FORMS AND DISTRIBUTION OF IRON AND MANGANESE IN RICE SOILS OF KERALA

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CERTIFICATE

This is to certify that the thesis herewith submitted contains the results of bona fide research work carried out by Sri P. Narayana Pisharody under my supervision. No part of the work embodied in this thesis has been submitted earlier for the award of any degree.

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VcL

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INTRODUCTION

CHAPTER I

INTRODUCTION

Rice is the major food crop of Kerala and covers an area of approximately two million acres. It is grown almost entirely under submerged conditions and on soils which vary widely in physical and chemical characteristics. Considerable amount of work has been done on the chemical and agronomic problems of rice soils but most of it pertains to the major plant nutrients only. Studies on micronutrients in these soils have received very little attention until quite recently.

Of the various micronutrients required for the nutrition of the rice plant, Iron and Manganese are needed in much larger amounts than the others and their essentiality for optimum growth and yield are well established. Hence, the forms and distribution of these two micronutrients in soils growing Paddy acquire considerable importance from the point of successful cultivation of this crop. This study assumes still greater importance as iron and manganese undergo profound changes in submerged soils which are liable to be detrimental to the growing crop under the water-logged conditions in which rice is commonly cultivated. In the paddy soils of Kerala these transformations are further complicated because of their strong acidity. It was, therefore, felt that it would be worthwhile to study the forms and distribution of iron and manganese in the different Paddy soils of this State both under submerged and dry conditions.

Iron and manganese occur in soils in various forms with widely divergent solubilities. Most of the soils in Kerala contain an abundance of iron but the bulk of it is present in forms that are of little use to crops. This is due to many interacting factors which affect and limit the iron that can be assimilated by plants. Deficiency of iron in available form which is manifested as chlorosis is a common occurrence in upland rice soils. In submerged soils, on the other hand, the problem is not one of deficiency of iron but of toxicity caused by excess amounts of soluble iron present under the reducing conditions prevailing in these soils.

According to Dhamija et al (1956), deficiency of manganese in rice soils of India is rare under field conditions. There is, however, danger of toxicity due to excess of soluble manganese in water-logged soils because manganese behaves exactly like iron under submerged conditions.

The need for precise data on the forms and distribution of iron and manganese in rice soils of Kerala is obvious and will be most useful in the efficient management of these soils. This problem assumes added importance in the context of the serious shortage in food in this state and the efforts that are being made to enhance rice yields.

In the light of the above observations, the present work was undertaken with the following main objectives:

(i) To assess the forms and distribution of iron and manganese in the rice soils of Kerala.

(ii) To investigate the influence of submergence on the various categories of these elements.

(iii) To study the correlations, if any, between the different forms of iron and manganese with the physical and chemical characteristics of the soil.

REVIEW OF LITERATURE

CHAPTER II

REVIEW OF LITERATURE

The literature reviewed here pertains to the forms and distribution of manganese and iron in soil profiles as influenced by environmental factors.

A: Forms of manganese:

Manganese occurs in soils in three widely different forms, viz., water soluble, exchangeable and higher oxides.

Kelley (1909) in a study of pine-apple soils of Hawaii recorded several patterns of distribution of total manganese in relation to the physical and chemical properties of these soils.

Investigations on the forms and availability of manganese in soils carried out by Piper (1931), Steenbjerg (1935) and Heintze (1938) revealed that only biv lent forms of manganese are available and not the higher oxides. Leeper (1935), however, held the view that not only bivalent manganese but a portion of higher oxides can also be assimilated by plants. This portion he termed as reducible oxides and the rest of the oxides as "inert oxides".

Sherman et al (1942-43) grouped water soluble, exchangeable and reducible oxides of manganese under 'active manganese'. Sherman and Harmer (1943) have also postulated that these forms of manganese remain in equilibrium in the soil as follows:

$$\text{Manganous Mn} \rightleftharpoons \text{Colloidal hydrated } MnO_2$$
$$\rightleftharpoons \text{inert Oxides.}$$

Biswas (1953) presented data on the distribution of different categories of manganese viz., total, active, exchangeable and water soluble, in the profiles of forty uncultivated soils from various parts of India.

Investigations on the forms and distribution of manganese in soils growing paddy were undertaken by Dhamija *et al* (1956) and they correlated the variations of the different categories with the physical and chemical properties of the soil.

Heintze (1957) from his experiments conducted at Rothamsted observed that in mineral soils low in organic matter, higher oxides of manganese approaching the manganese dioxide type were formed by oxidation of added manganese. But in alkaline organic soils no portion of difficultly reducible higher oxides of manganese were found or formed.

Nozdrunova *et al* (1958) investigated the seasonal variations in available and exchangeable manganese in sod podzolic soil and reported that the maximum content of exchangeable manganese was in summer.

Randhava et al (1961) examined forty-one soil samples from seven profiles for various forms of manganese viz., total, water soluble, exchangeable, reducible and active. He noted that several relationships exist between the chemical and physical properties of soils and the quantity and different forms of manganese.

Mandal (1961) carried out pot culture experiments with paddy and concluded that iron and manganese in the soil organic complex did not show any significant changes during the period of growth of the crop. ✓

B. Distribution of manganese in the profile:

Kelley (1909) noticed that manganese content generally decreased with depth of profile. Similar observations were made by Blair and Prince (1936).

Hoon and Dhawan (1943) found that in soils of the Punjab, manganese was present in the soil profile right down to the water table with slight accumulation in certain sections of the profile where the water table was low.

Koeings (1950) recorded the occurrence of a plough pan below the top soil followed by a hard pan layer rich in manganese dioxide in the profile of an irrigated paddy soil.

Shiori and Yoshida (1951) observed an accumulation of active manganese in the subsoil and attributed it to the leaching of surface soil.

Biswas (1953) found that the distribution of total and active manganese in black soils was either uniform throughout the profile or decreased slightly with depth with an accumulation in the subsoil, while in other soils, the distribution did not follow any regular pattern. His work also revealed that the level of both exchangeable and water soluble manganese was maximum in the surface soil and decreased gradually or remained uniform down the profile.

Ting and Yu (1958) followed the oxidation-reduction processes in paddy soils and reported that manganese content was highest in the illuvial horizon and much more than in the gley horizon.

Randhawa et al (1961) showed that in Punjab soils the total manganese increased with depth of profile, whereas other forms of this element decreased.

C. Influence of soil reaction on the forms and distribution of manganese:

It is now well established that soil reaction has a profound influence on the forms and distribution of manganese in the soil.

Willis (1932) observed that liming decreased the solubility of manganese and attributed this to the change in soil reaction from acidity to near neutrality. Later work of Blair and Prince (1936) has confirmed this finding. They noted that normal soils which were slightly to moderately acid usually contain sufficient manganese for plant growth, but when these soils were heavily limed the soluble manganese was converted into insoluble or slowly soluble forms.

Prince and Toth (1938) investigated the electro dialytic behaviour of solutions of $MnCl_2$ and soils and concluded that the mobility of manganese increased as the pH of the soil decreased.

Dhawan *et al* (1949) observed that no oxidation of manganese takes place in soils at pH values above 9.0.

Biswas (1951) reported that the relative amounts of replaceable forms of manganese in soils were greatly influenced by soil reaction. He found that increase in pH was followed by decrease in the amount of bivalent forms of manganese and vice versa.

The studies of Stenuit and Piot (1957) on the relationship between pH and manganese content of sandy soils indicated that deficiency of manganese in oats never occurs at pH less than 5.5 and only develops at pH greater than 7.0. He attributed this to the influence of soil reaction on the availability of manganese.

Similar results were obtained in experiments conducted by Eberhardt (1958) on the influence of deep and shallow ploughings on the distribution of manganese in soils. In soils of high acidity deep ploughing resulted in a slight increase in active manganese and shallow ploughing in a marked decrease. His work also revealed that since acidification of soil occurred much sooner with shallow than with deep ploughing, accumulation of active manganese took place in the subsoil of shallow ploughed plots due to a shift from easily reducible manganese to exchangeable manganese.

Sanchez and Kamprath (1959) concluded from incubation tests and field experiments that large portion of added manganese was rapidly converted to non-exchangeable form at pH 6.7 to 7.1.

Runge and Leon (1960) suggested that soil reaction was the best index of manganese availability.

Randhawa et al (1961) found more of water soluble, exchangeable, easily reducible and active manganese in acid soils than in alkaline soils.

D. Influence of water-logging on the forms and distribution of manganese:

Conner (1932) adduced evidence that when soil was kept under reduced conditions by water-logging the soluble form of manganese increased. Pearsal (1950) in a study on wet soils came to the conclusion that soils in the reducing state liberate large amounts of exchangeable cations, particularly manganese.

Clark and Resenicky (1956) investigating the mineral element levels in the soil solution of a submerged soil recorded a hundred fold increase of manganese.

