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Phosphate and micronutrient behaviour under flooded and aerated soil conditions

Ahmad, Fiaz

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PHOSPHATE AND MICRONUTRIENT BEHAVIOUR UNDER FLOODED AND AERATED SOIL CONDITIONS

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By

FIAZ AHMAD
B.Sc. Hons, M.Sc. Hons
(UAF, Pakistan)

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School of Agricultural and Forest Sciences,
Department of Soil Science,
University of Wales,
Bangor,
UK.

IN THE NAME OF ALLAH, THE COMPASSIONATE, THE MERCIFUL.

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DEDICATION

To my daughter AYMAN

(who was born in UK during my studies)

SUMMARY

The study was undertaken to investigate the behaviour of Phosphorus (P) and micronutrients (Fe, Mn, Cu & Zn) under waterlogged and aerated soil conditions. These soil conditions are common, in Pakistan, in areas where irrigated paddy rice-wheat rotations are practised. Soils undergo periods of flooding and aeration and changes in the availability of these nutrients take place. The study was carried out performing incubation studies, pot trials and sorption studies. Pyrophosphate (PP) was used with orthophosphate (OP), in most of the studies, to investigate its reported superiority as an amendment fertilizer compared with OP alone, its hydrolysis to OP and its role in affecting the availability of micronutrients, particularly zinc. "Organic acids" were used, in sorption studies, to evaluate their effectiveness in decreasing P sorption with or without added PP.

Flooded conditions during both laboratory incubations and pot trials increased the extractability of soil P. These increases varied with the soil type and flooding periods and were related to the amounts of iron oxides/ hydroxides "reduced" during the flooded periods. Moist aerated conditions favoured greater sorption/ precipitation of applied P, probably by iron oxides/ hydroxides, than the flooded conditions. Alternating flooded and moist aerated conditions greatly increased P sorption.

During a greenhouse grown paddy rice crop, soil P availability increased during an initial period of 4 weeks and then decreased until 10 weeks whereas during the wheat crop soil P decreased throughout the growth period. The decreases in P during the growth of paddy rice were probably due to P uptake and during the wheat crop due to both P sorption and plant uptake. The behaviour of soil micronutrients in laboratory incubations was different from that in pot trials. Generally, soil Fe, Mn and Cu increased with flooding during pot trials and soil Zn decreased. Soil Fe (NH_4HCO_3-DTPA extractable) decreased in the previously flooded soil (paddy rice) when subjected to moist aerated conditions during wheat crop (i.e 4* & 8* weeks). Extractable soil P also decreased during that period probably due to precipitation with Fe.

The addition of 10% lime, rather than 5%, during both paddy rice and wheat crops, increased soil P and decreased soil micronutrients (Fe, Mn, Cu & Zn), probably due to increases in soil pH.

Pyrophosphate (PP) hydrolysed more quickly in the soils than in solution, with the greatest hydrolysis being observed in a Pakistani soil compared with the local soils (brown earth & brown podzolic).

Pyrophosphate (PP) addition in small proportions with orthophosphate (OP) caused positive effects on the availability and plant uptake of soil P, Fe, Mn, Cu and Zn during both incubation studies and pot trials. Pyrophosphate (PP) addition to soils from Pen-y-Ffridd and Pakistan maintained lower pH values than OP alone during both flooded and moist incubations, which perhaps partially contributed in maintaining greater P availability.

During sorption studies, added PP clearly showed its superiority over OP alone. Addition of 10% PP with OP was found to be highly effective in totally inhibiting the sorption of P by $CaCO_3$ and a Pakistani soil. Added pyrophosphate (PP) also maintained pH values < 6.5 whereas in OP treated samples pH increased up to >7.5. Pyrophosphate probably blocked the sorption sites of $CaCO_3$ in these systems and prevented the formation of DCPD crystals. Added pyrophosphate also affected P sorption by brown podzolic soil, but the effects were much smaller. Added "organic acids", extracted from soil and rice straw, further decreased P sorption in most of the cases whereas 0.1M citric acid in the presence of $CaCO_3$ increased P sorption. In Pakistani soil, a PP extract of soil also increased P sorption probably by increasing the iron content in the solution. Sorption of P by brown podzolic soil increased on the addition of lime to this soil, probably because of increased "Ca" in the solution and/ or due to precipitation of Fe-P compounds as pH increased with liming.

Addition of pyrophosphate (PP) to soils, in the presence of Zn was also effective in decreasing P sorption, however Zn sorption increased in the presence of PP. In a soil free $CaCO_3$ system, added PP decreased Zn sorption compared with OP alone. Added Zn caused decreases in P sorption by $CaCO_3$ and the soils studied.

Keywords: aerobic, anoxic, micronutrients, organic acids, orthophosphate, paddy, phosphate, pyrophosphate, rice, waterlogged, wheat, zinc

CONTENTS

REFERENCES

APPENDICES

CHAPTER
1

Chapter 1: General Introduction

1.1. The Problem of Phosphate supply to rice and wheat in Pakistan

1.1.1. Pakistan: Physiography and Climate

Pakistan lies between latitude 14° and 37° north and longitude 61° and 75° east, with Kashmir extending to 80° east. Pakistan has its borders with India to the east, Iran to the west, Afghanistan to the north-west and with China to the north. Pakistan has a total area of 796,096 km^2 with four provinces, Balochistan (43.6%), Sind (17.7%), Punjab (15.9%), North Western Frontier Province (9.4%) and a Federally administered tribal area (3.4%) (Pakistan News, 1986). The country can be mainly divided into two distinct physical provinces: the Western Highlands and the Indus plains resulting from the deposition of sediments by the Indus river and its tributaries into shallow bays in the quaternary era (Khan, 1991). The Western Highlands can be divided into the following physiographic divisions: Mountainous North, Safed Koh and Waziristan Hills, Sulaiman and Kirthar Mountains, Balochistan Plateau and Potwar Plateau and the Salt ranges. Brief details about the Indus plains and their main divisions are given below as most of the agricultural land belongs to these divisions. The Indus Plains have been formed by the alluvium laid down by the Indus and its tributaries. The Indus is a mighty stream about 2,900 km (1800 miles) long and has a catchment area of 963,500 sq. km (372,000 sq. miles). From its source in the Mansarowar Lake down to Sazli, the Indus flows from east to west in a valley several miles deep between lofty mountains like the Karakoram and the Great Himalayas. The Indus Plains can be divided into the following physiographic divisions: Piedmont Plains, Alluvial Terraces, Active Flood Plains, Old Flood Plains, Deltaic Plains, Rolling Sand Plains and Dunes.

Extensive Piedmont Plains have developed between the Indus river and the Sulaiman-Kirthar mountains. They have been built by the alluvial fans developing along the rivers flowing eastward down the mountains. Two smaller areas of alluvial fans have emerged south of Siwaliks between the Jhelum and the Chenab River and between the Chenab and the Ravi river. These rivers become active during the rainy season and flow down the mountain slopes swiftly. They drop part of their sediment load as they slow down at the foothills and split into narrow channels as they move further.

Some parts of the interfluves of the Upper Indus Valley are occupied by alluvial terraces. These terraces are depositional and were formed during the Pleistocene times. The terraces are locally called "bars" and the interfluves, "doabs". Sandal Bar in the Chaj or Jech Doab (between the Jhelum and the Chenab), the Nili Bar in the Rachna Doab (between the Ravi and the Chenab) and the Ganji Bar in the Bari Doab (between the Ravi and the Sutlej-Beas) are the best known examples. The sediments of the terraces are called "old alluvium".

The active flood plains, locally called "bet", are narrow strips of land along the Indus River and its main tributaries, the Jhelum, the Chenab, the Ravi and the Sutlej. They are most extensive along the Indus (24-40 km width) and least along the Ravi (3-5 km width) and form important farming areas.

The old flood plains cover extensive areas between the "bet" and the "bar" uplands in the Upper Indus Valley and between the "bet" and the dessert areas in the lower Indus Valley. The old flood plains are one to two meters above the active flood plains and constitute the main agricultural areas of Pakistan.

The Indus River has built a large delta at its mouth. The area bounded by the Kalri and the Pinyari, two distributaries of the Indus River, is taken as the Indus Delta.

An extensive area in the south-west of Pakistan is covered with rolling sand plains and dunes. It is separated from the Indus valley by the dry channels of the Ghaggar river in the Punjab, which is called the Nara or Dhoro Purna River in Sind. This extensive dessert is called Cholistan in Bahawalpur, Pat in Northern Sind and Tharparker or Thar in Southern Sind. Agriculturally it is a poor area. With the extension of irrigation facilities some areas have been reclaimed. In patches "barani" (rain-fed) farming is practised.

The climatic regions in Pakistan may be divided into arid, semi arid, humid and the highland climate. The highlands experience high rainfall and cool temperatures. In the north, because of great heights, the mountain tops record freezing temperatures all year round. The hills and mountains also attract more rain than the plains. The monsoon winds which come in July and continue to blow until September bring rainfall. Pakistan receives only the tail-end of the monsoons, therefore the monsoon season is neither as prolonged nor as wet as in India. The temperature in the plains in winter (December-January) and summer (June-July) may range from 0°C to 50°C respectively.

1.1.2. Pakistan: Economy, Agriculture and Constraints

Pakistan, since its emergence in 1947, has been struggling for a strong economy. The annual per capita income was recorded to be about $30 in 1986-87 (Khan, 1991). The main sectors which contribute to the economy of the country include fishing, agriculture (crops and livestock), forestry and industrial products. The major contribution to the economy is through agriculture. Cotton (including yarn, raw cotton and cloth) and rice are the main exports which make up 34% and 8.8% respectively of the country's total exports. (Anonymous, 1981, 1985).

Agriculture in Pakistan concentrates on the production of food crops. Wheat is the staple food and covers about 37% (1981-85) of the cropped area, followed by rice which makes up about 10% of the total cropped area. Cotton is also an important cash crop for Pakistan and is grown on an area of 2.2 million hectares (Khan, 1991) which is still increasing. Other crops grown in Pakistan include maize, sugarcane, millet, pulses and oilseeds etc.

The main constraint in the development of the country is the rapidly increasing population. Pakistan had a population of 84.3 million (1981) with annual growth rate of 3.1% (Khan, 1991). The present population is thought to be over 120 million. Much of the agricultural growth is eaten away by the huge population increase. Other factors which have restricted development are political instability, lack of social justice, improper exploitation of the natural resources, illiteracy, soil salinity and water logging and some climatic and physiographic constraints. Urbanisation of people, and the building of houses and industries on fertile lands, have adversely affected the country's agriculture.

Most of the farmers have small holdings which are sometimes in scattered form. The access of heavy machinery to such fields is impossible and also uneconomic. Moreover the lack of resources has limited the use of modern machinery. Occasional and sometimes unwanted rains (annual floods) destroy the crops.

1.2. General Roles of Phosphorus

Phosphorus (P) makes up about 0.12% of the earth's crust (Cathcart, 1980). It is present in almost all soils and rocks, in water and in plant and animal remains. The world's supply of P comes from mineral deposits, a non-renewable natural resource. The most common of the minerals containing phosphorus are of the apatite group $[Ca_{10}(PO_4,CO_3)(F,OH)_{2-3}]$. Phosphorus, an indispensable element for life, plays key roles in animal as well as in plant metabolism.

In soils, available phosphorus usually exists in the form of orthophosphate ions i.e. $H_2PO_4^-$ and HPO_4^{2-}. Absorption of $H_2PO_4^-$ is greater at low pH values, whereas more HPO_4^{2-} is taken up at higher values of soil pH. In contrast to nitrate nitrogen, phosphate anions are either adsorbed by the soil or are precipitated as products with low solubility.

In plants, phosphorus occurs in concentrations between 0.1-0.4%, lower than those typically found for N and K (Tisdale *et al.*, 1993). In its prime importance in plant nutrition, phosphorus plays important roles in photosynthesis and oxidation-reduction reactions. The most essential function of P in plants is in energy storage and transfer. Energy obtained from photosynthesis and metabolism of carbohydrates is utilised in the synthesis of the energy-rich phosphate compounds (ADP and ATP) for subsequent use in growth and reproductive processes (Tisdale, *et al.*, 1993). Phosphorus is an important structural component of nucleic acids, coenzymes, nucleotides, phosphoproteins, phospholipids and sugar phosphates. A good supply of phosphorus is associated with increased root growth, early maturity of grain crops and greater straw strength. The quality of certain fruit, forage, vegetable and grain crops is also improved and disease resistance increased with satisfactory P nutrition (Tisdale, *et al.*, 1993). Furthermore, inorganic phosphorus controls some key enzyme reactions. For example, in fruit tissue of tomato, inorganic P released from the vacuoles into the cytoplasm can stimulate phosphofructokinase activity, an enzyme which can initiate the respiratory burst correlated with fruit ripening (Woodrow and Rowan, 1979). Delayed fruit ripening in phosphorus-deficient tomato plants (Pandita and Andrew, 1967) may be related to this function of inorganic phosphorus. The phosphorus requirement for optimal growth is in the range of 0.3-0.5% of the plant dry matter during the vegetative stage of growth (Marschner, 1995). Phosphorus deficiency is associated with a reduction in leaf expansion and leaf surface area (Freeden *et al.*, 1989) and number of leaves (Lynch *et al.*, 1991). Moreover, due to P deficiency flower initiation is delayed (Rossiter, 1978), the number of flowers decreased (Bould and Parfitt, 1973) and seed formation restricted in particular (Barry and Miller, 1989). Premature senescence of leaves may also limit seed yield in phosphorus-deficient plants (Batten *et al.*, 1986).

1.3. Phosphorus use in Pakistan

Due to the developments in agriculture and the need for better crop production in Pakistan, demand for greater fertiliser application has increased. The annual report (1993-94) of National Fertiliser Development Corporation in Pakistan has estimated the phosphate (P_2O_5) fertiliser requirement to be 475 thousand tonnes; with an increase of 5% over the previous year (1992-93). The local production in Pakistan supplies only 40% of the total demand and the remaining 60% is imported from overseas (Anonymous, 1993-94). Although the installation of a new DAP (diammonium phosphate) plant by FFC (Fauji Fertiliser Company), will produce about 450 thousand tonnes of DAP annually by 1996, the demand for fertilisers will not be met locally. An estimated 510 thousand tonnes of phosphate fertiliser have had to be imported (Anonymous, 1993-94).

Application of fertilisers in Pakistan is divided into two major agricultural seasons i.e. Rabi (October-March) and Kharif (April-September). Rabi is the crucial season both for application and planning fertiliser supplies. Phosphate consumption has been reported to be about 310 thousand tonnes and 145 thousand tonnes during Rabi and Kharif seasons respectively. About 60% of phosphate and 70% of DAP are consumed during November and December (Anonymous, 1992-93). Wheat and rice are the two major crops of Rabi and Kharif seasons respectively. A major part of the phosphorus is applied to the wheat crop at the time of cultivation to fulfil the fertiliser requirements for better crop production.

1.4. General Literature Review

1.4.1. Phosphorus behaviour under Flooded and Moist soil conditions

When air dried soils are flooded / submerged in water, a series of physical, chemical and biological processes are initialised. These processes can change and affect the qualities of soils as media for plant growth. The nature, pattern and extent of these changes may vary from soil to soil. Most of these changes are reversed on draining or drying the flooded soils. Flooding the soil has a marked effect on the behaviour of several important plant nutrients and on the growth and yield of crops like rice (Oryza sativa L.). The availability of some of the nutrients increases while others are subjected to greater fixation or loss from the soil as a result of flooding. Alternate flooding and drying of the soil is considered detrimental to the availability of both applied fertiliser and native resources of nitrogen and phosphate (PO_4^{3-}). These changes in plant nutrient availability resulting from flooding are largely due to biological oxidation-reduction processes brought into play by the exclusion of oxygen from the flooded soils.

The behaviour of phosphorus under submerged conditions is quite different from nitrogen or other major nutrients in soil. When oxic soils are submerged, changes in pH, Eh and availability of nutrients take place. Larsen *et al.* (1991) found that flooding lowered the redox potential to between -150 mv and -300 mv and stabilised the pH to 7 or so. During flooding, there is always a trend for pH change towards neutral soil reaction (pH 7). Submerging a soil causes an increase in pH of acidic soils and a decrease in pH of alkaline soils (Ponnamperuma, 1972). Increases in the availability of native and added P whether in terms of soil extractability or plant uptake have been reported by Shapiro (1958) and Mahapatra and Patrick (1969). Hydrolysis of iron and aluminium in association with a rise in pH during flooding are quoted as the source of increases in phosphate availability in acidic soils (Willet, 1989), with the liberation of sorbed and chemically bonded phosphate (Ponnamperuma, 1972).

Inorganic phosphorus in soil exists in different mineral forms. The solubility and forms of these minerals may change with flooding (Lindsay, 1979). In most soils, the Fe-P fraction increases due to flooding (Mahapatra and Patrick, 1969) possibly due to the transformation of variscite into vivianite (Lindsay, 1979). Alternate flooding and drying conditions may also affect the different fractions of P in soil. Sah and Mikkelsen (1986a) reported that Fe-P and Ca-P fractions increased due to flooding whereas Al-P and Rs-P (occluded P) decreased. They found decreases in Al-P and Fe-P and increases in Rs-P (occluded P) fractions during the drainage period in flooded rice cropped soils. Xiao (1988) concluded that P in gleyed paddy soils was dominated by occluded P while Fe-P was lower than that in non gley paddy soils; concluding that the lower contents of available P in the gley paddy soils were due to their lower rate of P release, greater P fixing capacity and also leaching of P during long term submergence.

Calcareous soils are dominated by calcium phosphates like flourapatite $[3Ca_3(PO_4)_2].CaF_2$ and most commonly carbonate apatite $[3Ca_3(PO_4)_2].CaCO_3$, a more reactive derivative of flourapatite (Chien and Black, 1976; Chien, 1977a,b). During flooding periods partial pressure of CO_2 rises and more phosphorus is released in soil solution due to the dissolution of calcium phosphates. Moreover, in alkaline soils increases in the solubility of P are consequences of the decrease in pH of these soils on flooding; for the solubility of hydroxyapatite increases as the pH decreases (Stumm and Morgan, 1970; Sah and Mikkelsen, 1986a).

Soil temperature in addition to moisture contents may also affect the solubility of soil phosphorus. Gill and Meelu (1983) reported that high temperature (33±2°C) in combination with high soil moisture content increased phosphorus availability significantly over the low temperature (13±2°C) and moisture contents. Decreases in ionic strength of the solution with flooding may also affect the availability of P in solution. Neue *et al.* (1990) stated that P retention increased with ionic strength but flooding of highly saline soils improved P availability. However such flooding changes not only the ionic strength but also pH and Eh. Curtin *et al.* (1992) concluded from the experiments on the influence of salt concentration and sodicity on the solubility of phosphate in soil that as the sodicity increased, water extractable P increased substantially. The main effect of sodicity was that it made the weakly absorbed P more labile. Increase in sodicity had little effect on the more strongly adsorbed P fraction (NaOH-P) or on Ca-bound P (HCl-P).

Mineralisation of organic phosphorus (OM) during flooding is a minor source of available phosphorus for plants (Patrick and Mahapatra, 1968) except in flooded organic soils (Racz, 1979). Organic forms of phosphorus are not important in the nutrition of rice as mineralisation of organic phosphorus releases only 2-4 % available phosphorus per year (Patrick, *et al.*, 1985).

Alternate flooding and drying conditions may cause considerable P transformations (Sah and Mikkelsen, 1986a); increase amorphous Fe levels and P sorption (Sah and Mikkelsen, 1986b, 1986c) and induce P deficiency, which may persist for several years (Willet and Higgins, 1978; Sah and Mikkelsen, 1986c), in crops grown after rice. Several Fe forms in soil are reported to correlate with P sorption (Willet and Higgins, 1980; Kuo and Mikkelsen, 1979; Torrent, 1987). Poorly crystalline or amorphous Fe-oxides due to their high reactivity and surface area play a considerable role in P sorption (Sah *et al.*, 1989; Kirk *et al.*, 1990).

During rice-wheat rotations soils undergo periods of alternate flooding and drying conditions. Rice cultivation is practised under complete submergence and hence considerable amounts of phosphorus become available to the crop whereas for the wheat crop, under oxic conditions, there is always a substantial need of phosphorus fertiliser application.

1.4.2. Phosphorus behaviour under Calcareous soil conditions

Most of the calcareous soils, which cover 30% of the world land surface (Chen and Barak, 1982), are deficient in soil P. Phosphorus deficiency in these soils is mainly due to their greater $CaCO_3$ contents which form insoluble compounds with P. Calcareous soils have been defined by Kadry (1973) as:

"The soils with high calcium carbonate content whose physical problems of land and water use for crop production are primarily dominated by the high content of $CaCO_3$, especially the active fraction with a large specific area."

Much work has been done on the reactions of phosphorus under calcareous conditions. It is well known that increasing the concentration of solution Ca^{2+} decreases P solubility (Barrow, 1972 and Lehr and van Wesemael, 1952) irrespective of reaction mechanism. Conversely, increasing solution P by adding ammonium-P fertiliser lowers the soil solution Ca^{2+} (Adams, 1966; Bennet and Adams, 1970). However the exact mechanism by which native or applied phosphorus reacts with the soil $CaCO_3$ is still disputed. It has been suggested that "adsorption" and "precipitation" may be involved. These reactions depend upon the amount of soluble phosphorus in soil solution. Cole *et al.* (1953) suggested that the lower concentration of P application will initiate adsorption while the greater P application will result in precipitation. Studies on the adsorption of P by calcite and calcareous soils have been reported by using Langmuir adsorption isotherms (Cole *et al.*, 1953; Kuo and Lotse, 1972). The fact that P precipitates and forms crystalline P compounds in soils has been shown by Lindsay *et al.* (1962) and Bell and Black (1970a, b, c,). Adsorption might be the first reaction followed by precipitation. Griffin and Jurinak (1973, 1974) concluded that the reaction was completed in two steps when P was applied to calcite. In the first step adsorption of P took place on the calcite surface and in the second step amorphous calcium phosphates were formed on the calcite surface which subsequently transformed into crystalline calcium phosphates. Sample *et al.* (1980) stated "P retention should be regarded as a continuum embodying precipitation, chemisorption and adsorption."

In calcareous soils adsorption on $CaCO_3$ surfaces and the precipitation of insoluble Ca-P compounds would greatly reduce plant available P. The reactions of phosphorus with $CaCO_3$ depend upon the amount of free $CaCO_3$ in soil suspension and its specific surface area. The reactivity of $CaCO_3$ and its surface area increases as effective $CaCO_3$ particle size distribution decreases (Holford and Mattingly, 1975a). The ratios of Ca^{2+} and P activity in the soil system may control the formation of initial P compounds and their subsequent transformation to other P compounds (Kissel *et al.*, 1985). The reaction products that take place when orthophosphate fertiliser is applied to calcareous soils are dicalcium phosphate dihydrate (DCPD) (Bell and Black, 1970b; Lindsay *et al.*, 1962), octacalcium phosphate (OCP) (Amer and Ramy, 1971; Larsen, 1967), and the more basic hydroxyapatite (HA) (Griffin and Jurinak, 1974; Lehr and Brown, 1958). Although DCPD and OCP are considered to maintain adequate levels of solution P required for maximum plant growth (Olsen and Khasawneh, 1980), their subsequent transformations into HA may limit the growth of most of the crops in calcareous soils.

1.4.3. Phosphate and Micronutrient Interactions

Interactions occur between phosphorus and different micronutrients. Such interactions may take place in the soil or in the plants. The major reactions of P in acid soils have been found to be with oxides and hydroxides of iron and aluminium as their concentration in these soils is much greater than that of $H_2PO_4^-$. Udo and Uzu (1972) have shown that the removal of Fe and Al oxides drastically reduced the capacity of soils to sorb P. In addition to $CaCO_3$, in calcareous soils Fe and Al oxides may also serve as P sorption sites. Holford and Mattingly (1975b) found that the high energy sorption sites which accounted for 22-37% of P sorption capacity in calcareous soils were closely related to dithionite extractable Fe. There is contradiction in the literature about the nature of reactions which take place between P and Fe in soils. One view holds that $H_2PO_4^-$ is adsorbed by the Fe oxide surface whereas the second view believes the $H_2PO_4^-$ and Fe^{III} to be stoichiometrically precipitated. These precipitates become increasingly insoluble with ageing (Brady, 1990). In soils dominated by $CaCO_3$, adsorption and precipitation of phosphorus (Freeman and Rowell, 1981) are related to $CaCO_3$ particle size distribution rather than to total chemically determined $CaCO_3$. Oxides of Fe and Al which dominate acidic soils (Mc Laughlin, *et al.*, 1981) may govern precipitation either through reaction with P or through a modifying effect of the $CaCO_3$ phase in calcareous soils. Any reaction that increases the Fe^{III} activity of Fe oxide will enhance the precipitation between Fe^{III} and $H_2PO_4^-$, resulting in soil P of very low solubility.

Different researchers have found P induced Fe-chlorosis in plants. Ayed (1970); Brown (1959) and Lingle *et al.* (1963) found high levels of P induced Fe-chlorosis in soybean tissues. Although they found the concentration of Fe to be normal, P/Fe ratio was higher in chlorotic plants. Mengel *et al.* (1984) attributed the elevated levels of phosphorus in chlorotic leaves to growth inhibition (concentration effect) rather than to the cause of iron chlorosis. It has been reported that the capacity of the plants to adsorb and hold Fe in a soluble form becomes less as the P concentration in the plant rises. Depression in Fe contents of plant tissues due to added phosphorus was noticed by Warnock (1970). As Fe^{III} ions are reduced to Fe^{II} prior to adsorption by plant roots (Brown *et al.*, 1961; and Chaney *et al.*, 1972), the reducing conditions in the rhizosphere may have a considerable effect on Fe uptake. Some reports indicate that Fe phosphate may precipitate externally on the roots (Ayed, 1970), but the interaction of Fe and P leading to Fe chlorosis appeared to be caused by an internal immobilisation of Fe probably due to the formation of Fe phosphate (Rediski and Biddulph, 1953). Since phosphate ions compete with the plant for Fe, the effectiveness of P in causing Fe deficiency should vary with the $H_2PO_4^-$ activity, pH and redox potential created by the adsorbing tissues (Adams, 1980). Thus if a plant can compensate for higher $H_2PO_4^-$ activity by lowering the pH and Eh, Fe availability can be maintained at a suitable level.

Soil solution concentration of Mn^{II} is governed by the solubility of Mn oxides such as Mn_2O_3 and MnO_2 which is related to pH and Eh (Adams, 1980). The availability of Mn^{II} like Fe^{III} is reported to be greater at low pH and Eh. Availability of Mn may increase with the application of phosphate fertilisers which are acidic in reaction. The decreased soil pH associated with high P rates can account for increased Mn uptake by plants (Bingham and Garber, 1960; Bingham *et al.*, 1958; Larsen, 1964; Page *et al.*, 1963; Smilde, 1973). Contrary to this P fertilisers may not affect (Bingham and Martin, 1956) or may decrease Mn uptake by plants (Heintze, 1969; Racz and Haluschak, 1974). In highly buffered soils, P fertilisers may have no effect on the availability of Mn due to little or no changes in pH (Adams, 1980). Furthermore, the cation in P fertiliser may increase the cationic antagonism associated with Mn uptake. Phosphorus induced Mn deficiency in Oats (Avena sativa L.) in alkaline soils reported by Heintze (1969) supported the effect of cation in P fertiliser.

Zinc plays some important roles in protein synthesis, numerous enzymatic functions, and production of chlorophyll and RNA. It is absorbed by plants by an active process that is influenced by biological and environmental factors (Bowen, 1969). In soils that are derived from limestone or calcareous sandstone, Zn content tends to be quite low (<150 $\mu g\ g^{-1}$ of soil) (Wedephol, 1978). However plant Zn cannot be estimated from the total soil Zn. Interaction of P and Zn has been studied by quite a few researchers in the past since 1936 (West, 1938; Boawn *et al.*, 1954, 1957; Thorne, 1957; Stuckenholtz *et al.*, 1966). The interaction or "P-induced Zn deficiency" has been connected with high levels of available P or with the application of P to the soil. The following four causes have been quoted by Mortvedt *et al.* (1972). (i) a P-Zn interaction in the soil (ii) a slower rate of translocation of Zn from the roots to the tops (iii) a simple dilution effect on Zn concentration in the tops owing to the growth response of P and (iv) a metabolic disorder within plant cells related to an imbalance between P and Zn, or an excessive concentration of P interfering with the metabolic functions of Zn at certain sites in the cell. Brief details about phosphorus and zinc interactions have also been reviewed in a separate chapter (Chapter 7).

Copper is not generally considered to be a problem micronutrient for plant growth. Its concentrations in soil solution are normally very low with a large proportion being present as organic complexes (Adams, 1980). The low levels of soluble Cu in soil may result due to high soil P, high organic matter and nitrogen and high soil Zn (Lucas and Knezek, 1972). Total Cu in soil may range from 2 to 100 ppm (Landon, 1991). The continuous use of the fertiliser may accumulate Cu to toxic levels which can cause Fe chlorosis (Reuther and Smith, 1952). Reports of P induced Cu deficiency are very limited, however heavy or prolonged use of phosphatic fertilisers may enhance such interactions (Bingham *et al.*, 1958; Bingham and Garber, 1960; Bingham, 1963; Spencer, 1966; and Landon, 1991). Copper toxicity in citrus, due to fungicide applications, has been reported to be corrected by the application of high P rates (Spencer, 1966). The reports of Bingham and Garber (1960) and Bingham and Martin (1956) also confirmed that high rates of P fertiliser to citrus reduced Cu contents of leaves, reduced growth and caused Cu deficiency symptoms. They attributed this deficiency to the interference of $H_2PO_4^-$ in soil solution with Cu absorption. Some contradictory reports in the literature consider the interaction of P and Cu to be synergistic rather than antagonistic (Greenwood and Hallsworth, 1960). They reported increases in the concentration and uptake of Cu with the application of P. As the availability of Cu decreases with an increase in pH (Landon, 1991), applied P fertilisers having acidic reaction may increase soil Cu in calcareous soils. Racz and Haluschak (1974) observed increases in water soluble Cu with the addition of ammonium hydrogen phosphate ($NH_4H_2PO_4$) fertiliser.

1.5. Aims and Scope of the Study

The consumption of P fertilisers in Pakistan is increasing day by day. Although, increases in agricultural crop production have been obtained in the last few years, the profit margins have declined due to huge increases in the cost of fertilisers. This study was carried out to investigate the behaviour of phosphate and its effect on micronutrients under flooded and moist conditions; a problem related to paddy rice-wheat grown areas in Pakistan. The study includes some basic laboratory based incubation experiments to investigate the behaviour of phosphorus under flooded and moist aerated conditions. It was decided that a simple flooded soil approach would be used rather than attempt to measure/ control redox potential. The effects of P fertilisation either as orthophosphate (OP) alone or in combination with pyrophosphate (PP) and two lime levels are investigated on paddy rice and wheat crops. Wheat and paddy rice are grown in pots in the green house, on the brown earth soil from Pen-y-Ffridd (Denbigh Series, Appendix I) treated with two lime levels (i.e. 5% and 10% on w/w basis). The effects of applied P fertilisers and their interaction with micronutrients under flooded and moist aerated conditions both in soil and plant tissues are investigated.

Studies on pyrophosphate (PP) hydrolysis and phosphate sorption are carried out. The effects of the addition of different organic acids, such as might be released from plant roots, on P sorption would also be included in the studies using agricultural lime and different soils. A separate chapter reports the effects of applied Zn on P sorption in the presence of agricultural lime and different soils.

CHAPTER

2

Chapter 2: Materials and Methods

The methods used in the experiments were as follows unless otherwise mentioned.

2.1. Soil Sampling

Soil sampling was done from 0-15cm depth of a typical UK cultivated land at Aber Farm, UCNW (SH652734), from a grass field (0-15cm depth) "overlimed" for 20 years near Pen-y-Ffridd research station, Bangor (SH 561702), from the Bs horizon of a brown podzolic soil at Gwydyr Forest (SH 757573), North Wales and from a field in the University of Agriculture Faisalabad, Pakistan. Samples were dried in the oven at 32±3° C, ground, sieved (< 2 mm) and stored in polythene bags.

2.2. Mechanical Analyses

The method was followed as described by Day (1965). Soil samples weighing 50g each in 1 litre glass beaker were boiled with 500 ml distilled water. The samples were cooled and 5 ml successive portions of 30 volume H_2O_2 were added until the effervescence ceased. The excess H_2O_2 was destroyed by boiling. The samples were transferred to plastic beakers along with 25 ml (5%) calgon solution and 25 ml distilled water. The soils were dispersed for 5 minutes with ultrasonic disintegrator at maximum output. After dispersion the material in each beaker was transferred to 1 litre measuring cylinders with hydrometers in place. The volumes were made up to 1 litre and additional 25 ml portions of distilled water were added to each cylinder. Soils were mixed thoroughly with plunger and starting times and temperatures were noted. Density of the suspensions were recorded as units g/l after time intervals of 40 seconds, 4.00, 37.5, and 120 minutes. The soils were removed from the cylinder after recording the final reading. Large fractions (630μm, 200μm and 63μm) were separated by suitable sieves. The weight of each fraction was recorded after labelling and oven drying at 105^oC.

2.3. Soil pH

Soil pH of each sample was determined in soil suspension (1:2.5) by using glass electrode. The suspensions were made with distilled water and with 0.01 M $CaCl_2$. The instrument was calibrated with buffer solutions of pH 4 and 9.2. Soil suspensions were stirred after small intervals and pH's were measured after 1 hour using Kent E11 2055 pH meter.

2.4. Cation exchange capacity (CEC) and Exchangeable Cations

Soil samples 5g each were placed in four 100 ml centrifuge tubes with 40 ml 1M ammonium acetate solution. The tubes were sealed with rubber bungs and soil was dispersed by shaking. The samples in tubes were centrifuged at 2000 rpm for 5 minutes and the supernatent decanted. This procedure was repeated three times and supernatent was collected in four flasks (200 ml vol.) each time. The volume in each flask was made up to 200 ml with 1N ammonium acetate. Exchangeable cations in each solution were determined by using atomic absorption for Mg (PYE UNICAM SP 2900) and flame photometer for Ca, Na and K.

Cation exchange capacity was determined by washing the soil in centrifuge tubes with ethanol and then displacing ammonium ions three times with successive portions of 1M KCl (acidified to pH 2.5). The supernatent was collected in 100 ml flasks and volume was made up to the mark. The NH_4^+ ions in the solutions were removed by steam distillation (Tecator Kjeldahl apparatus). Cation exchange capacity (CEC) was determined by titration against 0.025 M H_2SO_4 and calculated by using the relationship;

$$1 \text{ ml } 0.025 \text{ M } H_2SO_4 = 0.05 \text{ me } NH_4^+$$

2.5. Calcium Carbonate ($CaCO_3$) Contents (%)

Calcium carbonate contents of the soils were determined by the calcimeter method (Boscomb, 1961). The calcimeter was standardised by adding analytical reagent $CaCO_3$ to be digested with acid in order to saturate the acid in the container with CO_2. Soil samples (2g) were placed in the container and acid was poured slowly into it, then mixed and allowed to react for 30 minutes. More acid was added and allowed to react until no further reaction was noticed. The gas volume was recorded after equilibration and the temperature and the atmospheric pressure were also recorded at the same time.

Calcium carbonate content were calculated according to the following equation:

$$CaCO_3\,(\%) = \frac{\text{Gas volume (ml)}}{\text{Soil Wt. (g)}} \text{ X } \frac{\text{Barometric pressure}}{(\text{Temp. }^\circ\text{C}+273)} \text{ X F}$$

where F = constant (0.1604)

2.6. Free Iron Oxides

The method was followed as described by Coffin (1963) and Livesey (1964). Brief details are given below:

Soil samples (1.0g) in duplicate were put in 100 ml polythene bottles with 2.0g sodium dithionite and 40 ml citrate buffer solution (88.2g Sodium citrate dihydrate and 21.0g citric acid per 2000 ml). The samples were shaken overnight (16 hours) in an end-over-end shaker. The samples were filtered with Whatman no. 1 filter paper. Suitable aliquots were transferred to 100 ml volumetric flasks and volume was made up to approximately 70 ml with distilled water. Then 5 ml concentrated HCl, 0.5 ml 30 vol. H_2O_2 and 5 ml 15 % KCNS solution were added to each flask. The volume was made up to the mark with distilled water and read against a full reagent blank after 50 minutes on a spectrophotometer at 480 nm. The calibration curve was prepared over the range of 0.1 to 1.0 mg Fe_2O_3 using standard Fe solution.

2.7. Loss on Ignition

Loss on ignition between 105°C and 500°C is a rough estimation of the organic matter contents of a soil as most of the organic matter is burnt off at about 325°C (Rowell, 1994). However, this method may over estimate the OM contents as the sesquioxides present in the soil may lose structural water between 105°C and 500°C. For example goethite, FeOOH, dehydrates to haematite Fe_2O_3.

Soil samples (1g) in the porcelain crucibles were put in the furnace at 500°C for overnight. Another set of samples was put in the oven at 105°C. The soil samples were taken out of the furnace next morning and cooled in a desiccator and weighed. Loss on ignition was calculated.

2.8. Organic Carbon (OC)

Organic carbon (OC) was determined by using the Walkley-Black procedure modified by Mebius (1960).

2.9. Organic Carbon (OC) in Solution

This method was used to asses the net amounts of organic carbon (OC) in solution at a particular time. The method was used as suggested by Taylor (1990) which is described below. The method is based on the assumption that boiling chromic and sulphuric acids will oxidise nearly all of the organic carbon in a sample. The sample is refluxed for two hours with an aliquot of $K_2Cr_2O_7$ in an excess of H_2SO_4. The amount of dichromate consumed is determined by back titration with $Fe(NH_4)SO_4$. Also added were silver sulphate which is an oxidative catalyst and mercuric sulphate which overcomes Cl^-interference.

Reagents:

1) Standard Potassium Dichromate Solution

7.66g Analar Potassium Dichromate was dissolved in distilled water to a final volume of 1000 ml.

2) Ferrous Ammonium Sulphate (F.A.S.)

Made by adding 20 ml concentrated sulphuric acid to 200 ml distilled water and allowed to cool. 4.9015g of F.A.S. were dissolved in this and made up to 1000 ml.

3) Mercuric Sulphate

Made by dissolving 50g mercuric sulphate in a mixture of 225 ml distilled water and 25 ml concentrated sulphuric acid.

4) Silver Sulphate

Made by dissolving 5g silver sulphate in 500 ml M.A.R. sulphuric acid.

5) BDH Ferroin indicator

(1:10 phenanthroline/ferrous sulphate complex)

The apparatus was cleaned by refluxing with the appropriate amounts of reagents for two hours. The pipettes were cleaned thoroughly with distilled water.

The reagents were added as follows into each flask.

5.0 ml	sample
0.5 ml	mercuric sulphate solution
2.0 ml	potassium dichromate solution
7.5 ml	silver sulphate /sulphuric acid (added cautiously)

The contents were mixed and refluxed for two hours after which the flasks were allowed to cool for fifteen minutes. The condensors were then washed down with 5 ml distilled water. Finally, the contents of each flask were titrated against F.A.S. solution using two drops of ferroin as indicator. A blank was run in each set, the mean of titre values obtained for the blanks was used to calculate the back titre.

i.e. Back titre = Mean Blank titre - Sample titre

The carbon content in ug/ml of solution were calculated by the equation

Carbon content = Back titre x 7.63

NB. 7.63 is obtained by using 100 ppm carbon sucrose solution as standard.

2.10. Water Soluble P and Zn

The method was used to extract water soluble P and Zn. Soil samples were shaken overnight (16 hours) with a soil to water ratio of 1:5, centrifuged at 2000 rpm for 15 minutes and the extracts filtered with Whatman no. 42 filter paper to attain clear solution. The soil samples were than extracted with 0.5N NaOH as described in section 2.11. Phosphorus in the extracts was determined as described by Watanabe and Olsen (1965). Zinc was determined by using atomic absorption spectrophotometer (PYE UNICAM SP 2900).

2.11. 0.5N NaOH Extractable P and Zn

The method was used to extract organic and Fe oxide associated P and Zn. The extraction was done after 16 hours shaking using 0.5N NaOH (Xie and Mackenzie, 1988, 1989; Xie and Mackenzie, 1990) and 1M NaCl (Olsen and Sommers, 1982) with a ratio of 1:10 (soil:extractant). The bottles were centrifuged at 2000 rpm for 15 minutes and the extracts filtered with Whatman no. 42 filter paper. Phosphorus was determined by spectrophotometer and Zn by atomic absorption spectrophotometry.

2.12. Sodium Bicarbonate Extractable Phosphorus

Phosphorus from the soils was extracted as proposed by Olsen *et al.* (1954) using 0.5M $NaHCO_3$ adjusted at pH 8.5. Phosphorus in the extracts was determined by spectrophotometer (Cecil) using the ascorbic acid method of Watanabe and Olsen (1965).

2.13. Total Phosphorus

Finely ground soil samples (0.2g) were placed in the test tubes with 2 ml perchloric acid. The soil material was digested for 5 hours by putting the tubes in an electric dry block adjusted at $200 \pm 2^{o}C$. The tubes were cooled after complete digestion and volume was made up to a 15 ml mark on the tubes. An aliquot (1 ml) of each sample was taken and colour was developed, as described by Watanabe and Olsen (1965).

2.14. Readily Reducible Iron and Manganese

The method was used as described by Stewart-Jones (1980) to determine the amount of readily reducible iron oxides which might play an important role in phosphorus fixation during early stages of submergence. For this purpose 1,2,4-trihydroxybenzene (hydroxyhydroquinone) was used as reducing agent. The extraction of samples was done by using 0.2 % solution of hydroxyhydroquinone in 0.25 M solution of sodium sulphite (at pH 7.8 buffered with 0.1 M triethanolamine). The extracts were filtered with Whatman no. 1 filter paper after 10 minutes of reciprocal shaking in open polythene bottles. The extracts were acidified with 2M HCl in order to keep the extracted iron in solution form. Iron and manganese were determined by atomic absorption spectrometer (PYE UNICAM SP 2900).

2.15. $NH_4(HCO_3)$ - DTPA Extractable P, Fe, Mn, Zn and Cu

Soil samples, 10g, (unless otherwise mentioned) were put into 125 ml plastic bottles with 20 ml 1M NH_4HCO_3 and 0.005M DTPA solution (pH 7.6) (Lindsay and Norvell, 1978). The soil mixture was shaken on a reciprocal shaker for fifteen minutes at 175 cycles per minute with the bottles kept open. The extract was filtered through a Whatman no. 42 filter paper.

Phosphorus and Fe, Mn, Zn and Cu in the extracts were determined as above.

2.16. DTPA Soil Extract for Fe, Mn, Zn and Cu

Extraction was done by using the method proposed by Lindsay and Norvell (1978). Soil samples 10g each (unless otherwise mentioned) were put in polythene bottles with 20 ml DTPA extracting solution (0.005M DTPA, 0.01M $CaCl_2$, and 0.1M TEA buffered at pH 7.3). The soil mixtures were shaken for two hours with the bottles kept open. The mixtures were filtered through Whatman no. 42 filter paper. The micronutrients Fe, Mn, Cu and Zn in the extracts were determined by atomic absorption spectrophotometry.

2.17. Total P, Fe, Mn, Zn and Cu in Plant Shoots

Plant samples of paddy rice and wheat were dried at 70°C and finely ground. Samples 0.2g were put into test tubes with 1 ml concentrated nitric acid to destroy organic matter. The plant material was digested by putting the tubes in a dry block at a temperature of 200±2°C until no nitric acid was left. Then 2 ml perchloric acid was added to each tube and heated until complete digestion (3 to 4 hours) of the material took place. The samples were cooled, volume was made with distilled water up to 15 ml mark on the tubes. The samples were stored in glass vials for determination of P by spectrophotometry and of Fe, Mn, Zn and Cu by atomic absorption spectrophotometry.

2.18. Total P, Fe, Mn, Zn and Cu in Plant Roots

The method was as described in section 2.17 except that the plant roots were washed with distilled water, to remove the finer soil particles, before drying in the oven and 0.1g root material (unless otherwise mentioned) was used.

CHAPTER

3

Chapter 3: Laboratory based Incubation Studies

3.1. Experiment 1: Effects of flooded incubations on soil extractable P, solution pH and readily reducible Fe & Mn

3.1.1 Aims of the Experiment

The behaviour of phosphorus in soil samples collected from Aber Farm (Denbigh Series, Appendix I) under flooded conditions in the laboratory was investigated. Soil samples were collected from twelve sites in one field to investigate the variability. Changes in solution pH, and readily reducible iron and manganese under these conditions were also observed.

3.1.2 Treatments

The soil samples from twelve sites were numbered from S1- S12.

3.1.3 Experimental Procedure

Soil samples (10g), in triplicate, from each site were put into glass vials with 10 ml distilled water. The vials were sealed and put in the incubator at a temperature of 32±2°C. Samples for each site were taken out at five day intervals until 50 days, solution pH (1:5 soil:H_2O) was noted and the samples were analysed for $NaHCO_3$ extractable-P. A separate set of samples was incubated for the determination of readily reducible iron (Fe) and manganese (Mn).

3.1.4 Results

Results shown in figure 3.1 and in appendix 3.1 (a-e) represent the effects of flooded incubations on soil pH, P and readily reducible Fe and Mn. Incubating the soils under flooded conditions from 5 to 50 days caused increases in the solution pH. These increases in pH at 5 days of flooding ranged from 0.31-1.35 units compared with the initial pH (0 day) of the samples. Gradual increases in solution pH were observed with flooding period until 50 days. Overall increases in pH at 50 days of flooded incubation compared with the initial pH (0 days) and those at 5 days ranged from 0.76-1.75 units and 0.32-0.63 units respectively.

Table 3a: Some physical properties of soils

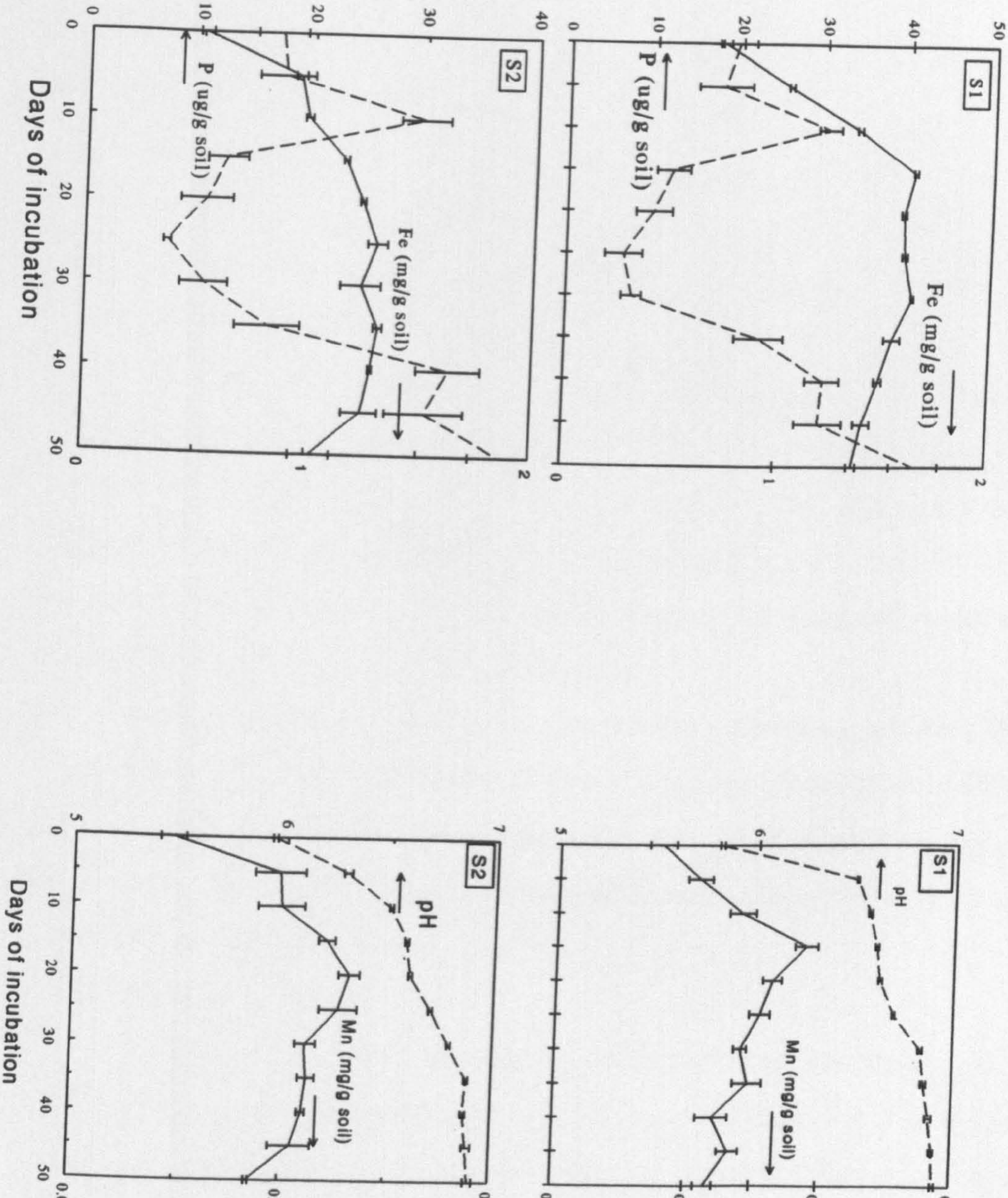
Soil Site	Aber Farm	Brown Podz. *	Pen-y-Ffridd	Pakistan
Land use	cultivated	conifer forest	grassland	cultivated
% Sand	36.28	72.86	63.98	12.10
% Silt	55.13	23.33	29.76	74.64
% Clay	8.6	3.91	6.26	13.26
Texture class	Sandy silt loam	Sandy loam	Sandy loam	silt loam
% $CaCO_3$ equi.	1.05	0.00	5.20	22.68

* soil was pretreated with citrate buffer solution and sodium dithionite to remove free iron oxides

Table 3b: Some chemical properties of soils

Soil Site	Aber Farm	Brown Podz.	Pen-y-Ffridd	Pakistan
pH (dist. H_2O)	5.93	4.51	7.33	8.49
pH (0.01M $CaCl_2$)	5.51	4.12	6.92	7.98
CEC (c moles/kg soil)	15.5	22.5	24.5	21.3
Exch. Na^+ (c moles/kg soil)	0.38	0.13	0.27	0.33
Exch. K^+ (c moles/kg soil)	0.31	0.10	0.61	0.89
Exch. Ca^{++} (c moles/kg soil)	8.50	xxx	9.20	17.4
Exch. Mg^{++} (c moles/kg soil)	1.20	xxx	1.80	2.30
Free Fe oxides (mg/g soil)	28.50	146.00	68.40	18.80
Loss on ignition (%)	7.04	8.63	9.72	1.92
Organic carbon (%)	2.70	3.15	3.53	0.70
$NaHCO_3$-P (ug/g soil)	19.60	9.45	21.54	10.16
DTPA-Fe (ug/g soil)	93.39	54.29	62.78	2.16
DTPA-Mn (ug/g soil)	37.49	6.95	56.25	5.73
DTPA-Cu (ug/g soil)	2.45	0.45	4.56	1.37
DTPA-Zn (ug/g soil)	2.07	1.92	2.39	0.88

Figure 3.1: Effects of flooded incubations on extractable soil P, reducible iron and manganese (Mn) and soil pH



*please see Appendix 3.1 (a-e) for the remaining samples

Overall increases in available phosphorus were observed after flooded incubation for 50 days compared with the initial soil phosphorus (0 day). These increases, however, were not regular throughout the incubation period. Increases in available P observed at 10 days of incubation were followed by decreases until 25 days. Increases in available P at 10 days compared with the initial P (0 day) concentrations ranged from 50-84% (S1-S12). The decreases observed at 25 days of incubation ranged from 25-67% and 55-81% respectively compared with the initial P (0 day) and those at 10 days of incubation. At 50 days of flooded incubation, the overall increases in extractable P compared with the initial P (0 day) ranged from 68-147%.

Increases in readily reducible iron, in general, compared with the initial iron (0 day), were observed after 50 days of flooded incubations. In most of the samples studied (except S11), increases in reducible iron were observed until 30 to 35 days of flooding; followed by modest decreases until 50 days. Overall increases at 30 and 50 days of flooded incubations compared with the initial iron concentrations (0 day) ranged from 63-198% and 50-133% (except S11) respectively.

Increases in reducible Mn were also observed with the flooded incubations. These increases were greatest (80-227%) after 20 days of incubation compared with the initial Mn concentration (0 day). As flooding proceeded from 25 to 50 days, decreases in reducible Mn were observed resulting in less overall increases (27-140%) compared with the initial Mn concentration (0 days).

3.1.5 Discussion

The shifts in pH towards neutrality due to flooded/ anaerobic conditions have been reported by many researchers in the past. These changes in pH in acidic soils take place mostly due to the reduction of Fe^{III} oxides, the extent of reduction depending upon the depletion of oxygen through microbial respiration, followed by proton consumption. Increases in pH of acidic soils during flooding (Willet, 1989) have been ascribed to proton consumption during the reduction of Fe^{III}, Mn^{III} and Mn^{IV} oxides.

Increases in pH of the soil samples (S1-S12) studied displayed the acidic nature of the soils.

Increases in phosphorus availability during flooding are reported to be due to the reductive dissolution of Fe^{III} oxides and the liberation of sorbed and occluded phosphate, changes in soil pH which increase the solubility of iron, aluminium and calcium phosphates and the desorption of phosphate from surfaces (Willet, 1986). However, the inconsistent increases in available P during the flooded incubations could not be attributed only to the above factors. The decreases in available phosphorus during 10 to 25 days might be attributed to a number of factors like (a) incomplete reduction of the soil (b) build up of acids which might have killed the microbes resulting in less consumption of oxygen and subsequently the oxidation of Fe^{II} to Fe^{III} (c) resorption of phosphorus by amorphous or poorly crystalline Fe and/or Mn oxide surfaces. These factors, however, cannot be isolated independently in the soil system due to their effects on each other. Increases in phosphorus availability during the first 10 days of flooding indicated the effects at the initiallization of the reduction process. Although, the levels of readily reducible Fe had already started to increase with flooding, the greater levels of readily reducible Fe (presumably recently oxidized Fe^{II} which has formed highly surface active Fe^{III} hydroxide) produced during 15 to 25 days (figure 3.1, Appendix 3.1 a-e) might have acted as active sites for P sorption. The decline in extractable phosphorus below the initial P levels may also support the sorption by amorphous Fe oxides having more exposed surface area compared with the crystalline Fe oxides in the original soil. Kirk *et al.* (1990) reported that solution P in flooded soils is mainly controlled by sorption on to charged surfaces such as poorly crystalline hydrous iron oxides. As the amount of Fe in the soil is usually much greater compared with the phosphorus concentration, minor changes in Fe may greatly alter the phosphorus concentration in solution. That is perhaps why a clear relationship between soil Fe and phosphorus may not always be found. Willet (1985) concluded that the addition of phosphate at levels less than the sorption capacity to reduced systems containing ferrihydrite will result in its sorption and an increase in the stability of the oxide, rather than an increase in the dissolution of oxide caused by vivianite formation. The reductive dissolution of strengite (Fe^{III} phosphate), in his study, was congruent for the first few days of flooding and then phosphate accumulated in excess of Fe^{2+}, probably because of vivianite (Fe^{II} phosphate) precipitation.

The results regarding reducible Mn confirmed the findings of Ponnamperuma (1972) and Antil *et al.* (1986) who also found a build up of high concentrations of Mn^{2+} within two weeks of submergence which was followed by a decline as flooding proceeded. The build up of reducible Mn concentration after 10 days of incubation might have depressed the solution phosphorus. Willet (1989) reported the results of 18 soils flooded in the laboratory which revealed that reduction of Fe^{III} during flooding was a main source for P release during flooding, however the reduction of Mn^{III} and Mn^{IV} also contributed as a source of P during flooding. The greater concentration of Mn might also have, to some extent, depressed the concentration of amorphous iron and probably masked the Fe-P relationship during that period. The antagonistic effects of Mn application on Fe concentration have been reported by Antil *et al.* (1986) and Verma *et al.* (1988).

