CHEMICAL CHANGES IN WATERLOGGED SOILS

by

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DEDICATED TO THE MEMORY OF MY FATHER

THE LATE ALHAJ TAYEB ALI CHOUDHURY

DECLARATION

I declare that I have composed this thesis myself. The work embodied in it is the result of my own investigations except where reference has been made to published literature.

F.A. Choudhury

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ABSTRACT

Incubation experiments were carried out to study the chemical changes which occur under waterlogged, and alternate flooded and moist conditions using four soils with and without added urea. Samples were analysed periodically to determine the concentrations of water and ammonium-acetate extractable phosphate, iron, manganese, calcium and potassium. The redox potential, pH and specific conductance of the samples were also measured. In addition, mineralisation of soil organic phosphorus and isotopically exchangeable pool of phosphate and iron were studied.

The results showed that with one exception, the redox potential became highly reducing after four weeks of waterlogging and soil pH values tended towards a neutrality. The amounts of extractable iron and manganese increased substantially within four weeks of waterlogging. The concentrations of calcium also increased whilst the concentration of potassium remained almost stable. The concentration of extractable phosphate increased in all soils but to different extents.

The results for the alternate flooded and moist conditions were very variable due to non-uniform aeration. The application of urea had no substantial effect on any of the values measured.

Water-soluble amounts of iron, manganese, calcium and potassium generally reached peak values after four weeks. The specific conductance values increased substantially within four weeks of waterlogging in all four soils.

The studies on mineralisation of organic soil phosphorus showed that, using existing techniques for phosphorus determination, it was

difficult to draw any firm conclusions. Isotopic exchange studies indicated a substantial increase in both exchangeable phosphate and iron compared with fresh, aerobic soils. However, whilst ammonium-acetate extracted most of the exchangeable iron, most of the exchangeable phosphate remained on the surface of the soil particles.

Glasshouse experiments were carried out to observe the response of rice to added fertiliser phosphorus. These studies showed that higher dry matter yield can be achieved by application of fertiliser phosphorus in a phosphate deficient soil although physical factors are also probably involved. The chemical composition of the rice plants was partially determined and related to the fertiliser treatments.

CONTENTS

1. INTRODUCTION

Rice is the staple food for about half the human population and is one of the most important tropical cereals. The total area under rice cultivation is about 100 million hectares, over 90% is grown in southern and eastern Asia, which are major centres of the world's population. About 185 to 200 million tons of rice is being eaten every year, of which, probably half is consumed on the farms where it is grown, while only 5% enters into international trade. There are usually three groups of rice grown in a year, namely, 'aman', 'aus' and 'boro'. The most important crop is 'aman'. The 'aman' grows during the monsoon period when rainfall is about 2000 to 4000 mm. The 'aman' is planted in May - June and harvested in September - December with a maturation period of 5 to 6 months. The 'aus' crop, of shorter duration, is planted in May - June and harvested in September - October. The 'boro' crop, if water is available, may be planted in December - January and harvested in March - April (Purseglove, 1972).

The importance of rice warrants good soil management. Most of the rice is grown in paddy fields which are flooded or waterlogged for considerable periods of time. This waterlogging causes considerable modifications to both the chemical and physical environment of the soil. Thus it is important to study the physicochemical properties of the waterlogged soils both to understand and maximise the utilisation of the system. Although many workers have studied the general changes which occur in a submerged soil (see e.g. Patrick and Mahapatra, 1968; Ponnamperuma, 1972 for reviews).

However, further information on the changes in the availability

of different plant nutrients under waterlogged soils is required. This work involves the study of the availability of plant nutrients and some of the physicochemical properties in waterlogged soils. Since phosphorus is one of the most essential major plant nutrients, its availability and mineralisation under waterlogged soil conditions was particularly studied. The distribution of phosphate in particle size fractions of the soil was also examined.

A glasshouse study was also made to observe the response of rice to added fertiliser phosphorus.

LITERATURE REVIEW

2. LITERATURE REVIEW

This review covers much of the literature dealing with the chemical changes which occur when a soil is waterlogged. One of the main objectives of this study was to examine the effects of waterlogging on the forms and availability of soil phosphorus and the response of paddy rice to added phosphorus. Accordingly, the literature relating to the forms, transformations, distribution and determination of soil phosphorus is also reviewed.

2.1. CHEMICAL CHANGES IN WATERLOGGED SOILS

When an aerobic soil is flooded it undergoes marked chemical changes. The oxidised constituents, e.g. NO_3^-, Mn^{4+}, Fe^{3+}, and SO_4^{2-}, that characterise a well-drained soil, virtually disappear and are replaced by their reduced counterparts, NH_4^+, Mn^{2+}, Fe^{2+}, and S^{2-}. The course of organic matter decomposition is diverted from carbon dioxide production to the generation of organic acids and methane. The solubility of phosphate is increased and accumulation of ammonia also occurs (Sankaram, 1969).

Waterlogging a soil usually brings about a number of other physicochemical changes in addition to those mentioned above. The more important of these are: (a) a decrease in redox potential; (b) an increase in pH of acid soils and a decrease in pH of alkaline soils; and (c) an increase in specific conductance.

The literature relating to some of the changes which may occur during waterlogging is reviewed below.

2.1.1. Redox Potential

The single physicochemical property that differentiates a

flooded soil from a well-drained soil is the oxidation-reduction or redox potential. Oxidation and reduction are chemical reactions in which electrons are transferred from a donor to an acceptor. The electron donor loses electrons and increases the oxidation number or is oxidised and the acceptor gains electrons and decreases its oxidation number or is reduced.

Redox potential measures the intensity of oxidation or reduction of the soil. High and positive redox potentials indicate oxidative conditions. The range of oxidation-reduction usually encountered in well-drained soils and in waterlogged soils is: oxidised, +400 to +700 mV; moderately reduced, +200 to +400 mV; reduced, -100 to +200 mV; and highly reduced, -300 to -100 mV (Patrick and Mahapatra, 1968).

The redox potential is usually measured by the electropotential (voltage) created between a platinum electrode in the system and a standard reference half-cell. The resulting potential, Eh, is represented by the equation (Hewitt, 1950)

$$Eh = Eo + \frac{RT}{nF} \ln \frac{(oxid.)}{(reduct.)}$$

where, Eh = the potential in volts, referred to the normal hydrogen electrode as zero, of the system under consideration

Eo = a constant characteristic of the system

R = gas constant

T = absolute temperature

n = number of electrons involved in the change from the oxidised to reduced form

(oxid.) = concentration of oxidised form

(reduct.) = concentration of reduced form

F = Faraday's constant.

The equation shows Eh to be dependent on the ratio of oxidant to reductant as well as on temperature and the particular system

under consideration. Also the system must be reversible, i.e. the oxidised form readily changing to the reduced form under the influence of suitable Eh and the reduced form readily changing to the oxidised form.

Reduction of various species in a flooded soil is more or less sequential and the sequence predicted is presented in Table 1.

Oxygen is the first soil component to be reduced and it becomes undetectable within a day after waterlogging (Ponnamperuma, 1972). After the disappearance of oxygen from a waterlogged soil the need for electron acceptors by facultative anaerobic and true anaerobic organisms results in the reduction of several oxidised components. If an energy source is available to the microorganisms, nitrate, the higher oxides of manganese, hydrated ferric oxide, and sulphate will be reduced. Nitrate and manganese dioxide are reduced at fairly high redox potentials, whereas sulphate is reduced only under the strictly anaerobic conditions associated with extremely low potentials. Ferric oxide reduction is intermediate.

The sequential reduction of oxygen, nitrate, manganic-manganese and ferric iron following the waterlogging of a soil has been reported by Turner and Patrick (1968). In some cases relatively complete reduction of one component is accomplished before the next component begins to undergo reduction (Patrick and Mahapatra, 1968). More usually one component is not completely reduced before the next most easily reduced component begins to reduce. Thus, the concept of a sequential reduction of oxidised components in a waterlogged soil may not necessarily always maintain a similar pattern. There could be some overlapping in the reduction of oxidised forms of iron and manganese. This may be attributed to the reduction of insoluble

Table 1. Sequence of reduction of oxidation-reduction systems in waterlogged soils*

Reaction	Redox potential in mV at pH_7, 25°C	Sequence
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	830	0
$NO_3^- + H_2O + 2e^- \rightleftharpoons NO_2^- + 2OH^-$	430	1
$MnO_2 + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O$	410	2
$Fe(OH)_3 + e^- \rightleftharpoons Fe(OH)_2 + OH^-$	-130	3
$Fe(OH)_3 + 3H^+ + e^- \rightleftharpoons Fe(OH)_2 + OH^-$	-140	
$CH_3COCOOH + 2H^+ + 2e^- \rightleftharpoons CH_3CHOHCOOH$	-180	4
$CH_3CHO + 2H^+ + 2e^- \rightleftharpoons CH_3CH_2OH$	-190	
$SO_4^{2-} + H_2O + 2e^- \rightleftharpoons SO_3^{2-} + 2OH^-$	-490	5
$SO_3^{2-} + 3H_2O + 6e^- \rightleftharpoons S^{2-} + 6OH^-$	-200	
$2H^+ + 2e^- \rightleftharpoons H_2$	-420	6
$CO_2 + 2H^+ + 2e^- \rightleftharpoons HCOOH$	-620	7
$H_3PO_4 + 2H^+ + 2e^- \rightleftharpoons H_3PO_3 + H_2O$	-700	
$H_3PO_3 + 2H^+ + 2e^- \rightleftharpoons H_3PO_2 + H_2O$	-920	8
$H_2PO_2^- + H^+ + 2e^- \rightleftharpoons P + 2H_2O$	-930	
$P + 3H^+ + 3e^- \rightleftharpoons PH_3$	-360	

* Source: Ponnamperuma (1965).

ferric oxide to the more soluble ferrous hydroxide and the subsequent release of manganese compounds that were occluded or coprecipitated with the ferric oxide. These manganese compounds were probably protected from reduction until the insoluble ferric oxide layer had been stripped away (Turner and Patrick, 1968).

When an aerobic soil is flooded, its redox potential (Eh) falls sharply and reaches a minimum within a few days, then it increases slightly before decreasing again asymptotically with time. The course of Eh changes is determined by the initial aerobic potential, the content of organic matter, the temperature, the nature and content of electron acceptors present in the soil and the duration of flooding (Ponnamperuma, 1965, 1972).

Organic matter may increase the intensity of reduction but does not necessarily produce significantly lower ultimate potentials. Green manure causes a steeper decline in Eh than straw (Ponnamperuma, 1965). Savant and Ellis (1964) also observed that a decrease in redox potential during the first 15 to 20 days of submergence was accelerated by additions of organic matter.

The influence of soil factors on redox potential changes have been summarized as follows: (a) soils high in nitrate (more than 275 ppm NO_3^-) have positive potentials for several weeks after submergence; (b) soils low in organic matter (less than 1.5%) or high in manganese (more than 0.2%) maintain positive potentials even six months after flooding; (c) soils low in active manganese and iron with more than 3% organic matter attain Eh values of -200 to -300 mV within two weeks of flooding; and (d) the fairly stable potentials reached after several weeks of flooding lie between +200 and -300 mV (Ponnamperuma and Castro, 1964; Ponnamperuma, 1965).

Temperature may play an important role in regulating redox potential. The rate of Eh decrease is maximum at temperature around 25°C but this varies somewhat with the soil (Cho and Ponnamperuma, 1971). The retardation of reduction is most pronounced in acid soils and hardly noticeable in neutral soils high in organic matter. The fairly stable potentials attained after about 12 weeks of flooding are practically independent of temperature in the range of 15 to 45°C (Ponnamperuma, 1972).

2.1.2. Soil pH

When an aerobic soil is flooded, its pH decreases during the first day or two, followed by an increase to a maximum constant value of 6.5 to 7.5 in two or three weeks (Ponnamperuma, 1965). The overall effect of flooding is to increase the pH of acid soils and to decrease the pH of sodic and calcareous soils. The tendency for soils of low pH to decrease in acidity and for soils of high pH to increase in acidity upon flooding indicates that the pH of a flooded soil remains more or less stable at a value near to the neutral point (Mahapatra, 1968).

The decrease in pH shortly after flooding might be due to the accumulation of carbondioxide produced by respiration of aerobic bacteria, because carbondioxide depresses the pH even of acid soils (Nicol and Turner, 1957). The subsequent increase in pH of acid soils is associated with reduction of the soil, and its course is determined by (a) the initial pH of the soil, (b) the nature and content of oxidised soil components, and (c) the content and kind of organic matter (Ponnamperuma, 1965).

Ponnamperuma (1965) found that the pH of acid soils, with an

initial pH of 4.6 to 5.7, increased sharply and remained in between 6.5 to 7.0 within three weeks of submergence. The values were maintained for the next 100 days. A common characteristic of these soils was their high content of active iron. Rodrigo and Pollard (1962) observed that when dry acid soils were submerged, the pH increased and equilibrium values were attained in 80 days.

The pH values of soils high in sodium sulphate may increase after submergence because Na_2SO_4 is reduced to H_2S and $NaHCO_3$ is formed. The pH values of sodic soils can be related to the Na_2CO_3 - H_2O - CO_2 equilibrium and those of calcareous soils to the $CaCO_3$ - H_2O - CO_2 equilibrium (Ponnamperuma, 1972), while in acid soils, rich in iron, by the equilibrium $Fe(OH)_2$ - H_2O - CO_2. In soils low in active iron but high in manganese, $Mn(OH)_2$ may be the dominant factor, while CO_2 tension may be important in soils low in both active iron and active manganese (Ponnamperuma, 1965).

The pH of a submerged soil has a marked effect on the availability of phosphate. Mineral phosphorus is present in soils mainly as iron and aluminum phosphates at low pH, and as calcium phosphates at high pH. The solubility of phosphorus in soils tends to be maximum in the pH range from 6.0 to 7.0 (Ponnamperuma, 1977a). Thus increase in pH of acid soils and the decrease in pH of calcareous and sodic soils as a result of flooding will increase the availability of phosphorus. The increase in pH of acid soils also eliminates aluminum toxicity and minimises iron toxicity.

2.1.3. Iron

A major chemical change that takes place when a soil is flooded is the reduction of iron from ferric compounds to ferrous compounds

by microorganisms. The occurrence of large amounts of reduced iron in waterlogged soils has been reported by several investigators (Pearsall, 1950; Patrick, 1964; Ponnamperuma, 1972; Olomu et al., 1973; Yoshida and Itoh, 1974). Submerged soil solutions are quite different from aerated soil solutions in that they contain high concentrations of iron. The high concentration of iron under reducing conditions is due to the reduction of insoluble ferric compounds to the more soluble ferrous forms.

Under well-drained conditions with oxygen present hydrated ferric oxide or ferric hydroxide is stable in the soil. Under reducing conditions, characterised by an absence of oxygen and a low redox potential, ferric hydroxide is reduced to ferrous hydroxide.

$$Fe(OH)_3 + \bar{e} \rightleftharpoons Fe(OH)_2 + OH^-.$$

This reduction results in the production of hydroxyl ions and an increase in pH (Patrick, 1964). De and Mandal (1957) found a gradual increase in ferrous contents of percolates from soils kept under waterlogged conditions for nine months. Rodrigo and Pollard (1962) observed that the iron content of the supernatant liquid above the waterlogged soil was very low. However, in the 'drained soil solution' from within the soil matrix it was much higher with fall of pH. The soil was treated with dilute acid to maintain a low pH, therefore, it was obvious to find more iron in the 'drained soil solution'. The 'drained soil solution' was not filtered so higher values for iron may also have resulted from colloidal material in suspension. Pearsall (1950) came to the conclusion that soils in the reducing state liberate large amounts of exchangeable cations. He observed that in a marsh soil, exchangeable ferrous iron was as high as 248 mg/100 g of dry soil.

The high concentration of iron is caused indirectly by microbiological action on the organic matter. In the absence of organic matter the solubility of iron is not increased under submerged soil conditions (Robinson, 1930). Meek et al. (1968) observed that flooding without addition of organic matter gave a very low concentration of ferrous iron in solution. Soils low in iron but high in organic matter give concentrations of iron that do not fluctuate for several months. In neutral and calcareous soils the concentration of water-soluble iron rarely exceeds 20 ppm (Ponnamperuma, 1972), presumably due to pH.

It is common to find high levels of available iron in flooded, acidic soils. Indeed, such high concentrations of iron may become toxic to plants. The build up of toxic concentrations of ferrous in the soil solution may be prevented by: (i) previous application of lime in the soil, (ii) avoiding addition of organic matter, (iii) providing internal drainage, and (iv) the addition of KNO_3 or $NaNO_3$ to retard reduction (Ponnamperuma et al., 1955).

Yoshida and Itoh (1974) found that in submerged soils ferrous iron constituted 22 to 30% of the total exchangeable cations but after exposure to air the exchangeable ferrous iron disappeared.

According to Ponnamperuma (1972) the reduction of iron brings about important chemical consequences: (a) the concentration of water-soluble iron increases; (b) pH increases; (c) cations are displaced from exchange sites; (d) the solubility of phosphorus and silica increases; and (e) new minerals are formed. The reduction of iron in a flooded soil is favoured by (i) the absence of substances at a higher level of oxidation such as NO_3^- and MnO_2; (ii) the presence of readily decomposable organic matter; (iii) high temperature

and (iv) a good supply of active iron (Islam, 1976).

During waterlogging the concentration of water-soluble iron increases and reaches a peak value and then decreases. The subsequent decrease is probably due to precipitation of ferric hydroxide [$Fe_3(OH)_8$]. The precipitation of ferric hydroxide is favoured by an increase in pH (Meek et al., 1968; Cho and Ponnamperuma, 1971; Ponnamperuma, 1972). Alexander (1977) observed that bacteria are able to oxidise ferrous iron to the ferric state, the latter precipitating as ferric hydroxide. He also found that many heterotrophic species attack soluble organic iron salts. The iron is converted to an inorganic form which is only slightly soluble and is precipitated from solution.

The presence of considerable amounts of exchangeable ferrous ions means that an equivalent amount of other cations have also been displaced from the exchange sites. From a nutritional view point this is desirable in soils of high cation exchange capacity, but in soils of low cation exchange capacity, it may lead to considerable loss of plant nutrients.

2.1.4. Manganese

The behaviour of manganese in waterlogged soils is similar to iron in many respects. After waterlogging, oxides of manganese (e.g. MnO_2, Mn_2O_3, Mn_3O_4) are reduced to much more soluble manganous (Mn^{2+}) compounds.

Manganese in flooded soils is generally considered to exist in at least four forms, viz., water-soluble, exchangeable, reducible and residual manganese. The first two forms are largely manganous-manganese, the third is composed of higher oxides of manganese and the fourth is a minor constituent of soil minerals (Patrick and

Turner, 1968; Gotoh and Patrick, 1972).

The presence of high concentration of reduced manganese in water-logged soils has been reported by many workers (Robinson, 1930; Ponnamperuma, 1972). The reduction of manganese is thought to be both chemical and biological. Yoshida and Kamura (1974) found that under sterile and non-sterile conditions manganese reduction in water-logged soils was mostly a microbial and partly a chemical process. In 1950 Pearsall found that soils in the reducing state liberate large amounts of exchangeable manganese. Robinson (1930) suggested that the high concentration of manganese is due to microbiological action on the organic matter. He found that in the absence of organic matter the solubility of manganese is not increased under submerged soil conditions. A similar observation was also made by Meek et al. (1968). They found that flooding without addition of organic matter produced only small increases in the concentration of exchangeable manganese.

The kinetics of water-soluble manganese vary from soil to soil. The concentration is low in high pH soils that are low in organic matter and active manganese, and is high in acid soils high in manganese and organic matter. Acid soils with a high content of manganese and organic matter build up water-soluble manganese concentrations within a week or two and show a slight decline in later stages of submergence. But the rate of decline is much less than that shown by iron. Alkaline soils usually contain very low concentrations of water-soluble manganese at any stage of submergence. The subsequent decline in water-soluble manganese might be due to precipitation of manganous carbonate $MnCO_3$ (Ponnamperuma et al., 1969). An increase in pH of the soil solution favours such

precipitation. Soil pH has a marked effect on the activity of soil manganese. Sims and Patrick (1978) extracted greater amounts of manganese at low soil pH.

2.1.5. Other Cations

As a result of flooding the concentration of different ions in the soil solution increases. In a reduced soil these ions are chiefly calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^{+}), sodium (Na^{+}), ammonium (NH_4^{+}), ferrous (Fe^{2+}), reduced manganese (Mn^{2+}) and bicarbonate (HCO_3^{-}). Of these calcium, potassium, magnesium and sodium are not involved in reduction processes; the increase in their concentration is a secondary effect of flooding and reduction, chiefly cation exchange reactions and the solvent action of carbon-dioxide (Ponnamperuma, 1965).

As a result of the displacement of potassium (K^{+}) from the clay complex, the concentration of potassium in the soil solution can be increased. Such an increase in flooded soils has been reported by IRRI (1963). The increases were highest in a sandy soil rich in organic matter and appeared to be associated with the content of soluble Fe^{2+} and Mn^{2+} (Ponnamperuma, 1965).

2.1.6. Specific Conductance

Specific conductance is now extensively used to appraise the total soluble salt content of soils. Specific conductance is one of the most frequently measured properties of aqueous solutions. Thus an accurate means of measuring the salt concentration from the easily measured specific conductance is of great value in evaluating the total soluble salt content of a particular soil.

The specific conductance of the solutions of most soils increases after flooding. The specific conductance of a soil increases

in the early stages of flooding, reaches a maximum roughly coincident with peak reduction and then decreases slightly to a fairly stable value, which varies with the particular soil.

When a soil is submerged or waterlogged the increase in specific conductance is caused by mobilisation of calcium (Ca^{2+}) and magnesium (Mg^{2+}) in neutral and alkaline soils and in acid soils by the increase in concentration by ferrous (Fe^{2+}) and the displacement of calcium (Ca^{2+}) and magnesium (Mg^{2+}) by cation exchange reactions (Ponnamperuma, 1965). The increase in specific conductance may also be due to the accumulation of NH_4^+, HCO_3^-, and $RCOO^-$ (Ponnamperuma, 1972, 1977a).

The kinetics of specific conductance varies largely with the soil and with the duration of flooding. Neutral and slightly alkaline soils starting with high conductances attain values exceeding 2,000 µmhos/cm (provided sufficient organic matter is present) and then show a slow decline. Strongly acid soils have low initial specific conductances, show steep increases to 2,000 to 4,000 µmhos/cm during the first four weeks of flooding and decline sharply thereafter. In slightly acid soils, specific conductance increases slowly reaches to an intermediate values between those of the alkaline and acid soils and declines slowly. A specific conductance exceeding 4,000 µmhos/cm is the harmful limit for rice and indicates the presence of excess salt. Values considerably in excess of 4,000 µmhos/cm are possible in submerged soils that have a low cation exchange capacity and are high in organic matter, and in acid sulphate soils (Ponnamperuma, 1965, 1972).

2.1.7. Phosphate

The effects of waterlogging on soil phosphate and the response of paddy rice to application of phosphate fertiliser are reviewed in section 2.2.4.

2.2. SOIL PHOSPHORUS

2.2.1. The Determination of Soil Phosphate

One of the objects of this work was to study the phosphorus status of the soils. Therefore, the different techniques used to determine phosphorus in soils by various workers are reviewed.

2.2.1.1. Analytical methods

Since the beginning of this century many methods have been developed for the determination of phosphate in soils. The main problem has been to devise methods giving accurate and reproducible results.

Early methods for the determination of phosphate were based on gravimetric procedures. Schollenberger (1918) extracted soil phosphate with ammonium solutions, ignited the extracts and converted into the phosphate to magnesium pyrophosphate ($Mg_2P_2O_7$) before weighing. For total phosphate Schollenberger (1918) used a wet combustion method.

Colorimetric methods are more often used for measuring soil phosphates because of their accuracy and the most common method involves the development of a blue colour in strongly acid solution. The reaction on which the method depends is the reduction of molybdate in the presence of phosphate. The development of the blue colour is due to the formation of a phospho-molybdate complex which is dependent on the final pH of the solution. The suitable pH value

of the final solution for developing blue colour can range from 0.3 to 1.5. In 1938 Dickman and De Turk determined the amount of phosphate in a soil extract by comparing the blue colour of the solution with the blue colour of a standard solution. However, neither the gravimetric nor the colour comparison methods were sufficiently accurate and these results gave only a rough indication of soil phosphate levels. These methods have been superseded by colorimetric methods together with accurate spectrophotometric measurement of colour intensity. The phospho-molybdate method has been widely used in this context although it does have some disadvantages. Sometimes instead of the phospho-molybdate blue colour other blue complexes are formed mainly due to certain interfering substances such as arsenate or antimonate, if present in the solution (Dyer and Wrenshall, 1938). It has also been established from the findings of several investigators that iron may interfere with the blue colour development (Truog and Meyer, 1929; Dyer and Wrenshall, 1938; Bornemisza et al., 1967). Usually the maximum colour intensity is developed in about five minutes after addition of the reducing agent and the peak of absorption occurs in the red part of the spectrum near 660 nm. However, for a solution containing more than 15 ppm of iron, maximum colour intensity is reached about four minutes after the addition of stannous chloride and thereafter the colour fades very rapidly and sometimes gives a greenish tinge instead of blue colour. This makes high concentration of ferric iron highly undesirable and for accurate work it is suggested (Dyer and Wrenshall, 1938) that the concentration of ferric iron should not exceed about 1 ppm. It has also been shown that ferrous iron inhibits the colour development if there is any considerable time

interval between the addition of molybdate and stannous chloride and even 1 ppm of ferrous iron is sufficient to have an appreciable effect. However, with an interval of 15 seconds no effect could be detected. It is, therefore, desirable that the stannous chloride be added within 15 seconds of the addition of acid molybdate if ferrous iron is present in the sample solution. Mehta et al. (1954) suggested that the concentration of stannous chloride can be increased to overcome interference by iron if the concentration of iron in the final solution to be measured is more than 75 ppm. Bornemisza et al. (1967) proposed a modification for the Mehta procedure when used with soils high in free iron where a strong interference occurs by the dissolved iron in the colorimetric determination of total and inorganic phosphate. The interference can be eliminated by passing the extracts through a strong-acid, cation-exchange resin which removes the interfering ions. Matt (1970) suggested that ascorbic acid, used instead of stannous chloride as a reducing agent, can tolerate interfering ions and showed that ferric iron concentration up to 800 ppm had no adverse effect on colour development.

2.2.1.2. Determination of organic phosphate

There are two basic methods used for the determination of soil organic phosphate. In the first, the organic phosphate is extracted from the soil and measured as the difference between the total and inorganic phosphate in the extract (Mehta et al., 1954; [illegible] MacLean, 1965; Bornemisza and Igue, 1967) and in the other organic phosphate is converted to inorganic phosphate by ignition of the soil and measured by the difference between the amounts of inorganic phosphate extractable from ignited and unignited samples (Legg and Black, 1955; Saunders and Williams, 1955; Dormaar and Webster, 1964). The most

probable source of error in extraction method is thought to be the partial conversion of organic phosphate to mineral forms during extraction, giving low values. In ignition methods the ignition is believed to increase the solubility of inorganic constituents, giving high values. If both methods are used to analyse soils, it is often found that extraction values are considerably lower than ignition (Williams and Walker, 1967; Ipinmidun, 1973). However, it has not been possible to assess the extent of the errors in each case and to determine which method gives the correct value. The method developed by Mehta et al. (1954) involves successive extractions with conc HCl and 0.5 N NaOH at room temperature and 0.5 N NaOH at 70°C for 10 minutes at 90°C. The difference in content of inorganic and total phosphate in the combined extracts was taken as total organic phosphate in the soil. MacLean (1965) extracted organic phosphate from soils with sodium bicarbonate. He observed that sodium bicarbonate extractable organic phosphate increased with increasing pH of extractant, temperature, time of extraction and soil/solution ratio. The inclusion of 0.5 N HCl pretreatment resulted in higher organic phosphate levels than those given by bicarbonate extraction only. This method extracted 98.8% of the total organic phosphate, as estimated by the method of Mehta et al. (1954).

Legg and Black (1955) determined organic phosphate in soils by an ignition method. Samples of soil were extracted with conc HCl before and after ignition for one hour at 240°C. The difference in inorganic phosphate content in the extracts before and after ignition is an estimate of the content of organic phosphate in the soil.

Dormaar and Webster (1964) studied the losses inherent in ignition procedures for determining total organic phosphate. A

mineral soil with known amounts of organically bound phosphate added to it, two organic soils, and five known phosphate esters were ignited at various temperatures to study losses of phosphate as a result of ignition. Recovery of phosphate from the mineral soil was found to be incomplete. For the organic soils incomplete combustion occurred at temperatures below 650°C and volatilisation at temperatures higher than 400°C. Either complex formation or resistance to oxidation occurred in the case of organic phosphates, RNA, phytin and lecithin giving a lower value. Anderson (1960) studied the factors affecting the estimation of phosphate esters in soil. He proposed a modification of Mehta's procedure by using a mild alkaline extraction before the acid extraction to obviate the hydrolysis of inositol hexaphosphate, glycerophosphate, glucose-1-phosphate and nucleic acids.

2.2.1.3. Determination of total and inorganic phosphates

The determination of organic phosphate is indirect. Most of the methods described above are based on first determining total phosphate and then inorganic phosphate. The soil is successively treated with acid and alkali in order to extract both inorganic and organic phosphate. Total phosphate is determined by digesting an aliquot of extract with perchloric acid. After taking out an aliquot for total phosphate, the suspended materials are allowed to flocculate. An aliquot from the supernatant is then taken out for inorganic phosphate measurement (Mehta et al., 1954).

2.2.1.4. Determination of available phosphate

The determination of organic, inorganic and total phosphate in soils is of somewhat limited value due to unavailability to plants. It is, therefore, important to know the amount of available phosphate

in soil for successful crop production. Since plants can only exploit the pool of available phosphate in soil, a number of extractants have been employed for the determination of this component. Truog (1930) used 0.002 N H_2SO_4, buffered to pH 3.0 with $(NH_4)_2SO_4$ as extractant for the determination of available phosphate. Morgan (1941) used 10% acetic acid (1.74 N) having a pH of 4.8. Bray and Kurtz (1945) treated soil samples with 0.1 N HCl and 0.03 N NH_4F solution in a soil to extracting solution ratio of 1:20 for the determination of available phosphate. Hende et al. (1952) used a solution of ammonium-acetate buffered to pH 4.5. This solution contains 6% glacial acetic acid (17.42 N) and 2.7% ammonia solution (15.5 N) of specific gravity 0.88. Olsen et al. (1954) employed 0.5 M $NaHCO_3$ buffered to pH 8.5 for determining the amount of readily available phosphate in soil. The use of extractants such as acetic acid and sodium bicarbonate instead of sulphuric acid and hydrochloric acid are based on the assumption that the strong acids extract much more phosphate than the plants can exploit which leads to an incorrect assessment of the availability of soil phosphate.

Ekpete (1976) used several extracting methods for the determination of available phosphorus (Bray, Truog, EDTA and Olsen methods) in waterlogged and air-dry soils. He observed that all the methods extracted more phosphorus from waterlogged than air-dry soils. He also found that the Olsen method was the most effective in extracting phosphorus from both waterlogged and air-dry soils. This method correlated with yield response of rice grown under waterlogged conditions.

The amount of exchangeable soil phosphate can also be determined by isotopic methods. The amount of phosphate in the soil (solid

phase plus soil solution) which can undergo isotopic exchange is known as the labile pool. Since there is no known extractant which can remove a labile fraction from soil, its measurement is possible only by the use of labelled phosphorus. Therefore, labile phosphorus is often determined by the direct method of equilibrating soil with a solution of phosphorus-32 labelled orthophosphate, assuming that the phosphate ions in solution exchange with the solid phase phosphate and phosphorus-32 becomes diluted throughout the total exchangeable pool in the soil.

Russell et al. (1954) suggested that the fraction of the total soil phosphate which is readily accessible to isotopic exchange may represent the amount of phosphate available to plants.

Fried (1964) has described the use of phosphorus-32 to determine the labile fraction of soil phosphates and has elucidated the various concepts used by different investigators concerning available and exchangeable phosphorus. Similarly Larsen (1967) reviewed the different methods of measuring and ascribing the labile pool of soil phosphates used by various workers.

2.2.2. Forms of Phosphorus in Soils

Phosphorus occurs almost exclusively as phosphate in soils. There are two classes of phosphate present in the soil: organic and inorganic. Both exist in various forms few of which are readily soluble. Since phosphorus plays an important role in the plant nutrition, it is necessary to know its different chemical forms.

2.2.2.1. Organic phosphate

The amount of organic phosphate present in the soil depends on the organic matter content of the soil. Williams and Steinbergs (1958) reported that the organic phosphate contents of soils range

from very small values, in mineral soils low in organic matter, up to 70-80% of the total phosphate in soils high in organic matter. Organic phosphate can, nonetheless, play an important role in soils where there is a lack of readily available phosphate to plants.

According to Black and Goring (1953) five groups of organic phosphate compounds have been well identified. They are:- (i) inositol phosphates; (ii) nucleic acids; (iii) phospholipids; (iv) phosphoproteins; and (v) "metabolic" phosphates. But these groups may not include a major proportion of soil organic phosphate, the remainder being largely unidentified (Anderson, 1967). Indeed Dormaar (1968) found that about 22-41% of the total organic phosphate was associated with humic acids in Chernozemic soils. Moyer and Thomas (1970) also indicated the presence of organic phosphate in polymeric forms. These materials do not fall into categories suggested by Black and Goring (1953).

(i) Inositol phosphates

Of the compounds of soil organic phosphate that have been identified so far inositol phosphates predominate and in some cases account for more than 50% of the total organic phosphate present (Anderson, 1967). Inositol has a number of stereoisomers, of which myo-, scyllo-, neo-, and D-chiroinositol in the form of phosphate esters have been isolated from the soil (Cosgrove, 1966, 1969; Anderson and Malcolm, 1974). Among the stereoisomers the myo- form is generally the major form in soil organic phosphate followed by scyllo-, chiro-, and neo- in decreasing order (Dalal, 1977).

Moyer and Thomas (1970) extracted soil organic matter and fractionated it into three fractions according to the molecular weight. Inositol phosphates were detected in the intermediate and lower

fractions but not in the higher fraction but phosphate was present in all the fractions. Inositol phosphates in the lower fraction were considered to be in the free from, while those in the intermediate fraction must be in either a polymeric form or bound to other organic compounds.

(ii) Nucleic acids

Nucleic acids occur in every living cell and in soil they come from the decomposition of plant, animal and microbial remains. Nucleic acids are of two types:- (a) ribonucleic acid (RNA) and (b) deoxyribonucleic acid (DNA), but since they represent only a small proportion (less than 3%) of the soil organic phosphate they are of limited interest here.

(iii) Phospholipids

A small proportion of soil phosphate is present as phospholipids. Phospholipids are soluble in alcohol or ether and if part of the soil phosphate is soluble in alcohol or ether this suggests the presence of phospholipids. Further evidence for their presence was provided when choline, another constituent of phospholipid, was detected in alkali extracts by Shorey (1913). The total amounts of phospholipids in soil obtained on the basis of its solubility in alcohol, ether or both, do not exceed 3 ppm (Black and Goring, 1953).