Tomlinson (1957) traced the seasonal variations in pH of the surface layer of some rice soils of Sierra Leone and did not find any regular variation in the availability of manganese. On the contrary, Kosegarten (1957) noted a decrease in exchangeable and active manganese and an increase in easily reducible manganese under drought conditions and the reverse under flooded conditions.

Runge and Leon (1960) reported that increasing wetness of soil profile resulted in loss of manganese from the A horizon and its accumulation in the lower part of the B horizon.

According to Shigenori (1961) water-logging converted manganese dioxide to manganous manganese.

Mandal (1961) studied the transformation of manganese in water-logged rice soils and came to the conclusion that the reducible manganese comprising higher oxides, such as, MnO_2, Mn_2O_3 and Mn_3O_4, decreased for sometime after the soil was water-logged and then increased to a level higher than that at the start. In later work he (1962) showed that the concentration of manganese in drainage water increased when soils were kept under an atmosphere of 10 percent oxygen and the content increased progressively with the period of water-logging.

E. Influence of organic matter on the forms and distribution of manganese:

Heintze and Mann (1951) in a study of the various fractions of manganese in neutral and alkaline organic soils found that the percentage of total soil manganese decreased with increase in soil organic matter which they attributed to the retention of bivalent manganese by the organic complex.

The work of Gopala Rao (1956) on the effect of green manuring on the availability of manganese in swamp paddy soils showed that the release of manganese on submergence was enhanced by green manuring.

Dhamija et al (1956) maintained that in paddy soils the distribution of the various forms of manganese depended on the organic matter content.

Heintze (1957) observed that manganese of a higher valency form remained in combination with organic matter. He also pointed out that manganese originally present in soluble organic matter fractions migrates anionically, whereas manganese added and retained by such fractions moved predominantly as a cation.

Kosegarten (1957) suggested that the increase in exchangeable manganese under water-logged conditions was due to the effect of soil organic matter.

The experiments of Sanchez and Kamprath (1959) illustrate the effect of organic matter on the availability of native and applied manganese. The results show that when peat was added to soil low in organic matter, the exchangeable manganese increased in acid soils and acid extractable manganese decreased in limed soils.

F. Influence of mechanical composition of soils on the forms and distribution of manganese:

Blair and Prince (1936) observed a significant relationship between the amount of clay and silt and the total manganese content of the soil. Hoon *et al* (1941, 1942) and Koch (1946) confirmed this finding.

Biswas (1953) pointed out that in Indian soils total manganese increased with clay content. Similar observations have been reported by Khanna *et al* (1954) Toth and Romney (1954) and Wahab and Bhatti (1958).

Karim *et al* (1960) found that in some East Pakistan soils the exchangeable manganese content of alluvial, coastal saline and hill tract soils were similar despite textural differences.

Pirta and Ollat (1961) reported that trace elements, especially manganese, tended to be high in clayey horizons. Zende and Pharaido (1961) also drew attention to the increase in extractable manganese with decreasing particle size and vice versa.

2: A: Forms and distribution of iron in the profile:

The element iron occurs in soils in the form of primary minerals, silicate clays and hydrated oxides with their organic and inorganic derivatives. According to Ponnamperuma (1955), of these different forms, the hydrated oxides are by far the most important and the seat of all the chemical and biochemical reactions involving iron.

Koeings (1950) reported the occurrence of a plough pan below the top soil followed by a hard pan rich in iron hydroxides in the profile of an irrigated rice soil. Shiori and Yoshida (1951) observed that free iron was leached from the furrow slice and accumulated in the subsoil.

Dhanija *et al* (1956) found that the percentages of ferrous and ferric iron were high in the presence of active manganese in paddy soils of India. Kamoshita (1956) recorded similar observations in paddy soils of Japan.

Ir. *et al* (1958) followed the transformations of iron in rice fields and recorded the seasonal variations. In the furrow horizon the percentage of ferrous iron was high and peak values were reached in August. In the A horizon, values were low but increased towards the B horizon. Appreciable amounts of ferrous iron occurred in the lower horizons.

Gile Jr. (1958) working on the fragi-pan and water table relationships of brown humic gley soils reported a concentration of Fe_2O_3 in the upper solum and in the fragi-pan. Ting and Yu (1958) observed that the iron content was highest in the illuvial horizon and much more than in the gley horizon.

Mandal (1961) found a sharp rise of insoluble ferrous iron when soils were water-logged.

B. Influence of organic matter on the forms and distribution of iron.

Mann (1930) noted increased solubility of iron when organic matter was added to soils.

Islam and lahi (1954) studied the reversion of ferric iron to ferrous iron in rice soils and reported that addition of oxidisable materials, especially organic matter, promoted reduction of iron.

Gopala Rao (1956) showed that the availability of iron in red loams increased in the presence of organic matter. Similar results were obtained by Ponnamperuma (1955) and Dhamija et al (1956).

Krishnamoorthy (1959) suggested the addition of green manure to paddy soils to render iron available. But according to Kiuchi and Omukai (1959), the solubility of iron in paddy soils is not affected by the organic matter content.

Mandal (1961) furnished evidence that in the presence of organic matter the reduction of iron from the ferric to ferrous form was more intensive under water-logged conditions.

C. Influence of water-logging on the forms and distribution of iron.

The occurrence of large amounts of iron in the reduced condition in water-logged soils has been reported by Pearsall (1950). He observed that in a marshy soil the exchangeable ferrous iron was as high as 248 mg. per 100 g. of dry soil. Islam and Elahi (1954) demonstrated that in laterite soils kept under water-logged conditions there was a progressive reduction of ferric iron to the ferrous form.

Ponnamperuma (1955) obtained 147 p.p.m. and 80 p.p.m. of ferrous iron respectively in percolates of a water-logged soil on the 67th day, with and without oat straw. Clark and Resnicky (1956) recorded as much as 100 percent increase in the iron content of soil percolates on continued submergence. Similar results were reported by De and Mandal (1957) and Gopala Rao (1956).

Iri et al (1957) studied the variations in ferrous iron content in profiles of rice soils under flooded conditions and noted that: (i) in a well drained site ferrous form in the furrow horizon increased when irrigation started and decreased almost to zero when it ceased, (ii) at 20-70 cm. depth the ferrous form was low but increased after flooding, (iii) at 70-100 cm. depth more iron occurred and the seasonal changes were only slight.

Gile (1958) recorded a concentration of Fe_2O_3 in the upper solum of the fragi-pan. But when the water table was above the fragi-pan, some of the FeO was laterally leached down and was oxidised. Investigations by Money and Kurup (1961) on the phenomenon of scum formation in the acid paddy soils of Kuttanad in Kerala revealed that appreciable amounts of iron are brought into solution by submergence. Further, iron in the reduced state is oxidised to the ferric form by atmospheric oxygen and insoluble ferric complex forms a reddish brown scum on the surface of water.

The transformation of iron from the ferric to ferrous form under water-logged conditions was also observed by Shigenori (1961) and Mandal (1961). Mandal (1962) and Rajaram (1964) recorded an increase in concentration of iron in soil percolates kept water-logged with increased period of submergence.

MATERIALS AND METHODS

CHAPTER III

MATERIALS AND METHODS

The material for this investigation consisted of six profiles from important paddy growing regions in Kerala. They include a wide range of soils which differ markedly in nature and characteristics.

It was necessary to collect the soil profiles in the submerged state as well as in the dry condition for the present study. It is well known that the collection of typical profiles of inundated soils is by no means a simple matter. This difficulty was got over by using a soil sampler improvised locally. It is extremely simple in design and consists merely of a piece of bamboo, 1.5 meters in length and about 8 cm. in diameter at the broad end. The internodes were knocked off and the wider end slightly pointed so that the sampler could easily penetrate into soft soil. This sampler proved quite satisfactory for the collection of profiles of soils in the waterlogged condition. It was driven into the soil with a wooden mallet to a depth of 75 cm. and then carefully withdrawn so that the column of soil inside remained unbroken. The excess water was drained off and both ends of bamboo closed with polythene paper. The profiles thus collected were taken to the laboratory without delay and the bamboos were split open longitudinally. In all cases the soil column was about 75 cm. long and unbroken. A separate soil sampler was obviously required for each profile but this was of little consequence as it is easily made and the cost is negligible.