3.2. Experiment II: Phosphorus and micronutrient behaviour under flooded and moist incubations

3.2.1. Aims of the experiment

The soil used in this experiment was the same as in experiment I. Due to the inconsistent results about P behaviour in flooded conditions, found in experiment I, the experiment was repeated with some modifications. A composite sample of S1, S2, S3 and S4 samples was prepared and used in the experiment. Air dried soil (< 2mm) had been stored for two and a half years at room temperature (22±2°C) prior to this study. The trial was conducted in the laboratory to investigate the effects of flooded (F) and moist (M) aerated incubations on the behaviour of soil P, Fe, Mn, Zn and Cu during flooded and moist aerated incubations. The fate of applied orthophosphate (OP) with or without pyrophosphate (PP) and its reactions with Fe, Mn, Zn and Cu were also investigated under both conditions. Potassium dihydrogen orthophosphate and tetra-potassium pyrophosphate were used as the sources of OP and PP respectively throughout the studies unless otherwise mentioned.

3.2.2. Treatments

The treatments were as follows

P0 = Control, P1 = Orthophosphate (OP) @ 100 µg P/g soil

P2 = Orthophosphate (OP) and pyrophosphate (PP) respectively @ (90+10) µg P/g soil

F and M = flooded and moist conditions respectively

3.2.3. Experimental Procedure

Soil samples (10g) in triplicate were put into the polythene bottles and the solutions of ortho- and pyro- phosphate fertilizers were prepared and added into the bottles for respective treatments. Distilled water was added in P0 treatment. In flooded samples 10 ml solution was added and in the moist aerated samples 1 ml solution per 10g soil was maintained. It was attained either by adding concentrated solutions or by blowing dry air into the samples. The moist and flooded samples were weighed on alternate days and loss in weight was corrected by adding distilled water. The samples were incubated at 32±2°C for 50 days and sampling was done every 10 days. Phosphorus, Fe, Mn, Zn and Cu in the extracts were measured (section 2.15).

3.2.4 Results:

The data regarding phosphorus behaviour under moist and flooded conditions with time is presented in tables 3.2.1 and 3.2.2 respectively and in figure 3.2.1. Addition of phosphorus both with or without pyrophosphate (PP) significantly ($p<0.01$) increased extractable phosphorus both during moist and flooded incubations. Extractable phosphorus, with or without added P, was found to be greater, throughout the incubation period, in the flooded compared with the moist samples. Extractable P in treatments P0, P1 and P2 respectively was 97%, 131% and 106% greater in flooded compared with the moist incubations after 50 days. Decreases in extractable P with time, were observed

Table 3.2.1: Effects of added OP with or without pyrophosphate (PP) on NH_4HCO_3-DTPA extractable-P during moist incubations

	Incubation time (days)				
Treatments	10	20	30	40	50
P0M	8.60	6.51	6.69	6.03	6.11
P1M	17.97	13.69	14.41	12.93	10.47
P2M	19.09	14.50	15.00	13.31	12.28
L.S.D.(0.05)	1.41	1.33	1.02	1.00	1.63
L.S.D.(0.01)	2.59	2.45	1.87	1.83	2.99

Table 3.2.2: Effects of added OP with or without pyrophosphate (PP) on NH_4HCO_3-DTPA extractable-P during flooded incubations

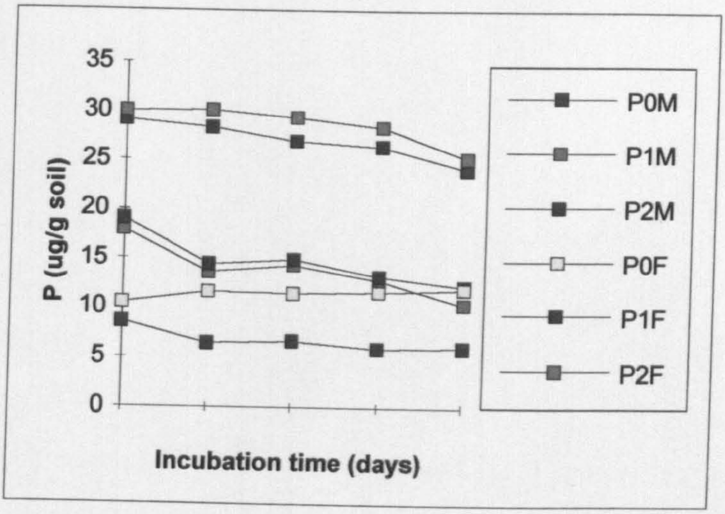
	Incubation time (days)				
Treatments	10	20	30	40	50
P0F	10.49	11.66	11.51	11.73	12.02
P1F	29.09	28.42	27.00	26.48	24.16
P2F	30.04	30.15	29.39	28.47	25.31
L.S.D.(0.05)	2.04	1.40	1.20	1.05	1.38
L.S.D.(0.01)	3.75	2.56	2.20	1.92	2.53

Table 3.2.3: Effects of added OP with or without pyrophosphate (PP) on NH_4HCO_3-DTPA extractable-Fe during moist incubations

	Incubation time (days)				
Treatments	10	20	30	40	50
P0M	126.8	97.33	94.95	93.75	72.46
P1M	133.5	91.77	79.84	73.88	58.81
P2M	142.7	98.52	90.18	82.23	63.58
L.S.D(0.05)	NS	NS	NS	14.99	6.03
L.S.D(0.01)	NS	NS	NS	NS	11.07

(each value is a mean of three replicates)

Figure 3.2.1: Effects of flooded and moist incubations on NH_4HCO_3-DTPA extractable soil phosphorus (P) and iron (Fe).



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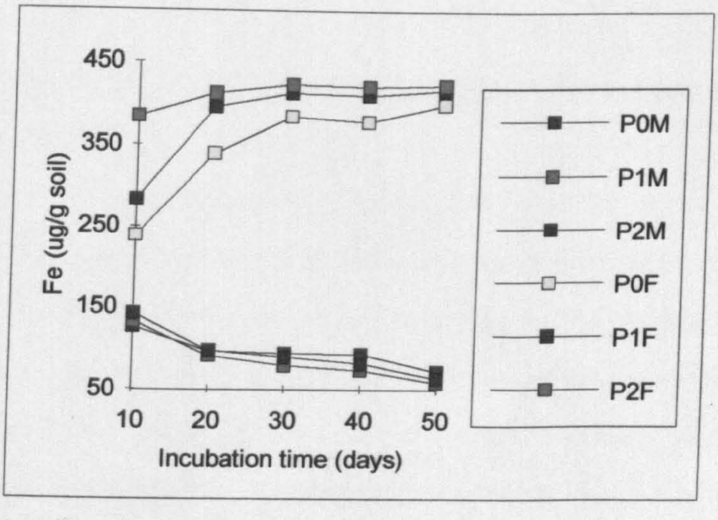


both under moist and flooded incubations; except in flooded control samples where 15% increases in P were observed. The decreases in P in moist samples after 50 days compared with 10 days were 29% (P0), 42% (P1) and 36% (P0). The decreases in flooded samples after that period were 17% (P1) and 16% (P2).

Increases in extractable Fe were observed during flooded incubations (table 3.2.4, figure 3.2.1) and decreases during the moist incubations (table 3.2.3, figure 3.2.1). Added phosphorus (P1 and P2 treatments) compared with control (P0) samples, caused decreases in the extractability of soil Fe during moist incubations and improved Fe extractability during flooded incubations. After flooded incubations, compared with the moist incubations for 50 days, about 5.5, 7.1 and 6.7 times greater extractable Fe was observed in P0, P1 and P2 treatments respectively.

The extractable levels of Mn were lower during the moist incubations (table 3.2.5, figure 3.2.2) and greater in the flooded incubations (table 3.2.6, figure 3.2.2). Flooded incubations caused increases in the extractability of soil Mn with the maximum values being observed at 20 days period. After 50 days of flooding compared with 10 days, extractable Mn changed less than 5% in all the treatments. About twice the levels of Mn, in treatments P0, P1 and P2 were extracted in flooded compared with the moist incubations at 20 to 50 days.

The behaviour of extractable Zn (tables, 3.2.7 & 3.2.8, figure 3.2.2) and Cu (tables 3.2.9 & 3.2.10, figure 3.2.3) was similar both under flooded and moist incubated conditions; showing greater levels during the moist and lower during the flooded conditions. In treatments P0, P1 and P2, during the moist compared with the flooded incubations of 50 days, about 1.4, 1.6, 1.6 and 3.1, 4.0, 3.9 times greater Zn and Cu respectively were observed. Decreases in extractable Zn and Cu both under moist and flooded incubations were observed as incubations proceeded from 10 to 50 days. Addition of phosphorus, with or without pyrophosphate, caused decreases in extractable Zn and Cu both under moist and flooded incubations. These decreases were, however, less in the presence of pyrophosphate (PP).

Table 3.2.4: Effects of added OP with or without pyrophosphate (PP) on NH_4HCO_3-DTPA extractable-Fe during flooded incubations

	Incubation time (days)				
Treatments	10	20	30	40	50
P0F	239.2	340.2	386.3	379.9	401.4
P1F	284.2	396.6	414.1	411.7	418.1
P2F	385.5	413.3	423.6	422.0	423.6
L.S.D(0.05)	20.7	17.9	21.9	24.9	NS
L.S.D(0.01)	38.0	32.8	NS	NS	NS

Table 3.2.5: Effects of added OP with or without pyrophosphate (PP) on NH_4HCO_3-DTPA extractable-Mn during moist incubations

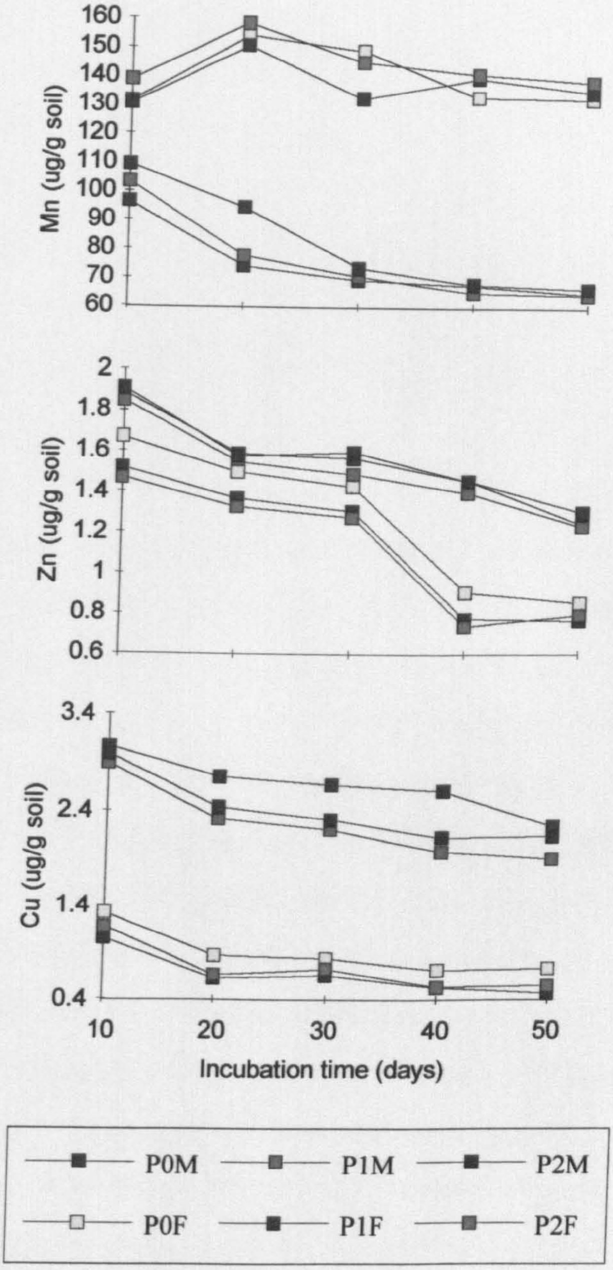
	Incubation time (days)				
Treatments	10	20	30	40	50
P0M	96.50	74.29	69.66	67.81	65.04
P1M	103.44	77.99	71.05	65.50	64.57
P2M	109.45	94.65	73.83	68.28	66.89
L.S.D(0.05)	10.68	10.33	NS	NS	NS
L.S.D(0.01)	NS	18.96	NS	NS	NS

Table 3.2.6: Effects of added OP with or without pyrophosphate (PP) on NH_4HCO_3-DTPA extractable-Mn during flooded incubations

	Incubation time (days)				
Treatments	10	20	30	40	50
P0F	131.56	154.46	149.32	133.5	132.85
P1F	130.87	150.99	132.95	139.89	135.24
P2F	139.20	158.63	145.44	141.35	138.71
L.S.D(0.05)	NS	NS	NS	NS	NS
L.S.D(0.01)	NS	NS	NS	NS	NS

(each value is a mean of three replicates)

Figure 3.2.2: Effects of flooded and moist incubations on NH_4HCO_3-DTPA extractable soil manganese (Mn), zinc (Zn) and copper (Cu).



3.2.5 Discussion

The results obtained in this trial were entirely different from those found in the previous experiment. The behaviour of phosphorus was not found to be exceptionally variable during the flooded incubations. A close relationship between P and Fe was found both during flooded and moist incubations. Decreases in P during the moist incubations were associated with the decreases in extractable Fe. This relationship might have developed due to the interactions of P and Fe which resulted in the sorption of applied P by the Fe-oxides followed by their precipitation as Fe-P compounds of low solubility. Decreases in the native soil P could simply be due the transformations of P into insoluble forms under moist conditions. Flooded incubations result in the reduction of Fe-oxides (Willet *et al.*, 1986), which play an important role in P sorption (Holford and Mattingly, 1975b; Hamad *et al.*, 1992; Udo and Uzo, 1972). Increases in native soil P during flooded incubations were associated with the increases in extractable Fe. Moreover, greater amounts of applied P remained available during the flooded conditions. These observations were in conformity to the reports, as quoted earlier, about the reduction of Fe-oxides and subsequent release of P during flooded conditions. The sorption of P during the flooded conditions, however, may be due to the amorphous Fe which might have precipitated with P in solution. Kirk *et al.* (1990) reported that P in flooded soils is mainly controlled by sorption onto charged surfaces such as poorly crystalline iron oxides. Pyrophosphate (PP) has been reported to act as a chelating agent (Giordano *et al.*, 1971; Mortvedt and Osborn, 1977) and to dissolve organic matter (Mortvedt and Osborn, 1977). In pyrophosphate (PP) treated samples, the greater amounts of Fe observed under both flooded and moist conditions may be attributed to these properties of pyrophosphate (PP). The greater amounts of P maintained in the presence of pyrophosphate (PP) might be due to the competition of organic anions, dissolved by pyrophosphate, with P for sorption onto surfaces of Fe. Competition between organic matter and phosphate for adsorption sites on soils is thought to be due to the chelating

Table 3.2.7: Effects of added OP with or without pyrophosphate (PP) on NH_4HCO_3-DTPA extractable-Zn during moist incubations

	Incubation time (days)				
Treatments	10	20	30	40	50
P0M	1.89	1.59	1.57	1.46	1.25
P1M	1.85	1.55	1.49	1.40	1.24
P2M	1.91	1.58	1.60	1.46	1.31
L.S.D(0.05)	NS	NS	NS	NS	NS
L.S.D(0.01)	NS	NS	NS	NS	NS

Table 3.2.8: Effects of added OP with or without pyrophosphate (PP) on NH_4HCO_3-DTPA extractable-Zn during flooded incubations

	Incubation time (days)				
Treatments	10	20	30	40	50
P0F	1.667	1.500	1.430	0.909	0.864
P1F	1.520	1.365	1.314	0.775	0.768
P2F	1.468	1.327	1.276	0.736	0.800
L.S.D(0.05)	0.147	NS	NS	NS	NS
L.S.D(0.01)	NS	NS	NS	NS	NS

Table 3.2.9: Effects of added OP with or without pyrophosphate (PP) on NH_4HCO_3-DTPA extractable-Cu during moist incubations

	Incubation time (days)				
Treatments	10	20	30	40	50
P0M	3.067	2.761	2.679	2.618	2.250
P1M	2.893	2.332	2.220	1.975	1.903
P2M	2.995	2.454	2.322	2.128	2.138
L.S.D(0.05)	NS	0.260	0.140	0.250	NS
L.S.D(0.01)	NS	NS	0.250	0.460	NS

Table 3.2.10: Effects of added OP with or without pyrophosphate (PP) on NH_4HCO_3-DTPA extractable-Cu during flooded incubations

	Incubation time (days)				
Treatments	10	20	30	40	50
P0F	1.332	0.872	0.842	0.719	0.729
P1F	1.046	0.627	0.658	0.525	0.474
P2F	1.179	0.668	0.729	0.535	0.546
L.S.D(0.05)	0.120	0.140	NS	0.140	0.190
L.S.D(0.01)	0.220	NS	NS	NS	NS

ability of hydroxyl-carboxyl ligands found in soil organic matter (Dalton *et al.*, 1952; Hue, 1991; Levesque and Schnitzer, 1967; and Parfitt, 1979).

Soil-solution concentrations of Mn^{2+}, as well as exchangeable Mn^{2+}, are governed by the solubilities of Mn oxides, such as Mn_2O_3 and MnO_2 (Adams, 1980); the dissolution and precipitation being governed by soil pH and redox potential (Eh). The greater effect of flooded conditions, compared with the moist conditions, on changes in extractable Mn might be attributed to the reduction of Mn-oxides. Increases in extractable Mn under the flooded conditions (low redox potential) have been reported by Mandal and Haldar (1980) and Ponnamperuma, (1972). The increases in extractable Mn with the application of P compared with the control samples (P0) might be due to the effect of P fertilizers in lowering solution pH. Phosphorus fertilizers may increase the level of soil-solution Mn in some soils probably because of the acidic reaction of dissolved superphosphate (Adams, 1980; Bingham and Garber, 1960; Racz and Haluschak, 1974).

Flooding caused declines in the extractable levels of soil Zn and Cu. The decreases in extractable Zn contents during flooding have been reported to be due to the coprecipitation of $ZnCO_3$ and $Zn(OH)_2$ (Sinha *et al.*, 1975), and the formation of ZnS (Yoshida and Tanaka, 1969). Moreover, competition between Fe and Zn for chelating ligands has been reported (Giordano and Mortvedt, 1972). The greater amounts of Fe extracted during the flooded conditions probably depressed the extraction of Zn and Cu. Applied P reacted with Zn and Cu during the moist and flooded incubations causing decreases in their availability. Antagonistic effects of P on Zn and Cu have been reported by different researchers like Ellis *et al.* (1964) and Mandal and Haldar (1980). Although, applied P caused declines in extractable levels of Zn and Cu compared with the control samples, slightly greater amounts of these elements in the presence of pyrophosphate (PP) are probably due to chelation / sequestering by pyrophosphate (PP).

3.3. Experiment III: Effect of alternate flooded-moist and moist incubations on soil extractable P and solution pH

3.3.1 Aims of the Experiment

This incubation experiment was conducted in the laboratory to explore the effects of alternate flooded-moist and moist conditions on the behaviour of soil phosphorus and solution pH.

3.3.2 Treatments

Two sets of treatments were prepared, one for alternate flooded-moist samples and the other for moist samples only.

(1) P0 (2) P1 (3) P2

where P0 = Control (0 μg P/g soil)

P1 = 100 μg P/g soil as OP

P2 = 100 μg P/g soil as OP & PP (90+10)

3.3.3 Experimental Procedure

Soil samples (5g) from Pen-y-Ffridd and Pakistan (table 3 a&b) in triplicate, were put into plastic bottles. Phosphorus fertilizer solutions were prepared and added to the respective bottles with a final volume of 5 ml for the flooded incubations. For the moist incubations either the concentrated solutions were added or a final volume of 1 ml was attained by blowing the air in the bottles. The weight of each bottle was recorded and then incubated at 32±2°C. The bottles for flooded incubations were sealed and for the moist incubations kept open. The weight of each bottle was corrected every two days by adding distilled water. Samples were taken out at three week intervals until 12 weeks. Solution pH was noted and extractable P was determined. To establish the alternate-flooded conditions, samples were incubated as shown in the table below. Moist conditions were attained, as described earlier, by drying the soil samples to 1 ml water contents.

Weeks of incubation	3W	6W	9W	12W
3W	flooded	X	X	X
6W	flooded	moist	X	X
9W	flooded	moist	flooded	X
12W	flooded	moist	flooded	moist

3.3.4 Results

Incubating the soils both under moist and alternate flooded-moist conditions caused decreases in extractable P. The behaviour of phosphorus in both soils from Pen-y-Ffridd and Pakistan was similar after 12 weeks of moist incubations. About 17%, 37% and 34% (tables 3.3.1 & 3.3.5) decreases in soil P in treatments P0, P1 and P2 respectively were observed after 12 weeks compared with the moist incubations of three weeks. During alternate flooded-moist incubations, the overall decreases in soil P in Pen-y-Ffridd soil (table 3.3.3) were 39%, 46% and 44% in treatments P0, P1 and P2 respectively. The decreases in soil P in Pakistani soil (table 3.3.7) under these conditions after 12 weeks were 34%, 33% and 26% respectively.

In Pen-y-FFridd soil (table 3.3.2), moist incubations of 12 weeks caused small increases (0.02 units) in solution pH in P1 and P2 treatments respectively whereas pH of control (P0) samples remained unchanged. After 12 weeks of alternate flooded-moist incubations, compared with three weeks, overall increases in solution pH of 0.2, 0.22 and 0.21 units were observed in treatments P0, P1 and P2 respectively (table 3.3.4). In Pakistani soil, after 12 weeks compared with 3 weeks, increases in solution pH in treatments P0, P1 and P2 during moist (table 3.3.6) and alternate flooded-moist (table 3.3.8) incubations were 0.03, 0.19, 0.06 and 0.12, 0.18 & 0.07 units respectively.

3.3.5 Discussion

Decreases in available P in Pen-y-Ffridd soil and the Pakistani soil observed during both alternate flooded-moist and moist aerated conditions could be due to the sorption of applied P. It has been reported that the sorption of most of the phosphorus takes place soon after its application (Sample *et al.*, 1980). The amounts and surface areas of Fe (Hamad, *et al.*, 1992), Al and Mn oxides and $CaCO_3$ contents in soil may

Table 3.3.1: Effects of moist incubations on $NaHCO_3$ extractable soil P (ug/g soil) in a soil from Pen-y-Ffridd

Treatments	3W	6W	9W	12W
P0	14.37	12.47	11.91	11.96
P1	34.82	28.44	25.70	21.82
P2	46.20	37.88	32.57	30.28
L.S.D(0.05)	4.07	4.38	4.24	3.04
L.S.D(0.01)	7.48	8.04	7.78	5.58

Table 3.3.2: Effects of moist incubations on solution pH (1:2 soil : H_2O) in a soil from Pen-y-Ffridd

Treatments	3W	6W	9W	12W
P0	7.99	7.98	8.00	7.99
P1	7.94	7.94	7.95	7.92
P2	7.89	7.88	7.89	7.91
L.S.D(0.05)	0.03	0.04	0.04	0.04
L.S.D(0.01)	0.06	0.07	0.07	0.07

(each value is a mean of three replicates)

Table 3.3.3: Effects of alternate flooded-moist incubations on $NaHCO_3$ extractable soil P (ug/g soil) in a soil from Pen-y-Ffridd

Treatments	3W	6W	9W	12W
P0	20.50	16.41	17.57	12.36
P3	39.83	29.95	33.33	21.47
P4	50.59	41.14	44.02	28.10
L.S.D(0.05)	6.43	4.96	4.31	5.65
L.S.D(0.01)	11.80	9.10	7.91	10.37

Table 3.3.4: Effects of alternate flooded-moist incubations on solution pH (1:2 soil : H_2O) in a soil from Pen-y-Ffridd

Treatments	3W	6W	9W	12W
P0	7.46	7.67	7.54	7.66
P3	7.41	7.64	7.51	7.63
P4	7.39	7.58	7.56	7.60
L.S.D(0.05)	0.03	0.026	NS	0.04
L.S.D(0.01)	0.06	0.048	NS	0.07

(each value is a mean of three replicates)

determine the extent of P sorption. Although, the sorption of P by $CaCO_3$ particles might have taken place in both soils, the greater sorption of applied P in Pen-y-Ffridd (5 % $CaCO_3$) soil during moist conditions may be expected due to the greater levels of Fe- and/or Mn-oxides. In Pakistani soil, however, the sorption of P probably is related to $CaCO_3$ contents (23% $CaCO_3$) rather than to the oxides of Fe and Mn. Increases in native soil P, with decreases in pH, in Pakistani soil were found to be greater during the first flooding (3 weeks) compared with the second flooding (9 weeks), following moist period (6 weeks); indicating that alternate flooded-moist conditions had adverse effects on P availability. Transformations of P compounds take place due to flooded-drained conditions (Mahapatra and Patrick, 1969; Sah and Mikkelsen, 1986a, b, c; and Sah *et al.*, 1989), which may result in the immobilization of P for several years (Willet and Higgins, 1980; Sah and Mikkelsen, 1986c). In Pen-y-Ffridd soil flooded periods caused increases in extractable P probably due to the reduction of Fe^{III} and Mn^{III}. The decreases in P during the moist periods following flooding might be due to the formation of amorphous Fe^{III} oxides / hydroxides with more sites for P sorption. The formation of amorphous Fe^{III} oxides / hydroxides takes place following the dissolution of crystalline Fe^{III} as Fe^{II} by reduction during flooding and subsequent oxidation and precipitation (Sah and Mikkelsen, 1986a); the amorphous Fe^{III} oxides / hydroxides having larger surface area than crystalline Fe (Borggaard, 1982). The results reported by Sah and Mikkelsen (1986 b, c) also indicated that flooding and subsequent draining caused increases in amorphous Fe levels and in P sorption. In Pakistani soil, compared with the Pen-y-Ffridd soil, alternate flooded-moist conditions had smaller effects on P levels probably due to the lower DTPA-Fe (2.16 µg Fe/g in Pakistani soil compared with 62.8 µg Fe/g in a Pen-y-Ffridd soil) and greater $CaCO_3$ contents. The increases in P, in Pakistani soil, during flooded periods might be partially related to the dissolution of Ca-P compounds through increases in partial pressure of CO_2 (Ponamperuma, 1972) resulting in increased Ca^{2+} activity in solution. Increased Ca^{2+} might also precipitate with P in solution (Sah and Mikkelsen, 1986b) and thus reduce P availability. Lower increases in P, in Pakistani soil,

Table 3.3.5: Effects of moist incubations on $NaHCO_3$ extractable soil P (ug/g soil) in a Pakistani soil

Treatments	3W	6W	9W	12W
P0M	11.41	10.08	10.15	9.46
P1M	31.47	26.19	21.97	19.67
P2M	37.18	30.01	32.91	24.65
L.S.D(0.05)	2.88	2.39	1.58	1.66
L.S.D(0.01)	5.29	4.39	2.91	3.05

Table 3.3.6: Effects of moist incubations on solution pH (1:2 soil : H_2O) in a Pakistani soil

Treatments	3W	6W	9W	12W
P0M	8.26	8.42	8.40	8.39
P1M	7.94	7.17	7.99	8.13
P2M	7.89	7.90	7.92	7.95
L.S.D(0.05)	0.05	0.04	0.04	0.04
L.S.D(0.01)	0.10	0.07	0.08	0.07

(each value is a mean of three replicates)

Table 3.3.7: Effects of alternate flooded-moist incubations on $NaHCO_3$ extractable soil P (ug/g soil) in a Pakistani soil

Treatments	3W	6W	9W	12W
P0	14.71	11.16	12.03	9.62
P1	36.09	28.67	27.32	24.13
P2	41.53	33.36	34.98	30.70
L.S.D(0.05)	2.40	2.43	2.14	1.30
L.S.D(0.01)	4.40	4.47	3.92	2.38

Table 3.3.8: Effects of alternate flooded-moist incubations on solution pH(1:2 soil : H_2O) in a Pakistani soil

Treatments	3W	6W	9W	12W
P0	8.14	8.24	8.17	8.26
P1	7.89	8.05	7.91	8.07
P2	7.87	7.96	7.88	7.94
L.S.D(0.05)	0.04	0.04	0.04	0.04
L.S.D(0.01)	0.07	0.07	0.07	0.07

(each value is a mean of three replicates)

during flooded periods following moist periods might be due to the coprecipitation of Ca^{2+} and phosphate ions in solution. Decreases in native soil P observed in both soils after 12 weeks of flooded-moist and moist incubations indicated the transformations of P into less soluble P compounds. Alternate flooded-moist and moist incubations of 12 weeks did not have much effect on P in control samples whereas small differences were observed in P treated samples. Longer incubation periods might be needed to establish the desired conditions in laboratory. The soil samples treated with pyrophosphate (PP) showed less sorption of applied P and maintained lower pH values under both conditions. Pyrophosphate (PP) has been reported to reduce P sorption through, the inhibition of DCPD crystal growth formation (El-zahaby and Chien, 1982) under calcareous conditions and also through the dissolution of organic carbon in solution (Xie and Mackenzie, 1989b) which may ultimately compete with P for sorption sites.

3.4 Conclusion

Incubating the soils for short periods under flooded conditions affected soil pH. Soil pH of each sample increased, as a result of flooding, and reached near to pH 7. Flooding also caused increases in $NaHCO_3$ extractable P. Increases in soil phosphorus were however somewhat reversed and resorption of released phosphorus, probably by amorphous Fe, took place during longer periods (15 to 25 days) of flooding. Flooded conditions might have induced the loss of easily degradable organic compounds and the build up of toxic organic substances; thus lowering the population of soil microbes which might otherwise enhance reducing conditions. The overall effect of flooding after 50 days of incubation was to increase soil phosphorus probably due to the reduction of Fe- and Mn- oxides. Readily reducible Fe was greater during 15-25 days of flooding which supported the idea that resorption of P might have taken place. Greater amounts of reducible Mn observed beyond 10 days of flooding were also found to be related to low P availability during that period. The effect of Mn was either by sorbing P directly or by depressing Fe concentration in solution and minimizing the Fe-P relationship.

Amounts of extractable phosphorus were found to be greater during the flooded compared with the moist incubations in all the treatments. Sorption of applied P took place during both incubations, greater sorption of P was observed during the moist incubations. Applied P caused decreases in extractable Fe during moist incubations, probably through precipitation, and increases during the flooded incubations, probably through pH effects on the dissolution of Fe oxides. Application of pyrophosphate (PP) increased extractable phosphorus and Fe under both conditions probably due to dissolution of organic matter (OM) and / or by lowering pH values. The greater amounts of extractable Mn during flooding were probably due to the reduction of Mn-oxides. Flooding caused decreases in the extractable Zn and Cu, probably due to their transformations into less soluble forms or due to the immobilisation by applied P and /or due to competition with Fe for the extracting solution.

Alternate flooded-moist and moist aerated conditions caused decreases in available P in the both soils. The decreases in P were greater in P treated samples compared with the control samples. These decreases were probably due to the sorption of applied P. In Pen-y-Ffridd soil, the sorption of applied P was expected due to Fe-oxides, amorphous and of large surface area, formed under alternate flooded-moist conditions, and in Pakistani soil due to the greater amounts of $CaCO_3$. It might be speculated that the surface area of $CaCO_3$ and the trapping of P in surface compounds would be affected by varying CO_2 in soil atmospheres and that $CaCO_3$ might be expected to dissolve and reprecipitate as conditions changed from waterlogged to aerated. Although these conditions affected the levels of extractable P, the effects were not large. Longer periods of incubations would be required for more definitive results. Changes in pH were also noted during the both conditions. Pyrophosphate (PP) treated samples were able to maintain greater levels of extractable P under both conditions.

CHAPTER

4

Chapter 4: Pyrophosphate (PP) as a Source of Phosphorus

4.1 Introduction

Orthophosphate (OP) is the major phosphate constituent of most phosphatic fertilisers and is well known as the major phosphate source in plant nutrition. The efficiency of applied phosphate is known to be quite low in calcareous soils as added fertiliser is quickly immobilised by $CaCO_3$ and gradually deposited as water insoluble calcium compounds. The major primary product of the orthophosphate fertiliser in calcareous soils is dicalcium phosphate dihydrate (DCPD) (Bell and Black, 1970b; Lindsay *et al*, 1962). With time DCPD is subsequently transformed into octacalcium phosphate (OCP) (Amer and Ramy, 1971; Larsen, 1967), and the more basic hydroxyapatite (HA) (Griffin and Jurinak, 1974; Lehr and Brown, 1958).

Polyphosphates are occasionally added to the soils as a phosphate source for plant nutrition. During the last 50 years or so there have been considerable increases in the fertiliser costs due to the increased use of fertilisers for better crop production. This has drawn the attention of scientists to the economical use of fertilisers. Polyphosphates (e.g. pyrophosphates etc) may be more economical due to their smaller volume and low transportation costs. Pyrophosphates (PP's) are water soluble and their condensed nature results in higher P analyses. In spite of their water solubility, pyrophosphates are not considered to be as efficient as orthophosphates in terms of plant nutrition and ease of plant uptake.

One technique developed to reduce the precipitation of fertiliser P in calcareous soils is the incorporation of small amounts of sodium pyrophosphate (NaPP) into orthophosphate (OP) fertiliser. Application of ammonium phosphate fertiliser containing 10% of its P in the form of PP to a calcareous soil has prevented the appearance of DCPD or HA (Larsen and Widdowson, 1966). Moreover, the addition of NaPP in small amounts to a solution supersaturated with DCPD has shown a remarkable inhibitory effect on the growth rate of DCPD crystals (Marshall and Nancollas, 1969). It has been reported by El-zahaby and Chien (1982) that more than 95% of the applied orthophosphate (OP) phosphorus disappeared from the solution after one hour reaction with $CaCO_3$. Addition of 2% NaPP to the total OP almost entirely prevented OP adsorption by $CaCO_3$ (El-zahaby and Chien, 1982). This inhibitory effect of NaPP was only effective if added before or with OP. They further indicated that the effect of NaPP was temporary and dependent on the ratio of $CaCO_3$ to NaPP and OP. Amer and Mostafa (1981) compared various ratios of PP to the P content of OP. They found that low rates of PP were ineffective in preventing the P adsorption but on the other hand higher rates considerably increased the soluble P. This was attributed to the effect of pyrophosphate (PP) in prohibiting DCPD crystal growth. Amer *et al.* (1985) concluded that pyrophosphate (PP) did not prevent OP sorption by $CaCO_3$ but inhibited its precipitation.

4.1.1. Pyrophosphate (PP) Hydrolysis

It is well known that pyrophosphate (PP) is a relatively ineffective source of P for plants prior to hydrolysis to the orthophosphate form (Sutton and Larsen, 1964). In soils pyrophosphate hydrolyses to orthophosphates; the main source of phosphate for plant nutrition. The effectiveness of pyrophosphate as a source of phosphorus for plants depends on its reactions with soil constituents and the distribution of phosphorus between ortho- and pyro- phosphates at different times during the growing season (Hughes and Hashimoto, 1971). The reactions of pyrophosphate with soil are slower than those of orthophosphate (Philen and Lehr, 1967). Studies on this aspect have revealed that pyrophosphate hydrolysis in soils is a reaction of both chemical and biochemically mediated processes (Dick and Tabatabai, 1986; Hons *et al.* 1986; Stott *et al.* 1985). Different factors which are reported to enhance pyrophosphate (PP) hydrolysis are the increases in temperature, H-ion concentration, enzymatic activity, colloidal gels, complexing cation concentrations and the ionic environment in the solution (Dick and Tabatabai, 1986 and 1987; Stott *et al.*, 1985; Sutton *et al.*, 1966; Van Wazer *et al.*, 1955). Other factors such as moisture content, soil texture and amounts of soil organic matter and their particular properties such as the molecular size and composition will also affect PP hydrolysis (Gilliam and Sample, 1968; Hons *et al.*, 1986; Hossner and Phillips, 1971; Tabatabai and Dick, 1979). Sutton *et al.* (1966) reported from a laboratory study that optimum temperature for pyrophosphate (PP) hydrolysis is in the range of 30-35°C. More rapid hydrolysis at high temperature is considered to be due to increased microbial and enzymatic activity (Engelstad and Allen, 1971; Sutton *et al.*, 1966). There is no consensus about the effect of pH on pyrophosphate (PP) hydrolysis. Some researchers have reported increases in pyrophosphate (PP) hydrolysis with increases in pH (Hons *et al.*, 1986; and Sutton and Larsen, 1964) whereas others have indicated decreases with rise in pH (Hossner and Melton, 1970; Philen and Lehr, 1967; and Subbarao and Ellis, 1975). Tabatabai and Dick (1979) observed a decrease in pyrophosphate (PP) hydrolysis in calcareous soils and attributed this decline to decreased magnesium ion (Mg^{++}) activity.

Pyrophosphate (PP) hydrolysis is catalysed by the pyrophosphatase (PPase) enzyme (Stott *et al.*, 1985), distributed within fauna, flora and soils (Tabatabai and Dick, 1979). The activity of this enzyme decreases with increases in $CaCO_3$ levels due to the binding of the essential Mg^{2+} ion by $CaCO_3$ (Tabatabai and Dick, 1979).

Pyrophosphate (PP) hydrolysis is also affected by soil moisture contents; flooded soils having more rapid hydrolysis than when at 1/3 bar moisture potential (Hossner and Phillips, 1971). Half-life values of applied pyrophosphate (PP) under flooded conditions ranged from about 0.5 to 4 days depending on other environmental factors. The half-life time required for pyrophosphate hydrolysis under aerobic conditions varied from 4 to 100 days (Blanchar and Hossner, 1969; Sutton *et al.*, 1966). Hons *et al.*, (1986) reported that pyrophosphate (PP) hydrolysis in calcareous soils was faster under drier conditions.

It is evident from the review of literature that pyrophosphate (PP) hydrolysis in the soils is not dependent on the effect of a single factor, rather it depends on the combination of biological, chemical and physical factors of complex nature.

4.2 Experiment I. Pyrophosphate Hydrolysis in Solution

4.2.1 Aims of the experiment

This experiment was designed to study the effects of temperature, $CaCO_3$, pH and added organic acids (water extract of rice straw) on pyrophosphate (PP) hydrolysis in solution. The effect of each factor was studied independently of the other in the absence of soil.

4.2.2 Treatments

The treatments were as follows

1) PPT1
2) PPT2
3) PPT3
4) PPCT1
5) PPCT2
6) PPCT3
7) PPOaT1
8) PPOaT2
9) PPOaT3
10) PPCOaT1
11) PPCOaT2
12) PPCOaT3
13) (OP+PP)T1
14) (OP+PP)T2
15) (OP+PP)T3
16) PPpH1
17) PPpH2
18) PPpH3

where PP= Potassium pyrophosphate (KPP) at 1000 µg P/ml of solution
C=$CaCO_3$ (5g added to 100ml solution)
T1, T2 & T3 represent three temperature levels at 5°C, 25°C & 45°C respectively
Oa= organic acid (H_2O-extract of rice straw) 10 ml added to make a total 100ml volume
OP = orthophosphate (80% of total P concentration)
pH1, pH2 & pH3 represent three pH levels at 4.5, 6.5 & 8.5 respectively

4.2.3. Materials and Methods

4.2.3.1. H_2O-extract of Rice Straw

Rice straw (2g) was added to 100ml water in polythene bottle, shaken for one hour at 175 cycles per minute. The extract was filtered and retained for the treatments.

4.2.3.2. Experimental Procedure

A series of small laboratory trials were conducted in this experiment. Potassium pyrophosphate was used as phosphate source. Phosphate solution was prepared and 100ml with a final concentration of 1000 µg P/ml was added in triplicate to 125 ml plastic bottles. Appropriate temperatures were provided to the samples using, a refrigerator, room temperature, and an incubator. In the first set (treatments 1-6) pyrophosphate (PP) solution in the presence and absence of $CaCO_3$ (5g) was incubated at different temperatures. In the second set (treatments 7-9) organic acid (10 ml rice straw extract) was added to pyrophosphate (PP) solution keeping the final solution concentration at 1000 μg P/ml and the final volume to 100ml. To another set of samples (treatments 10-12), $CaCO_3$ (5g) was added in the presence of organic acids. In another set (treatments 13-15), orthophosphate (OP) was added with pyrophosphate (PP) in solution with the ratio as mentioned earlier keeping the final concentration to 1000 μg P/ml of solution.

In another set of samples (treatments 16-18), three pH levels of 4.5, 6.5 and 8.5 were adjusted either by using dilute H_2SO_4 or NaOH. Phosphate remaining in solution was determined after 30, 60, 90, 120 and 240 days. Small portions of each sample were used to hydrolyse (total P) the remaining PP in solution at 95°C for 14 hours in the presence of 1ml H_2SO_4. Unhydrolyzed pyrophosphate (PP) was determined by subtracting the solution P from the total P (P after hydrolysis with acid) and the data are presented as unhydrolyzed PP(%).

4.2.4: Results

4.2.4.1: Effects of added $CaCO_3$, Organic acids and orthophosphate (OP) on pyrophosphate (PP) hydrolysis in solution at three temperature levels

Table 4.1a presents data about the effects of different amendments, added $CaCO_3$, organic acids and orthophosphate (OP) to pyrophosphate (PP) in solution, at different temperatures. The results are presented as unhydrolyzed PP (%) in solution observed after 30, 60, 90,120 and 240 days of incubation period. The effects of three temperature levels on PP hydrolysis in solution were observed in the presence and absence of $CaCO_3$. Different temperature levels did not affect pyrophosphate (PP) hydrolysis in solution greatly. At the highest temperature (45°C) more than 98% of the applied pyrophosphate (PP) was found in solution even after 240 days whereas more

Table 4.1a. Amounts of unhydrolysed pyrophosphate (%) in solution as affected by added $CaCO_3$, organic acids and OP at three temperature levels.

Treatments	Temperature (°C)	30 d	60 d	90 d	120 d	240 d
PP	5	100	100	99.9	99.7	99.6
PP	25	100	99.8	99.4	99.1	98.8
PP	45	99.8	99.6	98.9	98.5	98.3
PPC	5	100	99.7	98.9	98.3	97.5
PPC	25	99.4	98.5	97.9	97.2	96.6
PPC	45	98.7	97.3	96.3	95.3	94.6
PPOa	5	99.6	99.4	98.7	98.4	98.0
PPOa	25	99.4	98.6	97.3	96.5	95.7
PPOa	45	98.2	97.5	96.6	95.3	94.6
PPCOa	5	99.2	98.7	98.2	97.6	97.1
PPCOa	25	98.5	96.9	95.6	94.3	93.8
PPCOa	45	97.8	96.7	95.1	93.8	92.3
OP+PP	5	96.7	94.2	92.7	89.3	87.4
OP+PP	25	92.8	85.7	74.6	69.4	65.5
OP+PP	45	89.6	81.3	72.4	68.5	62.4

(each value is a mean of three replicates)

Table 4.1b Amounts of unhydrolysed pyrophosphate (%) in solution as affected by three pH levels

Treatments	pH level	30d	60d	90d	120d	240d
PPpH1	4.5	96.4	92.5	89.4	86.2	84.6
PPpH2	6.5	98.3	97.5	96.9	95.6	94.5
PPpH3	8.5	98.9	98.3	97.7	97.1	96.4

(each value is a mean of three replicates) than 99% PP remained in solution at the lowest temperature (5°C). Addition of $CaCO_3$ to the PP solution caused slight increases in the hydrolysis of applied PP showing more effect at the greatest than at the lowest temperature. About 97% and 94% of the applied PP were found in solution after 240 days at the greatest and the lowest temperatures respectively.

Addition of organic acids (H_2O-extract of rice straw) to PP solution caused slight increases in PP hydrolysis at all temperature levels. After 240 days of incubation about 4% and 2% increases in PP hydrolysis were observed at 5°C and 45°C respectively compared with the hydrolysis in the absence of organic acids. Further increases, in pyrophosphate (PP) hydrolysis, 1% at 5°C and 2% at 45°C, were observed when $CaCO_3$ was added to the solution. Maximum increases in PP hydrolysis compared with all the other treatments were observed when 80% OP was added to the total strength of PP solution showing more increases at the greatest temperature and less at the lowest temperature.

The effect of pH on PP hydrolysis was observed at three pH levels of 4.5, 6.5 and 8.5. Amounts of pyrophosphate hydrolysed after 240 days of incubation ranged from 3-15% of the applied PP with the maximum hydrolysis being observed at the lowest pH. The highest pH level causing the minimum hydrolysis of applied PP.

4.2.5: Discussion

The hydrolysis of pyrophosphate (PP) in solution was examined during a long incubation period for up to 240 days. It was found to be a slow process both in pure solution and in the presence of $CaCO_3$ and/or organic acids. Hydrolysis of condensed phosphates proceeds very slowly in sterile, neutral solutions at room temperatures (Gilliam and Sample, 1968). After the incubation period of 240 days less than 10% of the applied PP was hydrolysed either in the presence of $CaCO_3$ and/or organic acids or in their absence. In the presence of OP maximum increases in PP hydrolysis were observed. Hydrolysis of pyrophosphate (PP) increased slightly (1% only) in PP treated samples as temperature increased from 5°C-45°C which might be attributed to chemical hydrolysis which slightly increased with temperature. Pyrophosphate (PP) solution was used for the studies to exclude any possibility of biological hydrolysis. It is well known that PP hydrolysis is a reaction of both chemical and biochemically mediated processes (Dick and Tabatabai, 1986; Hons *et al.*, 1986; Stott *et al.*, 1985). It has also been reported from the studies on steam sterilised soils that 0 to 77% of the hydrolysis of pyrophosphate (PP) could be attributed to chemical hydrolysis depending on the soil type and length of incubation period (Gilliam and Sample, 1968; Hashimoto *et al.*, 1969; Dick and Tabatabai, 1978). Different researchers like Dick and Tabatabai, (1986) and (1987); Stott *et al.*, (1985); Sutton *et al.*, 1966; Van-Wazer *et al.*, 1955) have reported increases in pyrophosphate (PP) hydrolysis with the rises in temperature. Slight increases in pyrophosphate (PP) hydrolysis at higher temperature indicates that if pyrophosphate (PP) fertiliser is to be applied in solution forms, it may be stored at room temperature for long periods. Small increases in pyrophosphate (PP) hydrolysis were observed when $CaCO_3$ was added to the solution. These increases were slightly greater (2%) at higher temperature compared with those at lower temperature. Addition of $CaCO_3$ to solution might have caused positive effects on chemical hydrolysis of PP. The results are contrary to those of Searle and Hughes (1977) and Tabatabai and Dick (1979) who reported that the presence of $CaCO_3$ inhibited the biochemical hydrolysis of PP by pyrophosphatase. The results are, however, confirmed by the reports of Healy and Kilpatrick (1955) who found that water-soluble Ca^{2+} was involved in chemical hydrolysis and trimetaphosphate hydrolysis had been shown to be catalysed by Ca^{2+} in sterile water. As agricultural lime was used as source of $CaCO_3$ some amounts of Mg^{2+} might be present in the solution which would also promote chemical hydrolysis of pyrophosphate (PP). Magnesium (Mg^{2+}) ions are required for activation of pyrophosphate (PP) in pyrophosphatase assays (Searle and Hughes 1977) and has been shown to promote chemical hydrolysis of polyphosphates (TMP) in soils (Busman and Tabatabai 1985). Addition of rice straw extract to pyrophosphate (PP) solution further enhanced pyrophosphate (PP) hydrolysis which might either be due to its direct effect by lowering solution pH or probably due to the presence of pyrophosphatase enzyme in the extract which catalysed hydrolysis of pyrophosphate (PP). Maximum hydrolysis of pyrophosphate (PP) found in the presence of OP also supported the argument as its addition caused greater decreases in solution pH. The results of the trial with different pH levels (table 3.1b) also revealed that lower pH values enhanced the hydrolysis of pyrophosphate (PP) compared with the higher pH values. Hydrolysis in sterile aqueous systems normally decreases with the increase in pH (Van-Wazer, 1958).

4.3. Experiment II. PP Hydrolysis in Soil conditions

4.3.1. Aims of the Experiment

This experiment was conducted to see the effect of flooded and moist conditions on pyrophosphate (PP) hydrolysis in a brown podzolic soil, a brown earth soil from Aber Farm and a Pakistani soil. The effects of orthophosphate (OP) and/or organic acid additions on pyrophosphate (PP) hydrolysis under flooded and moist conditions were also included in the studies.

4.3.2. Hydrolysis under Flooded conditions

4.3.2.1. Treatments

The following treatments were included for studies for each soil.

1) P0T1	2) P0T2	3) P0T3	4) P1T1	5) P1T2	6) P1T3
7) P2T1	8) P2T2	9) P2T3	10) P3T1	11) P3T2	12) P3T3

Where P0= Control (no P), P1= PP @ 1000μg P/ml of solution as NaPP

P2= OP+PP @ (80%+20%), P3= P2+ Rice straw extract (10 ml)

4.3.2.2. Experimental Procedure

Soil samples (10g) from each soil were added into polythene bottles with 10 ml distilled water. Three replicates were used for each treatment. The bottles were sealed and kept at three temperatures of 5°C, 25°C and 45°C in the refrigerator, at room temperature and in the incubator respectively. Sampling was done after every week and solution P determined. Total P in solution was determined after hydrolysing the remaining PP in solution in the presence of 1 ml concentrated H_2SO_4 at 95°C for 14

Table 4.2.1. Amounts of unhydrolysed pyrophosphate (ug/g soil) in a brown podzolic soil during flooded incubations

Treatments	Temperature (°C)	1W	2W	3W	4W
P1	5	803.22	640.97	527.14	451.17
P1	25	622.31	535.41	443.79	347.97
P1	45	464.62	424.40	353.71	314.99
P2	5	188.79	177.71	164.21	128.27
P2	25	181.77	169.27	129.27	104.31
P2	45	169.29	151.63	103.50	85.64
P3	5	186.72	173.09	158.13	118.85
P3	25	181.35	163.43	122.29	89.40
P3	45	161.87	145.57	96.45	79.46
LSD (0.01)		(16.12)	(14.10)	(9.98)	(12.44)

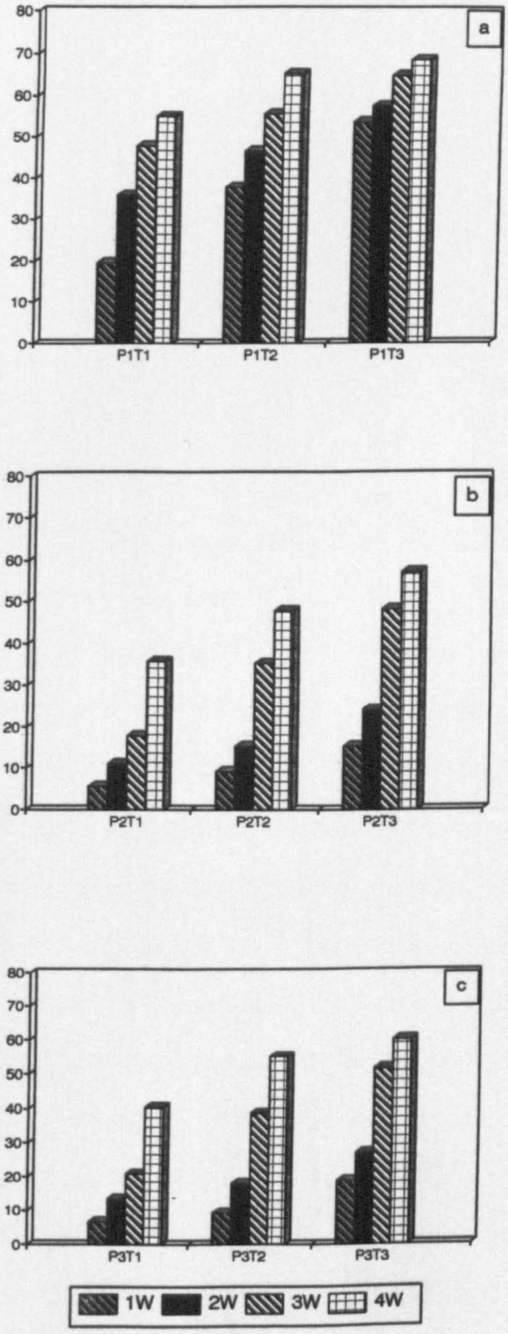
(each value is a mean of three replicates)

Table 4.2.2. Amounts of unhydrolysed pyrophosphate (ug/g soil) in a brown earth soil from Aber Farm during flooded incubations

Treatments	Temperature (°C)	1W	2W	3W	4W
P1	5	761.32	648.86	533.43	424.29
P1	25	688.78	557.99	414.47	340.59
P1	45	613.89	449.61	385.03	315.85
P2	5	193.51	184.73	164.04	129.29
P2	25	192.83	174.17	143.31	108.65
P2	45	182.69	160.92	137.80	94.76
P3	5	191.22	176.31	153.54	118.91
P3	25	189.62	157.61	122.07	79.25
P3	45	179.41	144.42	99.39	74.69
LSD (0.01)		(10.78)	(13.09)	(15.60)	(15.60)

(each value is a mean of three replicates)

Figure 4.1: Amounts of pyrophosphate (PP) hydrolysed (%) in a brown podzolic soil during 4 weeks of flooded incubation treated with (a) PP (b) OP + PP (c) OP + PP + Rice straw extract



hours. The effect of flooded conditions on native soil P was eliminated by deducting the solution P in control samples from P treated samples. Unhydrolyzed PP was determined by subtracting the solution P from total P.

4.3.2.3: Results

4.3.2.3.1: Effects of flooded incubations on pyrophosphate (PP) hydrolysis in a brown podzolic soil, an Aber Farm soil and a Pakistani soil

The results regarding the effects of flooded incubations with time on PP hydrolysis in a brown podzolic soil, a brown earth soil from Aber Farm and a Pakistani soil are presented in tables 4.2.1, 4.2.2 and 4.2.3 and in figures 4.1, 4.2 and 4.3 respectively. Hydrolysis of PP was found to be maximum in the Pakistani soil whereas the soil samples from Aber Farm and brown podzolic soil displayed similar less vigorous behaviour in hydrolysing PP. The effect of temperature was to increase pyrophosphate (PP) hydrolysis with the rise in temperature. Addition of OP to PP generally caused declines in pyrophosphate (PP) hydrolysis. Small increases in pyrophosphate (PP) hydrolysis were observed when rice straw extract was added with OP.

In brown podzolic soil (table 4.2.1) at 5°C about 45% (P1T1), 64% (P2T1) and 59% (P3T1) of the applied pyrophosphate remained unhydrolyzed after 4 weeks of flooded incubation. Increases in temperature caused more hydrolysis in all the treatments and about 10-14 % and 14-20% declines in unhydrolyzed pyrophosphate (PP) were found at 25°C and 45°C respectively. Addition of OP with PP solution to soil caused 19%, 17% and 11% declines in pyrophosphate (PP) hydrolysis at 5°C, 25°C and 45°C respectively. Addition of rice straw extract with OP caused slightly more hydrolysis of PP. These increases in pyrophosphate (PP) hydrolysis were 5%, 7% and 3% at 5°C, 25° C and 45°C respectively compared with when no rice straw extract was added. However total amounts of pyrophosphate (PP) hydrolysed were less than those observed with pyrophosphate (PP) alone.