2.2.2.2. Inorganic phosphate

Knowledge of the composition of inorganic phosphate in soil is of practical importance in evaluating the ability of the soil to supply readily available phosphates for the nutrition of the plants. According to Chang and Jackson (1957) inorganic phosphate can be classified into four main groups, namely, (i) calcium phosphate; (ii) aluminum phosphate; (iii) iron phosphate; and (iv) reductant soluble

phosphate extractable after removal of the first three forms.

(i) Calcium phosphate

Calcium phosphate exists mainly as apatite, but monocalcium phosphate $Ca(H_2PO_4)_2.H_2O$, dicalcium phosphate $CaHPO_4.2H_2O$ and octacalcium phosphate $Ca_8H_2(PO_4)_6.5H_2O$ also exist in soils in small amounts. Monocalcium phosphate is soluble in water but other forms of calcium phosphates are soluble in both acids and alkalies. They are more soluble in dilute hydrochloric acid than in dilute sodium hydroxide.

Fluorapatite $Ca_{10}(PO_4)_6F_2$ is the principal phosphatic constituent of many mineral phosphates while hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ is the phosphatic constituent of bones and teeth.

(ii) Aluminum phosphate

The aluminum phosphate compounds in soil include hydrates such as variscite, $AlPO_4.2H_2O$ and another, found in the sand, silt and clay fractions of soil, is wavellite, $Al_6(PO_4)_4(OH)_6.5H_2O$. In acid soils phosphate is precipitated on the surface of aluminum oxides or attached to silicate crystals such as kaolinite and montmorillonite.

(iii) Iron phosphate

Most of the iron phosphates in soil are hydrated compounds such as strengite $FePO_4.2H_2O$ and ferrous phosphate, vivianite $[Fe_3(PO_4)_2.8H_2O]$. The former was identified under oxidised and the latter under reduced conditions. Iron phosphates are more soluble in dilute alkalies than in dilute acids. In acid soils phosphate is also precipitated on the surfaces of iron oxides and as a result phosphate becomes unavailable or fixed.

2.2.3. Transformations of Soil Phosphates

Transformation of soil phosphates is influenced by: soil type, organic matter, microbial population, soil pH, soil moisture, soil temperature and can occur in a number of different ways.

2.2.3.1. Transformations of soil organic phosphates

Soil organic phosphate may play an important role in the nutrition of plants particularly in soils where there is a small amount of readily available phosphate. After the mineralisation of organic phosphate into inorganic forms plants can often take up phosphate derived from organic origin.

The transformation of phosphate during plant decomposition was studied by Birch (1961). He found that during plant decomposition microbial organic phosphate was rapidly formed from plant inorganic phosphate. Subsequently, with young plant material, much of the microbial organic phosphate was dephosphorylated and recovered as inorganic phosphate but with mature material there was little recovery even after three months decomposition. Plants generally contain sufficient inorganic phosphate for bacterial requirements during decomposition so that supplementary supplies obtained by mineralisation of other plant organic phosphate are unnecessary. Birch (1964) observed that application of 2:4 dinitrophenol in the study of phosphate transformation in soil indicated that one broad group of microorganisms utilised only inorganic soil phosphate, whereas another derived its phosphate solely through mineralisation of organic phosphate. The presence of the first group of organisms might lead to some immobilisation of inorganic phosphate when soil after a dry period became moistened by rain. Within a range of high to low C/P ratios, microorganisms may adsorb all the inorganic phosphate

produced by mineralisation, and only later after the death and lysis of cells would inorganic phosphate be released to the soil.

The gradual decrease in organic phosphate content of the soil is indicative of mineralisation and this process is generally studied by incubating soils in the laboratory. Incubation studies by various investigators (Thompson et al., 1954; Diest and Black, 1959) have revealed that the amount of extractable or readily available phosphate increases with the time of incubation.

Enwezor (1966) investigated the biological transformations of phosphate during the incubation of a soil treated with soluble inorganic phosphate and with fresh and rotted organic materials. The addition of inorganic phosphate increased the mineralisation of soil organic phosphate. During the decomposition of added organic materials there was an initial luxury adsorption of inorganic phosphate by soil microorganisms in the soil receiving high levels of soluble phosphate. This was followed by enhanced mineralisation of organic phosphate as incubation proceeded.

Ahmed and Islam (1974) observed that the mineralisation of soil organic phosphate was greater when samples were incubated in closed vials rather than in open tubes. Waterlogged or submerged conditions obviously enhance the mineralisation of soil organic phosphate. Islam and Ahmed (1973) studied the effect of waterlogging on the mineralisation of organic phosphate and reported that mineralisation of inositol phosphate increased under submerged conditions. Halstead et al. (1963) studied the effect of lime on the mineralisation of soil organic phosphorus. They found that liming resulted in an average decline of 3.6% in the total organic phosphorus content of the incubated soils. Some mineralisation also occurred in samples

incubated for nine months without lime. Islam and Mandal (1977) also observed that moisture and lime promoted mineralisation of organic phosphorus with time.

Ghoshal and Jansson (1975) conducted incubation experiments under aerobic conditions and evidence of biological consumption of added inorganic phosphorus was obtained. Organic phosphorus mineralisation was also indicated along with carbondioxide evolution but only to a small extent. Sekhon and Black (1968) studied the uptake of phosphorus by plants in relation to carbondioxide production and organic phosphorus mineralisation in soil. Statistical tests showed that the yield of phosphorus in the plants was correlated significantly with the organic phosphorus mineralised. The rate and amount of organic phosphate mineralisation is also effected by temperature. Acquaye (1963) found that at 50°C more organic phosphate was mineralised than below 50°C. He also observed that addition of nitrogen as urea and phosphorus as triple superphosphate to the soil increased the per cent of organic phosphate mineralisation. Furukawa and Kawaguchi (1969) reported that submerged paddy soils incubated at 40°C for two weeks resulted in decreased organic phosphate due largely to mineralisation of organic phosphate.

The determination of soil organic phosphate is always by an indirect method. Most of the above investigators have measured extractable phosphorus before and after incubation, and the difference was considered as the amount of organic phosphorus mineralised. Mineralisation of organic phosphorus during incubation can also be estimated by measuring the increase in inorganic phosphorus and the decrease in organic phosphorus.

Although mineralisation of organic phosphates has been studied

by several researchers the differences in the results presented were very small. A small decrease in organic phosphorus content is probably not a very clear indication of its mineralisation, since such small changes are very difficult to detect with existing techniques. It is obvious, therefore, that the results of studies on the mineralisation of organic phosphorus should be viewed with some caution.

2.2.3.2. Transformations of soil inorganic phosphates

Many investigations have been carried out studying the transformation and uptake of soil phosphates. This work has shown that the main source of phosphate nutrient taken up by the plants is inorganic forms. Inorganic phosphates present in the soils are usually soluble in acids and alkalies and a small amount may even be soluble in water.

Ghoshal (1975) observed that the process of inorganic phosphate transformation in soil was partly biological. He studied the relationships between biological immobilisation and chemical fixation of phosphate in soils under aerobic conditions. He concluded that the rate and extent of biological turnover was dependent on the type and amount of available energy material present at the site of decomposition, whereas the chemical fixation and release of phosphate was regulated by soil pH and by the content of clay minerals in the soil.

Yuan et al. (1960) studied the forms of newly fixed phosphate in soils. They observed that the ratio of aluminum phosphates to iron phosphates increased with the rates of applied phosphorus. They also studied the effect of temperature on alternate wetting and drying. The percentage of phosphate in the aluminum form decreased and iron phosphate increased as a result of increasing soil drying temperature and prolonged wetting and drying. Ivanov and Sauerbeck (1972) studied the transformation and availability of inorganic phosphate

fractions in soils. In pot experiments, $KH_2{}^{32}PO_4$ was applied in short-term seedling experiments, and KH_2PO_4 in longer experiments with older plants. Most of the added phosphate was transformed into aluminum phosphate and iron phosphate in non-calcareous soil. In soil containing carbonate, transformation was mainly into calcium phosphate and the extent of this transformation depended on the calcium content of the soil. Aluminum phosphate and iron phosphate were utilised to a significant extent only by older plants. The availability of aluminum phosphate and iron phosphate was greater in neutral soils. Soil acidity accelerated the transformation of aluminum phosphate into iron phosphate and decreased the availability of iron phosphate. In calcareous soils, newly formed calcium phosphate was more available to plants than the stable calcium phosphate pre-existing in the soil.

Chattopadhyay and Kar (1973) studied the fixation of soluble phosphate in acid soils and found that inorganic phosphate amounted to 70 to 90% of the total phosphate. The inorganic phosphate was distributed among the fractions investigated in the decreasing order: reductant-soluble phosphate (extractable after removal of calcium, aluminum and iron phosphate), iron phosphate, occluded aluminum phosphate. Reductant-soluble phosphate amounted to about 50% of the total inorganic phosphate. About 80-90% of soluble phosphate (KH_2PO_4) applied at a rate of 50 ppm phosphorus was fixed over a period of 30 days, resulting in an appreciable increase in the reductant-soluble phosphate and iron phosphate forms.

2.2.4. Phosphate

The occurrence of a marked increase in the availability of native and added phosphates in flooded soils as compared to well-drained

soils has been established (Shapiro, 1958a; Mahapatra and Patrick, 1969; Ponnamperuma, 1972).

It has been found that organic matter affects phosphate transformation in waterlogged soils through the mechanism of reduction and chelation. Both processes lead to increase in the solubility and availability of soil phosphate and less added phosphate is fixed (Shapiro, 1958b; Bhat and Bouyer, 1968).

Misra et al. (1970) studied the effect of prolonged waterlogging on phosphate retention. They worked with red and black soils and the soils were kept waterlogged for 30 days, 90% of the added soluble phosphate disappeared from solution. The retained phosphate was 60.5% and 50.4% in the inorganic fraction of black and red soils, respectively. Phosphate retention capacity was decreased when glucose, oxalate and ammonium sulphate were added with the phosphate under waterlogged conditions. Aluminum phosphate increased and iron phosphate decreased slightly. In an incubation study Singh and Ram (1976) demonstrated that most of the phosphate added (as KH_2PO_4) in the soil was present as inorganic soil phosphate fraction after five days of incubation. The percentage of phosphate transformed into aluminum phosphate decreased while that transformed into iron phosphate increased with time of incubation. Patrick et al. (1974) found that alternate flooding and moist conditions caused increased fixation or retention of added soluble phosphate and most of the added phosphate was in association with aluminum and iron phosphate fractions. Transformation of inorganic phosphate as influenced by organic matter and lime was studied by Mandal (1964), and Mandal and Mandal (1973). They observed that on waterlogging, control samples showed a slight increase in extractable phosphate, accompanied by a slight decrease

in the ferric phosphate; aluminum and calcium phosphates remained unchanged. In the presence of starch, extractable phosphate considerably increased while calcium phosphate decreased. The large amounts of carbondioxide formed by the decomposition of starch may have converted some of the insoluble tricalcium phosphate to more soluble mono- and dicalcium phosphates. Although a large amount of ferrous iron was formed, the ferric phosphate fraction showed no decrease and aluminum phosphate was not affected. In the presence of lime, ferric phosphate decreased considerably and aluminum phosphate decreased slightly. This decrease might be due to the hydrolysis of ferric and aluminum phosphates as a result of liming. Calcium phosphate was increased appreciably in the presence of lime. Some of the ferric phosphate was apparently converted to calcium phosphate.

The conversion of ferric iron to ferrous iron under waterlogged conditions and its relation to available phosphate was demonstrated by Islam and Elahi (1954). They found a progressive reduction of ferric to ferrous and an increase in readily soluble phosphate in lateritic soils incubated under waterlogged conditions in the laboratory. Addition of oxidisable materials, especially green manure, promoted the process of reduction and greatly increased the availability of phosphate. Islam (1970) found that in flooded soils the concentrations of water-soluble and ammonium-acetate extractable phosphorus first increased and then decreased. The increase in soluble phosphate in acid soils (pH 4.7 to 5.6) was related to a decrease in the concentration of iron, calcium and reductant-soluble phosphates, while the increase in slightly acid clay soil (pH 6.6) was associated with the decrease in iron and aluminum phosphates.

In a calcareous soil (pH 7.6), the increase in extractable phosphate corresponded to a decrease in the concentration of aluminum and reductant-soluble phosphates. Islam (1970) explained that the decrease in soluble phosphate at later stages of flooding was due to; the re-formation of insoluble aluminum, iron and calcium phosphates in two acid clay soils (pH 4.7 and 5.6); the formation of aluminum and calcium phosphates in slightly acid clay soil and to the formation of calcium phosphate only in acid fine sand soil (pH 5.2). Mahapatra and Patrick (1969) observed that waterlogging generally increased aluminum and iron phosphates, decreased reductant-soluble iron phosphate, and did not much affect calcium phosphate. When soil was incubated with $AlPO_4.2H_2O$, $FePO_4.2H_2O$ or $Ca(H_2PO_4)_2.H_2O$, they were almost completely recovered in the aluminum and iron phosphate fractions under both optimum moisture conditions and waterlogging. Extractable phosphate was increased by waterlogging, especially in soils that were richest in iron phosphate. Williams et al. (1958) found that soils containing appreciable amounts of ferric phosphate increased the phosphate supply to plants under anaerobic conditions, but soils without ferric phosphate showed a decrease in available phosphate. Thus the extent of availability of phosphorus depends on the extent of the reduction process and the iron content of the soil (Basak and Bhattacharya, 1962).

2.2.4.1. Response to added phosphate by paddy rice

It has been reported by several investigators that rice exhibits a very poor response to phosphorus fertilisation. As far as phosphorus nutrition is concerned, flooded rice appears to differ from non-flooded crops in at least two major aspects. Firstly, it appears that rice plants can absorb an adequate amount of phosphorus from a soil

solution with a low concentration of phosphate (Okajima, 1965). Tanaka (1962) observed that rice plants grew normally when supplied with a nutrient solution in which the phosphorus content was maintained at 0.1 ppm. Secondly, waterlogging releases phosphate from fixed forms to the soil solution as a result of reduction reactions, which probably ensures an adequate supply of phosphorus throughout most of the season in soils that contain appreciable amounts of iron phosphate and reductant-soluble phosphate (Patrick and Mahapatra, 1968). Without waterlogging, such soils would probably be phosphate deficient. Many experiments have shown inconsistent response of rice to phosphate fertilisation under waterlogged soil conditions (IAEA, 1970). However, Islam (1970) indicated the necessity of phosphorus fertilisation in flooded rice for soils which are low in phosphorus and high in active iron and aluminum.

2.2.5. Distribution of Phosphates with Respect to Soil Particle Size

Studies on the distribution of phosphates in different size fractions of soil are rather limited. The physical fractionation studies of Williams and Saunders (1956) showed that clay and silt together contain 85 per cent or more of the total soil organic phosphorus, but the sands also contain appreciable amounts present as coarse particles of organic matter. The phosphorus concentration of the fractions varied widely depending on the soil, but the total phosphorus was normally highest in the clay and lowest in the coarse sand, the main exceptions being the gleyed sub-soils where the fine sands were richer than the clays (Williams and Saunders, 1956). Goel and Agarwal (1960) working with some Indian soils found that 68-85% of the total phosphorus was concentrated in the clay fraction, and that the sand fraction contained the lowest amount. Hanley et al. (1965)

found that the sand fractions contained 10% of the total soil phosphorus and the clay fraction 60%. The amount present as organic phosphorus ranged from 39-70% of the total phosphorus with highest values for gleyed soils. Syers et al. (1969) observed that total phosphorus and organic phosphorus were concentrated in the clay separates. The amount (ppm) of total phosphorus and organic phosphorus in the coarse and fine sands was relatively low and the phosphorus was largely in the inorganic form. According to Swift and Posner (1972), and Watson and Parsons (1974) organic nitrogen and carbon are similarly associated with the clay and silt fractions of a soil. Omar (1977) observed that as much as 90% of the organic and inorganic phosphorus is associated with clay and silt fractions.

MATERIALS AND METHODS

3. MATERIALS AND METHODS

3.1. SOILS

Four soils were used for the incubation studies. Two from around Edinburgh (Macmerry series and Giffnock series) and two from Bangladesh (Tista floodplain and Old Brahmaputra floodplain soils).

3.1.1. Scottish Soils

3.1.1.1. Macmerry series

The soils of Macmerry series are formed on mixed tills derived from carboniferous sediments with partially sorted upper horizons. The soils are imperfectly drained, dark grey brown colour, medium blocky, friable with moderate organic matter content, occasional stones, some rounded or sub-rounded; and no mottles. It is a common arable soil of the Lothians; agriculturally it is regarded as a "medium" soil of light texture (Ragg and Futty, 1967).

Soil samples from Macmerry series were collected in May 1977. Samples (up to 30 cm depth) were collected from the different parts of the same field and mixed together. After air-drying the big clods were broken into small pieces and coarse roots and stones were removed. The soil was then passed through a 2 mm sieve and mixed by a rotary mixer for uniform mixing and then stored in covered plastic buckets.

3.1.1.2. Giffnock series

The soils of Giffnock series are formed on tills derived from carboniferous sediments, and are poorly drained gleys. The parent material is dominantly sand stones, with some shales, coals and limestone.

Soil samples from Giffnock series were collected in May 1977. Samples (up to 45 cm depth) were taken from the different parts of

the same field and mixed together. After air-drying the big clods were broken into small pieces and coarse roots and stones were removed. The soil was then passed through a 2 mm sieve and mixed by a rotary mixer for uniform mixing and then stored in covered plastic buckets.

3.1.2. Bangladesh Soils

Bangladesh lies astride the tropic of Cancer and 90°E meridian. Latitude ranges from 20°25′ to 26°38′ N. Longitude ranges from 88°01′ to 92°40′ E.

Bangladesh has a tropical monsoon climate. Monthly mean temperatures range from 18°C in winter to 30°C in summer. Rainfall is heavy and strongly seasonal, annual rainfall ranging from about 1,200 mm in the centre-west to about 4,000 mm in the north east of the country. About 90% of the rain falls in the summer months between May and October. Day length varies from approximately 10.7 hours in December to 13.6 hours in June.

3.1.2.1. Tista floodplain soils

The Tista floodplain soils were developed in noncalcareous alluvium (Tista river-borne deposits) and are shallow to deeply flooded in the monsoon season but drain early in the season. The soils are generally silt loam in texture and have a near neutral pH. These soils are highly productive and suitable for the cultivation of rice, jute, tobacco, sugarcane and other tropical crops.

The Tista floodplain soils were collected (up to 15 cm depth) in 1973 from a cultivated field near Gangachara, Rangpur, in northern Bangladesh. The soils were air-dried, coarse roots and stones were removed, well-mixed, passed through a 2 mm sieve, and then stored in covered plastic buckets.

3.1.2.2. Old Brahmaputra floodplain soils

The Old Brahmaputra floodplain soils were developed in Old Brahmaputra alluvium. These soils are intermittently flooded after heavy rainfall during the monsoon season. They are imperfectly drained soils. The soils are usually silt loam in texture and have an alkaline pH. These soils are very productive and suitable for the cultivation of rice and jute.

The Old Brahmaputra floodplain soils were collected (up to 15 cm depth) in 1977 from the east side of Sutiakhali market (west bank of Brahmaputra river). The soils were air-dried, coarse roots and stones were removed, well-mixed, passed through a 2 mm sieve, and then stored in covered plastic buckets.

3.2. ANALYTICAL TECHNIQUES

3.2.1. Soil pH

Soil pH was measured in a 1:2.5 suspension of soil and liquid on a Pye Unicam pH meter (model 290 Mk) using a combined glass/calomel electrode. But the pH of the incubated soils was determined at a 1:2 soil to water ratio. Prior to making pH measurements, the electrode was calibrated using standard buffer solutions at pH 4.0 and 7.0.

3.2.2. Particle Size Distribution

Particle-size analysis was carried out by the standard pipette method (Black, 1965a). Hydrogen peroxide was used to destroy the organic matter, followed by the addition of sodium hexametaphosphate and high speed stirring to disperse the soil.

The particles were separated according to U.S.D.A. size limits:

Sand : 2.00 to 0.05 mm

Silt : 0.05 to 0.002 mm

Clay : less than 0.002 mm

Textural classes of the soils were determined from the triangular co-ordinate diagram of U.S.D.A. (1951).

3.2.3. Organic Matter Content

Organic carbon was determined by the modified Tinsley method (Bremner and Jenkinson, 1960), using 0.5 g air-dried soil ground to pass through a 0.2 mm sieve. Organic matter was determined by multiplying per cent carbon by 1.72.

3.2.4. Total, Inorganic and Organic Phosphate

Soil samples were dried, ground and screened through a 0.2 mm sieve and analysed for total and inorganic phosphate. The phosphate was extracted from the soil and organic phosphate measured by the difference between the total and inorganic phosphate in the extract by following the method of Mehta et al. (1954). The colour development for the total and inorganic phosphate was carried out according to procedure described by Matt (1970). After colour development phosphate concentration was determined with a Pye Unicam SP 600 UV spectrophotometer with the wavelength set at 882 nm. A standard curve was prepared using standard phosphate solutions prepared from analytical reagent grade KH_2PO_4.

3.2.5. Fractionation of Aluminum, Iron and Calcium Phosphates

The fractionation of aluminum, iron and calcium phosphates in soils was carried out as described by Chang and Jackson (1957).

3.2.6. Extractable Phosphate, Iron, Manganese, Calcium and Potassium

Every 4 weeks for 16 weeks duplicate tubes of each soil were withdrawn from the incubator for the determination of ammonium

acetate (pH 4.5)-extractable phosphate, iron, manganese, calcium and potassium.

3.2.6.1. Phosphate

To determine extractable phosphate each soil sample was extracted in duplicate with ammonium acetate (pH 4.5) as described by Hende et al. (1952). The samples were shaken for $\frac{1}{2}$ hour with a soil solution ratio of 1:5. An aliquot of the extract was put into a 25 ml volumetric flask, then diluted to about 20 ml with the extracting solution, to which 4 ml molybdate reagent was added and mixed thoroughly. 0.45 ml of stannous chloride solution was added, mixed immediately, and made up to volume with the extracting solution. The same procedure was carried out on a blank, using all reagents. The maximum colour intensity was reached about 5 minutes after the addition of the reducing agent and the peak of absorption occurred in the red part of the spectrum near 660 nm. A Pye Unicam SP 600 spectrophotometer was used to measure the colour intensity at 660 nm. A standard curve was prepared using standard phosphate solutions prepared from analytical reagent grade KH_2PO_4.

3.2.6.2. Iron

Iron was determined, after appropriate dilution of the ammonium acetate extract, by feeding the solution into an atomic absorption spectrophotometer (Instrumentation Laboratory, Model 251) with the wavelength set at 248.3 nm. Iron in the ferrous state was complexed with α-α′-bipyridyl (Müller, 1933) and the resulting deep red complex was determined colorimetrically on a Pye Unicam SP 600 UV spectrophotometer at a wavelength 515 nm. Standard curves were prepared for the above methods from analytical reagent grade ferric chloride, $FeCl_3.6H_2O$. In the colorimetric determination of ferrous

iron, the ferric chloride standards were reduced with 10% sodium sulphite solution, thus rendering the standards capable of complex formation with α-α′-bipyridyl. The ferric iron was calculated as the difference between the total extractable iron and ferrous iron.

3.2.6.3. Manganese

Manganese was determined, after appropriate dilution of the ammonium acetate extract, by feeding the solution into an atomic absorption spectrophotometer (Instrumentation Laboratory, Model 251) with the wavelength set at 279.5 nm. A standard curve was prepared using solutions of manganous chloride.

3.2.6.4. Calcium

Calcium was determined, after appropriate dilution of the ammonium-acetate extract, by feeding the solution into an atomic absorption spectrophotometer (Instrumentation Laboratory, Model 251) with the wavelength set at 422.7 nm. A standard curve was prepared using solutions of calcium chloride.

3.2.6.5. Potassium

Potassium was determined, after appropriate dilution of the ammonium-acetate extract, by feeding the solution into an EEL flame photometer. A standard curve was prepared from analytical reagent grade potassium chloride.

3.2.7. 'Free' Iron and 'Free' Manganese

'Free' iron and manganese is defined here as that which is extracted after treatment with sodium dithionite/citrate buffer (Mehra and Jackson, 1960;). An aliquot from the extract was taken and after appropriate dilution it was analysed by feeding the extract into an atomic absorption spectrophotometer as described in 3.2.6.2. and 3.2.6.3., respectively.

3.2.8. Total Nitrogen

Total nitrogen was determined by the semimicro-Kjeldahl procedure, using a titrimetric end point (Black, 1965b).

3.2.9. Redox Potential

Redox potential measurements were made by placing the electrode 1-2 cm below the soil surface for two hours with a Pye Unicam pH meter (Model 290 Mk) using a combination platinum electrode in which a saturated KCl silver/silver chloride electrode was used as the reference half-cell. The combination electrode was supplied by Activion Glass Limited. Prior to making redox potential measurements, the operation of the platinum electrode was checked by using, as a standard, a suspension of pure quinhydrone in 0.05 M potassium acid phthalate, which has a redox potential of 463 mV at 25°C. In all redox potential measurements, the silver/silver chloride electrode saturated KCl half-cell emf of +200 mV was added to the measured emf.

3.2.10. Specific Conductance

Specific conductance was measured in a 1:2 suspension of soil and liquid on a Philips portable conductivity meter (PW 9504) using a standard immersion cell with a cell constant of 0.74. The cell constant was checked against a standard solution of 0.01 M KCl.

3.3. INCUBATION EXPERIMENTS

The four soils described in 3.1. were used for most of the incubation studies. All the incubation studies were carried out for 16 weeks in 100 ml polypropylene centrifuge tubes at 30°C. Each tube contained 35 g air-dry finely ground (<0.2 mm) soil and 70 ml of distilled water.

3.3.1. Completely Flooded Soils

A total of 64 polypropylene tubes were used for completely flooded studies, each soil having 16 tubes. In 32 tubes nitrogen at the rate of 45 μg N/g soil (equivalent to 112 kg N/ha) was added, as a solution of laboratory reagent grade urea, to observe if there were any differences between soil alone and soil fertilised with urea. The other 32 tubes contained soil and water only. Each tube was sealed, mixed thoroughly and then placed in the incubator.

Soil pH and specific conductance for the Macmerry and Giffnock soils were measured every day and redox potential every week. In the Tista floodplain and Old Brahmaputra floodplain soils, pH and specific conductance were measured every week and redox potential measurements were made every two weeks. After every 4 weeks for 16 weeks extractable phosphate, iron, manganese, calcium and potassium were determined. The analytical procedures are described in section 3.2.

3.3.2. Alternately Flooded and Moist Soils

Another 32 polypropylene tubes were incubated with soil subjected to alternately flooded and moist conditions. 16 tubes were used for soil containing nitrogen (as a solution of urea) at a rate similar to completely flooded samples. Initially the soil to water ratio was 1:2 in all the tubes. They were mixed thoroughly and then placed in the incubator. The tubes were kept open and after every 5 to 8 days a further addition of distilled water (about 30 ml) was made. The soil was never allowed to dry completely but aeration occurred between wetting cycles. Only Macmerry and Giffnock soils were incubated in this way.

After every 4 weeks for 16 weeks extractable phosphate, iron, manganese, calcium and potassium were determined. The analytical

methods are described in section 3.2.

3.3.3. Water-Soluble Iron, Manganese, Calcium and Potassium

Four soils were incubated in duplicate in 100 ml polypropylene tubes. To each tube 35 g of air-dry finely ground (<0.2 mm) soil and 70 ml distilled water was added, sealed, mixed thoroughly and then placed in the incubator. Samples were taken from the incubator every 4 weeks for 16 weeks for the determination of water-soluble amounts (i.e. soil solution concentration) of iron, manganese, calcium and potassium. The samples were shaken well and centrifuged. After centrifugation about 10 ml of the supernatant liquid was taken in a 20 ml millipore syringe and filtered through a 0.22 µm millipore filter paper. The amount of liquid taken out was replaced by addition of equal amount of distilled water and the tube replaced in the incubator. Iron, manganese, calcium and potassium were determined as described in section 3.2.

3.3.4. Mineralisation of Soil Phosphorus

Four soils in duplicate were incubated for the mineralisation studies. Soil samples were incubated in sealed polypropylene tubes for 16 weeks using a 1:2 soil water ratio and then removed from the incubator. They were air-dried and regrounded to pass through a 0.2 mm sieve.

Mineralisation of soil phosphorus was estimated by measuring the increase in inorganic phosphate and the decrease in organic phosphate during incubation. Determination of total, inorganic and organic phosphate was carried out by following the procedure described in 3.2.4.

3.3.5. Isotopically Exchangeable Phosphate and Iron in Soils

A total of 16 polypropylene tubes were used for the determination

of isotopically exchangeable phosphate and iron in soils, each soil having four replicates. In each tube 35 g of air-dry, finely ground (<0.2 mm) soil and 70 ml distilled water was introduced, sealed, mixed thoroughly and then placed in the incubator. The soil samples were withdrawn from the incubator after 16 weeks of incubation.

After the incubation period ammonium acetate (pH 4.5) was added (1:5 soil extractant ratio) to 16 tubes. They were shaken for $\frac{1}{2}$ hour and centrifuged. Then 12,500 μCi carrier-free phosphorus-32 was added to eight tubes and 2.5 μCi carrier-free iron-59 was added to remainder (duplicate samples for each soil). They were mixed thoroughly and mechanically shaken overnight to allow them to attain equilibrium. Ammonium acetate extractable phosphate and iron was determined by following the procedure as described in section 3.2.

The specific activity of the ammonium acetate extract was counted using a NaI well-type crystal detector for the iron-59 (γ-emitter) and a solid anthracene scintillator window for phosphorus-32 (β-emitter).

The amount of isotopically exchangeable phosphate was calculated by the following equation:-

$$\frac{\text{surface phosphate } {}^{32}P}{\text{solution phosphate } {}^{32}P} = \frac{\text{surface phosphate } {}^{31}P}{\text{solution phosphate } {}^{31}P}$$

Therefore,

$$\text{surface phosphate } {}^{31}P = \text{solution phosphate } {}^{31}P \times \frac{\text{surface phosphate } {}^{32}P}{\text{solution phosphate } {}^{32}P}$$

To obtain a value for the total isotopically exchangeable pool the values for surface and solution phosphate were added together.

Similar principles were applied to determine the isotopically exchangeable pool of iron in soils.

3.4. DISTRIBUTION OF PHOSPHATES IN SOIL PARTICLE SIZE FRACTIONS

The four soils described in section 3.1. were used to determine the distribution of phosphate in individual particle size fractions.

3.4.1. Ultrasonic Dispersion in Water

An MSE 150 watt ultrasonic disintegrator Mk 2 with a titanium vibrator probe was used. Duplicate 25 g samples of air-dried $<$2 mm soil were placed in a 100 ml polypropylene tubes, 75 ml of distilled water was added. Soil suspensions were disintegrated for 15 minutes with the tip of the probe immersed 2-3 cm below the liquid surface.

3.4.2. Separation of Particle Size Fractions

3.4.2.1. Clay ($<$2 μm)

After disintegration, the suspensions from 25 g soil were washed through a 0.2 mm sieve, to remove coarse sand. The $<$0.2 mm fraction was then collected and made up to 600 ml, with distilled water, in a beaker. The suspension was thoroughly stirred for one minute and then allowed to stand undisturbed for 8 hours, after which 7.5 cm of the clay suspension was syphoned off and collected in a 380 ml polypropylene centrifuge tube. After 15 minutes centrifugation at 2500 rpm the clear supernatant liquid was decanted into the beaker. The beaker was again made up to 600 ml level by adding a little more distilled water and then stirred thoroughly for one minute and allowed to stand overnight. The sample was syphoned again the next morning and collected in a 380 ml centrifuge tube used previously. The sample was centrifuged and recollected in the beaker by decantation of the clear supernatant liquid. The same

procedure was continued daily until all the clay was collected. All the clay was assumed to have been collected when a clear supernatant liquid was obtained in the beaker after the correct settling time. This usually required about 30 cycles and the clay collected was freeze-dried, weighed and stored in an air-tight glass bottle until required for analysis.

3.4.2.2. Silt (50 to 2 μm)

After the collection of clay, the beaker was again made upto 600 ml level with addition of distilled water. Then the suspension was thoroughly stirred for one minute and allowed to stand undisturbed for one minute thirty seconds, after which 7.5 cm of the suspended silt was decanted and collected in a 380 ml polypropylene centrifuge tube. After 15 minutes centrifugation at 2500 rpm the clear supernatant liquid was decanted into the beaker. The beaker was again made upto 600 ml level by small addition of distilled water and then stirred thoroughly for one minute and allowed to stand undisturbed. After the correct settling time, the suspended silt was decanted as before. The same procedure was continued until all the silt was collected. This procedure required about 25 to 30 cycles to collect all the silt. Then the sample was freeze-dried, weighed and stored according to the procedure adopted for clay.

3.4.2.3. Sand (2000 to 50 μm)

After the collection of silt, only fine sand remained in the beaker which was then dried at 100°C. The coarse sand retained on the 0.2 mm sieve from the original suspension was also dried at 100°C. Coarse and fine sand fractions were weighed in combination, well mixed and stored in an air-tight glass bottle until required for analysis.

3.4.3. Determination of Total, Inorganic and Organic Phosphate in Different Soil Fractions

Total, inorganic and organic phosphate in clay, silt and sand fractions were determined as described in 3.2.4.

3.5. GLASSHOUSE EXPERIMENTS

3.5.1. Experiment 1. Yield and Composition of Rice Plants

3.5.1.1. Soils

Macmerry and Giffnock series soils as described in 3.1.1. were used for the pot experiment which was carried out in a glasshouse.

3.5.1.2. Cultural operations

(a) Raising of seedlings

The rice seeds of variety 'IR 8' supplied by the National College of Agricultural Engineering, Silsoe in October 1975 were used as a test crop. The 'IR 8' rice variety developed in 1967 by the International Rice Research Institute, Philippines is high yielding, short (about 100 cm high), relatively insensitive to photoperiod, matures in 120 to 130 days, is resistant to lodging and responds to heavy fertilisation.

To test the viability of rice seeds, duplicate samples of 50 seeds were evenly distributed on moist filter paper on the bottom of a petridish. After 7 days 45% germination was recorded.

Rice seeds (250) were placed evenly on moist filter paper on the bottom of a plastic tray. The tray was kept in dark at about 22°C for 72 hours and seeds began germinating during that period. The seeds were then transferred equally into two plastic trays, one containing Macmerry soil (4.5 kg) and the other Giffnock soil (4.5 kg). The seeds were covered with a thin layer of soil. Both

the trays were then transferred to the glasshouse and covered with thick polythene sheets until germination was complete. The glasshouse was maintained at about 26°C. The trays were watered every alternate day. The seedlings were ready for transplanting after 30 days.

(b) Potting

Five white plastic buckets were used for each soil. Each bucket had a capacity of 15 litres. The buckets were numbered and there was no provision for any drainage. All the buckets were washed and dried before use. 7 kg of air-dry soil and 7 kg of sand (0.5 to 1.0 mm) were mixed thoroughly using a rotary mixer and placed in each bucket. The outside of the white bucket was painted with black paint. The buckets were saturated with water one day before transplanting. The buckets were randomly placed on a bench.

