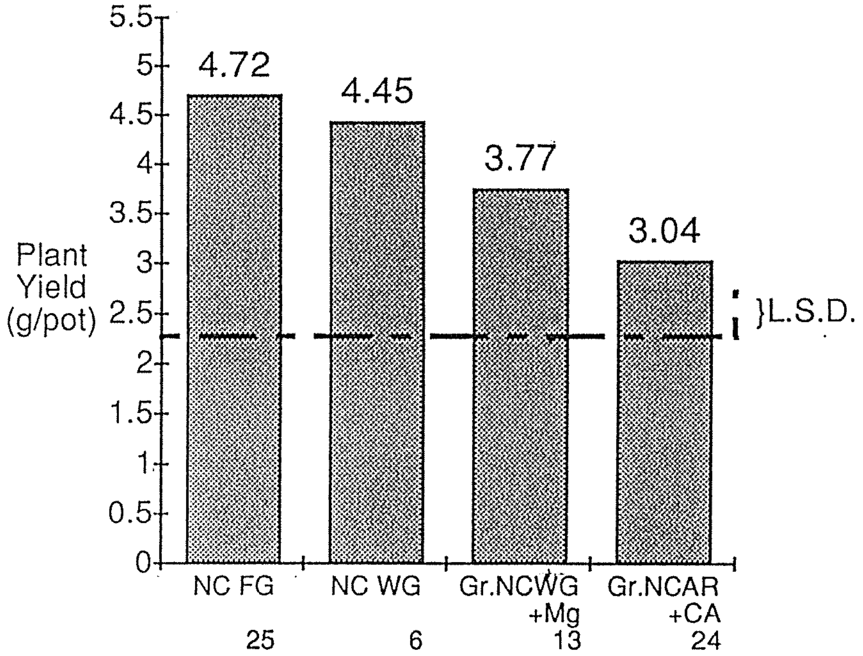


Figure 7.10: The accumulated yield (102 days) of ryegrass in the inverse isotopic dilution experiment, from pots fertilised with finely ground (FG) and works ground (WG) North Carolina phosphate rock (NC), and mini-granules (Gr) of NC WG made with $MgSO_4$ (Mg) and mini-granules of "as received" NC made a contaminated source of citric acid (CA). The broken line represents the yield of the unfertilised control pots. The number at the base of the chart is the treatment number, referring to appendix 1. L.S.D.=0.46

This work generally confirms the conclusion of Gillion *et al.* (1978), that the type of granulation agent may have no significant effect on the availability of phosphate from granulated phosphate rocks. Gillion *et al.* (1978) found that partial acidulation did effect the availability of the material but that effect was not confirmed by the particular product used in this study. The one granulation agent which did affect the availability of granulated NCWG was 20% w/w tallow which reduced the availability of the material.

7.3.5 Dry matter yields produced by different fertiliser application rates

(a) "Works ground" North Carolina phosphate rock

The accumulated yields derived from application rates of 40, 60 and 80 kgP/ha of NCWG (71.1, 106.0 and 141.0 mgP/pot) were not significantly different but were greater than yields obtained from pots with application rates of 10 and 20 kgP/ha (17.9, 35.0 mgP/pot) (see figure 7.12). Plant yields from pots with application rates of 10 and 20 kgP/ha were also not significantly different (see figure 7.12). Similarly there were no significant differences between the ryegrass growth rates produced by the different application rates until the 4th week after fertiliser application. After this time relative differences increased until the best separation of growth rates occured at the final harvest, where the differences in growth rates derived from the various application rates were the same as that obtained from the accumulated results, see (table 3, appendix 2).

The lack of yield response to increasing phosphate rock application rates above 40 kg/ha was perhaps surprising in view of the strong difference found between yields obtained from NCAR and NCWG, and because plant yields obtained from the MCP treatment were higher than the yields obtained from highest rate of application of the phosphate rock (Figure 7.14). These results suggested that the soil environment was conducive to the dissolution of phosphate rocks, and that plant yield was only limited by phosphate availability, but it would appear that the rate of phosphate rock dissolution did not increase when the application rate increased above 40 kgP/ha, suggesting that in fact the soil environment limited the dissolution

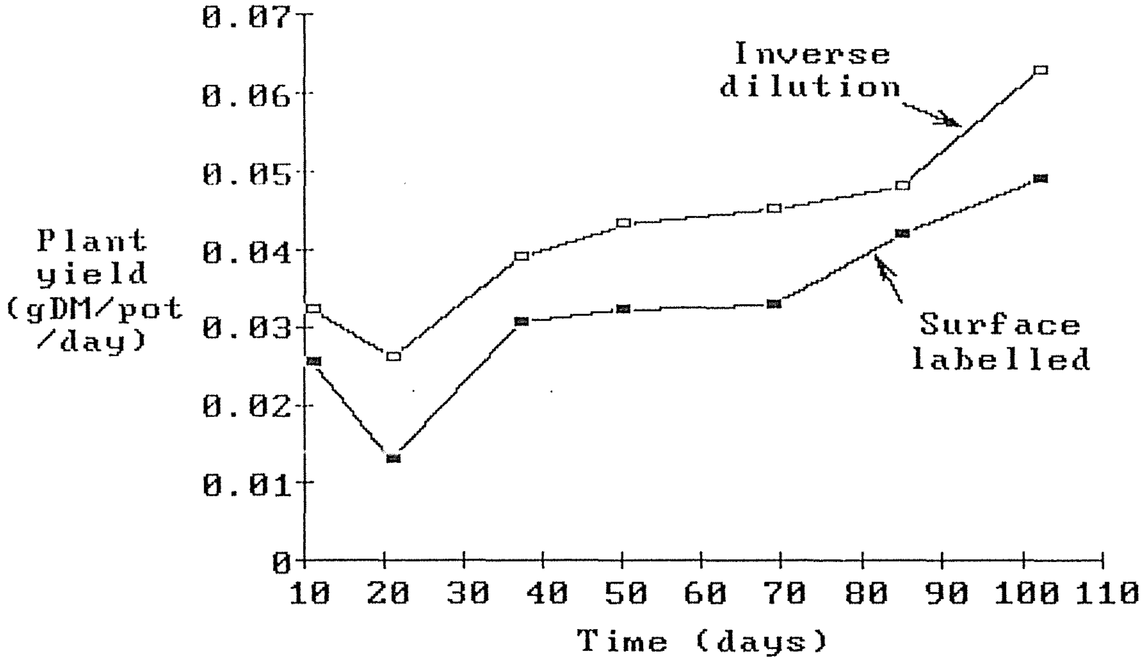


Figure 7.11: The effect of pot type (□ inverse isotopic dilution pots, or ▨, surface labelled treatment pots) on the rate of growth of ryegrass fertilised with works ground North Carolina phosphate rock.

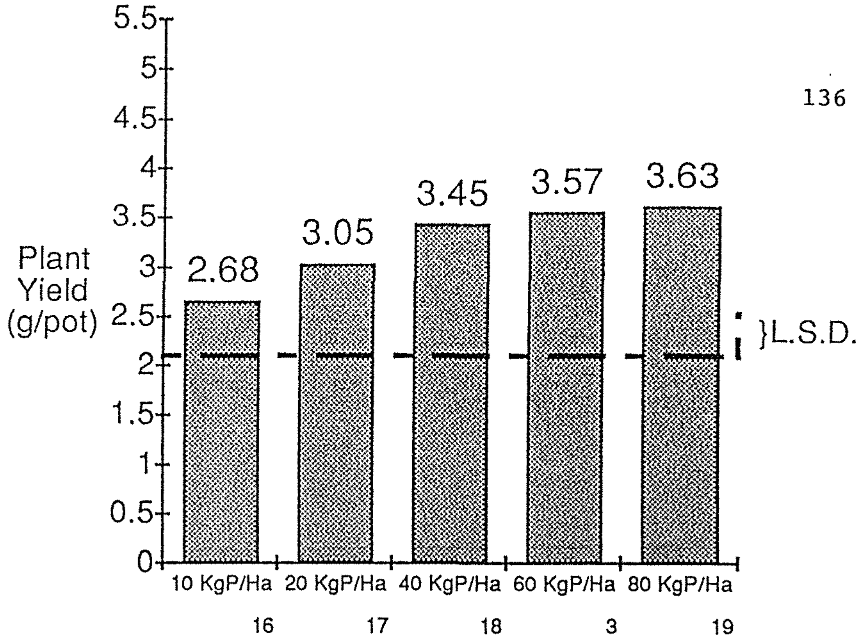


Figure 7.12: The effect of different rates (kgP/ha) of works ground North Carolina phosphate rock fertiliser on the accumulated yield (102 days) of ryegrass. The broken line represents the yield of the unfertilised control pots. The number at the base of the chart is the treatment number, referring to appendix 1. L.S.D.=0.44

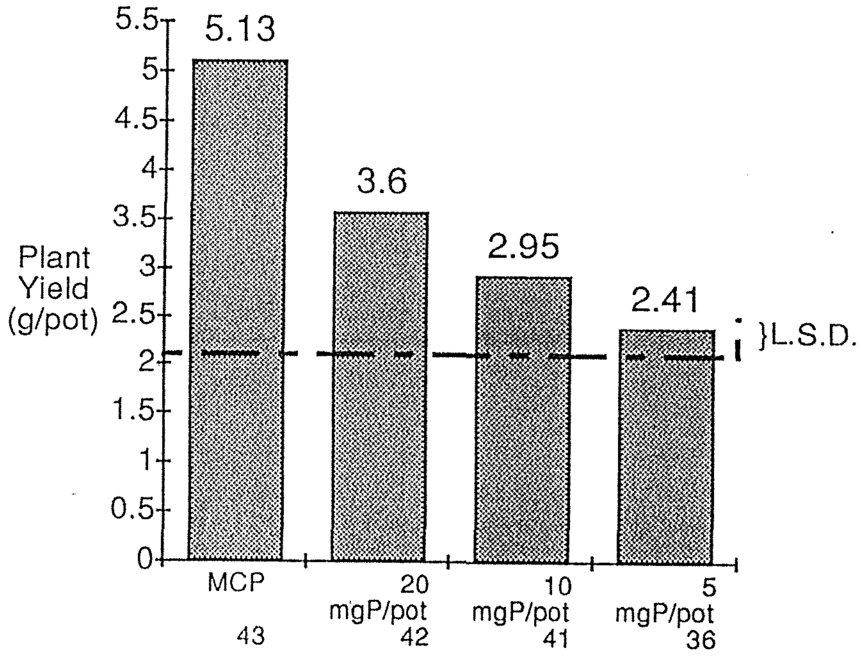


Figure 7.13: The effect of different rates water soluble phosphate (5, 10, 20 mgP/pot as K_2HPO_4) and MCP (106mgP/pot) on the accumulated yield (102 days) of ryegrass. The broken line represents the yield of the unfertilised control pots. The number at the base of the chart is the treatment number, referring to appendix 1. L.S.D.=0.34

of the NCWG. This suggestion was supported by soil fractionation (section 7.3.9) which found that only 4 to 16% of NCWG applied at 60KgP/Ha had dissolved ten weeks after the fertiliser was applied. A visual comparison between the amount of fertiliser dissolved from the NCWG and the amount of phosphate taken up from the K^2HPO^4 (Figure 7.14) suggests that all the phosphate which had dissolved from the phosphate rock was plant available, further supporting a hypothesis that the soil evironment was imposing limitations on the dissolution of the phosphate rock at higher rates of application.

(b) Potassium dihydrogen phosphate and monocalcium phosphate

In contrast to the limited response of plant yield to increasing application rates of NCWG (discussed above), plant yield increased significantly with each addition of KH_2PO_4 above 5mg of phosphate per pot (Figure 7.13 and 7.14). Yields obtained from the unfertilised pots and pots fertilised with 5mgP (as KH_2PO_4) were not significantly different. The accumulated yield from pots where MCP (106 mgP/pot) was applied were significantly greater than all the K_2HPO_4 (5 to 20 mgP/pot) treatments (Figure 7.13).

Differences in the plant growth rates between unfertilised pots and pots fertilised with K_2HPO_4 were most significant between the fourth and seventh weeks and thereafter declined so that none of the plant growth rates were significantly different from the control by the final harvest. In contrast, yield differences between the unfertilised control and pots fertilised with phosphate rocks tended to increase with time. Pots fertilised with MCP did not follow this pattern and maintained a steady growth rate which was significantly higher than that derived from all the other water soluble phosphate treatments from the third week onwards. These results are consistent with the findings in the field experiment (Chapter 6), and in other work (Bolan *etal.* 1990), that phosphate rock based fertilisers exhibit residual agronomic values that increase with time, when compared to water soluble fertilisers. For this reason the phosphate rock treatments in this experiment were not evaluated in terms of their relative agronomic effectiveness.

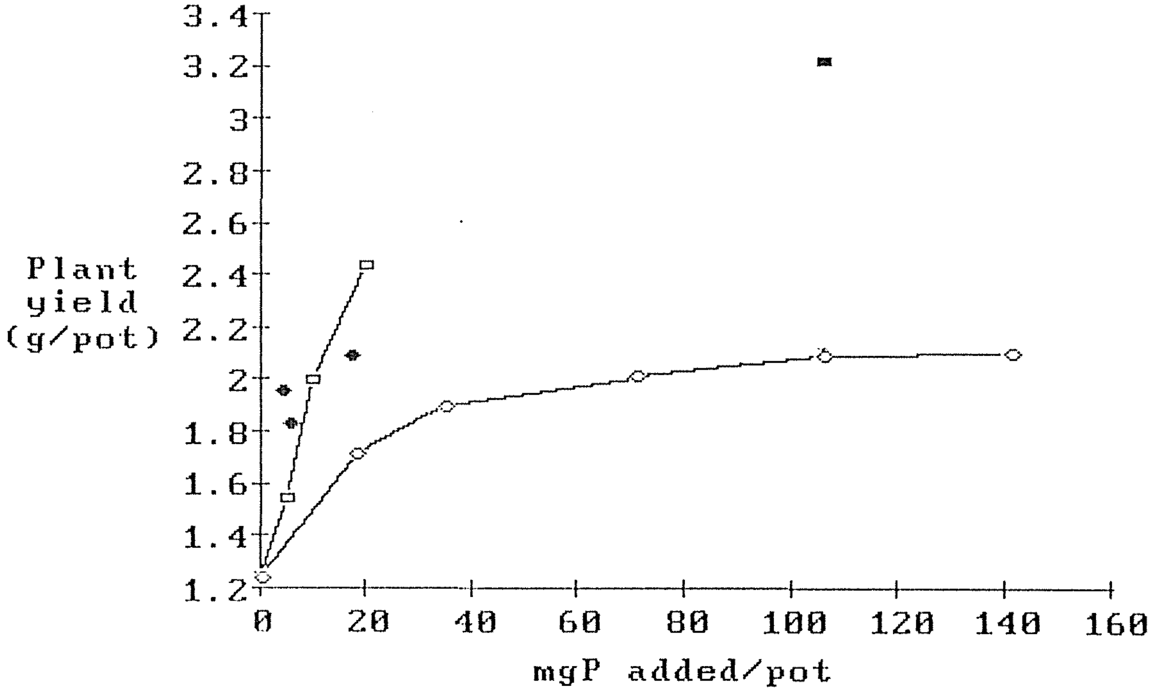


Figure 7.14: Comparison of the accumulated (69 days) plant yield from pots fertilised with different rates of North Carolina phosphate rock (◇), different rates of K_2HPO_4 (□), and also MCP (▩). Also included for comparison are soil fractionation results (taken at 69 days) of the amount of fertiliser which had dissolved from three works ground North Carolina phosphate rock treatments applied at 106mgP/pot (◆).