Hydrolysis of pyrophosphate (PP) showed similar trends in brown earth soil from Aber Farm (table 4.2.2) compared with the hydrolysis in brown podzolic soil (table

Table 4.2.3. Amounts of unhydrolysed pyrophosphate (ug/g soil) in a Pakistani soil during flooded incubations

Treatments	Temperature (°C)	1W	2W	3W	4W
P1	5	560.08	487.03	427.10	395.86
P1	25	473.54	417.11	357.34	333.39
P1	45	440.59	404.68	324.78	286.87
P2	5	195.55	178.95	163.19	143.44
P2	25	192.40	164.12	126.03	94.88
P2	45	184.39	146.68	102.78	83.47
P3	5	187.31	165.82	148.44	129.48
P3	25	180.60	122.32	90.75	64.21
P3	45	172.99	109.96	76.27	59.06
LSD (0.01)		(9.98)	(15.77)	(23.52)	(16.29)

(each value is a mean of three replicates)

Table 4.3.1 Amounts of unhydrolysed pyrophosphate (ug/g soil) in a Brown Podzolic soil during moist incubations

Treatments	Temperature (°C)	1W	2W	3W	4W
P1	5	897.25	753.16	642.28	530.82
P1	25	824.65	616.11	527.59	429.49
P1	45	784.65	596.82	466.61	350.07
P2	5	194.40	189.34	173.17	149.63
P2	25	189.69	174.04	150.41	129.58
P2	45	180.74	165.34	144.03	129.96
P3	5	191.23	182.44	165.49	140.24
P3	25	183.43	171.03	139.33	104.46
P3	45	172.61	158.18	135.83	112.62
LSD (0.01)		(10.78)	(15.42)	(10.78)	(12.22)

(each value is mean of three replicates)

Figure 4.2: Amounts of pyrophosphate (PP) hydrolysed (%) in a brown earth soil from Aber Farm during four weeks of flooded incubation treated with (a) PP (b) OP + PP (c) OP + PP + Rice straw extract

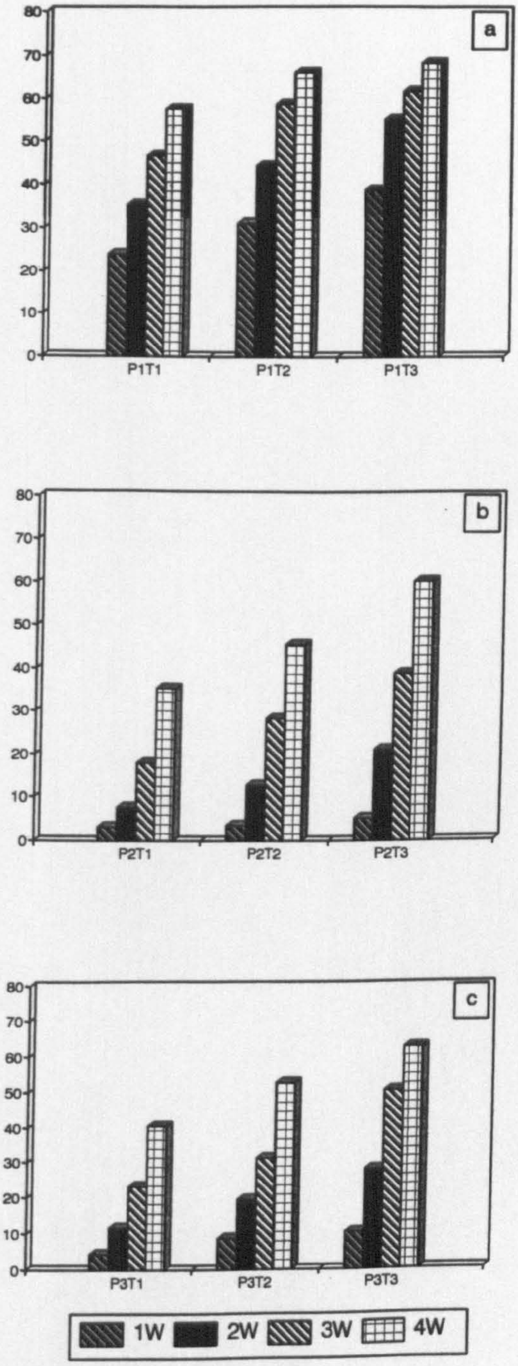
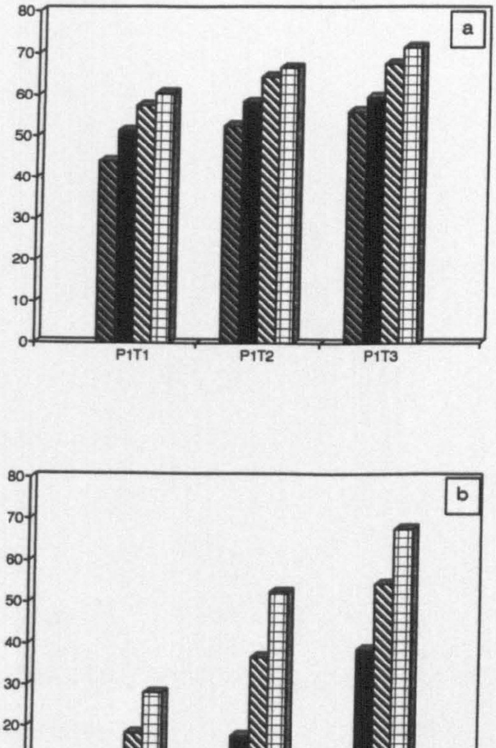


Figure 4.3: Amounts of pyrophosphate (PP) hydrolysed (%) in a Pakistani soil during four weeks of flooded incubation treated with (a) PP (b) OP + PP (c) OP + PP + Rice straw extract



4.2.1). In some treatments however slightly more hydrolysis of pyrophosphate (PP) was observed in a brown earth soil from Aber Farm. After 4 weeks of flooded incubations at 5°C about 59-64% of the applied pyrophosphate (PP) remained unhydrolyzed whereas at 25°C and 45°C these amounts were 34-54% and 31-47% respectively.

In Pakistani soil (table 4.2.3) after 4 weeks of flooded incubation at 5°C about 39% (P1T1), 71% (P2T1) and about 65% (P3T1) of the applied pyrophosphate (PP) remained unhydrolyzed. Increases in pyrophosphate (PP) hydrolysis with the rise in temperature levels were again noticed in this soil. These increases at 25°C and 45°C compared with those at 5°C amounted to be about 6% (P1T2), 24% (P2T2), 33% (P3T2) and 11% (P1T3), 30% (P2T3) and 35% (P3T3) respectively.

4.3.3: Hydrolysis under Moist conditions

4.3.3.1: Treatments

The treatments were the same as described in section 4.3.2.1.

4.3.3.2: Experimental Procedure

The experimental procedure was also the same as described in section 4.3.2.2 except that 1.5 ml distilled water was added to 10g soil in polythene bottles to achieve the moist conditions.

4.3.3.3: Results

The results regarding pyrophosphate (PP) hydrolysis under moist incubated conditions in a brown podzolic soil, a brown earth soil from Aber Farm and a Pakistani soil are presented in tables 4.3.1, 4.3.2 and 4.3.3 and in figures 4.4, 4.5 and 4.6 respectively. The amounts of pyrophosphate (PP) hydrolysed under moist incubations were less than those found under flooded conditions. In brown podzolic soil in treatment P1T1 about 53% of the applied pyrophosphate (PP) remained unhydrolyzed after 4 weeks of moist incubation.. This percentage declined to 43% and 35% as the temperature increased from 25°C (P1T2) to 45°C (P1T3) respectively. Addition of OP to pyrophosphate (PP) caused decreases in pyrophosphate (PP) hydrolysis. In orthophosphate (OP) treated samples, the amounts of unhydrolyzed pyrophosphate (PP)

Table 4.3.2. Amounts of unhydrolysed pyrophosphate (ug/g soil) in a brown earth soil from Aber Farm during moist incubations

Treatments	Temperature (°C)	1W	2W	3W	4W
P1	5	848.10	739.46	655.95	573.85
P1	25	788.23	631.28	513.49	451.10
P1	45	653.76	523.05	423.67	385.41
P2	5	194.14	183.29	170.46	153.98
P2	25	184.51	172.37	149.18	111.75
P2	45	182.37	162.81	135.96	98.70
P3	5	190.87	172.77	162.29	140.51
P3	25	188.27	166.20	134.81	87.24
P3	45	174.41	150.59	119.82	81.27
LSD (0.01)		**(13.30)**	**(9.41)**	**(11.99)**	**(17.60)**

(each value is a mean of three replicates)

Table 4.3.3. Amounts of unhydrolysed pyrophosphate (ug/g soil) in a Pakistani soil during moist incubations

Treatments	Temperature (°C)	1W	2W	3W	4W
P1	5	771.39	675.74	565.29	472.53
P1	25	671.68	521.36	461.54	382.35
P1	45	617.28	451.04	372.69	334.84
P2	5	199.14	191.84	182.39	172.29
P2	25	194.96	168.92	151.33	124.69
P2	45	185.89	164.58	147.69	127.34
P3	5	191.93	182.33	170.50	162.87
P3	25	181.91	146.15	122.59	93.62
P3	45	177.53	149.91	133.19	103.71
LSD (0.01)		**(14.11)**	**(15.24)**	**(12.88)**	**(18.21)**

(each value is a mean of three replicates)

Figure 4.4: Amounts of pyrophosphate (PP) hydrolysed (%) in a brown podzolic soil during four weeks of moist incubation treated with (a) PP (b) OP + PP (c) OP + PP + Rice straw extract

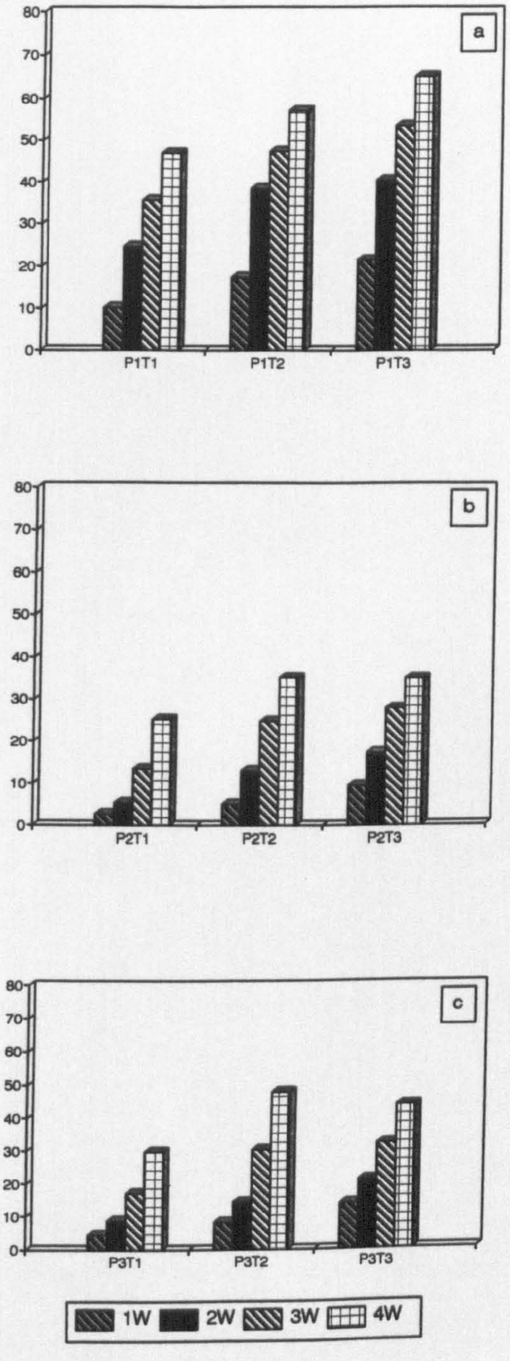
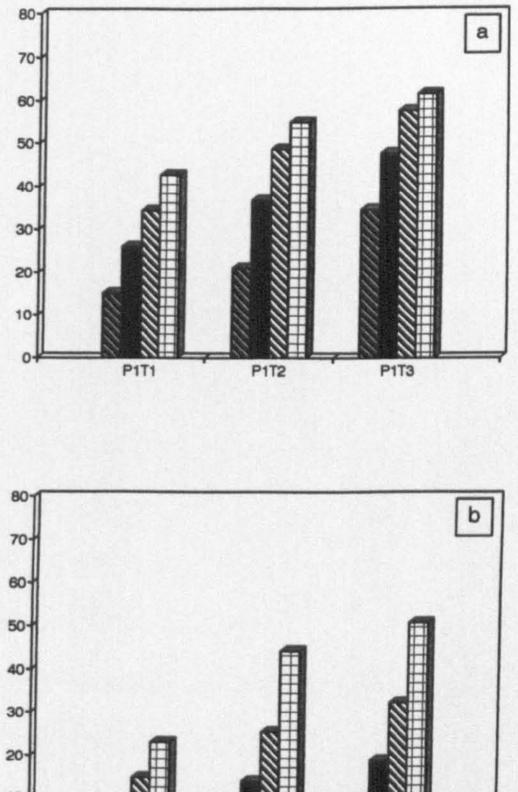


Figure 4.5: Amounts of pyrophosphate (PP) hydrolysed (%) in a brown earth soil from Aber Farm during four weeks of moist incubation treated with (a) PP (b) OP + PP (c) OP + PP + Rice straw extract



at 5°C, 25°C and 45°C after 4 weeks of moist incubations were 74%, 64% and 64% respectively. Addition of rice straw extract along with OP (table 4.3.1) caused slight increases in pyrophosphate (PP) hydrolysis and about 70% (P3T1), 52% (P3T2) and 56% (P3T3) of the applied pyrophosphate (PP) was found unhydrolyzed in solution at the above temperature levels.

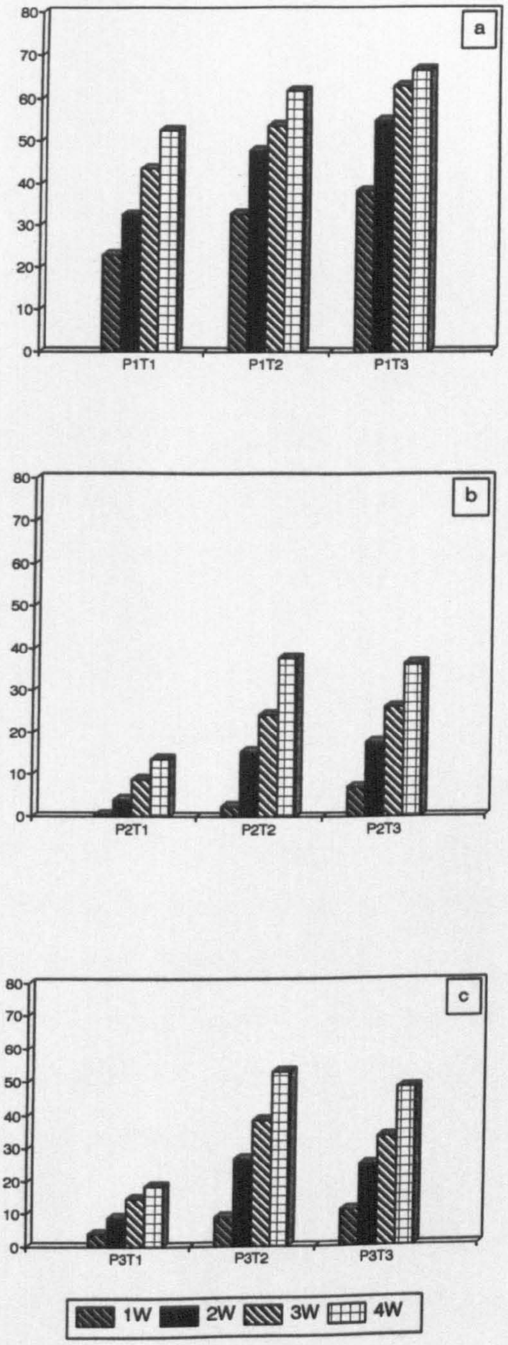
In brown earth soil from Aber Farm, after 4 weeks of moist incubation, pyrophosphate (PP) treated samples at all temperature levels showed less hydrolysis of pyrophosphate (PP) compared with those in brown podzolic soil. About 57%, 45% and 38% of applied pyrophosphate (PP) remained unhydrolyzed at 5°C, 25°C and 45°C respectively. Addition of OP to PP inhibited PP hydrolysis leaving about 77%, 56% and 49% pyrophosphate (PP) unhydrolyzed at 5°C, 25°C and 45°C respectively. Addition of rice straw extract along with OP slightly improved pyrophosphate (PP) hydrolysis and about 70%, 43% and 40% of applied pyrophosphate (PP) were observed in solution after 4 weeks of moist incubation at 5°C, 25°C and 45°C respectively.

In moist incubations also more rapid hydrolysis of applied pyrophosphate (PP) was observed in Pakistani soil compared with those in brown podzolic soil and a brown earth soil from Aber Farm. Similar effects of temperature on pyrophosphate (PP) hydrolysis were observed showing more hydrolysis at greater temperatures. After 4 weeks of moist incubation, in pyrophosphate (PP) treated samples, about 47%, 38% and 33% of the applied pyrophosphate (PP) remained unhydrolyzed at 5°C, 25°C and 45°C respectively. In the presence of OP treatment the amounts of unhydrolyzed pyrophosphate (PP) at the three temperature levels were 86%, 62% and 63% whereas these amounts in the presence of OP and rice straw extract were 81%, 46% and 52%.

4.4 Discussion

In this section pyrophosphate (PP) hydrolysis in the brown podzolic soil, a brown earth soil from Aber Farm and a Pakistani soil both under flooded and moist incubated conditions will be discussed together. Pyrophosphate (PP) hydrolysis was found to be directly proportional to temperature levels and moisture contents in all the soils studied.

Figure 4.6: Amounts of pyrophosphate (PP) hydrolysed (%) in a Pakistani soil during four weeks of moist incubation treated with (a) PP (b) OP + PP (c) OP + PP + Rice straw extract



Pyrophosphate (PP) hydrolysis was minimum in the brown podzolic soil with half life in the range of 1-3 weeks (flooded) and 3-4 weeks (moist) and maximum in the Pakistani soil with half life in the range of 1-< 2 weeks (flooded) and 2-4 weeks (moist) depending on the temperature levels. In brown podzolic soil, brown earth soil from Aber Farm and Pakistani soil about 1.1 to 2.5 times greater hydrolysis of pyrophosphate (PP) was observed during flooded compared with the moist incubations of 4 weeks. The greater rate of pyrophosphate (PP) hydrolysis under flooded conditions compared with the moist conditions may be due to changes in physical, chemical and microbiological processes that take place under these conditions. Changes that could affect rates of pyrophosphate (PP) hydrolysis when a soil is flooded include a rise in pH in acid soils and solubilization of Mn and Fe (Patrick and Fontenot 1976). Soil pH may affect the hydrolysis reaction by altering enzymatic activity (e.g. ionization states of enzymes and substrates) (Dick and Tabatabai, 1987). They also reported that polyphosphate hydrolysis was positively correlated with the solution pH which was inconsistent with the previous findings of Dick and Tabatabai (1986) and Sutton and Larsen (1964) on the effect of pH on pyrophosphate (PP) hydrolysis. Racz and Savant (1972) also reported greater rates of pyrophosphate (PP) hydrolysis in flooded conditions and attributed it to the greater pyrophosphatase activity of flooded soils. Hossner and Phillips (1971) attributed the greater rates of pyrophosphate (PP) hydrolysis to the low redox potentials in flooded soils that increased hydrolysis by a lowering of the activation energy for pyrophosphate hydrolysis. Increased solubilization of metals (e.g. formation of Fe^{2+}) would also decrease sorption of linear polyphosphates thus leaving them susceptible to hydrolysis reactions (Dick and Tabatabai, 1986). The greater amounts of pyrophosphate (PP) hydrolysed in the Pakistani soil compared with the brown earth soil from Aber Farm and brown podzolic soil suggested that less sorption of applied pyrophosphate (PP) might have taken place in the Pakistani soil. Pakistani soil used in the experiment had pH values more than 7 and contained relatively more $CaCO_3$ (23%) contents compared with the brown earth soil from Aber Farm (1% $CaCO_3$) and less DTPA extractable Fe-contents

(2.16 μg Fe/g in a Pakistani soil) compared with both the brown earth soil from Aber Farm (93.4 μg Fe/g soil) and brown podzolic soil (54.3 μg Fe/g soil). Moreover high pH values might have stimulated the activity of pyrophosphatase enzyme causing greater hydrolysis of pyrophosphate (PP). Dick and Tabatabai (1978) reported that optimum pyrophosphatase activity occurred at pH values between 7 and 8 in soils. Later studies of Dick and Tabatabai (1986) revealed that the highest percentage of pyrophosphate (PP) hydrolysis occurred in calcareous Canisteo soils. It has also been reported that alkaline soils tend to have both alkaline and acid phosphatase and acid soils to exhibit only acid phosphatase activity (Dick and Tabatabai 1984) which may partially account for increased hydrolysis rate with increasing pH. Hons and Stewart (1986) reported that more precipitation or adsorption of condensed phosphates or resulting orthophosphates may occur under acidic conditions. The greater sorption of applied pyrophosphate (PP) by brown earth soil from Aber Farm and brown podzolic soil was not unexpected due to their high Fe and /or probably Al contents (table 3b), because Fe and /or Al oxides/ hydroxides are known as active sorption sites for applied pyrophosphate (PP) and /or orthophosphate (OP). Polyphosphate hydrolysis was negatively correlated with dithionite extractable Fe^{3+} and Al^{3+} as linear polyphosphates (P2-P65) are sorbed by soils (Busman, 1984) and pyrophosphate (PP) reacts with Fe and Al in soil solution (Philen and Lehr, 1967; Hashimoto *et al.*, 1969). Moreover metal ions may inhibit enzyme reaction by complexing the substrate, by combining with the enzyme active group or by reaction with the enzyme substrate complex (Stott *et al.*, 1985). Tyler (1981) reported from his review on the effects of heavy metals on soil biology and biochemistry that heavy metals inhibit a variety of microbial enzymes, indicating that the nature and type of inhibition vary among the metals used and enzymes studied.

The addition of orthophosphate (OP) with pyrophosphate (PP) compared with pyrophosphate (PP) alone inhibited the hydrolysis of pyrophosphate (PP) both under flooded and moist incubations in all the soils studied. Inhibition of pyrophosphate (PP) hydrolysis by OP has also been reported by Kulaev (1979), Savant and Racz (1972) and

Stott *et al.* (1985). The exact mechanism by which OP inhibits pyrophosphate (PP) hydrolysis is not yet known. It has been suggested that competition among OP and pyrophosphate (PP) ions for sorption (probably on the enzyme) might be involved in inhibition process. Stott *et al.*, (1985) from their experiments using ions (e.g. BO_3^{2-}, AsO_4^{3-}, MoO_4^{2-}, VO_3^- and WO_4^{2-}), having similar ionic structure to OP, concluded that these ions are competitive inhibitors of pyrophosphatase in soils. Moreover, as OP was added at 80% of the total applied P, increased levels of OP in solution might have ultimately inhibited the chemical hydrolysis of pyrophosphate (PP) to OP. Inhibition of pyrophosphatase activity by the increased levels of inorganic P compounds have also been reported by Kulaev (1979).

Addition of rice straw extract in the presence of PP and OP promoted the hydrolysis of PP in the three soils studied. Increased hydrolysis of pyrophosphate (PP) might be attributed to less sorption of applied PP in the presence of rice straw extract. Organic anions might have competed with pyrophosphate and/or orthophosphate ions for the sorption sites on soil resulting in less sorption of applied pyrophosphate (PP). Moreover the addition of rice straw extract might also have increased the activity of pyrophosphatase enzyme. The presence of pyrophosphatase enzyme in fauna, flora and soils has been reported by Tabatabai and Dick (1979). Mnkeni and Mackenzie (1985) reported that increased pyrophosphate (PP) hydrolysis was due to decreased polyphosphate retention in soils in the presence of alfalfa residues. Later studies revealed that decreased recovery of PP in alfalfa amended topsoils was a function of both decreased polyphosphate sorption and increased enzyme activity (Mnkeni and Mackenzie, 1985). Racz and Savant (1972) found that adsorbed pyrophosphate (PP) hydrolysed at a slower rate than non-adsorbed PP. They concluded that the fixation (adsorption and/or chemical precipitation) of added PP reduces its enzyme-catalysed hydrolysis. Therefore it is most likely that soils with a high P-fixing capacity would hydrolyse PP at a relatively slower rate than would soils with a low phosphate fixing capacity.

More rapid hydrolysis at high temperature is considered to be due to increased microbial and enzymatic activity. In view of this, increased PP hydrolysis with the temperature from 5 to 45°C might be the result of both increased chemical hydrolysis and /or increased activity of pyrophosphatase enzymes in soils. The temperature range used in this experiment may practically exist in soils and thus might determine the amount of available P, if applied as pyrophosphate (PP), for the respective crops. As reported earlier optimum temperature for PP hydrolysis is in the range of 30-35°C (Sutton *et al.*, 1966). Increases in pyrophosphate (PP) hydrolysis with the increases in temperature from 10 to 30°C were also noted by Al-kanani and Mackenzie (1990); Dick and Tabatabai (1986). Sutton *et al.*, (1966) and Hashimoto and Wakefield (1974) also noted lower rates of PP hydrolysis at 10°C compared with 20°C and 30°C and concluded that cool temperatures limited the hydrolysis of pyrophosphate (PP). Hons *et al.*, (1986) found increases in PP hydrolysis with the increasing temperature from 5 to 35 °C. It might be concluded from the influences of temperature on PP hydrolysis that hydrolysis rate in cool soils might not be sufficient to supply the P demands for some cool season crops.

4.5. Conclusion

Hydrolysis of PP proceeded very slowly in solution media compared with that in the soil system. Addition of OP to PP in solution promoted hydrolysis of PP perhaps through increased chemical hydrolysis by lowering the pH of solution. Addition of $CaCO_3$ to the solution also increased PP hydrolysis by increasing the soluble Ca^{2+} and /or Mg^{2+} ions in solution which ultimately enhanced PP hydrolysis. Hydrolysis of PP decreased with the rises in solution pH suggesting that acidic media promoted chemical hydrolysis of PP and rise in solution pH decreased it. Addition of rice straw extract to PP in solution also lowered the solution pH which might have partially increased the chemical hydrolysis. Rice straw extract activated the pyrophosphatase enzyme probably by increasing its concentration in the solution.

The soils subjected to flooded incubations hydrolysed more PP than when subjected to moist incubations. More rapid hydrolysis in brown podzolic soil and brown earth soil from Aber Farm during flooded incubations might be due to rises in solution pH which probably increased the enzymatic activity. The solubilization of metal ions like Mn and Fe decreased the sorption of applied PP leaving it free to be hydrolysed by pyrophosphatase enzyme. More rapid hydrolysis in Pakistani soil during the flooded incubations might be the result of increased enzymatic activity due to favourable pH range (7-8) and also due to solubilization of Ca^{2+} and Mg^{2+} ions which are known to catalyse enzymatic activity.

More precipitation and/or adsorption of applied PP took place in brown podzolic soil and brown earth soil from Aber Farm, resulting in slower hydrolysis of PP compared with the Pakistani soil. Moreover the inhibition of pyrophosphatase activity by metal cations probably also contributed to slower hydrolysis of PP in these soils. Addition of OP in the presence of PP both under flooded and moist incubations decreased PP hydrolysis either by inhibiting the enzymatic activity or due to increased OP concentration in solution which restricted the hydrolysis of PP to OP. Addition of rice straw extract increased the hydrolysis of PP in the three soils studied both under flooded and moist incubations either directly by increasing the enzymatic activity or by decreasing the sorption of applied PP. Increasing levels of temperature increased PP hydrolysis in solution probably by increasing chemical hydrolysis. In soils, during flooded and moist incubations, the effect of temperature in increasing PP hydrolysis was probably by increasing both microbial and enzymatic activity.

CHAPTER
5

Chapter 5: Phosphate Sorption Studies

5.1. Introduction

The solubility of orthophosphate in calcareous soils is limited due to the rapid sorption (adsorption/ precipitation) of applied phosphorus on $CaCO_3$ surfaces. Reaction of phosphorus with $CaCO_3$ results in the formation of water insoluble compounds which may decrease the available phosphorus levels in soils for plant uptake. Dicalcium phosphate dihydrate (DCPD) is the major initial product of the reaction between water soluble OP fertilisers and calcareous soils (Lindsay *et al.*, 1962; Bell and Black, 1970b). Lehr and Brown (1958) found that after the time required for growth of two test crops in the green house, octacalcium phosphate (OCP) or hydroxyapatite (HA) could be identified in fertiliser bands in alkaline soils to which monocalcium phosphate (MCP) had been added. The order of the alteration is thought to be MCP, DCPD, OCP and HA. As the reaction products become more basic they are less soluble in water (Black, 1968).

Larsen and Widdowson (1966) did not find DCPD or HA in a calcareous soil that had reacted with ammonium phosphates containing 10% P as pyrophosphate (PP). The mechanism that prevented their formation was not understood; both reduced nucleation and crystal growth have been proposed (El-zahaby and Chien, 1982). Philen and Lehr (1967) pointed out the ability of high concentrations of polyphosphates to prevent the precipitation of orthophosphates (OP). Sodium pyrophosphate (NaPP) was shown to have a striking inhibitory influence upon the rate of crystal growth of DCPD (Marshal and Nancollas, 1969).

Researchers like Amer and Mostafa (1981) and El-zahaby and Chien (1982) etc. used $CaCO_3$ and calcareous soils to study the effects of pyrophosphate (PP) addition to orthophosphate (OP) in crystal growth inhibition. Their studies did not give information about the roles of pyrophosphate (PP) addition in acidic (iron rich) conditions and in the presence of organic acids. So it was thought necessary to add organic materials particularly as pyrophosphate (PP) can readily extract organic acids and humic materials from soil (Mc Keague, 1967) and the $CaCO_3$ used had no natural soil organic matter.

These studies were conducted to compare the effects of pyrophosphate (PP) and /or organic acid additions in reducing P sorption under calcareous and acidic (iron rich) conditions. The observations about the formation of DCPD crystals in the presence of pyrophosphate (PP) and / or organic acids on $CaCO_3$ particle surfaces were performed by using the techniques of EDAX and SEM.

5.2. Experiment I. Phosphate Sorption by Limestone ($CaCO_3$)

5.2.1. Aims of the Experiment

Sorption of applied P from solution by agricultural lime ($CaCO_3$) particles with time was studied using orthophosphate (OP) alone or in combination with pyrophosphate (PP) and /or organic acids. The concentration of phosphate used in the trials was 0.05M, a higher dose than usually applied to the field crops. However, this dose may be considered as realistic if microsites of the fertiliser granules are taken into account.

5.2.1.1. Materials and Methods

Solutions (0.05M) of orthophosphate (OP) alone or in combination with pyrophosphate (PP) and /or organic acids were used in different treatments. Amounts of pyrophosphate (PP) were 10% of total applied phosphates in solution. Organic acids were either extracted from soil and rice straw by PP (sections 5.2.1.2 and 5.2.1.3) and citric acid (5.2.1.5), from soil by chelex resin (section 5.2.1.4) or added in commercial form (trisodium citrate) to the solution. Agricultural lime ($CaCO_3$) weighing 25g was used for each treatment. The samples were shaken continuously and P determined after different intervals of time.

5.2.1.2. Pyrophosphate (PP) extract of soil

Sodium pyrophosphate (NaPP) weighing 2.23g was added to 100 ml distilled water along with 10g soil (Aber Farm) in polythene bottles, shaken for half an hour at 175 cycles per minute, centrifuged, filtered and 50 ml of the extract added to the main orthophosphate solution (0.045M) in polycarbonate bottles giving a final P concentration of 0.05M and total volume of 1000 ml.

5.2.1.3. Pyrophosphate (PP) extract of rice straw

Rice straw (0.5g) and 2.23g NaPP were added to 100 ml distilled water in polythene bottles, shaken for half an hour at 175 cycles per minute. The extract was filtered and 50 ml added to the OP solution (0.045M) in polycarbonate bottles. The pyrophosphate (PP) and orthophosphate (OP) concentrations being approximately the same as in the PP treatment in section 5.2.1.2.

5.2.1.4. Chelex resin extract of soil

Chelex resin (10g) and 20g soil were added to 100 ml distilled water in polythene bottles, shaken for half an hour at 175 cycles per minute, centrifuged, filtered and added to the OP solution in polycarbonate bottles.

5.2.1.5. Citric acid extract of Rice Straw

Rice straw (0.5g) and 100 ml citric acid solution (0.1M) were added to a polythene bottle and shaken for half an hour at 175 cycles per minute, filtered and 50 ml of the extract were added to the main solution in polycarbonate bottles for sorption studies.

5.2.2. Treatments

Following treatments were used for the experiment

i) LP1 ii) LP2 iii) LP3 iv) LP4
v) LP5 vi) LP6 vii) LP7 vii) LP8

where L & P are $CaCO_3$ and phosphate source respectively

P1= 0.05M OP solution, P2= 0.045M OP + 0.0025M PP*

P3= 0.045M OP + PP extract of soil (see 5.2.1.2)*

P4= 0.045M OP + PP extract of rice straw (see 5.2.1.3)*

P5= 0.05M OP + 0.1M citric acid

P6= 0.05M OP + 0.1M citric acid extract of rice straw (see 5.2.1.4)

P7= 0.05M OP + chelex resin extract of soil (see 5.2.1.5)

P8= 0.045M OP + 0.0025M PP + Chelex resin extract of soil*

* total P as OP+PP=0.05M

5.3. Results

5.3.1. Effects on solution P with sorption time

Initial solution P (OP) concentrations in each treatment were determined before adding lime to the bottles and are given in table 5.1 along with the data regarding P behaviour, with time, in the presence of $CaCO_3$. This shows that in OP treated samples considerable amounts of phosphorus were removed from the solution irrespective of organic acid additions. More than 50% of the applied P disappeared from the solution in first 24 hours of reaction time. Addition of citric acid and citric acid extract of rice straw to OP treatment had adverse effects on solution P and most of the P was removed from the solution. In the presence of citric acid extract of rice straw, however, removal of solution P was slightly lower in comparison to the citric acid alone. Further decreases in P removal from the solution were observed when chelex resin extract of soil was added to OP treatment. Overall decreases in solution P after 302 hours of sorption time in comparison to initial solution P in treatments LP1, LP5, LP6 and LP7 were 1093, 1233, 1222, and 976 µg P/1000 ml of solution respectively.

Addition of 10% sodium pyrophosphate (NaPP) to OP had a positive effect on P solubility and most of the applied P remained in solution even after 302 hours of reaction time. Addition of chelex resin extract of soil to OP+PP (LP8) treatment and PP-extract of soil to OP (LP3) treatment caused further increases in the solubility of P. The addition of pyrophosphate extract of rice straw (LP4) to OP treatment had similar effects on the solubility of P as in the presence of PP (LP2) alone. Increases in P over initial solution P in treatments LP2, LP3, LP4 and LP8 after 302 hours of reaction were 23, 80, 22 and 82 µg P/1000 ml of solution respectively.

5.3.2. Effects on Solution pH with Sorption Time

Effects on solution pH with sorption time are presented in table 5.1. Increases in pH in all the treatments up to 302 hours of reaction time were observed. These increases in pH in treatments LP1, LP2, LP3, LP4, LP5, LP6, LP7 and LP8 were 3.06, 0.51, 0.38, 0.58, 3.50, 1.95, 2.53 and 0.37 units respectively. The data in table 5.1 show that the increases in pH or final pH values at 302 hours of reaction were always higher in orthophosphate (OP) treated samples in the absence of pyrophosphate (PP). Addition of different organic acids, except citric acid, to OP and OP+PP treated samples resulted in less increases in the final pH values of the solution whereas addition of citric acid caused more increases. In treatments LP2, LP3, LP4 and LP8 final pH values of the solution were buffered around <6.5 by the addition of pyrophosphate (PP) and the "buffering effect" diminished in the presence of citric acid.

5.3.3. EDAX for Ca and P and SEM Observations

Solid material of $CaCO_3$ particles from the filter paper after final sampling (302 hours) were retained and attached on the stubs with double sided adhesive tape. The samples were coated with carbon prior to observations by Energy Dispersive X-ray analyses. The results are illustrated in figure 5.2 a & b.

5.4. Experiment II. Phosphate Sorption by a Pakistani soil

5.4.1. Aims of the experiment

A Pakistani soil (table 3a&b) was studied to investigate the effects of pyrophosphate and different organic acid extracts on the sorption of applied P with time.

5.4.2. Materials and Methods

5.4.2.1. Pyrophosphate (PP) extract of Soil

The procedure was followed as described in section 5.2.1.2 except that the organic acids/ humic materials were extracted using 20g soil (brown earth from Aber Farm) per 100ml of the extracting solution. The amount of soil was doubled to that stated in section 5.2.1.2 so that greater amounts of organic acids/ humic materials could be added as different ions present in soil may compete for chelation by organic ligands and thus minimise their effects.

5.4.2.2. Pyrophosphate (PP) extract of Rice straw

Method was followed as described in section 5.2.1.3 except that 2g rice straw per 100ml extracting solution was used for the extraction of organic acids/ humic materials.

Table 5.1. Effects of sorption time on solution P and pH in the presence of Calcium Carbonate ($CaCO_3$)

Treatments	P (ug/ 1000ml)			pH		
	0 hr	1 hr	302 hr	0 hr	1 hr	302 hr
LP1	1529	870	436	4.55	6.99	7.61
LP2	1409	1460	1432	5.98	6.18	6.49
LP3	1386	1460	1466	5.90	6.10	6.28
LP4	1414	1437	1436	5.90	6.14	6.48
LP5	1542	1540	309	4.43	6.42	7.93
LP6	1560	1597	338	5.85	6.30	7.80
LP7	1534	824	558	5.00	5.99	7.53
LP8	1412	1489	1494	5.99	6.08	6.45

Table 5.2. Effects of sorption time on solution P, pH and OC in the presence of a Pakistani soil

Treatments	P (ug/1000ml)			pH			OC (ug/ml)	
	0 hr	1 hr	384 hr	0 hr	1 hr	384 hr	1 hr	384 hr
PKP1	1592	1586	1318	4.55	5.80	6.22	2.25	9.16
PKP2	1455	1426	1498	5.98	5.98	6.10	6.10	18.31
PKP3	1483	1455	1476	5.90	5.92	6.07	6.87	15.26
PKP4	1392	1460	1502	5.90	5.91	6.10	16.79	21.36
PKP5	1472	1529	1369	5.00	5.82	6.20	1.53	10.68
PKP6	1369	1455	1541	5.99	6.00	6.11	9.16	19.08

5.4.2.3. Chelex resin extract of Soil

Method was followed as described in section 5.2.1.5.

5.4.3. Treatments

Following treatments were used for the experiment.

(i) PKP1 (ii) PKP2 (iii) PKP3 (iv) PKP4 (v) PKP5 (vi) PKP6

where PK & P are Pakistani soil and phosphate source respectively

P1= 0.05M OP solution

P2= 0.045M OP + 0.0025M PP *

P3= 0.045M OP + PP extract of soil (see 5.2.1.2) *

P4= 0.045M OP + PP extract of rice straw (see 5.2.1.3) *

P5= 0.05M OP + chelex resin extract of soil (see 5.2.1.5) *

P6= 0.045M OP + 0.0025M PP + Chelex resin extract of soil *

* total P as OP+PP= 0.05M

5.4.4. Experimental Procedure

Soil (50g) was put in polycarbonate bottles with 1000 ml phosphate solution, shaken continuously on a shaker and sampling was done after different intervals of time until 384 hours of reaction. Organic carbon in the solution was measured by using method as described in section 2.9 (chapter 2).

5.5. Results

5.5.1. Effects on solution P with sorption time

The data regarding initial solution P and effects on solution P with sorption time are presented in table 5.2. Solution P decreased in PKP1, PKP3 and PKP5 treatments and it increased in PKP2, PKP4 and PKP6 treatments. Decreases in solution P after 384 hours of reaction, compared with the initial solution P in treatments PKP1, PKP3 and PKP5 were 274.0, 7.0 and 103.0 micrograms per 1000 ml respectively whereas the increases in treatments PKP2, PKP4 and PKP6 were 43.0, 110.0 and 172.0 micrograms per 1000 ml respectively. The amounts of P removed from solution, after first hour of reaction, in treatments PKP1, PKP2 and PKP3 were 6.0, 29.0 and 28.0 micrograms per

1000 ml respectively and increases in the solubility of P were 68.0, 57.0 and 86.0 micrograms per 1000 ml in treatments PKP4, PKP5 and PKP6 respectively. Addition of chelex resin extract of soil to OP and OP+PP treated samples had positive effects on P solubility. Effects of adding chelex resin extract of soil to OP (PKP5) treatments were to decrease P sorption and to OP+PP (PKP6) treatment were to increase P solubility. Addition of PP extract of soil in the presence of OP (PKP3) caused slight increases in P sorption whereas addition of PP extract of rice straw (PKP4) increased P solubility.

5.5.2. Effects on solution pH with sorption time

Changes in pH of the solution with sorption time are presented in table 5.2. Increases in pH with sorption time in all the treatments were observed. These increases after 384 hours of reaction compared with the initial pH of the solution were 1.7, 0.12, 0.15, 0.20, 1.2 and 0.21 units in PKP1, PKP2, PKP3, PKP4, PKP5 and PKP6 treatments respectively. This shows that the maximum increases in pH (1.67 units) were observed in OP treated samples. Addition of PP, PP extracts of soil and rice straw in the presence of OP resulted in little changes in solution pH from 1 to 384 hours of reaction.. During first hour of reaction the increases in pH of 1.25 (PKP1) and 0.82 units (PKP5) were found in orthophosphate (OP) treated samples whereas an increase of only 0.02 units was found in the rest of the samples treated with pyrophosphate (PP).

5.5.3. Effects on Soluble organic carbon (OC) with sorption time

Data regarding changes in water soluble organic carbon (OC) with sorption time are presented in table 5.2. Organic carbon in solution in all the treatments increased with sorption time. During the first hour of reaction, the increases were minimum in treatment PKP5 and maximum in PKP4. Increases in the solubility of organic carbon (OC) after 384 hours compared with first hour of reaction were 4 (PKP1), 3 (PKP2), 2.2 (PKP3), 1.3 (PKP4), 7 (PKP5) and 2.1 (PKP6) times. After 384 hours of reaction maximum organic carbon (OC) in solution was found in PKP4 and minimum in PKP1 treatment. Addition of PP and PP extract of rice straw in the presence of OP increased the solubility of organic carbon (OC) whereas addition of PP extract of soil (PKP3) decreased its solubility after 384 hours of reaction compared with the treatments PKP2 and PKP4. Addition of chelex resin extract of soil to either OP (PKP5) or PP (PKP6) treated samples increased the solubility of organic carbon (OC) after 384 hours of reaction.

5.6. Experiment III. Phosphate Sorption by Brown Podzolic Soil

5.6.1. Aims of the experiment

Studies on the sorption of applied P with time were conducted in the presence of a brown podzolic soil (table 3a & b). The purpose was to investigate the roles of pyrophosphate (PP) and/ or organic acids in inhibiting P sorption by acidic brown podzolic soil. The effects of liming a brown podzolic soil on its behaviour for P sorption was also studied. This study emphasises the potential role of iron oxides/ hydroxides. It was thought that this would have some relevance to calcareous paddy soils since Fe^{II} is mobilised under flooded conditions and thus substaintial active Fe^{III} oxide/ hydroxide surfaces will be expected in the subsequent wheat soils.

5.6.2. Materials and Methods

5.6.2.1. Pyrophosphate (PP) extract of Rice Straw

Extraction was done as described in section 5.2.1.3.

5.6.2.2. Chelex Resin Extract of Soil

Extraction was performed by following the method as described in section 5.2.1.5.

5.6.3. Treatments

Two types of soil samples were used for the studies; original soil from the field and artificially limed soil with 5% & 10% lime levels.

5.6.3.1. Original Soil

(i) IP1 (ii) IP2 (iii) IP3 (iv) IP4 (v) IP5

where I & P are iron rich soil and phosphate source respectively

P1= 0.05M OP solution

P2= 0.045M OP + 0.0025M PP *

P3= 0.045M OP + PP extract of rice straw (section 5.2.1.3) *

P4= 0.05M OP + chelex resin extract of soil (section 5.2.1.5) *

P5= 0.045M OP + 0.0025M PP + Chelex resin extract of soil *

* total P as OP+PP=0.05M

5.6.3.2. Limed Soil

i) IL1P1 ii) IL2P1 iii) IL1P2 iv) IL2P2

where L1 & L2 are 5% and 10% lime levels on weight basis.

5.6.4. Results

Organic carbon (OC) in solution was measured by using the method as described in section 2.9 (chapter 2) and iron (Fe) contents in the solution were measured using the techniques of atomic absorption spectrophotometry.

5.6.4.1. Original Soil

5.6.4.1.1. Effects on solution P with sorption time

The data regarding changes in solution P with sorption time in the presence of brown podzolic soil are presented in table 5.3. Increases in P sorption with time were observed in all the treatments. The results regarding P sorption after first hour of reaction indicated that about 291.0 (IP1), 166.0 (IP2), 171.0 (IP3), 268.0 (IP4) and 172.0 (IP5) micrograms P per 1000 ml of the applied P disappeared from the solution. Amounts of P removed from the solution after 398 hours of reaction in the above cases were 658.0, 485.0, 483.0, 588.0 and 473.0 μg P/1000 ml of solution respectively. Addition of pyrophosphate (PP) and different organic acids to orthophosphate (OP) treated samples lowered the sorption of applied P by brown podzolic soil. After 398 hours of reaction time, the treatments IP2, IP3, IP4 and IP5 maintained 48.0, 55.0, 65.0 and 55.0 micrograms per 1000 ml respectively greater P in solution compared with that in IP1 treatment.

5.6.4.1.2. Effects on solution pH with sorption time

Changes in pH with sorption time are presented in table 5.3. After first hour of reaction increases in pH in IP1 (0.4 units) and IP4 (0.05 units) treatments and decreases in IP2 (0.19 units), IP3 (0.2 units) and IP5 (0.15 units) treatments were observed. A

Table 5.3. Effects of sorption time on solution P, pH, OC and Fe contents in the presence of a brown podzolic soil.

Treatments	P (ug/1000 ml)			pH			OC (ug/ml)		Fe (ug/ml)	
	0 hr	1hr	398hr	0 hr	1hr	398hr	1hr	350hr	1hr	350hr
IP1	1637	1346	979	4.59	4.99	5.72	98.2	271.4	0.6	10.3
IP2	1512	1346	1027	5.99	5.80	6.18	135.4	328.2	3.4	58.1
IP3	1517	1346	1034	6.00	5.80	6.21	104.9	325.8	4.0	57.6
IP4	1632	1364	1044	5.00	5.05	5.77	136.4	277.5	1.0	19.3
IP5	1507	1335	1034	6.00	5.85	6.20	188.8	372.0	4.9	66.0

Table 5.4. Effects of sorption time on solution P, pH, OC and Fe contents in the presence of a brown podzolic (limed) soil.

Treatments	P (ug/1000 ml)			pH			OC (ug/ml)		Fe (ug/ml)	
	0 hr	1hr	278hr	0 hr	1hr	278hr	1hr	278hr	1hr	278hr
IL1P1	1630	1283	976	4.55	5.83	6.50	95.4	195.6	0.2	1.2
IL2P1	1641	1397	918	4.55	5.91	6.58	106.8	184.7	0.6	0.4
IL1P2	1516	1340	987	5.99	6.06	6.60	133.5	230.0	9.2	5.3
IL2P2	1505	1346	1010	5.99	6.07	6.66	95.4	215.1	7.7	3.4

general increase in solution pH in all the treatments was observed and treatments IP1 and IP4 showed more increases. These increases in pH after 398 hours of reaction time compared with initial pH of the solution were 1.13 (IP1), 0.19 (IP2), 0.21 (IP3), 0.77 (IP4) and 0.20 (IP5) units.

5.6.4.1.3. Effects on Soluble organic carbon (OC) with sorption time

Amounts of organic carbon (OC) in solution was determined after 1, 36, 84, 182, 278 and 350 hours of reaction time and are illustrated in figure 5.4c. Data in table 5.3 show that in all the treatments increases in soluble organic carbon (OC) were observed with the sorption time. These increases after 350 hours of reaction compared with the first hour were 2.8 (IP1), 2.4 (IP2), 3.1 (IP3), and 2.0 (IP4 & IP5) times. Addition of pyrophosphate (PP) and /or organic acids in the presence of OP increased the solubility of organic carbon (OC) after each sampling time. These increases in treatments IP2, IP3, IP4 and IP5 after first & 350 hours of reaction ranged from 1.1-1.9 and from 1.0- 4.0 times respectively.

5.6.4.1.4. Effects on iron (Fe) contents in solution with sorption time

Iron contents (μg/ml) in solution with sorption time are presented in table 5.3. General increases in iron contents were observed with sorption time in all the treatments. These increases after 350 hours of reaction compared with the first hour were 17.4 (IP1), 17.2 (IP2), 14.3 (IP3), 18.9 (IP4) and 13.5 (IP5) times. Addition of pyrophosphate (PP) and /or organic acids to OP treated samples also increased the solubility of iron. These increases after first hour of reaction were 5.7 (IP2), 6.8 (IP3), 1.7 (IP4) ,8.3 (IP5) times and after 350 hours of reaction were 5.7 (IP2), 5.6 (IP3), 1.9 (IP4), and 6.4 (IP5) times respectively over IP1 treatment.

5.6.4.2. Limed Soil

5.6.4.2.1. Effects on solution P with sorption time

Changes in solution P with sorption time in the presence of brown podzolic limed soil samples are presented in table 5.4. The amounts of P removed from solution in the treatments IL1P1, IL2P1, IL1P2 and IL2P2 after first hour of reaction were 347, 244, 176 and 159 and after 278 hours of reaction were 654, 723, 529 and 495 micrograms per 1000 ml of solution respectively. Greater lime level (IL2P1), in OP treated samples, enhanced the removal of P from solution throughout the sorption time except at 1 hour of reaction. After 278 hours of reaction, the amounts of P removed per 1000 ml of solution were 74 micrograms greater in treatment IL2P1 (10% liming) compared with treatment IL1P1 (5% liming). Addition of PP (pyrophosphate) in the presence of OP (IL1P2, IL2P2) caused decreases in the removal of P by brown podzolic soil from solution. Slightly more decreases (17 & 34 ug P/1000 ml) were observed in IL2P2 compared with IL1P2 after first and 278 hours of reaction time.

5.6.4.2.2. Effects on solution pH with sorption time

Changes in pH of solution after liming the brown podzolic soil are presented in table 5.4. Data in table 5.4 show that increases in pH with sorption time and lime levels were observed. Increases in pH in treatments IL1P1, IL2P1, IL1P2 and IL2P2 after 1 & 278 hours of reaction were 1.28, 1.36, 0.07, 0.08 & 1.95, 2.03, 0.61 and 0.67 units respectively. Increases in pH in IL2P1 compared with IL1P1 after first & 278 hours of reaction were 0.08 units whereas these increases in IL2P2 compared with IL1P2 after first and 278 hours of reaction were 0.01 and 0.06 units respectively.

5.6.4.2.3. Effects on soluble organic carbon (OC) with sorption time

Table 5.4 presents data regarding the soluble organic carbon (OC) which show that increases in organic carbon (OC) in all the treatments were observed with sorption time. Greater levels of lime in both OP and PP treated samples decreased the solubility of organic carbon (OC). Increases in the solubility of organic carbon (OC) after 278 hours of reaction compared with the first hour were 2.1 (IL1P1), 1.7 (IL2P1), 1.7 (IL1P2) and 2.3 (IL2P2) times.

5.6.4.2.4. Effects on iron (Fe) contents of solution with sorption time

Table 5.4 presents data regarding iron contents in solution with sorption time. Data in table 5.4 show that the solubility of iron decreased with sorption time in all the treatments except in IL1P1 where an increase was observed. Greater levels of lime (i.e.

at 10% level in comparison to 5% level) decreased iron contents in the solution in all the treatments at all sampling times.

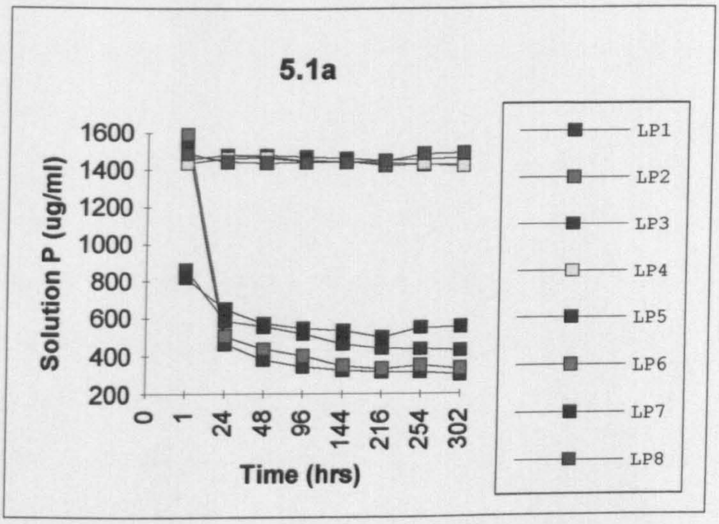
5.7. Discussion

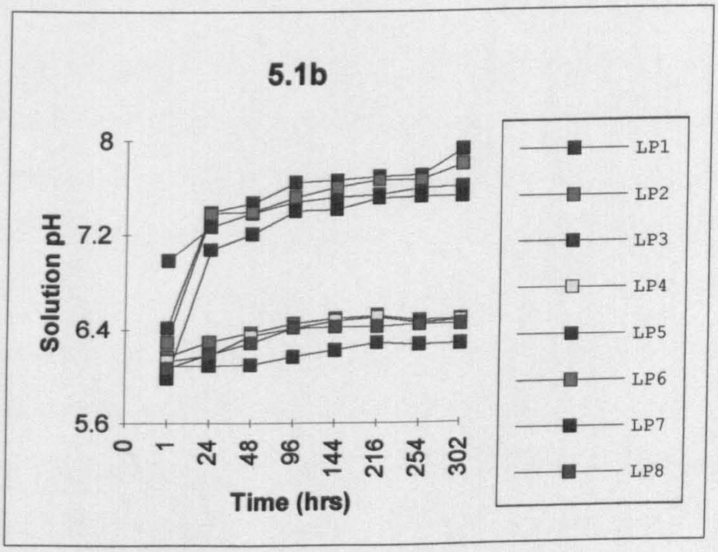
5.7.1. Sorption by agricultural lime ($CaCO_3$)

Sorption of P with time by agricultural lime ($CaCO_3$) and the effects of sorption on pH values of the suspensions are discussed below. Discussion about X-ray analyses and SEM observations will follow later. The experiment was run for 302 hours of reaction time which showed that in OP treated samples 64-80% of the applied P disappeared from the solution (Figure 5.1 a&b). This decrease in solution P was found to be maximum (80%) when citric acid was added in the presence of OP. The addition of a chelex resin extract of a soil to OP treated sample decreased P sorption and only 64% of the applied P disappeared from the solution at 302 hours of reaction. In the presence of pyrophosphate (PP) increases in solution P were observed in all the treatments except where citric acid and citric acid extract of rice straw were added. The decline in solution P in the presence of citric acid (LP5) after 302 hours of reaction was 79%. During the first 24 hours of reaction the decreases in solution P in treatments LP1, LP5, LP6 and LP7 were 61%, 69%, 68% and 57% respectively (figure 5.1a). Addition of citric acid with OP (LP5) caused 8% drop in solution P after 24 hours of reaction whereas 4% increases in solution P were observed in LP7 by the addition of chelex resin extract of soil. In the presence of PP increases of 5% (LP2), 7% (LP3), 4% (LP4) and 3% (LP8) in solution P were observed after 24 hours of reaction.

The decreases in solution P with time in LP1, LP5, LP6 and LP7 treatments might be due to the precipitation of phosphate with Ca. However these decreases were less (<70%) than those reported by El-zahaby *et al.*, (1982) who found more than 88% decreases in solution P after one day of reaction. The greater sorption of P found by El-zahaby *et al.*, (1982) could be attributed to their reagent grade $CaCO_3$ having more surface area and/or to the different P sources used in their experiments. The decreases in solution P with sorption time are reported to be due to the formation of (DCPD)

Figure 5.1: Changes in solution (a) P and (b) pH with sorption time in the presence of $CaCO_3$





dicalcium phosphate dihydrate (Bell and Black, 1970b; Larsen and Widdowson, 1966; Lindsay *et al.*, 1962). The decreases in solution P in the treatments LP1, LP5, LP6 and LP7 were associated with high pH values of the solutions. Final pH values of the solutions were more than 7.5 which are in conformity to the findings of El-zahaby *et al.*, (1982). Increases in pH values of the solutions might be due to the formation of DCPD crystals and hydroxide ions (OH^-) which might have controlled the pH of the solutions. El-zahaby *et al.*, (1982) suggested the following reaction under such conditions

$$H_2PO^-_4 + CaCO_3 + 2H_2O \Leftrightarrow CaHPO_4.2H_2O + CO_2 + OH^-$$

The greatest increases in pH in treatments LP5 and LP6 after 24 hours of reaction might have resulted, due to the acid solution, in the rapid formation of DCPD as compared to treatments LP1 and LP7.

More than 50% of the P sorption in OP treated samples occurred during the first 24 hours of reaction period (fig 5.1a). This indicates that most of the P applied in calcareous conditions is sorbed by $CaCO_3$ particles in a short time after application. However the sorption might vary with the amount and surface area of $CaCO_3$ used (Amer and Mostafa, 1981; Amer *et al.*, 1985). Kuo and Lotse (1972) reported that about 80% of the adsorption by $CaCO_3$ may be completed within 10 seconds. Amer and Mostafa (1981) found that the initial rapid drop in P sorption could be followed by a short period of relatively little change in concentration, then a second drop at a rate proportional to the initial concentration and finally a gradual decrease towards a relatively constant value. They called the period of relatively little change in P concentration separating the two drops as an induction period which precedes precipitation. In the present studies, rapid sorption of P during the first 24 hours was followed by gradual decreases in solution P and an induction period was not noticed.