(c) Transplanting first batch of rice seedlings

Eight 30 days old rice seedlings were transplanted to each bucket at equal spacing. Water was added to maintain the water level about 2 cm above the soil surface. Six days after transplanting, when the seedlings became fully established, the depth of water was raised to about 5 cm above the soil surface and maintained at this level throughout the growing period.

(d) Glasshouse maintenance

The day temperature of the glasshouse ranged from 26°C to 36°C and the night temperature ranged from 16°C to 20°C. Fluorescent lights were used to supply adequate light on dull days.

(e) Fertiliser application

Ten days after transplanting, nitrogen at the rate of 45 µg N/g soil (equivalent to 112 kg N/ha) was applied to all the buckets as a

solution of laboratory reagent grade urea.

(f) First harvest, drying, weighing and storage of plant material

Two months after transplanting, harvesting was carried out by cutting the rice plants at the soil surface. The cut ends of the plants were washed with water to remove any foreign material. The dry matter yield was recorded after drying at 80°C for 48 hours. The plants were then ground in a C & N Junior (Christy and Norris Ltd.) laboratory mill to pass through a 0.5 mm sieve and stored in air-tight plastic bottles.

(g) Removal of rice roots from buckets

Almost all the rice roots from the buckets were removed by hand after making a slurry. Special precaution was taken not to lose any soil. These buckets were again used to grow the second batch of rice.

(h) Transplanting second batch of seedlings

Eight 35 days old rice seedlings were transplanted to each bucket at equal spacing. Seven days after transplanting, when the seedlings were fully established, the depth of water was raised to about 5 cm above the soil surface and maintained at this level throughout the growing period. 18 days after transplanting, nitrogen at the rate of 45 μg N/g soil was applied to all the buckets as a solution of urea.

(i) Second harvest, drying, weighing and storage of plant material

Three months after transplanting, the plants were harvested by cutting at the soil surface. Washing, drying, weighing and storage were carried out as described in 3.5.1.2. (f).

3.5.1.3. Soil sampling and analysis

After the second harvest about 10 g of moist soil was taken from each bucket after making the soil into a slurry. The soil was air-dried, finely ground to pass through a 0.2 mm sieve and stored in polythene bags for subsequent analysis.

Soil samples were analysed for total and inorganic phosphate. The phosphate was extracted from the soil and organic phosphate measured by the difference between total and inorganic phosphate in the extract as described in 3.2.4.

3.5.1.4. Plant analysis and method of digestion

(a) Method of digestion

0.5 g plant sample was placed in a 50 ml Kjeldahl flask, to which 6 ml concentrated sulphuric acid (specific gravity 1.84)/ selenium (0.35%) mixture and 4 ml 30% analytical reagent grade H_2O_2 was added. The mixture was heated until the solution cleared and then heated for a further hour for complete digestion. After digestion the contents of the Kjeldahl flask were quantitatively transferred into a 50 ml volumetric flask and made upto volume with distilled water.

(b) Plant analysis

The plant samples collected from both the harvests were analysed for total phosphorus, iron, manganese, calcium and potassium, following acid digestion.

(i) Total phosphorus

Total phosphorus was determined by taking an aliquot from the digest and colour developed by the vanadate-molybdate-yellow method as described by Chapman and Pratt (1961). After colour development phosphorus concentration was determined with a Pye Unicam SP 600 UV

spectrophotometer at a wavelength of 395 nm. A standard curve was prepared in the same way using analytical reagent grade disodium hydrogen orthophosphate, $Na_2HPO_4.12\ H_2O$.

(ii) Total iron, manganese, calcium and potassium

Aliquots from the digest were taken and after appropriate dilution total iron, manganese, calcium and potassium were determined as described in section 3.2.

3.5.2. Experiment II. Effect of Added Phosphate on Rice Plants

3.5.2.1. Soils

Macmerry and Giffnock series soils as described in 3.1.1. were used for the pot experiment carried out in the glasshouse.

3.5.2.2. Cultural operations

(a) Raising of seedlings

The same variety of rice and a similar procedure was used for the raising of seedlings as described in 3.5.1.2. (a).

(b) Treatment combinations

There were four levels of phosphorus 0, 3.3, 6.6 and 13.2 µg/g soil (equivalent to 0, 7.34, 14.68 and 29.36 kg P/ha), two soils, two soil conditions (constantly flooded, and alternately flooded and moist), two harvests and two replicates; a total of 64 pots.

(c) Potting

64 earthern pots were numbered according to the soil and fertiliser treatment e.g. the pot receiving 6.6 µg P/g (equivalent to 14.68 kg P/ha) of Macmerry soil was numbered as $M(P_{2/1})$. There was a drainage hole at the bottom of each pot. The drainage holes of 32 pots were sealed with mastic and those remaining were modified to carry out alternately flooded and moist conditions. The modification consisted of inserting a small glass tube through a rubber

bung fitted to the drainage hole of each pot. One end of the glass tube was capped with glass wool and the other end was connected to a small length (about 15 cm) of rubber tubing with a screw clip which acted as a valve. All the pots were washed and dried before use. Each had a capacity of about 6 litres.

300 g of sand was first placed into each pot, onto which 5 kg of air-dry soil was placed. For constantly flooded conditions, 32 pots (16 for Macmerry and 16 for Giffnock soils) were placed at random on one bench and the rest on another. About a litre of water was first added to each pot one day before fertiliser application.

(d) Fertiliser application

A basal dose of nitrogen to give a final conc. in all pots of 45 µg N/g soil (equivalent to 112 kg N/ha) was applied to all the pots one day before transplanting, as a solution of laboratory reagent grade urea. On the same day fertiliser phosphorus was also applied to the pots at the rates of 0, 3.3, 6.6, 13.2 µg P/g soil (equivalent to 0, 7.34, 14.68 and 29.36 kg P/ha), as a solution of analytical reagent grade ammonium dihydrogen orthophosphate, $(NH_4)\ H_2PO_4$, containing 26.95% P.

(e) Transplanting

Three 23 days old rice seedlings were transplanted to each pot at equal spacing and water was added to bring the water level about 2 cm above the soil surface.

(f) Constantly flooded pots

Six days after transplanting when the seedlings became fully established, the depth of water was raised to about 5 cm above the soil surface and maintained at this level throughout the growing period.

(g) Alternately flooded and moist pots

Six days after transplanting the water level was raised to 4 cm above the soil surface. After 10 days all the water was allowed to drain through the bottom tube and the liquid collected in a 500 ml beaker. No water was supplied to the pots for 4 days and then the collected liquid, together with more water was added to restore the 4 cm water depth. The pots were kept 4 days flooded and 4 days moist for 42 days and then kept 4 days flooded and 3 days moist throughout the growing period.

Some weeds appeared during the early period of growth; they were uprooted and removed.

(h) Glasshouse maintenance

The glasshouse was maintained throughout the experiment in a similar way as described in 3.5.1.2. (d).

(i) Harvesting, drying, weighing and storage of plant material

Sixty days after transplanting, 32 pots were harvested by cutting the rice plants at the soil surface. Washing, drying, weighing and storage were carried out as described in 3.5.1.2. (f).

Similarly a second harvest was made 90 days after transplanting by cutting the remaining 32 pots.

(j) Soil sampling and analysis

After each harvest moist soil samples were collected from each pot for the determination of extractable phosphate and iron. The results were expressed on oven-dry basis. The pH was also measured in moist soil. The analytical techniques are described in section 3.2.

(k) Plant analysis

The plant samples collected from both the harvests were analysed for total phosphorus, following acid digestion. Digestion for the

determination of total phosphorus was carried out as described in 3.5.1.4.

3.5.3. Experiment III. Effect of Depletion of Soil Phosphate

3.5.3.1. Soils

Macmerry and Giffnock series soils as described in 3.1.1. were used to deplete the native phosphate content by growing ryegrass for about a year in pots and then using the same soil to grow rice.

Urea was applied in two splits, the first dose was applied 25 days after sowing ryegrass seeds and the second dose was applied two months from the date of the first application. Each time a solution of urea was applied at a rate equivalent to 112 kg N/ha. Grasses were growing very well in both the soils. The first harvest was made 75 days after sowing by cutting the grass just above the soil surface. Second, third and final harvests were made after 60, 90 and 105 days respectively from the date of the previous harvest. After the final harvest all the soils were taken out from the pots. They were air-dried, broken into small pieces and mechanically ground to pass through a 2 mm sieve.

3.5.3.2. Cultural operations

(a) Raising of seedlings

The same variety of rice and a similar procedure was used for the raising of rice seedlings as described in 3.5.1.2. (a).

(b) Treatment conbinations

There were two levels of phosphorus fertilisation, 0 and 20 µg P/g soil (equivalent to 0 and 50 kg P/ha). There were two soils and each treatment was replicated six times; a total of 24 pots.

(c) Potting

12 white plastic buckets were used for each soil. Each bucket

had a capacity of 15 litres. The buckets were numbered according to the soil and fertiliser treatment e.g. the bucket receiving 50 kg P/ha of Macmerry soil was numbered as $M(P_{50/1})$. There was no provision for any drainage. All the buckets were washed and dried before use. 7 kg of air-dry (phosphate depleted) soil and 7 kg of phosphate-free sand (0.5 to 1.0 mm) were mixed thoroughly by a rotary mixer and placed in each bucket. The outside of the bucket was painted with black paint. The buckets were saturated with water one day before application of phosphate and potassium fertilisers. The buckets were placed at random on a bench which was about 60 cm high from the floor.

(d) Fertiliser application

A solution of fertiliser phosphorus was uniformly applied to half the buckets one day before transplanting at the rate of 20 µg P/g soil as analytical reagent grade potassium dihydrogen orthophosphate, KH_2PO_4, containing 22.76% P. On the same day all the buckets also received sufficient of a solution of AR KCl to give a final concentration in all pots of 40 µg K/g soil. Eight days after transplanting, nitrogen at the rate of 40 µg N/g soil was applied to all the buckets as a solution of laboratory reagant grade urea.

(e) Transplanting

Eight 30 days old rice seedlings were transplanted to each bucket at equal spacing. Water was added to maintain the water level about 2 cm above the soil surface. Seven days after transplanting, when the seedlings became fully established, the depth of water was raised to about 5 cm above the soil surface and maintained at this level throughout the growing period.

(f) Glasshouse maintenance

The glasshouse was maintained throughout the experiment in a similar way as described in 3.5.1.2. (d).

(g) Harvesting, drying, weighing and storage of plant material

Sixty days after transplanting the buckets were harvested by cutting the rice plants at the soil surface. Washing, drying, weighing and storage were carried out as described in 3.5.1.2. (f).

(h) Plant analysis

The plant samples were analysed for total phosphorus, iron, manganese, calcium and potassium, following acid digestion by following the procedure as described in 3.5.1.4.

RESULTS AND DISCUSSION

4. RESULTS AND DISCUSSION

The soils used in this work are described in 3.1. and some of their physical and chemical properties are presented in Table 2. The Brahmaputra soil is slightly alkaline whilst the other three soils are moderately acidic. For agricultural purposes the extractable phosphate values are in the low categories for Macmerry, Brahmaputra and Tista whilst Giffnock is very low. The organic matter contents of Tista and Brahmaputra soils are relatively low compared with the other two soils. This low organic matter content was reflected in the low content of organic phosphorus. For general agricultural purposes the potassium values would be regarded as low in all four soils. 'Free' iron and manganese values are relatively high and low for the Macmerry and Giffnock soils respectively, while values for the Tista and Brahmaputra soils are in the medium level.

4.1. INCUBATION EXPERIMENTS

4.1.1. Redox Potential

As previously indicated (section 2.1.1.) the range of redox potential usually encountered in well-drained soils and in waterlogged soils is: oxidised zone +400 to +700 mV; moderately reduced +200 to +400 mV; reduced -100 to +200 mV; and highly reduced -300 to -100 mV (Patrick and Mahapatra, 1968).

The redox potential of the incubated waterlogged Macmerry and Giffnock soils measured every week for 16 weeks is reported in Appendix, Table A1 and for the Tista and Brahmaputra soils measured every two weeks is reported in Appendix, Table A2. After every four weeks of measurement the duplicate samples for each of the soils under

Table 2. Some physical and chemical properties of the soils

Soil	Texture	pH	Inorg. P	Org. P	Total P	Extractable P	Extractable K	'Free' Fe	'Free' Mn	O.M.	Total N	C:N
			µg/g soil							%		
Macmerry	Sandy clay loam	6.2	298	359	657	2.0	62	15750	410	5.7	0.20	16.5
Giffnock	Loam	5.6	53	89	142	0.5	32	3900	30	4.0	0.10	23.5
Tista	Silt loam	6.7	440	92	532	1.8	44	8000	270	1.5	0.07	11.6
Brahmaputra	Silt loam	7.6	710	53	763	3.0	77	7000	295	1.1	0.05	11.6

study were finally withdrawn from the incubator for other measurements. The data obtained on the basis of four week intervals are shown in Table 3 and Figure 1. After four weeks Brahmaputra soil was moderately reduced. Macmerry and Giffnock soils maintained highly reduced values upto 8 and 12 weeks of incubation, respectively and then became less reduced. The Tista soil also became less reduced from 8 weeks onward. In contrast Brahmaputra soil maintained only moderately reduced conditions throughout the incubation period.

The redox potential values for Macmerry, Giffnock and Tista soils returned to a relatively less reduced state towards the end of the incubation period. This was probably due to the depletion of reactive organic matter by the action of microorganisms which together are largely responsible for the reduction processes (Ponnamperuma, 1965), coupled with the slow diffusion of oxygen through the polypropylene tube (Posner, 1979). This would account for the observed increases in redox potential values.

Ponnamperuma (1965) observed that the redox potential falls sharply upon flooding, reaches a minimum within a few days, rises rapidly to a maximum, and then decreases asymptotically with time. With the exception of the Brahmaputra soil the results of the present investigation do indeed show that the redox potential follows the same trends indicated by Ponnamperuma (1965). However, the final asymptotic decrease observed by him was not observed here since the incubation was not carried on long enough.

It has been shown that soils low in organic matter (less than 1.5%) have maintained positive redox potential values for almost six months after submergence (Ponnamperuma, 1965). The Brahmaputra soil has a low organic matter content and this could be a reason for it

Table 3. Effect of waterlogging on redox potential of soils with time of incubation*

Time (weeks)	Soil			
	Macmerry	Giffnock	Tista	Brahmaputra
	Redox potential (mV)			
0	402 ± 2	128 ± 0	389 ± 41	282 ± 2
4	-227 ± 14	-161 ± 7	-161 ± 34	290 ± 28
8	-167 ± 21	-206 ± 18	-81 ± 11	211 ± 9
12	-42 ± 13	-122 ± 8	31 ± 4	199 ± 80
16	45 ± 36	-65 ± 5	45 ± 23	385 ± 5

* mean of duplicate samples

Table 4. Effect of waterlogging on redox potential of soils containing urea with time of incubation*

Time (weeks)	Soil			
	Macmerry	Giffnock	Tista	Brahmaputra
	Redox potential (mV)			
0	302 ± 2	72 ± 2	387 ± 25	309 ± 24
4	-227 ± 24	-173 ± 13	-119 ± 5	295 ± 22
8	-139 ± 7	-156 ± 5	-75 ± 19	254 ± 26
12	-31 ± 30	-104 ± 8	-65 ± 3	212 ± 168
16	39 ± 11	-94 ± 10	7 ± 2	262 ± 60

* mean of duplicate samples

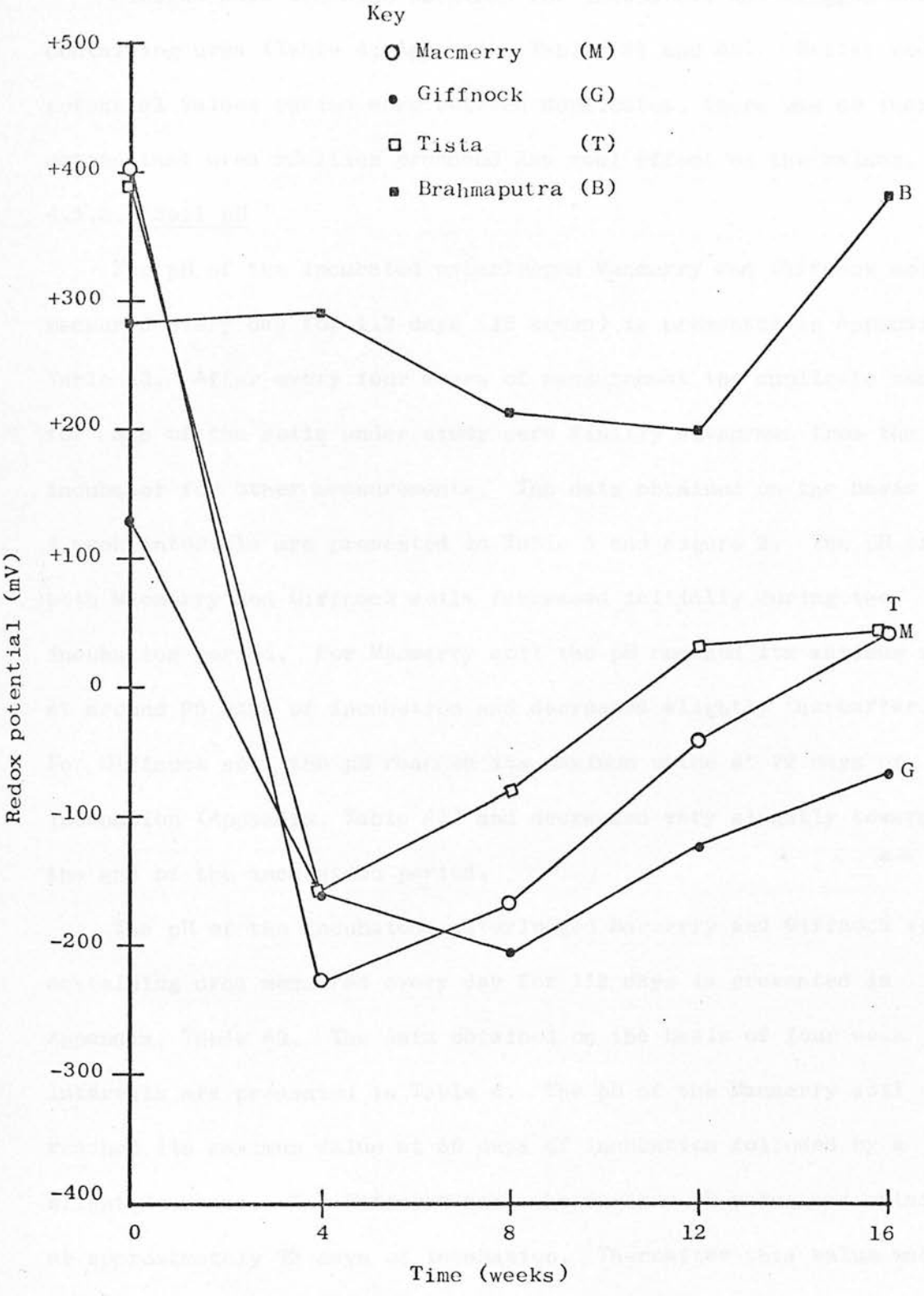

Figure 1. Plot of redox potential against time of incubation for waterlogged soils

maintaining positive redox potential values all through the study.

Similar data were also obtained for incubated, waterlogged soils containing urea (Table 4; Appendix, Tables A1 and A2). Whilst redox potential values varied more between duplicates, there was no indication that urea addition produced any real effect on the values.

4.1.2. Soil pH

The pH of the incubated waterlogged Macmerry and Giffnock soils measured every day for 112 days (16 weeks) is presented in Appendix, Table A3. After every four weeks of measurement the duplicate samples for each of the soils under study were finally withdrawn from the incubator for other measurements. The data obtained on the basis of 4 week intervals are presented in Table 5 and Figure 2. The pH of both Macmerry and Giffnock soils increased initially during the incubation period. For Macmerry soil the pH reached its maximum value at around 95 days of incubation and decreased slightly thereafter. For Giffnock soil the pH reached its maximum value at 79 days of incubation (Appendix, Table A3) and decreased very slightly towards the end of the incubation period.

The pH of the incubated, waterlogged Macmerry and Giffnock soils containing urea measured every day for 112 days is presented in Appendix, Table A3. The data obtained on the basis of four week intervals are presented in Table 6. The pH of the Macmerry soil reached its maximum value at 56 days of incubation followed by a slight decrease. For Giffnock soil the maximum pH value was obtained at approximately 73 days of incubation. Thereafter this value was more or less maintained for the duration of the experiment.

The pH of the incubated waterlogged Tista and Brahmaputra soils measured every week for 16 weeks is presented in Appendix, Table A4.

Table 5. Effect of waterlogging on pH of soils with time of incubation*

Time (weeks)	Soil			
	Macmerry	Giffnock	Tista	Brahmaputra
	pH			
0	6.4	5.5	6.8	7.6
4	7.1	6.8	6.9	7.0
8	7.3	6.7	6.9	7.0
12	7.0	6.7	6.9	7.2
16	7.1	6.6	7.0	7.2

* mean of duplicate samples
average error is ± 0.05

Table 6. Effect of waterlogging on pH of soils containing urea with time of incubation*

Time (weeks)	Soil			
	Macmerry	Giffnock	Tista	Brahmaputra
	pH			
0	6.4	5.5	6.8	7.6
4	7.1	6.7	7.0	7.1
8	7.4	6.9	7.0	7.1
12	7.1	6.9	6.9	7.2
16	7.2	6.8	7.0	7.2

* mean of duplicate samples
average error is ± 0.05

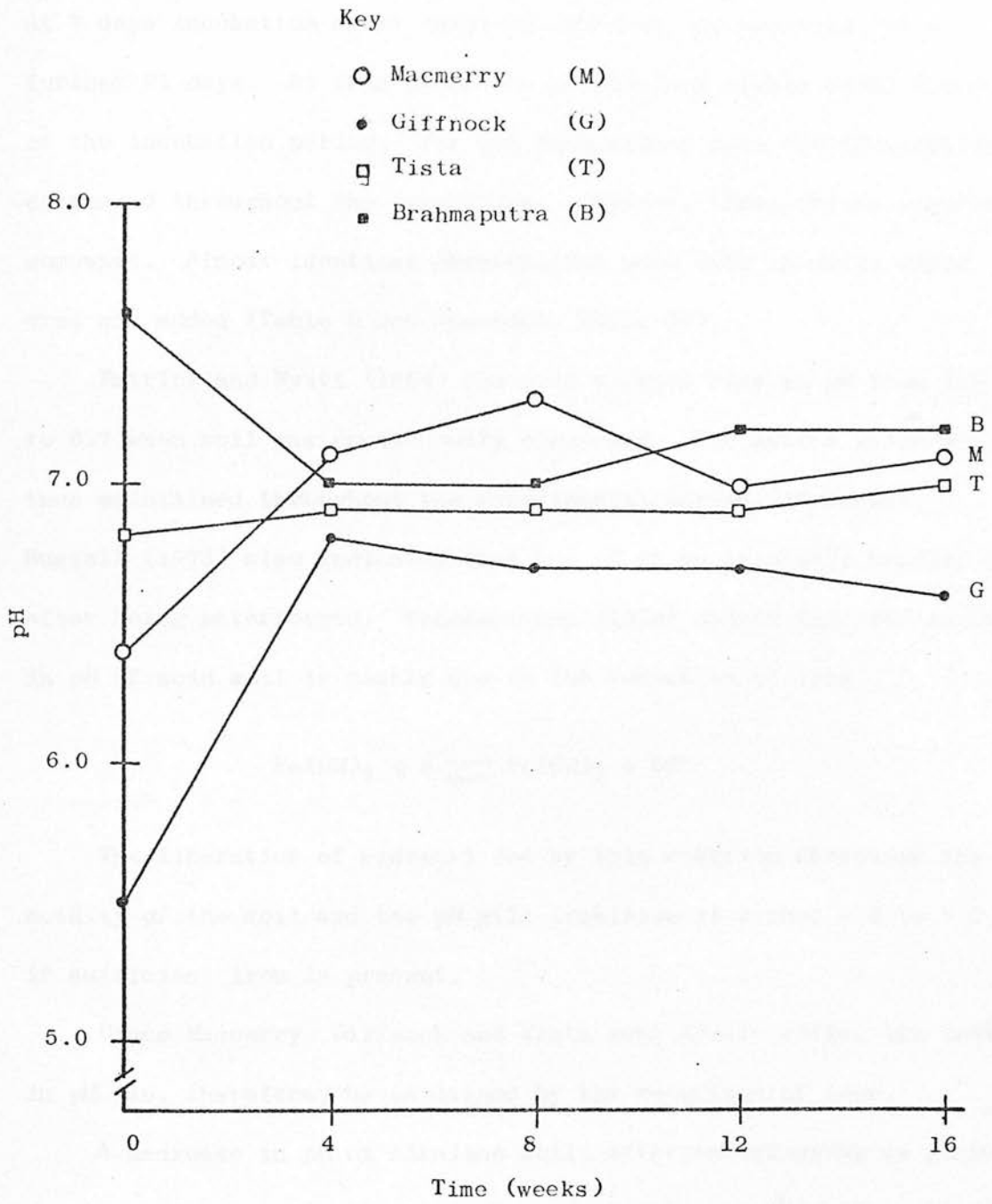

Figure 2. Plot of pH against time of incubation for waterlogged soils

The data obtained on the basis of four week intervals are presented in Table 5 and Figure 2. The pH of the Tista soil slightly decreased at 7 days incubation after which an increase was observed for a further 91 days. At this point the pH remained stable until the end of the incubation period. For the Brahmaputra soil the pH slightly decreased throughout the incubation. However, these values fluctuated somewhat. Almost identical observations were made in soils where urea was added (Table 6 and Appendix, Table A4).

Patrick and Wyatt (1964) observed a rapid rise in pH from 5.3 to 6.7 when soil was continuously submerged. The latter value was then maintained throughout the experimental period (60 weeks). Russell (1973) also indicated that the pH of an acid soil usually rises after being waterlogged. Ponnamperuma (1972) stated that the increase in pH of acid soil is mainly due to the reduction of iron.

$$Fe(OH)_3 + e^- \rightleftharpoons Fe(OH)_2 + OH^-$$

The liberation of hydroxyl ion by this reaction decreases the acidity of the soil and the pH will stabilise at around 6.5 to 7.0, if sufficient iron is present.

Since Macmerry, Giffnock and Tista were acidic soils, the increase in pH can, therefore, be explained by the reduction of iron.

A decrease in pH of alkaline soils after waterlogging is probably due to an increase in the partial pressure of carbondioxide. Nicol and Turner (1957) observed that carbondioxide depresses the pH even of acid soils. Ponnamperuma et al. (1966) found that the pH values of alkali and calcareous soils decreased, while those of the acid soils increased to a fairly stable pH value between 6.7 to 7.2 twelve weeks after flooding. They also observed that the pH of alkaline soils is

highly sensitive to changes in the partial pressure of carbondioxide. The Brahmaputra soil was alkaline in reaction, therefore, the decrease in its pH value is probably due to an increase in the partial pressure of carbondioxide.

Thus, previous findings suggest that overall effect of water-logging is to increase the pH of acid soils and to decrease the pH of alkaline soils. The results of the present investigation support this concept and show that the pH values of waterlogged soils tend towards neutrality.

4.1.3. Iron

The occurrence of large amounts of reduced iron in waterlogged soils has been reported by many workers (e.g. Pearsall, 1950; Patrick, 1964; Ponnamperuma, 1972; Yoshida and Itoh, 1974; Islam and Parsons, 1979). According to Alexander (1977) the increase in ferrous iron in a waterlogged soil is almost entirely due to the action of micro-organisms and no such changes occur in a sterile waterlogged soil.

When iron is reduced it can be extracted with ammonium acetate and small amounts of ferric iron can also be extracted. The concentrations of ammonium-acetate extractable iron with time of incubation under waterlogged soil conditions are presented in Table 7. The concentrations of extractable iron increased significantly upto 8 weeks of incubation in Macmerry and Tista soils, while in Giffnock and in Brahmaputra soils the peak values were reached after 4 weeks of incubation. In all soils most of the increase occurred within the first four weeks. Islam and Parsons (1979) also found that the reduction of iron increased with time and reached a maximum value at 32 days of anaerobic conditions.

It was observed that as a result of waterlogging the concentration

of extractable iron in the Macmerry, Tista and Giffnock soils increased dramatically with time, especially when compared with the values for fresh, aerobic soil samples. However, the amount of extractable iron depends both on the extent of reduction and on the iron content of the soil. The data presented in Table 7 show that as a result of waterlogging about 41, 37, 26 and 5% (these figures were based on the average of the data obtained at 4, 8, 12 and 16 weeks) of the 'free' iron (Table 2) has become extractable in the Giffnock, Tista, Macmerry and Brahmaputra soils, respectively. As can be seen, the proportion of extractable iron in the Brahmaputra soil is substantially less than the other three soils.

Data reported in Table 9 show that ferrous iron constituted most of the extractable iron, about 89 to 97% being in the ferrous state. A similar observation was also made by Patrick (1964). He found that a decrease in redox potential below +200 mV resulted in a very large release of ferrous iron, a concentration of 4400 ppm being present at a potential of -200 mV. However, iron brought into solution also depends on the pH of the soil. Alexander (1977) observed that the increases in acidity bring iron into solution. Three of the soils used here were in fact acidic in reaction. The occurrence of large amounts of iron in waterlogged, acidic soils have also been reported by Ponnamperuma (1972). The low concentration of extractable iron and low proportion of 'free' iron reduced in Brahmaputra soil was probably due both to the moderately reduced conditions which persisted throughout the experiment and to the higher pH of this soil.

Figure 3 shows clearly that the concentration of extractable iron decreases after 8 weeks of incubation in the Macmerry and Tista soils, and after 4 weeks in the Giffnock and Brahmaputra soils. The

Table 7. Concentration of ammonium acetate-extractable iron with time of incubation for waterlogged soils*

Time (weeks)	Soil			
	Macmerry	Giffnock	Tista	Brahmaputra
	Extractable Fe (μg/g soil)			
0	20 ± 0	675 ± 0	37 ± 0	11 ± 0
4	4300 ± 140	1740 ± 50	2899 ± 12	477 ± 78
8	4334 ± 34	1642 ± 25	3475 ± 25	406 ± 19
12	4125 ± 100	1621 ± 46	3106 ± 331	312 ± 63
16	3736 ± 61	1358 ± 17	2300 ± 0	197 ± 17

* mean of duplicate samples

Table 8. Concentration of ammonium acetate-extractable iron with time of incubation for waterlogged soils containing urea*

Time (weeks)	Soil			
	Macmerry	Giffnock	Tista	Brahmaputra
	Extractable Fe (μg/g soil)			
0	20 ± 0	675 ± 0	37 ± 0	11 ± 0
4	4360 ± 0	1395 ± 25	2956 ± 19	424 ± 12
8	4467 ± 100	1492 ± 42	3500 ± 125	525 ± 6
12	3814 ± 110	1381 ± 19	2912 ± 362	565 ± 40
16	3241 ± 59	1337 ± 63	2450 ± 180	512 ± 62

* mean of duplicate samples

Table 9. Concentration of ammonium acetate-extractable ferrous and ferric iron with time of incubation for waterlogged soils*

Time (weeks)	Soil			
	Macmerry		Giffnock	
	Ferrous iron	Ferric iron	Ferrous iron	Ferric iron
	Extractable Fe (μg/g soil)			
12	4018 ± 0	107	1481 ± 19	140
16	3587 ± 87	149	1169 ± 69	189

* mean of duplicate samples

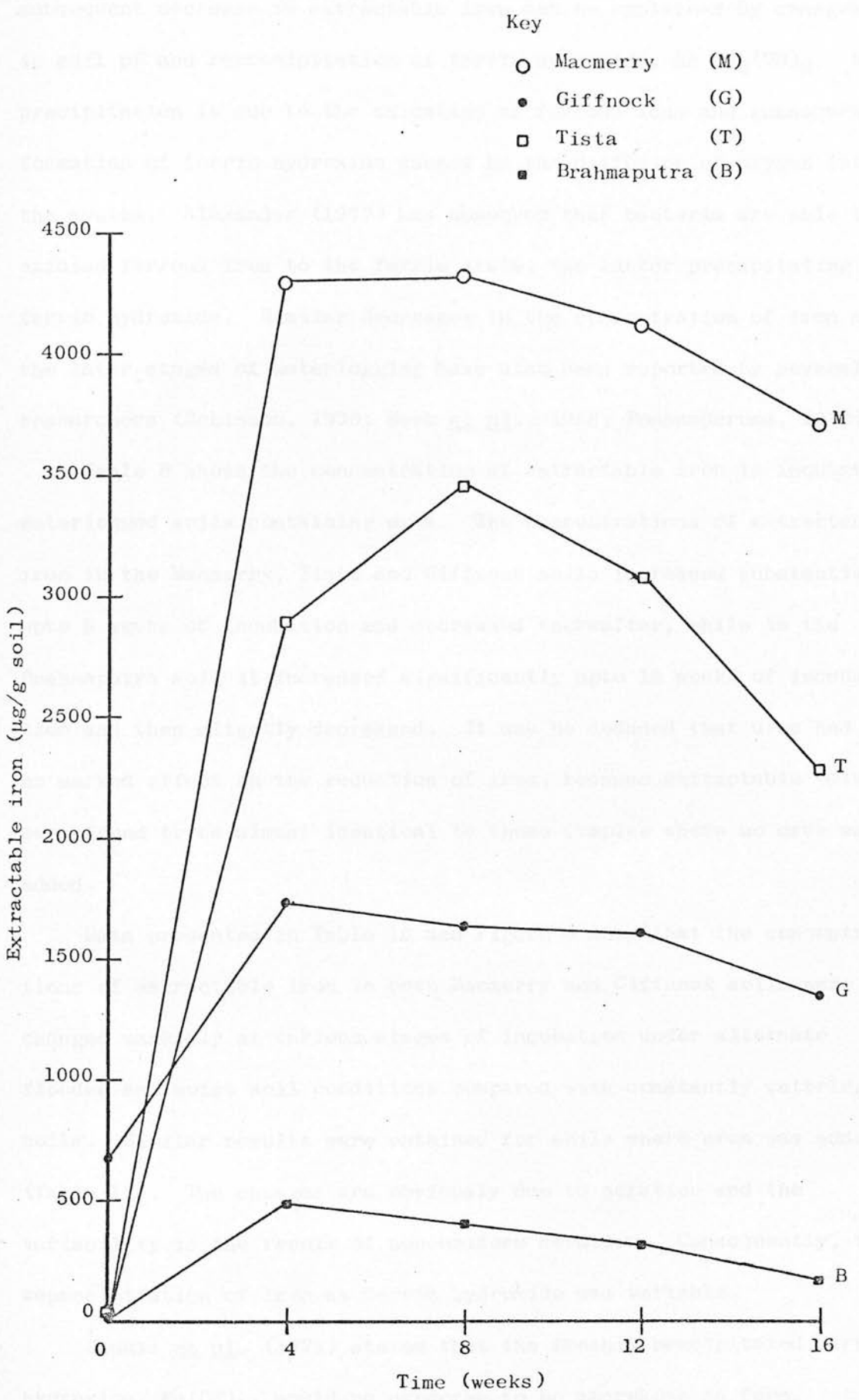

Figure 3. Plot of extractable iron against time of incubation for waterlogged soils

subsequent decrease in extractable iron can be explained by changes in soil pH and reprecipitation of ferric hydroxide, as $Fe_3(OH)_8$. Such precipitation is due to the oxidation of ferrous ions and subsequent formation of ferric hydroxide caused by the diffusion of oxygen into the system. Alexander (1977) has observed that bacteria are able to oxidise ferrous iron to the ferric state, the latter precipitating as ferric hydroxide. Similar decreases in the concentration of iron at the later stages of waterlogging have also been reported by several researchers (Robinson, 1930; Meek et al., 1968; Ponnamperuma, 1972).