Examination of the profiles showed that there was no horizon differentiation in any of them. Consequently, each profile was divided arbitrarily into two horizons, viz., a surface horizon (0 - 22 cm.) and a sub-surface horizon (22 - 75 cm.). As roots of the paddy plant seldom reach beyond this depth it was felt that there was no need to examine the soils at greater depths. Brief descriptions of the morphological characters of the different profiles together with important site features are given below:-

PROFILE I

Location:	Central Rice Research Station, Pattambi, Palghat District (Laterite region).
Topography:	Level
Rainfall:	281 cm.
Vegetation:	Rice
Special features:	Double crop land. Water-logged from July to January.
Depth (cm.):	Description
0 - 22	Yellowish brown (10 YR 5/6) soft sandy clay loam; gritty and loose, soft when wet; roots present; slightly acidic (pH. 6.1)

22 - 75	Yellowish brown (10 YR 5/6) sandy loam; gritty, loose and not sticky; roots absent; slightly acidic (pH 6.1)

PROFILE II

Location:	Agricultural Research Station, Monkombu. Alleppey District (Alluvial region)
Topography:	Level
Rainfall:	350 cm.
Vegetation:	Rice
Special features:	Single crop land. Water-logged from March to September.
Depth (cm.)	Description
0 - 22	Very dark brown (10 YR 2/2) Clay; very sticky when wet; forms hard lumps when dry; roots present; Acidic, (pH 5.2).
22 - 75	Very dark brown (10 YR 2/2) Silty Clay; sticky when wet and hard when dry; roots absent; very strongly acidic; (pH 2.9)

PROFILE III

Location:	Taliparamba - one mile from Taliparamba town on Taliparamba-Payyannur Road Cannanore District. (Laterite region)
Topography:	Level with hills on one side.
Rainfall:	354 cm.
Vegetation:	Rice
Special features:	Double crop land. Well drained.

Depth (cm.)	Description
0 - 22	Dark yellowish brown (10 YR. 4/4) sandy clay; grity and loose; soft when wet; roots present; slightly acidic (pH 6.4).
22 - 75	Dark yellowish brown (10 YR 4/4); sandy clay loam; grity and fribable; slightly acidic (pH 6.3)

PROFILE IV

Location: Rice Research Station, Mannuthy, Trichur District (laterite region).

Topography: Undulating but terraced. Hills on one side.

Rainfall: 326 cm.

Vegetation: Rice

Special features: Double crop land. Second crop raised with irrigation.

Depth (cm.)	Description
0 - 22	Dark yellowish brown (10 YR 3/4) sandy clay; grity very loose; not sticky; roots present; acidic (pH 5.4).
22 - 75	Dark yellowish brown (10 YR 3/4) sandy clay loam; grity and friable; roots absent, Acidic (pH 5.7).

PROFILE V

Location: Vechoor, on the Vaikom-Vechoor Road, Kottayam District (Kari Region)

Topography: Level

Rainfall: 295 cm.

Vegetation: Rice

Special features: Water-logged for the major part of the year.

Depth (cm.)	Description
0 - 22	Very dark grey (10 YR 3/1) clay; highly plastic and sticky when wet; forms hard lumps on drying; roots present; strongly acidic (pH 4.1).
22 - 75	Very dark grey (10 YR 3/1) silty clay; plastic and sticky when wet; forms hard lumps on drying; yellow mottlings and concretions present; slightly acidic, (pH 5.8).

PROFILE VI

Location: Rice Research Station, Kayamkulam Alleppey District (Sandy region).

Topography: Level

Rainfall: 281 cm.

Vegetation: Rice and Gingelly in rotation.

Depth (cm.)	Description
0 - 22	Dark grey (10 YR 4/1) sandy grity and very loose; roots present; slightly acidic (pH 5

22 - 75 Light grey (2.5 YR 7/2) sandy grity and very loose; organic matter practically absent; slightly acidic, (pH 5.7).

Analytical Procedures:

Standard analytical procedures as described by Piper (1950) and Jackson (1960) were adopted in the examination of the soils. The methods are outlined below:

1. Moisture:

10 g. soil was dried in an air oven at 100 to 105°C to constant weight and the loss in weight was expressed as percent on oven dry basis.

2. Mechanical analysis:

Mechanical analysis was carried out by the International Pipette method.

3. pH:

pH was measured in a 1:2.5 soil-water suspension using a Beckman pH meter.

4. Organic Carbon:

Organic carbon was estimated by Walkley and Black's method (1934).

Air dried soil ground to pass through a 80-mesh sieve was used. 1.0 g. soil was treated with 10 ml.

N. potassium dichromate and 20 ml. concentrated sulphuric acid and kept for half an hour. The excess of chromic acid was determined by titration with N/2 ferrous solution using diphenylamine as internal indicator.

5. <u>Cation Exchange Capacity</u>:

10.0 g. of soil was leached with neutral N. ammonium acetate solution. The adsorbed ammonium was determined by distillation with magnesium oxide and absorption in excess standard acid followed by titration with standard alkali.

6. <u>Analysis of clay fraction</u>:

(a) <u>Separation of clay</u>: The ammonium carbonate method, proposed by Puri (1934) was adopted.

50 g. soil was taken in a beaker, 250 ml. of N. ammonium carbonate added and boiled gently until the volume was reduced to half. 25 ml. of 0.5 N. sodium hydroxide was then added and the solution diluted to 250 ml. The volume was again reduced to half. The suspension was passed through a 70 mesh sieve and collected in a 500 ml. beaker marked at 8.6 cm. above the bottom. The clay was collected by decantation, air dried and stored in stoppered bottles.

(b) <u>Preparation of clay fusion extract</u>. The sodium carbonate fusion method was followed. 2 g. of clay was fused with sodium Carbonate in a Platinum crucible and the melt dissolved in dilute hydrochloric acid.

(c) Silica: The fusion extract was evaporated to dryness and dehydrated by heating in an air oven at 150°C for six hours. The residue was treated with dilute hydrochloric acid, filtered, washed, ignited, weighed and reported as SiO_2.

(d) Sesquioxides: The filtrate from silica estimation was made up to 500 ml. and the sesquioxides determined in a 50 ml. aliquot.

7. Iron:

Iron was estimated after reduction with hydroxylamine by the O - phenanthroline method as described by Fortune and Mellon (1938). Water soluble, exchangeable, easily reducible and total iron were determined in soils collected in the submerged condition as well as in the dry state (after harvest).

(a) Water soluble iron: 12.5 g. fresh soil was weighed into a conical flask, 125 ml. distilled water added and the flask stoppered tightly. The suspension was shaken in an end-over-end shaker for 30 minutes and then filtered through a Buchner funnel. The filtrate was evaporated to dryness, organic matter destroyed and water soluble iron determined by measuring the intensity of the colour of the ferrous orthophenanthroline complex in a Klett colorimeter.

(b) xchangeable iron: 125 ml. of N. neutral ammonium acetate was added to the 12.5 g. of soil from which water soluble iron had been removed and the suspension shaken vigorously for 20 seconds and filtered quickly through a Buchner funnel fitted with Whatman No.5 filter paper. The filtrate which contained exchangeable ferrous iron was freed from ammonium acetate by evaporation. The last traces of organic matter were removed by treatment with 10 ml. of aqua regia and repeated evaporation to dryness. The residue was dissolved in 1 ml. of N. hydrochloric acid and the iron was determined in the solution.

(c) educible iron: 125 ml. of N. ammonium acetate of pH 3 was added to the soil left after extraction of water soluble and exchangeable iron. The rate of filtration was so regulated that the time of contact of the extractant with the soil was more or less the same as in the determination of exchangeable iron. educible iron was estimated in the filtrate.

(d) Total iron: Total iron was determined in the hydrochloric acid extract of 5 g. of the air dried soil by reduction with zinc and sulphuric acid followed by titration with standard potassium permanganate.

8. Manganese:

Manganese was estimated by the periodate method proposed by Leeper (1935) as modified and described by Sherman *et al* (1942) after the oxidation of organic matter and removal of chlorides by evaporation with nitric acid. Water soluble, exchangeable, easily reducible and total manganese were fractionated and determined as follows:

(a) *Water soluble manganese:* 125 ml. of distilled water was added to 12.5 g. fresh soil in a flask and stoppered tightly. The suspension was shaken in an end-over-end shaker for 30 minutes and filtered through a Buchner funnel. The filtrate was then evaporated to dryness and organic matter destroyed by treatment with 30 percent H_2O_2 and 10 ml. concentrated nitric acid. The residue was treated with 35 ml. of water and 5 ml. of 85 percent H_3PO_4. To the clear colourless solution 0.3 g. of sodium periodate was added and the solution brought to boiling on a hot plate. After cooling, it was transferred to a 50 ml. volumetric flask and made up to volume with 5 percent phosphoric acid. The solution was mixed well and the intensity of colour measured in a Klett colorimeter.

(b) *Exchangeable manganese:* 125 ml. of N. ammonium acetate of pH 7 was added to the soil left after the extraction of water soluble manganese. The flask was stoppered and shaken continuously for 30 minutes and allowed to stand for six hours with occasional shaking.

It was then filtered through a Buchner funnel and exchangeable manganese determined in the filtrate as before.

(c) Easily reducible manganese: 125 ml. of N. ammonium acetate containing 0.2 percent of hydroquinone was added to the soil left over after the extraction of water soluble and exchangeable manganese. The suspension was shaken at frequent intervals for six hours and then filtered. In the filtrate easily reducible manganese was determined.

(d) Total manganese: 5.0 g. of the air dried soil was treated with 1:1 hydrochloric acid and the extract made up to volume; total manganese was determined in a 50 ml. aliquot.