The presence of pyrophosphate (PP) with orthophosphate (OP) caused a significant positive effect and little or no sorption of P even after 302 hours of reaction, compared with the initial solution P, was observed. In fact increases in solution P were observed throughout the reaction period compared with the initial solution P. This suggests that PP completely occupied or blocked the sorption sites of $CaCO_3$ particles and thus inhibited the sorption of applied P by $CaCO_3$. The increases in solution P in the presence of PP could be attributed to the hydrolysis of applied PP to OP during the shaking period. Amer and Mostafa (1981) also noted an increase in solution P between 24 and 96 hours of reaction and they attributed that increase to the hydrolysis of PP. Moreover in the presence of PP final pH values of the solutions were always maintained below 6.5 indicating the possible blocking of sorption sites of $CaCO_3$ by PP and thus inhibiting the formation of DCPD crystals and hydroxide (OH^-) ions (El-zahaby *et al.*, 1982).

The results reported by Amer and Mostafa (1981) and El-zahaby and Chien (1982) revealed that the effect of sodium pyrophosphate (NaPP) in reducing P sorption was temporary. Two explanations were given (i) sodium pyrophosphate (NaPP) acted as a crystal growth inhibitor for DCPD (Marshal and Nancollas, 1969). (ii) Sorption of NaPP may distort the surface structure of $CaCO_3$ due to its long chain P-O-P bonds which fit nicely into $CaCO_3$ lattices (Raistrick, 1949). El-zahaby and Chien (1982) reported from their experiments with $CaCO_3$ and DCPD crystals that PP ions sorbed on the $CaCO_3$ surfaces may inhibit the nucleation of DCPD. Their findings were partly in agreement with those of Amer and Mostafa (1981) who claimed that the inhibitory effect of NaPP on P sorption by $CaCO_3$ was due to its inhibition of DCPD nucleation and crystal growth. El-zahaby and Chien (1982) reported that the distorted surfaces of $CaCO_3$ may still sorb orthophosphate (OP) in the solution and thus lower the solution P. In the present studies, the first possibility seemed to be more likely as no distortion of $CaCO_3$ surfaces was observed during SEM studies (which will be discussed later). Pyrophosphate (PP) probably inhibited P sorption by binding to Ca on the $CaCO_3$ surfaces and thus reducing the surface area for OP sorption. This could also explain the inability of $CaCO_3$ to control the solution pH (<6.5) as $CaCO_3$ surfaces were blocked by NaPP. Similar results were reported by El-zahaby and Chien (1982).

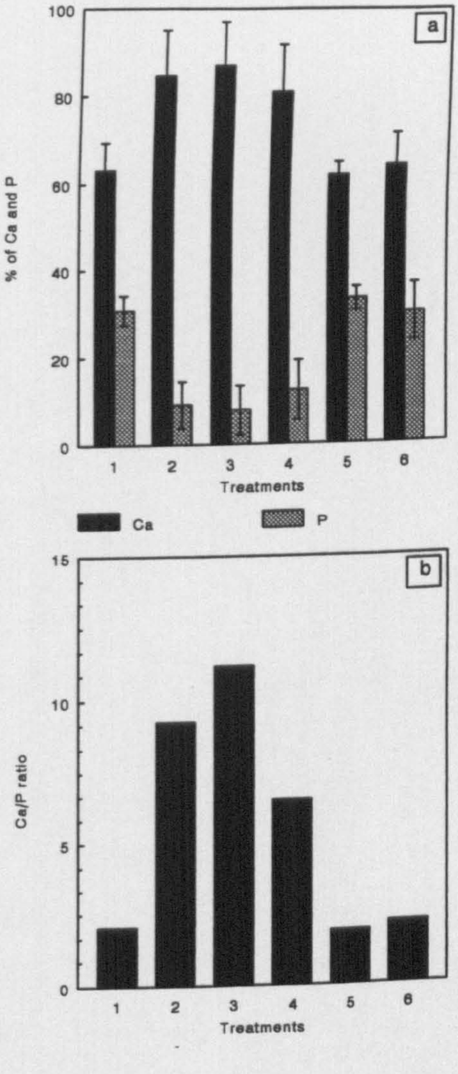
Addition of organic acids like humic acids extracted from soil and rice straw by PP and chelex resin extract of soil showed positive effects on solution P. Chelex extract of soil was found to be more effective in reducing P sorption and the effect was more pronounced in the absence of PP (LP7) where 11% reduction in P sorption compared with LP1 was observed. Moreover addition of organic acids also lowered the pH of the solution which might have, among the other factors, played an important role in reducing P sorption as organic ions are known to compete strongly with phosphate for sorption sites at low pH (Lopez-Hernandez, *et al.*, 1979; Sibanda and Young, 1986; and Traina, *et al.*, 1986). The other possibility of reduced P sorption could be that "C" of the soil organic acids was adsorbed on to seed crystal surfaces, inhibiting P precipitation by blocking sites for new crystal growth as suggested by Inskeep and Silvertooth (1988). It seems that organic acids (extracted from soil & rice straw) do not block all the sorption sites as P sorption was only reduced to some extent and not fully stopped (LP7). Moreover the lower effect of organic acids (extracted from soil & rice straw) in the presence of pyrophosphate (PP) could be the result of competition between PP and organic anions for sorption on $CaCO_3$ surfaces.

Increases in P sorption in the presence of citric acid and citric acid extracts of rice straw might be attributed to the large concentration (0.1M) of citric acid used for these trials which resulted in the dissolution of $CaCO_3$ and its subsequent precipitation with orthophosphate (OP). The results are contrary to Grossl and Inskeep (1991) who reported citric acid to be more effective in inhibiting DCPD crystals growth than humic, fulvic and tannic acids. However, the concentration of citric acids used by them was much lower (8 m mol L^{-1}).

5.7.2. X-ray Analyses and SEM Observations

Samples from the treatments LP1, LP2, LP3, LP4, LP5 and LP6 were prepared for the studies. Analyses were performed after coating the samples with carbon. Different points on each sample were randomly marked and analysed quantitatively for "Ca" and "P" contents. Data were statistically analysed for confidence limits at 95% probability

Figure 5.2: Percentage of (a) Ca and P and (b) Ca/ P ratio as determined by X-ray analyses



level. Percentages of Ca and P (fig 5.2a) and Ca/P ratio (fig 5.2b) were calculated. Greater concentrations of Ca and Ca/P ratios were found in the presence of PP and/or organic acids (soil and rice straw). Citric acid treated samples showed a lower Ca percentage and Ca/P ratio irrespective of PP treatment. In OP treated samples smaller sized (<50 um) $CaCO_3$ particles (Appendix-5.1, plate 1 a&b) revealed that possible reactions among lime particles and applied phosphorus had taken place during the sorption process resulting in the formation of DCPD crystals. The results are supported by the findings of Lindsay *et al.* (1962); Larsen (1967); and Bell and Black (1970b). The sorption process resulted in the formation of small sized fibrous crystals rather than with sharp edges. It is suggested that continuous shaking of the suspension might have favoured the formation of small sized fibrous crystals preventing the formation of rod shaped aged crystals. Moreover, the irregular sizes of the lime particles might have also affected the uniformity of the crystals. In the presence of pyrophosphate (10%PP), $CaCO_3$ particles were found to be greater in size (>50 µm) compared with the only OP treated samples. The presence of PP might have resulted in bond formation with Ca of the $CaCO_3$ particles rendering less surface area for reaction with OP. That is why probably a smaller concentration of P was found in the reaction products of PP treated samples as described earlier. Greater reaction among OP and $CaCO_3$ particles might have taken place in the absence of PP, resulting in greater P concentration in DCPD particles. X-ray analyses (appendix-5.1, plate 1 c&d) also revealed that in the presence of pyrophosphate (PP) inhibition of DCPD crystal formation took place possibly due to little reaction among $CaCO_3$ particles and applied phosphorus, supporting the work of previous researchers like Marshal and Nancollas (1969); Amer (1978); Amer and Mostafa (1981) and El-zahaby and Chien (1982). The aggregation of $CaCO_3$ particles at some data points was also noticed which might be the result of inter particle bonding by added PP. Addition of PP extract of soil also further reduced the P sorption as is clear from the figure 5.2a and appendix-5.1, plate 2 (a&b). However PP extract of rice straw did not produce the same results and was found to be less effective than PP alone

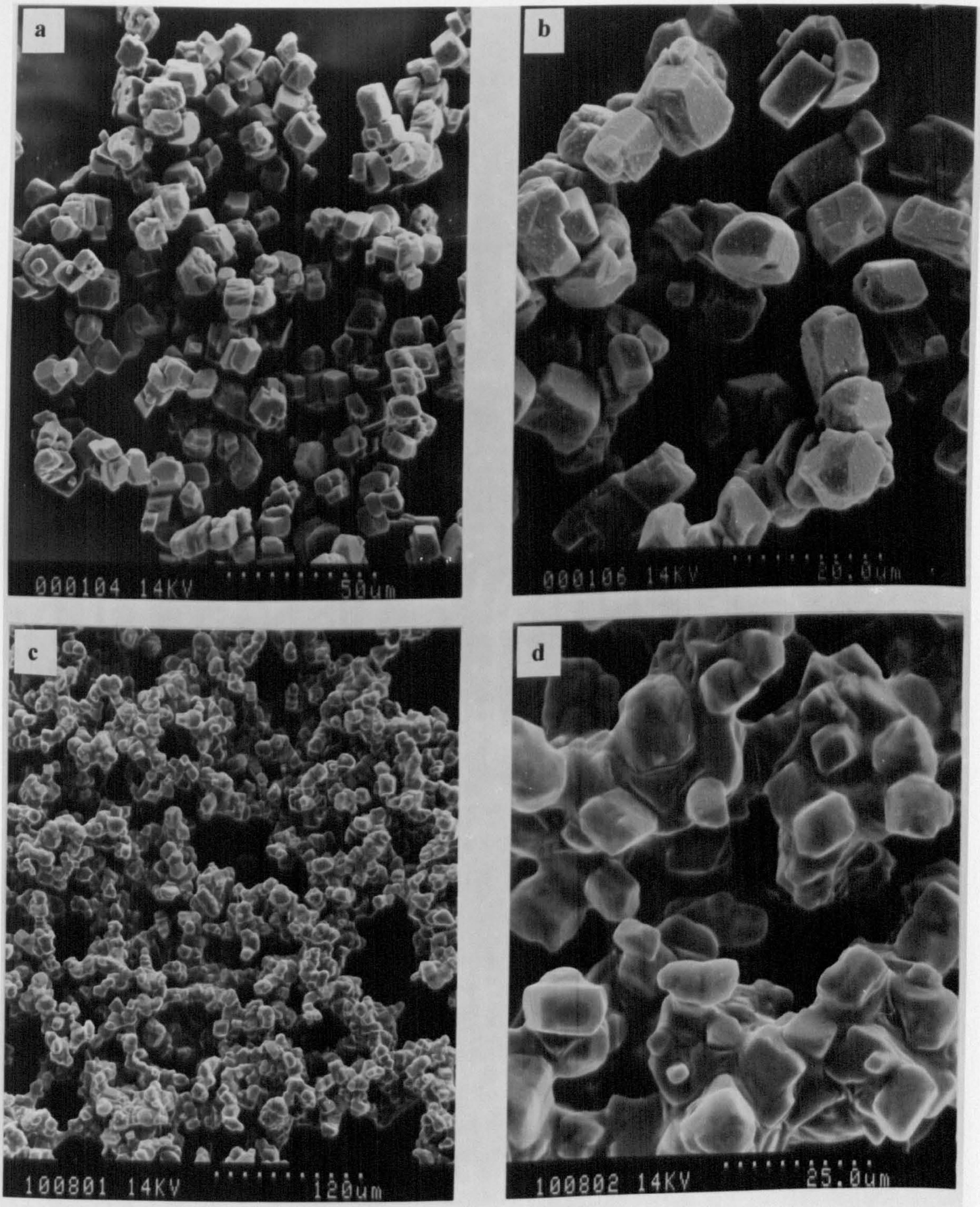


PLATE 1: (a) reagent grade lime particles (b) at higher magnification (c) reagent grade lime particles treated with PP (d) at higher magnification

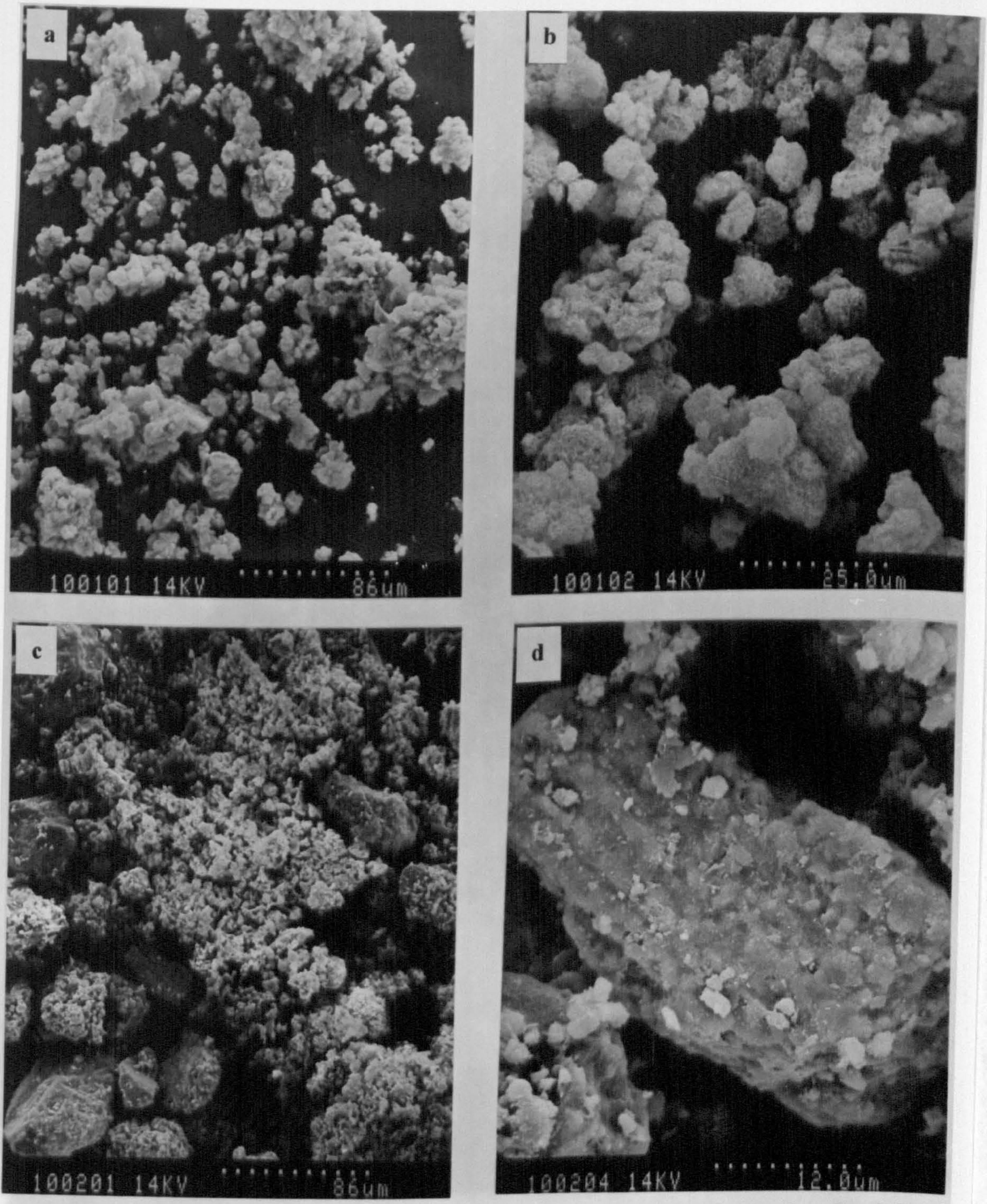


PLATE 2:(a) reaction products of agricultural lime and orthophosphate (OP) showing the formation of small fibrous DCPD (?) crystals (b) at higher magnification (c) reaction products of lime and applied phosphorus (OP+PP) showing interference by PP (d) surface of a larger lime particle at higher magnification showing little or no reaction with applied P

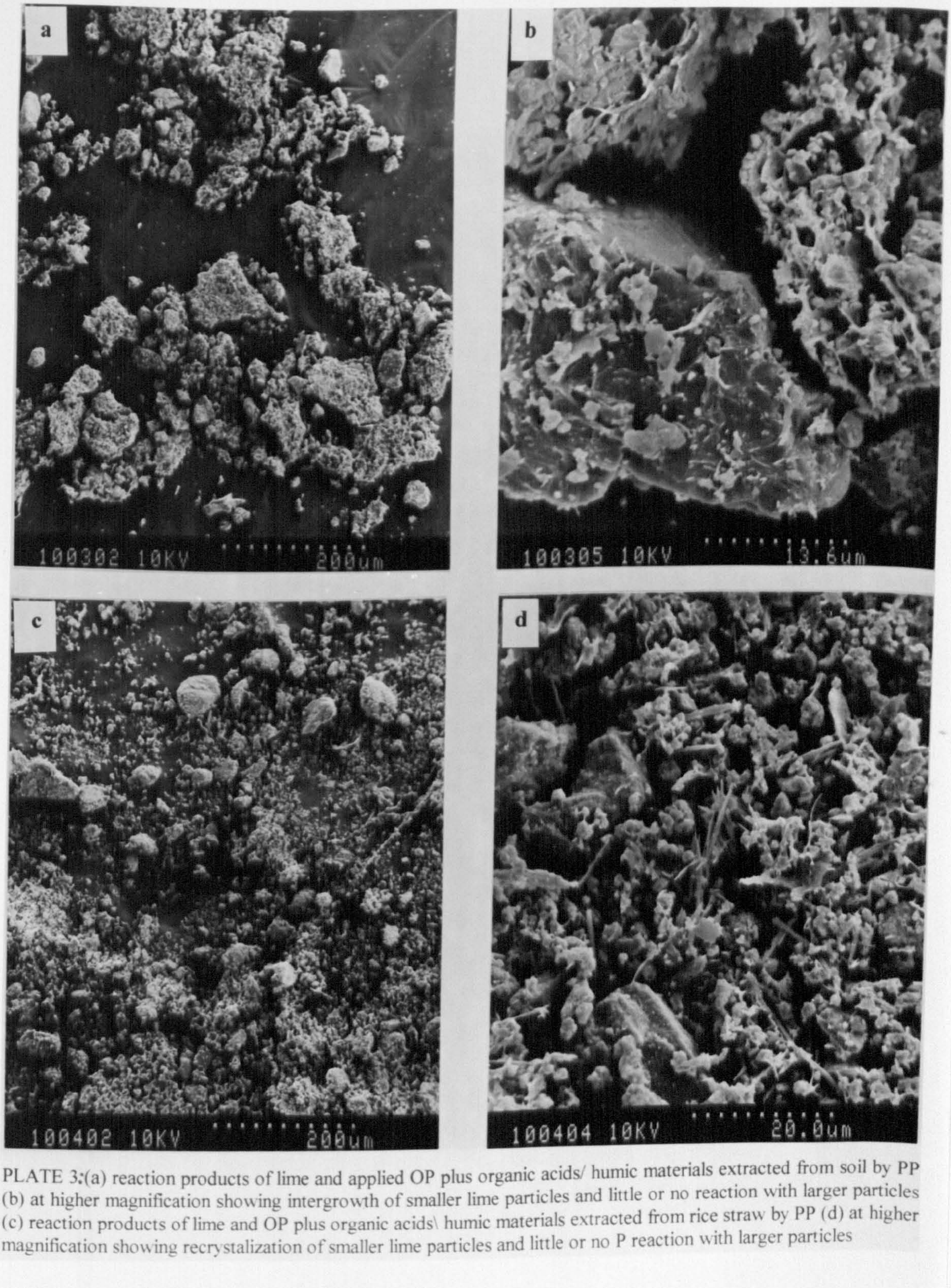


PLATE 3:(a) reaction products of lime and applied OP plus organic acids/ humic materials extracted from soil by PP (b) at higher magnification showing intergrowth of smaller lime particles and little or no reaction with larger particles (c) reaction products of lime and OP plus organic acids\ humic materials extracted from rice straw by PP (d) at higher magnification showing recrystalization of smaller lime particles and little or no P reaction with larger particles

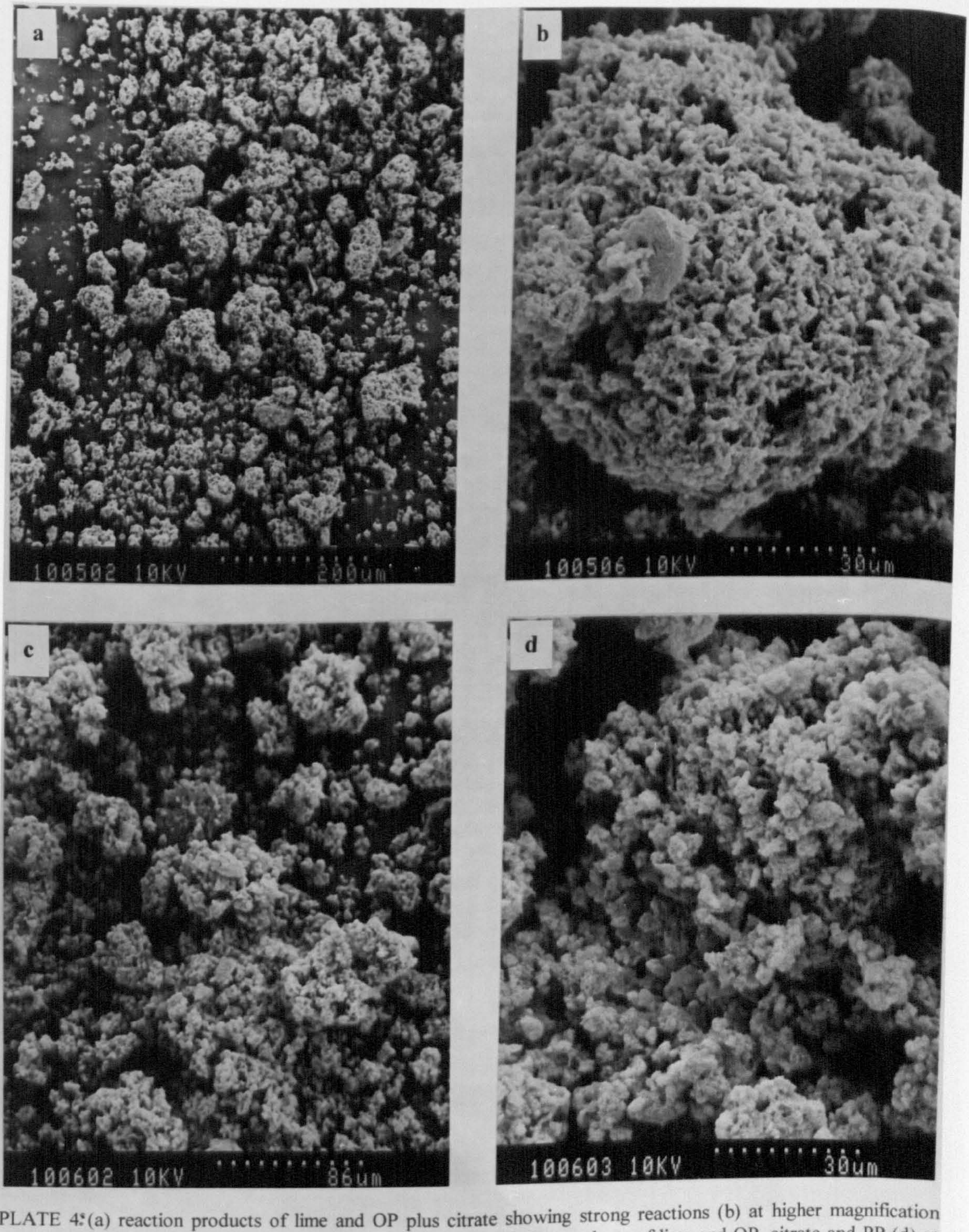


PLATE 4: (a) reaction products of lime and OP plus citrate showing strong reactions (b) at higher magnification showing the formation of small sized DCPD (?) crystals (c) reaction products of lime and OP, citrate and PP (d) at higher magnification showing some crystal growth and formation of small sized DCPD (?) crystals

(Appendix 5.1, plate 3c). Citric acid addition had adverse effects on the solution P and lowest levels of P were found in the solution as has been discussed earlier. Stronger reactions among lime particles and applied phosphorus, in the citric acid treated solution, were observed both in the presence and absence of PP (Appendix 5.1, plate 3 a, b, c&d). This may be due to citric acid dissolving $CaCO_3$ and maintaining a high Ca^{++} concentration in the solution, and hence greater phosphate/ Ca reaction.

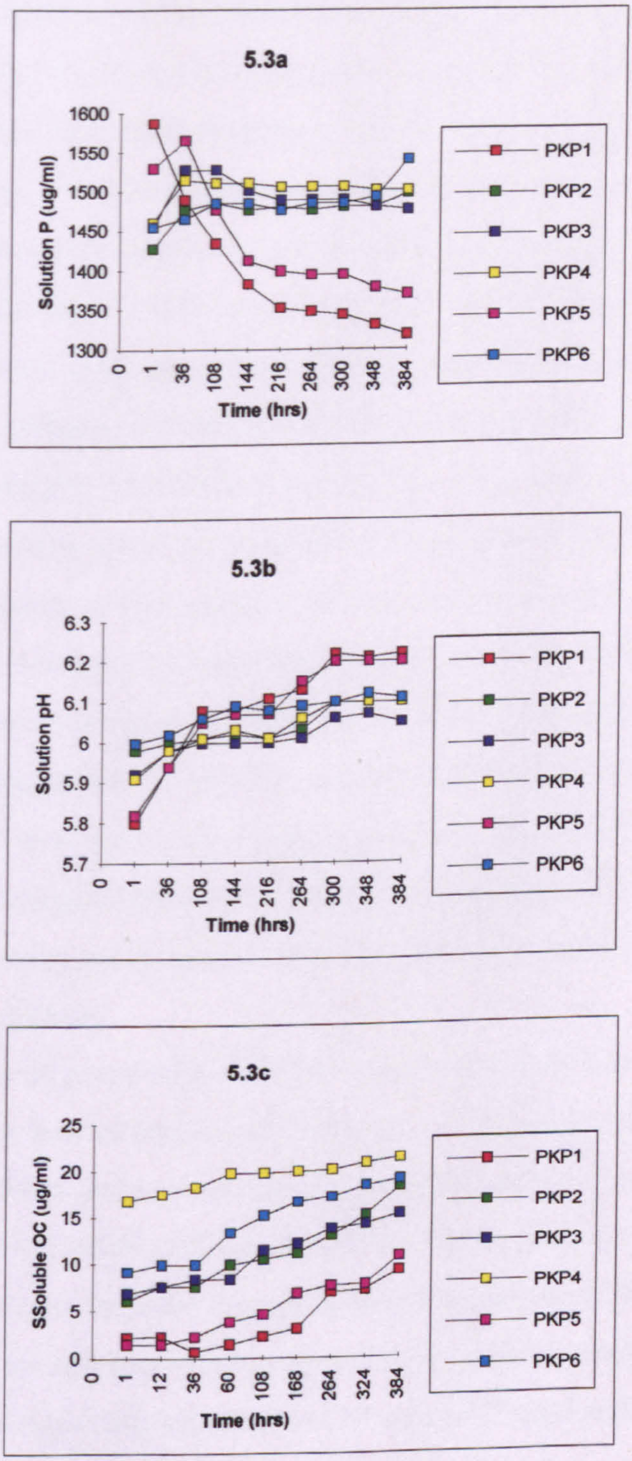
SEM micrographs (plates 1-4) have also been presented to verify the results obtained by EDAX studies. In plate number 1, photographs a & b show the reagent grade $CaCO_3$ particles without any P additions and photographs c & d show the interference caused by the addition of pyrophosphate (PP). In plate number 2, photographs a & b represent treatment LP1 and photographs c & d represent treatment LP2. The photographs a, b and c, d, in plate 3 represent treatments LP3 and LP4 respectively and in plate 4 represent treatments LP5 and LP6 respectively.

5.7.3. Sorption by different soils

In this section experiments II and III will be discussed together. The discussion concentrates on P sorption in Pakistani soil and brown podzolic original and limed soils. To compare the effects of treatments in these different types of soils each set of treatments will be discussed and compared separately along with the effects on solution pH, organic carbon (OC) and iron (Fe) contents where applicable.

In orthophosphate (OP) treatment of Pakistani soil during the first hour of reaction only 0.4% of the applied P disappeared from the solution (figure 5.3a) whereas the amounts in brown podzolic original (figure 5.4a) and limed soils (figure 5.5a) were 18%, 21% (5% lime) and 15% (10% lime) respectively. Removal of P during the first hour of reaction suggested that large amounts of Fe and probably Al in brown podzolic soil favoured the more rapid sorption of applied P compared with the Pakistani soil. Similar trends of P sorption were observed at the final sampling time, showing more sorption in brown podzolic soil than in Pakistani soil. In limed soils both levels of lime resulted in more P sorption after 278 hours of reaction compared with original brown

Figure 5.3: Changes in solution (a) P, (b) pH and (c) organic carbon (OC) with sorption time in the presence of a Pakistani soil



podzolic soil, with the 10% lime level causing greater P sorption than 5% lime. The sorption of P in brown podzolic (original) soil might be attributed only to the reaction of P with Fe and Al oxides as no $CaCO_3$ was detected in this soil. Many scientists reported that sesquioxides of Fe and Al were the main source of sorption sites in acid soils and provided the best indices of P retention (Ballard and Fiskall, 1974; Saunders, 1965; Xie and Mackenzie, 1991). It has been reported that oxalate extractable Fe and Al were significantly correlated with P sorption in podzolic horizons (Freese *et al.*, 1992; Kuo, 1986 and Laverdier and Karam, 1984). Lower sorption of P in Pakistani soil might either be attributed to the lower levels of iron oxides or to the moderate $CaCO_3$ levels (23% $CaCO_3$) in that soil. Increases in P sorption in brown podzolic soil with liming were associated with high pH, low organic carbon (OC) and iron (Fe) contents in the solution. Two possible explanations could be given for the enhanced P sorption by lime application. (i) Application of lime increased the lime contents of soil which acted as sorption sites for P in solution. (ii) Application of lime increased the pH of the solution which ultimately favoured precipitation of Fe with solution P. The second possibility seems more likely as the solubility of iron decreased with liming which indicated that the precipitation of Fe-P compounds might have taken place. The results are partly in agreement with the findings of Simard *et al.*, (1988) who reported increases in pH and calcium (Ca) concentration and decreases in dissolved organic carbon (DOC) and Al in solution with $CaCO_3$ addition.

In the presence of pyrophosphate (PP) treatment in Pakistani soil the less than 2% P sorbed after one hour of reaction was recovered as the reaction proceeded and after the final stage (348 hours) a greater than 2% increase in solution P was observed (fig 5.3a). In Pakistani soil addition of PP totally inhibited the sorption of applied P. The increases in solution P over the initial P might be due to hydrolysis of PP to OP. The results indicated that the inhibitory effect of PP in Pakistani soil was similar to that in $CaCO_3$ system. In brown podzolic soil addition of PP reduced P sorption throughout the reaction period in original as well as in limed samples. The effect was maximum at the

Figure 5.4: Changes in solution (a) P, (b) pH, (c) organic carbon (OC) and (d) soluble Fe with sorption time in the presence of a brown podzolic soil

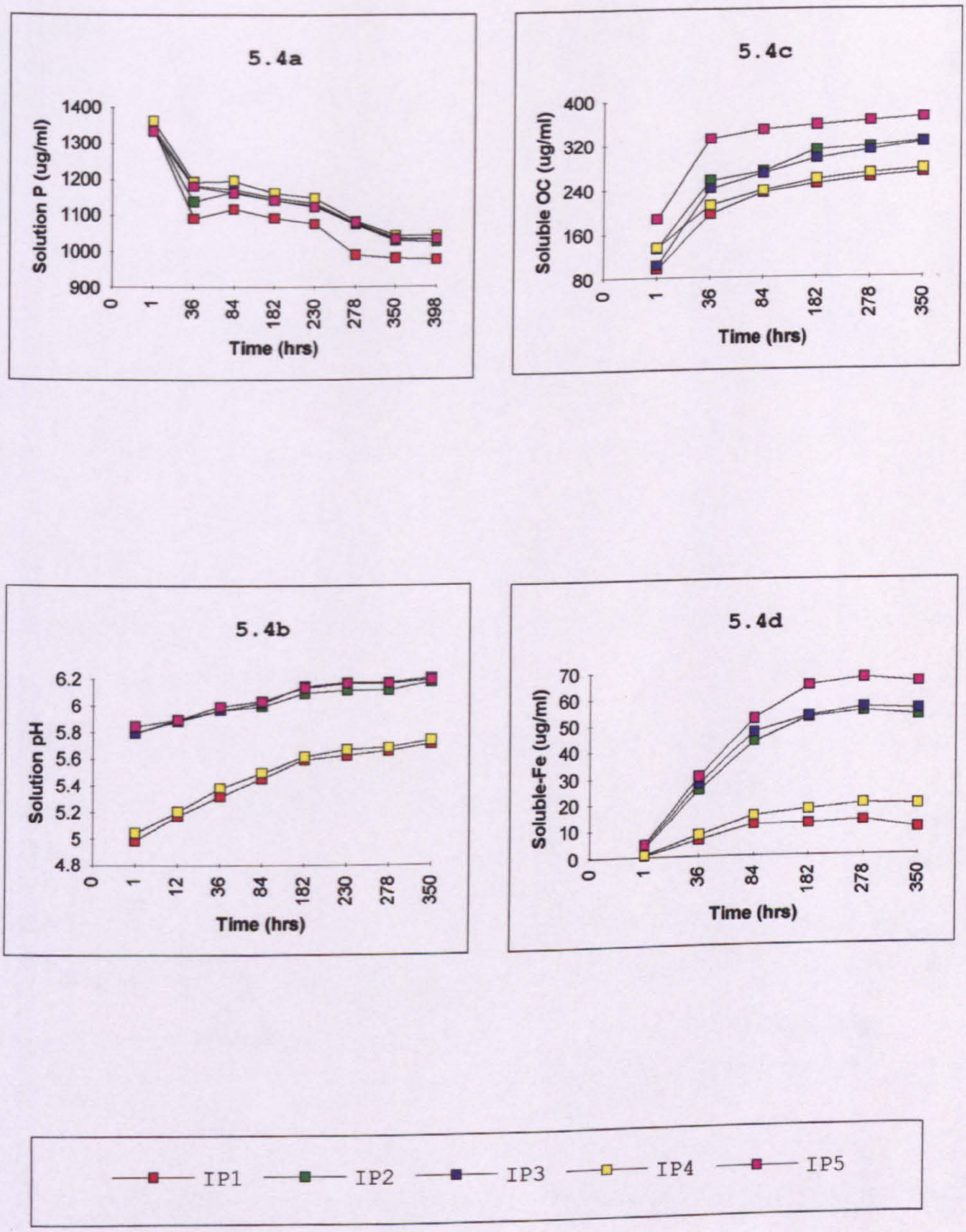
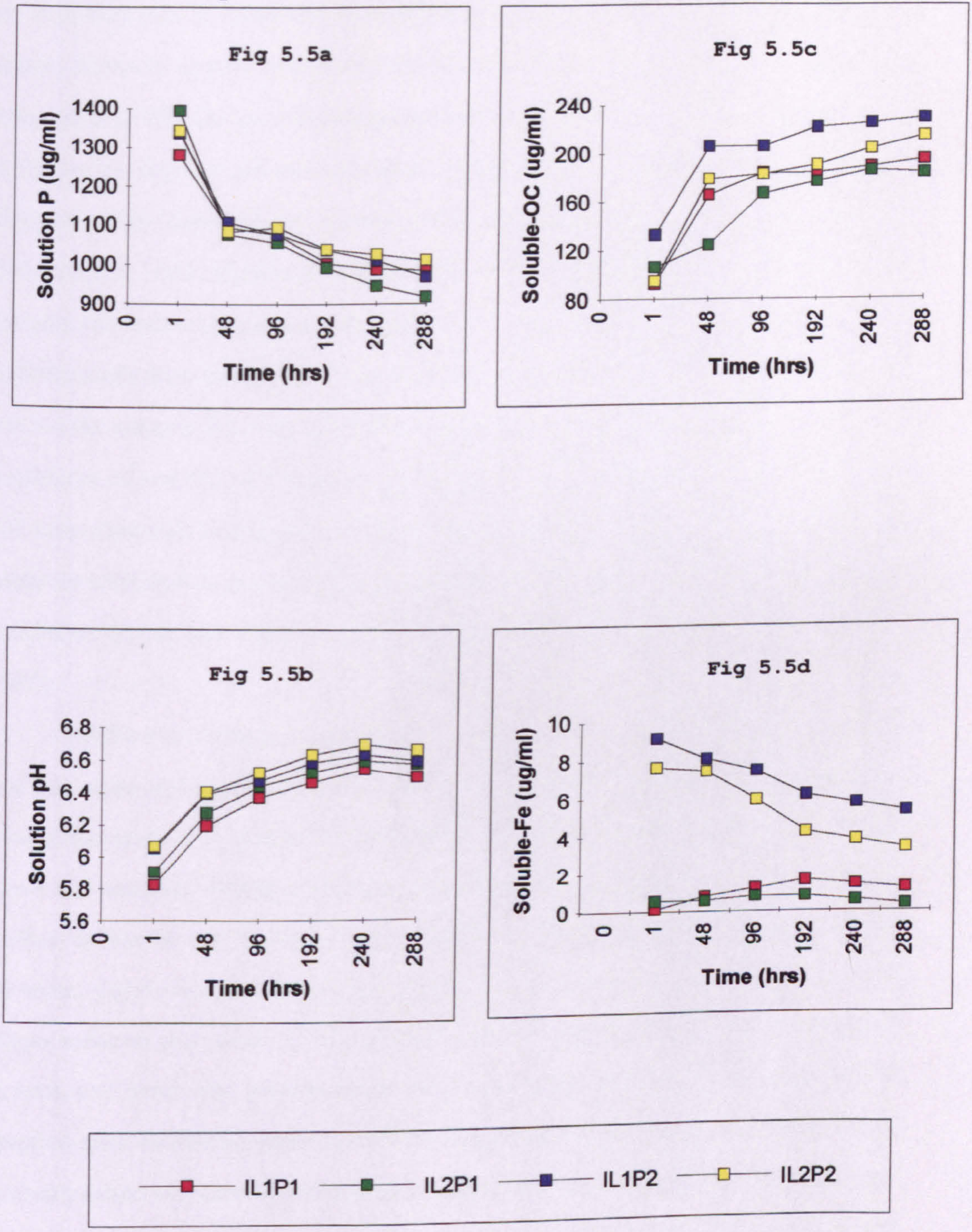


Figure 5.5: Changes in solution (a) P, (b) pH, (c) organic carbon (OC) and (d) soluble Fe with sorption time in the presence of a brown podzolic limed soil



10% lime level. The greater effect of PP in inhibiting the precipitation of applied P at the higher lime level suggested that the addition of PP under calcareous conditions may play an important role in enhancing P availability. Addition of PP in brown podzolic soil caused increases in iron contents of the solution. These increases might be due to the dissolution of OM and iron/OM complexes caused by the addition of PP. Pyrophosphate is known to disperse soil and solubilize organic matter (Bar-Yosef and Asher, 1983; Bremner, 1949; Mortvedt and Osborn, 1977) and thus increase solubility of Fe and Al (Mc Keague, 1967; Mnkeni and Mackenzie, 1985; and Xie and Mackenzie, 1990b). Greater amounts of organic carbon (OC) in solution as a result of dissolution by PP addition might have blocked the P sorption sites of Fe and Al. However the sorption was not totally stopped but only reduced to some extent. With the addition of lime, the solubilities of iron (Fe) and organic carbon (OC) were decreased and small increases in pH were observed. Less sorption of P by brown podzolic soil at increased lime levels might be attributed to the role of PP in inhibiting DCPD crystal formation in calcareous conditions (Amer and Mostafa, 1981; El-zahaby and Chien, 1982; and Amer *et al.*, 1982).

Addition of different organic acids, such as PP extracts of soil (in Pakistani soil) and rice straw and chelex resin extract of soil, to OP and /or OP+PP treated samples caused decreases in P sorption by both Pakistani soil and brown podzolic original and limed soil samples. Addition of chelex resin extract in the presence of PP caused a further decline in the P sorption. In Pakistani soil, addition of PP extract of soil, however, slightly increased P sorption. Slightly greater solution P concentration at initial stages indicates that some of the added PP had been hydrolysed during the extraction process and hence less pyrophosphate (PP) was left in solution for occupying the P sorption sites. Moreover, addition of PP extract of soil, in the presence of Pakistani soil, probably raised iron contents of the solution, dissolved by pyrophosphate (PP) during the extraction process (Mc Keague, 1967; Mnkeni and Mackenzie, 1985 and Xie and Mackenzie, 1990b). Applied P might have precipitated with iron (Fe) in solution and resulted in lower P solubility. The greatest effects in reduction in P sorption in Pakistani soil and brown podzolic soil were observed in the presence of chelex resin extracts of soil. In Pakistani soil, in OP treated samples, with the addition of organic acids, reduction in P sorption and in PP treated samples increases in solution P at the final stage of the experiment were observed compared with the initial solution P. These treatments in the presence of organic acids in brown podzolic soil only reduced P sorption. Moreover addition of organic acids in Pakistani soil caused a decline in solution pH compared with their absence (figure 5.3b). This decline could be attributed to the dissolution of $CaCO_3$ in Pakistani soil and then its subsequent precipitation. In brown podzolic soil however addition of organic acids slightly increased the pH (figure 5.4b). This increase in pH in brown podzolic soil might be related to the replacement of OH^- ions from Fe-hydroxides by organic ligands. The decreases in P sorption in brown podzolic soil might be due to the chelation of Fe and Al oxides by organic ligands thus reducing the P sorption sites (Dalton *et al.*, 1952; Levesque and Schnitzer, 1967; and Parfitt, 1979).

Most researchers have reported Al^{III} to be the dominant adsorbent for P in acidic soils (Haynes, 1982). It has been suggested that the hydroxyl and carboxylic ligands present in organic matter form complexes with Al, preventing the formation of aluminium phosphates (Dalton *et al.*, 1952; Levesque and Schnitzer, 1967; Parfitt, 1979; and Traina *et al.*, 1986). The effect of organic acids in reducing P sorption is associated with the pH of the system. At low pH, organic ions are thought to compete strongly with phosphate for sorption sites (Hingston *et al.*, 1972; Lopez-Hernandez *et al.*, 1979; Sibanda and young ,1986 and Traina *et al.*, 1986). However, the competition for P sorption between Fe and Al oxides may exist in iron rich conditions. The ability of citrate ions to form complexes with Fe and Al and thereby to decrease phosphate binding to the adsorption sites has been reported some time ago by Struthers and Sieling (1950).

Different explanations have been given for the reduced P sorption in calcareous conditions. Inskeep and Silvertooth (1988) stated that precipitation of HAP (hydroxyapatite) in the presence of organic acids was inhibited by "C" adsorption on to seed crystal surfaces by blocking sites for new crystal growth. Later studies by Grossl and Inskeep (1991) confirmed the presence of "C" on DCPD seed crystals. It was concluded by them that the level of inhibition is dependent on the amount of "C" adsorbed and degree of surface coverage of DCPD which are related to the functional group contents of the organic acids and their geometry (Inskeep and Silvertooth, 1988; Meyer and Nancollas, 1973). At pH 5.7, the majority of COOH functional groups should be dissociated and the adsorption of organic acids is probably due to COO^- binding with Ca^{2+} present at kinks and dislocations on DCPD surfaces (Inskeep and Silvertooth, 1988). Referring to the findings of the above scientists it could be speculated that in Pakistani soil organic acids reduced P sorption by masking the adsorption sites. Although the addition of organic acids did not totally stop the P sorption, even a slight increase in P availability might be helpful in maintaining adequate P levels for plant growth in calcareous conditions.

5.8. Conclusion

5.8a. Calcium Carbonate ($CaCO_3$) System

Sorption of P applied in the form of OP increased with time. More than 50% of the P sorption occurred during the first hour of reaction and was followed by small gradual increases throughout the 302 hour reaction period. Addition of organic acids in the form of chelex resin extract of soil to OP treated samples also decreased P sorption. Pyrophosphate (PP) either alone or with organic acids (PP extracts of soil & rice straw and chelex resin extract of soil) totally inhibited P sorption and increased solution P at final stages compared with the initial P. Further decreases in P sorption were noticed with the addition of organic acids to OP+PP treated samples suggesting that the blocking of sorption sites by "C" might have occurred. Addition of citric acid (0.1M) and citric acid extract of rice straw increased P sorption probably by increasing the surface area, pH and Ca^{2+} in solution by the dissolution of $CaCO_3$. Pyrophosphate (PP) and organic acids buffered the solution pH at less than 6.5. Inhibition of DCPD crystal formation was confirmed by X-ray analyses and SEM studies which showed higher Ca/P ratio in the presence of PP and organic acids and comparatively more established crystals in the absence of PP and organic acids respectively.

5.8b. Soil Systems

Sorption of P applied in the form of OP in Pakistani soil, brown podzolic original and limed (5% & 10%) soils was in the order of Pakistani < brown podzolic (O) < brown podzolic (5%) < brown podzolic (10%). Liming of brown podzolic soil increased P sorption & pH and decreased iron contents of the solution. Increases in solution P in Pakistani soil by the addition of PP and/ or organic acids were observed whereas decreases were observed in brown podzolic soil. Hydrolysis of PP to OP and dissolution of $CaCO_3$ by organic acids might have increased the solution P in Pakistani soil. In brown podzolic soil addition of PP and organic acids decreased P sorption probably by competing with OP for sorption sites of Fe- & Al-oxides. Increases in pH, organic carbon (OC) and iron (Fe) contents in solution (brown podzolic soil only) with sorption time in all the treatments in both soils were noticed. Addition of organic acids, however lowered pH in Pakistani soil whereas it increased it in brown podzolic soil in comparison to OP treatment. It can be concluded that the addition of pyrophosphate (PP) and / or organic acids, to local brown podzolic soils compared with the Pakistani soil studied, may not have significant effects in improving P availability, due to their greater Fe contents. This may perhaps indicate that the iron oxide/ hydroxide component in Pakistani calcareous soil is less affected by PP than the dominant $CaCO_3$ component.

CHAPTER
6

Chapter 6: Glass House Experiments

6.1. Soil Sampling

Soil samples for the pot experiments were collected from a field near Pen-y-Ffridd (Denbigh series, Appendix I) research station, Bangor. This UK soil was selected because it had been heavily limed for the previous twenty years and, with added lime, it was hoped that it would compare with calcareous paddy soils from the Indus Plains of Pakistan. Samples were collected in bulk from the surface (2-40 cms) after removing the top layer of grass. Samples were brought into the laboratory, dried at 32±2°C, ground and sieved (<2mm). The soil was stored in polythene bags in the laboratory. Physico-chemical analyses of the soil were performed as mentioned in tables 3a, b.

6.2 Experimental preparation and treatments

The trials were conducted from May to September 1993 in the glass house at Pen-y-Ffridd reserach station, Bangor. The mean temperature in the glass house during the experiment was about 27±3°C. Soil samples were put in the plastic pots, weighing 500g and 600g for the rice and the wheat trials respectively. Agricultural lime was added to the soils at the rate of 5% (L1) and 10% (L2) on w/w basis. For the rice trial, soil was put inside polythene bags in the pots in order to stop leaching of water and to establish waterlogged conditions. Expanded vermiculite weighing 20g was also put into each pot (5" size) and mixed thoroughly with the soil to improve aeration in the freely drained pots.

The treatments for rice were as follows

(1) A0B0 (2) AB0 (3) A1B1 (4) A2B2 (5) A3B3 [L1 (5% lime)]

(1) A0B0 (2) AB0 (3) A1B1 (4) A2B2 (5) A3B3 [L2 (10% lime)]

where A = orthophosphate (OP) and B = orthophosphate (OP) + pyrophosphate (KPP)

A0B0 = control, AB0=(150+0), A1B1=(135+15), A2B2=(120+30), A3B3=(105+45)

Phosphorus (KH_2PO_4) was applied at the rate of 150 mg P/ kg soil to each treatment.

Nitrogen was applied in the form of NH_4NO_3 @ 200mg N/ kg soil.

A similar set of treatments was prepared for the wheat trial.

6.3. Experiment I. Pot trials with rice and rice following a wheat crop

6.3.1. Aims of the experiment

The experiment was conducted to explore the effects of flooded conditions, during rice crop, on the behaviour of native and applied phosphorus on extractable soil P, Fe, Mn, Cu and Zn at two lime levels. The trial also included the cultivation of rice on a soil previously used for a wheat crop. The purpose was to investigate the behaviour of P and micronutrients (Fe, Mn, Cu and Zn) on flooding a soil previously subjected to wheat cultivation under moist aerobic conditions. Moreover, the effects of orthophosphate (OP) with or without pyrophosphate (PP) added to the soils on plant height and dry matter yields and on P and micronutrient uptake, were also investigated.

Quantities of P used in these experiments were more than the recommended dose of P for paddy rice and wheat crops in the field. The amounts are, however, comparable to those used for root crops like potatoes in UK.

6.3.2. Experimental procedure

Randomized complete block designs were used for the experiment.

6.3.2.1. Rice nursery and transplantation

Rice variety IRRI-6 was used for the trial. The rice nursery was grown in pots using peat as a growth medium. "Phostrogen" (mixed NPK fertilizer) was used to enhance the healthy growth of the nursery plants. Four week old rice seedlings were transplanted into the pots in standing water; transplantation was done at three points in the pots with two seedlings at each point.

6.3.3. Soil and plant sample handling

Soil and plant samples were collected after every two weeks until ten weeks. Plant heights were recorded. Pots were carefully drained, soil was uniformly mixed and samples were collected in the moist form and analyzed in the laboratory for $NaHCO_3$ extractable P and DTPA extractable Fe, Mn, Cu & Zn as described in section 2.16. Plant samples were washed thoroughly with tap water followed by distilled water, dried at

70°C, weighed for dry matter yields and ground for chemical analyses as described in sections 2.17 and 2.18.

6.3.4. Results

Mean values for plant height and dry matter yields are shown in tables 6.1.1 and 6.1.2 respectively. Sampling of the soil and plants was done after 2, 4, 6, 8 and 10 weeks unless otherwise mentioned. From the soil previously used for a wheat crop, sampling of plants and soil was done after 4 and 8 week growth periods. To distinguish these samples, these periods will be written as 4* and 8* in the following section. Statistical analyses of the results revealed that the interactions among phosphorus and lime treatments were not significant ($p<0.05\%$). The effects of applied P and lime levels on plant height and on nutrient behaviour were significant in some cases and are reported in the following section. The effects on dry matter yields were not significant but the results have been reported considering them as important yield parameters.

6.3.4.1. Plant height and dry matter yields

Application of phosphorus with or without pyrophosphate (PP) compared with the control (A0B0) treatments improved the height of paddy rice during the growth period of 10 weeks. Although, increases in plant height with growth period were observed in all the treatments, the greatest increases were observed in P treated samples. The data regarding the effects of applied P with or without pyrophosphate on plant heights of paddy rice are given in table 6.1.1. This shows that the greatest increases in plant height were observed during 8 to 10 weeks of growth period. Overall increases in plant height in treatments A0B0, AB0, A1B1, A2B2 and A3B3 after 10 weeks compared with the 2 weeks were 15.0cm, 16.5cm, 17.0cm, 17.67cm and 17.16cm respectively. Effects of P application with or without pyrophosphate (PP) compared with the control (A0B0) treatments were found to be greater, in improving plant height, from 6 to 10 weeks of growth. Paddy rice grown on the soil previously used for wheat cultivation gained less height compared with the soil used for rice crop only. Plant height observed

Table 6.1.1. Effects of applied P and lime levels on plant height (cm) of paddy rice at different stages of growth

Treatments	2W	4W	6W	8W	10W	4W*	8W*
A0B0	10.50	14.00	16.50	21.33	25.50	12.83	17.67
AB0	10.67	15.17	18.50	24.00	28.17	14.50	19.83
A1B1	12.50	16.00	19.83	26.00	29.50	15.00	21.00
A2B2	13.00	16.17	20.50	27.33	30.67	16.00	22.00
A3B3	14.17	17.17	20.83	27.67	31.33	17.33	23.50
LSD (0.05)	3.13	3.58^{ns}	3.67	3.54	3.73	3.78	3.71

(means of six values)

Lime levels	2W	4W	6W	8W	10W	4W*	8W*
L1	11.20	14.60	18.73	24.73	28.33	13.20	20.40
L2	13.13	16.80	19.73	25.80	29.73	17.07	21.20
LSD(0.05)	1.98^{ns}	2.27^{ns}	2.32^{ns}	2.24^{ns}	2.36^{ns}	2.39	2.35^{ns}

(means of fifteen values)

* Soil from previous wheat crop

Table 6.1.2. Effects of applied P and lime levels on dry matter yields (g/pot) of paddy rice at different stages of growth

Treatments	2W	4W	6W	8W	10W	4W*	8W*
A0B0	1.11	1.78	3.03	4.24	5.98	1.53	3.87
AB0	1.20	1.87	3.11	4.32	6.07	1.62	3.96
A1B1	1.28	1.95	3.20	4.41	6.15	1.71	4.05
A2B2	1.34	2.01	3.25	4.47	6.21	1.76	4.10
A3B3	1.36	2.03	3.27	4.48	6.23	1.78	4.12
LSD (0.05)	0.14^{ns}	0.14^{ns}	0.14^{ns}	0.14^{ns}	0.14^{ns}	0.14^{ns}	0.14^{ns}

(means of six values)

Lime levels	2W	4W	6W	8W	10W	4W*	8W*
L1	1.25	1.92	3.16	4.37	6.12	1.67	4.01
L2	1.27	1.94	3.18	4.39	6.14	1.70	4.04
LSD (0.05)	0.09^{ns}	0.09^{ns}	0.09^{ns}	0.09^{ns}	0.09^{ns}	0.09^{ns}	0.09^{ns}

(means of fifteen values)

* Soil from previous wheat crop

after 8* weeks (wheat soil) compared with the 8 weeks were 3.7cm, 4.2cm, 5.0cm, 5.3cm and 4.2 cm less in treatments A0B0, AB0, A1B1, A2B2 and A3B3 respectively.

Data regarding the effects of lime application on plant height (table 6.1.1) revealed that small increases in plant height were noticed in L2 (10%) over L1 (5%) lime level. The effects of both lime levels in improving plant height were not statistically ($p<0.05$) different. Similar effects of liming on plant height were observed in the soil previously used for wheat crop, however, after 4* weeks of growth period 10% liming in comparison to 5% liming significantly ($p<0.05$) improved plant height.

Increases in plant dry matter yields (table 6.1.2) were observed throughout the growth period of 2 to 10 weeks. Application of P with or without pyrophosphate slightly improved the dry matter yields over the control (A0B0) treatments. The effects of P additions in improving dry matter yields were not statistically significant ($p<0.05$). Maximum dry matter yields were observed at 10 weeks of growth period. Increases in dry matter yields observed, in the samples grown on soil previously used for wheat crop, i.e. 4* and 8* weeks were less than the 4 and 8 weeks period. Dry matter yields in treatments A0B0, AB0, A1B1, A2B2 and A3B3 obtained at 8* weeks were 0.37g, 0.36g, 0.36g, 0.37g and 0.36g respectively less than compared with 8 weeks.

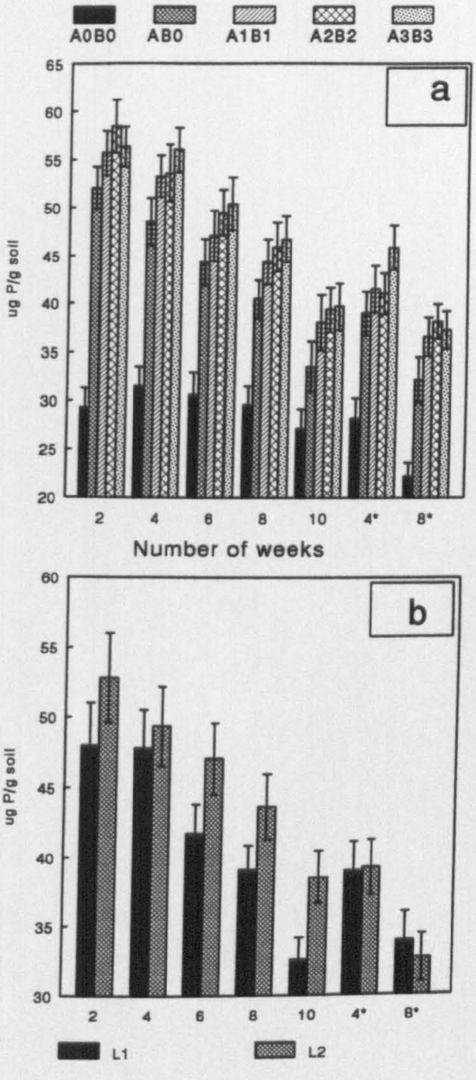
The effects of liming at 10% level over 5% level were to increase dry matter yields of plants (table 6.1.2). Statistical analyses revealed that both lime levels did not show significant ($p<0.05$) differences in increasing dry matter yields. The greatest amounts of dry matter yields were observed at 10 weeks of growth. Overall increases in dry matter yields after 10 weeks of growth period over 2 weeks were 4.87g at both lime levels. Increases in dry matter yields were again noticed in the samples grown on soil previously used for wheat crop. The increases were however less than those found in the samples grown on the current rice soil. Dry matter yields after 8* weeks of growth were 0.36g (L1) and 0.35g (L2) less than the 8 weeks of growth.