Table 8 shows the concentration of extractable iron in incubated waterlogged soils containing urea. The concentrations of extractable iron in the Macmerry, Tista and Giffnock soils increased substantially upto 8 weeks of incubation and decreased thereafter, while in the Brahmaputra soil it increased significantly upto 12 weeks of incubation and then slightly decreased. It may be deduced that urea had no marked effect on the reduction of iron, because extractable values were found to be almost identical to those samples where no urea was added.

Data presented in Table 10 and Figure 4 show that the concentrations of extractable iron in both Macmerry and Giffnock soils were changed markedly at various stages of incubation under alternate flooded and moist soil conditions compared with constantly waterlogged soils. Similar results were obtained for soils where urea was added (Table 11). The changes are obviously due to aeration and the variability is the result of non-uniform aeration. Consequently, the reprecipitation of iron as ferric hydroxide was variable.

Shukla et al. (1971) stated that the freshly precipitated ferrous hydroxide, $Fe(OH)_2$, would be expected to be amorphous in form.

Table 10. Concentration of ammonium acetate-extractable iron with time of incubation for alternate flooded and moist soils*

Time (weeks)	Soil	
	Macmerry	Giffnock
	Extractable Fe (μg/g soil)	
0	20 ± 0	675 ± 0
4	535 ± 335	1155 ± 960
8	46 ± 12	85 ± 2
12	32 ± 8	87 ± 23
16	13 ± 4	95 ± 21

* mean of duplicate samples

Table 11. Concentration of ammonium acetate-extractable iron with time of incubation for alternate flooded and moist soils containing urea*

Time (weeks)	Soil	
	Macmerry	Giffnock
	Extractable Fe (μg/g soil)	
0	20 ± 0	675 ± 0
4	2775 ± 225	755 ± 145
8	71 ± 23	153 ± 23
12	20 ± 9	83 ± 5
16	28 ± 5	61 ± 8

* mean of duplicate samples

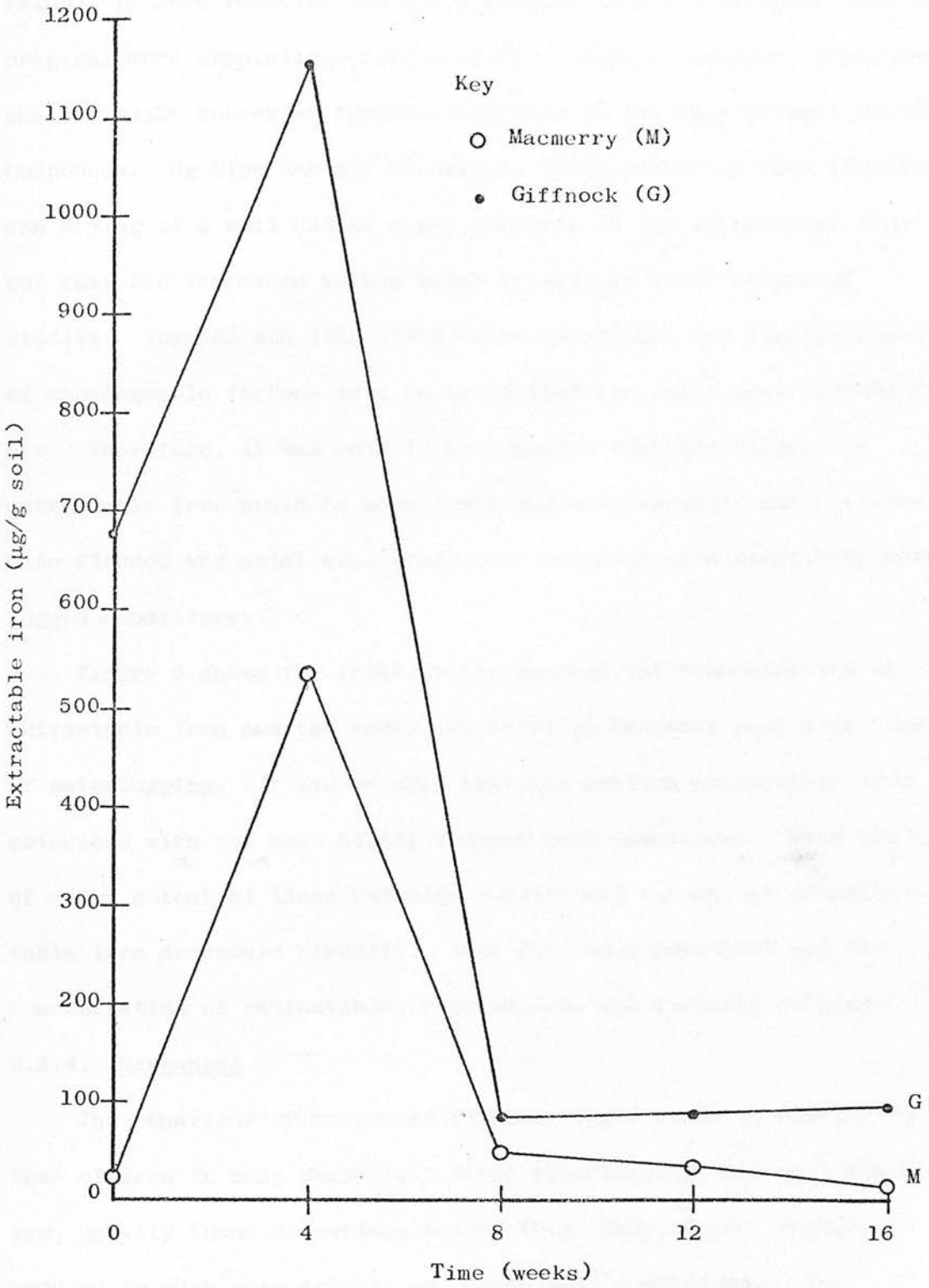

Figure 4. Plot of extractable iron against time of incubation for alternate flooded and moist soils

Holford and Patrick (1979) observed that this freshly precipitated $Fe(OH)_2$ is more reactive and has a greater sorption capacity than the original more crystalline ferric hydrous oxides. However, oxidation has obviously converted ferrous compounds to the less soluble ferric compounds. Ng Siew Kee and Bloomfield (1962) observed that flooding and drying of a soil causes a net increase in the extractable iron but that the increased values began to fall at later stages of studies. Yoshida and Itoh (1974) also found that the disappearance of exchangeable ferrous iron occurred when the soils were exposed to air. Therefore, it was only to be expected that the values for extractable iron would be much lower and more variable under alternate flooded and moist soil conditions compared with constantly waterlogged conditions.

Figure 5 shows the relationship between the concentration of extractable iron and the redox potential in Macmerry soil with time of waterlogging. It can be seen that the maximum extractable iron coincided with the most highly reduced soil conditions. With the rise of redox potential (less reducing conditions) the amount of extractable iron decreased steadily. Thus the redox potential and the concentration of extractable, reduced iron are directly related.

4.1.4. Manganese

The behaviour of manganese in waterlogged soils is similar to that of iron in many respects. After waterlogging, the soil manganese, usually found as various oxides (e.g. MnO_2, Mn_2O_3, Mn_3O_4), is reduced to much more soluble manganous (Mn^{2+}) compounds. The reduction processes are both chemical and biological (Yoshida and Kamura, 1974) and the occurrence of large amounts of exchangeable manganese in waterlogged soils is well established (Robinson, 1930;

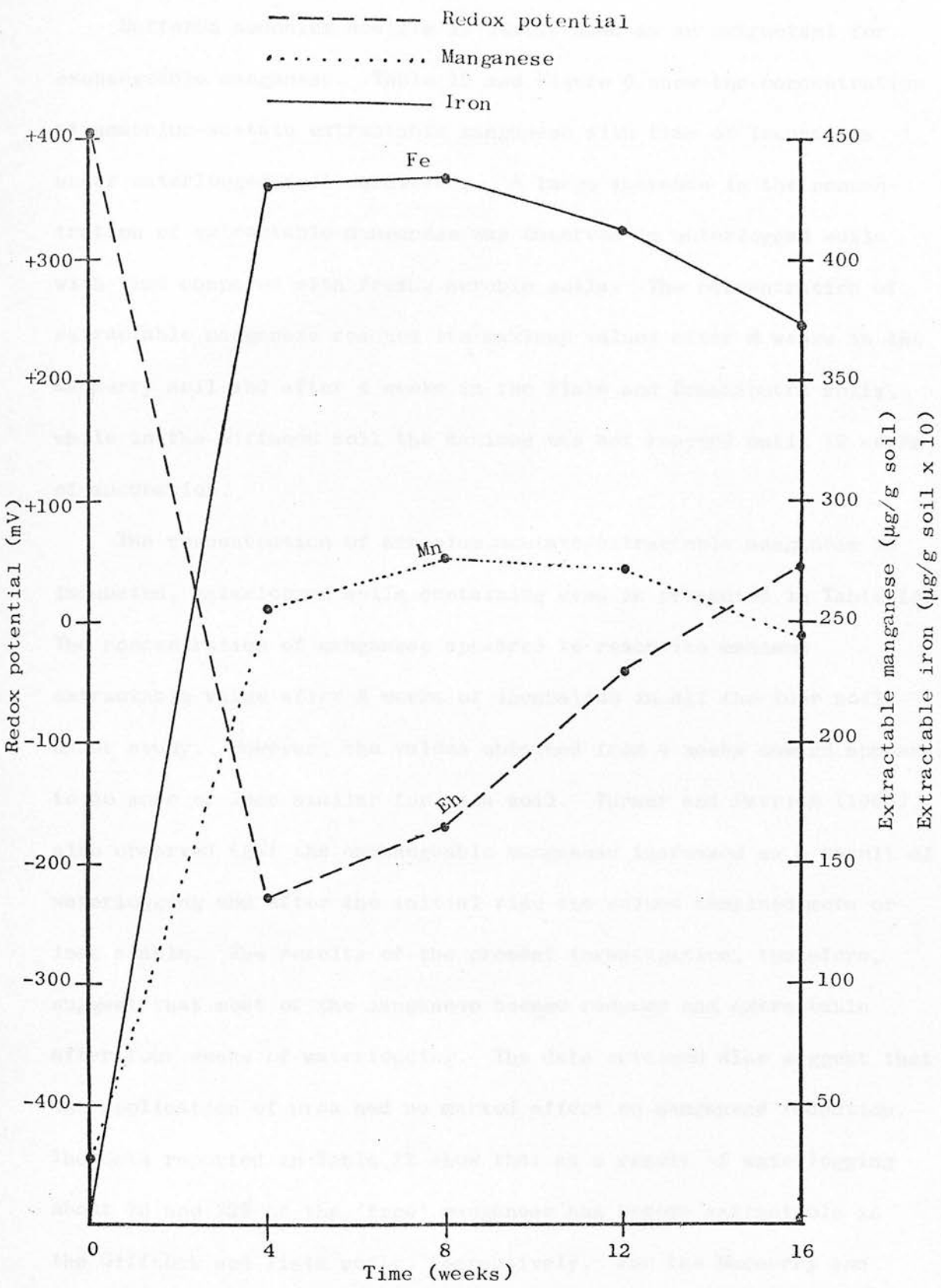

Figure 5. Plot of extractable iron, manganese, and redox potential against time of incubation for waterlogged Macmerry soil

Patrick and Turner, 1968; Ponnamperuma, 1972; Alexander, 1977).

Buffered ammonium acetate is widely used as an extractant for exchangeable manganese. Table 12 and Figure 6 show the concentration of ammonium-acetate extractable manganese with time of incubation under waterlogged soil conditions. A large increase in the concentration of extractable manganese was observed in waterlogged soils with time compared with fresh, aerobic soils. The concentration of extractable manganese reached its maximum values after 8 weeks in the Macmerry soil and after 4 weeks in the Tista and Brahmaputra soils, while in the Giffnock soil the maximum was not reached until 12 weeks of incubation.

The concentration of ammonium acetate-extractable manganese in incubated, waterlogged soils containing urea is presented in Table 13. The concentration of manganese appeared to reach its maximum extractable value after 8 weeks of incubation in all the four soils under study. However, the values obtained from 4 weeks onward appeared to be more or less similar for each soil. Turner and Patrick (1968) also observed that the exchangeable manganese increased as a result of waterlogging and after the initial rise the values remained more or less stable. The results of the present investigation, therefore, suggest that most of the manganese became reduced and extractable after four weeks of waterlogging. The data obtained also suggest that the application of urea had no marked effect on manganese reduction. The data reported in Table 12 show that as a result of waterlogging about 78 and 72% of the 'free' manganese has become extractable in the Giffnock and Tista soils, respectively. For the Macmerry and Brahmaputra soils about 65% of the 'free' manganese (Table 2) has become extractable (these figures were based on the average of the

Table 12. Concentration of ammonium acetate-extractable manganese with time of incubation for waterlogged soils*

Time (weeks)	Soil			
	Macmerry	Giffnock	Tista	Brahmaputra
	Extractable Mn (μg/g soil)			
0	28 ± 0	14 ± 0	48 ± 2	14 ± 0
4	255 ± 0	23 ± 0	210 ± 0	200 ± 0
8	277 ± 2	25 ± 0	193 ± 2	185 ± 0
12	273 ± 2	27 ± 2	185 ± 0	197 ± 2
16	245 ± 5	24 ± 0	192 ± 2	190 ± 5

* mean of duplicate samples

Table 13. Concentration of ammonium acetate-extractable manganese with time of incubation for waterlogged soils containing urea*

Time (weeks)	Soil			
	Macmerry	Giffnock	Tista	Brahmaputra
	Extractable Mn (μg/g soil)			
0	28 ± 0	14 ± 0	48 ± 2	14 ± 0
4	275 ± 0	20 ± 0	180 ± 0	197 ± 2
8	285 ± 0	24 ± 0	195 ± 10	200 ± 0
12	253 ± 7	21 ± 2	190 ± 5	195 ± 10
16	207 ± 22	24 ± 3	180 ± 0	180 ± 0

* mean of duplicate samples

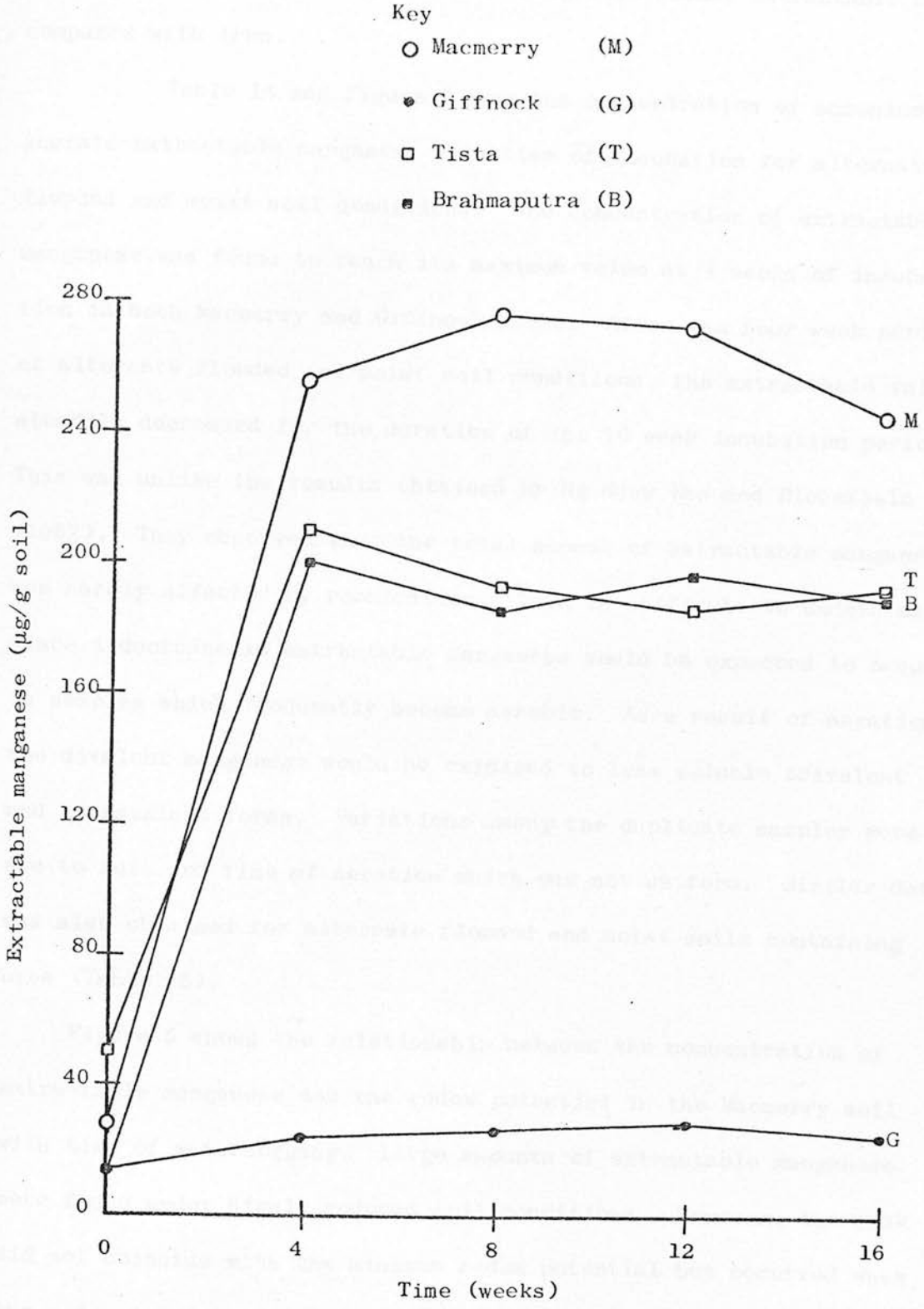

Figure 6. Plot of extractable manganese against time of incubation for waterlogged soils

data obtained at 4, 8, 12 and 16 weeks). It can be noted that a significantly greater proportion of manganese became extractable as compared with iron.

Table 14 and Figure 7 show the concentration of ammonium acetate-extractable manganese with time of incubation for alternate flooded and moist soil conditions. The concentration of extractable manganese was found to reach its maximum value at 4 weeks of incubation in both Macmerry and Giffnock soils. After the four week period of alternate flooded and moist soil conditions, the extractable values steadily decreased for the duration of the 16 week incubation period. This was unlike the results obtained by Ng Siew Kee and Bloomfield (1962). They observed that the total amount of extractable manganese was hardly affected by reoxidation. This is difficult to understand since a decrease in extractable manganese would be expected to occur in samples which frequently become aerobic. As a result of aeration the divalent manganese would be oxidised to less soluble trivalent and tetravalent forms. Variations among the duplicate samples were due to rate and time of aeration which was not uniform. Similar data was also obtained for alternate flooded and moist soils containing urea (Table 15).

Figure 5 shows the relationship between the concentration of extractable manganese and the redox potential in the Macmerry soil with time of waterlogging. Large amounts of extractable manganese were found under highly reduced soil conditions. However, the peak did not coincide with the minimum redox potential but occurred when the redox value began to rise. But with a further rise in redox potential the extractable values remained more or less stable. Whilst manganese is more readily reduced than iron, some of it is probably

Table 14. Concentration of ammonium-acetate-extractable manganese with time of incubation for alternate flooded and moist soils*

Time (weeks)	Soil	
	Macmerry	Giffnock
	Extractable Mn (μg/g soil)	
0	28 ± 0	14 ± 0
4	193 ± 25	22 ± 0
8	148 ± 47	18 ± 0
12	115 ± 15	15 ± 0
16	16 ± 0	13 ± 3

* mean of duplicate samples

Table 15. Concentration of ammonium-acetate-extractable manganese with time of incubation for alternate flooded and moist soils containing urea*

Time (weeks)	Soil	
	Macmerry	Giffnock
	Extractable Mn (μg/g soil)	
0	28 ± 0	14 ± 0
4	262 ± 8	22 ± 0
8	198 ± 2	19 ± 0
12	83 ± 31	16 ± 0
16	50 ± 10	14 ± 0

* mean of duplicate samples

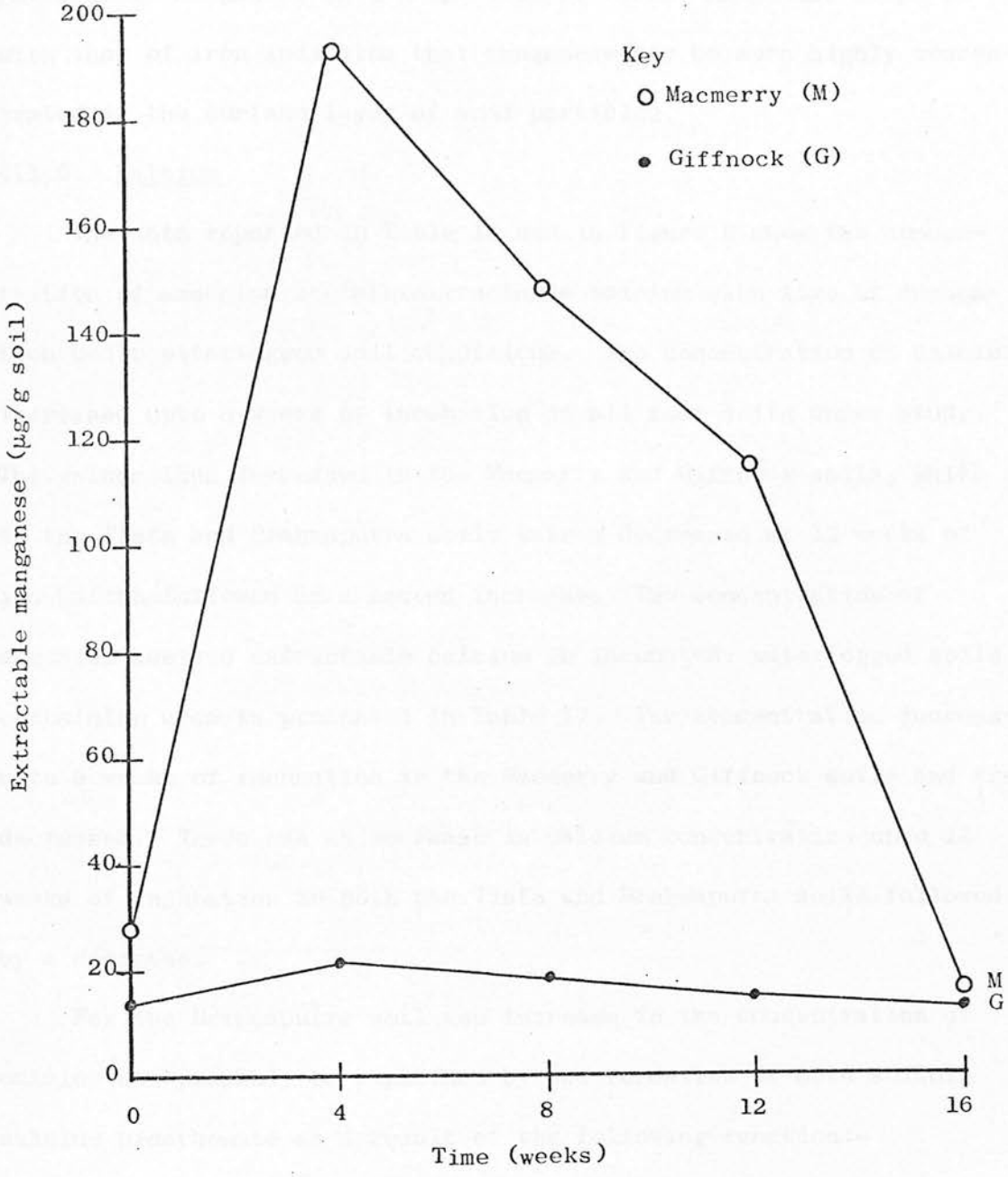

Figure 7. Plot of extractable manganese against time of incubation for alternate flooded and moist soils

occluded by iron compounds and can not be reduced until the iron is removed. This could account for the similar patterns of reduction for iron and manganese (Figure 5). However, the greater amounts of extractable manganese as a proportion of 'free' manganese compared with that of iron indicates that manganese may be more highly concentrated in the surface layer of soil particles.

4.1.5. Calcium

The data reported in Table 16 and in Figure 8 show the concentration of ammonium acetate-extractable calcium with time of incubation under waterlogged soil conditions. The concentration of calcium increased upto 8 weeks of incubation in all four soils under study. The values then decreased in the Macmerry and Giffnock soils, while in the Tista and Brahmaputra soils values decreased at 12 weeks of incubation followed by a second increase. The concentration of ammonium-acetate extractable calcium in incubated, waterlogged soils containing urea is presented in Table 17. The concentration increased upto 8 weeks of incubation in the Macmerry and Giffnock soils and then decreased. There was an increase in calcium concentration upto 12 weeks of incubation in both the Tista and Brahmaputra soils followed by a decrease.

For the Brahmaputra soil the increase in the concentration of calcium can probably be explained by the formation of more soluble calcium bicarbonate as a result of the following reaction:-

$$CaCO_3 + H_2O \overset{CO_2}{\rightleftharpoons} Ca(HCO_3)_2$$

The subsequent decrease in the concentration of calcium may be attributed to the fact that the reduced activity of microorganisms with time of waterlogging results in a decrease in carbondioxide

Table 16. Concentration of ammonium-acetate-extractable calcium with time of incubation for waterlogged soils*

Time (weeks)	Soil			
	Macmerry	Giffnock	Tista	Brahmaputra
	Extractable Ca (μg/g soil)			
0	1150 ± 0	750 ± 0	934 ± 3	1175 ± 13
4	1481 ± 19	863 ± 137	1050 ± 0	1425 ± 25
8	1625 ± 25	925 ± 25	1100 ± 0	1612 ± 137
12	1275 ± 25	750 ± 0	1037 ± 37	1237 ± 37
16	1200 ± 50	775 ± 25	1225 ± 125	1500 ± 0

* mean of duplicate samples

Table 17. Concentration of ammonium-acetate-extractable calcium with time of incubation for waterlogged soils containing urea*

Time (weeks)	Soil			
	Macmerry	Giffnock	Tista	Brahmaputra
	Extractable Ca (μg/g soil)			
0	1150 ± 0	750 ± 0	934 ± 3	1175 ± 13
4	1475 ± 0	737 ± 12	1087 ± 12	1462 ± 37
8	1850 ± 100	875 ± 25	1150 ± 0	1375 ± 100
12	1475 ± 25	825 ± 75	1262 ± 12	1537 ± 37
16	900 ± 100	575 ± 25	975 ± 0	1362 ± 12

* mean of duplicate samples

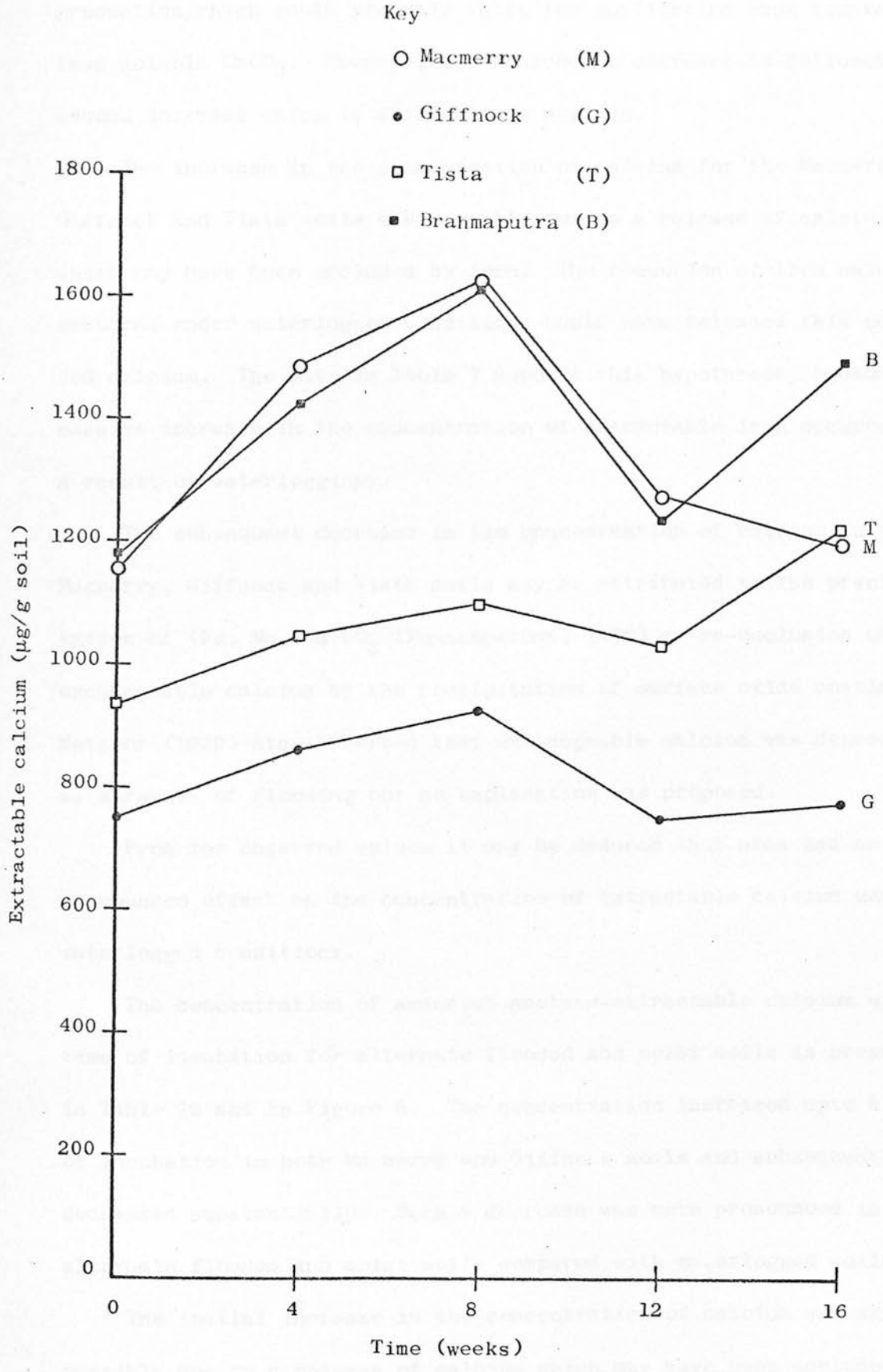

Figure 8. Plot of extractable calcium against time of incubation for waterlogged soils

production which would probably shift the equilibrium back towards the less soluble $CaCO_3$. However, the subsequent decrease is followed by a second increase which is difficult to explain.

The increase in the concentration of calcium for the Macmerry, Giffnock and Tista soils was possibly due to a release of calcium which may have been occluded by iron. The reduction of iron which occurred under waterlogged conditions could have released this occluded calcium. The data in Table 7 support this hypothesis, because a massive increase in the concentration of extractable iron occurred as a result of waterlogging.

The subsequent decrease in the concentration of calcium in the Macmerry, Giffnock and Tista soils may be attributed to the precipitation of $(Fe, Mn, Ca)CO_3$ (Ponnamperuma, 1972) or re-occlusion of exchangeable calcium by the precipitation of surface oxide coatings. Metzger (1929) also observed that exchangeable calcium was depressed as a result of flooding but no explanation was proposed.

From the observed values it may be deduced that urea had no pronounced effect on the concentration of extractable calcium under waterlogged conditions.

The concentration of ammonium acetate-extractable calcium with time of incubation for alternate flooded and moist soils is presented in Table 18 and in Figure 9. The concentration increased upto 8 weeks of incubation in both Macmerry and Giffnock soils and subsequently decreased substantially. Such a decrease was more pronounced in the alternate flooded and moist soils compared with waterlogged soils.

The initial increase in the concentration of calcium was again possibly due to a release of calcium which may have been occluded by iron. While the subsequent decrease was probably due to the fact that

Table 18. Concentration of ammonium acetate-extractable calcium with time of incubation for alternate flooded and moist soils*

Time (weeks)	Soil	
	Macmerry	Giffnock
	Extractable Ca (μg/g soil)	
0	1150 ± 0	750 ± 0
4	1725 ± 25	912 ± 63
8	2012 ± 12	1112 ± 38
12	940 ± 60	495 ± 20
16	850 ± 0	425 ± 13

* mean of duplicate samples

Table 19. Concentration of ammonium acetate-extractable calcium with time of incubation for alternate flooded and moist soils containing urea*

Time (weeks)	Soil	
	Macmerry	Giffnock
	Extractable Ca (μg/g soil)	
0	1150 ± 0	750 ± 0
4	1787 ± 12	950 ± 25
8	2075 ± 25	1112 ± 12
12	960 ± 35	517 ± 17
16	788 ± 0	475 ± 0

* mean of duplicate samples

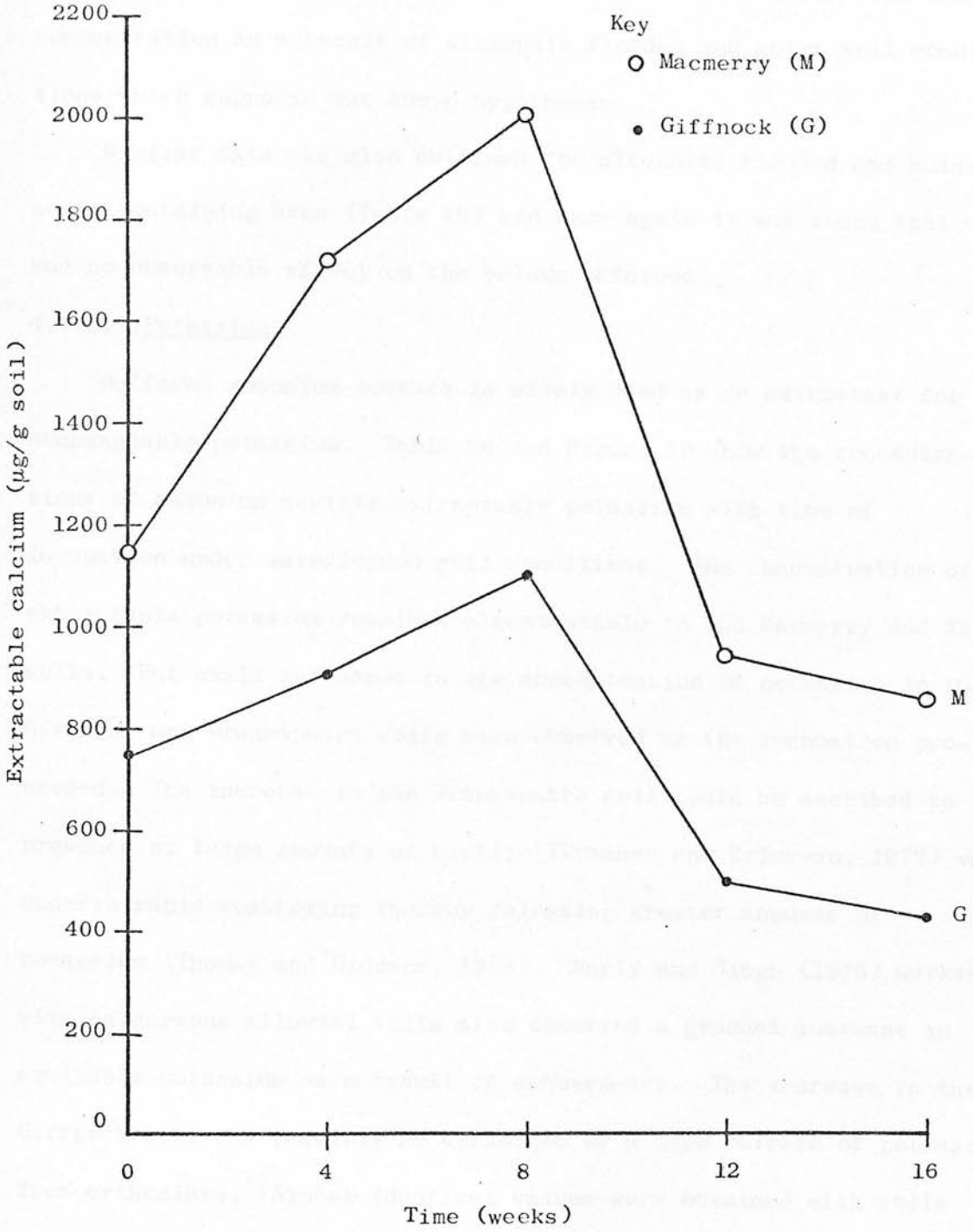

Figure 9. Plot of extractable calcium against time of incubation for alternate flooded and moist soils

calcium in the extractable form could be occluded by the ferric hydroxide resulting from frequent reprecipitation as a consequence of alternate flooded and moist soil conditions. As is evident from the Table 11 that there was a dramatic decrease in the extractable iron concentration as a result of alternate flooded and moist soil conditions which supports the above hypothesis.