7.3.6 The effect on dry matter yield of radioactively labelling the surface of the phosphate rock

A comparison of two treatments of NCAR granulated with the citric acid/$MgSO_4$ mix, one of which had been manufactured using surface labelled phosphate rock, found no significant difference between results from the two treatments (Figure 7.5), indicating that surface labelling did not effect phosphate availability.

7.3.7 Herbage phosphate content (P^{31})

The phosphate content of the herbage (P^{31}) at each harvest was consistently more variable between replicates than herbage dry matter yield. The average coefficient of variation for the rate of phosphate uptake per pot per day was 26.5%, which was considerably higher than that of the growth rate in dry matter per day per pot, this being 15.6%. One possible explanation for the high variability of the herbage phosphate data may have been a root knot nematode infection of the plant roots, (see appendix 5 for further details).

At the first harvest (taken 11 days after the fertiliser was applied) the KH_2PO_4 and MCP treatments, the 40, 60 and 80 kgP/ha NCWG treatments and also the "Hyphos" fertiliser treatment were the only treatments that produced herbage phosphate contents which were significantly greater than that of the unfertilised control. This is in contrast to the dry matter production data from the first harvest, which showed that only the pots fertilised with MCP (106mgP/pot) produced significantly more dry matter than the unfertilised control. This effect appears to have been caused by a lag between phosphate uptake and growth response, resulting in a short period of luxury uptake of phosphate.

Except for the MCP and 20mgP/pot KH_2PO_4 treatments, the luxury phosphate uptake effect did not occur at the second harvest, which was taken ten days later. At all subsequent harvests the pattern of the rate of uptake of phosphate was very similar to the growth rate pattern, and the percent phosphate content of the herbage was much the same, for all treatments.

Similar conclusions about the fertiliser treatment effects could therefore be drawn from both the phosphate uptake data and the plant yield results. Thus, because the variability of the phosphate content of the herbage was considerably higher than the plant yield data (possibly due to the effect of a root knot nematode infection, see appendix 5), the conclusions about the treatment effects have been based on the plant yield results discussed in section 7.3.1-6.

7.3.8 P^{32} uptake from surface labelled chromite and phosphate rock

The average coefficient of variation in P^{32} uptake data, across all treatments, was 23%, reflecting a high degree of variability between replicates in the data.

(a) Chromite controls

The accumulated P^{32} uptake from herbage harvested from pots fertilised with chromite and KH_2PO_4 were found to be similar except for the chromite treatment where no phosphate was applied, where P^{32} uptake was always very low relative to the other treatments (Table 7.3, rates of P^{31} and P^{32} in these treatments presented in appendix 3, table 4 and 5). Results like this are common when no carrier phosphate is used because much of the P^{32} appears to be irreversibly adsorbed (absorbed) by the soil surface.

Table 7.3 Accumulated ^{32}P and ^{31}P uptake per pot (ten weeks, 5th harvest) from treatments involving water soluble phosphate added to chromite. MgSO4 (0.0809g/pot) was added to all pots unless otherwise stated.

Treatment	P^{32} (uCi/pot)	P^{31} (mg/pot)
No phosphate	0.21 *a*	3.81*a*
5mg phosphate per pot	2.80 *b*	4.75*b*
5mg phosphate per pot, no $MgSO_4$	2.67 *b*	4.73*b*
5mg phosphate + 0.068g Citric acid per pot	2.39 *b*	4.56*ab*
10mg phosphate per pot	2.75 *b*	5.64*c*
20mg phosphate per pot	2.61 *b*	7.45*d*
*LSD (P=0.05)**	*0.56*	*0.87*

*A common postscript indicates no significant difference between treatments.

Addition of carrier phosphate ensures that solution phosphate is raised sufficiently for some P^{32} to remain exchangeable with the phosphate in solution (Mattingly and Talibudeen, 1960). The addition of 5mg of carrier P^{31} was sufficient to increase P^{32} uptake by the plants. Further increases in carrier P^{31} did not increase P^{32} uptake despite the fact that P^{31} uptake increased.

(b) labelled phosphate rock treatments

P^{32} uptake results from the labelled phosphate rock treatments are presented in table 7.4. The amounts of P^{32} taken up from all surface labelled, "as received" phosphate rock were not significantly different for the first two harvests. At the third harvest (5 weeks), there was an increase in P^{32} uptake from all these treatments and the greatest amount of P^{32} uptake occurred in the Sechura phosphate rock treatment. Lower amounts of P^{32} were taken up from pots fertilised with NCAR and YsfAR phosphate rocks, and the lowest amount of P^{32} was taken up from soil fertilised with AradAR. The order of these results (SAR> YsfAR> NCAR> AradAR) presented an interesting contrast to the order of accumulated herbage phosphate and plant yield results (SAR> AradAR> YsfAR> NCAR) and appears to reflect differences in the proportion of P^{32} which was strongly sorbed (or precipitated) on the phosphate rock surface.

The remainder of the P^{32} uptake results are also presented in table 7.4. The main points are that granulation with soluble salts had no effect on P^{32} uptake from NCWG treatments but caused a small increase in P^{32} uptake when this phosphate rock was in the NCAR form. The reasons for this effect are unclear. The uptake of P^{32} from pots fertilised with NCWG granulated with tallow was slow in comparison to other granulation agents. This result is consistent with the fact that the tallow bound granules were slow to disintegrate on the soil surface. The uptake of P^{32} when different rates of NCWG were applied to pots was found to increase in the same order as the P^{31} uptake, although not in direct proportion. This effect is discussed in section (d).

(c) Interpretation of the P^{31} and P^{32} uptake from the surface labelled materials

Assuming that all P^{32} and K_2HPO_4 applied with chromite was 100% availible for plant uptake, and that the P^{32} uniformly labelled the K_2HPO_4, then the specific activity of the $^{K}{}_2HPO_4$ in the soil would equal the specific activity of phosphate in the herbage which is derived from the K_2HPO_4. This assumption enabled the calculation of the *amount of phosphate in the herbage (at any harvest) (mgP/pot) which was derived from the K_2HPO_4* (PdfK). PdfK was equal to the *amount of ^{32}P in the herbage at that same harvest (μCi/pot) which was derived from the K_2HPO_4* (^{32}PdfK), divided by the *specific activity of the K_2HPO_4 (μCi/mgP) applied to the soil* (^{32}PK/PK). This was developed mathematically as follows;

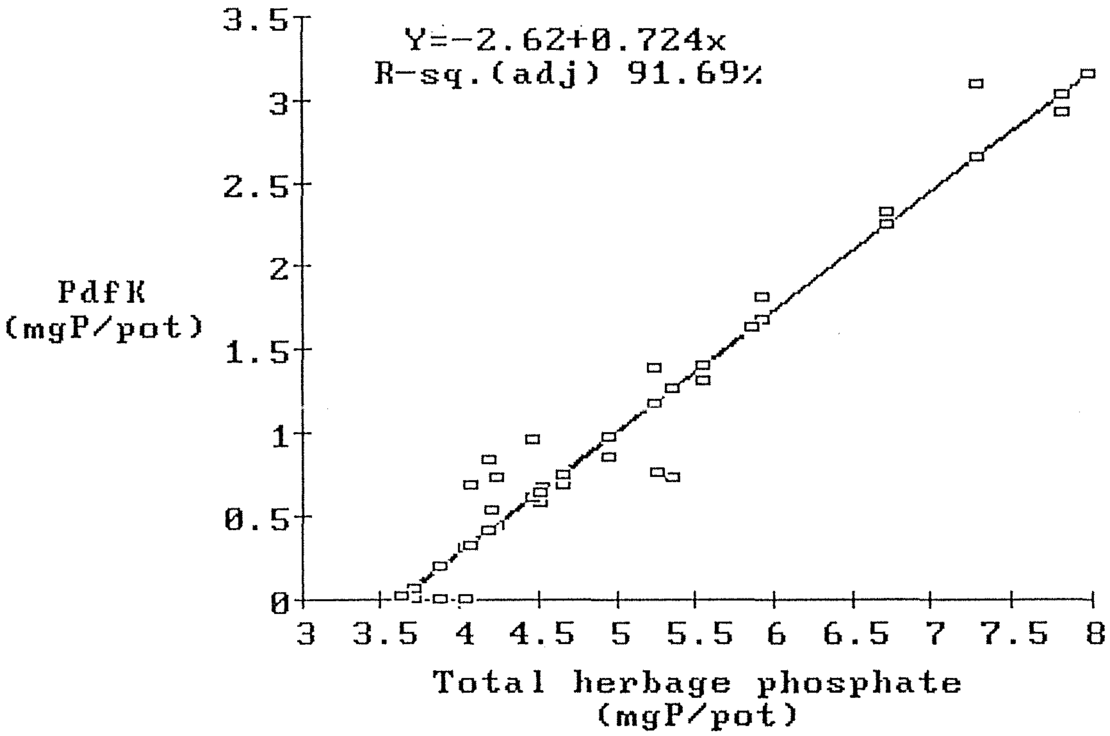


Figure 7.15: The relationship between the phosphate in plant herbage which was derived from labelled K_2HPO_4 fertiliser (PdfK, equation 1) and the accumulated (69 days) herbage phosphate.

$$\frac{^{32}PK}{PK} = \frac{^{32}PdfK}{PdfK}$$

which rearranges to $$PdfK = \frac{PK}{P^{32}K} *P^{32}dfK \qquad (1)$$

The amount of phosphate (mgP/pot) in the herbage which was derived from the K_2HPO_4 (PdfK) was calculated for all treatments involving chromite and K_2HPO_4 using P^{32} and P^{31} uptake data accumulated to the 5th harvest. PdfK was then found to be related to the *total accumulated phosphate (mg/pot) in the herbage* (Pt) by a linear relationship (2) (Figure 7.15):

$$PdfK = -2.62 + 0.72Pt \qquad (2)$$

PdfK was also calculated on a phosphate uptake per day basis and a similar linear relationship with total herbage phosphate was found.

The above relationship (2) may be expressed in more general terms of;

$$PdfK = -A + dPdfK/dPt*Pt \qquad (3)$$

where A is -2.62, the PdfK axis intercept, and dPdfK/dPt is 0.72, the slope of the PdfK:Pt relationship. This relationship may be rearranged to;

$$Pt\ (mgP) = (PdfK + A)(dPt/dPdfK) \qquad (4)$$

If no phosphate was applied then PdfK = 0 and the amount of phosphate in the herbage would be the same as *Pt in the control pots* (defined as **Ptc**, mgP/pot). This was shown as follows;

if PdfK=0 $$Pt = Ptc = A * dPt/dPdfK \qquad (5)$$

which rearranges to

$$A = Ptc * dPdfK/dPt \qquad (6)$$

substituting for A into equation (4)

$$Pt = [PdfK +(Ptc * dPdfK/dPt)](dPt/dPdfK)$$

which rearranged to

$$Pt = PdfK*(dPt/dPdfK) + Ptc \qquad (7)$$

Now dPt/dPdfK was consistantly found to be a fraction that was greater than one so [(dPt/dPdfK) - 1]*PdfK must represent *extra uptake of phosphate (mgP/pot) from the soil* (Pex), the amount of which was found to be proportional to the amount of phosphate taken up from the K_2HPO_4. Equation 7 therefore may be simplified to;

$$\text{Pt} = \text{PdfK} + \text{Ptc} + \text{Pex} \qquad (8)$$

$$\text{where Pex}=[(\text{dPt}/\text{dPdfK}) - 1]*\text{PdfK}$$

This equation described a model of the phosphate uptake by ryegrass where the herbage phosphate is composed of phosphate from the applied phosphate source (PdfK), plus phosphate from the soil. The phosphate uptake from the soil is composed of phosphate taken up in the same amount as if no phosphate had been applied (Ptc) plus an extra amount of soil phosphate taken up (Pex) which was found to be directly proportional to the amount of phosphate taken up from the applied K_2HPO_4. In this work that proportion, from the model, was 133% of PdfK at the first harvest, 62% of PdfK in the following harvests and 39% of PdfK when total phosphate is accumulated to the 5th harvest. This effect (Pex) is commonly called the priming effect, where fertilised plants are seen to utilise native soil nutrients more efficiently.

Table 7.4 Calculation of the amount of phosphate rock derived phosphate in the plant available pool, using equation 11. All results are on a per pot basis, accumulated to the 5th harvest.