6.3.4.2. Phosphorus and micronutrient (Fe, Mn, Cu and Zn) status of soil

Effects of applied P with or without pyrophosphate (PP) on extractable soil phosphorus during the paddy rice crop are illustrated in figure 6.1.1a. Slight increases in soil P in control (A0B0) samples were observed until 4 weeks followed by decreases until 10 weeks of growth period. In P treated samples gradual decreases in soil P were observed as the growth period proceeded from 2 to 10 weeks but extractable P in P treated samples, remained significantly greater ($p<0.05$) than the control samples. Overall decreases in soil P after 10 weeks over 2 weeks were 7%, 36%, 32%, 33% and 30% respectively in treatments A0B0, AB0, A1B1, A2B2 and A3B3. After 10 weeks about 23%, 40%, 45% and 46% greater soil P was extracted in treatments AB0, A1B1, A2B2 and A3B3 respectively compared with the control samples (A0B0). Lower levels of extractable P were observed in all the treatments in the soil previously used for wheat crop (4* & 8* weeks). Decreases in extractable soil P were again noticed as the growth period proceeded from 4* to 8* weeks. These decreases in treatments A0B0, AB0, A1B1, A2B2 and A3B3 were 21%, 18%, 12%, 7% and 21% respectively. Extractable P was again significantly greater in P treated samples. After 8* weeks the levels of extractable soil P were 44% (AB0), 64% (A1B1), 71% (A2B2) and 67% (A3B3) greater compared with the control (A0B0) samples.

Addition of 10% lime (L2) level compared with 5% lime (L1) level increased the extractability of soil phosphorus (figure 6.1.1b). The effect of liming to improve P availability was significant only from 6 to 10 weeks. After 10 weeks about 18% greater extractable soil P was observed in L2 lime level treatment. Overall decreases in extractable P were again observed with the growth period. These decreases after 10 weeks were 32% and 27% in L1 and L2 lime levels treatments respectively. No significant effect of liming on the extractability of soil P was observed in the soil previously used for wheat crop. Soil P decreased again as growth proceeded from 4* to 8* weeks. These decreases were 13% and 17% in L1 and L2 treatments respectively.

Figure 6.1.1: Effects of applied (a) P and (b) lime on extractable soil P under rice crop at different stages of growth



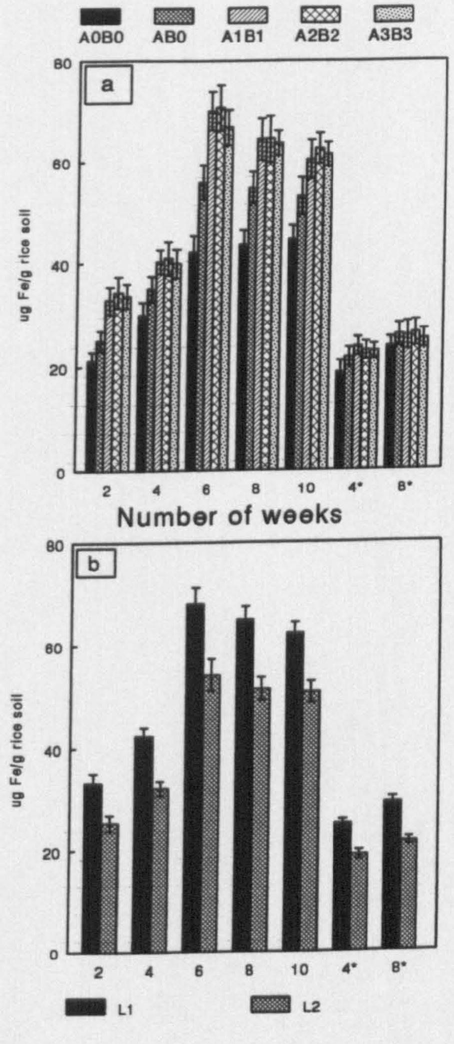
*Soil from previous wheat crop

Error bars (I) represent standard error of means

The effects of applied P and two lime levels on the extractability of soil Fe have been illustrated in figures 6.1.2a & b respectively. Increases in extractable soil Fe were observed until 8 weeks followed by slight decreases until 10 weeks. Overall increases in extractable soil Fe observed after 10 weeks over the 2 weeks were 112%, 112%, 84%, 83% and 83% in treatments A0B0, AB0, A1B1, A2B2 and A3B3 respectively. Applied P increased the extractable levels of soil Fe; causing significant ($p<0.05$) increases from 6 to 10 weeks compared with the control samples (A0B0). Addition of pyrophosphate (PP) with orthophosphate (OP) caused further increases in the extractability of soil Fe over orthophosphate (OP) alone. These increases were significant ($p<0.05$) from 2 to 10 weeks in comparison to the control samples (A0B0) and during 2, 6 and 8 weeks in comparison to orthophosphate treated samples (AB0). Slight increases in extractable soil Fe after 8* weeks compared with those after 4* weeks (soil from previous wheat crop) were observed but these P treatments did not differ significantly. Application of a greater level of lime (10%) significantly decreased the extractability of soil Fe throughout the growth period (figure 6.1.2b). Similar effects of liming in decreasing the extractability of soil Fe (4* & 8* weeks) were observed in the soil previously used for wheat cultivation.

Increases in extractable soil Mn (Table 6.1.3a) observed until 6 weeks were followed by decreases until 10 weeks of growth. Overall increases in extractable Mn were, however observed after 10 weeks compared with the 2 week period. These increases were 15.4, 10.6, 8.9, 8.4 and 8.7 times in treatments A0B0, AB0, A1B1, A2B2 and A3B3 respectively. Application of P in all forms (with or without pyrophosphate) in comparison to control samples significantly ($p<0.05$) increased the extractability of soil Mn throughout the growth period of 2 to 10 weeks (Table 6.1.3a). These increases after 10 weeks in treatments AB0, A1B1, A2B2 and A3B3 were 1.1, 1.3, 1.2 and 1.2 times respectively. Although the behaviour of extractable Mn was similar in the soil previously used for wheat cultivation, the extractable levels of Mn after 4* and 8* weeks of growth period were lower than those found in the rice soil. Greater levels of extractable Mn were again found in P treated samples, with the maximum levels being observed in

Figure 6.1.2: Effects of applied (a) P and (b) lime on extractable soil Fe under rice crop at different stages of growth



*Soil from previous wheat crop

Error bars (I) represent standard error of means

Table 6.1.3a. Effects of applied P on extractable soil Mn, Cu and Zn during paddy rice crop at different stages of growth

Treatments	2W	4W	6W	8W	10W	4W*	8W*
Mn (µg /g soil)							
A0B0	11.20	24.68	228.7	201.3	172.9	21.45	57.95
AB0	17.39	38.42	243.8	206.6	183.7	30.75	63.07
A1B1	24.55	55.34	330.0	239.2	219.2	40.04	70.53
A2B2	25.37	53.94	339.2	232.4	213.2	40.50	71.40
A3B3	24.41	54.25	332.2	229.3	212.4	41.18	65.23
LSD (0.05)	*2.31*	*3.35*	*7.27*	*5.80*	*9.08*	*3.85*	*4.42*
Cu (µg /g soil)							
A0B0	xx	2.37	2.70	2.97	3.05	2.05	2.59
AB0	xx	2.71	2.91	3.20	3.26	2.31	2.90
A1B1	xx	2.85	2.99	3.22	3.29	2.38	2.99
A2B2	xx	2.86	3.01	3.25	3.31	2.39	3.00
A3B3	xx	2.86	3.02	3.26	3.32	2.38	3.00
LSD (0.05)		*0.03*	*0.04*	*0.03*	*0.03*	*0.04*	*0.03*
Zn (µg /g soil)							
A0B0	1.96	1.85	1.53	1.35	1.27	1.45	1.00
AB0	2.02	1.92	1.63	1.51	1.42	1.51	1.17
A1B1	2.18	2.06	1.77	1.58	1.51	1.58	1.23
A2B2	2.22	2.13	1.77	1.63	1.53	1.56	1.25
A3B3	2.25	2.16	1.79	1.61	1.56	1.59	1.25
LSD (0.05)	*0.05*	*0.04*	*0.04*	*0.04*	*0.03*	*0.04*	*0.04*

(means of six values)

Table 6.1.3b. Effects of lime application on extractable soil Mn, Cu and Zn during paddy rice crop at different stages of growth

Lime levels	2W	4W	6W	8W	10W	4W*	8W*
Mn (µg /g soil)							
L1	20.90	56.50	315.6	234.8	214.7	43.20	70.06
L2	20.27	34.15	274.0	208.7	185.9	26.36	61.21
LSD (0.05)	*1.33^{ns}*	*2.10*	*4.54*	*3.62*	*5.67*	*2.41*	*2.76*
Cu (µg /g soil)							
L1	xx	3.11	3.33	3.53	3.56	2.48	3.19
L2	xx	2.35	2.52	2.83	2.94	2.12	2.60
LSD (0.05)		*0.02*	*0.02*	*0.02*	*0.02*	*0.02*	*0.02*
Zn (µg /g soil)							
L1	2.40	2.28	1.79	1.61	1.53	1.67	1.22
L2	1.86	1.77	1.60	1.46	1.39	1.40	1.13
LSD (0.05)	*0.03*	*0.03*	*0.02*	*0.02*	*0.02*	*0.02*	*0.02*

xx (not determined) (means of fifteen values)
* soil from previous rice crop

pyrophosphate (PP) treated samples. Liming of the soil caused decreases in extractable levels of Mn, with 10% lime level showing more decreases (Table 6.1.3b).

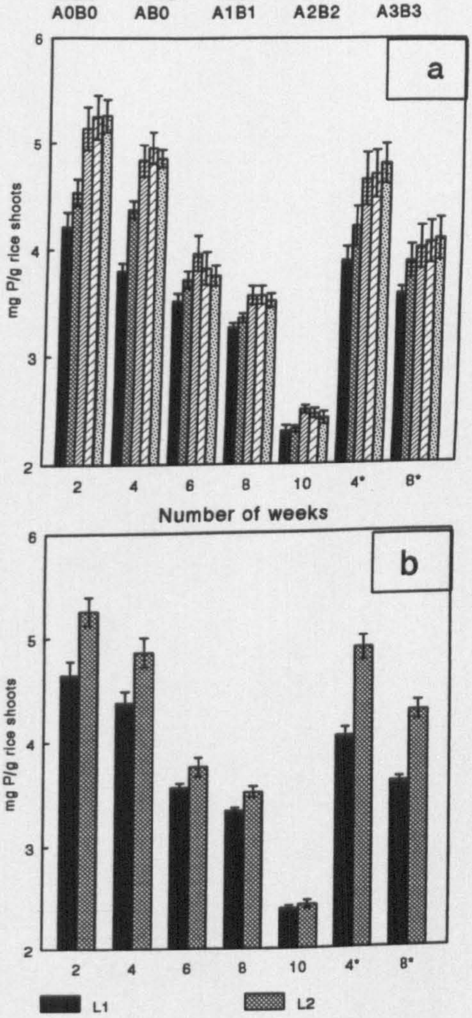
Extractable soil Cu was determined in soil extracts at 4 to 10 weeks and the results are reported in tables 6.1.3a & b. Increases in extractable soil Cu were observed with the growth period from 4 to 10 weeks. These increases at 10 weeks over 4 weeks were 29% (A0B0), 20% (AB0), 15% (A1B1), 14% (A2B2) and 16% (A3B3). Application of P in either form significantly ($p<0.05$) increased the extractability of soil Cu throughout the growth period. Similar effects on Cu behaviour were observed in the soil previously used for wheat cultivation; showing greater amounts of extractable Cu in P treated samples and also after 8* weeks compared with the 4* weeks. A greater level of lime (10%) compared with the lower level (5%) significantly decreased the extractability of soil Cu. This effect of liming was consistent throughout the growth period of 4 to 10 weeks and also from 4* to 8* weeks.

Decreases in extractable soil Zn were observed with the growth period of rice crop (Table 6.1.3a). Application of P in either form again significantly increased ($p<0.05$) the extractability of soil Zn. The behaviour of soil Zn was also similar in the soil previously used for wheat cultivation; showing decreases with the growth period and greater levels of soil Zn in the P treated samples. A greater level of lime (10%) caused decreases in the extractability of soil Zn (Table 6.1.3b). These decreases were significant ($p<0.05$) throughout the growth period from 2 to 10 weeks and from 4* to 8* weeks.

6.3.4.3. Phosphorus and micronutrient (Fe, Mn, Cu and Zn) status of rice shoots

Effects of applied P and lime on P concentrations of rice shoots are illustrated in figures 6.1.3a and 6.1.3b respectively. Decreases in P concentrations of rice shoots were observed as the growth proceeded from 2 to 10 weeks. Lowest contents of total P were observed at 10 weeks of growth period. Application of P in either form (with or without PP) significantly ($p<0.05$) increased the total P contents of shoots. These increases were consistent throughout the growth period of 2 to 10 weeks. Plant samples taken from the soil previously used for wheat cultivation also showed decreases in the P contents as

Figure 6.1.3: Effects of applied (a) P and (b) lime on P contents of rice shoots at different stages of growth



*Soil from previous wheat crop

Error bars (I) represent standard error of means

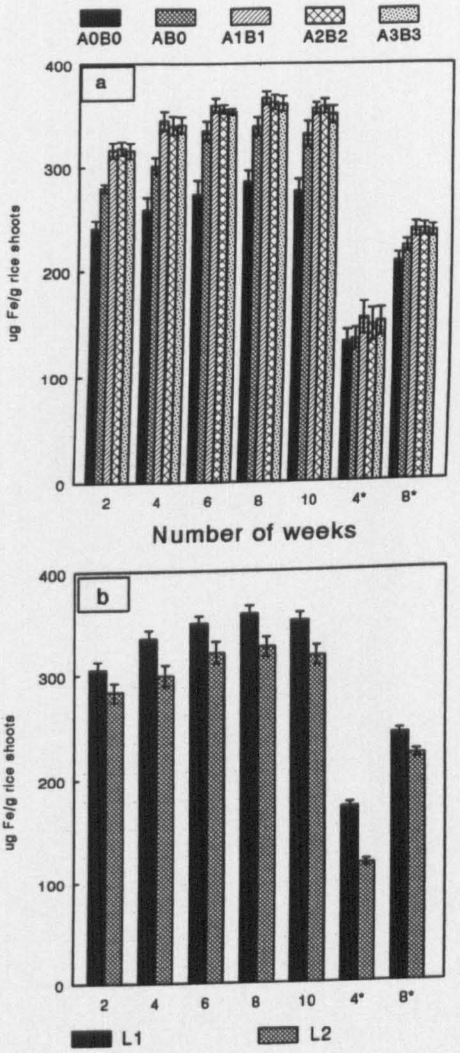
growth proceeded from 4* to 8* weeks. Liming of the soil at 10% level over 5% level caused increases in the P contents of shoots. These increases were significant ($p<0.05$) from 2 to 8 weeks and non-significant at 10 weeks. The effects of liming (10%) in increasing P contents of shoots (4* & 8* weeks) were again significant in plant samples grown on soil previously used for wheat cultivation.

Iron concentrations in shoots of paddy rice increased as the growth proceeded from 2 to 10 weeks. Application of P in either form (with or without PP) significantly ($p<0.05$) increased the Fe contents of shoots over the control samples (A0B0) throughout the growth period (figure 6.1.4a). Iron concentrations of shoots again increased as growth proceeded from 4* to 8* weeks in the soil previously used for wheat cultivation. The effects of added P on Fe contents of shoots were not significant after 4* weeks whereas significantly greater amounts of Fe were observed after 8* weeks. Application of greater level of lime (10%) over lower level (5%) significantly decreased the Fe contents of shoots throughout the growth period from 2 to 10 weeks and from 4* to 8* weeks (figure 6.1.4b).

Total Mn contents of shoots increased from 2 to 6 weeks and then decreased until 10 weeks of growth period (Table 6.1.4a). Overall decreases in Mn contents of shoots were observed as growth proceeded from 2 to 10 weeks. Total Mn contents of shoots were significantly ($p<0.05$) greater in the samples treated with P (with or without PP). Increases in Mn contents of shoots were observed with the growth period (4* to 8* weeks) in the samples collected from soil previously used for wheat cultivation. Total Mn contents in shoots were again significantly ($p<0.05$) greater in P treated samples during this period. Greater level of applied lime (10%) caused significant ($p<0.05$) decreases in the total Mn contents of shoots throughout the both growth periods (Table 6.1.4b).

Decreases in total Cu contents of shoots were observed with growth period from 4 to 10 weeks. Total Cu contents of shoots were significantly ($p<0.05$) greater in P treated samples compared with the control samples (Table 6.1.4a). Increases in Cu

Figure 6.1.4: Effects of applied (a) P and (b) lime on Fe contents of rice shoots at different stages of growth



*Soil from previous wheat crop

Error bars (I) represent standard error of means

Table 6.1.4a. Effects of applied P on total Mn, Cu and Zn concentrations in shoots of paddy rice plants at different stages of growth

Treatments	2W	4W	6W	8W	10W	4W*	8W*
			Mn (µg /g plant shoots)				
A0B0	523.1	662.5	608.0	543.7	506.6	108.1	132.8
AB0	584.9	729.0	650.7	601.1	568.7	127.9	145.5
A1B1	661.7	761.2	719.2	665.1	604.5	137.6	167.5
A2B2	648.3	753.8	723.5	672.3	611.5	140.0	208.4
A3B3	663.7	768.3	728.2	671.3	613.1	137.3	210.5
LSD (0.05)	*6.3*	*6.8*	*8.6*	*9.7*	*9.5*	*6.7*	*8.4*
			Cu (µg /g plant shoots)				
A0B0	xx	23.38	18.10	17.21	14.06	8.17	16.87
AB0	xx	24.65	21.83	18.71	15.86	12.37	19.75
A1B1	xx	27.33	23.86	21.33	18.45	14.58	24.92
A2B2	xx	26.16	22.76	20.56	18.04	15.24	24.64
A3B3	xx	25.45	23.34	19.87	17.76	16.01	24.93
LSD (0.05)		*1.91*	*1.48*	*1.85*	*1.92*	*2.09*	*1.99*
			Zn (µg /g plant shoots)				
A0B0	41.44	40.07	36.23	34.90	33.50	45.85	39.42
AB0	45.12	44.42	39.06	38.93	36.35	51.85	43.33
A1B1	49.56	46.47	42.76	40.73	38.37	53.18	45.73
A2B2	51.18	50.04	44.02	40.60	39.28	55.25	47.47
A3B3	54.39	51.55	46.95	42.72	41.42	56.67	48.90
LSD (0.05)	*3.08*	*3.60*	*4.06*	*3.39*	*3.42*	*3.11*	*3.49*

(means of six values)

Table 6.1.4b. Effects of lime application on total Mn, Cu and Zn concentrations in shoots of paddy rice plants at different stages of growth

Lime levels	2W	4W	6W	8W	10W	4W*	8W*
			Mn (µg /g plant shoots)				
L1	720.2	854.4	767.1	702.2	656.4	137.3	194.0
L2	512.4	615.4	604.7	559.2	505.3	123.0	151.8
LSD (0.05)	*3.9*	*4.3*	*5.4*	*6.1*	*5.9*	*4.2*	*5.3*
			Cu (µg /g plant shoots)				
L1	xx	25.38	24.99	23.97	19.16	14.07	20.77
L2	xx	24.20	18.96	15.10	14.51	12.48	23.68
LSD (0.05)		*1.19*^{ns}	*0.92*	*1.15*	*1.20*	*1.30*	*1.24*
			Zn (ug/g plant shoots)				
L1	54.01	50.97	46.37	44.18	42.05	54.70	46.95
L2	42.67	42.05	37.24	34.97	33.51	50.42	42.99
LSD (0.05)	*1.93*	*2.25*	*2.54*	*2.12*	*2.14*	*1.95*	*2.18*

xx (not determined) (means of fifteen values)

* soil from previous rice crop

contents of shoots with growth period (4* to 8* weeks) were observed in the plant samples collected from soil previously used for wheat cultivation. Addition of greater levels of lime (10%), compared with the lower level (5%), decreased the Cu contents of shoots, significantly ($p<0.05$) form 6 to 10 weeks (Table 6.1.4b). Although, a greater level of lime caused decreases in the Cu contents of shoots after 4* weeks, increases in Cu contents were observed after 8* weeks in samples collected from soil previously used for wheat cultivation.

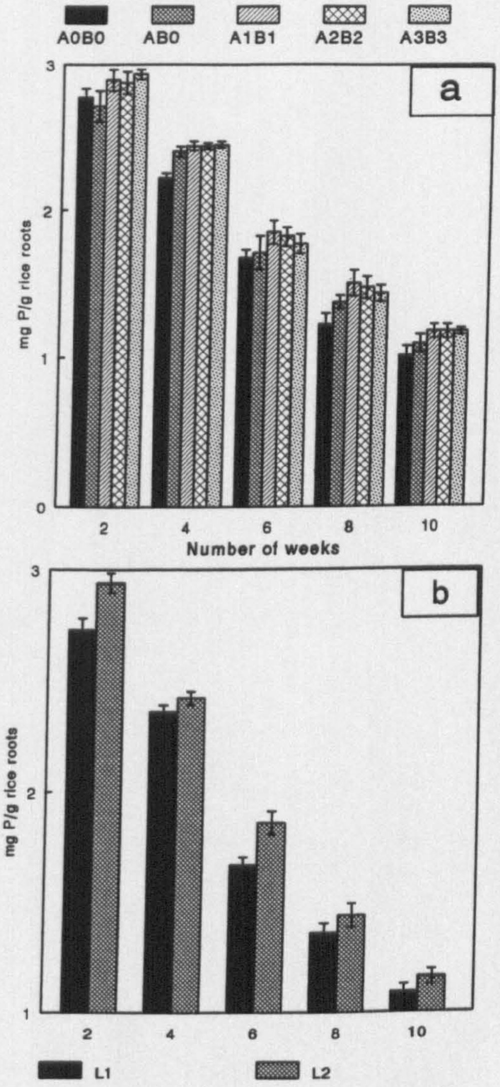
Decreases in Zn contents of shoots were observed as the growth proceeded from 2 to 10 weeks and from 4* to 8* weeks (Table 6.1.4a). Added P with or without pyrophosphate significantly ($p<0.05$) increased the total Zn contents of shoots throughout the entire growth period. Application of 10% lime level significantly decreased the Zn contents of shoots below the 5% lime level throughout the entire growth period of 2 to 10 weeks and from 4* to 8* weeks (Table 6.1.4b).

6.3.4.4. Phosphorus and micronutrient (Fe, Mn, Cu and Zn) status of rice roots

Phosphorus and micronutrient contents of rice roots were determined only from 2 to 10 weeks of growth period. Phosphorus contents of roots are illustrated in figures 6.1.5a and 6.1.5b. Decreases in P contents of roots were observed from 2 to 10 weeks. Lowest levels of P were found in the samples collected at 10 weeks of growth. Added P in either form (with or without PP) improved the P contents of roots throughout the growth period except at 2 weeks where OP treatment caused slight decreases (non-significant) over the control samples (A0B0). The greatest levels of P were however observed in pyrophosphate (PP) treated samples. These increases were not always significant in comparison to orthophosphate (OP) treated and control (A0B0) samples. Added lime at 10% level over 5% level caused increases in P contents of roots. These increases were consistent, although not always significant ($p<0.05$), throughout the growth period.

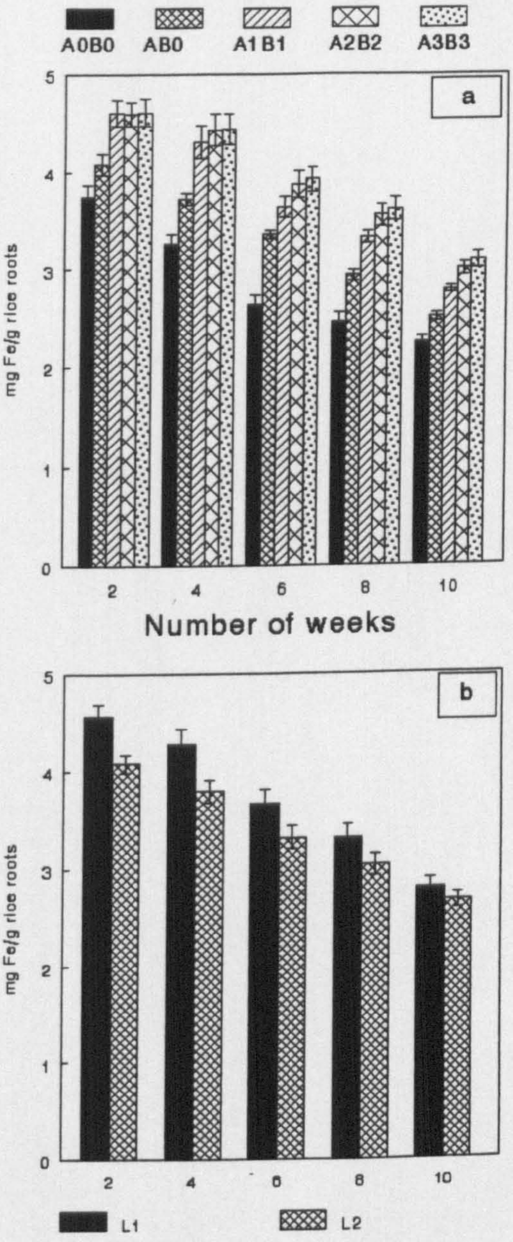
Total Fe, Cu and Zn contents of rice roots decreased as the growth proceeded from 2 to 10 weeks. The results are illustrated in figures 6.1.6 a & b for Fe and in table

Figure 6.1.5: Effects of applied (a) P and (b) lime on P contents of rice roots at different stages of growth



Error bars (I) represent standard error of means)

Figure 6.1.6: Effects of applied (a) P and (b) lime on Fe contents of rice roots at different stages of growth



Error bars (I) represent standard error of means

Table 6.1.5a. Effects of applied P on total Mn, Cu and Zn concentrations in roots of paddy rice plants at different stages of growth

Treatments	2W	4W	6W	8W	10W
Mn (mg /g plant roots)					
A0B0	1.247	1.404	1.675	0.379	0.227
AB0	1.313	1.584	2.500	0.643	0.311
A1B1	1.350	1.646	3.180	0.817	0.355
A2B2	1.381	1.681	3.177	0.883	0.374
A3B3	1.462	1.703	3.295	0.854	0.376
LSD (0.05)	*0.067*	*0.067*	*0.072*	*0.053*	*0.025*
Cu (μg /g plant roots)					
A0B0	xx	42.42	39.23	32.20	25.84
AB0	xx	60.84	51.74	39.67	32.96
A1B1	xx	64.48	53.38	41.87	32.11
A2B2	xx	64.41	53.72	42.81	30.28
A3B3	xx	65.93	53.65	39.30	29.60
LSD (0.05)		*3.04*	*3.38*	*3.49*	*2.36*
Zn (μg /g plant roots)					
A0B0	59.01	52.96	43.14	35.48	28.48
AB0	64.54	59.70	48.81	43.02	36.43
A1B1	80.37	75.81	57.89	50.93	41.12
A2B2	79.94	76.64	59.03	52.40	40.31
A3B3	79.56	73.65	58.12	50.70	39.82
LSD (0.05)	*3.28*	*4.56*	*3.23*	*3.61*	*3.35*

(means of six values)

Table 6.1.5b. Effects of lime application on total Mn, Cu and Zn concentrations in roots of paddy rice plants at different stages of growth

Lime levels	2W	4W	6W	8W	10W
Mn (mg /g plant roots)					
L1	1.507	1.726	3.335	0.753	0.349
L2	1.194	1.482	2.195	0.677	0.308
LSD (0.05)	*0.042*	*0.042*	*0.050*	*0.033*	*0.016*
Cu (μg /g plant roots)					
L1	xx	65.76	52.87	39.98	31.79
L2	xx	53.48	47.82	38.36	28.52
LSD (0.05)		*1.90*	*2.11*	*2.18*	*1.48*
Zn (μg /g plant roots)					
L1	83.72	78.61	58.53	49.83	40.53
L2	61.65	56.89	48.27	43.18	33.93
LSD (0.05)	*2.05*	*2.85*	*2.02*	*2.25*	*2.10*

xx (not determined)

(means of fifteen values)

6.1.5 for Cu and Zn. Added P with or without pyrophosphate caused significant ($p<0.05$) increases in total Fe, Cu and Zn contents of roots throughout the growth period. The effects of added pyrophosphate (PP) with orthophosphate (OP) in increasing the Fe, Cu and Zn contents of roots were found to be significant ($p<0.05$). Added lime at 10% level over 5% level caused decreases in Fe (figure 6.1.6b), Cu and Zn (Table 6.1.5b) contents of roots. The effects of liming were found to be consistent throughout the growth period, although not always significant ($p<0.05$).

Gradual increases observed in the Mn contents of rice roots until 6 weeks were decreased considerably during 8 to 10 weeks (Table 6.1.5a). Similar trends were observed in all the treatments. Added P with or without pyrophosphate (PP) raised the Mn contents of roots throughout the growth period. Significant ($p<0.05$) decreases in Mn contents of roots were observed with the application of 10% lime level compared with the 5% lime level (Table 6.1.5b).

6.4. Experiment II. Pot trials with wheat and wheat following a rice crop

6.4.1. Aims of the experiment

The experiment was conducted to investigate the effects of moist conditions, during wheat crop, on native and applied soil phosphorus and micronutrients at two lime levels. The trial also included the cultivation of wheat crop on the soil previously used for rice crop. The effects of applied P, with or without pyrophosphate, on plant height, dry matter yields and P and micronutrient uptake were also investigated.

6.4.2. Experimental procedure

Wheat seeds were soaked in water for 48 hours prior to sowing in the pots. Six seeds were sown in each pot and three seedlings were kept after germination. Randomized complete block design was used for the experiment.

6.4.3. Soil and plant sample handling

Soil samples were collected in moist conditions after removing the plants and mixing the soil thoroughly in the pots. Plant samples were collected in the same way as described in section 6.3.3. Soil and plant samples were analyzed as stated earlier in section 6.3.3.

6.4.4. Results

Statistical analyses of the results did not reveal significant ($p<0.05\%$) effects of lime and P interactions. Hence results regarding the effects of lime and P application on plant height, dry matter yields and on nutrient behaviour are reported in the following section. Sampling of the soil and plants was done as reported in experiment I (section 6.3.4).

6.4.4.1. Plant height and dry matter yields

The data regarding the effects of applied P and two lime levels on the heights of wheat plants are given in table 6.2.1. Increases in the height of wheat plants were observed with the growth period, the maximum increases were observed after 10 weeks of growth. Similar increases in plant height were observed in the plants grown on the soil previously used for rice cultivation, the total increases (4* & 8* weeks) were, however, less compared with those in the soil currently used for wheat cultivation (4 & 8 weeks). Added phosphorus with or without pyrophosphate (PP) caused slight increases in the heights of wheat plants throughout the growth period irrespective of the history of soil used. In pyrophosphate (PP) amended samples further increases in plant height were observed in comparison to orthophosphate (OP) treated samples. Treatment A2B2 caused significant increases in plant height compared with the control samples and treatment A3B3 caused significant increases in comparison to orthophosphate (OP) treated samples. These increases were significant at all growth periods except after 8* weeks where non-significant increases were noticed. Application of more lime (10%) over 5% lime level caused significant ($p<0.05$) increases in the height of wheat plants throughout the growth period (except after 2 weeks), irrespective of the history of soil used (table 6.2.1).

Data given in table 6.2.2 show that plant dry matter yields were also increased with the growth period and with the application of P with or without pyrophosphate

Table 6.2.1. Effects of applied P and lime levels on height (cm) of wheat plants at different stages of growth

Treatments	2W	4W	6W	8W	10W	4W*	8W*
A0B0	6.00	11.83	23.17	28.83	32.33	10.50	23.50
AB0	8.00	13.50	24.00	29.50	34.17	12.00	25.00
A1B1	9.00	14.50	25.50	31.50	35.67	13.50	26.50
A2B2	10.67	16.00	27.50	31.83	37.33	13.83	26.17
A3B3	11.83	17.67	28.50	33.00	38.00	14.50	27.33
LSD (0.05)	2.36	2.70	2.36	2.84	2.71	2.36	3.03

(means of six values)

Lime levels	2W	4W	6W	8W	10W	4W*	8W*
L1	8.40	13.13	23.87	29.33	33.93	11.73	24.40
L2	9.80	16.27	27.60	32.53	37.07	14.00	27.00
LSD(0.05)	1.49^{ns}	1.71	1.49	1.80	1.72	1.49	1.92

(means of fifteen values)

* Soil from previous rice crop

Table 6.2.2. Effects of applied P and lime levels on dry matter yields (g/pot) of wheat plants at different stages of growth

Treatments	2W	4W	6W	8W	10W	4W*	8W*
A0B0	0.52	1.80	3.88	6.45	8.95	1.34	5.77
AB0	0.75	2.03	4.11	6.69	9.18	1.57	6.00
A1B1	0.78	2.06	4.14	6.72	9.20	1.60	6.03
A2B2	0.80	2.08	4.17	6.74	9.23	1.62	6.06
A3B3	0.80	2.08	4.17	6.74	9.23	1.62	6.06
LSD (0.05)	0.15	0.15	0.15	0.15	0.15	0.15	0.15

(means of six values)

Lime levels	2W	4W	6W	8W	10W	4W*	8W*
L1	0.67	1.95	4.03	6.61	9.10	1.49	5.92
L2	0.79	2.07	4.16	6.73	9.22	1.61	6.04
LSD (0.05)	0.10	0.10	0.10	0.10	0.10	0.10	0.10

(means of fifteen values)

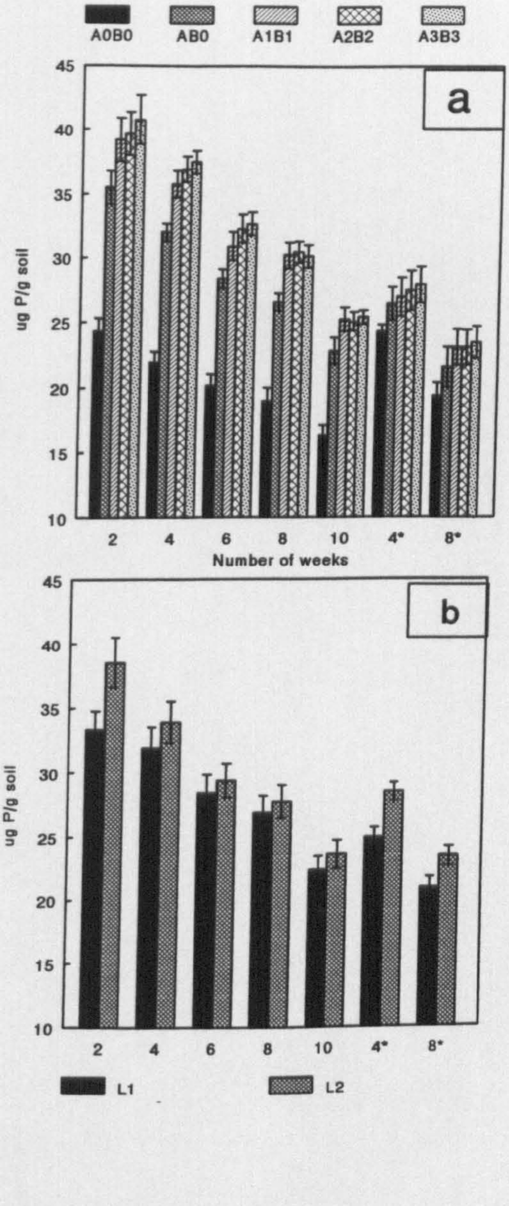
*Soil from previous rice crop

(PP). Maximum yields were observed after 10 weeks of growth period. Significantly greater ($p<0.05$) increases in dry matter yields were observed in P treated samples over the control samples (A0B0). Although addition of pyrophosphate (PP) with orthophosphate (OP) slightly improved the dry matter yields the effects were not statistically different. Liming of the soil at 10% level caused significant ($p<0.05$) increases in dry matter yields compared with the 5% lime level (table 6.2.2).

6.4.4.2. Phosphorus and micronutrient (Fe, Mn, Cu and Zn) status of wheat soil

Decreases in the extractability of soil phosphorus were observed with the growth period of 10 weeks (figure 6.2.1a). Overall decreases after 10 weeks over the two weeks were 33%, 36%, 36%, 37% and 38% in treatments A0B0, AB0, A1B1, A2B2 and A3B3 respectively. Addition of P with or without pyrophosphate (PP) significantly ($p<0.05$) increased the extractability of soil phosphorus throughout the growth period except after 8* weeks where OP treated samples did not show significant differences in comparison to control samples. The effects of pyrophosphate (PP) amendment were to significantly ($p<0.05$) increase the extractability of soil P over OP treated samples throughout the growth period of 10 weeks. These amounts after 10 weeks were 11% (A1B1), 10% (A2B2) and 11% (A3B3) greater compared with the AB0 treatment. In the soil previously used for rice cultivation (4* & 8* weeks), the effects of pyrophosphate additions on P availability were not significant in comparison to OP treated samples. Decreases in the extractability of soil P from 4* to 8* weeks were also noticed in the soil previously used for rice crop. These decreases after 8* weeks over the 4* weeks were 20%, 18%, 15%, 16% and 16% respectively in the treatments A0B0, AB0, A1B1, A2B2 and A3B3. Extractable levels of soil P at the same growth periods (4 & 8 weeks) were found to be lower in the soil previously used for rice cultivation (4* & 8* weeks). Addition of lime at 10% level, against 5% level, increased (significant after 2 weeks) the extractability of soil P until 10 weeks and significantly ($p<0.05$) after 4* and 8* weeks in the soil previously used for rice cultivation (figure 6.2.1b).

Figure 6.2.1: Effects of applied (a) P and (b) lime on extractable soil P under wheat crop at different stages of growth



*Soil from previous rice crop

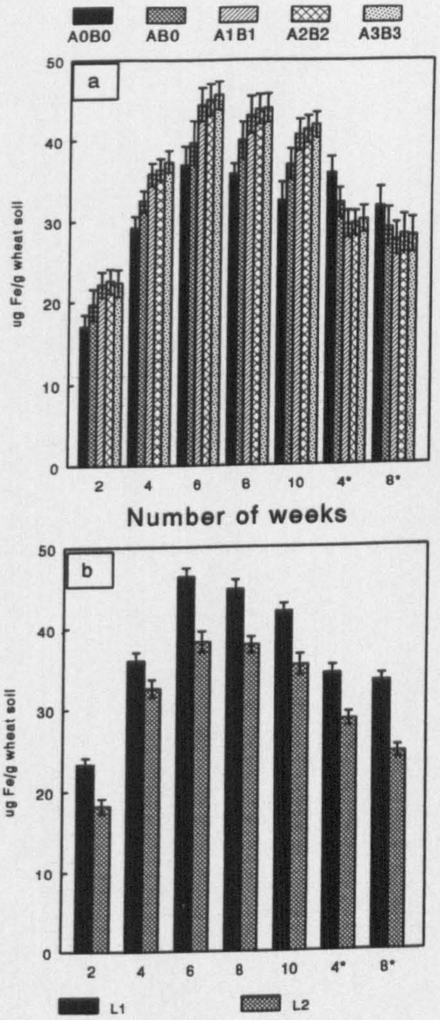
Error bars (I) represent standard error of means

Increases in extractable soil Fe were observed from 2 to 6 weeks and then slight decreases were observed until 10 weeks (figure 6.2.2a). Overall increases in extractable soil Fe after 10 weeks over the 2 weeks were 90%, 88%, 84%, 83% and 87% respectively in treatments A0B0, AB0, A1B1, A2B2 and A3B3. Overall decreases in extractable soil Fe with growth period were observed in the soil previously used for rice cultivation. These decreases after 8* weeks compared with the 4* weeks were 12%, 10%, 6%, 4% and 7% respectively in treatments A0B0, AB0, A1B1, A2B2 and A3B3. Added P with or without pyrophosphate (PP) increased the extractability of soil Fe during 2 to 10 weeks and decreased during 4* & 8* weeks in the soil previously used for rice cultivation. Addition of a greater level of lime (10%) over the lower level (5%) caused significant ($p<0.05$) decreases in the extractability of soil Fe during the both growth periods (figure 6.2.2b).

Extractable levels of soil Mn increased until 8 weeks of growth period followed by slight decreases after 10 weeks (table 6.2.3a). Overall increases in extractable soil Mn were observed after 10 weeks compared with the 2 weeks. These increases were 21.5, 30.2, 26.0, 23.5 and 23.4 times respectively in treatments A0B0, AB0, A1B1, A2B2 and A3B3. The increases observed after 8* weeks over the 4* weeks in the soil previously used for rice cultivation were 1.4, 1.5, 1.6, 1.5 and 1.4 times respectively in treatments A0B0, AB0, A1B1, A2B2 and A3B3. Significantly greater amounts of extractable Mn were observed in P treated samples. Further increases in the extractability of soil Mn were observed with the addition of pyrophosphate (PP) to orthophosphate (OP). Addition of greater level of lime (10%) over lower level (5%) significantly decreased the extractability of soil Mn in the both growth periods (table 6.2.3b).

Extractable soil Cu decreased as growth period proceeded from 2 to 10 weeks whereas increases in soil Cu were observed from 4* to 8* weeks in the soil previously used for rice cultivation (table 6.2.3a). Added P with or without pyrophosphate (PP) caused significant ($p<0.05$) increases in the extractability of soil Cu during the both growth periods irrespective of the history of soil use, except in AB0 treatment after 2

Figure 6.2.2: Effects of applied (a) P and (b) lime on extractable soil Fe under wheat crop at different stages of growth



*Soil from previous rice crop

Error bars (I) represent standard error of means

Table 6.2.3a. Effects of applied P on extractable soil Mn, Cu and Zn during wheat crop at different stages of growth

Treatments	2W	4W	6W	8W	10W	4W*	8W*
Mn (µg /g soil)							
A0B0	2.33	10.16	41.94	50.66	50.04	28.52	39.74
AB0	2.62	19.47	74.83	79.69	79.06	22.98	34.88
A1B1	3.22	21.82	84.68	90.54	83.87	21.63	33.77
A2B2	3.53	22.85	85.83	89.27	83.03	21.82	33.18
A3B3	3.50	23.91	85.02	88.62	82.04	23.33	33.62
LSD (0.05)	*0.14*	*1.81*	*5.69*	*6.26*	*3.54*	*2.85*	*2.48*
Cu (µg /g soil)							
A0B0	xx	2.93	2.82	2.61	2.39	2.71	3.08
AB0	xx	2.97	2.93	2.77	2.53	3.45	3.40
A1B1	xx	3.14	3.02	2.81	2.58	3.49	3.42
A2B2	xx	3.08	3.15	2.83	2.59	3.57	3.44
A3B3	xx	3.10	3.02	2.84	2.64	3.52	3.46
LSD (0.05)		*0.05*	*0.05*	*0.11*	*0.05*	*0.07*	*0.04*
Zn (µg /g soil)							
A0B0	1.23	1.55	1.87	1.67	1.50	1.33	1.08
AB0	1.17	1.53	1.74	1.55	1.27	1.30	1.04
A1B1	1.50	1.70	2.16	1.93	1.84	1.39	1.09
A2B2	1.40	1.87	2.14	1.99	1.90	1.48	1.14
A3B3	1.44	1.93	2.21	2.00	1.90	1.53	1.22
LSD (0.05)	0.51^{ns}	0.55^{ns}	0.58^{ns}	0.49^{ns}	0.53^{ns}	0.48^{ns}	0.51^{ns}

(means of six values)

Table 6.2.3b. Effects of lime application on extractable soil Mn, Cu and Zn during wheat crop at different stages of growth

Lime levels	2W	4W	6W	8W	10W	4W*	8W*
Mn (µg /g soil)							
T1	3.15	23.42	106.73	102.02	89.96	24.44	36.24
T2	2.92	15.86	42.19	57.49	61.26	22.87	33.84
LSD (0.05)	*0.10*	*1.13*	*3.55*	*3.91*	*2.21*	*1.78*	*1.55*
Cu (µg /g soil)							
T1	xx	3.48	3.38	3.10	2.87	3.42	3.61
T2	xx	2.61	2.59	2.44	2.22	3.27	3.11
LSD (0.05)		*0.03*	*0.03*	*0.07*	*0.03*	*0.04*	*0.03*
Zn (µg /g soil)							
T1	1.50	1.97	2.19	2.07	1.95	1.46	1.15
T2	1.19	1.47	1.86	1.58	1.42	1.35	1.07
LSD (0.05)	0.32^{ns}	*0.34*	0.36^{ns}	*0.31*	*0.33*	0.30^{ns}	0.32^{ns}

xx (not determined)

(means of fifteen values)

* soil from previous rice crop

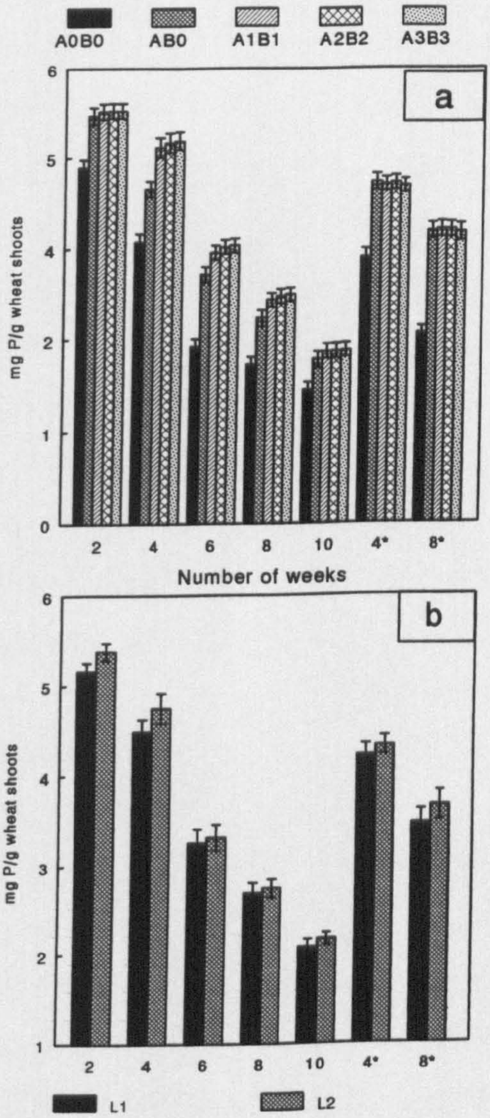
weeks where the effect was non significant. Added lime at 10% level compared with 5% level caused significant ($p<0.05$) decreases in the extractability of soil Cu during the both growth periods irrespective of the history of soil use (table 6.2.3b).

Increases (nonsignificant) in the extractability of soil Zn, were observed until 8 weeks followed by slight decreases after 10 weeks whereas decreases in soil Zn were observed from 4* to 8* weeks in the soil previously used for rice cultivation (table 6.2.3a). Added P (OP) slightly decreased whereas added pyrophosphate (PP) slightly increased the extractability of soil Zn during the both growth periods irrespective of the history of soil use. These changes in soil Zn were however, non significant ($p<0.05$). Addition of greater 10% lime level over 5% level decreased the extractability of soil Zn throughout the growth period. These effects were non-significant ($p<0.05$) during 2 & 6 weeks and during 4* and 8* weeks in the soil previously used for rice cultivation (table 6.2.3b).

6.4.4.3. Phosphorus and micronutrient (Fe, Mn, Cu and Zn) status of wheat shoots

Total P contents in wheat shoots decreased with the growth period from 2 to 10 weeks and also from 4* to 8* weeks in the plant samples collected from the soil previously used for rice cultivation (figure 6.2.3a). Overall decreases in P contents of shoots after 10 weeks over the 2 weeks in treatments A0B0, AB0, A1B1, A2B2 and A3B3 were 63%, 60%, 59%, 59% and 59% respectively. These decreases after 8* weeks over the 4* weeks were 29%, 14%, 14%, 14% and 14% respectively in treatments A0B0, AB0, A1B1, A2B2 and A3B3. Significantly greater levels of total P in shoots were observed in P treated samples. Addition of pyrophosphate (PP) with OP over OP alone significantly increased the P contents during 4 to 8 weeks but the effects were non-significant during 4* to 8* weeks. Greater lime level (10%) over the lower level (5%) increased P contents in shoots during the both growth periods (figure 6.2.3b). The effects were, however non-significant ($p<0.05$) during the both growth periods except after 2 weeks where significant increases were observed.

Figure 6.2.3: Effects of applied (a) P and (b) lime on P contents in wheat shoots at different stages of growth

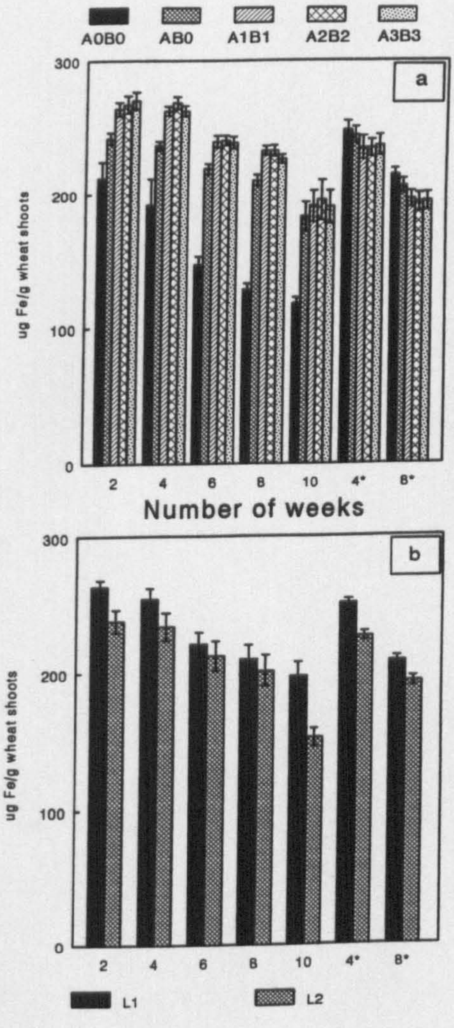


*Soil from previous rice crop

Error bars (I) represent standard error of means

Total Fe (figure 6.2.4a), Cu and Zn (tables 6.2.4a & b) contents of shoots decreased with the growth period from 2 to 10 weeks and also from 4* to 8* weeks in the samples collected from soil previously used for rice cultivation. Added P had different effects on the shoot contents of these elements. Total Fe contents of shoots increased significantly ($p<0.05$) with the application of P with or without pyrophosphate (PP). Addition of pyrophosphate (PP) with OP caused further increases in Fe contents of shoots. These increases were significant ($p<0.05$) during 2 to 8 weeks and non-significant after 10 weeks, in comparison to OP treated samples. In samples collected from soil previously used for rice cultivation, addition of P with or without pyrophosphate (PP) decreased the Fe contents of shoots, showing more decreases in pyrophosphate (PP) treated samples. Application of lime at 10% level over 5% level caused decreases in the Fe contents of shoots (figure 6.2.4b). These decreases were significant only during 2, 4 and 10 weeks and after 4* and 8* weeks of growth period. Addition of P (OP) decreased Cu contents in shoots during 4 to 8 weeks whereas the effects of adding pyrophosphate were not found to be consistent. Overall effects of P additions, in comparison to control samples, were to slightly increase the Cu contents of shoots after 10 weeks (table 6.2.4a). The effect of P addition in improving Cu contents of shoots in samples collected from soil previously used for rice cultivation were significant over control (A0B0) samples during 4* to 8* weeks of growth period. Overall effects of lime additions at 10% level compared with 5% level were to decrease the Cu contents of shoots (table 6.2.4b). Addition of pyrophosphate (PP) with orthophosphate (OP) increased, although not always significantly, the Zn concentrations in shoots whereas the addition of orthophosphate (OP) alone caused decreases compared with the control samples (table 6.2.4a). Decreases in Zn contents of shoots caused by OP addition, compared with the control samples (A0B0), were significant ($p<0.05$) during the growth period of 2 to 10 weeks and at 4* weeks whereas increases caused by the addition of different proportions of pyrophosphate were significant during 2 to 10 weeks. During 4* to 8* weeks added pyrophosphate failed to produce significant differences in

Figure 6.2.4: Effects of applied (a) P and (b) lime on Fe contents in wheat shoots at different stages of growth



*Soil from previous rice crop

Error bars (I) represent standard error of means

Table 6.2.4a. Effects of applied P on total Mn, Cu and Zn concentrations in shoots of wheat plants at different stages of growth

Treatments	2W	4W	6W	8W	10W	4W*	8W*
Mn (µg /g plant shoots)							
A0B0	28.54	34.49	41.48	50.64	61.33	76.59	54.44
AB0	31.74	38.33	47.71	60.76	71.56	71.94	45.74
A1B1	34.94	45.10	52.98	71.23	76.02	68.19	44.54
A2B2	36.62	42.83	54.96	69.21	78.50	67.35	44.80
A3B3	38.60	45.91	55.90	70.94	80.67	70.29	46.04
LSD (0.05)	*2.94*	*2.98*	*2.95*	*3.10*	*3.15*	*2.97*	*2.89*
Cu (µg /g plant shoots)							
A0B0	xx	12.15	10.05	7.60	5.33	9.08	7.63
AB0	xx	11.02	8.62	6.61	5.53	10.15	9.09
A1B1	xx	14.45	11.62	10.84	9.07	12.32	9.24
A2B2	xx	11.29	10.60	12.39	8.46	13.21	9.40
A3B3	xx	9.66	8.70	8.29	6.32	14.40	9.38
LSD (0.05)		*0.50*	*0.46*	*0.35*	*0.32*	*0.46*	*0.49*
Zn (µg /g plant shoots)							
A0B0	25.14	23.72	21.32	19.90	17.69	22.96	13.38
AB0	23.00	20.71	18.44	16.84	14.53	20.53	12.10
A1B1	27.08	25.27	24.02	21.94	20.34	21.57	13.48
A2B2	27.14	25.44	24.25	22.57	21.05	22.32	13.86
A3B3	27.01	25.34	24.45	22.88	21.52	22.04	13.82
LSD (0.05)	1.94	1.89	1.88	1.90	1.87	1.91	1.88^{ns}

(means of six values)

Table 6.2.4b. Effects of lime application on total Mn, Cu and Zn concentrations in shoots of wheat plants at different stages of growth

Lime levels	2W	4W	6W	8W	10W	4W*	8W*
Mn (µg /g plant shoots)							
L1	36.99	45.37	54.47	65.24	68.34	79.15	46.75
L2	31.19	37.29	46.75	63.87	78.90	62.58	47.47
LSD (0.05)	*1.84*	*1.86*	*1.84*	*1.94*	*1.97*	*1.86*	1.81^{ns}
Cu (µg /g plant shoots)							
L1	xx	12.73	10.31	8.95	7.09	12.43	9.60
L2	xx	10.70	9.52	9.35	6.80	11.23	8.29
LSD (0.05)		*0.31*	*0.29*	*0.22*	*0.20*	*0.29*	*0.31*
Zn (µg /g plant shoots)							
L1	28.22	26.67	24.85	23.10	20.47	26.55	15.01
L2	23.52	21.52	20.14	18.55	17.58	17.22	11.65
LSD (0.05)	*1.21*	*1.18*	*1.18*	*1.19*	*1.17*	*1.19*	*1.18*

xx (not determined) (means of fifteen values)

* soil from previous rice crop

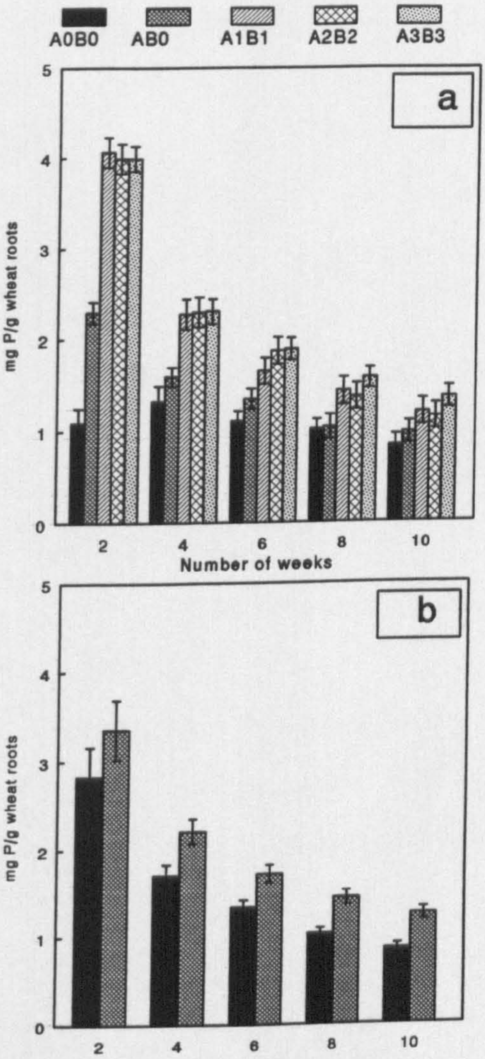
Zn concentration compared with both OP treated and control samples (A0B0). Decreases in Zn contents of shoots were again noticed in the samples treated with the greater lime (10%) level compared with the lower level (5%) (table 6.2.4b). These decreases were significant ($p<0.05$) throughout the both growth periods irrespective of the history of soil use.