Similar data was also obtained for alternate flooded and moist soils containing urea (Table 19) and once again it was found that urea has no observable effect on the values obtained.

4.1.6. Potassium

Buffered ammonium-acetate is widely used as an extractant for exchangeable potassium. Table 20 and Figure 10 show the concentrations of ammonium acetate-extractable potassium with time of incubation under waterlogged soil conditions. The concentration of extractable potassium remained almost stable in the Macmerry and Tista soils. But small increases in the concentration of potassium in the Giffnock and Brahmaputra soils were observed as the incubation proceeded. The increase in the Brahmaputra soil could be ascribed to the presence of large amounts of biotite (Brammer and Brinkman, 1977) which undergo rapid weathering thereby releasing greater amounts of potassium (Thomas and Giddens, 1958). Murty and Singh (1975) working with calcareous alluvial soils also observed a gradual increase in available potassium as a result of submergence. The increase in the Giffnock soil can possibly be explained by a slow release of potassium from orthoclase. Almost identical values were obtained with soils when urea was applied (Table 21).

The data presented in Table 22 and in Figure 11 show the concentration of extractable potassium with time of incubation for alternate

Table 20. Concentration of ammonium-acetate-extractable potassium with time of incubation for waterlogged soils*

Time (weeks)	Soil			
	Macmerry	Giffnock	Tista	Brahmaputra
	Extractable K (μg/g soil)			
0	62 ± 0	32 ± 0	44 ± 0	77 ± 2
4	59 ± 1	31 ± 4	48 ± 4	85 ± 0
8	52 ± 0	36 ± 2	51 ± 5	88 ± 0
12	62 ± 0	42 ± 1	47 ± 3	88 ± 0
16	58 ± 0	47 ± 1	44 ± 4	88 ± 0

* mean of duplicate samples

Table 21. Concentration of ammonium-acetate-extractable potassium with time of incubation for waterlogged soils containing urea*

Time (weeks)	Soil			
	Macmerry	Giffnock	Tista	Brahmaputra
	Extractable K (μg/g soil)			
0	62 ± 0	32 ± 0	44 ± 0	77 ± 2
4	56 ± 3	31 ± 4	42 ± 0	80 ± 0
8	56 ± 0	33 ± 0	49 ± 5	85 ± 0
12	44 ± 3	33 ± 0	46 ± 2	88 ± 0
16	52 ± 1	44 ± 1	46 ± 2	90 ± 3

* mean of duplicate samples

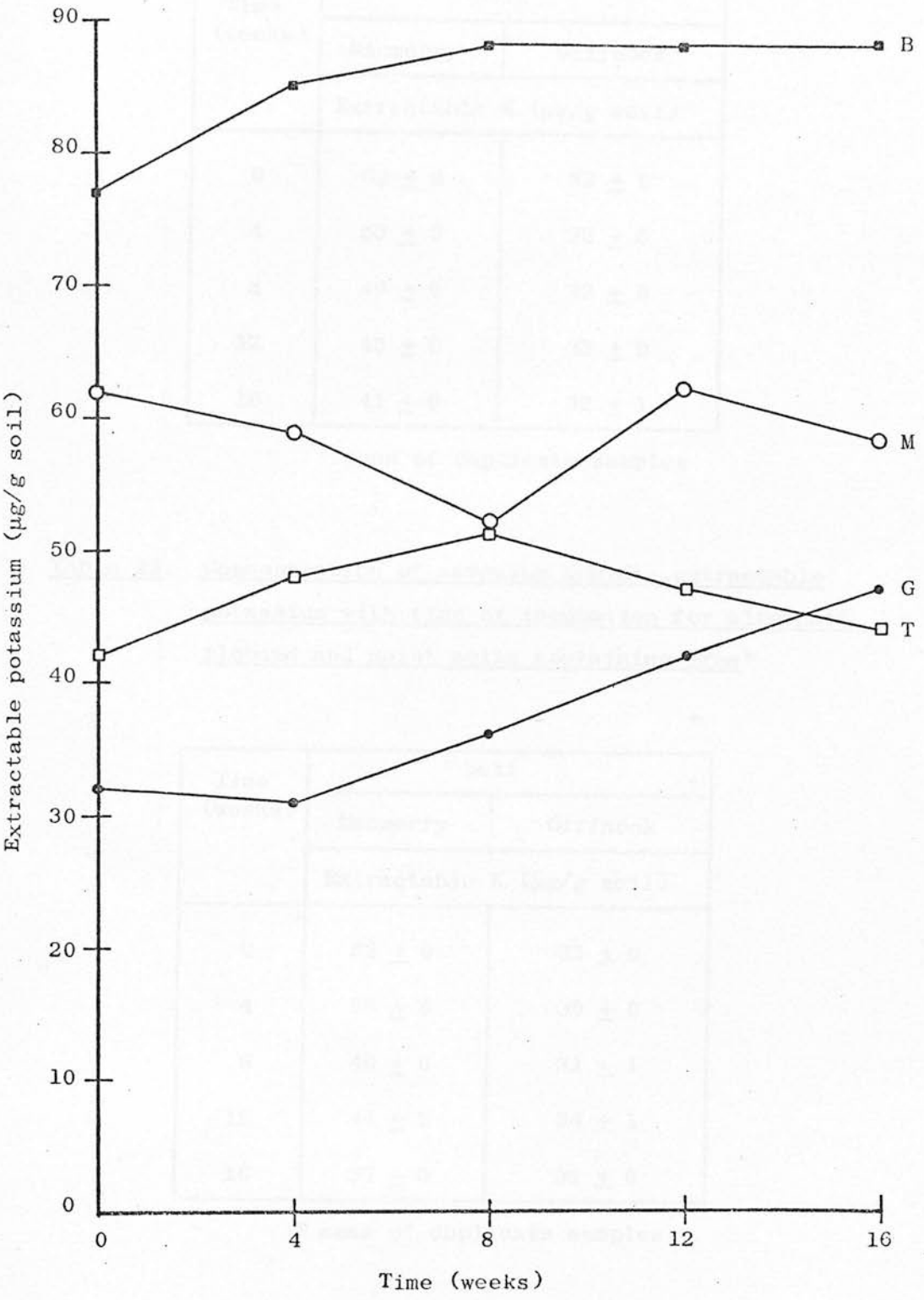

Figure 10. Plot of extractable potassium against time of incubation for waterlogged soils

Table 22. Concentration of ammonium acetate-extractable potassium with time of incubation for alternate flooded and moist soils*

Time (weeks)	Soil	
	Macmerry	Giffnock
	Extractable K (μg/g soil)	
0	62 ± 0	32 ± 0
4	53 ± 0	32 ± 0
8	49 ± 0	32 ± 0
12	45 ± 0	33 ± 0
16	41 ± 0	32 ± 1

* mean of duplicate samples

Table 23. Concentration of ammonium acetate-extractable potassium with time of incubation for alternate flooded and moist soils containing urea*

Time (weeks)	Soil	
	Macmerry	Giffnock
	Extractable K (μg/g soil)	
0	62 ± 0	32 ± 0
4	53 ± 0	30 ± 0
8	49 ± 0	31 ± 1
12	44 ± 2	34 ± 1
16	37 ± 0	32 ± 0

* mean of duplicate samples

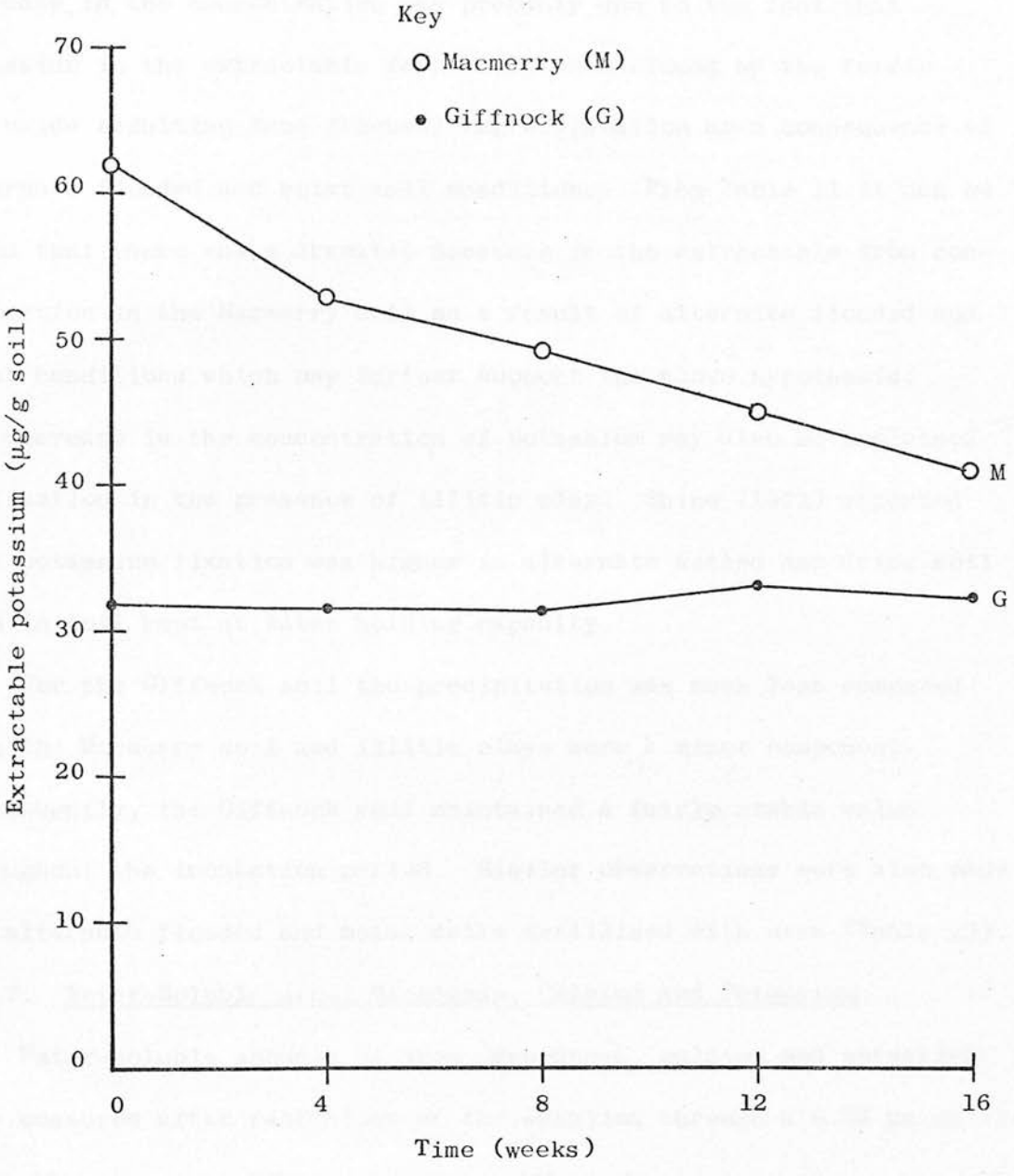

Figure 11. Plot of extractable potassium against time of incubation for alternate flooded and moist soils

flooded and moist soils. For the Macmerry soil the concentration of potassium decreased consistently with time of incubation. The decrease in the concentration was probably due to the fact that potassium in the extractable form could be occluded by the ferric hydroxide resulting from frequent reprecipitation as a consequence of alternate flooded and moist soil conditions. From Table 11 it can be noted that there was a dramatic decrease in the extractable iron concentration in the Macmerry soil as a result of alternate flooded and moist conditions which may further support the above hypothesis. The decrease in the concentration of potassium may also be explained by fixation in the presence of illitic clay. Shine (1971) reported that potassium fixation was higher in alternate wetted and dried soil than in soil kept at water holding capacity.

For the Giffnock soil the precipitation was much less compared with the Macmerry soil and illitic clays were a minor component. Consequently, the Giffnock soil maintained a fairly stable value throughout the incubation period. Similar observations were also made for alternate flooded and moist soils fertilised with urea (Table 23).

4.1.7. Water-Soluble Iron, Manganese, Calcium and Potassium

Water-soluble amounts of iron, manganese, calcium and potassium were measured after filtration of the solution through a 0.22 μm millipore filter paper. Without adequate filtration to amounts of iron measured in solution were anomalously high, due to the presence of colloidal material in suspension .

4.1.7.1. Iron

Data reported in Table 24 show the amount of water-soluble iron in incubated waterlogged soils. The concentration of water-soluble iron increased with time of incubation in all four soils under study.

Table 24. Concentration of water-soluble iron with time of incubation for waterlogged soils*

Time (weeks)	Soil			
	Macmerry	Giffnock	Tista	Brahmaputra
	Water-soluble Fe (μg/g soil)			
0	1.3 ± 0.2	2.8 ± 0.2	20.0 ± 0.0	0.3 ± 0.0
4	180 ± 36	132 ± 16	27 ± 12	0.4 ± 0.0
8	21 ± 1	92 ± 0	1.2 ± 0.1	1.5 ± 0.1
12	85 ± 25	25 ± 3	0.3 ± 0.1	n.d.
16	82 ± 2	23.5 ± 3.5	1.9 ± 0.1	n.d.

* mean of duplicate samples

n.d. = not detectable

Table 25. Concentration of water-soluble manganese with time of incubation for waterlogged soils*

Time (weeks)	Soil			
	Macmerry	Giffnock	Tista	Brahmaputra
	Water-soluble Mn (μg/g soil)			
0	0.1 ± 0.0	0.2 ± 0.0	0.4 ± 0.0	n.d.
4	35.5 ± 1.5	2.7 ± 0.3	18.0 ± 0.5	2.1 ± 0.1
8	28.5 ± 0.5	1.9 ± 0.0	11.8 ± 0.7	2.4 ± 0.0
12	25.5 ± 2.5	1.2 ± 0.0	10.5 ± 0.0	1.3 ± 0.0
16	24.8 ± 0.8	1.0 ± 0.1	6.5 ± 0.0	1.0 ± 0.1

* mean of duplicate samples

n.d. = not detectable

In the Macmerry, Giffnock and Tista soils the concentration reached peak values after four weeks of incubation, while in the Brahmaputra soil, a peak value was observed after 8 weeks. In the Macmerry and Giffnock soils the increases in iron concentration were substantial. For the Macmerry soil the concentration of water-soluble iron decreased at 8 weeks of incubation. This appears to be an abnormal result and the subsequent values are more in line with expected trends. For the Giffnock soil the concentration decreased from 8 weeks onward. In the Tista soil the concentration decreased from 8 to 12 weeks and again increased at 16 week measurement. It is difficult to understand the reason for the last increase. For the Brahmaputra soil there was no detectable iron in solution from 12 weeks onward.

As a result of waterlogging, the maximum release of water-soluble iron was 7.6, 4.2, 0.8 and 0.3% of the corresponding ammonium acetate-extractable values (Table 7) for the Giffnock, Macmerry, Tista and Brahmaputra soils, respectively (these figures were based on observed peak values). It appears from the results that waterlogging significantly increases the concentration of iron in the solution in both Macmerry and Giffnock soils. For the Tista and Brahmaputra soils the release of iron was very small compared with the other two soils. However, for all four soils the proportion released in the solution was small compared to the ammonium acetate-extractable values.

Ponnamperuma (1977b) observed that when an acid soil (pH 4.6) is waterlogged its Fe^{3+} compounds are directly or indirectly reduced to Fe^{2+} by microorganisms thus bringing a considerable amount (upto 600 ppm) of iron into solution. A proportion of this value may have resulted from colloidal material in suspension, if the solutions were not filtered properly. However, such an increase probably depends on

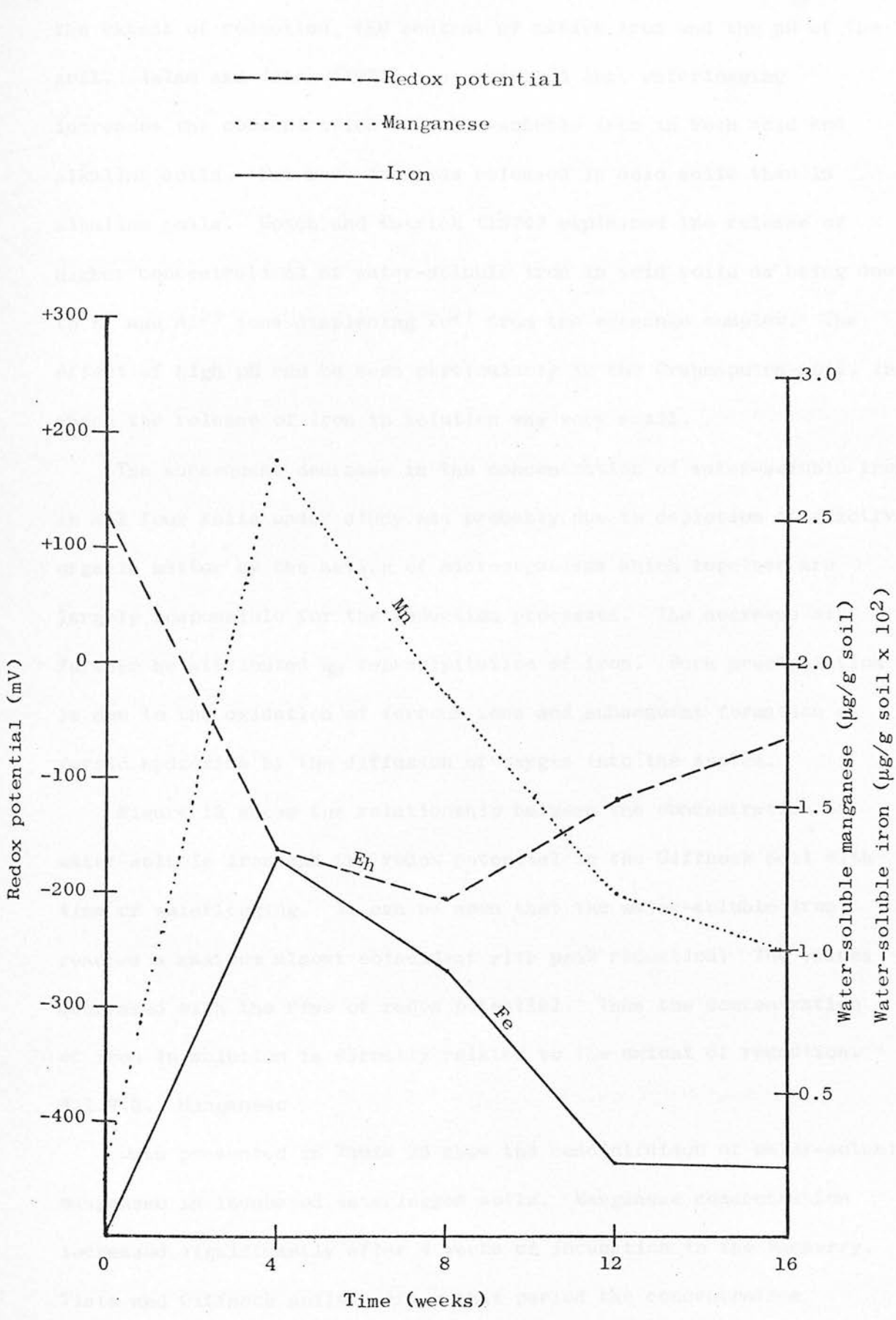

Figure 12. Plot of water-soluble iron, manganese and redox potential against time of incubation for waterlogged Giffnock soil

the extent of reduction, the content of native iron and the pH of the soil. Islam and Islam (1973) also reported that waterlogging increases the concentration of water-soluble iron in both acid and alkaline soils. But more iron was released in acid soils than in alkaline soils. Gotoh and Patrick (1974) explained the release of higher concentrations of water-soluble iron in acid soils as being due to H^+ and Al^{3+} ions displacing Fe^{2+} from the exchange complex. The effect of high pH can be seen particularly in the Brahmaputra soil, in which the release of iron in solution was very small.

The subsequent decrease in the concentration of water-soluble iron in all four soils under study was probably due to depletion of reactive organic matter by the action of microorganisms which together are largely responsible for the reduction processes. The decrease may further be attributed to reprecipitation of iron. Such precipitation is due to the oxidation of ferrous ions and subsequent formation of ferric hydroxide by the diffusion of oxygen into the system.

Figure 12 shows the relationship between the concentration of water-soluble iron and the redox potential in the Giffnock soil with time of waterlogging. It can be seen that the water-soluble iron reaches a maximum almost coincident with peak reduction. The values decreased with the rise of redox potential. Thus the concentration of iron in solution is directly related to the extent of reduction.

4.1.7.2. Manganese

Data presented in Table 25 show the concentration of water-soluble manganese in incubated waterlogged soils. Manganese concentration increased significantly after 4 weeks of incubation in the Macmerry, Tista and Giffnock soils. After that period the concentration decreased consistently but marginally for the duration of the

experiment. The peak value for the Brahmaputra soil reached at 8 weeks of incubation followed by a decrease. Islam and Islam (1973) also observed that the manganese concentration in soil solution increased with time of submergence. The increase in the concentration of manganese in a waterlogged soil is due to the reduction of oxides of manganese (Ponnamperuma, 1977a), and the amounts to be released in the solution may largely depend on the extent of reduction and on the native manganese content. The release of manganese in the solution precedes that of ferrous because oxides of manganese are reduced more readily than ferric oxides and conversely manganese is less readily oxidised (Tables 24 and 25).

The concentration of water-soluble manganese in the Brahmaputra soil was low probably due tc the fact that the soil remained only moderately reduced (Table 3) throughout the incubation period. The low concentration can also be attributed to its high pH and low organic matter content.

The significantly higher concentration of manganese released in the Macmerry, Giffnock and Tista soils results from the highly reduced (Table 3) conditions and lower pH values found in these soils. For the Macmerry and Tista soils the high values may also be explained by their high 'free' manganese content (Table 2).

As a result of waterlogging, the maximum release of manganese in the solution was 12.8, 10.0, 8.6 and 1.2% of the corresponding ammonium acetate-extractable values (Table 12) for the Macmerry, Giffnock, Tista and Brahmaputra soils, respectively (these figures were based on observed peak values). The results show that the proportion of manganese released in the solution was more than that of iron. However, the proportion found in soil solution was small

compared to the ammonium-acetate extractable manganese values.

Figure 12 shows the relationship between the concentration of water-soluble manganese and the redox potential in the Giffnock soil with time of waterlogging. Again the soil solution concentration of manganese was greatest, reduction was greatest and decreases as the redox potential rises. However, compared with the iron, a substantial proportion remained in solution confirming that manganese is more readily reduced and more able to persist in the reduced state.

4.1.7.3. Calcium

Data reported in Table 26 show the concentration of water-soluble calcium in incubated waterlogged soils. Very substantial increases were observed and values reached a peak after four weeks of incubation in all four soils under study.

The increase in the concentration of water-soluble calcium for the Macmerry, Giffnock and Tista soils may be attributed to the fact that as a result of waterlogging, due to the reduction processes, the concentration of Fe^{2+} and Mn^{2+} had increased in the solution (Tables 24 and 25). These ions preferentially replace other cations such as Ca^{2+} and K^{+} from their exchange sites. As a result of this exchange Ca^{2+} and K^{+} are released into the soil solution. The subsequent decrease in the concentration of calcium for the Macmerry, Giffnock and Tista soils was probably due to reprecipitation of iron and manganese in the system resulting in the movement of less iron and manganese away from exchange sites. Then calcium in solution would revert back to the original exchange sites leading to a decrease in the solution concentration of calcium. For the Macmerry soil a second increase (Table 26) was noted at the 12 week period. This rise and fall was probably correlated to the iron concentration (Table 24)

Table 26. Concentration of water-soluble calcium with time of incubation for waterlogged soils*

Time (weeks)	Soil			
	Macmerry	Giffnock	Tista	Brahmaputra
	Water-soluble Ca (μg/g soil)			
0	15.0 ± 2.0	12.0 ± 1.0	2.8 ± 0.2	43.0 ± 1.0
4	395 ± 5	131 ± 1	157 ± 1	123 ± 1
8	290 ± 0	86 ± 0	114 ± 0	101 ± 1
12	325 ± 15	63 ± 1	106 ± 2	91 ± 1
16	288 ± 12	47 ± 1	80 ± 0	81 ± 1

* mean of duplicate samples

Table 27. Concentration of water-soluble potassium with time of incubation for waterlogged soils*

Time (weeks)	Soil			
	Macmerry	Giffnock	Tista	Brahmaputra
	Water-soluble K (μg/g soil)			
0	2.4 ± 0.0	3.0 ± 0.0	4.2 ± 0.4	7.0 ± 0.0
4	9.5 ± 0.1	5.1 ± 0.5	5.1 ± 0.1	11.4 ± 0.2
8	9.4 ± 0.0	4.4 ± 0.0	4.4 ± 0.0	10.8 ± 0.0
12	9.5 ± 0.5	4.2 ± 0.2	3.6 ± 0.0	11.6 ± 0.0
16	7.9 ± 0.3	4.0 ± 0.0	3.4 ± 0.2	12.4 ± 0.4

* mean of duplicate samples

in the solution.

The increase in the concentration of water-soluble calcium for the Brahmaputra soil can probably be attributed, in part, to the formation of calcium bicarbonate which is formed as a result of the following reaction:-

$$CaCO_3 + H_2O \overset{CO_2}{\rightleftharpoons} Ca(HCO_3)_2$$

The subsequent decrease in the concentration of calcium may be explained by the fact that the reduced activity of microorganisms with time of waterlogging results in a decrease in carbondioxide production which would probably shift the equilibrium towards the less soluble $CaCO_3$.

As a result of waterlogging, the maximum release of calcium in the solution was 24.3, 14.2, 12.8 and 7.6% of the corresponding ammonium acetate-extractable values (Table 16) for the Macmerry, Giffnock, Tista and Brahmaputra soils, respectively (these figures were based on observed peak values). This represents a substantial amount of calcium in the solution as compared with the fresh, aerobic soil. The results indicate that when more iron and manganese were reduced, large amounts of calcium can be displaced from the exchange sites. It is apparent from the data that the Brahmaputra soil had a low concentration of iron and manganese in the solution. Therefore, it is expected, a relatively lower percentage of calcium in the solution compared with the other three soils.

The increase in the solution concentration of calcium, as a result of waterlogging, may be beneficial for the growth of plants.

4.1.7.4. Potassium

Data presented in Table 27 show the amount of water-soluble potassium in incubated waterlogged soils. The concentration of potassium substantially increased upto four weeks of waterlogging in the Macmerry, Giffnock and Tista soils, while in the Brahmaputra soil it increases throughout the experimental period.

The increase in the concentration of water-soluble potassium for the Macmerry, Giffnock and Tista soils can be attributed to the fact that as a result of waterlogging both iron and manganese came into solution (Tables 24 and 25). The iron and manganese cations replace other cations such as K^+, Ca^{2+} and Mg^{2+} from the exchange sites. As a result of these ion-exchange reactions, an increase in the solution concentration of potassium is observed. The increase for the Brahmaputra soil may also be partly due to weatherable minerals, especially biotite (Brammer and Brinkman, 1977). Clark and Resnicky (1956) stated that as a result of cation exchange reactions, potassium ions may be displaced from the clay complex and its concentration in the solution can be almost doubled. Increases of this order were also observed in several other waterlogged soils (IRRI, 1963).

The increased values remained more or less stable throughout the incubation period. As a result of waterlogging, the maximum release of potassium in the soil solution was 15.3, 14.1, 10.9 and 10.0% of the corresponding ammonium-acetate extractable values (Table 20) for the Macmerry, Brahmaputra, Giffnock and Tista soils, respectively (these figures were based on observed peak values). With the exception of the Brahmaputra soil, the proportion of potassium displaced is slightly higher than calcium in the Macmerry, Giffnock and Tista soils.

Potassium is an essential major plant nutrient; a significant increase in its concentration is probably one of the beneficial effects of waterlogging for the nutrition of crops grown under submerged conditions.

4.1.8. Specific Conductance

The specific conductance values for the incubated waterlogged Macmerry and Giffnock soils measured every day for 112 days with and without urea are reported in Appendix, Table A5. Results for the Tista and Brahmaputra soils measured every 7 days for 112 days with and without urea are presented in Appendix, Table A6. After each four week period of measurement duplicate samples of soils were finally withdrawn from the incubator for other determinations and measurements were continued on previously unopened samples.

Abbreviated data obtained at zero, 29, 57 and 85 days of incubation for the Macmerry and Giffnock soils with and without urea are shown in Table 28 and in Figure 13. Initially the values increased very rapidly and remained almost stable from 29 days onward. However, the peak values were attained after 29 days of incubation in both Macmerry and Giffnock soils.

Abbreviated data obtained at zero, 35, 63 and 91 days of incubation for the Tista and Brahmaputra soils with and without urea is reported in Table 29 and in Figure 14. The data indicate that there was a substantial increase in the specific conductance in both Tista and Brahmaputra soils with time. The values remained more or less stable from 35 days onward. However, the peak values were attained after 63 and 91 days of incubation in the Tista and Brahmaputra soils, respectively where no urea was added.