TREATMENT No.	 Description	$TotalP^{31}$ (mg)	PdfPR (mg)	$Accum.P^{32}$ (uCi)	SPACTPdfPR (uCi/mgP)
9.	S AR	4.59*a*	0.68	1.2 *a*	1.76
12.	ARAD AR	4.53*a*	0.64	0.8 *b*	1.25
17.	YSF AR	4.44*a*	0.57	1.0 *ab*	1.76
6.	NC AR	4.40*a*	0.55	1.0 *ab*	1.81
	LSD	*0.59*		*0.38*	
3.	NC WG	6.66*a*	2.17	1.55*a*	0.72
2.	gr.tallow	3.89*c*	0.18	0.47 *b*	3.8
4.	gr.$MgSO_4$	5.20 *b*	1.12	1.14*a*	1.02
5.	gr.CS	5.46 *b*	1.30	1.29*a*	0.99
	LSD	*0.93*		*0.53*	
25.	10 kgP/ha	4.93*b*	0.93	0.29*d*	0.32
26.	20 kgP/ha	5.45*b*	1.30	0.62*dc*	0.48
27.	40 kgP/ha	5.69*ba*	1.43	1.13 *cb*	0.79
3.	60 kgP/ha	6.66 *a*	2.17	1.55 *ba*	0.72
28.	80 kgP/ha	6.61 *a*	2.14	1.97 *a*	0.92
	LSD	*1.0*		*0.52*	
6.	NC AR	4.40*a*	0.55	1.0 *a*	1.81
7.	gr.$MgSO_4$	4.37*a*	0.53	1.28*ab*	2.4
8.	gr.CS	4.47*a*	0.59	1.39 *b*	2.35
	LSD	*0.4*		*0.37*	

* Least significance Difference figures based on 5% probabilty.
For PK(RPR) calculation Ptc=3.81, $P^{32}K$=18.11, and Ps=25.4

PdfK for the phosphate rock treatments (PdfPR) cannot be calculated using equation 1, but an estimate can be made using equation 2, on the somewhat tenuous assumption that a slowly available source of phosphate such as a phosphate rock will have the same priming effect on plant phosphate uptake pattern and generate the same Pex/Pt ratio (39% using accumulated results) as was found for the immediately available K_2HPO_4. The specific activity of the fertiliser phosphate (equation 9) in the herbage was found by dividing the total herbage P^{32} by PdfPR. The results are also in table 7.4.

$$\text{SPACTPdfPR} = \frac{\text{Accumulated herbage } P^{32} \text{ content}}{\text{PdfPR derived from accumulated } P^{31}} \qquad (9)$$

(d) Discussion

The only additional information about the phosphate rock which could be gained from the P^{32} surface labelling work was an estimate of the amount of phosphate in the herbage derived from the phosphate rock (PdfPR). The SPACTPdfPR was expected to indicate the specific activity of pool of phosphate in the soil which had dissolved from the phosphate rock and was sampled by the plant. The specific activity of the phosphate released from the fertiliser will be a function of the amount of P^{31} present in the soil pool interacting with the labelled surface of the phosphate rock prior to dissolution and will be modified by the amounts of P^{31} and P^{32} released as the phosphate rock dissolves. If significant quantities of P^{31} were released during dissolution then the specific activity of the dissolved pool may fall, but as the more reactive phosphate rock fraction is likely to dissolve first, and this is probably the fraction with which much of the P^{32} is associated, the specific acivity of the dissolved pool may not change significantly. The effects of these factors on the resulting specific activity could not be predicted but some information could be gained from comparisons of treatments which utilised the same phosphate rock.

The specific activity calculations based on PdfPR showed that the amounts of P^{32} taken up per unit of fertiliser phosphate from NCAR, SAR and YsfAR were similar, but that the amount was considerably lower for the AradAR.

Specific activities from the granulated treatments were always higher than the specific activity of the ungranulated parent materials, which may indicate that the clumping effect created a buffered zone within the clumps, reducing immobilization of the P^{32} by the soil and increasing the amount of P^{32} in solution.

The specific activity of the phosphate derived from the NCWG granulated with the tallow was very high, although the plant yield and phosphate uptake were not increased by the application of this fertiliser. This indicates perhaps that a small amount of phosphate rock dissolution did occurr in this treatment or that little of the P^{32} labelled surface PR phosphate became immobilised by interactions with the soil surface.

The specific activity of the phosphate derived from NCWG at different application rates dropped from 0.92 to 0.32 as the application rate dropped from 80 to 10 kgP/ha. This was accompanied by a rise in the proportion of the fertiliser applied which was taken up by the plant, indicating that the extent of dissolution of the fertiliser and/or the extent to which surface labelled P^{32} was diluted by PR phosphate (or adsorbed onto soil surfaces) increased as the application rate dropped. Based on PdfPR, the proportion of applied fertiliser which was in the herbage increased from 1.5% to 5.2%, as the application rate decreased from 80 to 10 kgP/ha. These results tend to confirm the conclusion of section 7.3.5, that the soil /phosphate rock chemical environment was limiting the amount of dissolution of the higher rates of application of NCWG.

A soil phosphorus fractionation (7.3.9) found that the average specific activity of phosphate released from NCWG, and the two mini-granulated NCWG treatments was 1.39 (The specific activity was calculated from the total P^{32} in the NaOH pool divided by the increase in P^{31} in the NaOH pool i.e. NCWG fertilised soil - control soil). If all the fertiliser phosphate in the herbage was derived from this pool then the specific activity of the fertiliser in the herbage and the fertiliser in the NaOH pool should be similar. In fact, the estimate of the average specific activity of the fertiliser in the herbage (SPACTPdfPR, table 7.4) for these three treatments was 0.91, which indicates that PdfPR was slightly overestimated. This may indicate that the phosphate rock had a slightly different priming effect on the plant, compared to the water soluble K_2HPO_4, and that more soil phosphate was taken up relative to the amount of fertiliser phosphate taken up (a lesser slope in equation 2).

7.3.9 Fractionation of soil

The objective of the soil phosphate fraction was to establish realistic estimates of the amount of fertiliser dissolution and the specific activity of the dissolved phosphate, in order to provide a check for the conclusions drawn from the herbage analyses. Further information was provided by extracting the root material from the soil of pots of these same four treatments and these results are presented in the following section (7.3.10). Soil samples were taken at four and ten weeks after fertiliser application from four treatments; NCWG (treatments 4 and 5), NCWG granulated with either $MgSO_4$ (treatments 11 and 12) or the $MgSO_4$/citric acid mixture (treatments 8 and 9), and 5mgP as K_2HPO_4 with chromite (treatments 37 and 38). See section 7.2.3 for details.

Finely sieved soil samples were sequentially extracted in 1M NaOH followed by 1M HCl (methods in chapter 3, section 3.5.4). The phosphate concentration in each extract was determined to give an estimate of non calcium bound phosphate and calcium bound phosphate, respectively. The difference in the amounts of noncalcium bound phosphate between fertilised and unfertilised soils was regarded as phosphate which had dissolved from the fertiliser (Equation 10). The difference in the amounts of calcium bound phosphate between fertilised and unfertilised soils was regarded as undissolved reactive phosphate (Equation 10) (Bolan and Hedley, 1989). All P^{32} recovered was regarded as having been derived from the fertiliser phosphate which was in the pool extracted.

Fertiliser P^{31}=

[P in fertilised soil (μgP/gsoil)-P in control soil (μgP/gsoil]
* [total weight of soil taken from pot (g)] (10)

(a) Recovery of phosphate fertiliser applied to soil

Recovery tests at time zero established that 100% of the fertiliser phosphate (average error ±15%) could be recovered from a soil sample by the fractionation procedure (table 7.5). All K_2HPO_4 P^{31} and P^{32} was expected to be recovered by the NaOH extraction. All of the applied P^{31} was recovered by the NaOH but recovery of some P^{32} in the HCl fraction from samples containing K_2HPO_4 may have been due to equilibration of P^{32} with the non-NaOH extractable phosphate during the NaOH extraction, so that not all P^{32} was extracted by the NaOH. Alternatively calcium phosphates were precipitated during the NaOH extraction.

Table 7.5 The percentage of fertiliser P^{31} and P^{32} recovered by sequential 1MNaOH and 1MHCl extracts of soil (mean of four replicates). P^{31} recovery from equation 10 divided by the amount of P^{31} mixed with the soil. P^{32} recovery expressed as total P^{32} recovered by either extractant divided by the amount applied with the fertiliser (see 7.2.3).

Extractant	NaOH		HCl		Total recovery	
	$\%P^{31}$	$\%P^{32}$	$\%P^{31}$	$\%P^{32}$	$\%P^{31}$	$\%P^{32}$
5mg K_2HPO_4 P	83	97	0.0	5	83±24	102±17
gr.NCWG+CS	2.8	41	97.6	73	100±10	114±8

There was a small (2.8%) recovery of phosphate in the NaOH fraction when phosphate rock was mixed with dry soil. Whilst the amount extracted was small the effect was consistent, so could not be solely attributed to error. A partial explanation may have been that the NaOH was extracting the small amount of water extractable phosphate found in phosphate rocks which had been produced during granulation with a mix of citric acid and $MgSO_4$. In another study approximately 1% of the phosphate in the fertiliser was found to have been solubilised by the granulation agent (see section 6.5.1). Further tests of granulated phosphate rock materials found that even when no citric acid was in the fertiliser up to 4.4% of the PR phosphate was extracted by the NaOH solution so that it does appear that the NaOH extraction did extract a small amount of undissolved phosphate rock. A similar effect was found when 0.5M NaOH was used to extract soil and phosphate rock mixtures (Bolan and Hedley, 1989).

The most notable point from the tests was that the pattern of P^{32} recovery was different to that of the P^{31}. The 41% recovery of P^{32} from the NaOH extraction of the phosphate rock contrasted with the 2.8% recovery of the P^{31}, and indicated that only a small fraction of the P^{31} in the phosphate rock became labelled with the P^{32}. This also caused the specific activity of the fertiliser phosphate to change depending on the type of extractant, so that phosphate derived from the phosphate rock in the NaOH had a relatively high specific activity and the phosphate in the HCl had a relatively low specific activity.

(b) Recovery of fertiliser applied to pots in the surface labelling experiment

The specific activity of the extractant solution and the recoveries of fertiliser phosphate and P^{32} are presented in Table 7.7 with the calculated specific activity of the phosphate derived from the fertiliser.

The K_2HPO_4 treatment for which the soil phosphate was fractionated was 5mgP as K_2HPO_4 mixed with chromite. The chromite was labelled with 18.11 µCi of P^{32} so the specific activity of the fertiliser was 3.62. The total recovery, in both extractants, of P^{31} from the fertiliser was greater than 100% at four weeks and 42% at ten weeks (actual recovery at four weeks was 243% which appears to be the result of a slight underestimate in the size of the unamended HCl pool. This underestimation was within the limits of the error margin but had a big effect on the relatively small quantity of phosphate (5mgP) added in the K_2HPO_4 treatment). The total recovery of P^{32} was 48% of the amount added to the soil at four weeks and 30% at ten weeks. If the P^{32} was uniformly labelling the P^{31} the recovery at four weeks is rather anomalous. Possibly the P^{31} recovery was overestimated, accurate estimations being difficult with the very small quantity of P^{31} applied and the high sampling error (average 27%).

Table 7.6 Recovery of fertiliser (% of total applied) based on six replicate measurements. These results are based on the more detailed results presented in table 7.7.

	Four weeks		Ten weeks	
TREATMENT	P^{31}	P^{32}	P^{31}	P^{32}
K_2HPO_4	243%	48%	42%	30%
NCWG	100%	65%	84%	45%
gr.NCWG+Mg	114%	78%	96%	66%
gr.NCWG+CS	95%	65%	94%	52%
Average for NCWG treatments				
	103%	69%	91%	54%

Granulated and ungranulated works ground North Carolina PR was applied at 106mgP per pot to the surface of the pots. The surface of the phosphate rock had been sprayed with 18.11 µCi of P^{32} so, if all the PR phosphate was uniformly labelled, the theoretical specific activity of the fertiliser was 0.17 µCiP^{32}/ mgP^{31}. The average total recovery of P^{31} dropped from 103% to 91% between the two fractionations. 69% of the applied P^{32} was recovered at four weeks and 54% at ten weeks. Much of the P^{31} and P^{32} which was not recovered can be accounted for by root and shoot uptake of plants, see the section on root separation from the soil (7.3.11). The different behaviour of the P^{31} and P^{32} is discussed in section (c).

(c) Distribution of ^{32}P and ^{31}P in the extractant solutions

Section (b) considered the total recovery of fertiliser from soil after two sequential extractions. Section (c) considers the distribution of the recovered fertiliser between the NaOH and HCl extracts.

Table 7.7 presents the recovery of labelled phosphate fertiliser from soils, using 1M NaOH and HCl extractants. Presented are the specific activities of the solution after the extraction, the apparent recovery of dissolved and residual fertiliser phosphate from each treatment (found by taking the increase in phosphate extracted compared to the unfertilised soil), and the total P^{32} recovered by the extractant. The apparent specific activity of the dissolved fertiliser phosphate is also presented, which is the total P^{32} recovered by the extractant divided by the amount of dissolved fertiliser P^{31} recovered by the extractant.The calculations are on a per pot basis, where 5mgP per pot was applied as K_2HPO_4 and 106 mgP applied to pots as phosphate rock, and 18.11 uCi of P^{32} was applied to all pots. The 1M NaOH extracted 99.5 ugP/g soil and 1M HCl extracted 37.4 ugP/g soil from the unfertilised control soil. The average coefficients of variation for the results presented in the table were P^{31}; NaOH 27%, HCl 10.4% and P^{32}; NaOH 10.6%, HCl 13.2%.

(c1) Soil containing K_2HPO_4 and chromite fertiliser

In soil where 5mgP as K_2HPO_4 was applied 30% of the recovered P^{31} was recovered in the NaOH at four weeks and 100% at ten weeks (cv 27%). The results at four weeks are rather in contrast to the recovery test (table 7.6) which suggested that 100% of the water soluble phosphate would have been in the NaOH at four weeks. This appears to be confirmed by the distribution of the P^{32} in the soil where 96% of the recovered P^{32} was in the NaOH pool at four weeks, increasing to 100% at ten weeks, so the 30% recovery appears to be an anomalous result probably caused by subsampling errors.

Table 7.7 Extraction of phosphate by 1MNaOH and 1MHCl from fertilised soil samples taken from pots destructively sampled at four weeks and ten after fertiliser application. See preceding text for further details.

EXTRACTANT:	1M NaOH				1M HCl		
	Extractant solution specific activity $(nCiP^{32}/\mu gP^{31})$	Dissolved fertiliser: P^{31} (mg)	P^{32} (μCi)	Dissolved fertiliser specific activity $(\mu CiP^{32}/mgP^{31})$	Extractant solution specific activity $(nCiP^{32}/\mu gP^{31})$	Undissolved fertiliser: P^{31} (mg)	P^{32} (μCi)
(a) Four weeks after fertiliser application							
K_2HPO_4	0.34	3.55	8.12	2.3	0.036	8.6	0.59
NCWG	0.31	4.45	7.01	1.57	0.043	102	4.73
gr.NCWG+Mg	0.22	4.77	6.85	1.43	0.058	116	7.32
gr.NCWG+CS	0.24	3.4	5.06	1.49	0.064	97	6.62
(b) Ten weeks after fertiliser application							
K_2HPO_4	0.29	0.8	5.52	6.9	0.0	1.3	0.0
NCWG	0.24	6.0	4.93	0.82	0.036	82.8	3.26
gr.NCWG+Mg	0.21	3.5	4.82	1.38	0.066	98.1	7.15
gr.NCWG+CS	0.17	2.0	3.23	1.62	0.060	97.3	6.21

(c2) Soil containing phosphate rock fertiliser

At four and ten weeks, approximately 4% of the PR phosphate was recovered in the NaOH pool. The distribution of P^{32} between the 1MNaOH and 1MHCl fractions did not change much over time, but appeared to be affected by the phosphate rock fertiliser form. 60% of the recovered P^{32} was found in the 1MNaOH extractable fraction for the ungranulated phosphate rock, decreasing to 40% for the granulated material. The recovery figures indicate that probably no more than 10 to 20 mgP was ever released from the phosphate rock fertilisers during the period of plant growth.