Increases in the Mn contents of shoots were observed with the growth period from 2 to 10 weeks whereas decreases were observed, during 4* to 8* weeks, in the samples collected from soil previously used for rice cultivation (table 6.2.4a). Significantly greater Mn contents were observed in the shoots treated with P (OP) either with or without pyrophosphate (PP). Pyrophosphate treated samples had significantly greater Mn contents of shoots compared with the orthophosphate (OP) treated samples. In samples, treated with either source of P, collected from soil previously used for rice cultivation., significantly ($p<0.05$) lower levels of Mn over the control samples were observed. Greater lime level (10%) over the lower level caused significant decreases in Mn contents of shoots throughout the growth period irrespective of the history of soil use except after 10 weeks where significant increases were observed and after 8* weeks where the effect was non significant (table 6.2.4b).

6.4.4.4. Phosphorus and micronutrient (Fe, Mn, Cu and Zn) status of wheat roots

Total P contents of roots as affected by the application of P and lime levels are illustrated in figures 6.2.5a & b respectively. Decreases in the P contents of roots were noticed as growth proceeded from 2 to 10 weeks. These decreases were greater in the pyrophosphate (PP) treated samples compared with the control (A0B0) and OP (AB0) treated samples. Addition of P caused increases, although not always significant ($p<0.05$), in P contents of roots throughout the growth period of 10 weeks. Total P contents in roots were significantly greater in the samples treated with pyrophosphate in addition to orthophosphate. Greater amounts of P were found in the samples treated with the greater lime level (10%). These amounts were significantly ($p<0.05$) greater during 4 to 10 weeks of growth (figure 6.2.5b).

Figure 6.2.5: Effects of applied (a) P and (b) lime on P contents in wheat roots at different stages of growth



Error bars (I) represent standard error of means

Total Fe contents of wheat roots decreased with the growth period from 2 to 10 weeks. The effects of added P with or without pyrophosphate (PP), on total Fe contents of roots, were not statistically significant ($p<0.05$) during the growth period of 2 to 10 weeks (figure 6.2.6a). Overall decreases in Fe contents of wheat roots were noticed with the application of lime at 10% levels compared with at 5% level.

Overall increases in Mn contents of wheat roots were observed with the growth period from 2 to 10 weeks (table 6.2.5a). Added P with or without pyrophosphate (PP) also caused significant increases in Mn contents of roots whereas significant decreases were observed in the samples treated with the greater (10%) lime level compared with the lower (5%) lime level (table 6.2.5b).

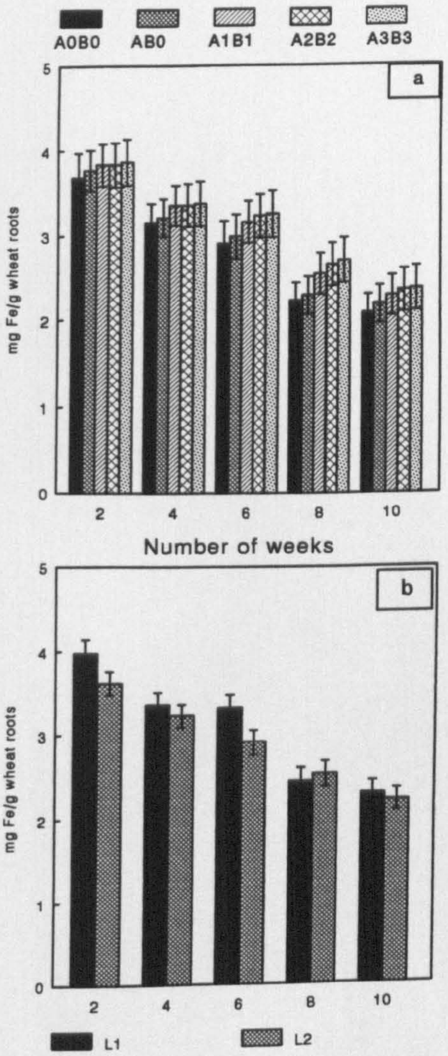
Decreases in the Cu contents of wheat roots were observed with the growth period from 4 to 10 weeks (table 6.2.5a). Application of P in either form of P (with or without PP) significantly increased the Cu contents of wheat roots, showing greater Cu contents in pyrophosphate (PP) treated samples. Total levels of Cu in wheat roots were found to be significantly greater in the samples subjected to 10% lime treatment compared with the 5% lime treatment (table 6.2.5b).

Total Zn contents of wheat roots also decreased with the growth period (table 6.2.5a). Phosphorus treated samples resulted in lower levels of Zn in wheat roots. Addition of P (OP) caused significant decreases in the Zn contents of roots compared with the control (A0B0) and pyrophosphate (PP) treated samples. Addition of pyrophosphate with orthophosphate slightly raised the Zn contents of roots, however, the amounts were lower, although not significantly, compared with the control samples. Greater lime level (10%) over lower level (5%) caused significant decreases in the Zn contents of roots from 2 to 8 weeks and non significantly after 10 weeks (table 6.2.5b).

6.5 Discussion

The pot experiments reported in the above sections (6.3 & 6.4) were conducted in a glass house. The aims of the experiments were to compare, under artificial calcareous conditions, the behaviour of applied and native soil P and their subsequent

Figure 6.2.6: Effects of applied (a) P and (b) lime on Fe contents in wheat roots at different stages of growth



Error bars (I) represent standard error of means

Table 6.2.5a. Effects of applied P on total Mn, Cu and Zn concentrations in roots of wheat plants at different stages of growth

Treatments	2W	4W	6W	8W	10W
Mn (µg /g plant roots)					
A0B0	231.7	201.8	225.0	231.7	233.2
AB0	238.9	237.0	252.7	262.3	283.3
A1B1	287.0	271.0	290.5	317.0	305.0
A2B2	293.2	274.7	299.9	311.4	304.6
A3B3	289.6	268.9	300.4	318.6	312.2
LSD (0.05)	*6.5*	*6.5*	*6.7*	*6.8*	*6.6*
Cu (µg /g plant roots)					
A0B0	xx	34.34	30.19	28.48	26.70
AB0	xx	37.44	32.68	31.11	29.61
A1B1	xx	41.27	34.38	30.58	29.50
A2B2	xx	40.42	35.30	32.31	31.23
A3B3	xx	40.26	37.89	36.80	36.14
LSD (0.05)	xx	*0.44*	*0.69*	*0.24*	*0.56*
Zn (µg /g plant roots)					
A0B0	115.1	97.8	76.5	58.9	42.8
AB0	91.0	77.8	59.9	46.1	30.2
A1B1	105.0	89.6	72.8	54.3	37.7
A2B2	108.4	95.2	78.2	56.4	40.5
A3B3	109.1	96.4	80.6	58.4	43.9
LSD (0.05)	*7.3*	*6.9*	*6.8*	*6.6*	*6.9*

(means of six values)

Table 6.2.5b. Effects of lime application on total Mn, Cu and Zn concentrations in roots of wheat plants at different stages of growth

Lime levels	2W	4W	6W	8W	10W
Mn (µg /g plant roots)					
L1	293.9	257.5	297.9	313.4	303.7
L2	242.2	243.8	249.5	263.0	271.6
LSD (0.05)	*4.1*	*4.1*	*4.2*	*4.3*	*4.1*
Cu (µg /g plant roots)					
L1	xx	37.79	32.68	29.49	28.01
L2	xx	39.70	35.49	34.21	33.26
LSD (0.05)	*xx*	*0.28*	*0.44*	*0.15*	*0.35*
Zn (µg /g plant roots)					
L1	118.2	100.9	83.5	59.1	40.3
L2	93.2	81.9	63.7	50.6	37.7
LSD (0.05)	*4.6*	*4.4*	*4.3*	*4.2*	4.3^{ns}

xx (not determined)

(means of fifteen values)

reactions with micronutrients during flooded (paddy rice) and moist aerated conditions (wheat) and flooded following moist (rice-wheat) and moist following flooded (wheat-rice) conditions. Results reported in experiments I & II will be discussed together in the following section in order to compare the effects of these alternate flooded / moist soil conditions on plant growth and nutrient status of soil and plants.

Plant height and dry matter yields of rice and wheat crops increased with the growth period. During the early stages of growth (after 2 weeks) paddy rice attained greater plant height and dry matter yields in comparison to the wheat plants. This might be due to the rice nursery which was transplanted after 4 weeks and had already gained some plant height and dry matter yields. Overall plant height and dry matter yields of wheat plants were greater than those found in the rice plants. Although greater levels of extractable soil P indicate that more P was available for rice plants than for the wheat plants, the dwarf nature of the rice variety might have restricted the gain in plant height and dry matter yields. Although, the nutrient phosphorus did not seem to be a limiting factor in the soil used for the trial, improvements in the heights of paddy rice and wheat plants with the application of P were associated with the greater levels of extractable soil P in P treated samples. It might be suggested that plants in soils even with "high" P levels (>15 μg P/g soil; Olsen and Dean, 1965) may respond, to some extent, to P additions and thus enhance the plant growth and probably the plant yield as well. Liming of the soil at 10% level in comparison to 5% level improved the plant height and dry matter yields of both paddy rice (non-significantly) and wheat plants (significantly) as reported in tables 6.1.1 & 6.1.2 and 6.2.1 & 6.2.2 respectively. Liming at 10% level caused increases in soil P extractability during wheat crop probably due to (i) increases in soil pH which may ultimately lower the activities of Fe-oxides. The solubility of Fe^{3+} ions which control the solubility of soil iron, has been reported to decrease 1000-fold for each unit increases in soil pH (Lindsay and Schwab, 1982). (ii) Original contents of $CaCO_3$ were about 5% in this soil (Table 3a) and lime application at 5% and 10% increased the levels approximately up to 10% and 15% respectively. The hydrolysis of $CaCO_3$ might have produced excess hydroxyl (OH^-) ions which precipitated with iron in the oxidizing environment and decreased its solubility (Olsen and Brown, 1980). Although, similar effects of greater lime level (10%) under paddy rice were observed, non-significant effects on plant height and dry matter yields under flooded rice conditions might be due to the reduction of Fe^{3+} to Fe^{2+} forms which would increase P availability under such conditions.

Decreases in extractable soil P under both paddy rice and wheat crops were observed with the growth period. Greater decreases in soil P in P treated samples might be attributed to the sorption of applied P under both conditions. Sorption of applied P varies from soil to soil depending upon the nature of soils and the soil conditions. Laverdiere and Karam (1984) have quoted a variety of soil properties, like hydrous oxides of Fe and Al, soil pH, clay content, soil organic matter and the interactive specific surface area, which have been identified as affecting the sorption of P in soils. Less sorption of applied P in rice soil, compared with the wheat soil, might be due to the reduced soil conditions which usually increase the availability of soil P (Patrick and Mahapatra, 1968; Ponnamperuma, 1972). The extent of increases may however, depend upon the combined effects of a number of factors like, the extent of soil reduction (Eh), decomposition of soil organic matter, the amounts and surface areas of $CaCO_3$, Fe and / or Al-oxides present in the soil, and also on the shifts in soil pH. The decreases observed in extractable soil P may also be attributed partly to uptake by plants. Uptake of P per pot was comparable with the "Olsen extractable soil P", at the final stages of growth. Slight increases and then decreases in the native soil P under rice conditions supported the effect of flooding followed by P uptake by the plants as growth proceeded. Addition of pyrophosphate (PP) at different proportions (10%, 20% & 30% of total applied P) with orthophosphate (OP), compared with the OP alone maintained greater levels of soil P, under both soil conditions. Pyrophosphate has been known to inhibit P adsorption and/or precipitation as DCPD crystals under calcareous conditions (Philen and Lehr, 1967; Marshall and Nancollas, 1969). The effects of adding pyrophosphate (PP) were greater during the growth of the wheat crop than during the rice crop. In rice soil, the lower effects might be due to hydrolysis of pyrophosphate to orthophosphate form as flooded conditions are reported to promote hydrolysis (Hossner and Phillips, 1971). Moreover, in flooded soil conditions, the solubility of phosphorus seemed to be controlled by Fe^{2+} ions rather than by the $CaCO_3$ contents as considerably greater Fe contents were observed in rice soil (figure 6.1.2) in comparison to wheat soil (figure 6.2.2). Addition of lime (5% & 10 % level) to wheat soil might have caused more increases in soil pH in wheat soil than in the rice soil, and considerably lowered the extractability of soil iron. This might also explain the query as to why greater P levels were found in the samples treated with 10% lime level. Lower levels of extractable soil P observed during the rice crop, in samples of soil previously used for wheat cultivation (4* & 8* weeks), might be due to the depletion of P by previous wheat crop. Uptake of P by previous wheat crop was about 50% of the "Olsen extractable P" per pot and this rice crop took up more P as growth proceeded. During the wheat crop, comparatively greater levels of extractable soil P, noticed at 4* & 8* weeks than at 4 & 8 weeks in the soil samples previously used for rice cultivation, might be due to the increases caused by flooded conditions during the previous rice crop.

Phosphorus contents in shoots and roots of paddy rice and wheat crops decreased with the growth period. After the first 2 weeks of growth, P contents in shoots (figure 6.2.3) and roots (figure 6.2.5) of wheat crop were greater compared with those in paddy rice (figures 6.1.3 & 6.1.5). Phosphorus contents in wheat samples compared with the rice samples decreased greatly with the growth period. These changes in P contents might be attributed to the greater sorption of applied P and to the greater gains in plant height and dry matter yields (dilution effects). In the flooded rice crop comparatively greater P contents in shoots and roots were maintained during the growth period. Flooded conditions and a smaller gain in plant height and dry matter yields might have favoured the rice crop maintaining greater levels of P in plant tissues. The overall decreases in P contents of shoots and roots of both crops with the growth period might be attributed to the "dilution effect". The effects of adding pyrophosphate (PP) on P contents of shoots and roots were also found to be similar in both soils (rice & wheat); showing greater P contents in pyrophosphate (PP) treated samples. However in wheat shoots, grown on the soil previously used for rice cultivation, lower P contents were observed in pyrophosphate (PP) treated samples. Addition of pyrophosphate (PP) caused increases in the extractability of soil Fe (figure 6.1.2) during the rice cultivation under flooded conditions. These increased levels of soil Fe might have precipitated, in amorphous forms, with soil P, under the moist conditions during wheat cultivation (figure 6.2.4). The formation of amorphous Fe^{III} oxides / hydroxides could take place due to the dissolution of crystalline Fe^{III} as Fe^{II} by reduction during flooding followed by subsequent oxidation and precipitation (Sah and Mikkelsen, 1986a), and would be expected to have larger surface area than crystalline Fe oxides (Borggaard, 1982). Sah and Mikkelsen (1986c,d) also reported that flooding and subsequent draining caused increases in amorphous Fe levels and P sorption. Greater level (10%) of applied lime caused decreases in the extractable levels of soil Fe either by increasing soil pH or by increasing its precipitation as reported earlier. Lower levels of extractable Fe probably helped the soil to maintain greater levels of P and P uptake by plants.

Flooded conditions have been known to increase the solubility of soil Fe. These increases might happen either due to decreases in soil pH of alkaline soils and/ or due to the reduction of Fe^{III} to Fe^{II} ions (Ponnamperuma, 1972; Willet *et al.*, 1986 and Willet, 1989); one of the most soluble forms of soil iron (Lindsay, 1979). Increases in extractable soil Fe and in Fe contents in rice shoots with the growth period might be attributed to the effects of flooded conditions, whereas in wheat soil, the extractable levels of soil Fe increased until 6 weeks and then decreased until 10 weeks of growth period. Application of P fertilizers might have caused decreases in soil pH (Adams, 1980; Bingham and Garber, 1960; Racz and Haluschak, 1974), resulting in increases in soil iron. Unfortunately the pH values in these trials were not recorded due to a large number of samples. In highly calcareous soils, lowering of soil pH, in general, due to applied P fertilizers might be impractical because the presence of $CaCO_3$ may buffer the soil system and minimize the possibility of changes in pH. However, pH changes in proximity to the fertilizer granule may take place and affect the solubility of Fe^{III} (Lindsay, 1979). Moreover, organic acids released by the roots of wheat plants might have also caused the reduction of Fe^{III} to Fe^{II} forms and thus increased their solubility. Pyrophosphate (PP) has been found to maintain lower levels of soil pH in calcareous conditions as reported in previous chapter (Chapter 5). Pyrophosphate also acts as a chelating agent (Giordano *et al.*, 1971; Mortvedt and Osborn, 1977) and has been reported to disperse soil and dissolve organic matter (Bar-Yosef and Asher, 1983; Bremner, 1949 and Mortvedt and Osborn, 1977) and thus increase the solubility of soil iron (Mc Keague, 1967; Mnkeni and Mackenzie, 1985 and Xie and Mackenzie, 1990b). These increases might happen either due to direct chelation of soil Fe by pyrophosphate (PP) or through organic acids /humic materials dissolved by pyrophosphate (PP). The greater levels of soil Fe and Fe contents of shoots and roots of paddy rice and wheat crops in pyrophosphate (PP) treated samples might be attributed to these properties of pyrophosphate (PP). The extractable levels of soil Fe and Fe content in shoots of wheat crop were lower in pyrophosphate (PP) treated samples at 4* & 8* weeks, i.e. in soil samples previously used for rice cultivation. These observations also support, as stated earlier, that the greater amounts of Fe released by pyrophosphate addition during flooded rice crop might have precipitated with soil P during moist aerated conditions. Decreases in Fe contents of roots with the growth period might be due to the movement of Fe from roots to shoots and / or to the dilution effect. Lower levels of soil Fe and Fe contents of shoots and roots of both paddy rice and wheat crops at 10% lime levels might be due to the increases in soil pH caused by the applied $CaCO_3$.

The effects of flooding have been reported to increase the solubility of soil Mn in addition to Fe. The increase might take place either due to the decreases in soil pH of calcareous soils or due to the reduction of Mn^{IV} and Mn^{III} to Mn^{II} under flooded conditions (Antil *et al.*, 1986 and Ponnamperuma, 1972). Flooded soil conditions during the rice crop caused increases in the extractability of soil Mn most probably due to the reduction of manganese compounds. Antil *et al.* (1986) and Ponnamperuma (1972) found that increases in Mn concentration, due to submergence of 2 weeks, were followed by decreases as flooding proceeded. The results reported by them correspond to acidic soils rich in Mn and organic matter. In the present study, increases in soil Mn were observed until 6 weeks followed by decreases until 10 weeks (table 6.1.3a). The results are also supported by the findings of Mandal and Haldar (1980). They performed incubation experiments on soils with pH>7 (7.85-8.00) and reported increases in soil Mn until 45 days followed by decreases until 95 days. Flooded conditions not only established the greater levels of extractable soil Mn throughout the growth but greater levels of Mn contents in rice shoots and roots were also noticed. Increases in the extractable soil Mn were also observed in wheat soil with the growth period, however, the contents were considerably lower in soil, wheat shoots and roots compared with those during flooded rice conditions. The increases in soil Mn under wheat crop could not be easily explained because the moist aerated conditions should adversely affect the solubility of soil Mn, and Mn-phosphate compounds ($MnPO_4 . 1.5H_2O$) of low solubility may form (Boyle, Jr. and Lindsay, 1986). The changes in soil pH, in the root rhizosphere, due to organic acids released by wheat roots and the complexing activity of the organic acids themselves might have played important roles in increasing the solubility of soil Mn. Increases in soil Mn due to applied P fertilizers might by attributed to the lowering of soil pH, to some extent, which increased the extractability of soil Mn and its uptake by plants. As the solubility of Mn^{2+} is pH dependent, its concentration may increase with the application of phosphate fertilizers having acidic reactions. The decreased soil pH associated with high P rates can account for increased Mn uptake by plants (Larsen, 1964; Page *et al.*, 1963 and Smilde, 1973). In contrast to this P fertilizers may decrease Mn uptake by plants (Heintze, 1969; Racz and Haluschak, 1974). Since P fertilizers are not likely to affect the pH of calcareous or highly buffered soils, P application should not increase solubility of Mn in such soils as there would be little or no effect on soil pH (Adams, 1980). It can be concluded that P may not directly lower soil pH in calcareous conditions but it may enhance release of organic acids, through increased plant growth, and may increase Mn extractability. Pyrophosphate (PP) additions to orthophosphate (OP) over the OP alone were more effective in increasing Mn availability, probably by lowering solution pH, and its subsequent uptake by both paddy rice and wheat plants. Increases observed in extractable soil Mn during flooded rice crop from 4* to 8* weeks in the soil samples previously used for wheat cultivation might also be due to the reduction of Mn compounds. During wheat crop, the extractable soil Mn, in samples previously subjected to flooded conditions under rice crop, increased from 4* to 8* weeks. However, extractable soil Mn after 8* weeks was less than that found after 8 weeks suggesting that the depletion of soil Mn took place during the previous rice crop. Liming of the soils at 10% level compared with at 5% level again caused decreases in extractable soil Mn during both rice and wheat crops probably due to increases in soil pH. The solubility of soil Mn, like Fe has been reported to be highly pH dependent and 100 fold decreases in Mn activity have been found with the each unit rise in soil pH (Lindsay, 1979).

Extractable soil Cu behaved differently under rice and wheat crops. During rice crop, soil Cu increased whereas it decreased with the growth period during wheat crop. Flooded conditions during rice cultivation might have increased soil Cu either by increasing its solubility in association with organic acids of small molecular size or by decreasing soil pH. The effect of flooded conditions was similar in increasing soil Cu from 4* to 8* weeks in the soil samples previously used for wheat cultivation. Total Cu contents in rice shoots and roots decreased with the growth period which might be attributed to the "dilution effect" as growth proceeded. Decreases in soil Cu in wheat soil and wheat soil following a rice crop (4* & 8* weeks) might be attributed to the transformations into insoluble forms of Cu compounds, perhaps with larger molecular weight insoluble humic organic materials, with time. Moreover, as the growth proceeded, more soil Cu was probably taken up by wheat plants causing decreases in the levels of soil Cu. Uptake of Cu by wheat plants increased from 1% to 3% and 1% to 2% of the DTPA soil Cu per pot as growth proceeded from 4 to 10 weeks and from 4* to 8* weeks respectively. Greater levels of soil Cu observed in P treated samples might be due to the effects of applied P fertilizers in lowering soil pH. In addition, some Cu-P compounds of greater solubility might have formed which increased the solubility of soil Cu. Lindsay (1979) reported that copper phosphates e.g. $Cu_3(PO_4)_2$ & $Cu_3(PO_4)_2.2H_2O$ are more soluble than soil-Cu especially as phosphate solubility is depressed by hydroxyapatite. These copper phosphates can dissolve sufficiently in soils to provide both available copper and phosphorus for plants. Greater lime levels (10%) again caused decreases in the extractability of soil Cu and its subsequent uptake both by paddy rice and wheat plants, probably due to increases in soil pH.

Flooded conditions have been reported to decrease or increase soil Zn. The effects may vary from soil to soil and with the soil conditions. Application of small amounts of Zn in rice growing areas of the world have been a continuous practice for the last few decades. Decreases in Zn contents observed in rice soil (table 6.1.3a) might have several causes. Increased levels of soil phosphorus, due to flooding might have adversely affected the extractability of soil Zn in rice soil and rice soil following a wheat crop (4* & 8* weeks). Moreover, the continuous uptake of Zn by rice plants might also have lowered its availability as the growth proceeded. Similar results regarding Zn extractability have been reported by Haldar and Mandal (1979). They observed sharp decreases in extractable Zn during flooding and attributed them to the antagonistic effects of increased levels of soil P, Fe and Mn. This "antagonism" should also take place with the application of P fertilizers and the extractability of Zn should decrease, whereas in the present study, during rice crop, addition of P increased the extractability of soil Zn, suggesting that some other mechanism might be involved. A number of factors might be involved which may increase soil Zn during flooded conditions e.g. (i) decreases in soil pH due to flooding (ii) application of P fertilizers might have stimulated root development and the demands for Zn uptake, encouraging the release into solution of soil Zn (iii) increases in the amounts of organic acids released by roots and/or microorganisms which may lower soil pH and increase the extractability of soil Zn (iv) the direct chelation of Zn by organic anions and (v) formation of $Zn_3(PO_4)_2$ which are reported to be much more soluble than normal soil Zn and a good source both for Zn and P (Lindsay, 1972). Significant increases in the extractability of soil Zn, in pyrophosphate (PP) treated samples were expected due to PP's roles in dispersing soil, dissolving organic matter and chelating micronutrients (Bar-Yosef and Asher, 1983; Bremner, 1949 and Mortvedt and Osborn, 1977). In contrast to rice, during the wheat crop addition of P (OP), decreased soil Zn in comparison to control samples (no P) suggesting that some interaction among soil P and Zn might have taken place. Precipitation of P and Fe^{III} might take place during moist aerated conditions as reported earlier. The possible formation of Fe-P-Zn complexes might take place under specific conditions (Lindsay, 1979 and Gupta, *et al.*, 1987) and decrease the solubility of Zn. Stanton and Burger (1966) reported that Zn bound to hydrated Fe oxides in soil through the medium of polyvalent P ions is unavailable to plants. Pyrophosphate (PP) treated samples were, however, able to maintain greater levels (non-significant at $p<0.05$) of soil Zn, probably due to chelation, soil dispersion and or due to the dissolution of organic matter. Moreover, pyrophosphate (PP) when added with OP has been shown to maintain lower pH values (chapter 5), which may also increase the extractability of soil Zn. Addition of greater lime level (10%) compared with 5% level probably increased the pH values even in the microniches within the soil and decreased the extractability of soil Zn. Lower levels of Zn in the samples previously used for rice and wheat crops (4* & 8* weeks) might be due to the depletion by the previous crops.

6.6 Conclusions

Increases observed in the extractability of native soil P during the first 6 weeks of flooded paddy rice growth were followed by decreases, probably caused by plant uptake and/ or due to resorption of P released during initial flooding. Extractable soil Fe, Mn, and Cu also increased with the flooded conditions and extractable soil Zn decreased.

Moist aerated conditions, during the wheat crop, caused decreases in the extractability of soil P and Mn throughout the growth period. Extractable soil Fe and Zn increased during 2 to 10 weeks and decreased during 4* to 8* weeks and soil Cu decreased during 4 to 10 weeks and increased during 4* to 8* weeks. Decreases in the extractability of applied P with or without pyrophosphate (PP) were observed, with the growth period, during both paddy rice and wheat crops. These decreases were greater during wheat crop indicating that moist aerated conditions stimulated sorption of P. Applied P with or without pyrophosphate (PP), significantly ($p<0.05$) improved plant height of both paddy rice and wheat crops and dry matter yields of wheat crop throughout the growth period, compared with the control samples. Extractable soil Fe, Mn and Cu increased with the application of P (OP). Addition of pyrophosphate (PP) in different proportions with OP caused further increases in the extractability of these elements. Extractable soil Zn decreased with applied P (OP) whereas it slightly increased with the addition of pyrophosphate (PP).

Phosphorus, Cu and Zn concentrations in shoots and roots of both paddy rice and wheat plants decreased throughout the growth period. Iron and Mn concentrations in rice shoots and Mn concentrations in rice roots increased. Iron concentrations in paddy rice and wheat roots and wheat shoots decreased and Mn concentrations in wheat shoots and roots increased from 2 to 10 weeks and decreased from 4* to 8* weeks (wheat shoots). Applied P with or without added pyrophosphate (PP) increased P concentrations in shoots and roots of both paddy rice and wheat crops. These increases were greater in the presence of pyrophosphate (PP). Overall effects of applied P were to increase the concentrations of Fe, Mn and Cu in shoots and roots of both crops; with greatest increases being observed in the presence of pyrophosphate (PP). Iron concentrations in wheat shoots, however, decreased from 4* to 8* weeks growth period, which were probably due to precipitation of Fe, released during previous flooded rice crop, during moist aerated conditions. Zinc concentrations in rice shoots and roots significantly ($p<0.05$) increased, over control samples (A0B0), with the application of P with or without pyrophosphate (PP). In wheat shoots applied P (OP) caused decreases in Zn concentrations over controls (A0B0) whereas applied pyrophosphate (PP) caused significant increases. Although applied pyrophosphate (PP), slightly increased Zn concentrations in roots of wheat plants, compared with OP alone, both forms of applied P decreased Zn concentrations in comparison to controls (A0B0).

Application of greater level of lime (10%) significantly ($p<0.05$) improved the plant height and dry matter yields of wheat plants. Extractable soil Fe, Mn, Cu and Zn and concentrations of these elements in shoots and roots of both paddy rice and wheat plants decreased significantly ($p<0.05$) throughout the growth period.

CHAPTER

7

Chapter 7: Roles of Phosphorus, Zinc and their Interaction

7.1. Introduction

Phosphorus plays an important role in plant nutrition, supporting life processes like photosynthesis, building and metabolism of carbohydrates, energy transfer and genetic reproduction. In calcareous soils adsorption on $CaCO_3$ surfaces and the precipitation of insoluble Ca-P compounds would greatly reduce plant available P. The reactivity of $CaCO_3$ on its surface area increases as effective $CaCO_3$ particle size distribution decreases (Holford and Mattingly, 1975b).

Zinc plays some important roles in protein synthesis, numerous enzymatic functions, production of chlorophyll and RNA. It is absorbed by plants by an active process that is influenced by biological and environmental factors (Bowen, 1969). In soils that are derived from limestone or calcareous sandstone, Zn content tends to be quite low (<150 ug g^{-1} of soil) (Wedephol, 1978). However plant Zn cannot be estimated from the total soil Zn. Although reactions of Zn with $CaCO_3$ in calcareous soils are the main cause of Zn deficiency, P induced Zn deficiency is also known to be common in plants. Phosphatic fertilizers have been identified as responsible for the induction or accentuation of Zn deficiency symptoms in some crops (Burleson, *et al.*, 1961; Ellis, *et al.*, 1964; Ward, *et al.*, 1963). The early suspicion that P-induced Zn deficiency resulted from precipitation of $Zn_3(PO_4)_2$ in the soil or on the roots was convincingly demolished by solubility experiments (Boawn, *et al.*, 1954; Jorinak and Inoye, 1962), by Zn source experiments (Boawn, *et al.*, 1954; 1957), and by extraction experiments (Bingham and Garber, 1960; McLean, 1974; Pauli, *et al.*, 1968; Racz and Haluschak, 1974). The solubility of $Zn_3(PO_4)_2$ is more than adequate to supply Zn to plants. Zinc phosphate is an effective Zn fertiliser and higher P rates generally increase extractable soil Zn. Olsen (1972) considered Zn deficiency a dilution effect as a result of stimulated growth caused by phosphorus application in P deficient soils. Barrow (1987) detected two ways by which fertiliser P can affect Zn sorption, on one hand by the effect of P in altering soil pH, depending upon the type of P fertilisation and its effect on the direction of pH changes (Barrow, 1987, Shuman 1988), and on the other hand by the effect of P sorption increasing the number of reactive sites for Zn sorption (Barrow, 1987; Xie and Mackenzie, 1989b). Some other studies reported that P-Zn interaction was a plant physiological phenomenon due to the interference of the two at the root surface absorption sites or in translocation within the plant (Burleson, *et al.*, 1961; Burleson and Page, 1967; Khan and Zende, 1977; Stukenholz, *et al.*, 1966; Warnock, 1970).

Barrow (1987) suggested four mechanisms in the soil when phosphorus fertiliser is added to the soil. (I) The reaction itself may change the pH due to release of hydroxide ions from the soil surface into the soil solution to maintain charge balance. (II) Phosphatic fertilisers which are acidic in nature can reduce soil pH. (III) Phosphate may induce indirect changes in pH through stimulated plant growth and nitrogen fixation (Williams, 1980; Bromfield, *et al.*, 1983), and (IV) contamination of phosphate fertiliser with Zn.

It is evident that increasing the inorganic phosphate availability in soil solution can depress Zn concentration in plants and induce zinc deficiency (Robson and Pitman, 1983). The most adverse effects appeared to occur when high levels of P were applied in the presence of low or deficient levels of Zn and led to increased inorganic phosphorus in the solution. This has been known as P-induced Zn deficiency. Increasing P in the soil solution depressed Zn concentration in plants and induced a true Zn deficiency (Robson and Pitman, 1983), enhanced the physiological requirements for Zn (Millikan, *et al.*, 1968; Cakmak and Marschner, 1987) and inactivated Zn in the plant tissues (Olsen, 1972; and Lecce, 1978).

Polyphosphates have been found to sequester metallic ions and form stable complexes which might increase micronutrient availability to plants. Giordano, *et al.* (1971) and Mortvedt and Osborn (1977) found that adding greater concentrations of polyphosphates to acid soils had only a temporary effect (3-4 weeks) in solubilising micronutrients while they did not alter calcareous soils even one day after application.

Al-Showk, *et al.*, (1987) conducted incubation experiments with different sources of orthophosphates and ammonium polyphosphate (APP) in two calcareous soils and reported no effect on DTPA-extractable Zn even after two months. Effect of pyrophosphate (PP) on Zn solubility can be summarised as (i) PP increases Zn solubility through the chelating effect (Bar-Yosef and Asher, 1983; Giordano, *et al.*, 1971; and Mortvedt and Osborn, 1977), and the effect is more significant at high pH (>8) while in most agricultural soils where the pH value is within a range of 5-8, the effect is limited due to rapid hydrolysis of PP (Dick and Tabatabai, 1986). (ii) PP has no effect on Zn solubility (Friesen *et al.*, 1980) and (iii) it decreases Zn solubility through increasing Zn specific sorption at constant initial pH (Giordano, *et al.*, 1971; Shield, *et al.*, 1978; Xie and Mackenzie, 1988) or increasing iron solubility and forming Fe-Zn precipitates (Mc Keague, 1967; and Pulford, 1986).

In soils, there exist shifts of $H_4P_2O_7 \rightarrow H_3P_2O_7^- \rightarrow H_2P_2O_7^{2-} \rightarrow HP_2O_7^{3-} \rightarrow P_2O_7^{4-}$ and $Zn^{2+} \rightarrow ZnOH^+ \rightarrow Zn(OH)_2$ as solution pH increases (Lindsay, 1979), the shifts are in reverse direction as pH decreases. Moreover PP has capacity to solubilize Fe and Al (Mnkeni and Mackenzie, 1985), to disperse soil more than OP and to dissolve organic matter (Mortvedt and Osborn, 1977). This capacity could mobilise micronutrients such as Zn, since soluble organic matter forms stable complexes with Zn (Hodgson, *et al.*, 1966), complexed Zn could be less subject to sorption by soil mineral components.

7.2. Incubation Studies

7.2.1. Aims of the experiment:

Incubation experiments were performed under conditions of flooding (Pen-y-Ffridd soil) and flooded and moist aerated conditions (Pakistani soil). Behaviour of P and Zn were investigated during these studies. Soil samples from a site near Pen-y-Ffridd Research Station and a soil from Pakistan were selected. Physical and chemical characteristics of these soils are given in tables 3a & b (chapter 3).

7.2.2. Treatments and Incubation Methods

7.2.2a. Pen-y-Ffridd soil

Soil was taken from the pots previously used for a wheat crop (chapter 6) and had 5% lime treatment on weight basis. No phosphate had been added to this soil during the wheat experiment. Treatments were as follows

(1) P0Z0	(2) P1Z0	(3) P2Z0	(4) P3Z0
(5) P0Z	(6) P1Z	(7) P2Z	(8) P3Z

P & Z represent Phosphate source & Zinc sulphate respectively

P0 = 0 ug P/g soil as OP (orthophosphate), P1 =100 ug P/g soil as OP

P2 =100 ug P/g soil as KPP (potassium pyrophosphate)

P3= (80 ug P/g soil as OP + 20 ug/g soil as KPP)

Z0 and Z1 are 0 and 100 ug Zn/g soil respectively.

Soil samples (10g) were put to 125 ml plastic bottles there being three replicates for each treatment. Solutions of each treatment were prepared and applied to their respective bottles. Final volume in the bottles was made up to 15 ml with distilled water to achieve submerged/ flooded conditions. Weight of each bottle was recorded. The bottles were then sealed and kept at room temperature (22± 2°C) for 10 days. After 10 days distilled water was added to attain a final 50 ml water in each bottle. The bottles were shaken overnight (18 hours approx.) on a horizontal shaker, centrifuged and filtered through Whatman no. 1 filter paper. The filtrate was kept for P and Zn analyses. The samples in the bottles were then extracted with 0.5N NaOH + 1M NaCl (1M NaCl was added to stop interference due to cloudiness by NaOH during P determination) after overnight shaking, centrifuged and filtered. Phosphorus was determined by spectrophotometer and Zn by atomic absorption.

7.2.2b. Pakistani Soil

The effects of flooded and moist incubations on the status of applied P and Zn were investigated for two and four week periods using a Pakistani Soil (see table 3a & b, chapter 3).

Soil was treated as follows

(1) P0Z0 (2) P0Z1 (3) P0Z2 (4) P1Z0 (5) P1Z1 (6) P1Z2
(7) P2Z0 (8) P2Z1 (9) P2Z2 (10)P3Z0 (11)P3Z1 (12)P3Z2

P = source of phosphate fertiliser, Z = zinc sulphate

Z1 and Z2 = 25 and 50 ug Zn/g soil respectively

P0 = 0 ug P/g soil as OP, P1 = 100 ug P/g soil as OP, P2 = 200 ug P/g soil as OP

P3 = OP(180) + PP(20) = a total of 200 ug P/ g soil

* PP = sodium pyrophosphate (NaPP)

Soil samples (5g) in triplicate were added to plastic bottles (65 ml vol.). Phosphate and Zn solutions were applied to the respective bottles. Final volume of 5 ml was attained in flooded samples with the addition of distilled water and that of 0.5 ml for the moist samples. The samples for moist incubations were dried by injecting air into the plastic bottles. The weight of each bottle was recorded. Bottles with flooded samples were sealed while those with the moist samples were kept open and the moisture contents were corrected after alternate days. Samples were then transferred to the incubator adjusted at $32^{o}C\underline{+}1$ for 2 and 4 weeks. The bottles were taken out after the required period, extracted with NH_4HCO_3-DTPA solution (Soltanpur and Schawab, 1977) by using appropriate concentrations to gain a final concentration of 0.05N NH_4HCO_3-DTPA solution in each bottle (soil to extractant ratio 1:4). Samples were shaken at 180 cycles per minute for 15 minutes, centrifuged, filtered and extractable-P was determined (Watanabe and Olsen, 1965) with spectrophotometer using 880 nm incident light and Zn by atomic absorption spectrophotometer.

7.3. Results

7.3.1. Pen-y-Ffridd Soil

Results regarding P and Zn interactions in soil samples from Pen-y-Ffridd area for 10 days flooded incubation are presented in table 7.1. Data on P behaviour are presented in H_2O and 0.5N NaOH extracts of soil. No detectable Zn was found in H_2O extracts, hence for Zn it is presented in 0.5N NaOH extract of soil only (table 7.1).

Table 7.1: Effects of applied P and Zinc on the behaviour of P (ug/g soil) and Zn (ug/g soil) in a soil from Pen-y-Ffridd during flooded incubations

	H_2O-P		0.5N NaOH-P		0.5N NaOH-Zn	
Treatments	Z0	Z	Z0	Z	Z0	Z
P0	2.54	0.92	226.98	251.00	0.911	44.21
P1 (OP)	3.27	2.08	267.39	297.26	1.105	44.56
P2 (PP)	3.09	1.56	257.44	274.42	1.156	45.22
P3 (OP+PP)	3.96	2.02	268.53	285.55	1.105	44.31
L.S.D (0.05)	(0.181)	(0.129)	(8.75)	(11.82)	(0.148)	(0.542)

Application of P in different forms with or without Zn significantly ($p<0.05$) increased solution P compared with control (P0) in both H_2O and 0.5N NaOH-extracts of soil. Addition of Zn (100 ug/g of soil) caused decreases in H_2O-soluble P and increases in 0.5N NaOH extractable-P in all the treatments.

Water failed to extract detectable amounts of Zn both in the absence and presence of Zn treatment, hence the 0.5N NaOH extracts were used for Zn determination. Application of P in different forms in the absence of Zn extracted significantly ($p<0.05$) more soil Zn than P0 treatment but in the presence of added Zn only PP treated samples extracted significantly ($p<0.05$) more Zn compared with the other treatments.

7.3.2. Pakistani Soil

Phosphorus behaviour in a Pakistani soil with different P and Zn levels under flooded and moist incubations of 2 and 4 weeks is presented in tables 7.2, 7.3, 7.4 and 7.5 respectively. Extractable soil P irrespective of moisture regime was found to be greater at 2 weeks and it decreased at 4 weeks of incubation. Samples incubated moist showed greater decreases in extractable soil P than the flooded incubated samples. Application of P at different levels significantly ($p<0.01$) increased extractable soil P compared with the control (P0) samples throughout the flooded and moist incubations, the flooded incubated samples showing greater P levels than the moist incubated samples. Application of different levels of Zn did not cause significant ($P<0.01$) changes in extractable P during 2 weeks of flooded incubation whereas Z2 treatment in comparison to control (P0) maintained significantly greater levels of extractable P after 4 weeks of flooding. During moist incubations of 2 and 4 weeks, applied Zn in comparison to Z0, increased the extractability of soil P.

Inclusion of 20% potassium pyrophosphate (KPP) with OP significantly increased ($p<0.01$) extractable soil P during flooded (2 & 4 weeks) and moist (2 weeks) incubations but during 4 weeks of moist incubation KPP addition resulted in a significantly lower extractable P in comparison to OP treatment. The decreases in P

Table 7.2: Effects of applied P and Zn on P availability (ug/g soil) in a Pakistani soil during 2 weeks of flooded incubation

Treatments	P0	P1	P2	P3	Means
Z0	35.47 ab	71.54 d	97.38 e	161.81 j	91.55 x
Z1	33.39 a	67.17 c	105.01 g	159.18 i	91.87 x
Z2	30.99 a	71.96 d	102.44 f	154.42 h	89.52 x
Means	33.28 A	70.22 B	101.61 C	158.47 D	

Table 7.3: Effects of applied P and Zn on P availability (ug/g soil) in a Pakistani soil during 4 weeks of flooded incubation.

Treatments	P0	P1	P2	P3	Means
Z0	33.54 ab	69.44 e	94.68 g	118.12 h	78.945 x
Z1	31.91 a	65.96 d	87.20 f	142.33 i	81.85 xy
Z2	29.98 a	62.93 c	94.37 g	148.38 j	83.92 y
Means	31.81 A	66.11 B	92.09 C	136.28 D	

* values with same letters do not differ significantly at 1% level

Table 7.4: Effects of applied P and Zn on P availability (ug/g soil) in a Pakistani soil during 2 weeks of moist incubation

Zn levels	P0	P1	P2	P3	Means
Z0	23.75 ab	67.34 d	87.59 e	122.23 h	75.23 x
Z1	22.58 a	63.31 c	95.02 g	126.57 j	76.87 xy
Z2	27.01 b	68.49 d	93.27 f	121.36 h	77.54 y
Means	23.78 A	64.71 B	91.96 C	123.39 D	

Table 7.5: Effects of applied P and Zn on P availability (ug/g soil) in a Pakistani soil during 4 weeks of moist incubation

Zn levels	P0	P1	P2	P3	Means
Z0	16.55 a	54.02 c	77.56 f	78.30 f	56.61 x
Z1	20.80 b	58.84 d	82.90 g	73.50 e	59.01 y
Z2	18.83 ab	59.56 d	84.29 g	72.47 e	58.79 y
Means	18.72 A	57.47 B	81.58 D	74.75 C	

* values with same letters do not differ significantly at 1% level

availability in P0, P1, P2 and P3 treatments from 2 to 4 weeks in flooded incubation were 4%, 6%, 9% and 14% and in moist incubation were 21%, 11%, 11% and 39% respectively. Addition of 20% KPP with OP resulted in increases of 56% and 48% in extractable soil P over OP during 2 and 4 weeks of flooded incubations respectively. During 2 weeks of moist incubations this increase was 34% whereas the reduction in P due to KPP addition after 4 weeks of moist incubation was 9% against OP treatment.

The effects of applied P and Zn on extractable soil Zn during 2 and 4 weeks of flooded and moist incubations are presented in tables 7.6, 7.7, 7.8 and 7.9 respectively. Application of different levels of Zn significantly ($p<0.01$) increased extractable soil Zn in flooded and moist incubated samples. The increases were greater in flooded than in the moist samples. Application of various P treatments significantly ($p<0.01$) lowered the extractability of Zn compared with P0 treatment after 2 weeks of flooded incubation. The maximum decrease was observed in the OP+PP treatment. A reverse effect of P treatments was observed after 4 weeks of flooded incubation showing significantly ($p<0.01$) greater Zn levels in P treated samples. In moist incubated samples slight increases in extractable soil Zn were observed from 2 to 4 week periods except in OP+PP (P3) treatment (4 weeks incubation) where a decrease in soil extractable Zn was observed.

7.4. Discussion

7.4.1. Pen-y-Ffridd soil

Addition of phosphorus to Pen-y-Ffridd soil significantly ($p<0.05$) increased water extractable-P during 10 days of flooded incubation showing comparatively more increases in all the treatments where no Zn was applied. Addition of PP to OP (P3Z0) increased extractable P compared with P0Z0, P1Z0 and P2Z0 treatments. This increase in H_2O soluble P may be related to the more rapid sorption of PP, due to multiple charge, on the sorption sites compared with OP and decreasing OP reaction with active sites on soil particles. Similar increases in solution-P with the addition of PP have been reported by Amer and Mostafa, (1981) and El-zahaby and Chien (1982). In the presence of Zn, the increases in H_2O soluble P were less which could be due to the possible formation of less soluble soil-phosphate-Zn complexes. However, P treated samples in the presence of Zn showed significant increases ($p<0.05$) in H_2O soluble P over the control (P0). The treatments P1Z and P3Z did not differ significantly and about a 50% reduction in water soluble P in PP treated samples occurred in the presence of Zn, perhaps reflecting the chelation of Zn by PP due to its sequestering properties. The results are contrary to Bremner (1949) and Mortevdt and Osborn (1977) who reported that the soil solution Zn increased with the application of ammonium pyrophosphate (NH_4-PP) and they attributed the enhanced concentration to the dissolution of organic matter which complexes Zn. But the probability of sequestration by PP itself cannot be discounted. However decreases in Zn desorption, or increases in Zn sorption, with PP were reported by Xie and Mackenzie (1990a). They concluded that PP was more effective in complexing Zn than OP. In 0.5N NaOH extracts of soil, P treatment significantly increased ($p<0.05$) extractable-P over control (P0) irrespective of Zn treatment. In the Zn treated soil, the treatments OP and OP+PP did not differ significantly, however PP treated samples showed a significant decrease ($p<0.05$) in solution-P which could be result of incomplete hydrolysis of PP to OP during this period. In the presence of Zn, although P1 (OP) and P3 (OP+PP) treatments did not vary significantly, OP treated samples had greater extractable P concentration than OP+PP treated samples. Pyrophosphate treated samples (P2Z) showed significantly lower P extractability than OP but not significantly different from OP+PP.

The concentration of Zn in H_2O-extracts was too low to be detected with the instrumentation available in Bangor so 0.5N NaOH extracts were analysed for Zn. In the absence of Zn slightly greater concentrations of Zn were observed with PP treated soil than in OP and OP+PP treatments. All the treatments gave significantly ($p<0.05$) greater values of Zn than the control (P0), they did not however, differ significantly from each other. In the presence of added Zn, the treatments P0Z, P1Z and P3Z did not differ significantly in terms of extractable soil Zn, extractable Zn in P2Z treatment was however found to be significantly greater ($p<0.05$) than the other treatments. This could be related to the ability of NaOH to extract PP-bound Zn. Moreover PP might have dissolved some of the organic matter, causing an increase in the organically bound Zn which was extracted by NaOH. The results are in agreement to those of Xie and Mackenzie (1988). They reported increases in Zn_{NaOH} (NaOH extractable-Zn) by the addition of P and PP and they attributed this increase to the Zn specifically adsorbed on Fe & Al hydroxides and on organic matter.

7.4.2. Pakistani Soil

The response of P application to a Pakistani soil was greater during flooded than the moist incubations. Lower extractability of P during moist aerated incubations (tables 7.4 and 7.5) compared with the flooded incubations (tables 7.2 and 7.3), was probably due to greater sorption of applied P. Decreases in P availability were not only observed in the P treated samples but P availability also decreased in the control samples (P0). These decreases were again greater in the moist aerated samples which probably favoured the transformation of P into insoluble compounds. Addition of 10% pyrophosphate (PP) of the total applied P increased the extractability of soil P. Pyrophosphate (PP) increased the extractability of P, over P0, P1 and P2, probably by lowering pH of the soil or by occupying the sites for P sorption. Decreases in P observed in P3 treatment, at 4 weeks of moist incubations, were probably due to precipitation of P with Fe and/ or Al oxides, dissolved by pyrophosphate (PP) (Mnkeni and Mackenzie, 1985).

Increases in the extractability of Zn, due to P (OP) application, were observed during 4 weeks of flooding (table 7.7) and decreases during 2 weeks of moist incubations (table 7.8). Lower levels of Zn extractability at 2 weeks of flooding were probably due to sorption of applied P, to maintain equilibrium in solution, which resulted in the formation of soil-P-Zn complexes. Increases in the extractability of soil P at 4 weeks of flooding might be due to several factors (i) release of Zn from the soil-P-Zn complexes (ii) decreases in pH caused by flooding, increased the solubility of Zn (iii) organic acids were

Table 7.6: Effects of applied P and Zn on Zn availability (ug/g soil) in a Pakistani soil during 2 weeks of flooded incubation

Zn levels	P0	P1	P2	P3	Means
Z0	1.96 a	2.27 a	1.80 a	1.75 a	1.95 x
Z1	24.23 b	26.31 c	25.39 c	23.62 b	24.89 y
Z2	43.27 e	27.16 d	27.62 d	24.46 bc	30.63 z
Means	23.15 C	18.58 B	18.27 B	16.61 A	

Table 7.7: Effects of applied P and Zn on Zn availability (ug/g soil) in a Pakistani soil during 4 weeks of flooded incubation

Zn levels	P0	P1	P2	P3	Means
Z0	3.65 a	4.08 a	3.96 a	4.00 a	3.92 x
Z1	20.30 b	26.47 d	25.62 d	23.31 c	23.92 y
Z2	21.07 b	26.78 d	25.62 d	24.00 cd	24.37 y
Means	15.01 A	19.11 D	18.40 C	17.10 B	

* values with same letters do not differ significantly at 1% level

Table 7.8: Effects of applied P and Zn on Zn availability (ug/g soil) in a Pakistani soil during 2 weeks of moist incubation

Zn levels	P0	P1	P2	P3	Means
Z0	1.80 a	1.79 a	1.71 a	1.79 a	1.78 x
Z1	6.74 b	9.74 c	6.81 b	10.36 c	8.43 y
Z2	15.75 e	16.14 e	13.44 d	20.07 f	16.35 z
Means	8.10 B	9.22 C	7.35 A	10.74 D	

Table 7.9: Effects of applied P and Zn on Zn availability (ug/g soil) in a Pakistani soil during 4 weeks of moist incubation

Zn levels	P0	P1	P2	P3	Means
Z0	3.67 b	3.64 b	3.58 b	2.34 a	3.31 x
Z1	10.13 e	9.20 e	9.82 e	5.27 c	8.61 y
Z2	19.99 g	17.06 f	17.60 f	7.12 d	15.45 z
Means	11.26 D	9.97 B	10.33 C	4.91 A	

* values with same letters do not differ significantly at 1% level

produced during flooded incubations which increased the solubility of Zn, either by lowering soil pH or by complexing with Zn. It has been reported that Zn sorption on soils is very much dependent on pH of the soil. For example 92% of the variation in Zn uptake from fertilizer could be attributed to pH (Lindsay, 1972). The large decreases in Zn availability with increases in pH suggests pH solubility of common Zn compounds such as $Zn(OH)_2$, $ZnCO_3$ or Zn SiO_3 (Tagwira, *et al.*, 1993). He reported 100% and 34% increases in Zn adsorption in the Chiota and Gwebi soils respectively per unit rise in pH.

Pyrophosphate (PP) addition to orthophosphate (OP) increased the extractability of Zn at 2 weeks of moist incubations. These increases were probably due either to formation of PP-Zn complexes, to decreases in pH caused by added PP, or to the dissolution of organic matter (Mortvedt and Osborn, 1977), which would ultimately complex Zn. Decreases observed in the extractability of Zn in P3 treatment (table 7.9) at 4 weeks of moist aerated incubations might have been due to the precipitation of Fe and /or Al, released by PP (Mnkeni and Mackenzie, 1985), probably in the form of Fe-P-Zn. Lower levels of extractable P in P3 also supported this assumption (table 7.5). Hydrolysis of applied pyrophosphate (PP) probably took place during that period, which favoured such precipitation. Added Zn probably increased the extractability of soil P either by lowering soil pH or by making soluble compounds like $Zn_3(PO_4)_2$ (Boawn, *et al.*, 1954; Jorinak and Inoye, 1962).

7.5. Sorption Studies

7.5.1. Sorption of P and Zn under Calcareous Conditions

7.5.1.1. Aims of the experiment

In this experiment agricultural lime ($CaCO_3$) was used to assess the sorption of applied P and Zn. Orthophosphate (OP) and sodium pyrophosphate (NaPP) were used in the presence of Zn. The effects of organic acids on sorption of P and Zn were also investigated.

Treatments were as follows

(1) P1Z (2) P2Z (3) P3Z (4) P4Z (5) P5Z

P = Phosphate source , Z = Zinc sulphate

P1 = 0.05M OP solution , P2 = 0.045M OP solution + 0.0025M NaPP solution

P3 = 0.045M OP solution + 55 ml of rice straw extract*

P4 = 0.05M OP solution + Chelex resin extract of soil**

P5 = 0.045M OP solution + 0.0025M NaPP solution + Chelex resin extract of soil,

Zinc = 20 ug/ml of solution

* Method for the extraction of rice straw see 7.5.2.3.1

**Method for extraction of soil by the resin see 5.2.1.4

7.5.1.2 Materials and Methods

Solution (1000 ml) for each treatment was added to 1.5 litre polycarbonate bottles. Initial pH and soluble-P contents of each solution were determined. Agricultural lime (25g) was added to each bottle. The bottles were tightly sealed and attached to the end to end shaker. Continuous shaking was done so that an equilibrium could be established between solution P and $CaCO_3$ particles. Samples (10 ml) of the suspension were collected in centrifuge tubes after 6, 24, 48, 72, 120, 168, 216, 364, and 412 hours. They were centrifuged at 3000 revolutions per minute for 10 minutes and filtered through Whatman no. 1 filter paper and pH values of the aliquots were recorded. Phosphorus in solution was measured by ascorbic acid method (Olsen, 1965) and Zn by using atomic absorption. Organic carbon in treatment numbers 3, 4 and 5 was also measured (section 2.9, chapter 2)

7.5.2. Sorption of P and Zn by a Pakistani Soil

7.5.2.1. Aims of the experiment

Soil used in this experiment was imported from Pakistan. Physical and chemical characteristics are shown in tables 3a & b. Sorption of applied P and Zn were investigated using this soil. Effects of inclusion of sodium pyrophosphate (NaPP) and organic acids on sorption of P and Zn were also studied.

7.5.2.2. Treatments

The following treatments were included in this experiment.