The increase in specific conductance can be attributed mainly to

Table 28. Effect of waterlogging on specific conductance of soils incubated with and without urea as a function of time*

Time (days)	Soil			
	Macmerry		Giffnock	
	Without urea	With urea	Without urea	With urea
	Specific conductance (μ mhos/cm)			
0	70 ± 0	76 ± 0	70 ± 0	67 ± 0
29	1850 ± 0	1762 ± 0	674 ± 31	682 ± 3
57	1850 ± 0	1762 ± 0	642 ± 30	602 ± 70
85	1749 ± 20	1843 ± 2	436 ± 1	552 ± 16

* mean of duplicate samples

Table 29. Effect of waterlogging on specific conductance of soils incubated with and without urea as a function of time*

Time (days)	Soil			
	Tista		Brahmaputra	
	Without urea	With urea	Without urea	With urea
	Specific conductance (μ mhos/cm)			
0	173 ± 0	155 ± 13	269 ± 3	288 ± 1
35	1175 ± 19	1194 ± 19	676 ± 3	747 ± 0
63	1189 ± 5	1276 ± 11	673 ± 12	903 ± 11
91	1117 ± 4	1208 ± 5	679 ± 6	788 ± 25

* mean of duplicate samples

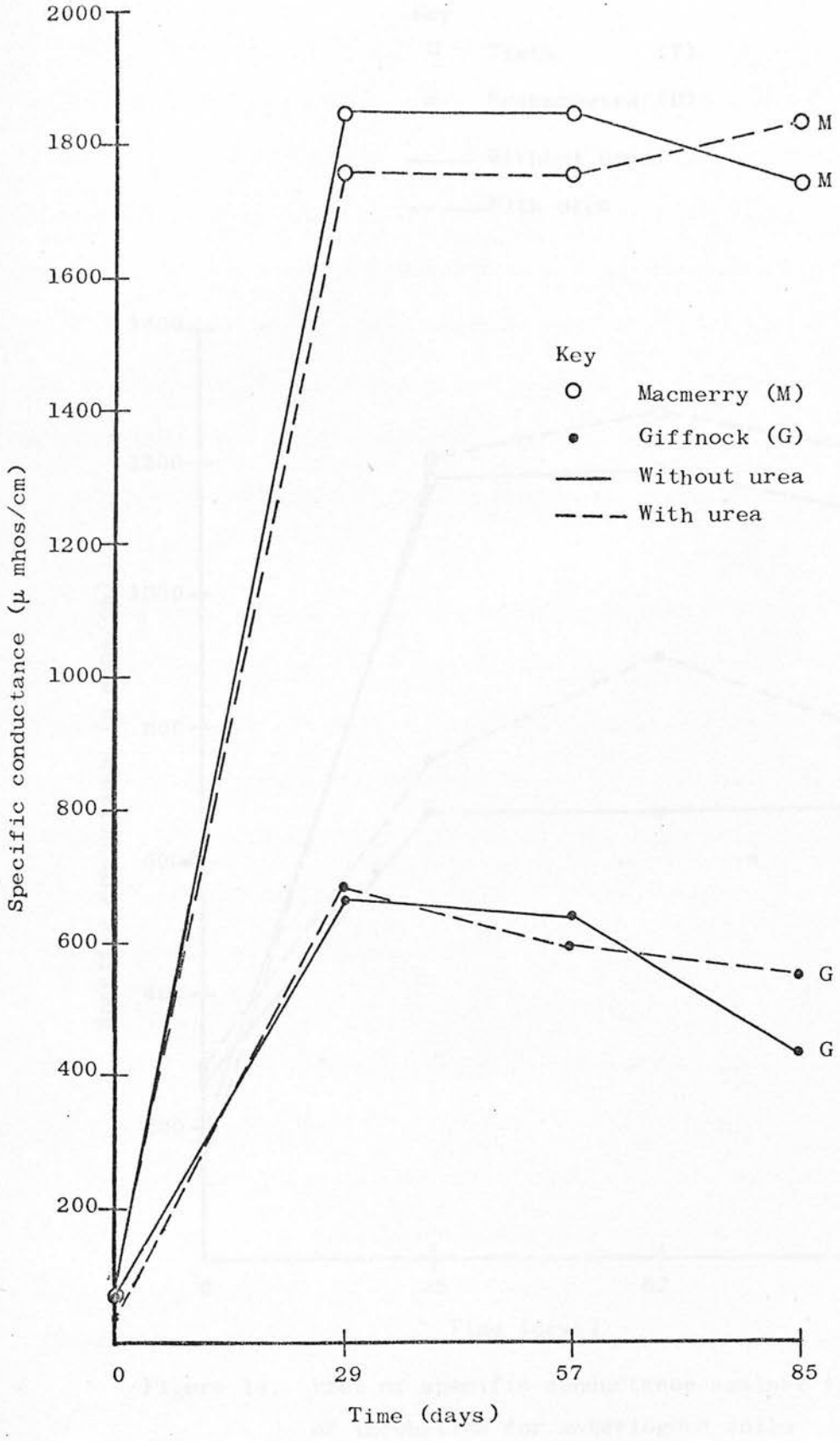

Figure 13. Plot of specific conductance against time of incubation for waterlogged soils

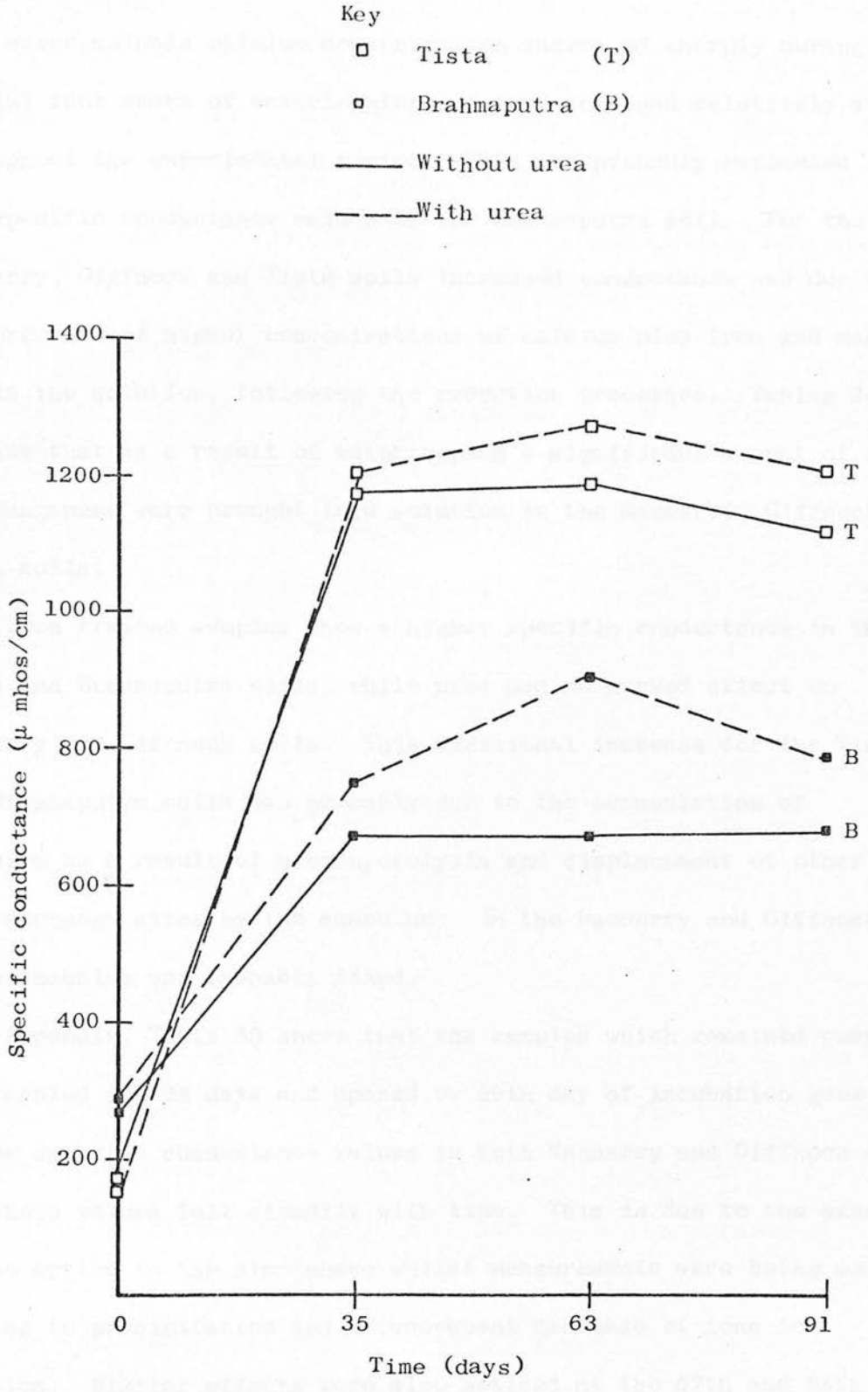

Figure 14. Plot of specific conductance against time of incubation for waterlogged soils

the mobilisation of calcium in the Brahmaputra soil which is supported by the water-soluble values of calcium (Table 26). The data show that water-soluble calcium concentration increased sharply during the initial four weeks of waterlogging and then remained relatively stable throughout the experimental period. This was probably reflected in the specific conductance values of the Brahmaputra soil. For the Macmerry, Giffnock and Tista soils increased conductance was due to the presence of higher concentrations of calcium plus iron and manganese in the solution, following the reduction processes. Tables 24 and 25 show that as a result of waterlogging a significant amount of iron and manganese were brought into solution in the Macmerry, Giffnock and Tista soils.

Urea treated samples show a higher specific conductance in the Tista and Brahmaputra soils, while urea had no marked effect on Macmerry and Giffnock soils. This additional increase for the Tista and Brahmaputra soils was probably due to the accumulation of ammonium as a result of urea hydrolysis and displacement of other ions from exchange sites by the ammonium. In the Macmerry and Giffnock soils ammonium was probably fixed.

Appendix, Table A5 shows that the samples which remained completely sealed for 28 days and opened on 29th day of incubation gave much higher specific conductance values in both Macmerry and Giffnock soils. But these values fall steadily with time. This is due to the exposure of the system to the atmosphere whilst measurements were being made leading to precipitation and a consequent decrease of ions in solution. Similar effects were also noticed at the 57th and 85th day of incubation. The Tista and Brahmaputra soils exhibited the same behaviour at the 5th, 9th and 13th week of incubation (Appendix,

Table A6).

It can, therefore, be concluded that waterlogging causes substantial increases in the specific conductance and the peak values are reached after about four weeks of incubation followed by a slight decrease. However, when the samples were completely sealed throughout, the values remained fairly stable. Urea application had increased the specific conductance in the Tista and Brahmaputra soils over the soils where no urea was added.

Figure 15 shows the specific conductance, and water-soluble iron, manganese, calcium and potassium plotted against time of incubation for waterlogged Giffnock soil. It is evident from the figure that maximum specific conductance values were related to maximum release of iron, manganese, calcium and potassium. Likewise a decrease in concentration of iron, manganese, calcium and potassium was reflected in decreasing values of specific conductance. Therefore, as would be expected, there is a direct relationship between specific conductance and concentration of iron, manganese, calcium and potassium in the solution.

4.1.9. Phosphate

Increases in the availability of soil phosphate due to waterlogging have been reported by several workers (Islam and Elahi, 1954; Shapiro, 1958a; Patrick and Mahapatra, 1968; Ponnamperuma, 1972). Phosphate associated with ferric iron and aluminum predominates in acid soils, whereas calcium phosphates predominate in neutral and alkaline soils (Jackson, 1964). Iron and aluminum phosphates tend to release phosphate as the soil pH increases while calcium phosphates liberate phosphate as the pH decreases (Stumm and Morgan, 1970).

Thus the release of phosphate in flooded soils may be explained

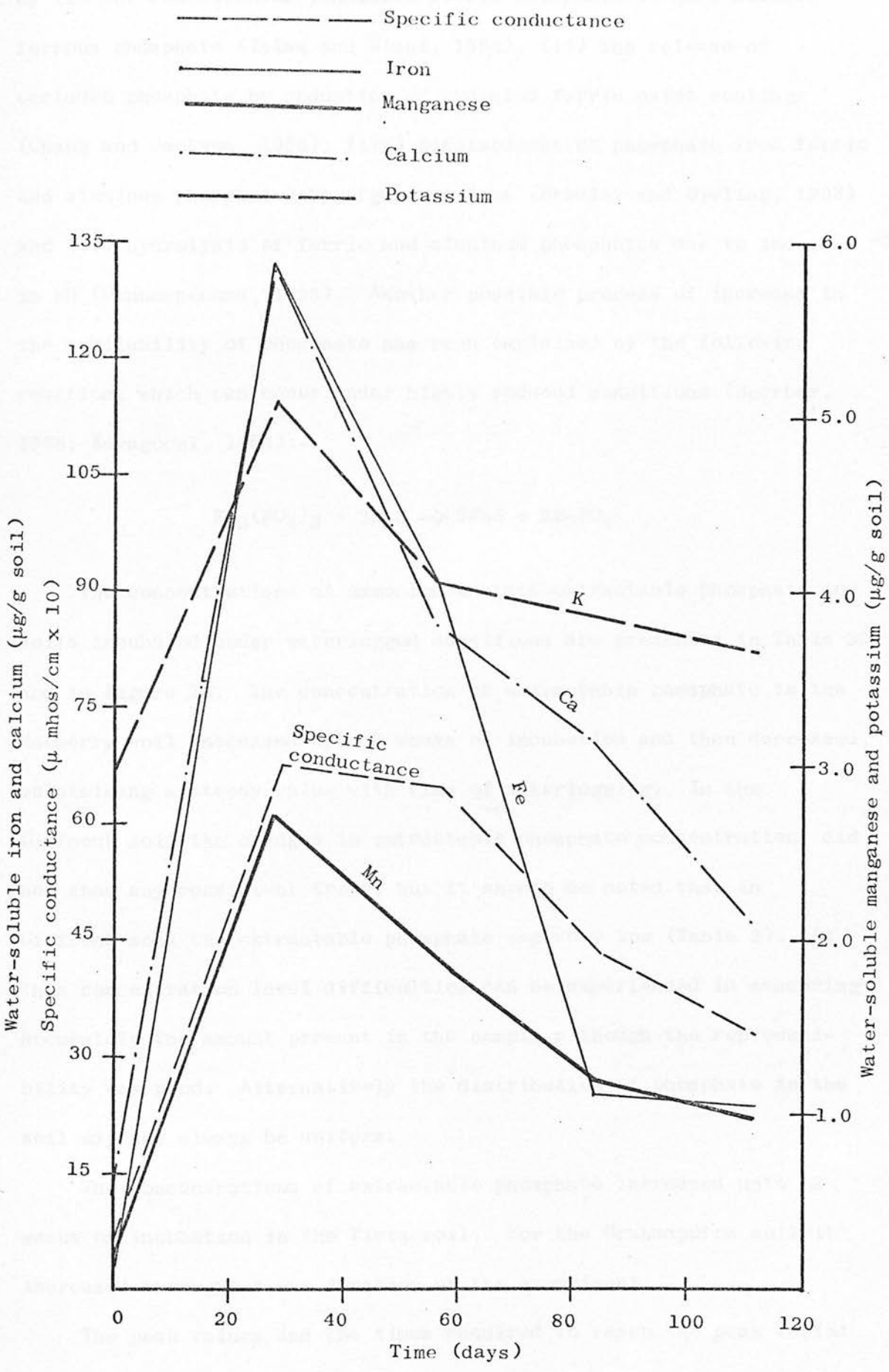

Figure 15. Plot of specific conductance, and water-soluble Fe, Mn, Ca and K against time of incubation for waterlogged Giffnock soil

by (i) the reduction of insoluble ferric phosphate to more soluble ferrous phosphate (Islam and Elahi, 1954), (ii) the release of occluded phosphate by reduction of hydrated ferric oxide coatings (Chang and Jackson, 1958), (iii) displacement of phosphate from ferric and aluminum phosphates by organic anions (Bradley and Sieling, 1953) and (iv) hydrolysis of ferric and aluminum phosphates due to increase in pH (Ponnamperuma, 1955). Another possible process of increase in the availability of phosphate has been explained by the following reaction, which can occur under highly reduced conditions (Sperber, 1958; Kawaguchi, 1965):-

$$Fe_3(PO_4)_2 + 3H_2S \rightarrow 3FeS + 2H_3PO_4$$

The concentrations of ammonium acetate-extractable phosphate in soils incubated under waterlogged conditions are presented in Table 30 and in Figure 16. The concentration of extractable phosphate in the Macmerry soil increased upto 8 weeks of incubation and then decreased, maintaining a steady value with time of waterlogging. In the Giffnock soil the changes in extractable phosphate concentrations did not show any consistent trend, but it should be noted that in Giffnock soil the extractable phosphate was very low (Table 2). At this concentration level difficulties can be experienced in measuring accurately the amount present in the sample although the reproducibility was good. Alternatively the distribution of phosphate in the soil may not always be uniform.

The concentrations of extractable phosphate increased upto 12 weeks of incubation in the Tista soil. For the Brahmaputra soil it increased throughout the duration of the experiment.

The peak values and the times required to reach the peak varied

Table 30. Concentration of ammonium acetate-extractable phosphate with time of incubation for waterlogged soils*

Weeks	Soil			
	Macmerry	Giffnock	Tista	Brahmaputra
	Extractable P (μg/g soil)			
0	2.0 ± 0.0	0.5 ± 0.0	1.8 ± 0.1	3.0 ± 0.3
4	3.3 ± 0.1	1.1 ± 0.1	9.8 ± 0.4	3.6 ± 0.1
8	4.2 ± 0.0	0.7 ± 0.1	11.5 ± 0.4	4.9 ± 0.1
12	3.9 ± 0.0	1.6 ± 0.2	14.2 ± 0.1	8.6 ± 0.2
16	3.9 ± 0.8	0.8 ± 0.3	10.7 ± 0.5	10.2 ± 0.5

* mean of duplicate samples

Table 31. Concentration of ammonium acetate-extractable phosphate with time of incubation for waterlogged soils containing urea*

Weeks	Soil			
	Macmerry	Giffnock	Tista	Brahmaputra
	Extractable P (μg/g soil)			
0	2.0 ± 0.0	0.5 ± 0.0	1.8 ± 0.1	3.0 ± 0.3
4	3.0 ± 0.0	0.8 ± 0.1	12.7 ± 0.1	3.6 ± 0.1
8	5.2 ± 0.1	0.7 ± 0.1	11.7 ± 1.7	4.1 ± 0.5
12	5.0 ± 0.3	0.7 ± 0.1	10.1 ± 0.4	6.7 ± 0.2
16	3.9 ± 0.3	0.6 ± 0.0	10.1 ± 1.9	8.8 ± 0.7

* mean of duplicate samples

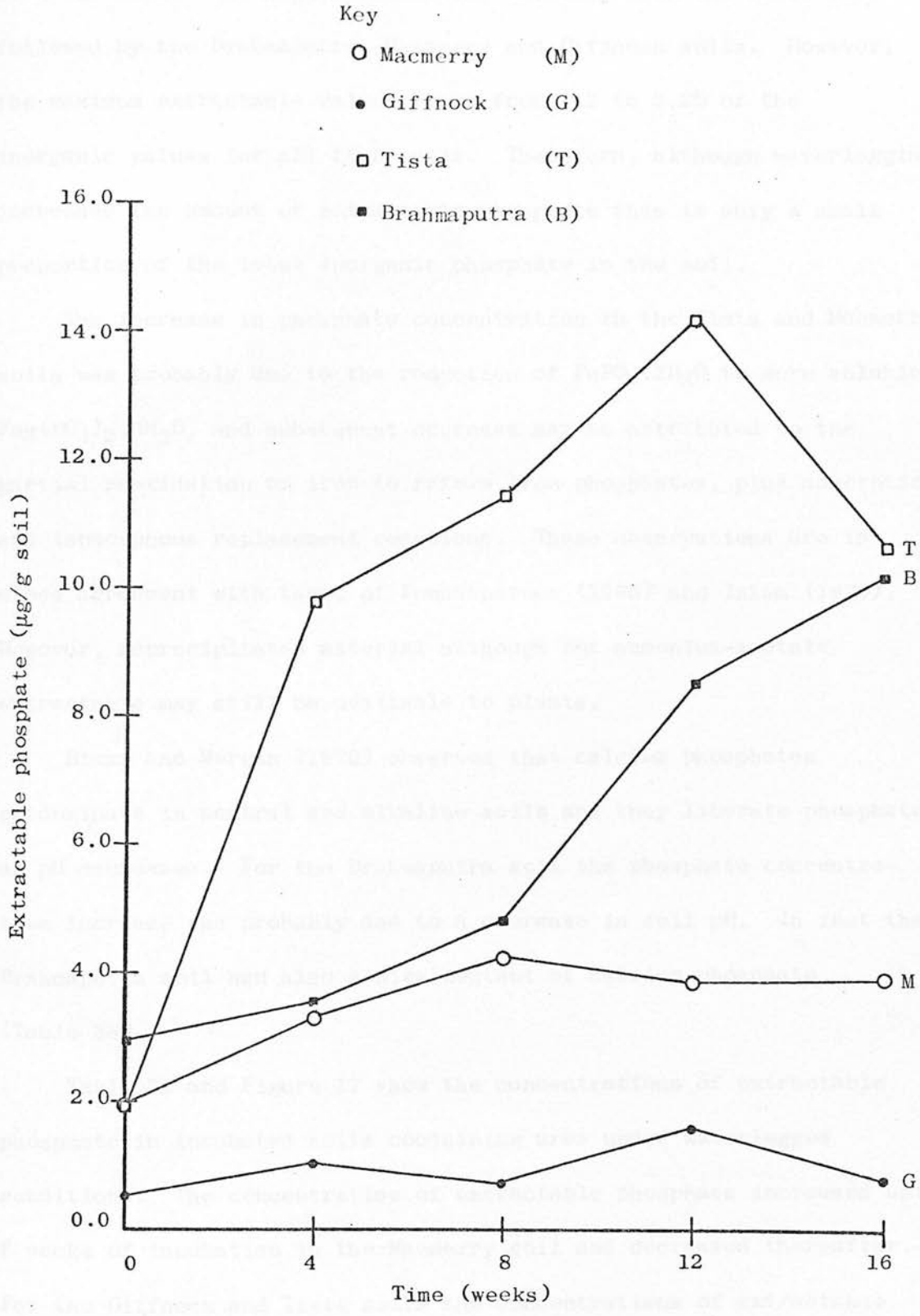

Figure 16. Plot of extractable phosphate against time of incubation for waterlogged soils

with the soil. The highest value was obtained with the Tista soil followed by the Brahmaputra, Macmerry and Giffnock soils. However, the maximum extractable values range from 1.2 to 3.2% of the inorganic values for all four soils. Therefore, although waterlogging increases the amount of extractable phosphate this is only a small proportion of the total inorganic phosphate in the soil.

The increase in phosphate concentration in the Tista and Macmerry soils was probably due to the reduction of $FePO_4.2H_2O$ to more soluble $Fe_3(PO_4)_2.8H_2O$, and subsequent decrease may be attributed to the partial reoxidation of iron to reform iron phosphates, plus adsorption and isomorphous replacement reactions. These observations are in close agreement with those of Ponnamperuma (1965) and Islam (1970). However, reprecipitated material although not ammonium-acetate extractable may still be available to plants.

Stumm and Morgan (1970) observed that calcium phosphates predominate in neutral and alkaline soils and they liberate phosphate as pH decreases. For the Brahmaputra soil the phosphate concentration increase was probably due to a decrease in soil pH. In fact the Brahmaputra soil had also a high content of calcium phosphate (Table 38).

Table 31 and Figure 17 show the concentrations of extractable phosphate in incubated soils containing urea under waterlogged conditions. The concentration of extractable phosphate increased upto 8 weeks of incubation in the Macmerry soil and decreased thereafter. For the Giffnock and Tista soils the concentrations of extractable phosphate increased upto 4 weeks of incubation and then decreased. But in the Brahmaputra soil it increased throughout the incubation period. The data, however, indicate that the application of urea had

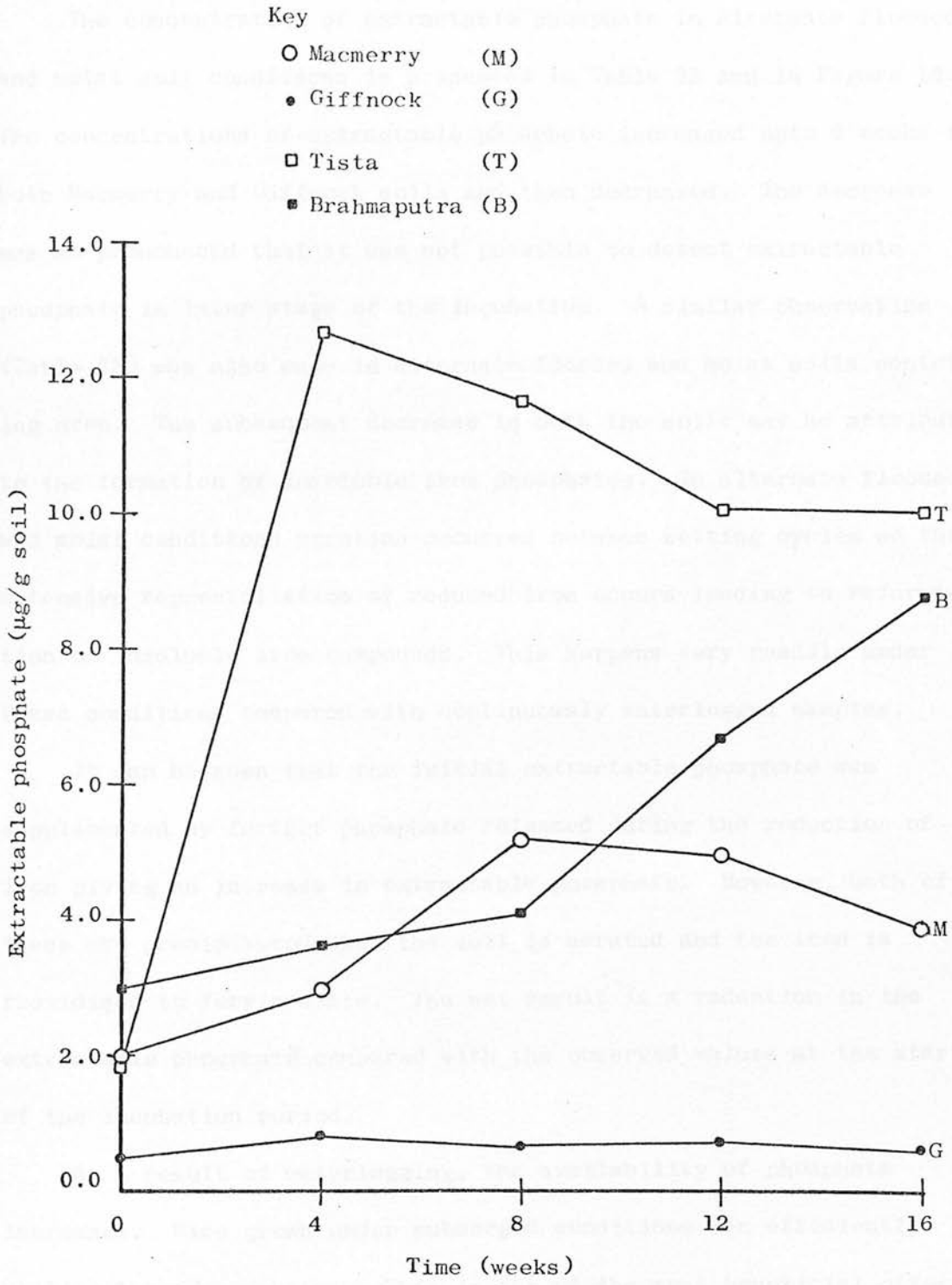

Figure 17. Plot of extractable phosphate against time of incubation for waterlogged soils containing urea

no marked effect on the extractable phosphate values in any of the four soils under study.

The concentration of extractable phosphate in alternate flooded and moist soil conditions is presented in Table 32 and in Figure 18. The concentrations of extractable phosphate increased upto 4 weeks in both Macmerry and Giffnock soils and then decreased. The decrease was so pronounced that it was not possible to detect extractable phosphate in later stage of the incubation. A similar observation (Table 33) was also made in alternate flooded and moist soils containing urea. The subsequent decrease in both the soils may be attributed to the formation of insoluble iron phosphates. In alternate flooded and moist conditions aeration occurred between wetting cycles so that extensive reprecipitation of reduced iron occurs leading to reformation of insoluble iron compounds. This happens very readily under these conditions compared with continuously waterlogged samples.

It can be seen that the initial extractable phosphate was supplemented by further phosphate released during the reduction of iron giving an increase in extractable phosphate. However, both of these are precipitated when the soil is aerated and the iron is reoxidised to ferric state. The net result is a reduction in the extractable phosphate compared with the observed values at the start of the incubation period.

As a result of waterlogging, the availability of phosphate increases. Rice grown under submerged conditions can efficiently utilise these phosphates. This is one of the most beneficial effects of waterlogging.

Table 32. Concentration of ammonium-acetate-extractable phosphate with time of incubation for alternate flooded and moist soils*

Time (weeks)	Soil	
	Macmerry	Giffnock
	Extractable P (μg/g soil)	
0	2.0 ± 0.0	0.5 ± 0.0
4	3.2 ± 0.2	1.1 ± 0.2
8	1.1 ± 0.4	0.2 ± 0.1
12	1.0 ± 0.0	0.3 ± 0.1
16	n.d.	n.d.

* mean of duplicate samples

n.d. = not detectable

Table 33. Concentration of ammonium-acetate-extractable phosphate with time of incubation for alternate flooded and moist soils containing urea*

Time (weeks)	Soil	
	Macmerry	Giffnock
	Extractable P (μg/g soil)	
0	2.0 ± 0.0	0.5 ± 0.0
4	2.6 ± 0.2	1.3 ± 0.1
8	1.2 ± 0.2	0.4 ± 0.1
12	1.0 ± 0.0	0.3 ± 0.0
16	n.d.	n.d.

* mean of duplicate samples

n.d. = not detectable

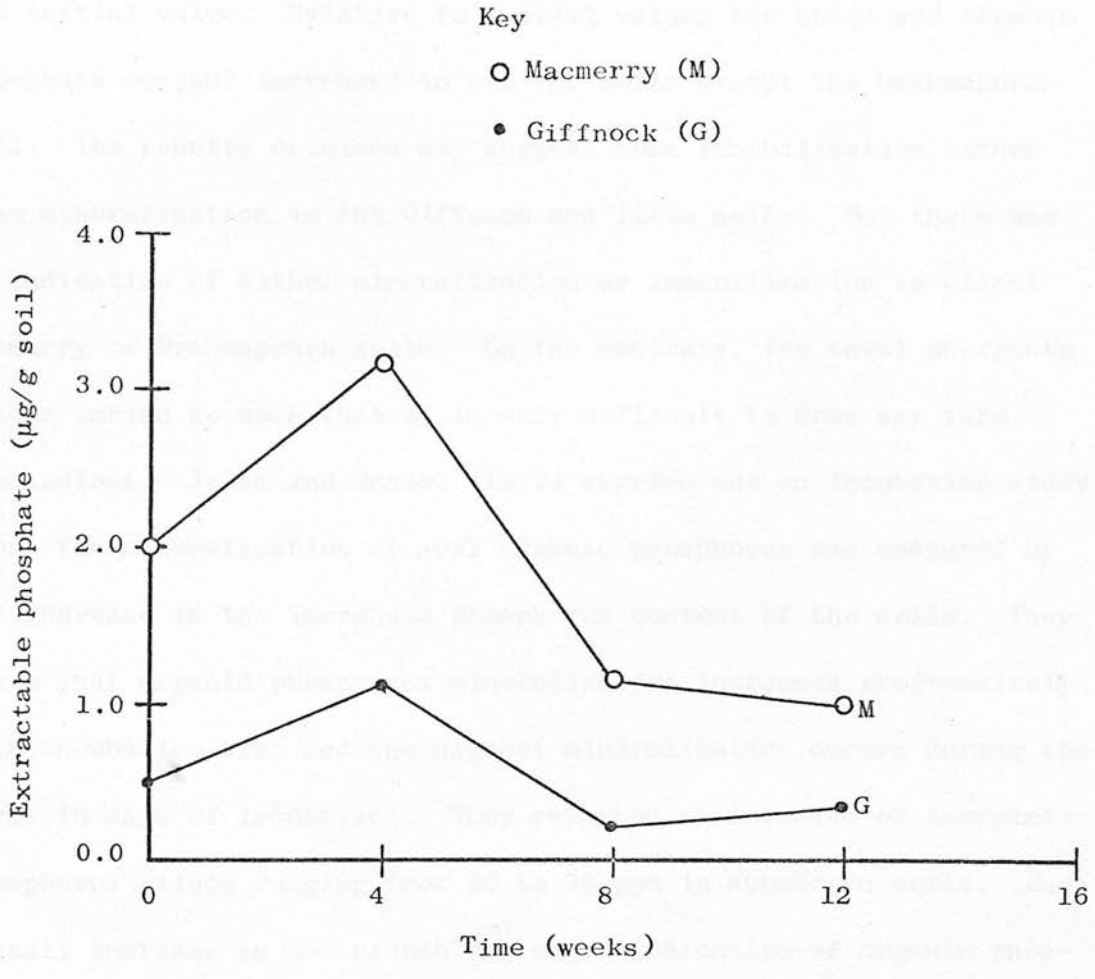

Figure 18. Plot of extractable phosphate against time of incubation for alternate flooded and moist soils

4.1.10. Mineralisation of Soil Phosphorus

Table 34 shows the amounts of inorganic, organic and total phosphate in waterlogged soils incubated for 16 weeks. The values for inorganic phosphate content of Giffnock, Tista and Brahmaputra soils show a decrease while in the Macmerry soil the value increased from the initial value. Relative to initial values the total and organic phosphate content increased in all the soils except the Brahmaputra soil. The results obtained may suggest some immobilisation rather than mineralisation in the Giffnock and Tista soils. But there was no indication of either mineralisation or immobilisation in either Macmerry or Brahmaputra soils. On the contrary, the total phosphate values varied so much that it is very difficult to draw any firm conclusions. Islam and Mandal (1977) carried out an incubation study where the mineralisation of soil organic phosphorus was measured by the increase in the inorganic phosphorus content of the soils. They found that organic phosphorus mineralisation increases progressively with incubation time and the highest mineralisation occurs during the first 15 days of incubation. They reported an increase of inorganic phosphorus values ranging from 20 to 25 ppm in submerged soils. Such a small increase is probably not a clear indication of organic phosphorus mineralisation as it could have resulted from the analytical error. If a small amount of mineralisation does occur during waterlogging, it is difficult to detect with existing analytical techniques. However, mineralisation studies could be more accurately monitored by incorporating labelled phosphorus-32 either into the organic or inorganic phosphorus fractions.

Table 34. Concentration of inorganic, organic and total phosphate content in waterlogged soils incubated for sixteen weeks*

Soil	Inorganic	Organic	Total	Total (original)
	µg P/g soil			
Macmerry	347	424	771	657
Giffnock	46	116	162	142
Tista	399	184	583	532
Brahmaputra	537	50	587	763

* mean of duplicate samples

4.1.11. Isotopically Exchangeable Phosphate and Iron

Isotopically exchangeable material is usually defined as the amount which is held on the surface of soil particles and is in dynamic equilibrium with similar species in the soil solution. It is often partly or completely extractable using suitable reagents. Since the concentration of the material in the natural soil solution is usually small compared with the total exchangeable amount in the soil, the solution component is often ignored. However, in these experiments an extracting reagent was used, thus bringing a substantial portion of the extractable material into solution. Hence, the isotopically exchangeable pool consists of material on both the soil surface and in the extracting solution.

Table 35 shows the amounts of isotopically exchangeable phosphate and iron in fresh soils and in waterlogged soils incubated for sixteen weeks. It is evident from the data that waterlogging substantially increased the amounts of isotopically exchangeable phosphate and iron in all four soils as compared with the fresh soils. It has also been shown that ammonium acetate-extractable phosphate (Table 30) and iron (Table 7) values increased as a result of waterlogging.

It is clear from the data (Table 35) that most of the exchangeable iron extracted by the ammonium acetate was in the solution phase rather than adsorbed. This indicates that as a result of waterlogging, insoluble ferric compounds are reduced to much more soluble ferrous compounds and which can readily be extracted by buffered ammonium acetate solution. It can be seen that waterlogging increases the isotopically exchangeable pool of iron by a factor of 9.9, 5.8, 4.6 and 1.3 in the Macmerry, Tista, Giffnock and Brahmaputra soils, respectively as compared with the fresh soils.

Table 35. Amounts of isotopically exchangeable phosphate and iron*

Soil	Non-extractable (surface) µg/g		Extractable (solution) µg/g		Isotopically exchangeable pool (µg/g soil)	
	P	Fe	P	Fe	P	Fe
(a) Fresh soil						
Macmerry	49.7	384	2.8	531	52.5	915
Giffnock	6.1	126	0.9	881	7.0	1007
Tista	13.9	16	2.0	631	15.9	647
Brahmaputra	27.9	36	3.8	525	31.7	561
Standard error	0.87	6.20	0.09	19.30	1.30	16.30
(b) Waterlogged soil						
Macmerry	90.5	1868	17.5	7175	108.0	9043
Giffnock	7.8	1490	1.6	3150	9.4	4640
Tista	30.8	455	14.0	3300	44.8	3755
Brahmaputra	88.9	276	11.9	470	100.8	746
Standard error	2.08	24.40	0.42	14.60	2.48	37.80

* mean of duplicate samples

As is evident from the data, the isotopically exchangeable fraction of phosphate was more associated with soil surfaces. Thus the true increase in available phosphate is much greater than indicated by ammonium-acetate extraction in earlier incubation experiments (Table 30). However, the observations are in close agreement with the findings of Holford and Patrick (1979). They stated that the higher labile phosphate must have been responsible for the higher solution phosphate concentration. The isotopically exchangeable pool of phosphate was increased by a factor of 3.2, 2.8, 2.1 and 1.4 in the Brahmaputra, Tista, Macmerry and Giffnock soils, respectively as compared with the fresh soils. The results indicate that with the increase in the isotopically exchangeable pool of iron, the exchangeable pool of phosphate was also increased. However, this relationship between iron and phosphate was not directly proportional. The data presented in Table 38 also indicate that there are significant amounts of iron phosphate present in the fresh samples of Macmerry, Tista and Brahmaputra soils and under reduced soil conditions the solubility of these materials would be increased. Holford and Patrick (1979) also observed that the changes in phosphate availability in reduced soils are dependent on the solubility of iron phosphates.

4.1.12. Conclusions

The incubation experiments were conducted in the laboratory to study the chemical changes which occur during waterlogging. The results of the experiments have shown that with the exception of the Brahmaputra soil, the redox potential values for the Macmerry, Giffnock and Tista soils became highly reduced after four weeks of waterlogging and then rose slightly. The intensity of reduction in soils, however, depends on the organic matter content and the amounts

of reducible materials present in the soil.

The results of the pH values for the Macmerry, Giffnock and Tista soils show an increase and for the Brahmaputra soil a decrease as a result of waterlogging. The findings of the present work support the concept that waterlogging increases the pH of acid soils and decreases the pH of alkaline soils. Therefore, the pH of waterlogged soils have a tendency to approach and to remain close to a neutral value.

Waterlogging substantially increases the amounts of extractable iron in all four soils under study. Most of the iron reduction took place within four weeks of waterlogging. But the values began to fall at the later stages of waterlogging. The subsequent decrease in the concentration of iron may be attributed to the fresh precipitation of ferric hydroxide $Fe_3(OH)_8$, as a result of the exhaustion of metabolically labile organic materials and the diffusion of oxygen into the system. The results of the alternate flooded and moist soil conditions were very variable. The extent of aeration was probably not uniform in all the samples thus the reprecipitation of iron as ferric hydroxide was variable. Oxidation has obviously converted ferrous compounds to the less soluble ferric compounds.