RESULTS

TABLE I

MECHANICAL COMPOSITION OF SOILS

Profile No.	Locality	Depth (cms)	Coarse sand %	Fine sand %	Silt %	Clay %	Textural class
I	Pattambi	0 - 22	55.8	23.6	9.3	29.3	sandy clay loam
		22 - 75	56.2	17.3	11.5	18.2	sandy loam
II	Monkombu	0 - 22	2.5	17.4	22.0	57.8	clay
		22 - 75	0.4	3.8	37.3	57.9	silty clay
III	Taliparamba	0 - 22	34.1	11.3	8.2	49.0	sandy clay
		22 - 75	49.4	10.9	10.5	30.7	sandy clay loam
IV	Mannuthy	0 - 22	41.7	12.2	5.2	40.1	sandy clay
		22 - 75	61.6	13.4	3.6	27.5	sandy clay loam
V	Vaikom	0 - 22	——	1.8	21.3	69.9	clay
		22 - 75	0.1	1.4	47.4	44.1	silty clay
VI	Kayamkulam	0 - 22	21.9	67.0	2.9	8.2	sandy
		22 - 75	41.7	53.4	2.9	3.6	sandy

TABLE II

IMPORTANT CHEMICAL CHARACTERISTICS OF SOILS

Profile No.	Locality	Depth (cms)	pH		Organic carbon %	Organic matter %	Cation Exchange capacity m.e./ 100 g. soil	$\frac{SiO_2}{R_2O_3}$
			Dry	Waterlogged				
I	Pattambi	0 - 22	5.1	6.1	0.91	1.57	24.2	1.97
		22 - 75	5.1	6.1	0.11	0.19	21.6	
II	Monkombu	0 - 22	4.5	5.2	2.04	3.51	15.0	2.90
		22 - 75	4.8	2.9	2.73	4.70	17.0	
III	Taliparamba	0 - 22	5.2	6.4	1.65	1.19	16.4	1.87
		22 - 75	5.2	6.3	1.57	2.70	18.9	
IV	Mannuthy	0 - 22	5.2	5.4	0.68	1.17	19.7	1.46
		22 - 75	5.4	5.7	0.27	0.46	20.6	
V	Vaikom (Kari)	0 - 22	3.9	4.1	2.86	4.92	8.5	2.70
		22 - 75	6.0	5.8	2.83	4.87	11.3	
VI	Kayamkulam	0 - 22	5.3	5.5	0.14	0.24	2.4	1.96
		22 - 75	5.4	5.7	0.03	0.05	2.3	

CHAPTER IV

RESULTS

The mechanical analysis of the soils is given in Table I.

The data show that the clay content in the different profiles varies from 3.6 to 69.9 percent. The soils range in texture from sandy to clay. The maximum amount of clay is found in profile V and the minimum values for both horizons are recorded in profile VI. xcept in profile II, there is marked decrease in the clay content in the subsoil. The sand fractions predominate in profile VI.

Data regarding pH, organic carbon, organic matter, cation exchange capacity and SiO_2/R_2O_3 ratio are presented in Table II.

(i) pH.

It will be observed that all the soils are acidic in reaction. The pH values of the water-logged soils range from 2.9 to 6.4 and that of the dry soils from 3.9 to 6.0. As expected, in all cases the dry soils register lower values than the water-logged soils. The variation in pH with depth is not uniform.

(ii) Organic carbon

The amount of organic carbon in the various profiles

TABLE III

DISTRIBUTION OF DIFFERENT FORMS OF MANGANESE IN WATER-LOGGED SOILS

Profile No.	Locality	Depth (cms)	Manganese (p.p.m.)					$\frac{\text{Active}}{\text{Total}}$
			Water soluble	Exchange-able	Easily Reducible	Active	Total	
I	Pattambi	0 - 22	10.5	11.7	104.8	126.9	524.0	0.242
		22 - 75	9.4	14.2	55.2	78.7	591.0	0.133
II	Monkombu	0 - 22	14.8	20.5	124.2	159.6	355.0	0.450
		22 - 75	14.0	17.4	109.3	141.7	367.0	0.386
III	Taliparamba	0 - 22	2.1	38.9	20.2	61.2	625.0	0.098
		22 - 75	2.5	40.0	18.9	61.4	764.0	0.083
IV	Mannuthy	0 - 22	1.8	15.3	28.9	46.1	554.0	0.085
		22 - 75	2.1	21.1	23.0	46.3	670.0	0.069
V	Vaikom	0 - 22	13.2	49.7	75.6	138.5	382.0	0.363
		22 - 75	12.4	80.0	52.6	145.0	573.0	0.253
VI	Kayamkulam	0 - 22	9.4	10.2	15.9	35.5	432.0	0.082
		22 - 75	6.9	54.9	8.9	70.7	655.0	0.181

TABLE IV

DISTRIBUTION OF DIFFERENT FORMS OF MANGANESE IN DRY SOILS (AFTER HARVEST)

Profile No.	Locality	Depth (cms)	Manganese (p.p.m.)					Active / Total
			Water soluble	Exchangeable	Easily Reducible	Active	Total	
I	Pattambi	0 - 22	1.7	16.3	9.8	27.7	550.0	0.050
		22 - 75	1.3	14.2	18.8	34.3	604.0	0.056
II	Monkombu	0 - 22	2.8	28.8	17.6	49.1	367.0	0.134
		22 - 75	2.8	36.6	20.0	59.4	360.0	0.165
III	Taliparamba	0 - 22	1.8	17.6	12.2	31.7	611.0	0.085
		22 - 75	1.4	9.8	9.8	21.0	775.0	0.027
IV	Mannuthy	0 - 22	0.9	18.5	16.5	35.9	516.0	0.070
		22 - 75	2.4	15.2	96.8	114.4	655.0	0.174
V	Vaikom	0 - 22	2.3	18.4	11.4	32.1	393.0	0.082
		22 - 75	8.1	64.8	32.8	105.7	579.0	0.182
VI	Kayamkulam	0 - 22	3.0	10.9	10.1	24.1	415.0	0.058
		22 - 75	1.8	14.3	7.8	23.9	647.0	0.037

TABLE VII

RANGE OF VARIATION IN DIFFERENT FORMS OF MANGANESE IN WATER-LOGGED AND DRY SOILS

Form of Manganese	Mn (p.p.m.)					
	WATER-LOGGED			DRY		
	Minimum	Maximum	Mean	Minimum	Maximum	Mean
	SURFACE SOIL (0 - 22 cms)					
WATER SOLUBLE	1.8	14.9	8.7	0.9	3.0	2.1
EXCHANGEABLE	10.2	49.7	24.4	10.9	28.9	18.4
EASILY REDUCIBLE	15.9	124.2	61.6	9.8	17.6	12.9
ACTIVE	35.5	159.6	94.6	24.1	49.2	35.1
TOTAL	355.0	625.0	479.0	367.0	611.0	475.0
	SUB SOIL (22 - 75 cms)					
WATER SOLUBLE	2.1	14.0	7.9	1.3	8.1	2.9
EXCHANGEABLE	14.2	80.0	37.9	9.8	64.8	25.8
EASILY REDUCIBLE	9.0	109.3	44.7	7.8	96.8	31.0
ACTIVE	46.3	145.0	90.7	21.0	114.4	59.8
TOTAL	367.0	764.0	603.3	360.0	775.0	603.3

varies from 0.03 to 2.86 percent. Profiles II and V are rich in this constituent indicating heavy accumulation of organic matter in these soils. Except in profile II, organic carbon decreases with depth.

(iii) Cation exchange capacity

The cation exchange capacity of the soils shows wide variation the values ranging from 2.4 to 24.2 m.e./100 g. soil.

(iv) SiO_2/R_2O_3 ratio

The silica sesquioxide ratio of the surface soils varies from 1.46 to 2.9.

The distribution of the different forms of manganese in soils under both water-logged and dry conditions is shown in Tables III and IV.

The range of variation of the different forms of manganese under water-logged and dry conditions is shown in Table VII.

(1) Total Manganese

Total manganese varies from 350 to 625 p.p.m. in the surface soil and 367 to 764 p.p.m. in the subsoil of the water-logged profiles. Profile II registers the minimum values and profile III the maximum values for both horizons. In all the profiles, there is definite mobilization of total manganese in the subsoil.

The amount of total manganese in the dry soils is practically the same as that present in these soils when they are water-logged. It ranges from 367 to 611 p.p.m. in the surface layer and 360 to 775 p.p.m. in the second layer. The subsoil records higher values than the surface soil in all the profiles, with the exception of profile II.

(2) Water soluble Manganese

Manganese in this form is very low in the water-logged soils. It varies from 1.8 p.p.m. in profile IV to 14.8 p.p.m. in profile II. It may be noted that water soluble manganese constitutes the smallest fraction of total manganese. There is very little variation down the profile.

The data reveal that there is a marked decrease in this category of manganese in all the soils under dry conditions. The amount present is extremely small, most of the value lying between 1.0 and 3.0 p.p.m. There is very little variation in water soluble manganese with depth.