(1) P1Z0 (2) P1Z (3) P2Z (4) P3Z (5) P4Z (6) P5Z (7) P6Z

P = phosphate solution

Z0 = no Zn , Z = zinc sulphate applied @ 50 ug/ml of solution

P1 = 0.05M OP, P2 = OP+PP (0.045M OP + 0.0025M NaPP)

P3 = 0.05M OP + 90 ml water extract of rice straw

P4 = P2 + 90 ml water extract of rice straw

P5 = P1 + Chelex resin extract of soil (70 ml)

P6 = P2 + Chelex resin extract of soil (70 ml)

7.5.2.3. Materials and Methods

7.5.2.3.1. Extraction of rice straw

Samples (2g) of dried, finely ground rice straw were weighed in two plastic bottles and 120 ml of distilled water was added to each bottle. The samples were shaken on a horizontal shaker for two hours at 175 cycles per minute to extract "organic acids" in the water. The extract was filtered and added to the respective solutions.

7.5.2.3. Experimental Procedure

Solutions (1000 ml) were added to the polycarbonate bottles. Initial solution P of each solution was determined and pH recorded. Soil samples (50g) were added to each bottle. The bottles were sealed and attached to the end to end shaker for continuous shaking. Samples (10 ml) of the suspension from each bottle were taken after intervals of 24, 72, 120, 168, 216, 264 and 312 hours. The suspensions were centrifuged, filtered and analysed for P contents (Watanabe and Olsen, 1965). pH of the aliquots was also recorded. Water soluble Zn for each sample was measured by atomic absorption (Pye-UNICAM). Organic carbon in solution was measured (section 2.9, chapter 2).

7.5.3. Brown podzolic soil

7.5.3.1. Aims of the experiment

Soil samples of a brown podzolic soil were used for these studies. No detectable $CaCO_3$ was present in this soil (table 3a) so it was assumed that the effects on sorption of applied P and Zn in this soil would be associated with the different forms of Fe and/ or Al in the soil.

7.5.3.2. Treatments

The following treatments were used for this experiment.

(1) P1Z (2) P2Z (3) P3Z (4) P4Z

P = phosphate source, Z = zinc sulphate (100 ug Zn/ g of soil.)

P1 = 0.05 M solution of OP, P2 = 0.045 M sol. of OP + 0.0025 M solution of NaPP

P3 = P1 + 50 ml of rice straw extract see 7.5.2.3.1

P4 = P2 + 50 ml of rice straw extract see 7.5.3.2.1

7.5.3.2.1. Extraction of rice straw

Duplicate samples (2g) of finely ground rice straw were added to plastic bottles with 50 ml distilled water, shaken for 1 hour at 200 cycles per minute, filtered and then added to the respective treatments.

7.5.3.3. Experimental Procedure

Samples (50g) of brown podzolic soil were added to 1.5 litre polycarbonate bottles containing already prepared solutions (1000 ml) for each treatment. Initial pH of each solution was recorded and P contents determined. The bottles were sealed and attached to the end to end shaker for continuous shaking. Samples (10 ml) from each bottle were taken after 1, 48, 96, 144, 192, 264, and 336 hours. Clear filtrates were achieved by centrifugation and filtration. The pH values were recorded and P contents determined after each sampling time. Organic carbon (OC) and soluble iron contents were measured.

7.5.4. Sorption by Pen-y-Ffridd soil

7.5.4.1. Aims of the experiment

The soil used here was sampled from Pen-y-Ffridd Research area, Bangor. This soil had a history of heavy liming for about 20 years. Physical and chemical characteristics are given in the table 3a & b. Two types of samples were used, samples as collected from the field and samples which had received 5% lime during rice/ wheat pot experiments (chapter 6). This soil had not received phosphate fertiliser during the pot experiment.

7.5.4.2. Treatments

The soils were treated as follows

L0	(1) P1Z0	(2) P2Z0	(3) P3Z	(4) P4Z
L5%	(5) P1Z0	(6) P2Z0	(7) P3Z	(8) P4Z

L0, L5% = 0 & 5% liming respectively

P = phosphate source, Z0 = no zinc

Z = zinc sulphate (100 ug Zn /ml of sol.)

P1, P3 = 0.05 M OP solution, P2, P4 = 0.045 M OP solution. + 0.0025 M NaPP solution

7.5.4.3. Experimental Procedure

The experiment was performed in the same way as mentioned in 7.5.3.3.

7.5.5. Sorption of P and Zn by agricultural lime ($CaCO_3$), Pakistani soil, and brown podzolic soil (Comparison of Sorption)

7.5.5.1. Aims of the experiment

In this experiment agricultural lime ($CaCO_3$), a Pakistani soil and a brown podzolic soil were used to assess the sorption of P and Zn with lower levels of P (0.025 M) and greater levels of Zn (200 ug/ml). The effects of using pyrophosphate along with OP on P and Zn sorption was also studied.

7.5.5.2. Treatments

The following treatments were used for this experiment.

(1) LP1Z (2) LP2Z (3) KP1Z (4) KP2Z (5) IP1Z (6) IP2Z

L = lime, P = phosphate source, K= Pakistani soil, I= Brown podzolic soil

Z = zinc sulphate (200 ug Zn / ml of solution)

P1= 0.025M OP, P2 = 0.02M OP + 0.0025M NaPP

7.5.5.3. Experimental Procedure

Calcium carbonate (25g) and soil (50g) were used for the sorption studies. The rest of the procedure was the same as described in 7.5.3.3.

7.6. Results

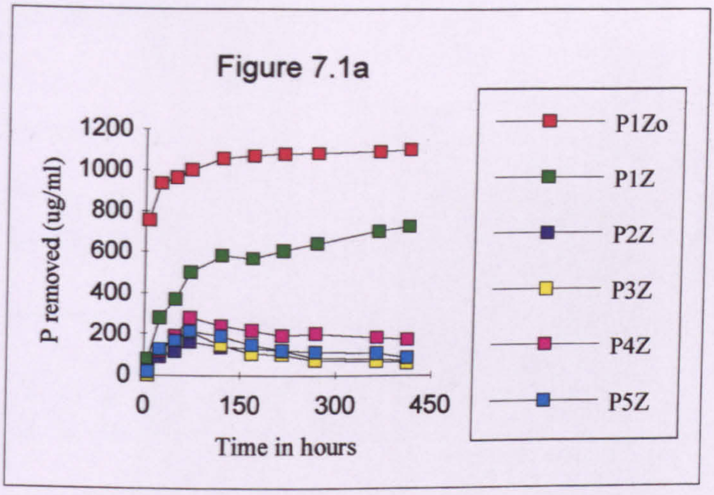
7.6.1. Sorption Studies

7.6.2. Sorption of P and Zn in Calcareous Conditions

Figure 7.1a represent P sorption by $CaCO_3$ with time either in the absence or presence of Zn. It is evident from the data that larger amounts of P were sorbed by $CaCO_3$ in the absence of Zn compared with its presence. The addition of PP, rice straw extract and chelex resin extract of soil caused considerable decreases in P sorption. The sorption of P at 6 hours of reaction time was 49%, 5%, 1%, 0.4%, 1% and 1% of the total applied P in P1Z0 (OP), P1Z (OP), P2Z (OP+PP), P3Z (P1+ rice straw extract), P4Z (P1+ chelex extract of soil) and P5Z (P4+PP) respectively. An increase in P sorption was found with sorption time and at 412 hours duration, the sorption of P increased 71%, 47%, 5%, 4%, 12% and 6% of the total applied P in the treatments P1Z0, P1Z, P2Z, P3Z, P4Z and P5Z respectively. Maximum sorption of P was observed at 72 hours of sampling in treatments P2Z, P3Z, P4Z and P5Z. A slight increase in solution P was observed after 72 hours until the final sampling at 412 hours.

Zinc sorption with time by $CaCO_3$ is presented in figure 7.1b. Amounts of Zn sorbed from solution were determined from 6 to 364 hours of reaction period. In OP treated samples, sorption of Zn seemed to be a rapid process and 99% of the applied Zn disappeared from the solution at 6 hours of reaction time. The sorption of Zn was inhibited by the addition of pyrophosphate (PP) and "organic acids". However, a rapid sorption of Zn was found after 6 hours in P2Z and P3Z treated samples, followed by some release of Zn at 24 hours. After 24 hours further sorption of Zn was observed until

Figure 7.1: Amounts of (a) P and (b) Zn removed from solution by agricultural lime ($CaCO_3$) with sorption time



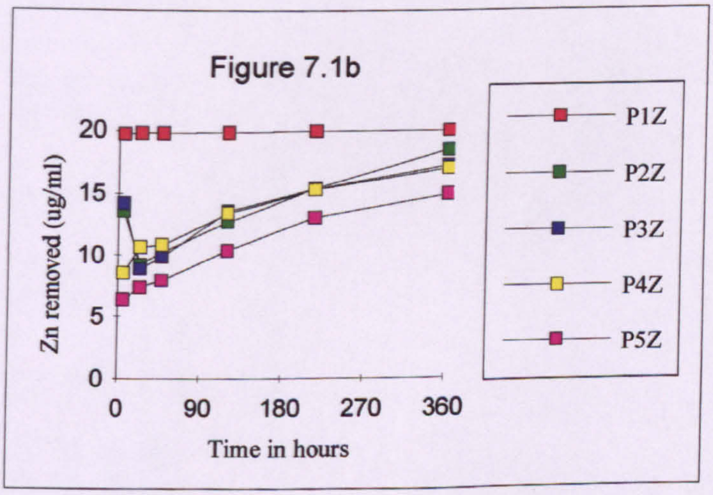


Table 7.10: Changes in solution pH with sorption time in the presence of agricultural lime ($CaCO_3$)

Treatments	0 H	6 H	24 H	120 H	168H	216 H	268 H	364 H	412 H
P1Z0	4.55	7.11	7.27	7.52	7.51	7.50	7.60	7.78	7.82
P1Z	4.53	5.83	6.31	6.71	6.86	6.89	6.90	7.00	7.03
P2Z	5.96	6.00	6.05	6.0	6.13	6.18	6.21	6.32	6.43
P3Z	5.93	6.00	6.01	6.09	6.12	6.13	6.17	6.22	6.22
P4Z	5.01	5.41	5.53	5.69	5.72	5.77	5.80	5.89	5.89
P5Z	6.00	6.05	6.10	6.14	6.18	6.18	6.19	6.23	6.25

Table 7.11: Changes in organic carbon (OC) in solution (ug/ml) with sorption time in the presence of agricultural lime ($CaCO_3$)

Treatments	6 H	48 H	120 H	216 H	268 H	364 H
P3Z	19.08	14.50	14.50	8.39	9.92	10.68
P4Z	38.15	32.24	34.34	28.61	24.80	22.89
P5Z	51.50	45.78	43.87	36.27	36.27	32.43

364 hours. In the samples taken at 6 hours, the sorption of applied Zn in treatments P1Z, P2Z, P3Z, P4Z and P5Z was 68%, 72%, 43% and 32% respectively and it increased to 100%, 92%, 86%, 85%, and 74% at 364 hours of reaction. Addition of PP and "organic acids" with OP decreased the sorption of Zn by $CaCO_3$.

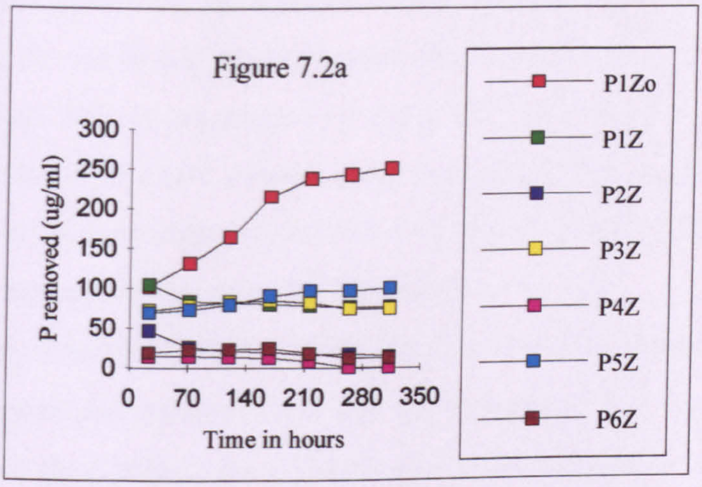
Changes in pH of solution are presented in table 7.10. An increase in pH of the solution with time was observed. The treatment P1Z0 showed the maximum overall increase in pH of 3.0 units at 412 hours. The increase in pH in other treatments like P1Z, P2Z, P3Z, P4Z and P5Z was 2.5, 0.5, 0.3, 0.9, and 0.3 units respectively. Application of Zn with OP caused a decrease in pH (0.79 units) of solution after 412 hours compared with P1Z0. Further decreases in pH of solution were observed with the introduction of PP or organic acids to treatment P1Z and this reduction was 0.6, 0.8, 1.1, and 0.8 units in P2Z, P3Z, P4Z and P5Z respectively.

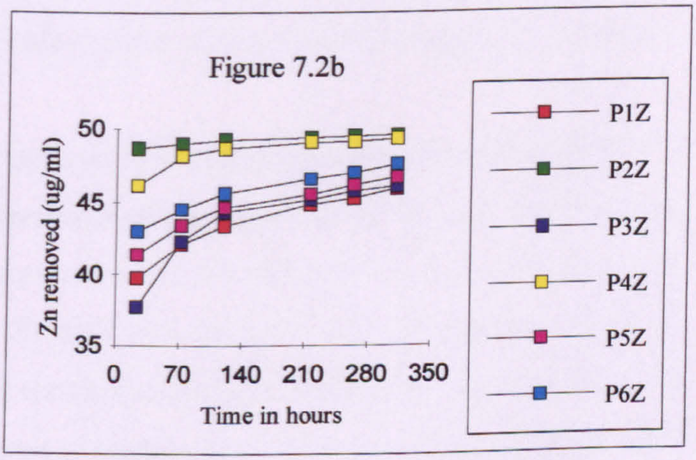
Table 7.11 presents the data about organic carbon (OC) contents in solution after 6, 48, 120, 216, 268 and 364 hours of reaction time. A decline in organic carbon (ug/ml) in solution was observed with sorption time. This decrease after 364 hours of reaction time compared with the 6 hours was 44%, 40% and 37% in treatments P3Z, P4Z and P5Z respectively. As no organic acids were applied to the other treatments no change was expected due to reaction with lime ($CaCO_3$). The same amount of organic carbon (OC) was applied to treatments P4Z & P5Z, however treatment P4Z had 26% less organic carbon than P5Z after 6 hours of reaction time. This decrease was found to be 29% after 364 hours of reaction time, showing a further slight decline with reaction time. This might be because without PP treatment, reactions between OP, $CaCO_3$ and "organic acids" were faster and most of the applied "organic acid" was precipitated or metabolised within a few hours.

7.7. Sorption of P and Zn by a Pakistani soil

Figure 7.2a presents the sorption of P by a Pakistani soil in the presence and absence of Zn. It is evident that the amount of P sorbed was much higher with P1Z0 compared with P1Z treatment. Sorption of P was almost the same after 24 hours but

Figure 7.2: Amounts of (a) P and (b) Zn removed from solution by a Pakistani soil sorption time





after 312 hours of reaction time sorption of P in P1Z was 69% lower than P1Z0. In all the treatments except P1Z0, P3Z and P5Z desorption of P rather than sorption was observed. The effects of the addition of Zn in reducing P sorption were also considerable. An overall reduction in sorption after 312 hours over 24 hours was 26%, 68%, 92% and 35% in treatments P1Z (OP), P2Z (OP+PP), P4Z (P2+ rice straw extract) and P6Z (P2+ chelex extract of soil) respectively. The increases in sorption at 312 hours over 24 hours in treatments P1Z0 (OP), P3Z (P1+ rice straw extract) and P5Z (P1+ chelex extract of soil) were 144%, 5% and 43% respectively.

Zinc sorption by Pakistani soil with time is presented in figure 7.2b which shows that the minimum sorption occurred in P1Z and maximum in P2Z treatment (OP+PP). After 24 hours about 97% of the applied Zn disappeared from the solution in treatment P2Z whereas in P1Z, the amount of Zn sorbed was 80%. The amounts of Zn sorbed after 302 hours of reaction were 92%, 99%, 92%, 99%, 93% and 95% in treatments P1Z, P2Z, P3Z, P4Z, P5Z and P6Z respectively. Addition of "organic acids" in the presence of PP decreased the sorption of Zn whereas their addition in OP treated samples increased it.

Changes in pH with sorption time are presented in table 7.12. An overall increase in pH was observed in all the samples up to 312 hours of reaction time. The increases in pH at 312 hours over initial pH were 1.67, 1.0, 0.17, 0.96, 0.13, 0.71, and 0.13 units in treatments P1Z0, P1Z, P2Z, P3Z, P4Z, P5Z, and P6Z respectively. Application of Zn to OP (i.e. P1Z) treatment caused a decrease in pH compared with P1Z0. This decrease in pH at 312 hours of reaction was 0.74 units. Addition of organic acids (H_2O-extract of rice straw and chelex resin extract of soil) to P1Z treatment (i.e. P3Z and P5Z) increased pH at 312 hours.

Organic carbon (OC) in solution is presented in table 7.13, showing increases in P1Z0, P1Z and P2Z and decreases in P3Z, P4Z, P5Z and P6Z treatments at 264 hours of sorption time.

Table 7.12 Changes in solution pH with sorption time in the presence of a Pakistani soil

Treatments	0 H	24 H	72 H	120 H	168 H	216 H	264 H	312 H
P1Z0	4.55	5.87	6.03	6.08	6.09	6.11	6.13	6.22
P1Z	4.48	5.19	5.29	5.31	5.38	5.40	5.40	5.48
P2Z	5.90	5.92	6.00	6.00	6.00	6.01	6.02	6.01
P3Z	4.60	5.25	5.39	5.40	5.45	5.49	5.50	5.56
P4Z	5.87	5.93	6.00	6.01	6.01	6.02	6.04	6.04
P5Z	4.90	5.30	5.39	5.42	5.49	5.50	5.62	5.61
P6Z	5.92	5.97	5.99	6.01	6.02	6.03	6.06	6.09

Table 7.13: Changes in organic carbon (OC) in solution (ug/ml) with sorption time in the presence of a Pakistani soil

Treatments	24 H	72 H	120 H	168 H	216 H	264 H
P1Z0	2.25	2.34	2.87	3.05	4.86	6.87
P1Z	7.50	7.63	9.92	10.68	11.45	12.97
P2Z	12.21	12.21	11.45	12.21	14.50	24.47
P3Z	24.42	22.13	18.31	16.79	19.84	19.08
P4Z	38.91	34.34	25.18	25.18	24.42	22.84
P5Z	38.92	32.05	33.57	32.81	32.05	30.52
P6Z	51.88	48.07	45.78	44.25	48.07	48.07

7.8. Brown Podzolic Soil

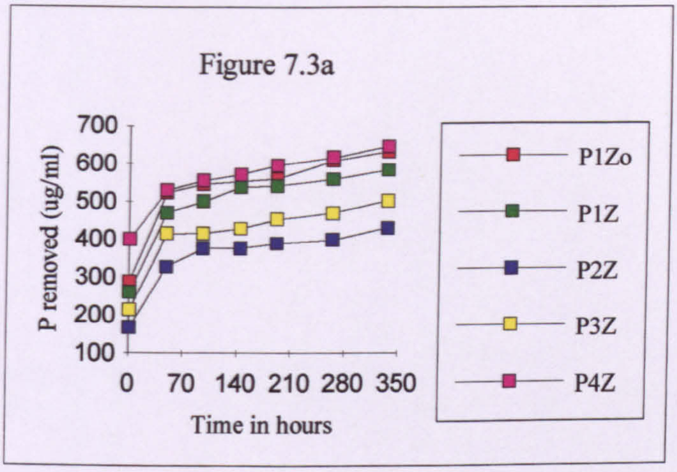
Changes in P sorption with time in brown podzolic soil are presented in figure 7.3a. Application of Zn decreased sorption of P in P1Z (OP). This decrease in P sorption after 336 hours was 8%. Generally an increase in P sorption was observed from 1 to 336 hours of reaction, showing that 50% of the sorption occurred within the first 48 hours of reaction time. Further decreases of 26% and 14% in P sorption were noticed in treatments P2Z (OP+PP) & P3Z respectively in comparison to P1Z0 treatment. Addition of rice straw extract to P2Z (i.e P4Z treatment), caused a significant increase in P sorption, showing 11% and 50% greater sorption at 336 hours in comparison to P1Z and P2Z respectively.

Sorption of Zn by brown podzolic soil seemed to be a rapid process (figure 7.3b) and most of the applied Zn disappeared from the solution during the first hour of reaction. A slight increase in Zn sorption was observed from 48 to 264 hours. At 264 hours of reaction the sorption was 96%, 96%, 97%and 95% of the total applied Zn in P1Z (OP), P2Z (OP+PP), P3Z (P1+ rice straw extract) and P4Z (P3+PP) respectively.

Changes in pH, organic carbon (OC) and iron (Fe) contents of the solution with sorption time are presented in tables 7.14, 7.15 and 7.16 respectively. An increase in pH was observed with sorption time. Application of Zn to OP treatment decreased the pH by 0.17 units at 336 hours. Addition of rice straw extract to P1Z & P2Z (i.e P3Z & P4Z respectively) caused increases in pH of 0.17 and 0.1 units at 336 hours respectively.

Increases in organic carbon (OC) with sorption time were much greater in the absence than in the presence of Zn. An overall increase of 172%, 61%, 110%, 21% and 30% was observed, in treatments P1Z0, P1Z, P2Z, P3Z and P4Z respectively, after 192 hours compared with first hour of shaking period for treatments P1Z0, P1Z, P2Z, P3Z and P4Z respectively. Addition of rice straw extract , however, caused an increase in OC in solution by up to 37% and 17% in the treatments P3Z and P4Z compared with the treatments P1Z & P2Z respectively.

Figure 7.3: Amounts of (a) P and (b) Zn removed from solution by a brown podzolic soil with sorption time



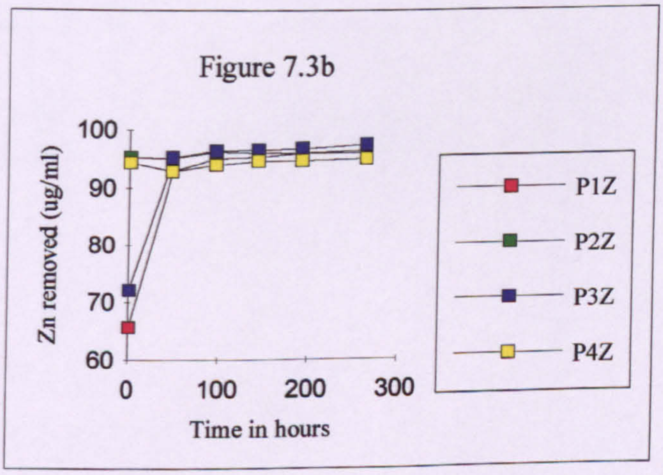


Table 7.14: Changes in solution pH with sorption time in the presence of a brown podzolic soil

Treatments	0 H	1 H	48 H	96 H	144 H	192 H	264 H	336 H
P1Z0	4.59	4.99	5.38	5.43	5.50	5.61	5.64	5.70
P1Z	4.50	4.50	4.92	5.03	5.14	5.20	5.27	5.31
P2Z	5.79	5.52	5.74	5.80	5.85	5.88	5.91	5.93
P3Z	4.61	4.59	5.13	5.21	5.31	5.35	5.40	5.48
P4Z	5.81	5.59	5.78	5.83	5.95	6.00	6.02	6.03

Table 7.15: Changes in organic carbon (OC) in solution (ug/ml) with sorption time in the presence of a brown podzolic soil

Treatments	1 H	48 H	96 H	192 H
P1Z0	98.24	207.25	245.58	267.28
P1Z	90.03	127.17	141.16	144.97
P2Z	93.09	164.05	190.75	195.84
P3Z	164.05	148.79	155.90	198.38
P4Z	175.49	217.46	221.27	228.90

Table 7.16: Changes in iron (Fe) contents of solution (ug/ml) with sorption time in the presence of a brown podzolic soil

Treatments	1 H	48 H	96 H	192 H
P1Z0	0.59	6.89	12.46	14.12
P1Z	0.34	1.12	1.19	2.11
P2Z	1.72	23.30	25.07	27.62
P3Z	0.55	1.72	2.50	3.09
P4Z	0.74	21.14	23.69	24.21

Addition of Zn to OP treatment decreased the iron content of solutions by up to 85% but increases in iron content in solutions were observed with sorption time. Greatest iron content were found in P2Z treatment. Added "organic acids" increased the solubility of iron by up to 46% in treatment P3Z over P1Z and decreased its solubility by up to 12% in P4Z treatment compared with P2Z treatment.

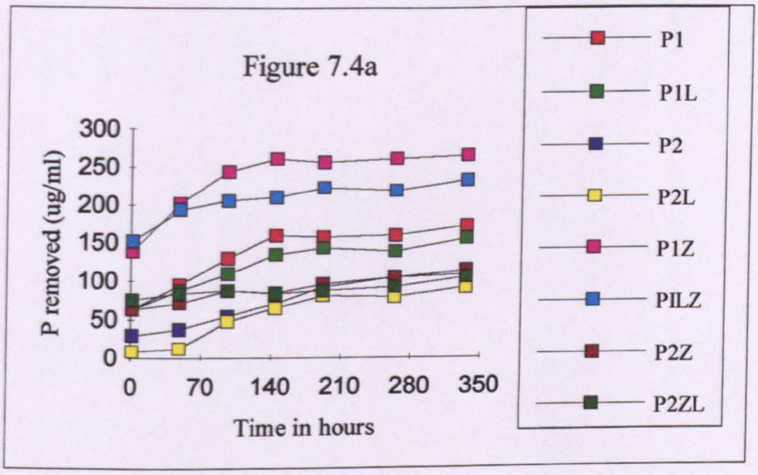
7.9. Pen-y-Ffridd Soil

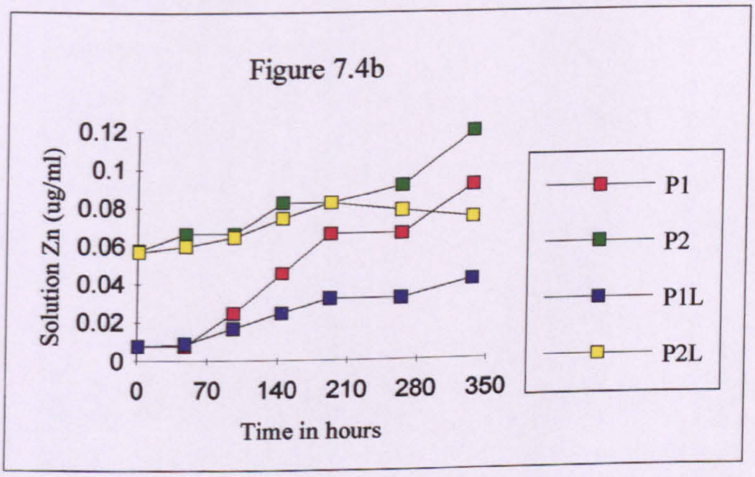
Sorption of P by soil samples (original & limed) from Pen-y-Ffridd area in the presence and absence of Zn is illustrated in figure 7.4a. Increases in sorption of P with time were observed in both the soils, PF(5%) soil however, showed greater sorption of P than PF(0) in all the treatments. The increases in P sorption at 336 hours in PF(5%) compared with PF(0) were 54%, 4%, 50% and 14% in treatments P1Z0, P2Z0, P1Z, and P2Z respectively. Addition of Zn in both the soils PF(0) & PF(5%) caused a decrease in P sorption. These decreases in treatments P1Z and P2Z were 10% and 16% in PF(0) and 13% and 7% in PF(5%) respectively.

Changes in native soil Zn are illustrated in figure 7.4b, showing the behaviour of Zn in PF(0) and PF(5%) soil samples with sorption time. An increase in the solubility of native soil Zn was found with sorption time. The greatest increases were observed in PF(0) in treatment P2Z0 and the lowest levels of Zn were observed in PF(5%) in P1Z0 treatment. Most of the applied Zn disappeared from the solution within the first 48 hours of reaction time (figure 7.4b). Minimum sorption of Zn (97% of applied Zn) was observed in treatment P1Z in PF(0) soil and maximum sorption (99%) in treatment P2Z in PF(5%) soil (figure 7.4c). Liming of soil increased Zn sorption by up to 1.5% and 1% in P1Z and P2Z respectively. Moreover liming caused a decrease in the solubility of native soil Zn by up to 55% and 38% in P1Z0 and P2Z0 treatments.

Changes in pH and organic carbon (OC) in solution with sorption time in the presence of Pen-y-Ffridd soil [PF(0) and PF(5%)] samples are presented in tables 7.17, 7.18, 7.19 and 7.20 respectively. An increase in pH of solution was observed with sorption time of 336 hours. Liming of soil caused an increase of 0.23, 0.19, 0.31 and

Figure 7.4: Amounts of (a) P removed from solution, (b) changes in native soil Zn and (c) Zn removed from solution by a soil from Pen-y-Ffridd (PF 0, PF 5%) with sorption time





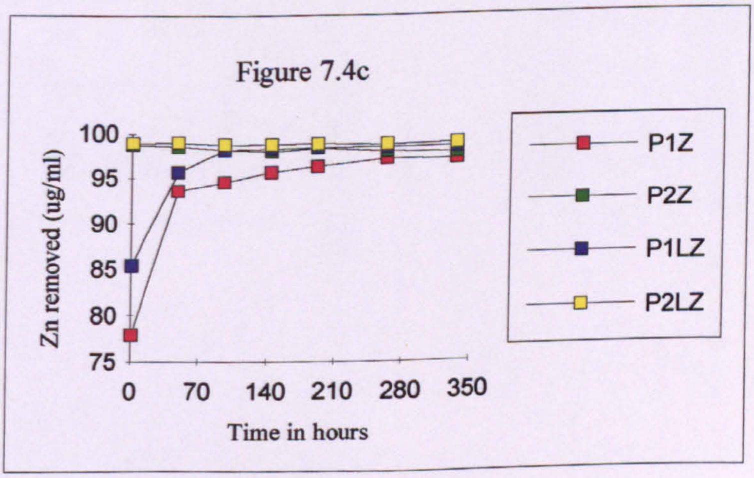


Table 7.17: Changes in solution pH with sorption time in the presence of a soil from Pen-y-Ffridd (PF O)

Treatments	0 H	1 H	48 H	96 H	144 H	192 H	264 H	336 H
P1Z0	4.60	5.40	5.71	5.72	5.77	5.80	5.83	5.87
P2Z0	6.00	5.97	6.07	6.02	6.05	6.08	6.10	6.11
P1Z	4.50	5.05	5.22	5.26	5.30	5.33	5.37	5.40
P2Z	5.80	5.80	5.90	5.90	5.90	5.92	5.96	5.98

Table 7.18: Changes in solution pH with sorption time in the presence of a soil from Pen-y-Ffridd (PF 5%)

Treatments	0 H	1 H	48 H	96 H	144 H	192 H	264 H	336 H
P1Z0	4.60	5.80	5.98	5.98	6.00	6.03	6.08	6.10
P2Z0	6.00	6.10	6.20	6.20	6.21	6.25	6.28	6.30
P1Z	4.50	5.39	5.59	5.59	5.61	5.66	5.70	5.71
P2Z	5.80	5.99	6.09	6.09	6.09	6.10	6.15	6.15

Table 7.19: Changes in organic carbon (OC) in solution (ug/ml) with sorption time in the presence of a soil from Pen-y-Ffridd (PF 0)

Treatments	1 H	48 H	96 H	144 H	192 H	264 H
P1Z0	33.57	59.13	68.67	76.54	82.02	85.42
P2Z0	40.44	104.91	106.82	107.25	110.64	115.26
P1Z	16.53	49.60	52.14	53.41	55.95	61.04
P2Z	26.71	87.75	89.02	90.29	94.10	94.10

Table 7.20: Changes in organic carbon (OC) in solution (ug/ml) with sorption time in the presence of a soil from Pen-y-Ffridd (PF 5%)

Treatments	1 H	48 H	96 H	144 H	192 H	264 H
P1Z0	24.42	44.25	46.54	46.54	48.83	51.12
P2Z0	32.81	74.77	79.35	80.88	88.51	91.56
P1Z	24.42	40.44	50.36	45.78	54.94	57.23
P2Z	47.31	61.04	67.14	70.20	72.49	74.77

0.17 units at 336 hours in P1Z0, P2Z0, P1Z and P2Z treatments respectively. Addition of Zn in PF(0) decreased pH by up to 0.47 and 0.13 units and in PF(5%) by up to 0.39 and 0.15 units in treatments P1Z and P2Z respectively.

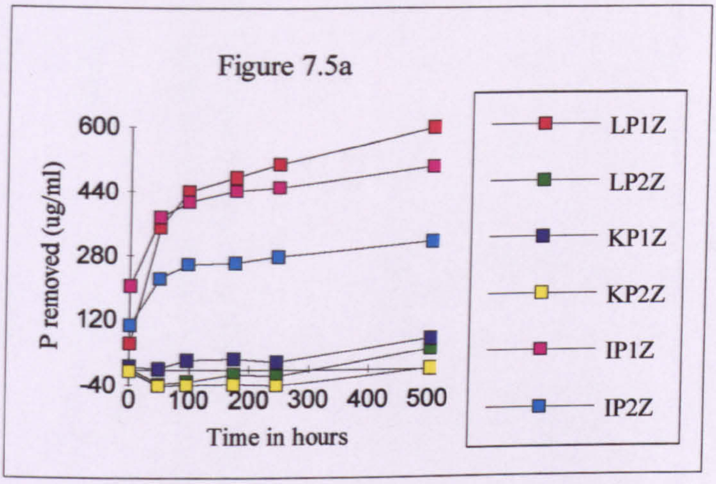
Soluble (OC) increased with sorption time until 264 hours. The increase was found to be greater in PF(0) than in PF(5%) soil. Liming of the soil caused a decrease in organic carbon (OC) in solution by up to 41%, 22%, 6% and 21% after 264 hours in treatments P1Z0, P2Z0, P1Z and P2Z treatments respectively. Application of Zn also caused further decreases in OC in solution. This decrease in PF(0) soil in P1Z and P2Z treatments was 29% & 20% respectively. In P1Z treatment in PF(5%) soil a slight increase of 11% in OC in solution was observed whereas the decrease in organic carbon (OC) in P2Z treatment was 18%.

7.10. Sorption of P and Zn by Calcium carbonate ($CaCO_3$), a Pakistani soil and a Brown podzolic soil (Comparison of Sorption)

Figure 7.5a shows the amount of P remaining in solution with the sorption time in $CaCO_3$ (LPZ), a Pakistani Soil (KPZ) and brown podzolic soil (IPZ). An overall decrease in solution P was observed with time up to 504 hours. After 504 hours of reaction 80%, 8%, 10%, 0.4%, 66% and 51% of applied P disappeared from the solution in treatments LP1Z (OP), LP2Z (OP+PP), KP1Z (OP), KP2Z (OP+PP), IP1Z (OP) and IP2Z (OP+PP) respectively. Sorption of P was maximum in LP1Z and minimum in KP2Z. Addition of pyrophosphate (PP) to $CaCO_3$ and Pakistani soil considerably decreased P sorption after 504 hours by up to 92% and 97% in treatments LP2Z and KP2Z respectively in comparison to brown podzolic soil where only 37% decreases in P sorption were observed in IP2Z treatment. In treatments LP2Z and KP2Z, solution P increased until 48 hours of reaction period and then it decreased until 504 hours of reaction.

Sorption of Zn was maximum in $CaCO_3$ and minimum in Pakistani soil (figure 7.5b). More than 90% of the applied Zn disappeared from the solution after the first hour of reaction time in $CaCO_3$. At 246 hours of reaction 100% Zn was sorbed in LP1Z

Figure 7.5: Amounts of (a) P and (b) Zn removed from solution by agricultural lime ($CaCO_3$), a Pakistani soil and a brown podzolic soil with sorption time



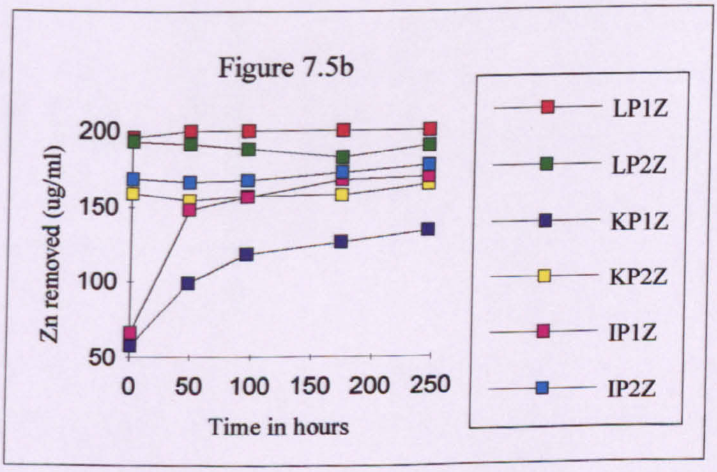


Table 7.21: Changes in solution pH with sorption time in the presence of agricultural lime ($CaCO_3$), a Pakistani soil and a brown podzolic soil

Treatments	1 H	48 H	96 H	174 H	246 H	504 H
LP1Z	4.33	4.66	4.78	4.88	4.93	5.12
LP2Z	5.52	5.78	5.83	5.90	5.92	6.03
KP1Z	4.79	4.88	4.92	4.90	4.99	5.10
KP2Z	5.98	6.05	6.09	6.09	6.11	6.16
IP1Z	5.59	6.71	7.01	7.05	7.23	7.53
IP2Z	6.09	6.20	6.23	6.23	6.29	6.62

Table 7.22: Changes in organic carbon (OC) in solution (ug/ml) with sorption time in the presence of agricultural lime ($CaCO_3$), a Pakistani soil and a brown podzolic soil

Treatments	1 H	96 H	174 H
KP1Z	3.82	6.10	8.39
KP2Z	9.16	9.16	12.21
IP1Z	67.91	131.24	136.58
IP2Z	70.96	178.03	189.48

and 95% was sorbed in LP2Z. In Pakistani soil and brown podzolic soil Zn sorption at 246 hours was greater in PP treated samples in comparison to OP treated samples.

Tables 7.21 and 7.22 represent pH and organic carbon (OC) in solution after varying sorption times. Solution pH and organic carbon (OC) increased with sorption time. The highest pH values, after 504 hours of reaction, were observed, in both treatments, in brown podzolic soil compared with the Pakistani soil and agricultural lime ($CaCO_3$). The effects of pyrophosphate (PP) were to lower suspension pH in the presence of brown podzolic soil (0.91 units) and to increase the pH in the presence of Pakistani soil (1.06 units) and $CaCO_3$ (0.91 units). Solution organic carbon (OC) is presented only for Pakistani soil and brown podzolic soil, showing that greatest amounts of organic carbon (OC) were solubilised due to the high organic matter content of this soil. Addition of PP increased the solubility of organic carbon (OC) in both the soils. These increases after 174 hours of reaction were 45% and 39% in KP2Z and IP2Z treatments respectively.

7.11. Discussion

7.11.1. Sorption Studies

Sorption of P and Zn in the $CaCO_3$ system, in a Pakistani soil, a brown podzolic soil and a brown earth soil from Pen-y-Ffridd are discussed together as sorption of P and Zn showed similar trends. However, sorption of Zn in the $CaCO_3$ system was different from sorption in soils. The effect of different treatments on P, Zn, solution pH & OC and iron contents (brown podzolic soil) will be discussed where appropriate.

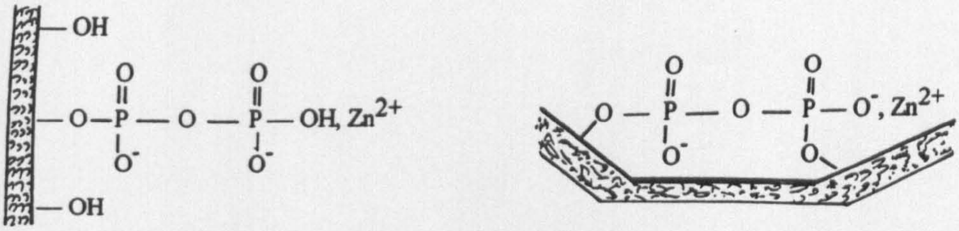
Application of Zn with OP caused substantial decreases in P sorption by calcium carbonate ($CaCO_3$) and all the soils studied. The reduction in P sorption was 34%, 69%, 8%, 37% and 57% in $CaCO_3$, Pakistani soil, brown podzolic, PF(0) and PF(5%) soils respectively. Moreover Zn addition caused a drop in pH by up to 0.79, 0.74, 0.39, 0.47 and 0.39 units in $CaCO_3$, Pakistani soil, brown podzolic soil, PF(0) and PF(5%) soil samples respectively. Although the sorption time scales for each experiment were slightly different, it is evident that P sorption and pH at the later stages of the experiment did not vary greatly. The drop in pH caused by Zn addition could be attributed to the acidic nature of the applied $ZnSO_4$ salt. One of the possible factors reducing P sorption could be the shifts in pH of the solution. This shift was more in the $CaCO_3$ system, giving a final pH of 7.03, a favourable pH range for P availability, after 412 hours of reaction. This change in pH could have played an important role in reducing P sorption in $CaCO_3$, Pakistani soil, PF(0) and PF(5%) soil. A second possibility could be the formation of $Zn_3(PO_4)_2$. As P and Zn were applied in the solution form a rapid reaction was expected. The solubility of $Zn_3(PO_4)_2$ is great enough (Boawn *et al.*, 1954; Jorinak and Inoye, 1962) to maintain high levels of P in solution, and $Zn_3(PO_4)_2$ is considered to be an effective Zn fertiliser and higher P rates generally increase extractable soil Zn (Adams, 1980). However during the first six hours of reaction 99% of the applied Zn disappeared from the solution. This shows that some reactions other than the formation of $Zn_3(PO_4)_2$ might have taken place. It can be suggested that $ZnSO_4$ reacted with $CaCO_3$ to form $ZnCO_3$ and $CaSO_4$, reducing the active sorption sites for applied P fertiliser and maintaining higher P levels in solution. As the solubility of $ZnCO_3$ is suggested to be strongly pH dependent (Tagwira, *et al.*, 1993), a small change in pH could increase or decrease its solubility. Solution pH in the presence of $CaCO_3$ was slightly above 7, and as Zn is more soluble under acidic conditions, so less soluble Zn was expected. Thirty fold reductions in Zn concentration in soil solution for every unit of pH increase in the range of 5-7 have been observed (Tisdale and Nelson, 1993). Moreover, the adsorption of Zn to the $CaCO_3$ surfaces itself cannot be ignored. Tisdale and Nelson (1993) reported that Zn is adsorbed by magnesite ($MgCO_3$), dolomite [$CaMg(CO_3)_2$] and calcite ($CaCO_3$), specifically in the crystal surfaces (magnesite & dolomite) at sites in the lattice occupied by Mg atoms. As the $CaCO_3$ used in the experiment was commercial grade (agricultural lime), some magnesite or dolomite might be present which acted as sorption sites for Zn.

Maximum decreases in pH were noticed in Pakistani soil with Zn addition to OP treatment, with a final pH of 5.48 at 312 hours of reaction time. Data regarding Zn sorption show that 92% of the applied Zn was sorbed at 312 hours of reaction time. The effect of Zn addition in reducing P sorption in PF(5%) soil was greater than in PF(0) and brown podzolic soil. This shows that addition of Zn can be more effective in decreasing P sorption in calcareous soils with high pH (pH>7). Amounts of Zn sorbed by brown podzolic soil at 264 hours, by PF(0) and PF(5%) soils at 336 hours was 96%, 97% and 98% respectively.

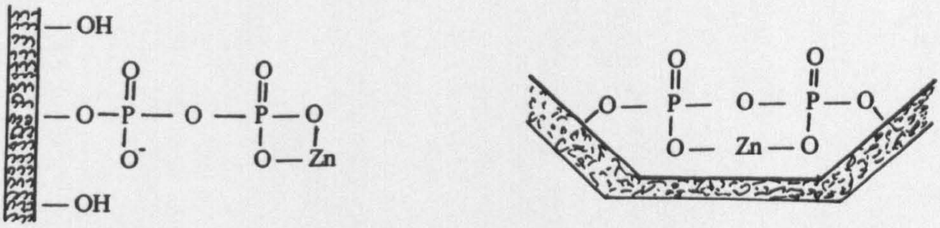
Reduction in P sorption in Pakistani soil and PF(0) and PF(5%) soils by the addition of Zn is most probably due to the shift in pH, which resulted due to the acidic reaction of $ZnSO_4$ salt and its high concentration in solution. In Pakistani soil desorption rather than P sorption with time was observed and maximum sorption was observed after 24 hours of reaction. This desorption of P might have taken place in two possible ways (a) a quick sorption of applied P for first 24 hours and then the release of adsorbed P at 72 hours (b) the addition of $ZnSO_4$ reacted with Ca-P in the soil and increased the solution P by the dissolution of Ca-P. Bohn *et al.* (1979) suggested that there is an initial rapid reaction between P and the soil involving adsorption and ligand exchange followed by a slower reaction involving mineral dissolution. However this sort of reaction did not occur in PF(O), PF(5%) and brown podzolic soil as increases in P sorption were observed. Addition of Zn to the brown podzolic soil (P1Z treatment) caused a slight decline in pH. This decline in pH was within the favourable range (pH 5-7) of P availability, therefore it can partially be regarded as a factor for reduced P sorption. The reduction in P sorption was only 8% in comparison to P1Z treatment. In "iron rich" soils adsorption of P is dominated by Fe and/ or Al oxides (Young *et al.*, 1985). Xie and Mackenzie (1989b) found positive correlations between sorbed P and extractable Fe & Al contents, supporting the speculation that sorption was occurring on the edges of clay minerals and Fe oxide /hydroxide crystallites (Parfitt *et al.*, 1975).

Addition of PP to OP in the presence of Zn caused significant decreases in P sorption in $CaCO_3$ and in the soils studied. This reduction was 90%, 80%, 26%, 41% and 55% in $CaCO_3$, Pakistani soil, brown podzolic soil, PF(0) and PF(5%) soil respectively. This shows maximum reduction of P sorption in $CaCO_3$ and minimum in brown podzolic soil. It could be speculated that the effect of PP in reducing P sorption is greater in calcareous soils (high pH) compared with acidic soils rich in Fe and/ or Al oxides (low pH). In calcareous conditions PP acts as a crystal growth inhibitor (Marshall and Nancollas, 1969), reducing P sorption (El-zahaby *et al.*, 1982). The effect of sodium pyrophosphate (NaPP) decreases with the decrease in pH and the sorption of PP itself increases (Xie and Mackenzie, 1989a), due to greater availability of sites for PP sorption at lower pH, and greater contents of Fe and/ or Al materials (Xie and Mackenzie, 1988) involved in PP sorption. Xie and Mackenzie (1991) reported that reduced P adsorption or increased P desorption was associated, among the other factors, with the decreases in extractable Fe & AL. In the $CaCO_3$ system, addition of PP-extract of rice straw to OP caused greatest decrease of 91% in P sorption whereas the decrease caused by the addition of chelex resin extract of soil to OP and OP+PP treated samples was 76% and 88%. The effects of adding organic acids to Pakistani soil in reducing P sorption at 312 hours were 2% (P3Z), 98% (P4Z) and 84% (P6Z) whereas in P5Z an increase of 30% in P sorption was observed. In brown podzolic soil, addition of H_2O-extracts of rice straw to OP treated sample caused a decline of 14% in P sorption whereas its addition to OP+PP treated samples caused significant increases in P sorption by up to 11% compared with OP and 50% compared with OP+PP treated samples. Addition of "organic acids" along with PP played an important role in reducing P sorption in $CaCO_3$ and Pakistani soils, whereas the effect was minimum in brown podzolic soil. It could be suggested that under calcareous conditions added "organic acids" might have played an important role in chelating cations such as Ca^{++} in solution, reducing the sorption sites for P. Moreover the effect of organic acids in reducing P sorption was greater in the presence of PP. The minimal effect of organic acids in reducing P sorption in iron rich soils could be attributed to the solubilization of Fe & Al oxides from the soil and then reprecipitation with phosphorus because hydrous Fe-oxide is capable of concurrently retaining phosphate and Zn, Cd or Cu (Kuo, 1986). Organic anions in solution can either compete with P sorption or increase P retention by the soil. Organic matter can induce P retention with cations such as Fe, Al, and Ca which join P attached to OM (Wild, 1950) by complex formation between humic acids and Al which would be active for P sorption (Appelt *et al.*, 1975). Greater P sorption in P5Z treatment in Pakistani soil could be the result of more iron contents in chelex resin extract of soil which increased sorption sites for P. In brown podzolic soil however, a more pronounced effect of Fe & Al can be suggested due to the combined effect of PP and rice straw extract in solubilising more native Fe and Al oxides and thus providing more sites for P sorption. This assumption is supported by the lower Fe contents in solution in P4Z treatment (table 7.16) compared with P2Z treatment which indicated that reprecipitation of P with Fe in solution might have taken place. Addition of PP and "organic acids" caused considerable decreases in Zn sorption in the $CaCO_3$ system. Maximum effect was found in P4Z. However in Pakistani soil and in PF(0) and PF(5%) soil samples maximum sorption of Zn was observed in PP treated samples and minimum in OP treated samples. In brown podzolic soil slight variations in Zn sorption were observed with more sorption taking place in P3Z and P4Z treatment. Addition of "organic acids" to OP treatment increased Zn sorption, probably by increasing pH, whereas in PP treated samples addition of "organic acids" decreased Zn sorption slightly. Greater sorption of Zn was observed in PF(5%) soil compared with PF(0) soil samples in both the treatments. Moreover PP extracted more native Zn in PF(0) and PF(5%) soils compared with OP, limed soil [PF(5%)] however showed less extractable Zn than the PF(0) soil.

An overview of the results indicates that PP and organic acids played an important role in reducing Zn sorption in $CaCO_3$ systems. Addition of PP and "organic acids" also caused reduction in pH of the suspension after 412 hours of reaction . As Zn sorption is highly pH dependent as described earlier, reduction in pH resulted in greater Zn concentrations in solution. This reduction in pH was observed in all the treatments including PP and/ or organic acids. Different studies on Zn have reported decreases in solution Zn concentration with the increase in pH (Ghanem and Mikkelsen, 1988), as a result of Zn sorption both through increasing Zn adsorption and Zn precipitation (Lindsay, 1979; Pulford, 1986; Tiller *et al.*, 1984). Moreover as PP is known to increase Zn solubility through chelating effects (Bar-Yosef and Asher, 1983; Giordano *et al.*, 1971), the reduced sorption in $CaCO_3$ could have occurred due to chelation by PP in PP treatments. However, in soil systems like in Pakistani soil, PF(0) and PF(5%) soils, PP failed to maintain higher levels of Zn in solution when compared with OP treated samples, perhaps due to comparatively higher final pH in PP treated samples. Addition of organic acids to PP treated samples decreased the Zn sorption but their addition to OP treatments increased the sorption of Zn. Organic acids in OP treatments increased the pH of the suspensions and thus increased Zn sorption. Although increases in pH were also found in brown podzolic soil these increases were less than in OP treated samples. Moreover PP in the soils caused additional dissolution of organic matter along with Fe & Al oxides which in turn competed with Zn for chelation by PP and thus Zn was released for sorption by the soil active sites. It is supported by data shown in table 7.15 which show more OC in solution in PP treated samples and more Fe contents (table 7.16) in P2Z treatment. Xie and Mackenzie (1990b) suggested that PP could expose more surfaces for Zn sorption due to increased dissolution of OM, Fe, Al and Mn for subsequent coprecipitation of PP, Fe, Al, or other ions with Zn ions. Precipitation of Zn-NH_4-PP, as suggested by Adrino and Murphy (1970), would reduce bioavailable Zn in solution. It is speculated that PP sorption may be similar to the binuclear sorption of OP (Parfitt *et al.*, 1975). Thus PP could increase cation exchange capacity (CEC) or complex with Zn depending on the geometry of PP sorption to the soil surface (Xie and Mackenzie, 1990a). They proposed three possible mechanisms in soil which could increase Zn sorption with added PP sorption. (i) a coulombic effect which increases Zn sorption through increases in surface charge. (ii) a bridge effect , when Zn ions attach to sorbed PP through covalent bonds between Zn and O of PP. (iii) specific sorption of Zn through Zn-PP-Soil complex formation, resulting from PP sorption.



a: Coulombic effect



b: Bridge effect

c: Complexes of Zn-PP-soil

Schematic representation of proposed mechanisms for pyrophosphate and zinc interactions on the surface of soil particles. Schematics on the left show mononuclear and on the right show binuclear bonds of pyrophosphate with the soil surface (Xie and Mackenzie, 1990 a)

7.11.2 Sorption of P and Zn by agricultural lime ($CaCO_3$), Pakistani soil and brown podzolic soil (Comparison of Sorption)

Sorption of P and Zn was studied in the $CaCO_3$ system, a Pakistani soil and brown podzolic soil with greater levels of Zn (200ppm) and low levels of applied P (0.025M). The reaction time of 504 hours resulted in maximum sorption of P by $CaCO_3$ in OP treated samples (80%) and minimum sorption by Pakistani soil (10%). The sorption of P by brown podzolic soil was 66%. Addition of PP decreased P sorption by up to 97% in Pakistani soil and 90% and 22% in $CaCO_3$ and in brown podzolic soil respectively. The results indicated that greater concentrations of Zn caused significant decreases in solution pH of $CaCO_3$ and Pakistani soil and increases in brown podzolic soil (table 7.21). In the $CaCO_3$ system in OP treatment, greater concentrations of Zn caused drastic effects on P in solution and 80% of the applied P disappeared from the solution. Moreover all of the applied Zn disappeared after 246 hours of reaction time. From the results it can be suggested that greater Zn concentrations produced highly acidic solution which dissolved most of the $CaCO_3$ in the solution, followed by a possible coprecipitation of Ca-Zn-P complex. Lowering of pH caused favourable effects in Pakistani soil and only 10% of applied P was sorbed after 504 hours of reaction. In PP treated samples the sorption was almost negligible. Although high pH was observed in OP treatment in brown podzolic soil compared with PP treatment, yet more Zn disappeared from the solution in PP treated samples. This can probably be related to greater dissolution of organic matter by PP in comparison to OP (table 7.22) which resulted in organic carbon-Zn complex in the solution (Mc Keague, 1967; Pulford, 1986; Xie and Mackenzie, 1990b). Similar explanation for more Zn sorption in Pakistani soil can be made. Increases in soluble organic carbon (OC) with the sorption time in Pakistani soil and brown podzolic soil were observed. More increases were observed in PP treated samples which can probably be related to the ability of PP to dissolve more OM than OP (Mortvedt and Osborn, 1977).

7.12. Conclusion

7.12.1. Incubation Studies

Extractability of soil P, in Pen-y-Ffridd soil, in P treated samples, increased both in H_2O and 0.5N NaOH extracts of soil. Pyrophosphate (PP) increased the extractability of native soil Zn in 0.5N NaOH extracts of soil in comparison to OP, irrespective of the Zn treatment. Addition of Zn caused significant increases in 0.5N NaOH extractable P and Zn and decreases in P in H_2O extract. Application of Zn to PP treated samples decreased the availability of P in both H_2O and 0.5N NaOH extracts of soil.

Extractabilities of soil P and Zn increased in Pakistani soil, due to applied P and Zn fertilizers, both during flooded and moist incubations. Sorption of applied P took place under both incubation conditions, showing greater sorption during moist aerated incubations. Added pyrophosphate (PP) significantly increased the extractability of P over P0, P1 and P2 treatments during 2 and 4 weeks of flooded and 2 weeks of moist aerated incubations whereas it decreased P availability during 4 weeks of moist incubations. Applied P with or without pyrophosphate (PP) increased the extractability of soil Zn at 4 weeks of flooding and 2 weeks of moist aerated incubations whereas at 4 weeks of moist incubations both forms of applied P decreased Zn availability, with PP treated samples showing greater decreases. Overall effects of Zn were to increase the extractability of P at 4 weeks of flooding and 2 and 4 weeks of moist incubations.

7.12.2. Sorption Studies

Application of Zn caused decreases in P sorption in the order of Pakistani soil > PF(0) > PF(5%) > $CaCO_3$ > brown podzolic soil. Decreases in pH in the $CaCO_3$ system and all the soils studied were also noticed with the addition of Zn. Moreover addition of PP and/ or organic acids to OP caused significant decreases in P sorption by the $CaCO_3$ and all the soils except brown podzolic soil where P4Z treatment increased P sorption. In the $CaCO_3$ system maximum sorption of Zn was found in OP treatment whereas in the soil system generally minimum sorption was found in OP treated samples. Addition of PP and/ or organic acids to OP decreased Zn sorption by $CaCO_3$. In the soil system however, OP+PP treated samples increased Zn sorption compared with OP treated samples. Addition of organic acids to OP treatment caused increases in the sorption of Zn but their addition to OP plus PP treatments decreased Zn sorption in Pakistani and brown podzolic soil.