The results also revealed that most of the manganese became reduced and extractable after four weeks of waterlogging. The results of the experiment also show that as a result of waterlogging about 78 and 72% of the 'free' (dithionite/citrate extractable) manganese became ammonium-acetate extractable in the Giffnock and Tista soils, respectively. For the Macmerry and Brahmaputra soils about 65% of the 'free' manganese became extractable. However, the amount of extractable iron or manganese depends both on the extent of reduction and on their native content.

Waterlogging increased the concentrations of ammonium-acetate extractable calcium upto 8 weeks in the Macmerry and Giffnock soils, while it increased upto 12 weeks in the Tista and Brahmaputra soils. Such an increase for the Macmerry, Giffnock and Tista soils was probably due to release of calcium which may have been occluded by iron. As a result of waterlogging, the iron was reduced and came into solution, this may open the blockage of calcium releasing more calcium in the solution. Subsequent decrease may be due to re-occlusion of exchangeable calcium by the precipitation of surface oxide coatings. For the Brahmaputra soil the increase was probably due to formation of calcium bicarbonate. In the alternate flooded and moist soils the subsequent decrease in the concentration of extractable calcium was more pronounced probably due to occlusion of calcium by the ferric hydroxide resulting from frequent precipitation of iron as a consequence of alternate flooded and moist soil conditions.

During waterlogging, the concentration of extractable potassium remained almost stable in the Macmerry and Tista soils, and slightly increased in the Brahmaputra and Giffnock soils. For alternately flooded and moist soils the potassium concentration in the Macmerry soil decreased consistently with time. This was again probably due to re-occlusion of potassium by the precipitation of oxide coatings.

Waterlogging increases the amounts of water-soluble iron, manganese, calcium and potassium in all four soils under study. Water-soluble iron, manganese, calcium and potassium reached peak values after four weeks of waterlogging in the Macmerry, Giffnock and Tista soils. For the Brahmaputra soil peak values for iron and manganese were reached at 8 weeks, calcium at 4 weeks and potassium increased all through the experimental period.

The observations on specific conductance showed clearly that the values substantially increased within four weeks of waterlogging and that if the system remained completely anaerobic the values remained more or less stable throughout the incubation period. The increased values were related to the concentration of iron, manganese, calcium and potassium in the solution.

Waterlogging increases the concentration of extractable phosphate upto 8 weeks, 12 weeks and all through the experimental period in the Macmerry, Tista and Brahmaputra soils, respectively. Inconsistent results were obtained with the Giffnock soil. This was probably due to a very low concentration of extractable phosphate. For the alternate flooded and moist soil conditions the concentration increased upto four weeks and then decreased in both Macmerry and Giffnock soils.

The results of the present work suggest that the application of urea had no marked effect on redox potential, pH, iron, manganese, calcium, potassium and phosphate content of all four soils under study. However, urea application increased the specific conductance of the Brahmaputra and Tista soils but had no marked effect on the Macmerry and Giffnock soils.

The studies on mineralisation of soil phosphorus under water-logged conditions revealed that, using the existing determining techniques, it was difficult to draw any firm conclusions about mineralisation of soil phosphorus.

Isotopic studies show that buffered ammonium acetate can extract most of the exchangeable iron while most of the exchangeable phosphate remained on the surface of the soil particles.

4.2. DISTRIBUTION OF TOTAL, INORGANIC AND ORGANIC PHOSPHATE WITH RESPECT TO SOIL PARTICLE SIZE

It can be seen from Table 36 that the particle size distribution obtained by ultrasonic dispersion method and the conventional sedimentation method showed very close agreement. The percentage recovery by ultrasonic dispersion method varied from 93.8 to 95.5 per cent.

The distribution of phosphate in different fractions of soil is presented in Table 37. The highest values for total and inorganic phosphate were found to be associated with the clay fraction in all four soils under study. For the Macmerry and Giffnock soils, total and inorganic phosphate increases with decreasing particle size, whereas in the Tista and Brahmaputra soils a similar order was not maintained. In these soils the sand fractions contain more total and inorganic phosphate than silt fraction. Organic phosphate was found to be highest with the clay fraction of all four soils. Results of the Macmerry and Giffnock soils substantiate the findings of other investigators (Williams and Saunders, 1956; Hanley et al., 1965; Syers et al., 1969; Omar, 1977).

Table 39 shows that the organic phosphate as a proportion of total phosphate was highest in the clay fraction followed by silt and sand in the Macmerry, Tista and Brahmaputra soils but the Giffnock soil behaves reversely. Such an observation for the Giffnock soil is probably due to the presence of organic material in the form of plant fragments associated with coarser soil fractions and the very low values for inorganic phosphate found in this soil. A similar observation was also made by Oades and Turchenek (1978). They found that organic phosphorus had accumulated particularly in sand fractions in the form of plant fragments.

Table 36. Particle size distribution of soils

(a) By conventional dispersion method

Soil	Sand (%)	Silt (%)	Clay (%)
Macmerry	50.58	26.05	22.10
Giffnock	48.50	29.60	22.00
Tista	12.36	71.62	15.73
Brahmaputra	12.05	73.38	13.72

(b) By ultrasonic dispersion method

Soil	Sand (%)	Silt (%)	Clay (%)
Macmerry	53.33	23.47	17.12
Giffnock	52.88	22.36	18.95
Tista	11.88	67.52	16.12
Brahmaputra	14.20	67.18	12.40

Table 37. Distribution of total, inorganic and organic phosphate in each soil fraction*

Soil	Total phosphate (μg/g)			Inorganic phosphate (μg/g)			Organic phosphate (μg/g)		
	Sand	Silt	Clay	Sand	Silt	Clay	Sand	Silt	Clay
Macmerry	173 ± 2	815 ± 9	1725 ± 6	146 ± 4	426 ± 8	717 ± 0	27	389	1008
Giffnock	13 ± 1	167 ± 5	440 ± 10	n.d.	46 ± 3	142 ± 0	13	121	297
Tista	459 ± 5	408 ± 8	1012 ± 6	430 ± 1	353 ± 7	750 ± 0	29	55	262
Brahmaputra	525 ± 25	509 ± 16	1187 ± 0	519 ± 6	464 ± 1	992 ± 8	6	45	195

* mean of duplicate samples

n.d. = not detectable

Table 38. Fractionation of aluminum, iron and calcium phosphate in soils*

Soil	Al-fraction	Fe-fraction	Ca-fraction
	μg/g soil		
Macmerry	20.5 ± 2.0	87.5 ± 0.0	66.8 ± 1.8
Giffnock	12.8 ± 1.8	13.0 ± 0.0	6.8 ± 0.3
Tista	23.5 ± 5.0	88.0 ± 1.0	293.0 ± 3.0
Brahmaputra	24.3 ± 1.8	80.5 ± 2.0	354.0 ± 16.0

* mean of duplicate samples

Table 39. Organic phosphate as a percentage of total phosphate in each fraction

Soil	Sand	Silt	Clay
Macmerry	15.60	47.7	58.4
Giffnock	100.00	72.5	67.6
Tista	6.30	13.5	25.9
Brahmaputra	1.14	8.8	16.5

Table 40 shows the percentage distribution of total, inorganic and organic phosphate in clay fractions. For all soils the highest value for each of the categories of phosphate was found in the clay fractions. The lowest values were observed in the sand fractions of the Macmerry and Giffnock soils but in the silt fractions of the Tista and Brahmaputra soils. The high concentration of phosphate in clay fractions may be explained by greater phosphate retention capacity of the clay (Syers et al., 1969) and the formation of organo-clay complexes.

4.2.1. Conclusions

The studies show that satisfactory dispersion of soil particles can be achieved using ultrasonic techniques.

The studies on the distribution of total, inorganic and organic phosphate in individual soil particles of the Macmerry, Giffnock, Tista and Brahmaputra soils revealed that the highest values of total, inorganic and organic phosphate was found to be associated with the clay fraction.

4.3. GLASSHOUSE EXPERIMENTS

4.3.1. Experiment 1. Yield and Composition of Rice Plants

A glasshouse pot experiment was set up to study the yield and composition of rice plants grown under waterlogged conditions.

4.3.1.1. Growth conditions and dry matter yield

The rice plants started tillering two weeks after transplanting. Algae began to grow in the water of all pots one week after transplanting but disappeared with time. In the Macmerry soil, although the plants were growing very well some brown spots appeared near the end of some leaves about one month after transplanting. The tips of

Table 40. Distribution of percentage of total, inorganic and organic phosphate in each soil fraction

Soil	Total phosphate			Inorganic phosphate			Organic phosphate		
	Sand	Silt	Clay	Sand	Silt	Clay	Sand	Silt	Clay
Macmerry	6.4	30.0	63.6	11.3	33.0	55.7	1.9	27.3	70.8
Giffnock	2.0	27.0	71.0	n.d.	24.4	75.6	3.0	28.0	69.0
Tista	24.4	21.7	53.9	28.0	23.0	49.0	8.4	15.9	75.7
Brahmaputra	23.6	22.9	53.5	26.3	23.5	50.2	2.4	18.3	79.3

n.d. = not detectable

some leaves were desiccated after four weeks of transplanting as a result of mottling. Forty five days after transplanting many of the older leaves were completely senescent. In the Giffnock soil the plants were growing well. Four weeks after transplanting brown spots were noticed near the end of some leaves and most of the edges of those leaves were desiccated. The appearance of brown spots in the leaves for both Macmerry and Giffnock soils was probably due to iron toxicity. Tanaka et al. (1966) reported that rice leaves containing more than 300 ppm iron exhibit iron toxicity symptoms known as bronzing; tiny brown spots appear first, followed by development of a uniform brown colour. However, better growth performance was observed with the Macmerry soil than the Giffnock soil. This may be attributed to the better physical condition and higher fertility status of the Macmerry soil compared with the Giffnock soil (Table 2).

The first harvest of rice plants was made two months after transplanting. After the first harvest the same soil was used to grow another batch of rice. The second harvest was made three months after transplanting.

Table 41 shows the dry matter yield of rice in two harvests. For the Macmerry soil the dry matter yield was found to be almost similar in both harvests, while for the Giffnock soil a higher dry matter yield was observed in the second harvest.

4.3.1.2. Chemical composition of the rice plants

(a) Phosphorus

The concentration of phosphorus (μg P/g dry matter) in the rice plants at both harvests for the Macmerry and Giffnock soils is presented in Table 42 and the data for the individual pots are reported in Appendix, Tables A7 and A8. The total uptake by plants

Table 41. Yield of rice grown under flooded conditions

Buckets	Soil			
	Macmerry		Giffnock	
	First harvest	Second harvest	First harvest	Second harvest
	Plant yield (g/pot)			
1	34.3	40.4	16.8	27.9
2	36.6	33.6	17.0	26.1
3	36.6	36.7	15.6	28.0
4	38.9	38.0	16.3	31.8
5	37.5	35.0	15.1	23.1
Mean	36.8	36.7	16.2	27.4
Standard deviation	1.7	2.6	0.8	3.2

from individual pots is shown in Appendix, Tables A9 and A10. The data show that there was a greater conc. of phosphorus in the plants grown in the Macmerry soil than in the Giffnock soil, by factors of 1.6 and 2.2 in the first and second harvests, respectively. Similarly the total uptake (mg P/pot) of phosphorus by the plants (Table 43) was much higher in the Macmerry soil than in the Giffnock soil by factors of approximately 3.6 and 3.0 for the first and second harvests, respectively.

Data presented in Table 42 show that for both soils the concentration of phosphorus in the plants was higher at the first harvest. Both the concentration of phosphorus in the plant material and total uptake by the plants was higher during the first harvest for the Macmerry soil. This was probably due to much of the easily available phosphate taken up by the plants grown of the first batch. For the Giffnock soil the concentration of phosphorus in the plants was also higher at the first harvest, while the total uptake was greater for the second harvest. As is evident from the Table 41, there was significantly more dry matter yield in the second harvest for the Giffnock soil which accounts for the greater concentration of phosphorus. However, the results indicate that the concentration or total uptake of phosphorus by the plants is largely dependent on the soil properties and the availability of native phosphate.

(b) Iron

The mean concentration of iron in rice plants at both harvests for the Macmerry and Giffnock soils is shown in Table 42. Similar data on the basis of individual pots are reported in Appendix, Tables A7 and A8 and the total uptake by plants from individual pots is reported in Appendix, Tables A9 and A10. The data show that at both

Table 42. Concentration of phosphorus, iron, manganese, calcium and potassium in rice plants*

	Soil									
	Macmerry					Giffnock				
	P	Fe	Mn	Ca	K	P	Fe	Mn	Ca	K
	Plant content (μg/g dry matter)									
First harvest										
Mean	2722	800	1240	10100	6710	1720	755	235	7400	8730
Standard deviation	305	127	82	518	567	121	169	29	783	825
Second harvest										
Mean	2507	310	2097	9725	4070	1122	255	480	9200	4340
Standard deviation	243	137	482	495	514	127	29	72	1099	654

* mean of five replicates

Table 43. Total uptake (mg/pot) of phosphorus, iron, manganese, calcium and potassium by rice plants*

	Soil									
	Macmerry					Giffnock				
	P	Fe	Mn	Ca	K	P	Fe	Mn	Ca	K
	Plant uptake (mg/pot)									
First harvest										
Mean	100.49	29.53	45.62	370.96	247.38	27.86	12.07	3.79	119.23	141.47
Standard deviation	15.46	5.62	3.80	13.02	30.34	3.19	2.63	0.40	9.57	19.10
Second harvest										
Mean	91.70	11.30	77.09	357.63	148.88	30.75	6.78	13.24	250.31	118.85
Standard deviation	4.84	4.64	18.79	35.78	13.39	5.42	0.97	2.90	26.60	22.21

* mean of five replicates

harvests the concentration of iron in the plants is similar for both soils. However, because of the differences in yield, the total uptake (Table 43) is much higher in the Macmerry soil than in the Giffnock soil. The total uptake of iron by the plants was significantly less in the second harvest for both soils. This may be due to the fact that most of the iron is reduced within four weeks of waterlogging (Table 7) and as such the concentration was much higher during the first harvest than the second harvest. The decreased concentration of iron in the second harvest was probably due to the fact that much of the available iron was taken up by the plants at the first harvest. Data obtained in the laboratory incubation studies (Table 9) indicate that in the Giffnock soil most of the reduced iron was taken up by the rice plants by both harvests. For the Macmerry soil about $\frac{1}{4}$th of the reduced iron was taken up by the rice plants by both harvests. The decreased concentration of iron in the second harvest might have also occurred as a result of pH rise. It can be noted that waterlogging increases the pH of the soils (Table 5). Van Der and Van Diest (1979) also observed that with increasing pH the translocation of iron to the shoots was reduced. Moreover, after the first harvest the soils were disturbed to remove all the roots from the soils. This may have lead to the reoxidation and reprecipitation of some of the iron.

It may, therefore, be deduced from the results that the concentration of iron in the rice plants was for the most part similar in both soils. Total uptake was largely dependent on the dry matter yield and on the native iron content of the soil.

(c) Manganese

Table 42 shows the concentration of manganese in the rice plants

at both harvests for the Macmerry and Giffnock soils and the figures for individual pots are shown in Appendix, Tables A7 and A8. There was significantly higher concentration of manganese in plants at both harvests in the Macmerry soil compared with the Giffnock soil, by factors of 5.3 and 4.4 in the first and second harvests, respectively. Similarly, the total uptake of manganese was substantially higher in the Macmerry soil than in the Giffnock soil by factors of 12.0 and 5.8 for the first and second harvests, respectively (Table 43). Such increases in the amount of manganese were probably due to a large difference in the 'free' manganese content of both soils (Table 2) and to dry matter yield difference. It is noted that a higher concentration of iron occurred during the first harvest, while in the case of manganese more concentration was observed in the second harvest. The results suggest that there is an antagonistic effect of iron and manganese in the nutrition of rice. Karim and Mohsin (1964) observed a similar interaction between iron and manganese in the nutrition of rice.

(d) Calcium

Table 42 shows the mean concentration of calcium in the rice plants at both harvests for the Macmerry and Giffnock soils and the total uptake is presented in Table 43. The data indicate that there was a higher concentration of calcium in the plants grown on the Macmerry soil compared with the Giffnock soil at both harvests. In the Macmerry soil the total uptake was almost identical at both harvests. However, greater total uptake was observed in the second harvest with the Giffnock soil. As with iron and manganese this can be explained by the higher dry matter yield difference between the harvests. In addition, the concentration of calcium is also dependent on the native content of the soils.

(e) Potassium

The concentration of potassium in the rice plants at both harvests for the Macmerry and Giffnock soils is reported in Table 42 and the total uptake is presented in Table 43. The data show that the concentration of potassium in the plants grown on the Giffnock soil was higher than those grown on the Macmerry soil, although the Giffnock soil contains less potassium than the Macmerry soil. This may be attributed to the low dry matter yield obtained from the Giffnock soil leading to increased potassium concentration in the plants. The data also indicate that the concentration of potassium was greater in the rice plants at the first harvest in both soils. This suggests that the rice plants exploited much of the available potassium during this period thereby depleting the amount available for growth in the second harvest. The total uptake was also more at the first harvest. Despite an increase in dry matter yield during the second harvest, rice grown on the Giffnock soil exploited more potassium during the first harvest. Thus the maximum uptake of potassium occurred during the first harvest irrespective of dry matter yield. This is further evidence for the phenomenon of luxury uptake of potassium by plants.

4.3.1.3. Total, inorganic and organic phosphate content of soils

Inorganic, organic and total phosphate contents of soils are presented in Table 44. The data show that there was an increase in the inorganic phosphate content for the Macmerry soil and a decrease for the Giffnock soil compared with the initial values (Table 2). Total phosphate and organic phosphate values were decreased for both Macmerry and Giffnock soils as a result of flooding. A decrease in the phosphate content may be explained by the fact that phosphate

Table 44. Inorganic, organic and total phosphate content of soils following rice grown under flooded conditions

Buckets	Soil					
	Macmerry			Giffnock		
	Inorganic	Organic	Total	Inorganic	Organic	Total
	µg P/g soil					
1	320	247	567	51	56	107
2	331	309	640	43	67	110
3	331	224	555	45	58	103
4	315	232	547	46	68	114
5	350	245	595	44	58	102
Mean	329.4	251.4	580.8	46	61	107
Standard deviation	13	34	38	3	6	5

uptake by the rice grown on both soils probably depleted native forms. The data further suggest that in both soils there could have been some mineralisation. But the total phosphate values vary so much compared with the initial values that it is difficult to draw any firm conclusions. Similar difficulties were also found in the laboratory studies (Table 34).

4.3.2. Experiment II. Effect of Added Phosphate on Rice Plants

A glasshouse experiment was conducted to study the effect of fertiliser phosphorus on the yield of rice grown under constantly flooded and alternately flooded and moist soil conditions.

4.3.2.1. Growth conditions and dry matter yield

The rice plants started tillering two weeks after transplanting in both soils. Algae began to grow in the water of all pots one week after transplanting and the amount of algal growth was greater with the Macmerry soil. In time, first the algae in the Giffnock soil and then in the Macmerry soil disappeared. The plant growth was relatively luxurious with the Macmerry soil probably due to better physical condition and higher fertility status of this soil. More tillers and better growth was observed with alternately flooded and moist soils than in the constantly flooded state.

The first harvest of the rice plants was made two months after transplanting and the second harvest was made three months after transplanting. The data presented in Table 45 show the effect of fertiliser phosphorus on dry matter yield of rice. For the Macmerry soil there was no evidence of response to fertiliser phosphorus in either harvests and in both soil conditions. For the Giffnock soil, however, there was a consistent effect of phosphorus fertilisation in the first harvest under both soil conditions. Total dry matter

Table 45. Effect of fertiliser phosphorus on dry matter yield of rice grown under constantly flooded, and alternately flooded and moist soils*

Treatment	Soil							
	Macmerry				Giffnock			
	Flooded		Flooded and moist		Flooded		Flooded and moist	
	First harvest	Second harvest	First harvest	Second harvest	First harvest	Second harvest	First harvest	Second harvest
	Plant yield (g/pot)							
P_0	14.5 ± 1.0	27.0 ± 2.5	17.8 ± 1.2	26.5 ± 3.5	2.8 ± 0.2	9.3 ± 0.7	5.3 ± 0.2	14.5 ± 3.5
P_1	14.0 ± 1.5	26.3 ± 1.7	17.8 ± 0.8	29.0 ± 3.0	6.2 ± 0.8	14.0 ± 0.0	6.3 ± 1.2	16.0 ± 2.0
P_2	13.8 ± 0.2	24.3 ± 1.8	17.0 ± 0.0	27.3 ± 1.3	7.0 ± 0.5	16.8 ± 0.8	8.5 ± 0.5	17.0 ± 3.5
P_3	17.0 ± 1.0	26.5 ± 0.5	17.0 ± 0.5	28.8 ± 0.3	7.5 ± 0.5	16.8 ± 0.8	9.0 ± 1.0	15.5 ± 1.0

* mean of duplicate samples

yield of rice increased significantly with increasing levels of phosphorus fertilisation. In the second harvest there was a significant trend of increasing dry matter yield with increasing levels of phosphorus under constantly flooded conditions. In the alternate flooded and moist soils dry matter yield increased over the control as a result of added phosphorus but the increases were not consistent with increasing fertiliser increments.

The data show an increase in the dry matter yield for both soils with alternate flooded and moist conditions compared with constantly flooded soils. Decreased dry matter yield in the flooded soils may well have been due to loss of nitrogen as a result of enhanced denitrification under waterlogged conditions (Patrick and Mahapatra, 1968). Decreased yield may also have resulted from the presence of large amounts of reduced iron and manganese. Such high concentrations of iron and manganese can be toxic to rice plants. Terman and Allen (1974) also observed that the yields of rice supplied with just adequate levels of water can equal or even exceed those achieved under constantly flooded conditions.

A significant response to phosphorus fertilisation was observed for the Giffnock soil, particularly in the first harvest. This may be attributed to the low phosphate content of the soil (Table 2). However, response by rice to phosphorus fertilisation, as visually observed, decreased with age of the plants. The results suggest that the major requirement of phosphorus for the rice plants is at the early stages of growth. Indeed, Davide (1965) had stated that the rice plants take up the bulk of the phosphorus during early growth stages.

4.3.2.2. Phosphorus content in the rice plants

Table 46 presents the concentration of phosphorus in the rice plants grown under constantly flooded, and alternately flooded and moist conditions at different levels of phosphorus fertilisation. For the Macmerry soil the highest concentration of phosphorus occurred at the first harvest under constantly flooded conditions. Increasing amounts of fertiliser phosphorus did not effect the concentration of phosphorus in plants at both harvests or under both soil conditions. For the Giffnock soil there was a consistent effect of fertiliser phosphorus on phosphorus concentration in the rice plants at both harvests under both soil conditions.

The total uptake of phosphorus by the rice plants grown in this experiment is reported in Table 47. The data indicate that in the Macmerry soil total uptake of phosphorus was greater in the second harvest, due mainly to higher dry matter yields. However, there was no consistent effect of phosphorus fertilisation on total uptake with respect to the harvests or the soil conditions.

The trend of total uptake of phosphorus for the Giffnock soil was similar to that observed for the phosphorus concentration in plants grown in this soil.

The concentration of phosphorus in the plant material and total uptake by the plants was different for each soil. This was due to their different physical characteristics and native available phosphate content.

4.3.2.3. Extractable phosphate and iron, and soil pH

(a) Phosphate

The concentrations of ammonium acetate-extractable phosphate for constantly flooded, and alternately flooded and moist soils at different

Table 46. Concentration of phosphorus in rice plants grown under constantly flooded, and alternately flooded and moist soils at different levels of fertiliser phosphorus*

Treatment	Soil							
	Macmerry				Giffnock			
	Flooded		Flooded and moist		Flooded		Flooded and moist	
	First harvest	Second harvest	First harvest	Second harvest	First harvest	Second harvest	First harvest	Second harvest
	Plant content (μg P/g dry matter)							
P_0	3056 ± 131	2649 ± 112	2437 ± 37	2668 ± 18	1475 ± 100	1487 ± 12	1368 ± 18	1543 ± 43
P_1	3031 ± 69	2956 ± 69	2625 ± 50	2668 ± 118	1825 ± 100	1756 ± 94	1556 ± 56	1625 ± 75
P_2	3618 ± 68	2825 ± 0	2481 ± 106	2529 ± 95	2281 ± 106	2106 ± 44	1775 ± 75	1687 ± 37
P_3	3268 ± 93	2931 ± 19	2199 ± 262	2712 ± 12	2562 ± 187	2050 ± 0	1793 ± 56	2018 ± 56

* mean of duplicate samples

Table 47. Total uptake of phosphorus by rice plants grown under constantly flooded, and alternately flooded and moist soils at different levels of phosphate fertiliser*

Treatment	Soil							
	Macmerry				Giffnock			
	Flooded		Flooded and moist		Flooded		Flooded and moist	
	First harvest	Second harvest	First harvest	Second harvest	First harvest	Second harvest	First harvest	Second harvest
	Plant uptake (mg P/pot)							
P_0	44.44±4.96	66.69±0.98	43.41±3.71	70.65±8.85	4.03±0.09	13.75±1.00	7.18±0.25	22.23±4.77
P_1	42.54±5.51	77.72±6.99	46.63±2.86	77.74±11.44	11.48±2.00	24.58±1.32	9.80±1.30	26.15±4.45
P_2	49.74±0.04	68.51±2.12	42.18±1.80	69.05±5.76	15.91±0.40	35.24±0.84	15.05±0.25	28.56±5.27
P_3	55.47±1.68	77.66±0.96	37.26±3.36	77.98±0.32	19.13±0.13	34.34±1.54	16.09±1.29	31.23±1.14

* mean of duplicate samples

levels of fertiliser phosphorus are presented in Table 48. The data show that the concentration of phosphate in the Macmerry soil at the first harvest increased with increasing rates of fertiliser phosphorus under constantly flooded conditions. Such increases were proportionate with the amounts of added fertiliser phosphorus.

For the Giffnock soil no marked effect of fertiliser phosphorus on levels of phosphate availability was observed under either soil condition. This was probably due to the fixation of added fertiliser phosphorus. Likewise no marked effect of fertiliser phosphorus was observed for the Macmerry soil in the second harvest under constantly flooded conditions and at both harvests under alternate flooded and moist conditions. More fixation of added fertiliser phosphorus might have taken place in the alternate flooded and moist conditions, while in the flooded soil fixation of added fertiliser phosphorus might have occurred in the later stage of waterlogging.

Due to constant submergence, the phosphate concentration increased significantly as compared with the initial values in both soils (Table 2). Such increases in the phosphate concentration were also observed in the laboratory studies under waterlogged soil conditions (Table 30). However, in the alternate flooded and moist conditions the extractable phosphate values for the Macmerry soil decreased substantially compared with constantly flooded soils. The concentration of extractable phosphate in the Giffnock soil at the first harvest was very low but at the second harvest the decrease was so pronounced that it was not possible to measure. A similar observation was also made in the laboratory studies under alternate flooded and moist soil conditions (Table 32).

However, it can be seen from Table 47 that the total uptake of

Table 48. Extractable phosphate for constantly flooded, and alternately flooded and moist soils at different levels of fertiliser phosphorus following plant growth*

Treatment	Soil							
	Macmerry				Giffnock			
	Flooded		Flooded and moist		Flooded		Flooded and moist	
	First harvest	Second harvest	First harvest	Second harvest	First harvest	Second harvest	First harvest	Second harvest
	μg P/g soil							
P_0	6.4 ± 1.5	5.7 ± 0.5	1.2 ± 0.2	3.2 ± 0.3	1.0 ± 0.0	0.6 ± 0.0	0.3 ± 0.0	n.d.
P_1	8.6 ± 0.4	4.9 ± 0.5	1.4 ± 0.4	4.0 ± 0.0	1.0 ± 0.1	0.6 ± 0.0	0.4 ± 0.0	n.d.
P_2	14.9 ± 1.8	5.5 ± 0.1	1.4 ± 0.4	5.2 ± 0.7	1.4 ± 0.1	0.6 ± 0.0	0.4 ± 0.1	n.d.
P_3	18.3 ± 4.7	6.1 ± 0.4	1.0 ± 0.3	2.2 ± 0.0	0.9 ± 0.1	0.5 ± 0.0	0.3 ± 0.1	n.d.

* mean of duplicate samples

n.d. = not detectable

phosphorus by the rice plants was hardly affected by the lower level of extractable phosphate. This indicates that the rice plant can exploit phosphate from the soil even at the level when it is not detectable in an ammonium-acetate extract. Therefore, ammonium acetate-extractable phosphate values are not a clear indication of available phosphate.

The reasons for the increase in the concentration of extractable phosphate as a result of waterlogging, and decrease in the alternate flooded and moist soil conditions are discussed in section 4.1.9.

(b) Iron

The concentrations of ammonium-acetate extractable iron for constantly flooded, and alternately flooded and moist soils at different levels of fertiliser phosphorus are shown in Table 49. The data show that as a result of constantly flooded conditions the concentration of extractable iron in both soils at both harvests increased dramatically as compared with fresh, aerobic soils (cf. zero-week observation in Table 7). There was no observable effect of phosphorus fertilisation and the extractable values were similar in all pots. However, as a result of flooding, the values for extractable iron were substantially higher for the Macmerry soil compared with the Giffnock soil as observed also in the laboratory studies (Table 7).

In the alternate flooded and moist soil conditions, the extractable iron values obtained for the Macmerry soil at both harvests were very variable. This variability resulted from the non-uniform aeration of the pots. In the Giffnock soil the amount of extractable iron was decreased by factors of approximately 2 and 3 at the first and second harvests, respectively compared with the constantly flooded conditions. However, the values were more or less similar in

Table 49. Concentration of extractable iron for constantly flooded, and alternately flooded and moist soils at different levels of fertiliser phosphorus*

Treatment	Soil							
	Macmerry				Giffnock			
	Flooded		Flooded and moist		Flooded		Flooded and moist	
	First harvest	Second harvest	First harvest	Second harvest	First harvest	Second harvest	First harvest	Second harvest
	μg Fe/g soil							
P_0	6684 ± 257	6674 ± 0	234 ± 6	3373 ± 2341	1095 ± 38	1080 ± 31	584 ± 201	388 ± 67
P_1	6365 ± 674	7119 ± 411	327 ± 32	1508 ± 323	1168 ± 136	1148 ± 6	575 ± 33	344 ± 34
P_2	6071 ± 292	6367 ± 424	249 ± 79	1099 ± 621	1276 ± 132	1035 ± 22	559 ± 25	308 ± 66
P_3	6576 ± 731	6746 ± 212	1382 ± 392	2728 ± 2423	1086 ± 72	1055 ± 29	305 ± 67	444 ± 54

* mean of duplicate samples

all the treatments. The reasons for the increase in the concentration of extractable iron as a result of waterlogging, and decrease in the alternate flooded and moist soil conditions are discussed in section 4.1.3.

(c) Soil pH

The pH of the constantly flooded, and alternately flooded and moist soils at different levels of fertiliser phosphorus is shown in Table 50. The values indicate that phosphorus fertilisation has no marked effect on pH for both soils under both conditions. In the constantly flooded soils the values remained more or less stable in all the treatments. The pH values were slightly higher compared with the initial values (Table 2).

For the Macmerry soil, a small decrease in the pH value was observed under alternately flooded and moist conditions. However, a significant decrease was noticed with the Giffnock soil in the second harvest. In the first harvest the values were identical to those observed under constant flooded conditions. Savant and Kibe (1969) also observed that alternate submergence and drying of soil depresses the pH slightly after 30 days. At later stages, pH depression was more pronounced with time. It is difficult to suggest an explanation to account for these observations but it could be due to reoxidation of iron in a poorly buffered soil.

4.3.3. Experiment III. Effect of Depletion of Soil Phosphate

In the previous experiment, response of rice to phosphorus fertilisation was observed only for the Giffnock soil which has a very low level of available phosphate. In an attempt to induce deficiency conditions in both soils, depletion of native phosphate was carried out by growing ryegrass for about a year. Then a glasshouse

Table 50. The pH of the constantly flooded, and alternately flooded and moist soils*

Treatment	Soil							
	Macmerry				Giffnock			
	Flooded		Flooded and moist		Flooded		Flooded and moist	
	First harvest	Second harvest	First harvest	Second harvest	First harvest	Second harvest	First harvest	Second harvest
	pH							
P_0	6.3 ± 0.0	6.2 ± 0.2	6.0 ± 0.0	6.0 ± 0.0	5.8 ± 0.0	5.6 ± 0.0	5.9 ± 0.0	5.2 ± 0.0
P_1	6.4 ± 0.1	6.3 ± 0.2	6.1 ± 0.0	5.9 ± 0.2	5.7 ± 0.1	5.4 ± 0.1	5.7 ± 0.0	5.3 ± 0.1
P_2	6.3 ± 0.2	6.0 ± 0.0	6.1 ± 0.0	6.0 ± 0.4	5.6 ± 0.0	5.5 ± 0.1	5.7 ± 0.0	5.3 ± 0.2
P_3	6.5 ± 0.0	6.0 ± 0.0	6.1 ± 0.1	6.1 ± 0.1	5.8 ± 0.1	5.5 ± 0.1	5.7 ± 0.0	5.2 ± 0.0

* mean of duplicate samples

experiment was carried out to study the effect of phosphorus fertilisation on the rice plants grown in phosphate depleted soils under flooded conditions. As a result of phosphate depletion, by growing grass, the extractable phosphate values decreased from 2.0 μg P/g soil to 0.25 μg P/g soil in the Macmerry and from 0.5 μg P/g soil to 0.12 μg P/g soil in the Giffnock.

4.3.3.1. Growth conditions and dry matter yield

The rice plants started tillering twelve days after transplanting in the Macmerry soil where fertiliser phosphorus was added. In the buckets where no phosphorus was added tillering started two weeks after transplanting. For the Giffnock soil tillering started two weeks after transplanting where phosphorus was applied but without phosphorus addition, tillering started 18 days after transplanting.

Six days after transplanting algae began to grow in the water of both soils but only in buckets where fertiliser phosphorus was applied. No algal growth was observed in any buckets where fertiliser phosphorus was not added. This effect was noticed in both soils. This may be attributed to the fact that in the absence of adequate phosphorus algal growth is limited even when nitrogen is plentiful. The algal mass disappeared about four weeks after transplantation in the Macmerry soil, while in the Giffnock soil it disappeared about five weeks after transplanting.

In the Giffnock soil, the older leaves of the rice plants began to brown about 35 days after transplanting and they were gradually desiccated where phosphorus was added. However, no such symptoms were noticed in the buckets where fertiliser phosphorus was absent. Similarly for the Macmerry soil, the older leaves of the rice plants began to brown about 40 days after transplanting and they were

gradually desiccated. These symptoms were noticed only in the buckets where phosphorus was added. This may be explained by the fact that algal growth in the phosphorus treated buckets results in aeration which leads to the formation of nitrate. This can be denitrified; hence leading to preferential loss of nitrogen from the phosphorus treated buckets. Also as a result of algal growth in the phosphorus treated buckets much of the nitrogen applied might have been utilised by the algae for their nutrition and metabolism. Thus, there may have been insufficient supply of nitrogen for the normal growth of the rice plants.