These fractionation results confirm previous conclusions that the extent of phosphate rock dissolution was overestimated by calculations using herbage P^{32} specific activities from the surface labelling and inverse isotopic dilution experiments.

The specific activity of the total phosphate present in the phosphate rock fertiliser applied to the soil was 0.17 so these results showed that the specific activity of the fertiliser phosphate recovered in 1MNaOH was disproportionately high (range 0.82 to 1.62) compared to the applied fertiliser phosphate and disproportionately low (range 0.039 to 0.073) in the 1MHCl fraction. These effects were further exaggerated in the zero time recovery tests of the NCWG treatment granulated with the citric acid/ $MgSO_4$ mix, where the small amount of P^{31} that dissolved in the NaOH extractant had a specific activity of 3.04, while the specific activity of the undissolved fertiliser phosphate was was 0.004. (Specific activities calculated using the total P^{32} recovered by the extractant and the fertiliser P^{31} recovered by the extractant). This confirms the conclusion from the surface labelling experiment, that the ^{32}P was not simply labelling the phosphate in the phosphate rock. For the NCWG, at four and ten weeks, approximately 50% of the P^{32} was in the NaOH pool, that is, readily exchangeable with the extractant and probably labelling the soil phosphate pool which is associated with the dissolving surface of the phosphate rock. The other half of the P^{32} was extracted with the majority of the phosphate rock, by the HCl, and was probably closely associated with the phosphate on the surface of the phosphate rock and may have exchanged with P^{31} within the structure of the rock.

In general the fractionation results have provided useful information about the distribution of the P^{32} label between the dissolved and residual fertiliser phosphate and have proved valuable in measuring the specific activity of phosphate that dissolved from the surface labelled phosphate rock.

7.3.10 Fractionation of roots

In the above soil fractionation section it was found that not all the P^{31} and P^{32} was recovered. These discrepancies may be accounted for by plant uptake. One pot of each of the treatments which were fractionated was reserved and the roots washed free of soil.

The root fractionations were not replicated so that the results were not conclusive but the fractionation did suggest that there was approximately a 3g increase in the plant dry weight of roots and non-harvested above ground herbage per pot for all the pots over the duration of the experiment. The root separation also suggested that a small growth response occurred in the roots in a pattern which was similar to the cut herbage phosphate response (Figure 7.16). Root weights were greatest in the pots fertilised with ungranulated NCWG and lowest in the unfertilised control. The concentration of phosphate in the roots also increased as herbage phosphate response increased as well as the shoot to root ratio (Table 7.8).

Table 7.8 Distribution of phosphate throughout a ryegrass plant eleven weeks after fertiliser application

	Roots %P	Stubble %P	Herbage %P	Shoot/Root ratio w/w
NO PHOSPHATE	0.13	0.11	0.25	0.58
K_2HPO_4	0.20	0.14	0.28	0.61
NCWG	0.27	0.17	0.28	0.73
gr.NCWG+Mg	0.31	0.15	0.29	0.63
gr.NCWG+CS	0.37	0.15	0.28	0.61

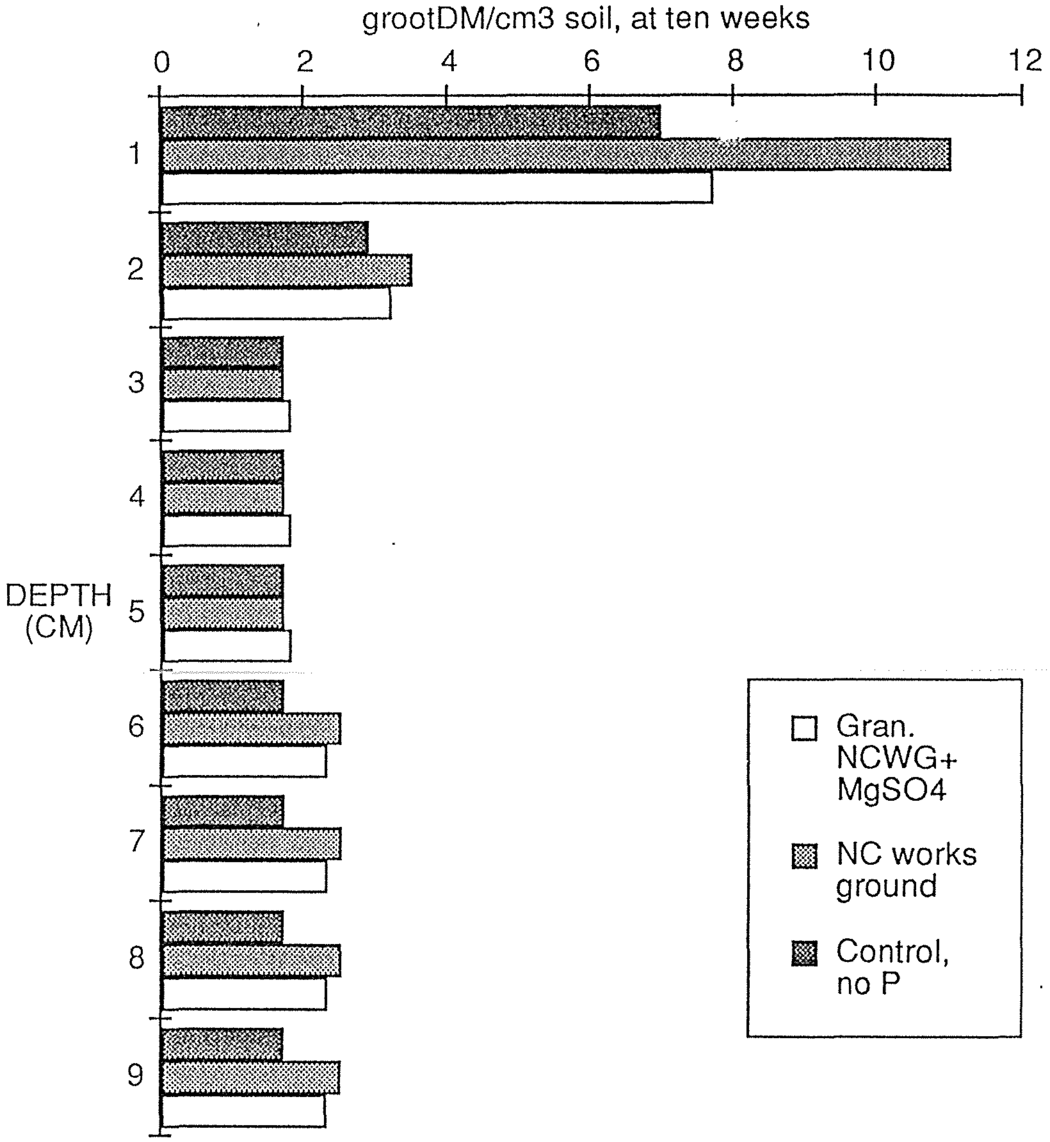


Figure 7.16: The distribution of root mass (g root DM/cm^3 soil) at different soil depths in unfertilised pots (control), in pots fertilised with works ground North Carolina (NC) phosphate rock, and in pots fertilised with mini-granules of works ground North Carolina phosphate rock made using $MgSO_4$ (Gran. NCWG+$MgSO_4$).

This increase in plant dry matter and accompanying increase in phosphate content could account completely for the 58% loss of phosphate from the soil to which K_2HPO_4 had been added and the 6% drop in recovery of phosphate from the phosphate rock treatments (Table 7.9).

Information on the recovery of P^{32} from the plants was only available for the first soil fractionation. The results are presented in table 7.9, and suggest that most of the P^{32} not recovered from the soil had been taken up by the plants.

Table 7.9 Recovery of P^{32} from all roots plus shoots harvested from pots (also presented as a percentage of the total P^{32} applied to the pots), and total recovery of P^{32} from plant and soil fractionations, four weeks after fertiliser application. The final two columns present the specific activity of the phosphate in the herbage harvested from the pots at four and ten weeks.

Treatment	Roots plus Shoots: Total P^{32} (μCi)	Roots plus Shoots: fraction of P^{32} applied (%)	Plant plus Soil: total P^{32} recovered (%)	Herbage Specific activity 4 weeks	Herbage Specific activity 10 weeks
NCWG	5.02	28	93	0.44	0.23
gr.NCWG+CS	3.61	20	85	0.51	0.21
gr.NCWG+Mg	3.41	19	97	0.21	0.18
K_2HPO_4	6.47	36	84	1.23	0.33

The herbage specific activities at four weeks were rather higher than the soil NaOH extractable phosphate for the same time. This difference was most marked in the 5mg of soluble phosphate treatment. The specific activity of phosphate in the extracted NaOH solution at ten weeks (Table 7.7) was not significantly different from the specific activity of herbage phosphate from the herbage cut taken at ten weeks (Table 7.9). While this similarity between the two sets of specific activities may have been only coincidence, it does tend to suggest that the plant was taking up phosphate from the NaOH extractable soil pool.

An infection of the roots by nematodes was noted at eleven weeks and the possible effects of this are discussed in a following section (7.3.11). Just how much these root fractionation results were modified by the effects of the nematodes is not known. It is possible that total root weights were reduced and that the root dry matter response to the fertiliser was modified. The shoot to root ratios may have been increased and the total phosphate content of the roots may have increased because the nematodes act as nutrient sinks.

7.3.11 Inverse isotopic dilution experiment

The general aim of the "A" value concept is to accurately distinguish between the soil and the fertiliser contribution to plant phosphate. In this experiment an isotopic dilution technique was employed to estimate the quantity of phosphate available from a phosphate rock fertiliser as it dissolved in soil. This technique had previously been tested in a field trial (Chapter 5), where, under conditions of no growth response to the fertiliser, the technique yielded no useful information. The technique was re-evaluated under glasshouse conditions where a growth response to the fertiliser was expected.

All fertilised pots produced plant dry matter yields significantly above the unfertilised control pots; the results are discussed elsewhere in the sections relevant to the various treatments. Accumulated plant dry matter yields are presented in table 7.10, and the rates of dry matter production per day in table 7, appendix 2.

When the experiment was set up it was expected that the soil conditions in the pots in the isotopic dilution experiment would replicate the conditions in the surface labelled experiment. This assumption was disproved in that the plant yield and herbage phosphate uptake from the inverse isotopic dilution pots was considerably higher than from the same treatments in the surface labelled pots. The average accumulated dry matter plant yield from the unfertilised control pots was 2.09g in the surface labelled experiment and 2.26g in the inverse isotopic dilution experiment. This was not a significant increase but the yield response to the fertiliser was greatly increased in the inverse isotopic dilution experiment. For example NCWG produced 168% of the control yield in the surface labelled pots increasing to 197% in the inverse isotopic dilution pots, similarly yields NCWG granulated with $MgSO_4$ increased from 149% to 167% of the control yield. There was a similar effect on the herbage phosphate content. This change in the scale of fertiliser response limited the comparisons which could be made between common fertiliser treatments in the two experiments, and also limited comparisons of information derived from the two isotopic techniques.

(a) P^{32} uptake

Accumulated P^{32} uptake (Table 7.10) also increased when fertiliser was applied to pots, following the pattern of the P^{31} uptake and dry matter responses, although the extent of the increased P^{32} was high relative to the yield and P^{31} uptake responses, particularly in the granulated treatments.

Table 7.10 Accumulated (fourteen and a half weeks) dry matter, P^{31} and P^{32} in herbage grown in the inverse isotopic dilution experiment.

Treatment	Dry matter (g)	P^{31} (mgP)	P^{32} (μCi)	specific activity
Unfertilised control	2.26 *a*	5.07 *a*	32.25*a*	6.36
NCWG	4.45 *d*	11.48*d*	63.40*bc*	5.52
NCFG	4.72 *d*	12.83*d*	67.8 *cd*	5.28
Gr.NCWG+Mg	3.77 *c*	8.96 *c*	72.97 *d*	8.14
Gr.NCAR + CA	3.04 *b*	6.85 *b*	58.44*b*	8.53
Least significant difference	*0.46*	*1.37*	*6.19*	

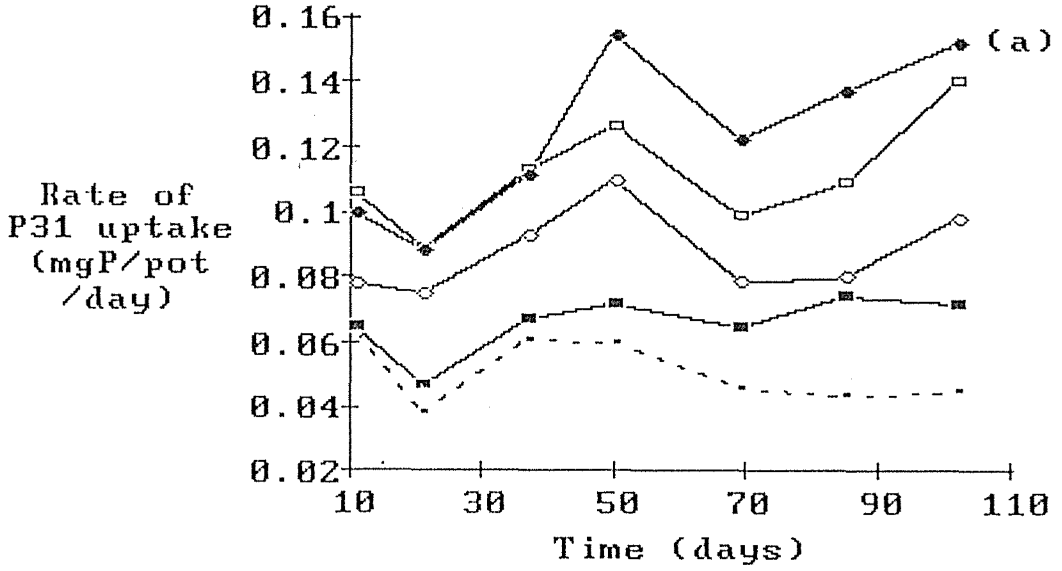
The unexpectedly high uptake of P^{32} by the granulated fertiliser treatments was confirmed by a comparison of the rates of P^{31} and P^{32} uptake by the plants (Figure 7.17, and appendix 3, table 2 and 3), which showed that P^{32} uptake was not well related to P^{31} uptake and that both the granulated treatments caused high rates of P^{32} uptake between the first and third harvests (from one and a half to five weeks) after the fertiliser was applied to the pots. Subsequently the rate of P^{32} uptake from these two treatments tailed off so at the final two harvests the rates of uptake from all treatments were not significantly different.