Increases in solution pH and organic carbon (OC) in the soil system and decreases in the soluble "organic carbon" (OC) in the presence of $CaCO_3$ were noticed with the sorption time. Pyrophosphate (PP) was found to be effective in decreasing P sorption even with the higher initial Zn and lower P concentrations. Sorption of Zn was similar to those reported in the previous experiment. Greater concentrations of Zn increased solution pH of brown podzolic soil in OP treated samples and decreased in OP+PP treated samples in brown podzolic soil and Pakistani soil. Solution pH was buffered around 6 by the addition of PP to OP. Organic carbon (OC) in solution increased with sorption time in Pakistani soil and brown podzolic soil, with pyrophosphate (PP) treatments showing more increases than OP treatments.

Pyrophosphate (PP) dcreased P sorption in the presence of Zn, with the greatest effects being observed in case of $CaCO_3$ and the minimum in the brown podzolic soil. The effects of PP in lowering P sorption, at higher Zn concentrations, were slightly more in the Pakistani soil than the $CaCO_3$. Although greater reduction in P sorption due to PP addition, was observed in brown podzolic soil at high Zn levels, the effects were still less compared with the $CaCO_3$ and Pakistani soil.

CHAPTER
8

Chapter 8: General Discussion

Availability of soil phosphorus is believed to be affected by a number of factors, like soil pH, amounts and surface area of Fe and Al oxides/ hydroxides and calcium carbonate (Hamad *et al.*, 1992), soil moisture contents, amounts and decomposition of soil organic matter and organic acids etc. Moreover the amounts and types of added fertilizers will also change the status of P available to plants. The effects of all these factors cannot be isolated from each other in soil systems and considerable changes in soil P and other micronutrients (Mn, Cu and Zn) would take place if any of them were altered. When soils are subjected to flooding, a series of physical, chemical and biological changes take place which might be reversed when the soils are dried.

The current studies were performed to investigate the effects of different factors on the behaviour of soil phosphorus. The features included were (i) incubation studies under flooded (anaerobic) and moist aerated conditions and under alternating flooded/ moist conditions (ii) use of pyrophosphate (PP) as an amendment fertilizer (iii) phosphate sorption, in the presence or absence of pyrophosphate (PP) and organic acids/ humic materials extracted from soil and rice straw, by agricultural lime and different soils with or without applied Zn and (iv) pot experiments with paddy rice and wheat crops. In addition to changes in phosphate, in some cases, the effects on soil pH and on the behaviour of micronutrients (Fe, Mn, Cu and Zn) were also included in the studies. In the following section, discussion will concentrate on the main factors which affected the availability of soil phosphorus in the current studies.

8.1. Soil moisture contents and effects on Phosphorus (P) and micronutrient (Fe, Mn, Cu & Zn) availability

Flooded conditions compared with the moist aerated soil conditions caused positive effects on the extractability of soil phosphorus (P). Overall increases in extractable soil P were observed in all the soil samples subjected to flooded conditions during the laboratory incubations. The extent of increases, however, varied with flooding periods and from soil to soil. During flooded incubations for 50 days, amounts of extractable soil phosphorus almost doubled, increasing from 23 to 46 μg P/g soil (experiment I, chapter 3). Flooded incubations also increased the pH values (5.7 to 6.9) and iron contents (0.74 to 1.28 mg reducible-Fe/g soil) of the soil. These increases were, however not regular and drops in P availability over the initial P were observed during 10-25 days. It was assumed that resorption of P, released during flooding, on to amorphous Fe oxides/ hydroxides might have taken place. The conditions of the "flooded" samples in this study were not perhaps rigorously truly anoxic but simply relied on rapid O_2 consumption by degrading organic materials and on slow O_2 and CO_2 diffusion through water. Such conditions (partially anoxic/ anaerobic) would favour the mobilisation of Fe^{II} and then formation of amorphous Fe^{III} oxides/ hydroxides in more aerated microsites. Moreover, the greater amounts of iron in solution, reduced during early stages of flooding, might have favoured the formation of amorphous or poorly crystalline Fe^{III} oxides/ hydroxides, with larger surface area (Borggaard, 1982) and so a greater capacity/ tendency for P sorption than crystalline Fe oxides. Such oxides may control P availability in flooded soils (Kirk *et al.*, 1990). These results were not reproducible and regular, however, and rather less increases in P extractability were observed when the experiment was repeated (experiment II, chapter 3). This later experiment was conducted two years after the first trial using different shape vessels. The samples had been stored, in air dried conditions, in the laboratory for two years. Phosphorus probably reacted with the soil particles during storage which caused the transformation of P into different compounds of lower P solubility. Bartlett and James (1980) suggested that storing dry soil samples may have marked effects on the results obtained from measurements of a range of soil chemical properties. If any reaction between P and dry soil continues, an analysis performed some time after sampling may not reflect the P status of soil at sampling. Such reactions between P and soil particles have been suggested to be through the diffusion of P into the adsorbing particles (Barrow, 1983). Bramely *et al.*, (1992) suggested that the continuing reaction occurred in limited regions of the surface, presumably in zones of crystal imperfection having thin layers of silicate between adjacent micro-crystals of iron oxide. The products formed, involving such reactions, might transform, with time, into aged crystals with very low solubility and might not be fully dissolved/ "reduced" when the soils are flooded. Reduction of Fe^{III} to Fe^{II} during flooding is considered to be the main source of P increases in flooded acidic soils (Willet, 1986). Thus the amounts of "reducible Fe" (Fe^{III}) in a soil would determine the extent of P increases upon flooding.

In contrast to flooded conditions, moist aerated conditions enhanced the reactions between Fe^{III} oxides and P that would lower the solubility of soil P. The results obtained from the later experiments (experiments II & III, Chapter 3) also revealed that extractability of soil P increased during flooded and decreased during moist aerated incubations. In soil samples from Aber Farm and Pen-y-Ffridd, moist/ aerobic soil conditions favoured the sorption of applied P probably due to reaction/ precipitation with Fe-oxides (Holford and Mattingly, 1975; Hamad *et al.*, 1992; and Udo and Uzo, 1972); the prime active sites for P sorption.

Alternate flooded and moist aerated soil conditions caused greater decreases in the extractability of soil P compared with the soils subjected to moist aerated conditions only. These decreases were 3.4 and 2.6 times in the soils from Pen-y-Ffridd and Pakistan respectively. Soils subjected to alternate flooded-moist conditions have been reported to have greater tendency to fix P. Moist soil conditions following flooding reverse the physical and chemical changes that take place during flooding. Among the other changes, Fe^{II} may be oxidised to the Fe^{III} form. This oxidation may involve the precipitation of Fe-P compounds in amorphous forms. In acidic soils, such reactions might be the main reasons for lower P availability when flooded soils are re-oxidised. Availability of P in flooded-drained soils may decrease due to build up of amorphous or poorly crystalline Fe^{III} oxides/ hydroxides (Sah and Mikkelsen, 1986a). These decreases would, however, depend upon the amounts of Fe^{III} oxides reduced during flooded conditions. Unfortunately, determination of Fe contents in this experiment were not made. In Pen-y-Ffridd soil compared with Pakistani soil, probably greater amounts of iron (due to greater

DTPA-Fe in Pen-y-Ffridd soil than Pakistani soil, Table 3b) were "reduced" during flooding which precipitated in amorphous forms during moist aerated conditions and resulted in greater sorption of P than the Pakistani soil. In Pakistani soil lower levels of DTPA-Fe (2.16 ug Fe/g soil) might have partially contributed to the increases in soil P during flooding and resorption of P during moist aerated conditions.

Extractability of soil P, during pot trials with flooded paddy rice and aerated moist wheat crops, decreased with the growth period of 2 to 10 weeks and from 4* to 8* weeks (* represent soils from previous wheat and paddy rice crops). Although, increases in extractable P during the paddy rice crop were observed, soil P decreased as growth proceeded from 4 to 10 weeks, probably due to plant uptake. Decreases in P during the wheat crop were greater, probably due to greater rate of P sorption during moist aerated conditions and to P uptake by plants. The availability of soil Fe and Mn increased at 10 weeks compared with the 2 weeks, during both paddy rice and wheat crops, paddy rice soil, however, showed considerably greater increases than the wheat soil. These results support the findings of Mandal and Haldar (1980) who reported increases in the extractability of soil Fe and decreases in the extractability of soil Zn during flooded incubations. In wheat soil, however, extractability of soil Fe decreased at 8* weeks which was probably due to the precipitation of iron oxides/ hydroxides (Holford and Mattingly, 1975b: Hamad *et al.*, 1992; and Udo and Uzo, 1972) released during the previous flooded rice crop. Availability of soil Cu increased during flooded rice crop and decreased during wheat crop (10 weeks only). Flooded conditions had adverse effects on soil Zn the availability of which decreased during both growth periods whereas in moist aerated conditions, during wheat crop, it decreased only at 8* weeks of growth, probably due plant uptake and/ or due to precipitation as Fe-PP-Zn complexes.

Liming had positive effects on P availability, which increased with the greater lime levels (10%) but the availabilities of micronutrients were negatively affected, showing greater decreases with high lime levels (10%). These decreases were most probably due to increases in pH as result of lime application.

8.2. Pyrophosphate as an amendment fertilizer

Pyrophosphate (PP) was used with orthophosphate (OP) in small proportions of the total applied P in most of the studies performed i.e. incubation studies, pot trials and sorption studies. The amounts of PP ranged from 10-30% of the total applied P. Although added PP with OP proved to be more effective in maintaining greater P levels than the orthophosphate (OP) alone, the effects varied with the experimental conditions. The effects of added PP in improving P availability, in general, were minimum during incubation studies in a brown earth soil from Aber Farm and maximum during sorption studies in the presence of agricultural lime ($CaCO_3$).

During the incubation studies, PP treated samples in comparison to OP treated samples, maintained 3% and 17% greater P at 50 days of flooded and moist incubations respectively. The greatest effects of PP addition were found in a brown earth soil from Pen-y-Ffridd, showing 31% and 39% greater levels of P after 12 weeks of alternate flooded-moist and moist aerated incubations respectively. The response of a Pakistani soil to PP addition was slightly less than the soil from Pen-y-Ffridd, showing 27% and 25% greater levels of P in PP treated samples compared with OP treated samples. The marginal effects of PP addition to Aber farm soil, in improving P availability, were expected due to greater iron contents (DTPA-Fe 93.4 ug/g soil) in that soil, which might have precipitated with the added PP and minimised its effectiveness in reducing P sorption. Although the amounts of DTPA extractable Fe were greater in a soil from Pen-y-Ffridd, greater levels of "available" P which were maintained in that soil compared with the Pakistani soil suggested that some other factors were also involved. During alternate flooded-moist and moist incubations of 12 weeks, the pH values in the soils from Pen-y-Ffridd and Pakistan, in PP treated samples, were 7.60, 7.91, 7.94 and 7.95 respectively. Due to the high pH values in both soils, most of the iron oxides/ hydroxides were probably precipitated and near their ZPC (zero point of charge) (Lindsay, 1979) and did not play a major role in affecting P availability. Lower pH values of the Pen-y-Ffridd soil probably helped it to maintain greater levels of P than the Pakistani soil. The marginal effects of PP in improving P availability during flooded incubations were probably due to more rapid hydrolysis of PP to OP (Hossner and Phillips, 1971), which would otherwise block sites for P sorption (Giordano *et al.*, 1971; and Mortvedt and Osborn, 1977).

During pot trials, the behaviour of added pyrophosphate (PP) in improving P availability was slightly different from the incubation studies. The effects of added PP, at 10 weeks and 8* weeks (soil from previous wheat crop), were greater in flooded paddy rice soil than the moist aerated wheat soil, maintaining about twice the levels of P found in the wheat soil. Flooded conditions of the paddy rice soil, probably helped it to maintain greater levels of P as most of the iron oxides/ hydroxides were reduced to soluble Fe^{II} forms (Ponnamperuma, 1972) and did not remove P from solution. After 8* weeks of growth compared with the 10 weeks period, during both paddy rice and wheat crops about 28% and 46% respectively less P were maintained in PP treated samples than the OP treated samples. Most of the added pyrophosphate (PP) was probably hydrolysed to OP during the 8* weeks period (a total of 19 weeks) and ultimately precipitated in insoluble forms. Hydrolysis of pyrophosphate (PP) has been reported to be variable with the soil moisture content, with a half-life ranging from 0.5 to 4 days in flooded and 4 to 100 days in moist conditions (Blanchar and Hossner, 1969 and Sutton *et al.*, 1966). Pyrophosphate (PP) treated samples in comparison to OP treated samples maintained greater P levels in plant shoots (5-6%) and roots (9%) of paddy rice, showing slightly less P in shoots at 8* weeks period. Lower levels of "available" P at that period, as reported earlier, probably decreased uptake of P by plants. Pyrophosphate (PP) failed to show significant ($p<0.05$) differences from OP treatment in affecting uptake of P by wheat plants.

Pronounced effects of pyrophosphate (PP) addition were found during the sorption studies, using agricultural lime ($CaCO_3$) and soils of varied nature. The greatest effects of PP in decreasing P sorption were noticed in the presence of agricultural lime ($CaCO_3$) whereas in the presence of brown podzolic soil, PP addition caused marginal effects. In PP treated samples almost all of the applied P remained in solution when reacted with agricultural lime ($CaCO_3$) for about 302 hours. In OP treated samples, only 30% of the applied P was found in solution after that period. In brown podzolic soil, about 60% and 68% of the applied P remained in solution after 398 hours of reaction time. Sorption of P by brown podzolic soil increased when lime was added to this soil, maintaining about 60% (IL1P1, i.e. 5% lime+OP), 56% (IL2P1, i.e. 10% lime+OP), 65% (IL1P2, i.e. 5% lime+OP+PP) and 67% (IL2P2, i.e. 10% lime+OP+PP) of the applied P in solution at 278 hours of reaction. These observations indicated that the application of pyrophosphate (PP) as an amendment fertilizer might be useful only under calcareous conditions. Pyrophosphate (PP) probably reacted with "Ca" in the system blocking the sites for P sorption and inhibiting the formation of DCPD crystals and hydroxide (OH^-) ions (El-zahaby and Chien, 1982). In PP treated samples, in the presence of agricultural lime ($CaCO_3$), pH values were maintained below 6.5 whereas in OP treated samples, sharp increases in pH were observed rising up to 7.61 after 302 hours of reaction time. These results also confirm the possibility of the inhibition of DCPD crystal formation and OH^- formation in PP treated samples. Pyrophosphate (PP) did not prove to be as effective in brown podzolic soil as in the presence of agricultural lime ($CaCO_3$), most probably due to the greater amounts of iron oxides/ hydroxides in the brown podzolic soil which minimised its effects. Added pyrophosphate (PP) might have been covalently bound to most of the iron oxides/ hydroxides present in the system (Bar-Yosef and Asher, 1983: Giordano *et al.*, 1971 and Mortvedt and Osborn, 1977), but some of the iron oxide/ hydroxides may be still free to react with P in solution. Moreover, the dissolution of organic matter (OM) by added PP (Mnkeni and Mackenzie, 1985), probably resulted in the exposure of more sites in the system, which served as a sink for phosphate molecules in the solution. Addition of lime to brown podzolic soil increased P sorption probably due to, increases in pH which caused precipitation of iron oxides/ hydroxides. Some of the applied P perhaps precipitated with iron oxides/ hydroxides in solution, which accounted for the increased P sorption by that soil. The effectiveness of pyrophosphate (PP), however, slightly increased with the increasing levels of added lime.

This observation also supported the idea that the use of pyrophosphate (PP) as an amendment fertilizer could be more effective in calcareous systems. The sorption of P by Pakistani soil was 17% of the total applied P in OP treated samples whereas in PP treated samples slight increases in the solubility of P were observed. Although the sorption of applied P by the Pakistani soil was less than would be expected in a calcareous soil, the effectiveness of pyrophosphate (PP) in reducing P sorption was still high. Lower iron contents (DTPA-Fe 2 ug/g soil) in this soil probably helped PP to maintain greater levels of P in solution. The effectiveness of PP in reducing P sorption by the Pakistani soil was almost similar to that in the presence of agricultural lime ($CaCO_3$), as all of the applied P in the presence of agricultural lime ($CaCO_3$) and Pakistani soil, remained in solution after the reaction periods of 302 and 398 hours respectively. It may be concluded from the results that the use of pyrophosphate (PP) added in small proportions (~10%) to OP fertilizers, in calcareous soils would probably give better results than in the acidic soils rich in iron contents.

8.2.1: Pyrophosphate (PP) role in affecting micronutrient (Fe, Mn, Cu & Zn) availability

Inclusion of pyrophosphate (PP) with OP had positive effects on the availability of micronutrients (i.e. Fe, Mn, Cu & Zn) during incubation studies (chapter 3), pot trials (chapter 6) and sorption studies (chapter 7). During incubation studies, the behaviour of OP in affecting micronutrient availability was variable during flooded and moist aerated incubations. Extractable soil Fe and Mn increased during flooded incubations of 50 days and decreased during moist aerated incubations. Extractable soil Cu and Zn decreased both during flooded and moist aerated incubations. Added OP, however, did not change the extractability of soil Zn in comparison to control (P0) samples during both incubations. Added pyrophosphate (PP), in comparison to OP, improved the extractabilities of soil Fe, Mn, Cu & Zn during both incubation conditions. Pyrophosphate (PP) in comparison to OP, probably dissolved more organic matter (OM) from the soil, increasing "organic anions" in soil solution, which ultimately reacted with metallic cations to form soluble complexes and thus increased the solubility of these nutrients. Moreover, PP itself has been reported to act as a chelating agent (Bar-Yosef and Asher, 1983; Giordano *et al.*, 1971; and Mortvedt and Osborn, 1977).

Pyrophosphate (PP) addition caused fairly similar effects on micronutrient availability during pot trials, resulting in increases in their solubility in both flooded paddy rice and moist aerated wheat soils. In most cases, the uptake of these nutrients was also increased by added PP. In wheat soil at 8* weeks (soil from previous rice crop), extractability of soil Fe and Mn decreased in PP treated samples compared with OP (AB0) and P0 (A0B0) treatments. These decreases were probably because greater Fe and Mn were mobilised by added PP during the previous paddy rice crop, and they precipitated with P during the current wheat crop under moist aerated conditions. Added P as OP decreased extractable Zn during wheat crops whereas added PP increased its levels over both P0 (A0B0) and OP (AB0) treatments, supporting the idea of chelation either directly by PP or through "organic anions" produced due to the dissolution of organic matter (OM). Moreover, PP might also have increased the solubility of Zn by maintaining lower soil pH than the OP treated samples. The results found in the sorption studies (chapter 5 and 7), in the presence of agricultural lime ($CaCO_3$), revealed that lower pH values were maintained in PP treated samples (pH <6.5) than the OP treated samples (pH >7.0). Although pH values in this trial were not recorded, it was expected that PP would maintain lower pH than OP in this soil, as it was limed prior to the pot trials and was expected to be slightly calcareous.

During sorption studies (chapter 7), the behaviour of PP in affecting Zn solubility was different in the "pure" $CaCO_3$ system and soil systems. In general, PP decreased Zn sorption by agricultural lime in comparison to OP whereas in soil systems, PP increased sorption of Zn. The increased sorption of Zn due to added PP might have happened in a number of ways. (i) Pyrophosphate (PP) probably occupied some of the sites of $CaCO_3$, which resulted in the lowering of solution pH and Zn sorption. In all the soils used for sorption studies, pH values were higher in PP than the OP treated samples, which probably increased sorption or precipitation of Zn, the solubility of Zn being highly pH dependent (Lindsay, 1979). (ii) In PP treated samples, in the presence of soils, other metallic cations such as iron oxides/ hydroxides were dissolved in solution which probably competed with Zn for chelation by PP. This competition probably left Zn free in the solution to be sorbed by soil surfaces. This assumption is supported by the greater iron contents in solution (brown podzolic soil) in PP treated samples (table 7.16). (iii) Pyrophosphate (PP) itself was probably sorbed by the soils, causing increases in the cation exchange capacity (CEC) of the soils and specific Zn sorption by the formation of Zn-PP bond (Xie and Mackenzie, 1990b). (iv) Added pyrophosphate (PP) might have exposed new sites through organic matter (OM) dissolution (Mnkeni and Mackenzie, 1985) and enhanced Zn sorption.

8.3: Role of organic acids

Added "organic acids", such as would be released into soil solution by the decomposition of organic matter (OM), showed positive effects in maintaining greater P levels in solution in line with the literature (Lopez-Hernandez, *et al.*, 1979). The effects, however, varied with the kind of organic acids used. For example, PP extract of rice straw in the absence of Zn and water extract of rice straw in the presence of Zn were the most effective in reducing P sorption by agricultural lime ($CaCO_3$). In Pakistani soil, chelex resin extract of soil in the absence of Zn and water extract of rice straw in the presence of Zn were the most effective in reducing P sorption. Commercial organic acids like citric acid did not play convincing roles, in improving P availability, in the presence of agricultural lime ($CaCO_3$) but clearly the concentrations of citric acid used in this study were too great. Inconsistency in the behaviour of "organic acids" suggests that further research needs to be conducted to clarify their specific role in such reactions, at the concentrations likely to be encountered in rhizosphere soil solutions.

8.4: Conclusions and suggestions for further research

The aim of this study was to investigate the behaviour of soil phosphorus under flooded and moist aerated soil conditions, the conditions prevailing in the field during alternating paddy rice and wheat rotations. The studies included a series of laboratory incubation experiments and glass house trials on wheat and paddy rice. The experiments were conducted under flooded and moist aerated conditions to investigate the behaviour of soil phosphorus and micronutrients (Fe, Mn, Cu & Zn). Studies included the use of pyrophosphate (PP) as a source of P, its hydrolysis to OP which may determine the amounts of P available to plants and also its reactions with the micronutrients (Fe, Mn, Cu & Zn). The effects of added organic acids/ humic materials, such as would be dissolved by pyrophosphate (PP) and/ or released due to the decomposition of organic matter, on P availability, were also investigated. Studies on the sorption of applied P by agricultural lime and different soils in the presence and absence of Zn were also performed.

Flooded incubations, in general, caused increases in the extractability of soil P subjected to laboratory incubations and pot trials. The soils subjected to flooded conditions maintained greater levels of P than the moist aerated soils. Alternating flooded- moist conditions decreased P availability over the moist aerated samples, suggesting that more sorption sites probably of iron oxides/ hydroxides (amorphous forms) were exposed due to these conditions. Amorphous iron oxides/ hydroxides were probably also produced during the 10-25 day period of flooding when a brown earth soil from Aber Farm was incubated for 50 days. Incomplete reduction of the soil was probably responsible for the accumulation of these amorphous iron oxides/ hydroxides. During incubation experiments in the laboratory it seemed very difficult to maintain uniform conditions of moisture, temperature and flooded conditions for each sample in the small volumes used in this work. Due to limitation in the UK of conducting paddy rice trials in the field, the conditions may be improved greatly by using larger volumes of soil for incubations and performing analyses using sub samples from the bulk incubated samples.

Flooded and moist aerated conditions, during the pot trials, increased the extractability of soil Fe and Mn. These increases were considerably greater in the flooded than in the moist conditions. The extractability of soil Fe decreased in the moist aerated soil which was previously subjected to flooded conditions. Flooded conditions increased the extractability of soil Cu whereas moist conditions decreased it. The extractability of soil Zn decreased with the flooded and increased with the moist conditions.

Sorption of applied P as OP was greatest in the presence of agricultural lime ($CaCO_3$) compared with the soils studied. Added pyrophosphate (PP) and different organic acid extracts of soils and rice straw inhibited P sorption by $CaCO_3$ and the soils, the effects being greatest in the case of $CaCO_3$ and least in brown podzolic soil. Pyrophosphate (PP) and added organic ligands probably blocked the sorption sites on $CaCO_3$ particles and prevented the formation of DCPD crystals. It might be suggested that the addition of pyrophosphate (PP) and organic acids could improve P availability in highly calcareous soils to a greater extent, and to a lesser extent in moderately calcareous soils. As the effects were not found to be convincing in brown podzolic soil and in a soil from Pen-y-Ffridd probably due to their greater Fe contents, the effectiveness of added pyrophosphate (PP) and/ or organic acids in calcareous soils would, however, depend upon their "active" Fe contents.

If the soils are subjected to flooded conditions, iron oxides/ hydroxides are mobilised and may precipitate in amorphous forms when these soils are aerated. These iron oxides/ hydroxides may play a major role in determining the fate of soil P, even in soils with low total Fe. The "active" iron oxides/ hydroxides of a soil should be taken into account if the effectiveness of pyrophosphate (PP) is to be tested on that soil.

Further studies are needed to investigate the roles of "active" iron oxides/ hydroxides, in determining the fate of applied P, which may be present as coatings on the surfaces of $CaCO_3$ in calcareous paddy rice soils which have been subjected to cycles of aeration and anaerobism.

Organic acid extracts used in these studies probably contained organic acids of different kinds, some of which might contribute like to the reduction in P sorption. Techniques should be developed to isolate the specific natural organic ligands responsible for such reactions and root exudates in rhizospheres of living plants could also be investigated in addition to organic materials produced by microbial degradation of plant debris.

Overall effects of Zn addition were to decrease P sorption by $CaCO_3$ and a Pakistani soil. Added Zn caused decreases in pH of the solutions, perhaps producing a favourable pH range for P availability. Added pyrophophate (PP), in comparison to OP, increased the extractability of micronutrients (Fe, Mn, Cu & Zn) during both flooded paddy rice and moist aerated wheat conditions. During sorption studies, PP treated samples maintained greater amounts of organic carbon and iron contents in solution. The sorption of Zn by the soils, however, increased in PP treated samples compared with OP alone.

Liming a brown earth soil from Pen-y-Ffridd caused decreases in the extractability of micronutrients and increases in the extractability of soil P. Phosphorus availability seemed to be more closely related to the extractable soil Fe than the other micronutrients.

The current studies were performed in the laboratory and in the glass house (pot trials) as it was not possible to conduct trials in the field. It seems difficult to make solid recommendations for paddy rice and wheat rotations on the basis of laboratory studies which may not truly represent the actual field conditions, however, the information obtained from such studies may be used as a basis for further investigations in the field.

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APPENDICES

Appendix I

Series	*Denbigh*	*Manod*
Soil type	Brown earth, low base status	Podzolized
Locality	Aber	Gwydyr High Park
Grid Ref.	SH/636716	SH/793591
Relief	Gentle to moderate unifrom slope at 180 ft. N. aspect	Moderate uniform slope from crest oflong ridge, 700 ft. S.W. aspect
Profile Drainage	Free	Free
Site Drainage	Normal	Normal
Land use	Ley grass	Spruce forest about 25-30 years old with very sparse ground flora
Parent Material	Drift dominantly of Ordovician shale, with some grits and igneous rocks	Ordovician slaty shale with possible slight igneous influence

Profile Description (inches)

(0-7) A

Brown (10 YR 5/3) loam with numerous small and medium size shale, some larger grit and occasional igneous pebbles; moist medium and small cloddy structure; porous; slightly compact at top becomming friable lower; moderate to high organic matter; frequent roots; abundant earthworms; fairly sharp boundary.

(7-17) B

Yellowish brown (10 YR 5/4) loam to clay loam with frequent small shale stones; moist; weak large cloddy breaking to small cloddy and crumb; porous; friable; frequent roots; earthworms in upper part of horizon; merging boundary.

(17-27) (B)C

Clay loam as above with faint paler mottle in lower part of horizon; very small cloddy to crumb structure; fewer grass roots than above.

Profile Description (inches)

(0-2) Ao

Black (5 YR 2/1) mor humus horizon with top inch of little decomposed litter (F layer) over 1 inch H layer; weak crumb structure; porous; loose; fluffy; structure; porous; loose; fluffy; abundant roots; sharp boundary

(2-2 3/4) A$_2$

Grey to grey-brown (10 YR 5/1-5/2) loam with occasional small shale stones; moist; small cloddy structure; porous; initially rather compact breaking to friable; high organic matter; abundant roots; sharp boundary

(2 3/4-6) AB

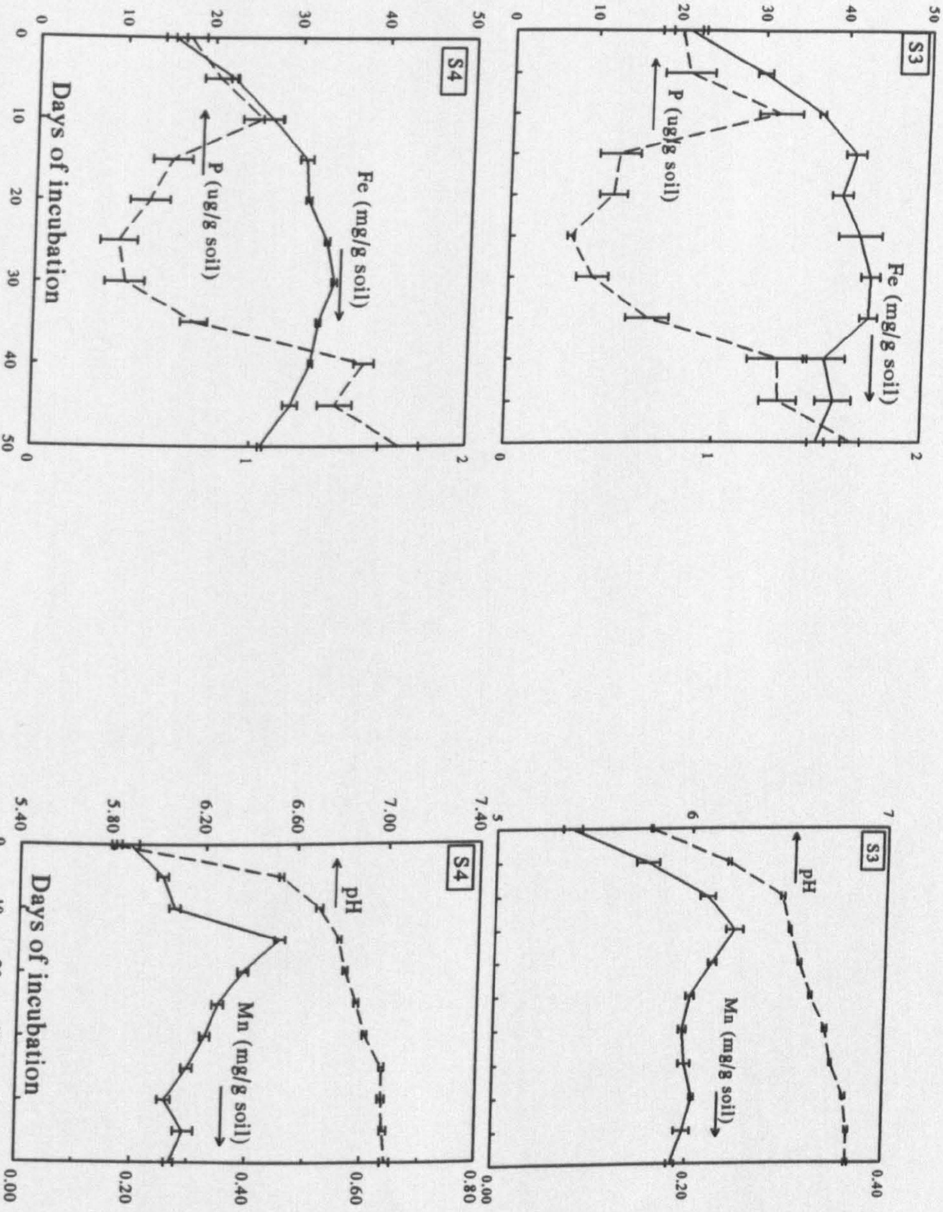
Brown (7.5 YR 4/4) faintly mottled with brighter brown; loam with many small shale stones; moist; cloddy structure; porous; initially compact breaking to friable; moderate organic matter; frequent roots; fairly sharp boundary

(6-24) B

Strong brown (7.5 YR 5/6) loam with abundant shale stones; moist; very small crumb structure; very porous; loose; moderate organic matter; frequent roots; over shale rock

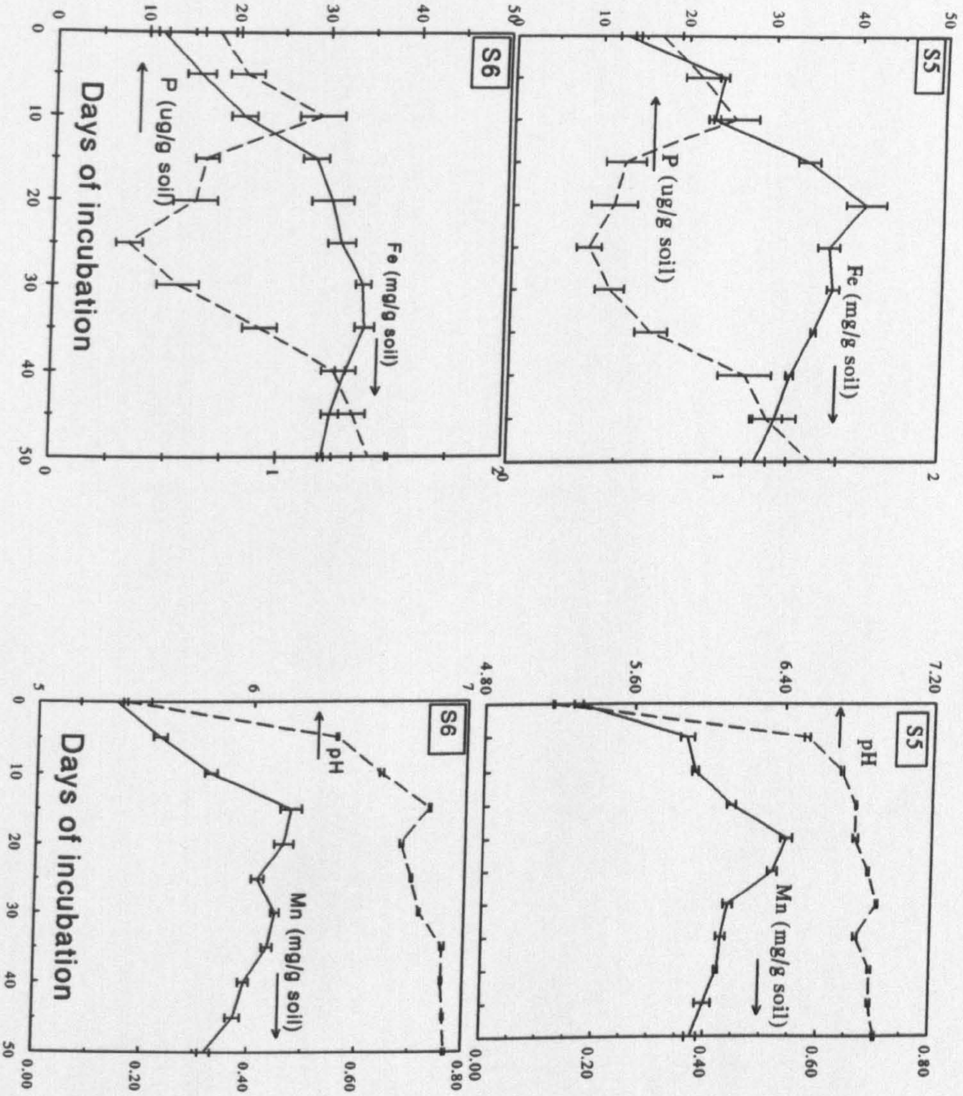
Analytical Data

Series	**Denbigh**	**Manod**
Number	Cn 55/1	Cn 84/4
Depth (inches)	0-7 A	6-24 B
Silt % (0.02-0.002mm)	31	35
Clay% (<0.002mm)	16	17
Loss on ignition (%)	10.8	8.0
pH (Water)	6.1	5.7
pH (0.01M $CaCl_2$)	5.7	5.1
Exchangeable Cations me/100g		
Ca^{++}	5.70	0.39
Mg^{++}	1.31	0.11
Na^{+}	0.30	0.08
K^{+}	0.71	0.08
Exchange Capacity me/100g	26.0	11.6
Percentage Saturation	31	6

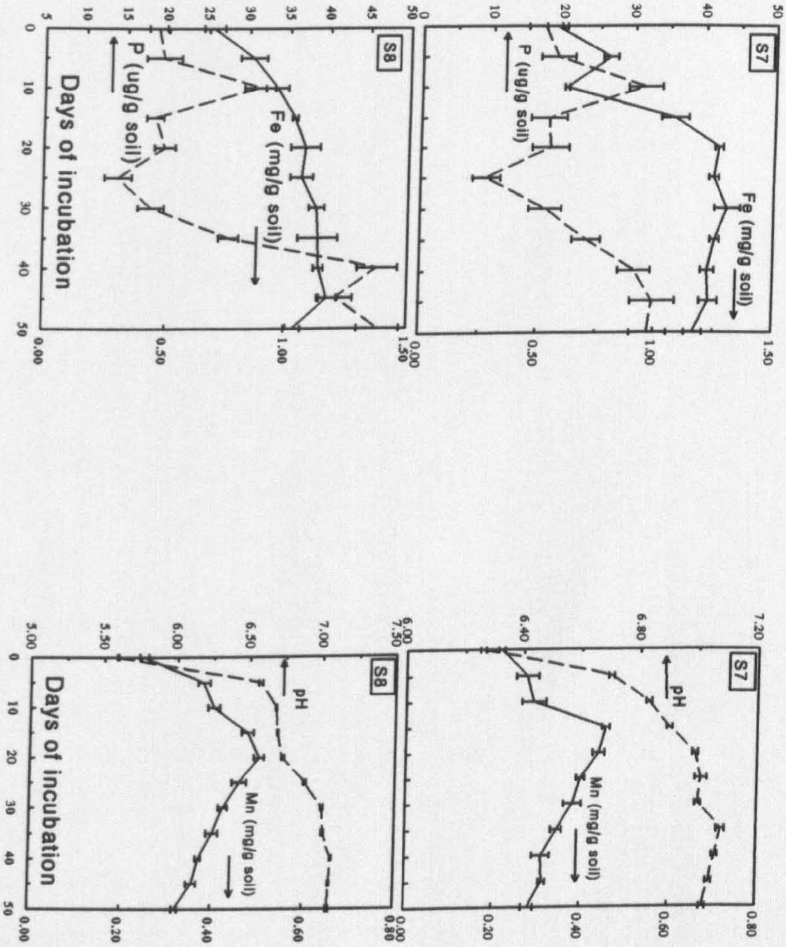


APPENDIX 3.1a

(Effects of flooded incubations on extractable soil P, reducible Fe & Mn and pH)

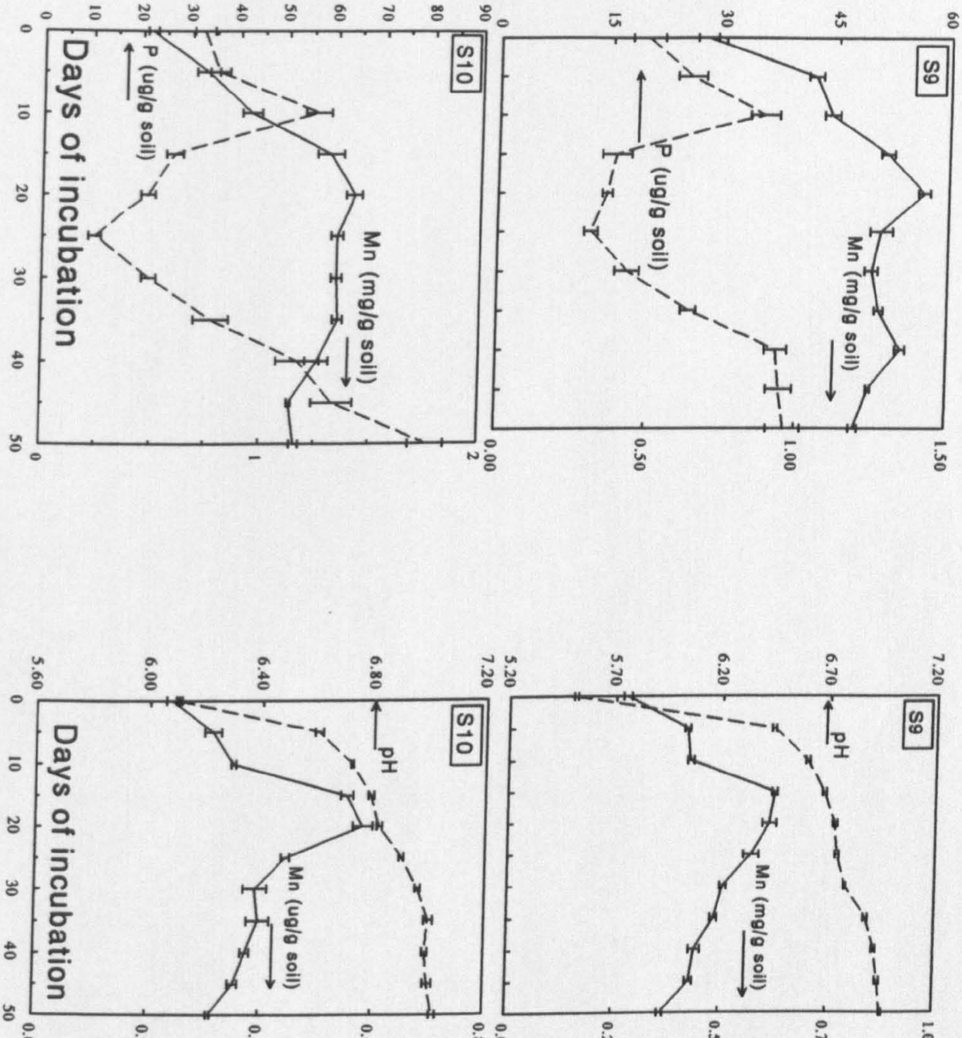


APPENDIX 3.1b
(Effects of flooded incubations on extractable soil P, reducible Fe & Mn and pH)



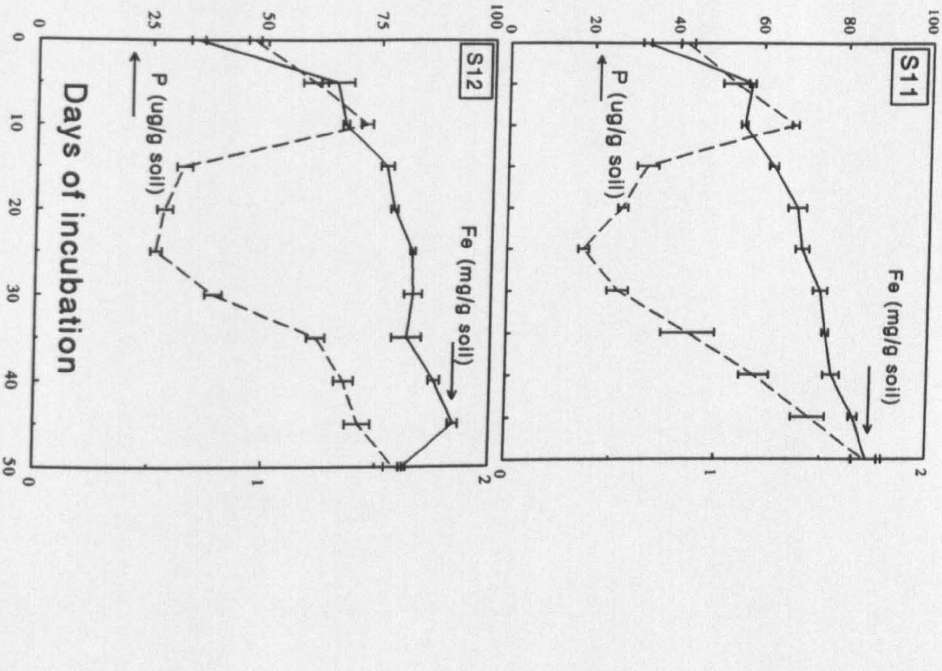
APPENDIX 3.1c

(Effects of flooded incubations on extractable soil P, reducible Fe & Mn and pH)



APPENDIX 3.1d

(Effects of flooded incubations on extractable soil P, reducible Fe & Mn and pH)



APPENDIX 3.1e
(Effects of flooded incubations on extractable soil P, reducible Fe & Mn and pH)

Appendix 5.1 EDAX analyses

Photograpghs (plates 1-3) are presented which show that $CaCO_3$ particles/ DCPD (?) crystals were marked at different points in the photograpghs and then analysed for Ca and P contents.

PLATE 1 : (a, b): Treatment LP1 ($CaCO_3$ + OP)

(c, d): Treatment LP2 ($CaCO_3$ + OP +PP)

PLATE 2 : (a, b): Treatment LP3 ($CaCO_3$ + OP +PP extract of soil)

(c): Treatment LP4 ($CaCO_3$ + OP +PP extract of rice straw)

PLATE 3: (a, b): Treatment LP5 ($CaCO_3$ + OP + citric acid)

(c, d): Treatment LP6 ($CaCO_3$ + OP + citric acid extract of rice straw)

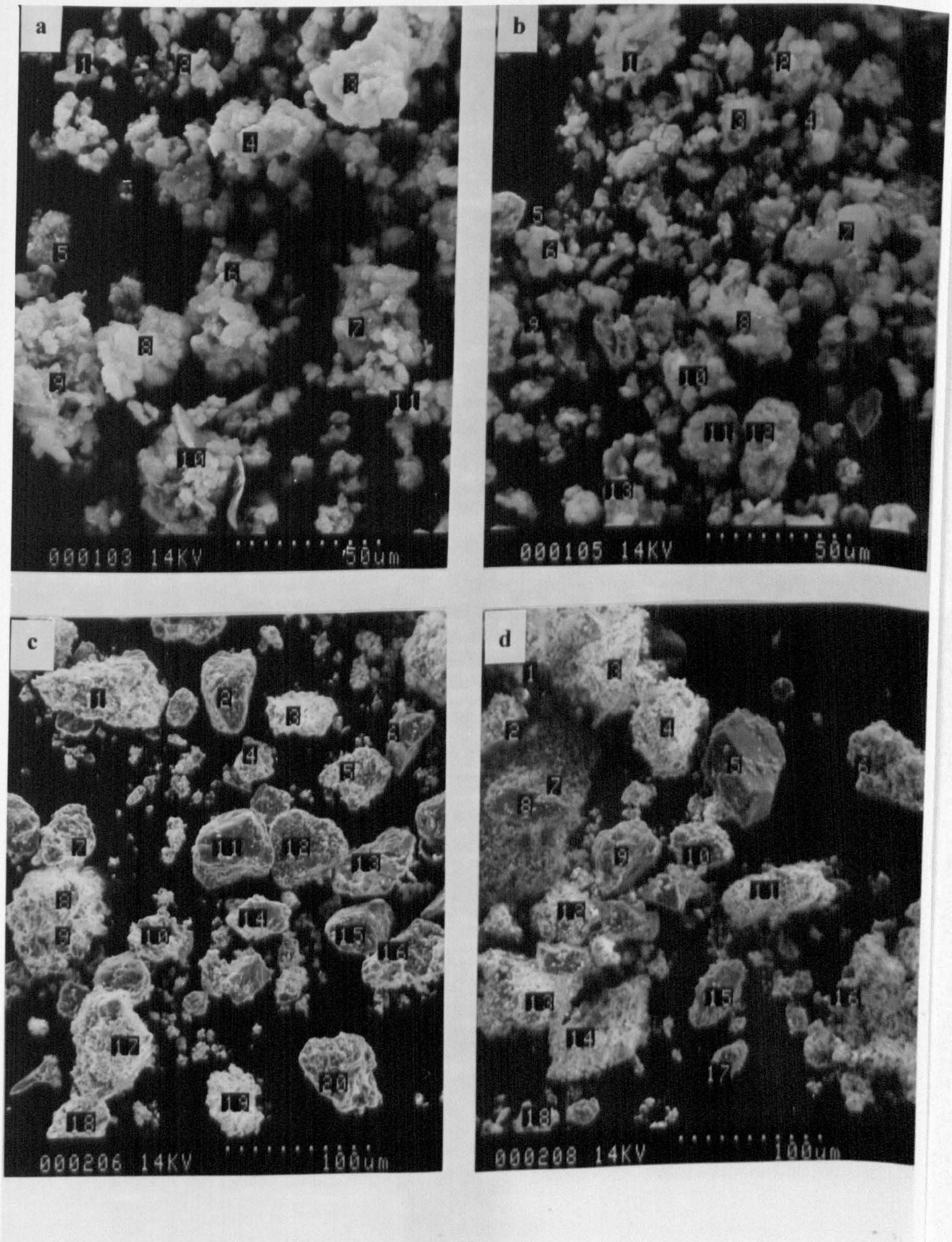

a
000103 14KV 50um
b
000105 14KV 50um
c
000206 14KV 100um
d
000208 14KV 100um

PLATE 1

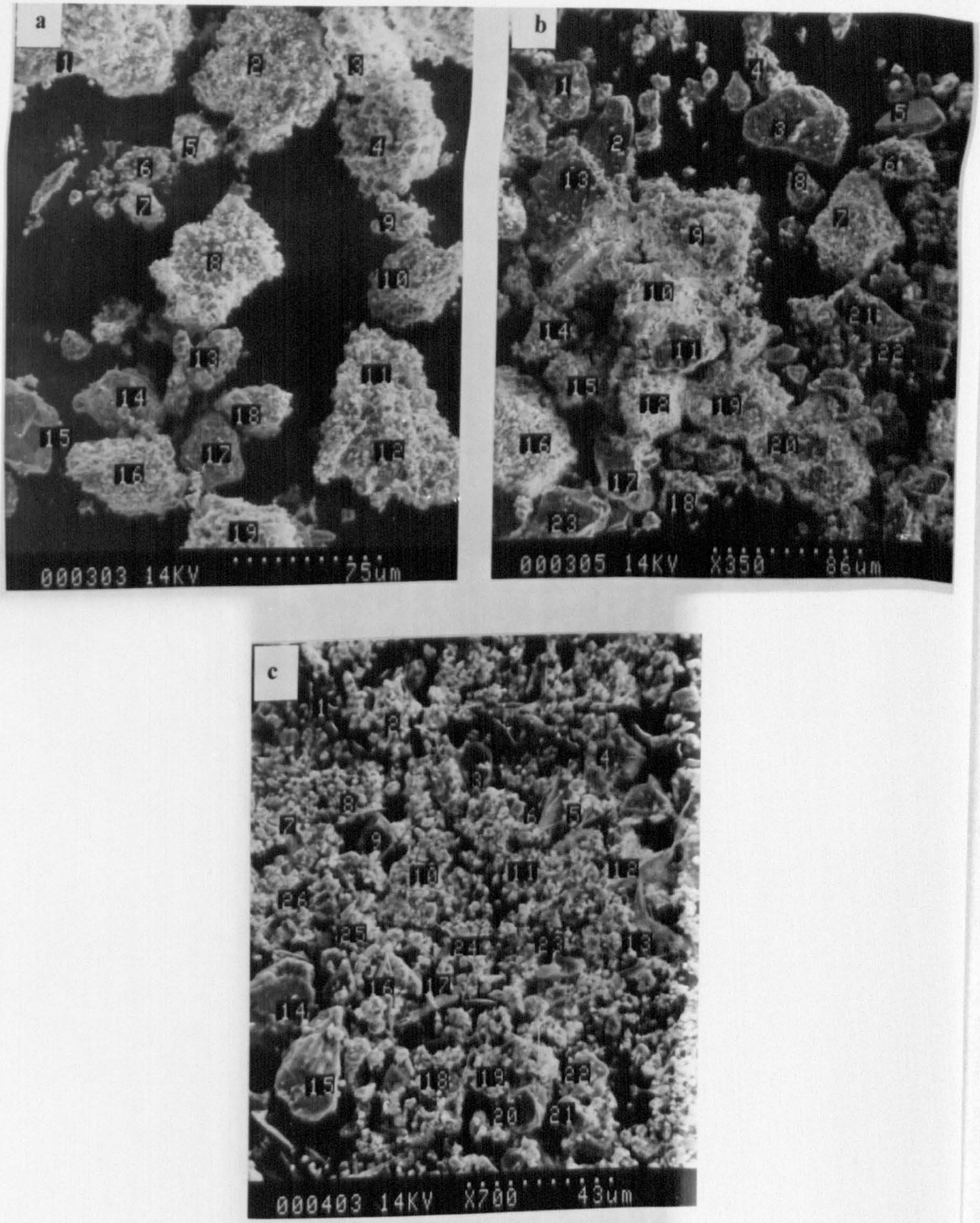
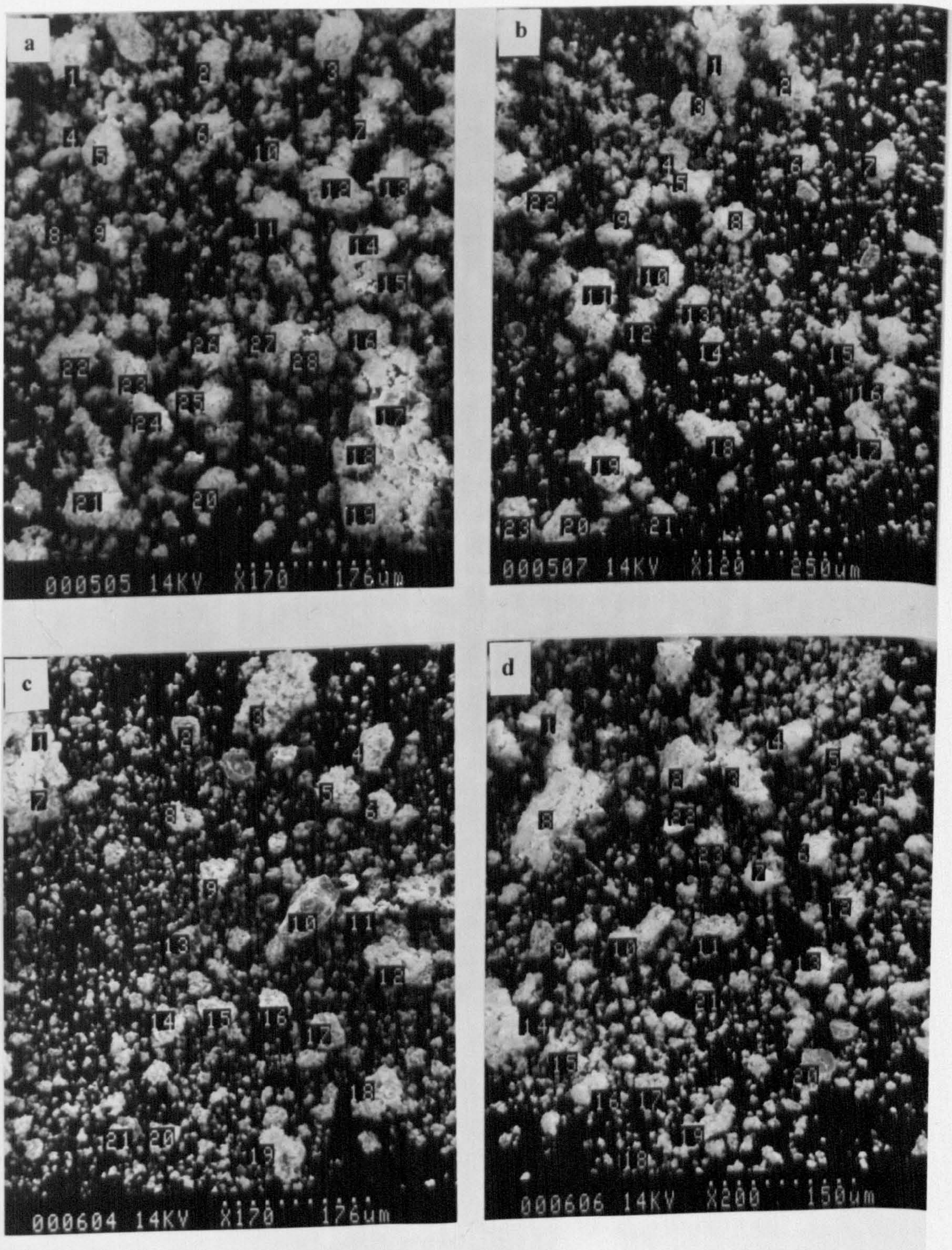

a
000303 14KV 75um
b
000305 14KV X350 86um
c
000403 14KV X700 43um

PLATE 2


a
1
2
3
4
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6
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12
13
8
9
11
14
15
26
27
28
16
22
23
25
17
24
18
21
20
19
000505 14KV X170 176um
b
1
2
3
4
5
6
7
22
9
8
10
11
13
12
14
15
16
18
17
19
23
20
21
000507 14KV X120 250um
c
3
1
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4
7
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20
19
000604 14KV X170 176um
d
1
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17
19
18
000606 14KV X200 150um

PLATE 3