Plates 1 and 2 show the response of rice to phosphorus fertilisation grown under flooded conditions in the Macmerry and Giffnock soils, respectively four weeks after transplanting. It is clear from the plates that plants grown in the Macmerry soil responded less to phosphorus fertilisation compared with the Giffnock soil. This may be attributed to the fact that the Giffnock soil was more deficient in phosphorus than the Macmerry soil. It can also be noted that waterlogging increases by only a small amount of available phosphate in the Giffnock soil compared with the Macmerry soil (Table 48).

As the rice plants mature the response to phosphorus fertilisation becomes less pronounced. This is because the major requirement for phosphorus of the rice plants is at the early stages of growth.

Sixty days after transplanting the rice plants were harvested. Table 51 shows the effect of flooding on dry matter yield of rice grown in the presence and absence of added fertiliser phosphorus. Appendix, Table A11 presents the data on the basis of individual buckets. The data show that both soils responded to phosphorus fertilisation with increases in dry matter yield. For the Giffnock soil,

Plate 1. Showing the effect of fertiliser phosphorus on rice plants grown in phosphate depleted Macmerry soil

Plate 2. Showing the effect of fertiliser phosphorus on rice plants grown in phosphate depleted Giffnock soil

Table 51. Dry matter yield of rice grown in the presence and absence of added phosphorus under flooded conditions*

Treatment		Soil	
		Macmerry	Giffnock
		Plant yield (g/pot)	
P_0	Mean	46.50	23.57
	Standard deviation	2.66	1.18
P_{50}	Mean	48.62	31.75
	Standard deviation	2.66	1.28

* mean of six replicates

phosphorus application brings a substantial increase in the dry matter yield. Thus the results suggest that the application of phosphorus is essential for soils deficient in phosphorus for the better growth of rice plants.

It is not easy to establish a criterion for the identification of deficient soils. However, this work would indicate that soils with less than 0.5 μg ammonium acetate-extractable P/g soil may be responsive to applications of phosphorus fertiliser. In terms of normal agriculture on aerobic soil, this would represent a very low level of phosphate indeed.

4.3.3.2. Concentrations of phosphorus, iron, manganese, calcium and potassium in the rice plants

Table 52 shows the effect of flooding on the concentration of phosphorus, iron, manganese, calcium and potassium in the rice plants in the presence and absence of added phosphorus. The data obtained on the basis of individual buckets are reported in Appendix, Table A12.

For the Macmerry soil, the concentration of phosphorus and potassium in the rice plants increased with the application of phosphorus and potassium. The concentrations of manganese and calcium were not markedly effected by application of fertiliser phosphorus. The concentration of iron in the rice plants grown on both soils was much less than found in the previous experiment (Table 42). This may be due to better growth exhibited by the rice in this experiment leading to greater transport of oxygen to the roots giving rise to less intensively reduced conditions. This could result in greater oxidation of iron at the roots surface and consequently decrease the uptake by the plant.

In the Giffnock soil, the concentration of phosphorus increased

Table 52. Concentrations of phosphorus, iron, manganese, calcium and potassium in rice plants in the presence and absence of added phosphorus

Treatment		Soil									
		Macmerry					Giffnock				
		P	Fe	Mn	Ca	K	P	Fe	Mn	Ca	K
		Plant content (μg/g dry matter)									
P_0	Mean	2546	241	1583	9833	15750	1750	251	451	8667	25167
	Standard deviation	103.0	26.7	108.0	258.2	524.4	90.8	19.0	54.0	258.2	1211.0
P_{50}	Mean	2733	211	1583	9750	17587	3042	205	575	9333	24167
	Standard deviation	167.0	15.9	230.0	612.4	801.0	78.5	23.5	39.1	861.2	816.5

substantially with phosphorus fertilisation as compared with the control. With the application of phosphorus fertiliser, the concentration of calcium and manganese increased and potassium decreased slightly.

Table 53 presents the total uptake of phosphorus, iron, manganese, calcium and potassium by the rice plants in the presence and absence of added phosphorus. The data obtained on the basis of individual buckets are reported in Appendix, Table A13. The total uptake of phosphorus, potassium, calcium and manganese increased markedly in both soils as a result of phosphorus fertilisation but especially in the Giffnock soil. Once again this may be due to the increased yield and also probably to the synergistic effect of phosphorus application.

4.3.4. Conclusions

The glasshouse experiments were conducted to determine the yield and composition of the rice plants, the effect of added fertiliser phosphate and the effect of depletion of soil phosphate on the growth and chemical composition of the rice plants. The above observations were made with crops grown on the Macmerry and Giffnock soils under waterlogged, and alternate flooded and moist conditions.

The results revealed that better growth and an increased dry matter yield can be obtained by the application of fertiliser phosphorus. This effect is more pronounced with the soil particularly deficient in phosphate. However, the major requirement for phosphorus of the rice plants is at the early stages of growth. There was no marked effect of fertiliser phosphorus on both the concentration of phosphorus in the plant material and total uptake by the plants grown on the Macmerry soil indicating that this soil had adequate supplies of phosphate. However, for the Giffnock soil there was a

Table 53. Uptake of phosphorus, iron, manganese, calcium and potassium by rice plants in the presence and absence of added phosphorus

Treatment		Soil									
		Macmerry					Giffnock				
		P	Fe	Mn	Ca	K	P	Fe	Mn	Ca	K
		Plant uptake (mg/pot)									
P_0	Mean	118.5	11.2	73.7	458	731.7	41.2	5.9	10.6	204	592.0
	Standard deviation	10.2	1.25	6.5	30.8	34.9	2.4	0.52	1.0	11.4	13.9
P_{50}	Mean	135.8	10.2	77.3	475	854.6	96.5	6.5	18.3	297	766.6
	Standard deviation	7.9	0.68	14.1	47.9	54.4	3.0	0.92	1.5	30.6	18.8

consistent and marked effect of fertiliser phosphorus on yield and phosphorus uptake by the rice plants.

Iron uptake occurred at the early stages of growth in both soils. This was probably due to most of the iron being reduced within four weeks of waterlogging. The uptake of manganese probably depends on the iron present in the solution. When there is much more available iron the uptake of manganese is found to be less. Relative to iron, manganese stays for longer periods in the reduced state, therefore, greater uptake of manganese occurs at the later stages of growth. This indicates that there is an antagonistic effect of iron and manganese in the nutrition of rice. The application of fertiliser phosphorus had no marked effect on the uptake of calcium and potassium by the rice plants.

APPENDIX

Table A1. Effect of waterlogging on redox potential of soils incubated with and without urea as a function of time*

Time (weeks)	Soil			
	Macmerry		Giffnock	
	Without urea	With urea	Without urea	With urea
	Redox potential (mV)			
0	402 ± 2	302 ± 2	128 ± 0	72 ± 2
1	-123 ± 11	-145 ± 0	-121 ± 8	-115 ± 0
2	-135 ± 5	-175 ± 12	-143 ± 3	-130 ± 2
3	-188 ± 21	-182 ± 17	-157 ± 7	-157 ± 12
4	-227 ± 14	-227 ± 24	-161 ± 7	-173 ± 13
5	-345 ± 25	-301 ± 51	-161 ± 3	-166 ± 6
6	-270 ± 50	-220 ± 7	-186 ± 23	-155 ± 14
7	-190 ± 40	-159 ± 7	-121 ± 9	-160 ± 19
8	-167 ± 21	-139 ± 7	-206 ± 18	-156 ± 5
9	-147 ± 14	-185 ± 17	-120 ± 15	-135 ± 5
10	-134 ± 3	-166 ± 14	-88 ± 9	-117 ± 1
11	-72 ± 14	-109 ± 8	-70 ± 22	-114 ± 5
12	-42 ± 13	-31 ± 30	-122 ± 8	-104 ± 8
13	-108 ± 34	-110 ± 19	-86 ± 8	-75 ± 2
14	-38 ± 23	17 ± 7	-51 ± 11	-28 ± 13
15	25 ± 6	42 ± 7	-43 ± 11	-82 ± 25
16	45 ± 36	39 ± 11	-65 ± 5	-94 ± 10

* mean of duplicate samples

Table A2. Effect of waterlogging on redox potential of soils incubated with and without urea as a function of time*

Time (weeks)	Soil			
	Tista		Brahmaputra	
	Without urea	With urea	Without urea	With urea
	Redox potential (mV)			
0	389 ± 41	387 ± 25	282 ± 2	309 ± 24
2	-119 ± 12	-161 ± 14	191 ± 56	126 ± 31
4	-161 ± 34	-119 ± 5	290 ± 28	295 ± 22
6	-127 ± 10	-96 ± 8	307 ± 30	161 ± 12
8	-81 ± 11	-75 ± 19	211 ± 9	254 ± 26
10	-41 ± 9	-102 ± 9	117 ± 55	99 ± 50
12	31 ± 4	-65 ± 3	199 ± 80	212 ± 168
14	51 ± 43	-49 ± 10	179 ± 7	135 ± 65
16	45 ± 23	7 ± 2	385 ± 5	262 ± 60

* mean of duplicate samples

Table A3. Effect of waterlogging on pH of soils incubated with and without urea as a function of time*

Time (days)	Soil			
	Macmerry		Giffnock	
	Without urea	With urea	Without urea	With urea
	pH			
0	6.4	6.4	5.5	5.5
1	6.4	6.4	5.7	6.1
2	6.5	6.6	6.1	6.3
3	6.6	6.5	6.2	6.2
4	6.7	6.5	6.3	6.2
5	6.5	6.6	6.1	6.3
6	6.6	6.7	6.2	6.4
7	6.8	6.8	6.4	6.6
8	6.8	6.8	6.3	6.7
9	6.8	6.9	6.5	6.7
10	6.9	6.9	6.5	6.7
11	6.9	6.8	6.5	6.7
12	7.0	6.9	6.5	6.8
13	6.9	7.0	6.6	6.8
14	6.9	6.9	6.6	6.8
15	7.0	7.1	6.7	6.9
16	7.0	7.0	6.8	6.8
17	7.1	7.1	6.9	6.9
18	6.9	7.1	6.6	6.9
19	6.9	7.1	6.7	7.0

Table A3. (Continued)

Time (days)	Soil			
	Macmerry		Giffnock	
	Without urea	With urea	Without urea	With urea
	pH			
20	7.0	7.2	6.7	7.0
21	7.0	7.1	6.7	6.9
22	7.2	7.2	6.9	7.0
23	7.2	7.2	6.9	7.0
24	7.1	7.2	6.8	7.0
25	7.1	7.2	6.9	6.9
26	7.1	7.2	6.8	6.9
27	7.1	7.2	6.8	6.9
28	7.1	7.1	6.8	6.7
29	6.8	6.7	6.5	6.5
30	6.7	6.8	6.4	6.5
31	6.8	7.0	6.3	6.7
32	6.9	7.0	6.4	6.7
33	6.9	7.1	6.6	6.7
34	7.1	7.0	6.6	6.7
35	7.1	6.9	6.6	6.5
36	7.0	7.0	6.6	6.6
37	7.0	6.9	6.7	6.7
38	6.9	7.0	6.4	6.7
39	6.8	7.0	6.3	6.6

Table A3. (Continued)

Time (days)	Soil			
	Macmerry		Giffnock	
	Without urea	With urea	Without urea	With urea
	pH			
40	6.9	7.0	6.3	6.6
41	6.8	7.0	6.3	6.4
42	6.9	6.9	6.3	6.4
43	6.9	7.0	6.3	6.5
44	6.9	6.9	6.5	6.3
45	6.8	6.7	6.3	6.3
46	6.8	6.9	6.3	6.4
47	6.7	6.8	6.1	6.3
48	6.9	6.9	6.2	6.3
49	6.7	6.7	6.1	6.2
50	6.7	7.2	6.1	6.9
51	6.7	7.2	6.1	6.8
52	7.2	7.2	6.7	6.8
53	7.1	7.2	6.6	6.8
54	7.1	7.2	6.6	6.8
55	7.1	7.3	6.6	6.8
56	7.3	7.4	6.7	6.9
57	7.0	7.0	6.6	6.5
58	6.9	6.8	6.5	6.5
59	6.9	7.0	6.4	6.6
60	6.9	7.1	6.4	6.7

Table A3. (Continued)

Time (days)	Soil			
	Macmerry		Giffnock	
	Without urea	With urea	Without urea	With urea
	pH			
61	7.0	7.1	6.5	6.7
62	7.1	7.1	6.6	6.8
63	7.2	7.3	6.7	6.9
64	7.2	7.1	6.9	6.8
65	7.3	7.2	6.9	6.8
66	7.1	7.2	6.7	6.9
67	7.2	7.2	6.8	6.9
68	7.2	7.2	6.7	6.9
69	7.2	7.2	6.8	6.9
70	7.2	7.2	6.8	6.9
71	7.2	7.2	6.8	6.9
72	7.3	7.2	6.9	6.9
73	7.2	7.3	6.8	7.0
74	7.1	7.2	6.7	7.0
75	7.1	7.1	6.8	6.9
76	7.1	7.2	6.8	6.9
77	7.1	7.2	6.7	6.9
78	7.1	7.2	6.7	7.0
79	7.2	7.2	7.0	7.0
80	7.1	7.2	6.8	7.0

Table A3. (Continued)

Time (days)	Soil			
	Macmerry		Giffnock	
	Without urea	With urea	Without urea	With urea
	pH			
81	7.1	7.2	6.7	7.0
82	7.1	7.1	6.8	6.9
83	7.1	7.1	6.7	6.9
84	7.0	7.1	6.7	6.9
85	7.3	7.0	6.3	6.4
86	7.2	7.0	6.4	6.5
87	7.2	7.0	6.4	6.6
88	7.2	7.1	6.5	6.6
89	7.2	7.1	6.6	6.6
90	7.2	7.2	6.6	6.7
91	7.3	7.2	6.7	6.8
92	7.3	7.3	6.8	6.9
93	7.3	7.2	6.8	6.9
94	7.3	7.2	6.8	6.9
95	7.3	7.2	6.8	6.9
96	7.3	7.2	6.7	6.9
97	7.3	7.2	6.7	6.9
98	7.3	7.3	6.7	6.9
99	7.3	7.3	6.8	6.9
100	7.3	7.3	6.9	6.9
101	7.2	7.2	6.8	6.9

Table A3. (Continued)

Time (days)	Soil			
	Macmerry		Giffnock	
	Without urea	With urea	Without urea	With urea
	pH			
102	7.3	7.2	6.7	6.9
103	7.2	7.2	6.7	6.9
104	7.2	7.2	6.7	6.9
105	7.2	7.2	6.7	6.8
106	7.2	7.3	6.8	7.0
107	7.1	7.2	6.8	6.9
108	7.1	7.2	6.7	6.9
109	7.1	7.2	6.7	6.8
110	7.1	7.2	6.7	6.8
111	7.1	7.2	6.6	6.8
112	7.1	7.2	6.6	6.8

* mean of duplicate samples

average error is $\pm$ 0.05

Table A4. Effect of waterlogging on pH of soils incubated with and without urea as a function of time*

Time (weeks)	Soil			
	Tista		Brahmaputra	
	Without urea	With urea	Without urea	With urea
	pH			
0	6.8	6.8	7.6	7.6
1	6.7	6.9	7.1	7.1
2	6.8	6.9	6.9	7.0
3	6.9	6.9	7.0	7.0
4	6.9	7.0	7.0	7.1
5	6.9	7.1	6.8	7.2
6	6.6	7.0	6.5	7.0
7	6.8	7.1	6.8	7.1
8	6.9	7.0	7.0	7.1
9	6.9	6.9	6.9	7.0
10	6.9	6.9	7.1	7.0
11	6.9	7.1	7.1	7.1
12	6.9	6.9	7.2	7.2
13	6.9	7.0	7.0	7.0
14	7.0	6.9	7.1	7.0
15	7.0	7.0	7.2	7.1
16	7.0	7.0	7.2	7.2

* mean of duplicate samples

average error is $\pm$ 0.05

Table A5. Effect of waterlogging on specific conductance of soils incubated with and without urea as a function of time*

Time (days)	Soil			
	Macmerry		Giffnock	
	Without urea	With urea	Without urea	With urea
	Specific conductance (μ mhos/cm)			
0	70 ± 0	76 ± 0	70 ± 0	67 ± 0
1	111 ± 1	178 ± 2	101 ± 3	143 ± 1
2	166 ± 2	276 ± 13	134 ± 0	189 ± 0
3	308 ± 13	356 ± 8	157 ± 0	204 ± 6
4	361 ± 9	428 ± 6	178 ± 1	207 ± 3
5	469 ± 7	489 ± 3	190 ± 1	216 ± 0
6	522 ± 22	548 ± 0	207 ± 2	255 ± 6
7	567 ± 11	643 ± 0	213 ± 2	293 ± 3
8	635 ± 19	654 ± 0	239 ± 1	299 ± 0
9	664 ± 21	666 ± 6	261 ± 8	308 ± 0
10	691 ± 20	759 ± 19	282 ± 0	332 ± 4
11	751 ± 11	795 ± 9	309 ± 1	334 ± 1
12	808 ± 13	822 ± 0	320 ± 0	340 ± 1
13	835 ± 5	891 ± 0	326 ± 2	359 ± 7
14	907 ± 5	936 ± 11	326 ± 2	359 ± 7
15	925 ± 0	954 ± 6	326 ± 2	359 ± 7
16	948 ± 0	1020 ± 7	331 ± 7	374 ± 4
17	954 ± 6	1049 ± 7	333 ± 5	400 ± 11
18	986 ± 0	1057 ± 0	342 ± 6	391 ± 2
19	1020 ± 7	1072 ± 0	337 ± 12	382 ± 3

Table A5. (Continued)

Time (days)	Soil			
	Macmerry		Giffnock	
	Without urea	With urea	Without urea	With urea
	Specific conductance (μ mhos/cm)			
20	1057 ± 0	1096 ± 8	333 ± 8	393 ± 7
21	1080 ± 8	1203 ± 9	335 ± 13	385 ± 9
22	1080 ± 8	1203 ± 9	335 ± 13	388 ± 5
23	1080 ± 8	1223 ± 10	330 ± 12	425 ± 2
24	1080 ± 8	1241 ± 8	354 ± 15	419 ± 8
25	1080 ± 8	1254 ± 21	358 ± 12	425 ± 14
26	1121 ± 17	1265 ± 11	359 ± 7	415 ± 8
27	1166 ± 28	1265 ± 11	345 ± 6	396 ± 11
28	1175 ± 19	1276 ± 22	346 ± 5	387 ± 2
29	1850 ± 0	1762 ± 0	674 ± 31	682 ± 3
30	1542 ± 0	1644 ± 0	545 ± 16	609 ± 2
31	1542 ± 0	1574 ± 0	530 ± 5	571 ± 6
32	1542 ± 0	1542 ± 0	481 ± 18	530 ± 1
33	1510 ± 0	1450 ± 0	458 ± 28	485 ± 5
34	1465 ± 15	1541 ± 0	439 ± 26	499 ± 3
35	1321 ± 24	1541 ± 0	390 ± 24	499 ± 3
36	1436 ± 13	1450 ± 0	400 ± 40	440 ± 8
37	1309 ± 11	1436 ± 13	391 ± 31	436 ± 6
38	1286 ± 11	1409 ± 13	381 ± 27	432 ± 7
39	1276 ± 22	1409 ± 13	355 ± 19	430 ± 10
40	1299 ± 45	1409 ± 13	355 ± 19	437 ± 2

Table A5. (Continued)

Time (days)	Soil			
	Macmerry		Giffnock	
	Without urea	With urea	Without urea	With urea
	Specific conductance (μ mhos/cm)			
41	1310 ± 34	1321 ± 23	352 ± 19	379 ± 5
42	1310 ± 34	1451 ± 0	351 ± 21	414 ± 1
43	1276 ± 22	1357 ± 12	329 ± 21	372 ± 6
44	1233 ± 0	1321 ± 23	316 ± 22	360 ± 1
45	1254 ± 21	1345 ± 0	321 ± 31	378 ± 0
46	1254 ± 21	1345 ± 0	309 ± 27	377 ± 1
47	1298 ± 22	1345 ± 0	320 ± 35	370 ± 2
48	1254 ± 21	1345 ± 0	313 ± 31	370 ± 2
49	1254 ± 21	1383 ± 13	304 ± 31	369 ± 3
50	1254 ± 21	1309 ± 11	296 ± 32	343 ± 8
51	1194 ± 19	1265 ± 11	281 ± 27	342 ± 6
52	1233 ± 20	1276 ± 22	286 ± 29	337 ± 7
53	1233 ± 20	1298 ± 0	286 ± 33	325 ± 3
54	1233 ± 20	1194 ± 0	279 ± 28	299 ± 2
55	1213 ± 19	1276 ± 0	274 ± 27	324 ± 5
56	1156 ± 18	1265 ± 11	242 ± 24	302 ± 6
57	1850 ± 0	1762 ± 0	642 ± 30	602 ± 70
58	1574 ± 0	1542 ± 0	501 ± 38	549 ± 28
59	1682 ± 0	1542 ± 0	518 ± 50	519 ± 9
60	1626 ± 17	1542 ± 0	455 ± 44	496 ± 3
61	1574 ± 0	1526 ± 16	432 ± 32	483 ± 9

Table A5. (Continued)

Time (days)	Soil			
	Macmerry		Giffnock	
	Without urea	With urea	Without urea	With urea
	Specific conductance (μ mhos/cm)			
62	1574 ± 0	1526 ± 16	414 ± 33	482 ± 11
63	1574 ± 0	1510 ± 0	401 ± 29	466 ± 1
64	1526 ± 16	1465 ± 14	383 ± 27	440 ± 2
65	1480 ± 0	1451 ± 0	362 ± 29	414 ± 1
66	1542 ± 0	1451 ± 0	362 ± 29	432 ± 2
67	1511 ± 31	1423 ± 0	347 ± 32	414 ± 1
68	1511 ± 31	1396 ± 26	334 ± 26	409 ± 3
69	1465 ± 15	1409 ± 13	325 ± 27	403 ± 3
70	1436 ± 13	1423 ± 0	309 ± 23	394 ± 5
71	1409 ± 13	1383 ± 13	300 ± 21	373 ± 2
72	1298 ± 23	1345 ± 0	282 ± 20	368 ± 2
73	1409 ± 13	1333 ± 12	291 ± 19	368 ± 2
74	1383 ± 13	1333 ± 12	283 ± 11	374 ± 6
75	1370 ± 25	1276 ± 0	277 ± 13	347 ± 9
76	1345 ± 24	1276 ± 0	277 ± 13	346 ± 8
77	1276 ± 22	1287 ± 11	251 ± 12	348 ± 12
78	1276 ± 22	1213 ± 20	255 ± 10	318 ± 10
79	1204 ± 29	1223 ± 10	234 ± 13	331 ± 8
80	1214 ± 39	1203 ± 10	237 ± 17	334 ± 12
81	1194 ± 38	1214 ± 39	235 ± 13	339 ± 9
82	1184 ± 28	1157 ± 36	243 ± 19	330 ± 14

Table A5. (Continued)

Time (days)	Soil			
	Macmerry		Giffnock	
	Without urea	With urea	Without urea	With urea
	Specific conductance (μ mhos/cm)			
83	1166 ± 28	1139 ± 35	242 ± 19	329 ± 10
84	1113 ± 25	1148 ± 27	238 ± 22	333 ± 11
85	1749 ± 20	1843 ± 2	436 ± 1	552 ± 16
86	1737 ± 16	1705 ± 16	411 ± 19	498 ± 5
87	1721 ± 20	1682 ± 0	404 ± 19	488 ± 4
88	1682 ± 30	1641 ± 0	386 ± 16	470 ± 7
89	1654 ± 28	1558 ± 0	385 ± 17	449 ± 14
90	1627 ± 36	1495 ± 0	370 ± 18	422 ± 13
91	1609 ± 35	1537 ± 11	351 ± 18	422 ± 13
92	1534 ± 39	1440 ± 11	330 ± 18	390 ± 16
93	1526 ± 16	1416 ± 7	319 ± 16	383 ± 12
94	1534 ± 39	1480 ± 0	313 ± 15	397 ± 8
95	1511 ± 46	1423 ± 0	315 ± 21	375 ± 10
96	1488 ± 38	1375 ± 0	314 ± 21	362 ± 8
97	1485 ± 40	1376 ± 6	306 ± 24	359 ± 9
98	1440 ± 40	1383 ± 13	291 ± 19	353 ± 9
99	1376 ± 26	1333 ± 12	288 ± 19	353 ± 9
100	1268 ± 35	1281 ± 5	266 ± 17	330 ± 8
101	1272 ± 29	1304 ± 6	257 ± 16	335 ± 13
102	1260 ± 27	1272 ± 7	261 ± 14	325 ± 5
103	1250 ± 37	1213 ± 0	266 ± 19	308 ± 10

Table A5. (Continued)

Time (days)	Soil			
	Macmerry		Giffnock	
	Without urea	With urea	Without urea	With urea
	Specific conductance (μ mhos/cm)			
104	1237 ± 43	1231 ± 2	261 ± 18	308 ± 10
105	1182 ± 40	1222 ± 28	247 ± 16	311 ± 10
106	1182 ± 40	1168 ± 21	244 ± 16	302 ± 4
107	1118 ± 38	1145 ± 10	239 ± 15	302 ± 4
108	1118 ± 38	1125 ± 4	242 ± 14	299 ± 3
109	1031 ± 11	1038 ± 17	239 ± 15	302 ± 4
110	1081 ± 39	1048 ± 32	236 ± 16	281 ± 5
111	1074 ± 39	1094 ± 37	239 ± 17	289 ± 4
112	1051 ± 37	1086 ± 44	230 ± 17	287 ± 3

* mean of duplicate samples

Table A6. Effect of waterlogging on specific conductance of soils incubated with and without urea as a function of time*

Time (days)	Soil			
	Tista		Brahmaputra	
	Without urea	With urea	Without urea	With urea
	Specific conductance (μ mhos/cm)			
0	173 ± 0	155 ± 13	269 ± 3	288 ± 1
7	667 ± 6	759 ± 19	490 ± 13	550 ± 10
14	943 ± 6	1064 ± 7	598 ± 29	684 ± 6
21	1027 ± 0	1088 ± 16	646 ± 19	691 ± 0
28	1027 ± 14	1080 ± 8	669 ± 16	714 ± 10
35	1175 ± 19	1194 ± 19	676 ± 3	747 ± 0
42	1049 ± 7	1157 ± 36	655 ± 0	755 ± 0
49	1035 ± 22	1141 ± 53	658 ± 3	729 ± 4
56	1035 ± 22	1123 ± 70	664 ± 3	740 ± 0
63	1189 ± 5	1276 ± 11	673 ± 12	903 ± 11
70	1138 ± 0	1224 ± 30	673 ± 12	846 ± 5
77	1054 ± 26	1175 ± 19	667 ± 6	804 ± 8
84	970 ± 10	1043 ± 36	644 ± 17	747 ± 7
91	1117 ± 4	1208 ± 5	679 ± 6	788 ± 25
98	1039 ± 11	1097 ± 0	664 ± 3	717 ± 31
105	1001 ± 20	1081 ± 16	658 ± 3	709 ± 23
112	957 ± 3	1069 ± 27	606 ± 10	693 ± 32

* mean of duplicate samples

Table A7. Concentration of phosphorus, iron, manganese, calcium and potassium in rice plants after first harvest

Buckets	Soil									
	Macmerry					Giffnock				
	P	Fe	Mn	Ca	K	P	Fe	Mn	Ca	K
	Plant content (μg/g dry matter)									
1	2400	700	1200	10500	6200	1900	850	225	7250	9700
2	2437	750	1150	10750	6050	1775	700	200	6250	9150
3	2775	700	1350	10000	6800	1675	975	275	7250	7500
4	3125	850	1200	9500	7250	1662	725	250	8000	8850
5	2875	1000	1300	9750	7250	1587	525	225	8250	8450
Mean	2722	800	1240	10100	6710	1720	755	235	7400	8730
Standard deviation	305	127	82	518	567	121	169	29	783	825

Table A8. Concentration of phosphorus, iron, manganese, calcium and potassium in rice plants after second harvest

Buckets	Soil									
	Macmerry					Giffnock				
	P	Fe	Mn	Ca	K	P	Fe	Mn	Ca	K
	Plant content (µg/g dry matter)									
1	2200	362	1662	9875	3600	1300	250	575	10000	5300
2	2875	525	2000	10000	4900	1137	237	475	8000	4100
3	2525	262	2600	9750	3900	1150	300	500	9000	4700
4	2512	200	2600	10125	4200	1075	225	475	8375	3700
5	2425	200	1625	8875	3750	950	262	375	10625	3900
Mean	2507	310	2097	9725	4070	1122	255	480	9200	4340
Standard deviation	243	137	482	495	514	127	29	72	1099	654

Table A9. Total uptake (mg/pot) of phosphorus, iron, manganese, calcium and potassium by rice plants after first harvest

Buckets	Soil									
	Macmerry					Giffnock				
	P	Fe	Mn	Ca	K	P	Fe	Mn	Ca	K
	Plant uptake (mg/pot)									
1	82.32	24.01	41.16	360.15	212.66	31.92	14.28	3.78	121.80	162.96
2	89.19	27.45	42.09	393.45	221.43	30.18	11.90	3.40	106.25	155.55
3	101.57	25.62	49.41	366.00	248.88	26.13	14.43	4.29	113.10	117.00
4	121.56	33.07	46.68	369.55	282.03	27.09	11.82	4.08	130.40	144.26
5	107.81	37.50	48.75	365.63	271.88	23.96	7.93	3.40	124.58	127.60
Mean	100.49	29.53	45.62	370.96	247.38	27.86	12.07	3.79	119.23	141.47
Standard deviation	15.46	5.62	3.80	13.02	30.34	3.19	2.63	0.40	9.57	19.10

Table A10. Total uptake (mg/pot) of phosphorus, iron, manganese, calcium and potassium by rice plants after second harvest

Buckets	Soil									
	Macmerry					Giffnock				
	P	Fe	Mn	Ca	K	P	Fe	Mn	Ca	K
	Plant uptake (mg/pot)									
1	88.88	14.63	67.15	398.95	145.80	35.75	6.98	16.04	279.00	147.87
2	96.60	17.64	67.20	336.00	164.64	29.68	6.19	12.40	208.80	107.01
3	92.67	9.62	95.42	357.83	143.13	32.20	8.40	14.00	252.00	131.60
4	95.46	7.60	98.80	384.75	159.60	34.19	6.30	15.11	266.33	117.66
5	84.88	7.00	56.88	310.63	131.25	21.94	6.05	8.66	245.44	90.09
Mean	91.70	11.30	77.09	357.63	148.88	30.75	6.78	13.24	250.31	118.85
Standard deviation	4.84	4.64	18.79	35.78	13.39	5.42	0.97	2.90	26.60	22.21

Table A11. Dry matter yield of rice grown in the presence and absence of added phosphorus

Treatment	Buckets	Soil	
		Macmerry	Giffnock
		Plant yield (g/pot)	
P_0	1	50.10	24.30
	2	49.00	22.20
	3	43.30	24.50
	4	47.00	24.10
	5	44.80	21.90
	6	44.80	24.40
	Mean	46.50	23.57
	Standard deviation	2.66	1.18
P_{50}	1	50.60	30.20
	2	46.10	32.50
	3	53.00	32.60
	4	48.20	32.70
	5	47.00	32.50
	6	46.80	30.00
	Mean	48.62	31.75
	Standard deviation	2.66	1.28

Table A12. Concentrations of phosphorus, iron, manganese, calcium and potassium in rice plants in the presence and absence of added phosphorus

Treatment	Buckets	Soil									
		Macmerry					Giffnock				
		P	Fe	Mn	Ca	K	P	Fe	Mn	Ca	K
		Plant content (µg/g dry matter)									
P_0	1	2700	200	1500	10000	15000	1850	260	420	8500	24500
	2	2575	265	1725	10000	16000	1825	280	555	9000	26500
	3	2500	265	1625	10000	16000	1600	255	465	9000	23500
	4	2400	260	1525	9500	15500	1775	230	415	8500	25500
	5	2600	230	1675	10000	16500	1750	230	425	8500	26500
	6	2500	225	1450	9500	15500	1700	250	425	8500	24500
	Mean	2546	241	1583	9833	15750	1750	251	451	8667	25167
	Standard deviation	103.0	26.7	108.0	258.2	524.4	90.8	19.0	54.0	258.2	1211.0

Table A12. (Continued)

Treatment	Buckets	Soil									
		Macmerry					Giffnock				
		P	Fe	Mn	Ca	K	P	Fe	Mn	Ca	K
		Plant content (μg/g dry matter)									
P_{50}	1	2700	195	1650	10000	17500	3050	175	545	10250	24500
	2	2450	215	1200	9000	16500	3100	195	530	10000	23500
	3	2800	205	1825	10000	17000	3000	210	615	8500	24500
	4	2850	210	1450	10500	18500	2925	245	545	10000	23500
	5	2925	200	1775	10000	18500	3025	210	615	9000	23500
	6	2675	240	1600	9000	17500	3150	195	600	8250	25500
	Mean	2733	211	1583	9750	17587	3042	205	575	9333	24167
	Standard deviation	167.0	15.9	230.0	612.4	801.0	78.5	23.5	39.1	861.2	816.5

Table A13. Uptake of phosphorus, iron, manganese, calcium and potassium by rice plants in the presence and absence of added phosphorus

Treatment	Buckets	Soil									
		Macmerry					Giffnock				
		P	Fe	Mn	Ca	K	P	Fe	Mn	Ca	K
		Plant uptake (mg/pot)									
P_0	1	135.3	10.0	75.2	501	751.5	45.0	6.3	10.2	207	595.4
	2	126.2	13.0	84.5	490	784.0	40.5	6.2	12.3	200	588.3
	3	108.3	11.5	70.4	433	692.8	39.2	6.2	11.4	221	575.8
	4	112.8	12.2	71.7	447	728.5	42.8	5.5	10.0	205	614.6
	5	116.5	10.3	75.0	448	739.2	38.3	5.0	9.3	186	580.4
	6	112.0	10.1	65.0	426	694.4	41.5	6.1	10.4	207	597.8
	Mean	118.5	11.2	73.7	458	731.7	41.2	5.9	10.6	204	592.0
	Standard deviation	10.2	1.25	6.5	30.8	34.9	2.4	0.52	1.0	11.4	13.9

Table A13. (Continued)

Treatment	Buckets	Soil									
		Macmerry					Giffnock				
		P	Fe	Mn	Ca	K	P	Fe	Mn	Ca	K
		Plant uptake (mg/pot)									
P_{50}	1	136.6	9.9	83.5	506	885.5	92.1	5.3	16.5	310	739.9
	2	129.9	9.9	55.3	415	760.7	100.8	6.3	17.2	325	763.8
	3	148.8	10.9	96.7	530	901.0	97.8	6.8	20.0	277	798.7
	4	137.4	10.1	69.9	506	891.7	95.6	8.0	17.8	327	768.5
	5	137.5	9.4	83.4	470	869.5	98.3	6.8	20.0	293	763.8
	6	125.2	11.2	74.9	421	819.0	94.5	5.9	18.0	248	765.0
	Mean	135.8	10.2	77.3	475	854.6	96.5	6.5	18.3	297	766.6
	Standard deviation	7.9	0.68	14.1	47.9	54.4	3.0	0.92	1.5	30.6	18.8

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