(b) Estimates of the amount of phosphate in the soil which has been released from fertiliser

The development of the "A" value concept and application to the inverse isotopic technique was previously discussed in chapter 5, section 5.2.5. The relationships developed in the field experiment could not be directly applied to results from the glasshouse experiment because the assumption that the efficiency of plant uptake from the soil pool was the same in fertilised and unfertilised pots under the glasshouse conditions of a growth response to fertiliser was not upheld by the results from the surface labelling technique. Equation 8, section 7.3.8 suggested that the addition of fertiliser caused an increased efficiency in the uptake of the soil phosphate. Even a small increase in the efficiency of soil phosphate recovery would considerably inflate an estimate of the size of plant available pool of the fertilised pots by equation 3 and 4 in section 5.4.1 of the field experiment.

Based on the simplest application of the inverse isotopic technique an estimate of the size of the plant available pool for a pot can be made, if it is assumed that the average specific activity of the plant available phosphate in the pot is the same as the average specific activity of the plant material harvested from the pot (Equation 11).

$$\frac{P^{32}\text{ plant available pool}}{P^{31}\text{ plant available pool}} = \frac{P^{32}\text{ herbage}}{P^{31}\text{ herbage}} \qquad (11)$$



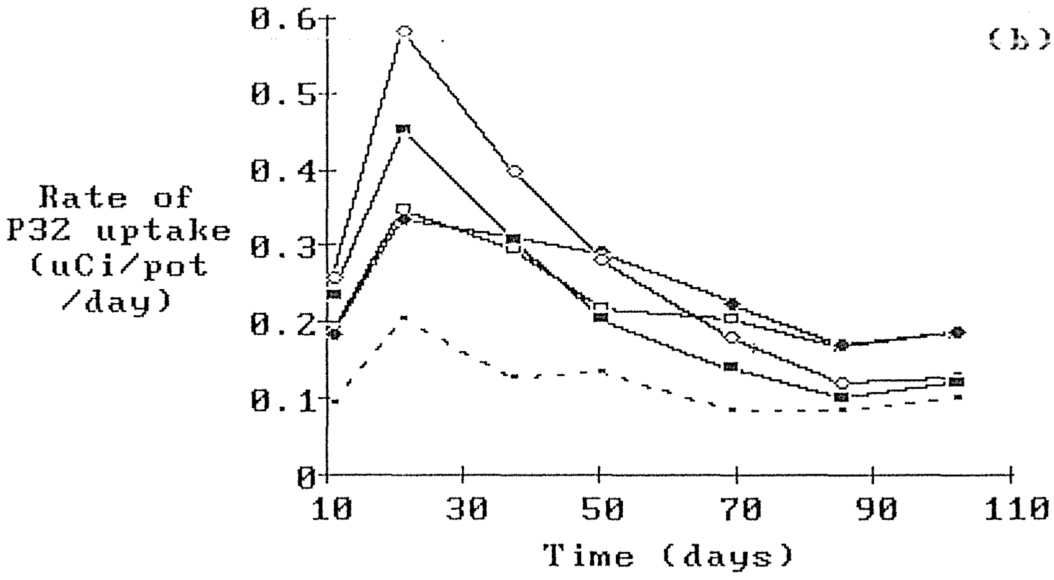


Figure 7.17: A comparison of the P^{31} uptake (a) and P^{32} uptake (b) in the inverse isotopic dilution experiment from unfertilised pots (•) and pots fertilised with North Carolina phosphate rock in the forms; works ground (□), works ground mini-granuled with $MgSO_4$ (◇), finely ground (◆), and "as received" mini-granulted with citric acid (▩). L.S.D.(a)=0.023 L.S.D.(b)=0.088

This relationship may be simply rearranged to find the amount of P^{31} in the plant available pool at any harvest. The difference in size between the plant available pools of the unfertilised control pots and the fertilised pots should provide an estimate of the amount of phosphate released into the plant available pool from the fertiliser. The basic assumption of this relationship is that all the injected P^{32} remained in the plant available pool and that any difference in the specific activity of phosphate in plants from different treatments was entirely due to dilution of the P^{32} by phosphate released from the fertiliser into the plant available pool. To increase to the accuracy of the estimate, the amount of P^{32} injected into the plant available pool was adjusted to account for P^{32} which had previously been removed in the harvested herbage. The amount of P^{31} added with the P^{32} (3.99µgP/pot) was regarded as negligible and not included in this calculation. The difference between the size of the plant available pools in fertilised and unfertilised soils was found for each treatment, using the specific activity of the herbage found at each harvest and the results are presented in table 7.11.

Table 7.11 Estimate of the size of the plant available pool in unfertilised pots, and the amount of phosphate released from the fertiliser into the plant available pool, based on the difference in plant available pool size of fertilised and unfertilised pots, as calculated by equation 12.

Treatment Harvest:	2	3	4	5	6	7
Size of the unfertilised plant available pool (mgP/pot)						
	16.2	39.5	38.4	50.9	49.9	36.4
Amount of fertiliser phosphate in the plant available pool (mgP)						
NCWG	4.9	-8.1	-8.6	-14.1	-0.7	20.1
NCFG	6.3	-11.6	3.37	-10.0	9.6	23.3
granules: NCWG + Mg	-5.6	-21.0	-9.6	-19.3	-1.7	19.1
granules: NCAR + CA	-7.6	-22.3	-10.9	-13.9	10.2	13.0

The estimates of dissolved fertiliser phosphate were expected to be approximately in proportion dry matter and phosphate uptake responses to the fertiliser. In fact the estimates were inversely related to the herbage specific activity and were not closely related to the dry matter yield or phosphate uptake. In the third and fifth harvests the estimate of size of the plant available pool in the fertilised pots was found to be smaller than the unfertilised pots, leading to negative values for the amount of dissolved phosphate in the plant available pool. This effect also occurred for the two granulated treatments in the second and fourth harvests.

Soil fractionation of surface labelled pots (Table 7.7) found that the amount of increase in the NaOH pool when amended with works ground NCPR was between 2 and 6 mg of phosphate, tending to confirm that negative values found were incorrect (ranging from -0.7 to -14) and suggesting that the herbage specific activities of the fertilised treatments were high and did not properly reflect a dilution in the herbage caused by the uptake of (unlabelled) dissolved fertiliser phosphate, which was the predicted effect.

The general increases in the estimated size of the unfertilised plant available soil pool during the experiment (Table 7.11) suggested that some P^{32} was being removed from the plant available pool, causing an artificial increase in the estimate of the pool size. Possible mechanisms, such as absorption and immobilisation, causing the removal of P^{32} from the plant available pool were discussed in section 5.3.3 of chapter 5. Because close to 100% of the P^{32} injected was recovered from the NaOH pool at ten weeks this effect, of an increasing plant available pool size, suggested that the plant was not withdrawing phosphate from the entire NaOH extractable pool, or the plant available pool size would not have changed. The quantity of phosphate extracted by a 1:40 w/v water extraction of wet injected soil at ten weeks was 25.3 mgP/pot which was close to the 16.4 mgP per pot estimate of the size of the plant available pool at the second harvest. In subsequent harvests the magnitude of the estimate of the size of the plant available pool may have been artificially inflated by the removal of P^{32} from the exchangeable pool and replacement with P^{31}.

(c) Estimates of the amount of phosphate in the herbage which was derived from the fertiliser

With no reasonable estimate of the amount of dissolved fertiliser phosphate in the plant available pool (section b) a model was developed (Appendix 4), to find PdfPR(2), the quantity of phosphate in the herbage which was derived directly from the fertiliser. (The (2) denotes that this is the second isotopic technique which has been used to estimate this quantity.) This quantity might possibly give a better estimate of the relative availability of the different fertilisers than the calculations in section (b) because no estimate of the size of the soil pool is necessary.

In the field experiment (Chapter 5) there was no dry matter response and the model estimating PdfPR(2) yielded no more information than finding the difference in phosphate uptake response between the different treatments. The technique was tried again in a glasshouse environment, in order to test the performance of the model when a dry matter response was attained. A significant dry matter response to the presence of various phosphate rock fertilisers was found, see section 7.3.1.

The only assumption in this model was that an extra quantity of soil phosphate will be taken up as a result of the dry matter response. No assumptions are made about the nature of this response except that the specific activity of the extra soil phosphate is the same as that of the rest of the soil phosphate which is taken up by the fertilised plant. It is also assumed that phosphate taken up from the soil will have the same specific activity regardless of whether fertiliser was applied to the pots or not.

PdfPR(2) was calculated utilising equation 12. The results of the calculation are presented in table 7.12.

$$\mathrm{PdfPR(2)} = \mathrm{Pt} - \frac{\mathrm{P^{32}t}}{\mathrm{SpactC}} \qquad (12)$$

Where:

SpactC: Specific activity of the phosphate in herbage cut from a pot where no phosphate rock fertiliser was applied.

Pt: Total phosphate content of herbage cut from pots where phosphate rock fertiliser was applied.

PdfPR(2): Amount of phosphate derived from the fertiliser in herbage cut from a pot where phosphate rock fertiliser was applied.

$P^{32}t$: Total P^{32} content of herbage cut from pots where phosphate rock fertiliser was applied.

Table 7.12 Estimates of the amount of fertiliser phosphate taken up from treatments where the inverse isotopic dilution technique was employed, based on the model developed in Appendix 4. Estimates were found for phosphate taken up at each harvest, excluding the first harvest, using equation 12.

	PdfPR(2) at each harvest (mgP/pot)					
Treatment	2	3	4	5	6	7
NCWG	0.08	-0.58	0.34	-0.29	0.34	0.96
NCFG	0.17	-0.75	0.40	-0.08	0.74	1.12
Gr.NCWG+Mg	-0.52	-1.89	-0.18	-0.38	0.25	0.68
Gr.NCAR+CA	-0.30	-1.97	-0.28	-0.14	0.33	0.44

As was found in the "A" value calculations the results appear to be anomalous, the estimates of the amount of phosphate in the herbage which is derived from the fertiliser being negative in many cases.

The results in section (b) suggested that the negative values may have been an artifact of high herbage specific activities. In order to examine the effect of the herbage specific activity a rough estimate of the fertiliser content of the herbage was made using equation 7, from the model developed from the pots where different amounts of labelled K_2HPO_4 had been applied. An assumption was made that 70% of the phosphate uptake response was derived from the fertiliser (although this was possibly an overestimation, section 7.3.8) and the calculation based on phosphate uptake results accumulated to the final harvest (accumulated PdfPR(1) in table 7.13). The PdfPR(1) calculation suggested that between 1.2 and 5.4 mg of the total phosphate taken up the plant in the inverse isotopic dilution pots may have been derived from the fertiliser. Using this estimate, the amount of P^{32} which might have been taken up by the plants was predicted, if the specific activity of the phosphate taken up from the soil in unfertilised herbage from pots in the inverse isotopic dilution experiment was the same for the other inverse isotopic dilution treatments.

Table 7.13 The accumulated amount of fertiliser phosphate in plant herbage in pots in the inverse isotopic dilution experiment as found by two different models (equations 7 yielded PdfPR(1) and equation 12 PdfPR(2)). A comparison is also presented of the actual accumulated P^{32} uptake in the plant herbage and the amount of P^{32} uptake predicted based on the results of PdfPR(1). The difference between the actual and predicted P^{32} uptake is presented as a percentage of the predicted uptake.

Treatment	Fertiliser P^{31} PdfPR(2) (mgP)	PdfPR(1) (mgP)	ActualP^{32} uptake (μCi)	Predicted P^{32} uptake (μCi)	P^{32} uptake difference
NCWG	1.5	4.5	63.4	44.4	143%
NCFG	2.2	5.4	67.8	47.2	144%
Gr.NCWG+Mg	-2.5	2.7	73.0	39.8	183%
Gr.NCAR+CA	-2.3	1.2	58.4	35.9	163%

The amount of P^{32} uptake for the duration of the experiment per pot as predicted by this calculation ("Predicted P^{32}" table 7.13) may be compared with the actual accumulated P^{32} uptake from pots in table 7.13. The extent that the actual P^{32} uptake was greater than the predicted amount is also presented as a percentage of the predicted amount.

Within the limitations of the assumptions that similar proportions of soil and fertiliser phosphate were taken up by plants in surface labelled and isotopic dilution pots, it becomes evident that considerably more P^{32} was taken up than if the labelled soil plant system was behaving as predicted. The extent of the effect of extra uptake also varied depending on the treatment, granulated treatments taking up considerably more P^{32} than expected compared to the phosphate rock treatments which were not granulated. These comparisons suggest a confirmation of the effect found in section (b), of higher than predicted herbage phosphate specific activities in the fertilised treatments. Section (c) further suggests that the reason for this effect was anomalously high P^{32} uptake in the fertilised treatments, particularly when the fertiliser was granulated. The cause of this effect is discussed in section (d).

(d) Fractionation of soil labelled by injection

One unfertilised pot in the inverse isotopic dilution experiment was cut into six sections ten weeks after P^{32} was injected. The sections were extracted sequentially in 1MNaOH and 1MHCl as described previously (see section 7.3.9 for details). The distribution of the P^{32} was found to be much as predicted (figure 7.18), with the original injection zone being between 1 and 5 cm depth and the actual distribution 88% of P^{32} between 1 and 5.5cm. The recovery of the amount of P^{32} originally injected was 85.9%, plant herbage uptake accounting a further 8.7%, the remaining fraction (5.4%) may have been in the roots.