(3) Exchangeable Manganese

The amount of exchangeable manganese in the waterlogged soils ranges from 10.2 to 80.00 p.p.m. It is highest in the subsoil of profile V and lowest in the surface soil of profile VI. Except in profile II, exchangeable manganese is higher in the subsoil than in the surface soil.

In the dry soil studied, manganese in the exchangeable form varies between 9.8 and 64.8 p.p.m. The variation with depth is irregular.

(4) Easily Reducible Manganese

Easily reducible manganese constitutes the major fraction of total manganese in most of the waterlogged soils. The amount present shows considerable variation ranging from 8.9 p.p.m. in profile VI to 124.2 p.p.m. in profile II. Surface concentration of easily reducible manganese is very noticeable in all the profiles.

The content of this category of manganese in the dry soils is very low as compared to that in waterlogged soils, the values lying between 9.8 and 32.8 p.p.m. The distribution of easily reducible manganese in the profile does not follow any regular pattern.

(5) Active Manganese

The sum of the water soluble, exchangeable and easily reducible manganese represents the active manganese in the soil.

In the water-logged soils studied, active manganese varies from 35.5 p.p.m. in profile VI to 159.6 p.p.m. in profile II. The distribution of this form of manganese in the profile is erratic.

TABLE V

DISTRIBUTION OF DIFFERENT FORMS OF IRON IN WATER-LOGGED SOILS

Profile No.	Locality	Depth (cms)	Fe (p.p.m.) Water soluble	Exchange-able	Reducible	Active	Total ppm x 10^{-4}
I	Pattambi	0 - 22	29.8	12.3	80.5	122.5	11.6
		22 - 75	45.1	21.4	10.8	77.3	13.2
II	Monkombu	0 - 22	25.3	40.7	75.7	141.6	2.8
		22 - 75	43.1	58.6	100.8	202.4	3.2
III	Taliparamba	0 - 22	33.8	30.8	37.7	102.2	10.8
		22 - 75	18.4	33.0	33.0	84.4	12.8
IV	Mannuthy	0 - 22	45.1	17.5	26.3	89.0	4.8
		22 - 75	30.7	38.9	22.4	92.0	6.8
V	Vaikom	0 - 22	24.4	24.4	19.5	68.3	5.2
		22 - 75	33.3	37.0	39.0	109.3	6.8
VI	Kayamkulam	0 - 22	13.2	6.2	9.2	28.6	2.4
		22 - 75	9.0	12.9	5.0	26.9	1.6

TABLE VI

DISTRIBUTION OF DIFFERENT FORMS OF IRON IN DRY SOILS (AFTER HARVEST)

Profile No.	Locality	Depth (cms)	Fe (p.p.m.)				Total ppm x 10^{-4}
			Water soluble	Exchange-able	Reducible	Active	
I	Pattambi	0 - 22	24.3	16.4	60.9	101.6	11.68
		22 - 75	29.3	30.8	68.4	128.5	13.60
II	Monkombu	0 - 22	17.1	30.4	68.6	116.1	3.20
		22 - 75	35.3	60.7	106.6	202.6	3.04
III	Taliparamba	0 - 22	4.0	5.0	10.9	19.9	11.62
		22 - 75	4.3	13.3	10.0	27.6	12.48
IV	Mannuthy	0 - 22	17.0	12.0	33.7	62.7	4.64
		22 - 75	22.0	22.0	11.7	55.7	6.72
V	Vaikom	0 - 22	15.5	19.1	18.7	53.3	5.60
		22 - 75	17.6	58.8	50.4	126.8	6.40
VI	Kayamkulam	0 - 22	18.3	15.3	21.9	55.5	2.08
		22 - 75	9.3	18.5	24.7	52.5	1.92

TABLE VIII

RANGE OF VARIATION IN DIFFERENT FORMS OF IRON IN WATER-LOGGED AND DRY SOILS

FORM OF IRON	Fe (p.p.m.)					
	WATER-LOGGED			DRY		
	Minimum	Maximum	Mean	Minimum	Maximum	Mean
			SURFACE SOIL (0 - 22 cms)			
WATER SOLUBLE	13.2	45.1	28.6	4.0	24.3	16.0
EXCHANGEABLE	6.2	40.2	21.9	5.0	30.4	16.4
REDUCIBLE	9.2	80.5	41.5	10.9	68.6	34.1
ACTIVE	28.6	141.6	92.0	19.9	116.1	68.2
TOTAL (Fe_2O_3) p.p.m. x 10^{-4}	2.4	11.6	6.27	2.1	11.7	6.5
			SUB SOIL (22 - 75 cms)			
WATER SOLUBLE	9.0	45.1	29.9	4.3	35.3	14.4
EXCHANGEABLE	12.9	58.6	33.3	13.3	60.7	33.9
REDUCIBLE	5.0	100.8	35.2	10.0	106.6	45.3
ACTIVE	26.9	202.4	96.7	27.6	202.6	102.3
TOTAL (Fe_2O_3) p.p.m. x 10^{-4}	1.6	13.2	7.4	1.9	13.6	7.2

The active manganese content of the dry soils lies in the range 21.0 to 114.4 p.p.m. In most of the profiles, the level is higher in the subsoil than in the surface layer.

The distribution of the different forms of iron in soils under water-logged and dry conditions is shown in Tables V and VI.

The range of variation of different forms of iron under water-logged and dry conditions is shown in Table VIII.

(i) Total Iron

The total iron present in the water-logged soils varies from 16,000 to 1,32,000 p.p.m. The lowest values are recorded in profile VI and the highest values in profile I for both horizons. All the profiles, with the exception of profile VI, show concentration of total iron in the subsoil.

The amount of total iron in the dry soils is of the same order as that in the water-logged soils. It ranges from 19,200 to 1,36,000 p.p.m. It may be noted that here also the subsoil is richer in total iron than the surface soil in the majority of the profiles.

(ii) Water soluble iron

The level of water soluble iron varies from

9.0 p.p.m. in profile VI to 45.1 p.p.m. in profile IV in the water-logged soils. The variation with depth is irregular.

In the dry soils, iron of this category ranges from 4.0 to 35.3 p.p.m. Except in profile VI, water soluble iron increases with depth.

(iii) Exchangeable iron

The content of exchangeable iron in water-logged soils fluctuates from 6.2 to 58.6 p.p.m. It is highest in profile II and lowest in profile VI. In all the profiles there is marked increase in this fraction of iron in the subsoil.

The level of exchangeable iron ranges from 5.0 to 60.7 p.p.m. in the dry soils. As in the water-logged soils, it increases with depth in all the profiles studied.

(iv) Reducible Iron

The amount of reducible iron in the water-logged soils varies from 5.0 p.p.m. in profile VI to 100.8 p.p.m. in profile II. The distribution of this category of iron appears to bear no relation to depth.

The content of reducible iron in the dry soils lies in the range 10.0 to 106.6 p.p.m. The variation with depth is not uniform.

(v) Active Iron

The level of active iron in the water-logged soils varies within wide limits, viz., 26.9 to 202.4 p.p.m. Profile VI registers the minimum value and profile II the maximum values for both horizons. There is no regularity in the variation with depth.

The dry soils give similar values for this category of iron which range from 19.9 to 202.6 p.p.m. In the majority of the profiles active iron tends to accumulate in the subsoil.

DISCUSSION

CHAPTER V

DISCUSSION

Total Manganese

Viswanath and Ukil (1944) in a study of the Manganese status of Indian soils recorded mean values of 807.4 p.p.m. and 962.3 p.p.m. for surface soils and subsoils respectively of the humid region. The corresponding figures for the rice soils of Kerala under dry conditions obtained in the present investigation are 475.0 p.p.m. and 603.3 p.p.m. respectively. The lower level of total manganese in Kerala soils may be largely due to the low cation exchange capacity of the clay minerals present in these soils and the drastic leaching that they are subjected to.

Though profile II (Monkompu) registers the highest values for the various fractions of iron it ranks lowest as regards total manganese content. The strong acidity and high level of organic matter in this soil seems to be responsible for this situation as it favours the formation of active manganese which is easily lost by leaching.

The accumulation of total manganese in the subsoil is an important feature of both the dry and submerged profiles. This is obviously the consequence of leaching of manganese from the surface horizon and its deposition in the subsoil. Similar results have been reported by Biswas (1953) and Randhava et al (1961).

Of the several factors which influence the amount of total manganese in soils the clay content is one of the most important. It is interesting to note that a close relationship exists between total manganese and clay content in the soils studied. Higher values are recorded with increase in clay. It will be seen from Table III that of the various forms of manganese, the exchangeable category is predominate. This fraction is naturally associated with the clay complex. Hence this close correlation of total manganese with clay. The correlation between clay content and total manganese is highly significant (r =   ) and this finding is in accord with the observations of Biswas (1953), Wahab and Bhatti (1958) and other workers.

The data clearly show that waterlogging has not produced any significant change in the total manganese content of rice soils.