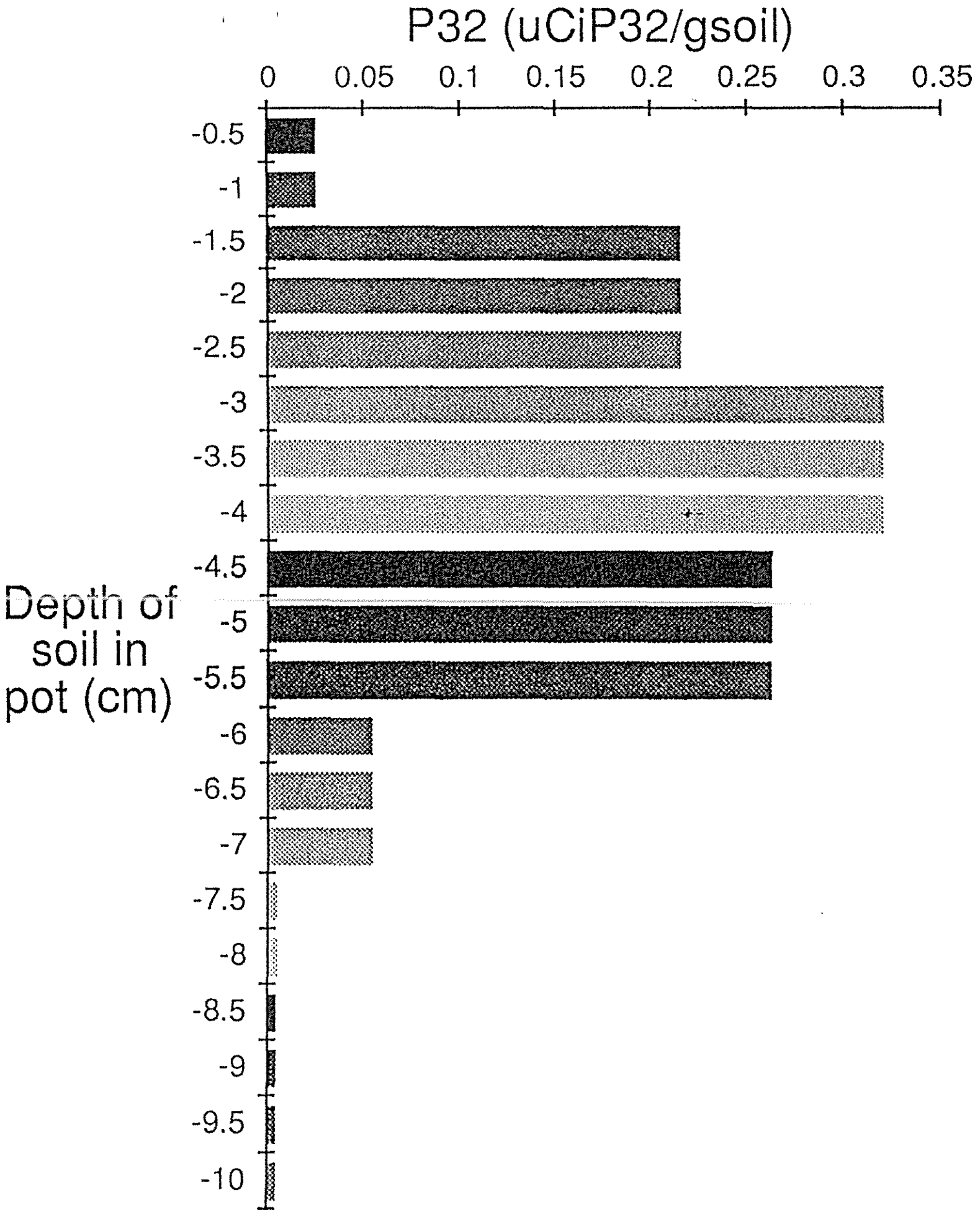


Figure 7.18: The vertical distribution of P^{32} activity (CiP^{32}/gsoil) in a pot from the inverse isotopic dilution experiment which was dissected 69 days after injection of the label into approximately the 1-5cm depth zone.

The majority of the P^{32} was found in the NaOH extraction, only 4% of the quantity recovered was found in the HCl fraction. The average specific activity of the NaOH solution extracted from all depths was 1.25. The highest specific activity of an NaOH solution was 2.77. Figure 7.18 indicates that most of the P^{32} was injected between 2.5 and 4cm pot depth. Soil samples from this depth were also extracted with water and an Olsen solution before the soil was dried and the respective specific activities were 0.054 and 0.341. These specific activity results contrast with the specific activity of phosphate recovered from the plant herbage, which was 4.49 at the time that the soil was fractionated, and generally higher for harvests taken previous to the fractionation. A possible explanation for this apparent concentration of P^{32} in the plant may have been that the plant roots were preferentially growing down the small holes created by the injector needles in the fertilised treatments (an increase in root mass in fertilised and unfertilised pots over the duration of the experiment was found in the surface labelled pots, section 7.3.10).

The observed plant yield response to fertiliser was probably also accompanied by a root growth response, as was demonstrated in the surface labelled pots (Figure 16). If the extra root growth was associated with the injector holes then the effect of increased P^{32} uptake would have been accentuated in the fertilised pots, providing the effects observed in sections (b) and (c). This is not a completely satisfactory explanation because the greatest increases in P^{32} uptake were observed in the granulated fertiliser treatments (table 7.13), which had the lowest plant yield responses. The reasons why this effect occurred are not known.

7.4 Conclusions

1. Grinding "as received" North Carolina phosphate rock to a commercial works ground particle size resulted in a significant increase in plant yield. A further reduction in particle size, and also grinding "as received" Arad phosphate rock to the works ground particle size, resulted in no increase in the plant yield. The significant result when the particle size of the "as received" North Carolina phosphate rock was reduced suggested that grinding phosphate rock increased the rate of dissolution of the material. Results from varying the rate of application of works ground North Carolina phosphate rock showed that the soil environment was imposing limitations on the dissolution of this material. This result suggests that the lack of response to the Arad and finer North Carolina materials was also caused by limitations on dissolution imposed by the soil environment.

2. Mini-granulation of "as received" North Carolina and Sechura phosphate rocks caused no reduction in phosphate availability from these materials. Mini-granulation of works ground North Carolina phosphate rock caused no decrease in phosphate availability when the material was applied to pots in the surface labelled experiment but the application of the same treatment to the inverse isotopic dilution pots caused a significant reduction in phosphate availability compared to the ungranulated material. Mini-granulation of "as received" and works ground Arad PR caused a significant reduction in phosphate availability.

   The significant reduction in availability in some treatments led to the conclusion that the objective of creating granules small enough to cause no significant reduction in availability (no significant clumping effect) had not been fulfilled. It appeared that mini-granulation reduced the actual availability of the phosphate rock materials in environments where there was sufficient rate of dissolution of the phosphate rock for the "clumping" effect to be limiting (i.e. the greater plant growth in the inverse isotopic dilution pots). In some cases the environment of the phosphate rock imposed limitations on the rate of dissolution of the particular phosphate rock material and limited the availability of the material to a level which was not reduced further even when the material was granulated.

These conclusions call into question the conclusion from the field experiment, the mini-granulation did not limit the availability of the works ground North Carolina phosphate rock. In view of the conclusions reached in the glass house experiment it seems possible that the field environment may have been limiting the dissolution of the phosphate rock and a granulation effect was not evident because the dependence of the plants on phosphate derived from phosphate rock dissolution was small.

3. The nature of the two principal granulation agents (10% w/w $MgSO_4$ and a 10% mix of 1:0.6 citric acid and $MgSO_4$) caused no significant difference in plant yeilds. There was also no significant difference in availability when works ground North Carolina phosphate rock was applied as a commercially granulated partially acidulated product, compared to the other granulated products. Granulation of works ground North Carolina phosphate rock with tallow, however, reduced the availability of the phosphate rock compared to the other granulated products.

4. The plant availability of "as received" White Youssafia phosphate rock was found to be intermediate between "as received" North Carolina and Arad phosphate rocks. This result contrasted with the results of the formic acid solubility tests (Chapter 4) which suggested that White Youssafia would have the lowest agronomic performance in the series studied, namely Sechura, North Carolina, Arad and White Youssafia phosphate rocks.

5. A very limited amount of information about phosphate rock dissolution could be gained from radioactively labelling the surface of phosphate rocks, because P^{32} uptake from the surface labelled phosphate rock materials was not simply related to P^{31} uptake. Fractionation of fertilised soil from pots sampled during the experiment revealed that the P^{32} was labelling both the soil pool associated with dissolved fertiliser and the residual fertiliser, but that the exact distribution of the P^{32} was highly dependent on the type and particle size of the phosphate rock and therefore very few comparisons could be made between the different phosphate rock treatments.

The use of labelled water soluble phosphate as a control for this experiment provided sufficient information to allow the plant uptake from soil and fertiliser sources of phosphate to be modelled. A fertiliser priming effect was identified in which the uptake of fertiliser phosphate by a ryegrass plant was associated with the uptake of "extra" soil phosphate, compared to the uptake of soil phosphate by unfertilised plants. The amount of "extra" soil phosphate taken up was linearly related to the amount of fertiliser phosphate taken up, in pots fertilised with small amounts of K_2HPO_4.

If radioisotopes are to be used to study phosphate rock dissolution in field soils then improved methods of isotope placement in the soil need to be investigated. Surface labelling of phosphate rock materials did not provide a simple method to significantly increase the amount of information that could be gained on phosphate rock dissolution in soils. The use of such material in conjunction with soil phosphate chemical fractionation did allow some comparisons to be made between the specific activity of the dissolved and residual fertiliser phosphate pools and the specific activity of the phosphate in the plants.

6. A re-evaluation of the inverse isotopic technique found that basic assumptions necessary to derive information from the results could not be supported. The uptake of P^{32} from the soil was found to be highly sensitive to unpredictable variables caused by the different fertiliser treatments and not well related to the uptake of P^{31}. Attempts to gauge the amount of fertiliser derived phosphate in the soil or to partition the dry matter and phosphate uptake response of the herbage into that derived from the soil and that derived from the fertiliser were abandoned. Increased P^{32} uptake by fertilised plants in the inverse isotopic dilution pots did confirm, however, that the addition of fertiliser did stimulate root growth at depth, in unfertilised regions of the soil. This presumably was part of the fertiliser priming effect identified in the surface labelled experiment.

CHAPTER 8: SUMMARY OF CONCLUSIONS

Mechanics of granulation

After extensive trialling of granulation agents, the best granulation agent for the efficient production of strong mini-granules (0.5-1mm diameter) was found to be a mixture of citric acid and magnesium sulphate. The small granule size requirement necessitated two drying steps and also a cutting step which reduced the yield and the speed of the process. The temperature and moisture content of the granules at the commencement of the final drying step were found to be important factors controlling the strength of the granules. The strength and yield of the mini-granules were also influenced by the type and particle size distribution of the phosphate rock used for granulation. The formic solubility of the phosphate rock was increased after granulation. This increase was roughly proportional to the amount of binder in the granules so was probably caused by a decrease in the ratio to formic acid volume ~~basis~~.

Effect of grinding

A theoretical model of phosphate rock dissolution in the soil suggested that the initial particle size of phosphate rocks would be a principle factor influencing the agronomic performance of the material. Decreasing the particle size of Arad and North Carolina phosphate rocks rocks increased the solubility of the phosphate in these materials in 2% formic acid by approximately 12%. However, in a glass house trial no consistent increase in agronomic performance (ryegrass yields) could be associated with decreasing particle size of phosphate rock. The agronomic performance of North Carolina phosphate rock was improved by grinding to less than 250µm in particle size, no further improvement occurred if the phosphate rock was more finely ground (<42µm particle size). The agronomic performance of the "as received" Arad phosphate rock was not improved by grinding.

The agronomic performance and percentage dissolution of the works ground North Carolina phosphate rock in a glasshouse trial was reduced by an increasing rate of application. This provided evidence that soil factors were controlling the rate of phosphate rock dissolution at higher levels of application, including the application rate at which the majority of the treatments were applied (60 kgP/ha). The extent of this effect may have varied with phosphate rock type and particle size and may have caused the inconsistent treatment effect of phosphate rock particle size on agronomic performance.

The increase in formic solubility with decreasing particle size and the increased agronomic performance of North Carolina phosphate rock suggests that grinding will increase the potential agronomic performance of reactive phosphate rocks, but, with respect to other phosphate rocks, the rock type and application rate will interact with the soil environment to determine whether the rate of dissolution of the material can be significantly increased by a reduction in particle size.

Effects of Granulation

A field trial in which different sized granules of finely ground North Carolina phosphate rock were applied to permanent ryegrass-clover pasture demonstrated that mini-granulation (granule diameter 0.5 to 1mm) did not reduce the agronomic performance of the phosphate rock, compared to granules of a greater diameter, but this result was not regarded as conclusive. Significant reductions in agronomic performance occurred when reactive phosphate rocks were mini-granulated and surface applied in a glasshouse trial. This suggested that, unlike the glasshouse trial, in the field environment the dependence of the sward on phosphate dissolved from the reactive phosphate rock was small and could be sustained by the mini-granulated material.

In the glasshouse trial mini-granulation of "as received" North Carolina and Sechura phosphate rocks caused no reduction in phosphate availability from these materials. The effect of mini-granulation of works ground North Carolina phosphate rock had variable effects depending on the treatment of the soil being used. Application of mini-granules to injected pots of soil, which were being used for in inverse isotopic dilution technique, caused a significant reduction in phosphate availability compared to the non-granulated material but application of the same mini-granules to undisturbed pots of soil caused no decrease in phosphate availability. However, application to undisturbed pots of mini-granulated of "as received" and works ground Arad phosphate rock caused a significant reduction in phosphate availability.

The significant reduction in agronomic value when some materials were granulated led to the hypothesis that mini-granulation reduced the availability of the phosphate when the rate of dissolution of the phosphate rock was significantly reduced by the "clumping" effect, of interactions between groups of particles. When phosphate rock dissolution was slow, or limited by the soil plant environment the "clumping" effect was reduced and granulation had minimal effect on plant yield.

The type of granulation agent had no significant effect on the agronomic performance of the granulated materials, except when tallow was used as a granulation agent and reduced the availability of works ground North Carolina phosphate rock.

The granulation effect does need to be put in perspective. This research necessitated the use of relatively small experimental plots and a limited time frame. In real systems, of greater variability and probably where much stronger forces will contribute to particle breakdown, the reduction in agronomic performance caused by granulation may be an insignificant effect.

Evaluation of different phosphate rocks

Comparisons of results from publications on phosphate rock research proved difficult because the materials are often not clearly characterised. Clear definitions of the origins, particle size distribution, and method of determining reactivity need to be made.

The reactivity of White Youssafia phosphate rock was assessed in terms of solubility in 2% formic acid, relative to North Carolina, Arad and Sechura phosphate rocks. These materials were tested in the form in which they were imported into New Zealand and the results demonstrated that the phosphate in White Youssafia phosphate rock was only 44% soluble in formic acid (30 minute extraction) and therefore less chemically reactive than either Sechura, North Carolina, or Arad phosphate rocks.

A glass house trial of surface applied Arad, North Carolina, Sechura, and White Youssafia phosphate rocks found that their agronomic performance bore little relation to the reactivity or particle size of these materials. The phosphate rocks increased ryegrass yield above the unfertilised control to similar extents, the only significant difference being that the yield derived from Sechura phosphate rock was greater than the yield from North Carolina phosphate rock. As previously there was evidence that the soil/plant environment limited the dissolution of these materials in a manner that was unpredictable. It is suggested that more extensive agronomic evaluations of these phosphate rocks include a range of application rates of both phosphate rock and water soluble phosphate. In this way environmental effects on dissolution can be separated from the effects of the type and form of the phosphate rock, and correct assessments of agronomic performance can be made.