It has to be borne in mind that total manganese content is not a true index of the manganese status of the soil. It is of little importance from the point of view of plant growth though it may serve as a reserve of this micronutrient for plants.

Water soluble Manganese

This form of manganese is present in very small amounts in all the soils examined. It is of the order of 2.1 p.p.m. in the surface layer and 3.0 p.p.m. in the subsoil under dry conditions. Bhamija et al (1956) found that manganese of this category was absent in many rice soils of Bihar, Uttar Pradesh and Punjab.

The distribution of water soluble manganese is fairly uniform and varies little with depth which may be ascribed to the free movement of this form of manganese in the soil.

The influence of soil reaction on this category of manganese is very evident. The amount of water soluble manganese increases as pH decreases. This is obviously due to the formation of bivalent manganous ions under acidic conditions. High negative correlation was obtained between pH and water soluble manganese in the soils studied which corroborates the results of Biswas (1951) and Randhava et al (1961).

The maximum values for water soluble manganese are recorded in profile II (Monkombu) and profile V (Kari). These soils are rich in organic matter in the presence of which most of the reducible oxides of manganese are converted into soluble bivalent forms. This accounts for the higher content of the water soluble category of manganese in these soils.

The data reveal that water soluble manganese increases when soils are waterlogged. The amount of manganese of this category in submerged soils though small is three to four times higher than that found in soils under dry conditions. This observation is supported by the work of Pearsall (1950), Runge and Leon (196) and Mandal (1961). According to Ponnamperuma (1955), the peculiar conditions obtaining in rice soils, viz., absence of oxygen, the metabolism of anaerobic bacteria and the generation of powerful reducing agents by the anaerobic decomposition of organic matter, favour the reduction of manganese to water soluble forms

Exchangeable Manganese

This category of manganese is the bivalent form which is extractable with normal ammonium acetate solution at pH 7.0. It is a bigger fraction than water soluble manganese and the mean values for exchangeable manganese for rice soils under dry conditions are 18.4 p.p.m. and 25.8 p.p.m. for the surface and subsurface layers respectively.

It is seen that in the majority of the profiles there is mobilization of exchangeable manganese in the subsoil. It may be noted in this context that manganese is one of the most easily exchangeable bases, particularly in acid soils. Further, as pointed out by Andredy (1940) under conditions of high rainfall and acidity most of the reducible oxides of manganese are liable to be converted into bivalent manganous ions in the soil. These manganous ions are very mobile and are leached down and may be carried away in the drainage water. In the soils examined they have accumulated in the subsoil which accounts for the higher concentration of exchangeable manganese in this layer.

It will be noticed that as the fine fractions comprising clay and silt increase there is proportionate increase in the content of exchangeable manganese.? Under conditions of heavy rainfall and fairly high acidity the coarse fractions of soils are rendered very poor in exchangeable bases, particularly manganese, which is perhaps the most easily exchangeable base. Consequently, the fine fractions hold increasing amounts of manganese with greater tenacity than the coarser fractions. A highly significant correlation (r = 0.696) was obtained between the fine fractions and exchangeable manganese content. This observation is not, however, in agreement with the finding of Karim and Hussain (1960) who reported that the exchangeable manganese content of alluvial, coastal saline and hill tract soils of East Pakistan are similar notwithstanding textural differences.

As in the case of water soluble manganese, the soils examined registered higher values for exchangeable manganese under waterlogged conditions for the same reasons. This is in conformity with the results of Fosegarton (1957) who found less exchangeable and active manganese under drought conditions and the reverse under flooded conditions.

Easily reducible Manganese

This fraction represents the easily reducible portion of the higher oxides of manganese which vary in composition from MnO_2 to Mn_3O_4. Easily reducible manganese is present in the soil either in a colloidal hydrated form in the clay and silt fractions or in a finely divided state in the finer fractions.

In all the profiles there is surface concentration of this category of manganese. This may be explained as follows:

Due to continuous cropping the surface soil is subjected to greater spells, the oxides of manganese present in the top horizon alternatively pass through the processes of oxidation and reduction to a greater extent than those in lower horizon. Hence there is greater possibility for the oxides of manganese in the top horizon to undergo reduction than those in the subsoil.

The highest values for easily reducible manganese are recorded in profile II (Monkombu) and profile V (Kari). The high level of both organic matter and fine fractions in these soils accounts for this.

Low values for reducible manganese indicate low availability of manganese in soils. According to Sherman and Harmer (1943), at least 100 p.p.m. of manganese in this form must be present in the soil for satisfactory crop production. Judged by this standard, all the soils in the dry condition are very low in this category of manganese. But when these soils are submerged reducible manganese increases in most cases. This can best be explained as being due to the reduction of higher oxides of manganese.

Active Manganese

The distribution of active manganese in the surface and subsurface horizons of each profile is fairly uniform. The ratio of active to total manganese ranges from 0.069 to 0.450 in waterlogged soils and from 0.027 to 0.182 in dry soils.

The level of active manganese in the soils increases with increasing organic matter and clay contents as in the case of both water soluble and exchangeable manganese. The reasons for this are the same in all the three cases. The influence of soil texture is very marked in profile II (Monkombu) and profile V (Kari) which register the maximum values for active manganese. A high positive correlation ($r = 0.952^{***}$) exists between clay and active manganese content in the soils examined. There is also a close relationship ($r = 0.577$) between active manganese and organic carbon. Dhamija et al (1956) and other workers have also noted a similar relationship.

The amount of active manganese in the soils is greatly influenced by waterlogging. In the majority of cases, submerged soils gave values for active manganese which are much higher than those for dry soils. The reducing conditions brought about by waterlogging are very conducive for the formation of bivalent forms of manganese which constitute part of the active manganese in soils. This accounts for the higher content of active manganese in submerged soils.

The highest SiO_2/R_2O_3 ratios were recorded by profile II (Monkombu) and profile V (Kari) which also gave the maximum values for active manganese. This suggests that the level of this category of manganese is influenced not only by texture and organic matter but also by the nature of the clay minerals present in soils. Raychaudhuri and Anantharaman (1960) in a study of Indian acid soils growing paddy indicated that the clay minerals in kari soils consist of a mixture of kaolinite and illite. Gopalaswamy (1958) however, suggested that the Kuttanad soils contain a mixture of montmorillonite and illite types of clays. The Monkombu soil and the Kari soil belong to the same region (Kuttanad) and have many similar characteristics. They are entirely different from the other soils studied which are either lateritic or sandy. Leeper (1947) found that soils containing montmorillonite can fix large amounts of active manganese while heavily leached soils of low pH containing kaolinite can fix very little. In the latter case, the mobile manganous forms of manganese are either quickly absorbed by the plant or removed in drainage water. This explains the high values for active manganese registered by the Monkombu and Kari soils.

From the results of the present study no relationship could be drawn between active manganese content and pH of soils.

Total Iron

The maximum values for total iron for both the surface soil and subsoil were recorded by profile I (Pattambi). This observation holds good in the case of dry soils as well as submerged soils. As expected, profile VI (Kayamkulam) which is a typical light sandy soil registered the lowest figures. In all the profiles, with the only exception of profile VI, there is concentration of total iron in the subsoil which is brought about by eluviation from the surface. The amounts present correspond with the content of fine fractions in the surface and subsurface layers. This relationship between the total iron content and the fine fractions of the soil was earlier noted by Kubotta (1958) and Pinta and Ollat (1961).

Water soluble iron

The distribution of this fraction of iron in the profile does not follow any regular pattern in submerged soils. In dry soils, however, water soluble iron tends to accumulate in the subsoil. Shiori and Yoshida (1951) who made the same observation attributed this to the leaching of ferrous iron from the surface to the subsurface horizon.

Soil reaction has a pronounced influence on the solubilization of iron. More iron goes into solution with decrease in pH of the soil as is evident from the negative correlation ($r = -0.58^*$) that exists between pH and water soluble iron. This conclusion is supported by the work of Rodrigo (1962) who showed that the amount of iron brought into solution is inversely proportional to the pH. A characteristic feature of submerged soil is that the carbon dioxide content is several hundred times higher than in air. The carbonic acid formed as a consequence lowers the pH of the soil and brings about the precipitation and subsequent solution of ferrous iron as demonstrated by Ponnamperuma (1955).

Exchangeable Iron

Profile II (Monkombu) and profile VI (Kayamkulam) gave the highest figures for exchangeable iron for both the surface and subsoil under waterlogged conditions. It is noteworthy that these soils record the minimum values for this category of iron for both horizons under dry conditions. It was further observed that in most of the profiles examined the subsoil layer contained more exchangeable iron than the surface layer under both submerged and dry conditions. There is clear evidence that submergence brings about the reduction and solubilization of iron. The soluble product is carried down in the drainage water to the zone of high oxygen concentration in the soil where it is deposited as concretions. This explains satisfactorily the depletion of iron in the surface horizon and its concentration in the subsoil.