Value of the radioisotopic techniques

Surface labelling of phosphate rock was undertaken as a method of avoiding the problems of trying to generate uniformly P^{32} labelled phosphate rocks. However, only a very limited amount of information about phosphate rock dissolution could be gained from herbage specific activities, because the P^{32} labelled only a small fraction of the rock phosphate and the amount varied with type and particle size distribution of the phosphate rock. The dissolution of different forms of phosphate rock could not be compared using this labelling technique.

The use of chromite labelled with $K_2HP^{32}O_4$ as a control for the surface labelled experiment provided sufficient information to model the plant uptake from soil and fertiliser sources of phosphate, demonstrating that fertilised plant took up more soil phosphate, but the model could not be directly applied to results from the phosphate rock treatments. A soil phosphate fractionation of the phosphate rock treated soil did indicate that 4 to 16% of the works ground North Carolina phosphate rock dissolved during the experiment and it was demonstrated graphically that plant response to this dissolved phosphate was similar to phosphate derived from the K_2HPO_4/chromite treatments.

The injection method was used for the inverse isotopic dilution technique as the only viable method of labelling *in situ* pasture soils, but these results demonstrated that the uptake of fertiliser phosphate by plants does not just cause a simple dilution of P^{32} labelled soil phosphate. Fertiliser treatment stimulated unpredictable uptake of labelled soil phosphate, thus changes in herbage specific activity could not be used to calculate the extent of phosphate rock dissolution in the soil, or the amount of phosphate in the plants which was derived from the phosphate rock fertilisers. The high inherent variability of the isotope data combined with the variability of soil-phosphate rock dissolution systems does not appear to be a combination that is likely to produce meaningful results in these types of short term experiments.

Recommendations for future research

More extensive examination of the interactions between application rate, reactive phosphate rock type, and soil environmental factors such as soil moisture content and soil solution anion concentrations is required, in order to better predict the agronomic availability of reactive phosphate rocks. Factors such as the variability of reactivity within ore samples and the nature of the surface unground reactive phosphate rocks also require consideration.

The effect of surface application of different particle and granule sizes of reactive phosphate rocks needs to evaluated in extensive grazed trials under as realistic conditions as possible, in association with a study of the requirements of the fertiliser industry to generate products with acceptable handling characteristics. The results of such a study would be amenable to a cost/benefit analysis which would determine the viability of granulation.

APPENDIX 1: TREATMENT LIST OF THE GLASSHOUSE EXPERIMENT

The treatments which were applied to pots in the glasshouse experiment are cataloged in the following table in terms of: treatment number, fertiliser parent material, parent material particle size, granulation agent (implies that the fertiliser was granulated), whether the surface of the fertiliser was labeled with P^{32}, the type of pot, the amount of phosphate applied to each pot, whether the treatment involved destructive soil sampling, and designated pots for each treatment. (See ensuing notes for further explanations.)

No.	Fert.	Grind	Gran.	P^{32} label	Pot type	μgP/ pot	Soil fract.	Pot numbers
1.	-	-	-	-	IID	0	-	60 65 70 75
2.	-	-	-	-	SL	0	10	28 88 127 166
3.	NC	WG	-	+	SL	106	-	17 56 116 155
4.	NC	WG	-	+	SL	106	4	26 86 125 164
5.	NC	WG	-	+	SL	106	10	7 46 106 145
6.	NC	WG	-	-	IID	106	-	64 69 74 76
7.	NC	WG	CS	+	SL	106	-	16 55 115 154
8.	NC	WG	CS	+	SL	106	4	22 82 121 160
9.	NC	WG	CS	+	SL	106	10	2 41 101 140
10.	NC	WG	Mg	+	SL	106	-	35 95 134 173
11.	NC	WG	Mg	+	SL	106	4	32 92 131 170
12.	NC	WG	Mg	+	SL	106	10	20 59 119 158
13.	NC	WG	Mg	-	IID	106	-	61 66 71 77
14.	NC	WG	H_2SO_4	-	SL	106	-	1 40 100 139
15.	NC	WG	Tallow	+	SL	106	-	31 91 130 169
16.	NC	WG	-	+	SL	17.9	-	3 42 102 141
17.	NC	WG	-	+	SL	35.0	-	34 94 133 172
18.	NC	WG	-	+	SL	71.1	-	38 98 137 176
19.	NC	WG	-	+	SL	141.0	-	21 81 120 159
20.	NC	AR	-	+	SL	106	-	15 54 114 153
21.	NC	AR	CS	+	SL	106	-	23 83 122 161
22.	NC	AR	CS	-	SL	106	-	6 45 105 144

Appendix 1 continued.

Fertiliser treatments applied in the glass house experiment.

No.	Fert.	Grind	Gran.	P^{32} label	Pot type	µgP/ pot	Soil fract.	Pot numbers
23.	NC	AR	Mg	+	SL	106	-	19 58 118 157
24.	NC	AR	CA	-	IID	106	-	63 68 73 -
25.	NC	FG	-	-	IID	106	-	62 67 72 78
26.	Arad	AR	-	+	SL	106	-	5 44 104 143
27.	Arad	AR	Mg	-	SL	106	-	36 96 135 174
28.	Arad	WG	-	-	SL	106	-	37 97 136 175
29.	Arad	WG	Mg	-	SL	106	-	14 53 113 152
30.	Arad	WG	CS	-	SL	106	-	12 51 111 150
31.	Sechura	AR	-	+	SL	106	-	4 43 103 142
32.	Sechura	AR	Mg	-	SL	106	-	10 49 109 148
33.	Sechura	AR	CS	-	SL	106	-	9 48 108 147
34.	W. Ysf.	AR	-	+	SL	106	-	25 85 124 163
35.	Chromite	AR	-	+	SL	0	-	18 57 117 156
36.	Chromite	AR	-	+	SL	5	-	30 90 129 168
37.	Chromite	AR	-	+	SL	5	4	27 87 126 165
38.	Chromite	AR	-	+	SL	5	10	24 84 123 162
39.	Chromite	AR	-	+	SL	5,no Mg	-	33 93 132 171
40.	Chromite	AR	-	+	SL	5,+CS*	-	13 52 112 151
41.	Chromite	AR	-	+	SL	10	-	29 89 128 167
42.	Chromite	AR	-	+	SL	20	-	11 50 110 149
43.	MCP	AR	-	-	SL	106	-	39 99 138 177

* The material in this pot was not granulated but these pots were fertilised with an equivalent amount of the CS granulation agent.

(a) $MgSO_4$ was applied to all pots, unless otherwise specificed, so as to supply the same amount of $MgSO_4$ as was applied to pots in the fertilisers granulated with $MgSO_4$. The exception was treatment 39.

(b) The surface of some fertilisers was labelled with P^{32}. This is expressed as "+" in the "P^{32} label" column.

(c) Abbreviations used:

1. Fertiliser type ("Fert."): NC = North Carolina phosphate rock.

2. Fertiliser grind ("Grind"): WG = commercial "works" grind.
AR = as received into New Zealand.
FG = Very finely ground (<30μm).

3. Granulation agents ("Gran"): CS = 10% w/w 1:0.6 mix of citric acid and MgSO$_4$, granulating 10% w/w.
Mg = 10% w/w MgSO$_4$.
CA = Contaminated Citric acid.
H$_2$SO$_4$ = commercial partially acidulated product, "Hyphos".
Tallow = 25% w/w animal fat.

4. Type of experimental pot SL = Surface label experimetntal pot (plain PB5).
IID = Inverse isotopic dilution pot (metal ring around pot).

(d) Some treatments (3,7,10 and 36) were repeated and the soil in the pots destructively sampled four or ten weeks after fertiliser was applied (expressed as 4 or 10 in the "Soil fract." column).

APPENDIX 2: EXPERIMENTAL DATA; RATE OF DRY MATTER PRODUCTION

LSD for comparing data from the same harvest only. Within each harvest of each table data not significantly different have the same character postscript and data with no postscript is significantly different from all other data from that harvest.

Table 1 Comparison of the rate of dry matter production (g/pot/day) derived from pots fertilised with different "as received" phosphate rocks in the main glass house experiment .

	Days after fertiliser application						
Treatment(no.)	11	21	37	50	69	85	102
Control(35)	0.0128a	0.0098a	0.0174a	0.0168a	0.0152a	0.0195	0.0325a
NCAR(20)	0.022a	0.0098a	0.022ab	0.021ab	0.0201ab	0.0257a	0.0355a
W.YsfAR(34)	0.0224a	0.0122a	0.0227ab	0.0194ab	0.0223b	0.0271a	0.038ac
AradAR(26)	0.0231a	0.0113a	0.0236b	0.0208ab	0.024b	0.0297a	0.0439b
SechuraAR(31)	0.0247a	0.0108a	0.0231b	0.0226b	0.0246b	0.0309a	0.042bc

LSD(P<0.05)=0.0054

Table 2 Comparison of the rate of dry matter production (g/pot/day) derived from pots fertilised with various fertilisers based on works ground North Carolina phosphate rock in the main glass house experiment.

	Days after fertiliser application						
Treatment(no.)	11	21	37	50	69	85	102
Control(35)	0.0128a	0.0098a	0.0174a	0.0168a	0.0152a	0.0195a	0.0325a
Gr.Mg(10)	0.0248a	0.0111a	0.0281ab	0.0272ac	0.0267b	0.036b	0.0427b
Gr.CS(7)	0.0272a	0.0134a	0.0287ab	0.028c	0.0283b	0.0367b	0.051bc
NCWG(3)	0.0254a	0.0129a	0.0305b	0.0321bc	0.0328bc	0.0418bc	0.049bc
Gr.H_2SO_4(14)	0.0246a	0.0151a	0.035b	0.0372b	0.039c	0.0453c	0.0546c
Gr.Tallow(15)	0.0226a	0.0094a	0.0189a	0.0158a	0.0178a	0.0218a	0.0338a

LSD(P<0.05)=0.00819

Table 3 Comparison of the rate of dry matter production (g/pot/day) derived from pots fertilised with different rates of application of works ground North Carolina phosphate rock in the main glass house experiment.

	Days after fertiliser application						
Treatment(no.)	11	21	37	50	69	85	102
Control(35)	0.0128a	0.0098a	0.0174a	0.0168a	0.0152	0.0195a	0.0325a
10kgP/ha(16)	0.027a	0.0118a	0.0242ab	0.023ab	0.0246a	0.0238ab	0.035a
20kgP/ha(17)	0.0237a	0.0126a	0.0259b	0.0279bc	0.0308bc	0.0304bc	0.04a
40kgP/ha(18)	0.0275a	0.0127a	0.0276b	0.0284bc	0.0323bc	0.0365cd	0.0514b
60kgP/ha(3)	0.0254a	0.0129a	0.0305b	0.0321c	0.0328bc	0.0418d	0.049b
80kgP/ha(19)	0.023a	0.013a	0.0301b	0.0326c	0.0343c	0.0434d	0.0504b

LSD(P<0.05)=0.00835

Table 4 Comparison of the rate of dry matter production (g/pot/day) derived from pots fertilised with different of forms of Arad phosphate rock ("as received" and "works" ground) in the main glass house experiment.

	Days after fertiliser application						
Treatment(no.)	11	21	37	50	69	85	102
Control(35)	0.0218a	0.0098a	0.0174a	0.0168a	0.0152a	0.0195a	0.0325a
AradWG(28)	0.0241a	0.0115a	0.0253c	0.02698	0.0251b	0.0302b	0.0428c
AradAR(26)	0.0231a	0.0113a	0.0236bc	0.0208a	0.024bc	0.0297b	0.0439c
Gr.WG+CS(30)	0.0237a	0.008a	0.0184ab	0.0164a	0.201abc	0.0268b	0.041bc
Gr.AR+Mg(27)	0.0223a	0.0101a	0.0195ab	0.0167a	0.0192ac	0.026b	0.0348a
Gr.WG+Mg(29)	0.0215a	0.0093a	0.0194ab	0.0166a	0.0177a	0.025ab	0.036ab

LSD(P<0.05)=0.00573

Table 5 Comparison of the rate of dry matter production (g/pot/day) derived from pots fertilised with chromite and different amounts of K_2HPO_4, in the surface labeled experiment.

	Days after fertiliser application						
Treatment(no.)	11	21	37	50	69	85	102
Control(35)	0.0128a	0.0098a	0.0174a	0.0168a	0.0152a	0.0195a	0.0325a
20mgP(42)	0.0303a	0.0168a	0.0403c	0.0378c	0.0315b	0.034b	0.0363a
10mgP(41)	0.0304a	0.0137a	0.0328cb	0.0277bc	0.0251ab	0.0244ab	0.034a
5mgP,noMg(39)	0.024a	0.0125a	0.026ab	0.0236ab	0.0189a	0.0234a	0.0306a
5mgP (36)	0.0249a	0.0121a	0.0257ab	0.0199ab	0.0178a	0.0216a	0.0316a
5mgP,+CS(40)	0.0227a	0.0111a	0.0246ab	0.021ab	0.0173a	0.0176a	0.0287a

LSD($P<0.05$)=0.0103

Table 6 Comparison of the rate of dry matter production (g/pot/day) derived from pots fertilised with Mono calcium phosphate and different forms of Sechura phosphate rock in the surface labeled experiment.

	Days after fertiliser application						
Treatment(no.)	11	21	37	50	69	85	102
Control(35)	0.0128a	0.0098a	0.0174a	0.0168a	0.0152a	0.0195a	0.0325a
MCP(43)	0.034	0.0177a	0.0555	0.0485	0.0512	0.0536	0.0636
Gr.SAR+CS(33)	0.0233a	0.0111a	0.0222a	0.0235a	0.0258a	0.0341a	0.0455b
SechuraAR(31)	0.0247a	0.0108a	0.0231a	0.0226a	0.0246a	0.0309a	0.0424b
Gr.SAR+Mg(32)	0.0218	0.0103a	0.0208a	0.0204a	0.0237a	0.0325a	0.039ab

LSD($P<0.05$)=0.0084

Table 7 Rate of dry matter production (g/pot/day) derived from inverse isotopic dilution pots in the glass house experiment fertilised with different forms of North Carolina phosphate rock

	Days after fertiliser application						
Treatment(no.)	11	21	37	50	69	85	102
Control(1)	0.024a	0.0178a	0.0198a	0.0218a	0.0193	0.0205	0.0325
NCWG(6)	0.0318b	0.0258b	0.039bc	0.0433bc	0.0453a	0.0458b	0.0625b
NCFG(25)	0.0298ab	0.028b	0.0445b	0.049b	0.0518a	0.0475b	0.061ab
Gr.WG+Mg(13)	0.0268ab	0.0255b	0.036c	0.0375c	0.036b	0.035a	0.0543a
Gr.AR+CA(24)	0.0253ab	0.021ab	0.025a	0.026a	0.0293b	0.031a	0.0448

LSD($P<0.05$)=0.00703

APPENDIX 3: EXPERIMENTAL DATA; PHOSPHATE UPTAKE BY HERBAGE

Least significant difference (LSD) for comparing data from the same harvest only. Within each harvest of each table data not significantly different have the same character postscript and data with no postscript is significantly different from all other data from that harvest.