The influence of organic matter on the exchangeable iron content of the soils studied is apparent from the positive correlation that exists between them. Mandal (1961) has also reported a similar relationship in water logged soils. The decomposition of organic matter in soils under submerged conditions produces appreciable amounts of organic acids which enhance the mobility of iron resulting in increased amounts of exchangeable iron in the soil.

Reducible Iron

The distribution of this fraction of iron in the profile is not uniform. In profile II (Monkombu) and profile V (Kari) the subsoil contains more of reducible iron whereas in the other profiles the order is reversed.

The maximum values for this category of iron are registered in profiles II and V. The high organic matter content of these soils is responsible for this.

Active Iron

Under waterlogged conditions there is not much variation in the distribution of this form of iron in the profiles whereas under dry conditions the subsoil shows twice as much active iron as the surface soil. Iri et al (1957) reported similar data in a study of the variation in ferrous iron content of soil profiles at various stages of submergence. They noted that the active iron content of the furrow slice was depleted when the field was dried but increased progressively with the period of submergence. This may be attributed to the formation of active iron from inert oxides of iron under the reducing conditions created by waterlogging.

As in the case of manganese, the fine fractions influence the content of active iron in the soil and show a linear relationship (r = 0.712***).

The effect of organic matter on this category of iron is also discernible from the data. Active iron is found to be significantly correlated with organic carbon content (r = 0.755 *) for all the soils examined. This observation upholds the findings of Krishnamoorthy (1959) and Mandal (1961).

It is clear from the above discussion that the availability of iron and manganese in rice soils of Kerala is altered markedly by their environment. The results also reveal that submergence of soils brings about profound changes in the forms and distribution of these two elements, particularly in the strongly acid soils of the Kuttanad region. These transformations are beneficial within limits but are liable to adversely affect the fertility of these soils and may even prove to be limiting factors in crop production under intensely acid conditions. The present work has only touched the fringe of this problem. Many important phases of this problem remain to be investigated, the more important of them being:

(i) The inter-relationships between iron and manganese in the soil.

(ii) Seasonal transformations of iron and manganese in relation to crop growth in submerged soil.

It is hoped that these problems will receive the attention of soil scientists interested in this subject.

SUMMARY AND CONCLUSIONS

CHAPTER VI

SUMMARY AND CONCLUSIONS

A study was made of the forms and distribution of iron and manganese in six profiles representing typical rice soils of Kerala. Samples were examined both under water-logged and dry conditions. Correlations were worked out between the physical and chemical characteristics of the soils and the forms and distribution of these elements. The findings are summarised below:

(1) The sub soils are richer in total manganese than the surface soils both under water-logged and dry conditions.

(2) The total manganese is correlated with the finer fractions of the soils, the content increasing with increase in clay.

(3) The active manganese fraction bears little relation to total manganese content.

(4) Distribution of water soluble manganese follows a uniform pattern throughout the profile and shows little variation between surface and sub soil layers.

(5) The solubilisation of manganese increases with decrease in soil pH and Vice Versa.

(6) The content of exchangeable manganese is higher in sub soil and increases with increase in fine fractions.

(7) The easily exchangeable nature of manganese is clearly brought about by the negative correlation obtained with the cation exchange capacity of the soils.

(8) The easily reducible manganese accumulates in the surface layer of all the profiles.

(9) The active manganese exhibits a uniform pattern of distribution in the profile and shows little variation between the two horizons.

(10) The organic matter content has a marked influence on the forms, solubilization and mobilisation of soil manganese.

(11) Water logging has resulted in bringing more manganese into solution.

(12) The total iron content is higher in the subsoils than in the surface soils in most of the profiles.

(13) Total iron tends to increase with increase in fine fractions.

(14) Water soluble iron accumulates in the sub soil under dry conditions but there is no regularity in distribution under submerged conditions.

(15) More iron is brought into solution as soil reaction tends towards acidity.

(16) The sub soil contains more of exchangeable iron both under dry and submerged conditions.

(17) Exchangeable iron shows a relationship with soil texture, the amount being higher in heavy soils.

(18) The reducible fraction of iron follows no regular trend of distribution in the profiles.

(19) The active iron is uniformaly distributed in the profile under submerged conditions but under dry conditions the sub soils record higher values.

(20) The active iron tends to increase with the increase in fine fractions.

(21) Organic matter influences the amount and distribution of water soluble, exchangeable, reducible and active forms of iron.

(22) Water-logging appears to be one of the controlling factors in the solubilization and mobilization of iron, the effect bean more pronounced in the subsoil.

LITERATURE CITED

BISWAS, T.D. 1951 Manganese status of some Indian soils Indian J. Agri. Sci. 21: 2; 97.107

BISWAS, T.D. 1953 Distribution of manganese in profiles of some Indian soils. J. Indian Soc. soil Sci. 1: 21 - 31

BLAIR, A.W., and PRINCE, A.L. 1936 Manganese in New Jersey soils. Soil Sci. 42: 327 - 33

CONNER, S.D. 1932 Factors affecting Manganese availability in Soils. Jour. Amer. Soc. Agron. 24: 726 - 733

*CLARK, F.E., and RESNICKY, J.W. 1956 Some mineral element levels in the Soil solution of a submerged Soil in relation to rate of organic matter addition and length of flooding. Proc. Intern. Congr. Soil Sci; 6th Congr. Paris. Vol. 9, 545 - 548

DE, P.K., and MANDAL, L.N. 1957 Physiological diseases of rice Soil Sci. 84: 367 - 376

DHAMIJA, O.P., MURTHY, R.S. and RAYCHAUDHURI, S.P. 1956 Studies on soils growing Paddy J. Indian Soc. Soil Sci. 4: 193 - 204

DHAWAN, C.L., JAGJIWAN SINGH and BHATNAGAR. 1949 Indian J. Agri Sci. 20: 3, 343 - 345

*EBERHARDT, W. 1958 The effects of cultivation and liming on active manganese levels in soils. Proc. Crop Sci. Soc. Japan. 26: 205 - 210 Abst. Soils and ferts. Vol XXI: 4, 1293.

*FORTUNE, W.B. and MELLON, M.G.	1938	Determination of iron with O-Phenanthroline Ind. Eng. Chem. anal. Ed. 10: 60-64 quoted by Jackson, M.L. 1962 Soil Chemical Analysis. Asia Publishing house Madras.
*GILE, L.H. Jr.	1958	Fragipan and water table relationships of some brown podsolic and low humic gley soils. Proc. Soil Sci. Soc. Amer. 22, 560 - 565
GOPALA RAO, H.G.	1956	Effect of green manuring to Red loamy soil freshly brought under Swamp Paddy cultivation with particular reference to iron and Manganese. J. Indian Soc. Soil Sci. 4: 225 - 235.
*GOPALA SWAMY, V.	1958	Studies on the fertility status of some peaty, marshy and swampy soils. M.Sc. Thesis, Indian Agrl. Res. Inst.
HEINTZE, S.G.	1938	Readily Soluble manganese of Soil and "Marsh Spot" of Peas. J. Agr. Sci. 28: 175 - 186
HEINTZE, S.G.	1957	Studies on Soil manganese. J. Soil Sci. 8: 287 - 300
HEINTZE, S.G. and MANN, P.J.G.	1951	A study of various fractions of the manganese of Neutral and Alkaline organic Soils. J. Soil Sci. 2: 237 - 242.
HOON, R.C., and DHAWAN, C.L.	1943	The occurrence and significance of trace elements in relation to crop Production. Indian J. Agric. Sci., 13: 601 - 608
HOON, R.C., DHAWAN, C.L., and MADAN, M.L.	1941	Effect of certain Soil factors on the yield of wheat in Punjab. Soil Sci. 51: 339 - 349

IRI, H., MARUTA, I., and TAKHASHI, I. 1957 The variation in ferrous iron content in soil profiles under the flooded conditions of rice fields (Part I) *Soil and Plant food* **2**: 36 - 47

*IRI, H., MARUTA, I., and TAKHASHI, I. 1958 Studies on the transformation of iron in rice fields under flooded condition 1. Seasonal variation of iron in different horizons. *Abst. Soils & Fertis* Vol **XXII**: **5**; 24 - 54 *J. Sci. Soil, Tokyo.* **28**, 477 - 482

ISLAM, M.A., and ELAHI, M.A. 1954 Reversion of ferric iron to ferrous iron under water-logged condition and its relation to available Phosphorus. *J. Agric. Sci.* **45**: 1 - 2.

JACKSON, M.L. 1962 *Soil Chemical Analysis.* Asia publishing house, Madras.

*KAMOSHITA, Y. 1956 On the Chemical constituents of the principal Soil types on Japanese paddy field area. *VIth International Congress of Soil Science, Paris.*

KARIM, A.Q.M.B., HUSSAIN, M., and CHOWDHARY, S. 1960 Studies on the manganese content and its distribution in some East Pakistan Soils. *Soil Sci.* **90**: 129 - 132.