Table 1 Phosphate uptake per core (mgP) from different forms of North Carolina phosphate rock, and MCP, in the field experiment.

	Days after fertiliser application						
Treatment	17	29	49	70	92	112	131
No Fertiliser	1.9 a	2.1 a	2.7 a	1.7 a	2.7 a	2.4 a	1.4 a
NCWG	2.1 a	2.1 a	3.3 ab	2.6 ab	3.6 ab	3.5 abc	1.9 a
NCFG	2.2 a	2.2 a	4.0 b	3.1 b	3.8 ab	3.6 bc	2.1 a
Gr.WG 0.5-1mm	2.1 a	2.8 ab	3.9 b	3.0 b	4.1 b	3.5 bc	2.1 a
1-2mm	2.1 a	2.5 ab	3.5 ab	3.0 b	3.4 ab	3.4 abc	1.9 a
2-4mm	2.4 a	2.5 ab	4.2 bc	3.2 b	3.2 ab	3.0 ab	1.9 a
MCP	3.7 b	3.4 b	5.2 c	3.5 b	3.5 ab	4.1 bc	2.3 a

LSD($P<0.05$)=1.06

Table 2 Rate of phosphate (P^{31}) uptake (mgP/pot/day) derived from inverse isotopic dilution pots in the glass house experiment fertilised with different forms of North Carolina phosphate rock.

	Days after fertiliser application						
Treatment(no.)	11	21	37	50	69	85	102
Control(1)	0.0631a	0.0378a	.0.605a	0.06a	0.0455a	0.044	0.045
NCWG(6)	0.1055b	0.0885b	0.113b	0.1263b	0.0985bc	0.1085	0.014a
NCFG(25)	0.10bc	0.0878b	0.1105b	0.1535b	0.122b	0.1368	0.152a
Gr.WG+Mg(13)	0.0778ac	0.0753b	0.0933b	0.1095b	0.0790cd	0.0795a	0.0983
Gr.AR+CA(24)	0.0653a	0.0468a	0.0673a	0.072a	0.065ad	0.074a	0.072

LSD($P<0.05$)=0.0228

Table 3 Rate of uptake of P^{32} (µCi/pot/day) derived from inverse isotopic dilution pots in the glass house experiment fertilised with different forms of North Carolina phosphate rock.

	Days after fertiliser application						
Treatment(no.)	11	21	37	50	69	85	102
Control(1)	0.0963a	0.205a	0.128a	0.136a	0.085a	0.085a	0.101a
NCWG(6)	0.189b	0.348b	0.295b	0.217ab	0.205b	0.167a	0.186a
NCFG(25)	0.185b	0.334b	0.312bc	0.29b	0.226b	0.173a	0.189a
Gr.WG+Mg(13)	0.2598b	0.583c	0.398c	0.280b	0.181b	0.122a	0.129a
Gr.AR+CA(24)	0.235b	0.45d	0.31bc	0.206ab	0.140ab	0.101a	0.121a

LSD($P<0.05$)=0.088

Table 4 Rate of phosphate (P^{31}) uptake (mgP/pot/day) derived from surface labeled experiment pots in the glass house experiment fertilised with chromite and different amounts of K_2HPO_4.

	Days after fertiliser application						
Treatment(no.)	11	21	37	50	69	85	102
Control(35)	0.0588a	0.0173a	0.0435a	0.053a	0.0725a	0.0365a	0.0498a
20mgP(42)	0.1163d	0.0575b	0.1025c	0.1028	0.102	0.0595	0.0565a
10mgP(41)	0.0973cd	0.0365ab	0.082bc	0.078b	0.076a	0.0363a	0.0478a
5mgP,noMg(39)	0.0743ab	0.028a	0.0623ab	0.063ab	0.0773a	0.0373a	0.04a
5mgP (36)	0.0918bc	0.028a	0.063ab	0.059ab	0.071a	0.0338a	0.042a
5mgP,+CS(40)	0.0693a	0.0365ab	0.059a	0.0573ab	0.0688a	0.0303a	0.415a

LSD($P<0.05$)=0.0214

Table 5 Rate of uptake of P^{32} (μCi/pot/day) derived from surface labeled experiment pots in the glass house experiment fertilised with chromite and different amounts of K_2HPO_4.

	Days after fertiliser application						
Treatment(no.)	11	21	37	50	69	85	102
Control(35)	0.0032	0.0018	0.0028	0.0023	0.0028		
20mgP(42)	0.0312ab	0.0277a	0.042a	0.036a	0.0278a		
10mgP(41)	0.0383b	0.0289a	0.052a	0.0285a	0.027a		
5mgP,noMg(39)	0.0229a	0.036a	0.0485a	0.034a	0.0233a		
5mgP (36)	0.0278ab	0.0377a	0.053a	0.032a	0.0228a		
5mgP,+CS(40)	0.0286ab	0.0259a	0.0488a	0.0315a	0.0188a		

LSD($P<0.05$)=0.0128

APPENDIX 4: AlGEBRAIC PROOF FOR SPECIFIC ACTIVITY EQUATIONS

1. Definition

SpactC	Specific activity of the phosphate in herbage cut from a pot where no phosphate rock fertiliser was applied.
SpactPR	Specific activity of the phosphate in herbage cut from a pot where phosphate rock fertiliser was applied.
Pc	Total phosphate content of herbage cut from pots where phosphate rock fertiliser was not applied.
Pt	Total phosphate content of herbage cut from pots where phosphate rock fertiliser was applied.
Pr	Amount of phosphate derived from the fertiliser in herbage cut from a pot where phosphate rock fertiliser was applied.
Pex	Any increase in the amount of herbage phosphate derived from the soil when phosphate rock fertiliser was applied, as compared to Pc.
$P^{32}c$	Total P^{32} content of herbage cut from pots where phosphate rock fertiliser was not applied or where fertiliser was applied but no growth response occurred.
$P^{32}t$	Total P^{32} content of herbage cut from pots where phosphate rock fertiliser was applied.
$P^{32}ex$	Any increase in the amount of herbage P^{32} derived from the soil when phosphate rock fertiliser was applied, as compared to $P^{32}c$.

2. Derivation of specific activity relationship when no growth response to phosphate fertiliser occurs.

$$\text{SpactC} = \frac{P^{32}c}{Pc} \qquad \text{SpactPR} = \frac{P^{32}c}{Pt} = \frac{P^{32}c}{Pc + Pr}$$

It is assumed that if no growth response occurs, but a phosphate uptake response occurs, then all extra phosphate in the herbage, (as compared to the phosphate content of herbage where no fertiliser was applied), was derived from the fertiliser. It is also assumed that the amount and specific activity of phosphate taken up from the soil is the same for the pots where no phosphate fertiliser was applied and pots where fertiliser was applied.

$$\frac{\text{SpactC}}{\text{SpactPR}} = \frac{P^{32}c}{Pc} . \frac{Pc + Pr}{P^{32}c}$$

$$= \frac{P^{32}c.Pc}{Pc.P^{32}c} + \frac{P^{32}c.Pr}{Pc.P^{32}c}$$

$$= 1 + \frac{Pr}{Pc}$$

$$\frac{\text{SpactC}}{\text{SpactPR}} = \frac{Pc}{Pc} + \frac{Pr}{Pc}$$

$$\frac{P^{32}c.Pt}{Pc.P^{32}c} = \frac{Pc}{Pc} + \frac{Pr}{Pc}$$

$$Pr = Pc.\left\{\frac{P^{32}c.Pt}{Pc.P^{32}c} - \frac{Pc}{Pc}\right\}$$

$$Pr = Pt - Pc$$

3. Derivation of specific activity relationship when a growth response to phosphate fertiliser did occur.

$$\mathrm{SpactC} = \frac{P^{32}c}{Pc} \qquad \mathrm{SpactPR} = \frac{P^{32}t}{Pt} = \frac{P^{32}c + P^{32}ex}{Pc + Pr + Pex}$$

The equation for herbage specific activity, under conditions of a growth response to fertiliser, assumes that an extra quantity of soil phosphate will be taken up as a result of the dry matter response. No assumptions are made about the nature of this response except that the specific activity of the extra soil phosphate is the same as that of the rest of the soil phosphate which is taken up by the fertilised plant. It is also assumed, as in section 2, that phosphate taken up from the soil will have the same specific activity regardless of whether fertiliser was applied to the pots or not.

$$\frac{\mathrm{SpactC}}{\mathrm{SpactPR}} = \frac{P^{32}c}{Pc} \cdot \frac{Pc + Pr + Pex}{P^{32}c + P^{32}ex}$$

$$\text{if } Pex = \frac{Pc}{P^{32}c} \cdot P^{32}ex$$

$$= \frac{P^{32}c}{Pc} \cdot \frac{\left(Pc + Pr + \frac{Pc}{P^{32}c} \cdot P^{32}ex\right)}{P^{32}c + P^{32}ex}$$

$$= \frac{(P^{32}c \cdot Pc) + (P^{32}c \cdot Pr) + (\overset{Pc\ .\ {}^{32}Pex}{\cancel{P^{32}c\ .\ Pex}})}{Pc \cdot (P^{32}c + P^{32}ex)}$$

$$= \frac{Pc}{Pc} \cdot \left(\frac{P^{32}c + P^{32}ex + \left(\frac{P^{32}c\ .\ Pr}{Pc}\right)}{(P^{32}c + P^{32}ex)}\right)$$

If $\frac{\mathrm{SpactC}}{\mathrm{SpactPR}} = \frac{P^{32}c}{Pc} \cdot \frac{Pt}{P^{32}t}$

then
$$\frac{P^{32}c}{Pc} \cdot \frac{Pt}{P^{32}t} = \frac{P^{32}c + P^{32}ex + \left(\frac{P^{32}c \,.\, Pr}{Pc}\right)}{(P^{32}c + P^{32}ex)}$$

$$(P^{32}c + P^{32}ex)\,\frac{P^{32}c}{Pc} \cdot \frac{Pt}{P^{32}t} = P^{32}c + P^{32}ex + \left(\frac{P^{32}c \,.\, Pr}{Pc}\right)$$

$$Pr = \left\{\left(P^{32}c \cdot \frac{P^{32}c}{Pc} \cdot \frac{Pt}{P^{32}t}\right) + \left(P^{32}ex \cdot \frac{P^{32}c}{Pc} \cdot \frac{Pt}{P^{32}t}\right) - P^{32}c - P^{32}ex\right\} . \frac{Pc}{P^{32}c}$$

$$Pr = P^{32}c \cdot \frac{Pt}{P^{32}t} + P^{32}ex . \frac{Pt}{P^{32}t} - P^{32}c - P^{32}ex \cdot \frac{Pc}{P^{32}c}$$

$$P^{32}ex = P^{32}t - P^{32}c$$

$$Pr = P^{32}c \cdot \frac{Pt}{P^{32}t} + (P^{32}t - P^{32}c) . \frac{Pt}{P^{32}t} - P^{32}c - (P^{32}t - P^{32}c) . \frac{Pc}{P^{32}c}$$

$$Pr = P^{32}c \cdot \frac{Pt}{P^{32}t} + Pt - P^{32}c \cdot \frac{Pt}{P^{32}t} - P^{32}c - P^{32}t \cdot \frac{Pc}{P^{32}c} + Pc$$

$$= Pt - P^{32}t \cdot \frac{Pc}{P^{32}c}$$

$$Pr = Pt - \frac{P^{32}t}{\mathrm{SpactC}}$$

APPENDIX 5: THE PROBLEM OF NEMATODES

When some of the fractionation pots were sampled for root growth at eleven weeks extensive root galling was found. The cause of these was identified by Dr T.M. Stewart (Massey dept. of Plant Health) as being a heavy infestation of the root knot nematode *Meloidogyne Naasi*. Recordings of this nematode infecting ryegrass are apparently rare in New Zealand although Franklin (1978) recorded that in England the principal hosts of *M. naasi* were barley and ryegrass.

Franklin (1978) reported that the egg masses of *Meloidogyne* spp. were embedded in a gelatinous meshwork with spaces that contained water. Drought conditions (or the air drying of experimental soils) caused this matrix to dehydrate, shrink and harden, so inhibiting the hatching of the eggs until the soil was rewetted. Upon hatching the larvae moved through the films of moisture on the soil particle surfaces to the plant roots. The most favourable conditions for larval movement being a soil at field capacity, so that adequate oxygen as well as water was present, and temperatures of 20 to 30°C. The length of the life cycle will be laregly dependant on the soil temperature being six to seven weeks at 20-26°C and twelve to fourteen weeks in English field conditions of soil temperatures of less than 10°C.

Bird (1974) found that the larvae move enter the root and move into a favourable position (near a vascular bundle) and puncture the surrounding cell walls, possibly introducing growth regulators. Multinucleate giant cells develop around the nematode forming galls. Franklin (1978) found that these galls were commonly inconspicuous and cylindrical and that ryegrass appeared unaffected by the infestation. Bird (1974) reported that the effects of heavy galling would be the stunting of top growth, a relatively greater shoot to root ratio, increased susceptibility to water stress and root infection, and also disturbances of protein synthesis at root exudate patterns.

The effect of fertilisation on plants which have been infected by nematodes has been found to be variable. Yeates (1976) found that the effect of different rates of fertiliser on nematode infested plants depended on the growth stage of the plant and on the presence of other plant pathogens. The plants showed variously a good differential response to different rates of fertiliser, or no response at all.

In this experiment there was a significant yield response upon the application of fertiliser, although the presence of nematodes may explain why there was no significant growth rate response at the second harvest from any treatment. It is possible that total yields were reduced overall and also possible that the degree of differentiation between the treatments may have been affected. Nematodes may have been the cause of the high variability of the phosphate content of the herbage (section 7.3.7), and also the unaccountable drop in the phosphate to dry matter ratio which occurred in some treatments, although this effect was not statistically significant.

Nematodes may have been the cause of the decrease in yield between the treatments in black polythene bags and those of the isotopic dilution experiment where the bags were inside a cylinder of galvinised iron. The presence of the cylinders may have reduced the soil temperature and therefore reduced the extent of the nematode infection.

The conditions and duration of the experiment were ideal for root knot nematode infection and no nematicides were ever applied to the pots. While the general growth trends in the experiment may not have been affected by the nematodes the general applicabilty of the results, especially those concerning relative comparisons, must be called into question. Results most likely to be affected were the ratios found in the various P^{32} models expressing the extent of fertiliser phosphate uptake compared to native soil phosphate uptake.

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