*KELLEY, W.P. 1909 Pine apple Soils. *Hawai Station reports.* 58-63 (1909)

KHANNA, K.L., BHATTACHARYA, P.B., and JONEJA, K.L. 1954 Characterisation and classification of Soil in white sugar belt of Bihar. *J. Indian Soc. Soil Sci.* **2**: 106 - 109.

KIUCHI, T. and OMUKAI, S. 1959 Influence of organic matter content and Plant roots on the leaching of cations from Paddy Soils. *Soil and Plant food* **5**: 108-113

KOCH, D.E.V.	1946	Manganese content of some Ceylong Soils. Trop. Agro. 102.
*KOENIGS, F.F.R.	1950	A "Sawah" profile near Bogor (Java) Trans. 4th Int. confr. Soil Sci. 1: 297 - 300. quoted by Ponnamperuma 1955.
*KOSEGARTEN, E.K.	1957	Variations of active manganese in Soil samples depending on moisture content and microbial activity. LandW. Forsch. 10: 214-22 Abst. Soils and Fertis Vol. XXI No.3, 902-1958.
*KRISHNAMOORTHY, C.	1959	Improving Soil fertility condition with special reference to minor elements. Proc. Indian Acad. Sci. 49 B. 338-348 Abst. Soils and Fertis Vol XXII 5: 2464. 1959
* LEIPER, G.W.	1935	Manganese deficiency of Cereals. Pot Experiments and a new hypothesis. Proc. Roy. Soc. Victoria 47: 225-261.
MANDAL, L.N.	1961	Transformation of iron and manganese in waterlogged rice soils. Soil Sci. 91: 121-126
MANN, H.B.	1930	Availability of manganese and iron. Soil Sci. 30: 117-131
MANDAL, L.N.	1962	Levels of iron and manganese in Soil solution and the growth of rice in waterlogged soils in relation to the Oxygen Status of Soil solution. Soil Sci. 94: 387-391
MONEY, N.S., and BALAKRISHNA KURUP T.K.	1961	Investigation on the phenomenon of scum formation in paddy fields of Kerala State. J. Indian Soc. Soil Sci. 9: 4, 253-255

*NOZDRUNOVA, E.M., RYTIKOVA, M.N., and SHEMYAKINA, A.F. 1958 The question of seasonal variation in the available and Exchangeable manganese content in sod podzolic soils. Dokl. Skh. Akad. Timiryazera 34: 157 - 159 (R) Abst. Soils and Fertis 24: 2, 590.

*PEARSALL, W.H. 1950 The investigation of wet soils and its agricultural implications. Empire J. Exp. Agr. 18: 289-298 quoted by Mandal, L.N. 1961.

PINTA, M. and OLLAT, C. 1961 Physico-chemical investigations of trace elements in tropical soils. 1. A study of some soils in Dahomey. Soils and Fertis 24: 6, 2945

PIPER, C.S. 1931 Availability of manganese in soils. J. agric. sci. 21: 762 - 779

PIPER, C.S. 1950 Soil and plant analysis. Inter science publishers, New York.

PONNAMPERUMA, F.N. 1955 Chemistry of submerged soils in relation to the growth and yield of Rice. Ph.D Thesis Cornell. Univ.

PRINCE, A.L. and TOTH, S.J. 1938 Studies on the behaviour of manganese in soils. Soil Sci. 46: 83 - 94

PURI, A.N. 1935 Soil Sci., 29: 263-70

RAJARAM, K.P. 1964 Study of transformations of nitrogen and phosphorus in acid paddy soils of Kerala State in relation to crop growth and yield. Dissertation submitted to the University of Madras in partful filment for M.Sc.(Ag)

RANDHAWA, N.S., KANWAR, J.S. and NIJHAWAN, S.D. 1961 Distribution of different forms of Manganese in the Punjab soils. Soil Sci. 92: 2, 106-112.

*HONGE, E.C.A., and LOON, L.D.	1960	Distribution of Manganese in a bio topo sequence of South Eastern Iowa soils. Proc. Iowa acad. Sci. 67: 232 - 236 Abst. Soils and Fertis 24: 6, 2933.
SANCHEZ, C., and KAMPRATH, E.J.	1959	Effect of liming and organic matter content, on the availability of native and applied manganese. Proc. Soil Sci. Soc. Amer. 23: 302-304
SHERMAN, G.D., and HARMER, P.M.	1943	Manganous manganic equilibrium in soils. Proc. Soil Sci. Soc. Amer. 7: 398 - 405
SHERMAN, G.D., Mc HARGUE, J.S. and HODGKISS, W.S.	1942	Determination of active manganese in the soil. Soil Sci. 54: 253 - 257
SHIGEMORI, A.	1961	A review of research on redox potentials of Paddy soils. Soil Sci. 94: 1, 6 - 11
SHIOHIRI, M., and YOSHIDA, M.	1951	Studies on the manganese in the paddy soils. Jour. Sci. Soil Tokyo. 22: 50 - 56
*STEENBJERG, F.	1935	The exchangeable manganese in Danish Soils and its relation to Plant growth. Trans. Inter. Cong. Soil Sci. 3rd. Congr., Oxford. 198-201 Quoted by Mandal, L.N. 1961.
STENUIT, D., and PIOT, R.	1957	The relationship between pH and Manganese content of sandy soils and development of manganese deficiency symptoms in oats. Soils and Fertis 13: 59, 1336
*TING, C.P. and YU, T.J.	1958	Oxidation and Reducation Processes in Paddy Soils. IV The activities of Iron and Manganese in paddy soils derived from red earth. Abst. Soils and Fertis. 22: 1, 19.

TOMLINSON, T.E.	1957	Seasonal Variation of the surface pH values of some rice soils of Sierra Leone. Trop. agri. Trin. **34**: 287-294
TOTH, S.J., and ROMNEY, E.M.	1954	Manganese studies with some New Jersey soils. Soil Sci. **78**: 298-303
WAHABA, A. and BHATTI, H.M.	1958	Trace element status of some West Pakistan soils. Soil Sci. **86**: 319 - 323
WALKLEY, A. and BLACK, I.A.	1934	Soil Sci. **37**: 29-38
WILLIS, L.G.	1932	The effect of liming soils on the availability of manganese and iron. Jour. Amer. Soc. Agron. **24**: 716 - 726
ZENDE, G.K., and PHARANDE, K.S.	1961	Effect of Particle size on the level of Extractable manganese in the soil. J. Indian Soc. Soil Sci. **9**: 89 - 98

* Originals not seen

LIST OF CORRELATIONS WORKED OUT

A. Water-logged condition

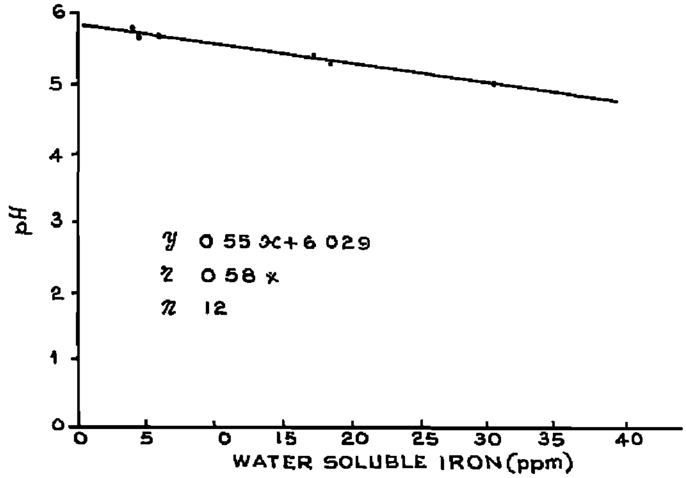
1.	Base Exchange Capacity Vs Exchangeable manganese	-0.68^{**}
2.	Water soluble manganese Vs pH	-0.56^{*}
3.	Active manganese Vs Exchangeable manganese	0.80^{**}
4.	Organic carbon Vs Exchangeable iron	0.642^{*}
5.	Clay Vs Exchangeable iron	0.62^{*}
6.	Fine fractions Vs Exchangeable iron	0.706^{**}
7.	pH Vs Active manganese	0.88^{**}
8.	Clay Vs Total manganese	0.964^{**}
9.	Active iron Vs Active manganese	Not significant
10.	Active iron Vs Fine fractions	0.712^{**}
11.	Active manganese Vs Fine fractions	0.952^{***}
12.	Organic carbon Vs Active iron	0.755^{**}
13.	Organic carbon Vs Active manganese	0.577^{*}

B. Dry condition

14.	pH Vs water soluble iron	-0.58^{*}
15.	Fine fractions Vs Exchangeable iron	0.605^{*}
16.	Organic carbon Vs Exchangeable iron	0.58^{*}
17.	Organic carbon Vs Active iron	0.689^{**}
18.	Water soluble manganese Vs Exchangeable manganese	0.88^{**}
19.	Organic carbon Vs Exchangeable manganese	0.65^{*}
20.	Fine fractions Vs Exchangeable manganese	0.696^{**}

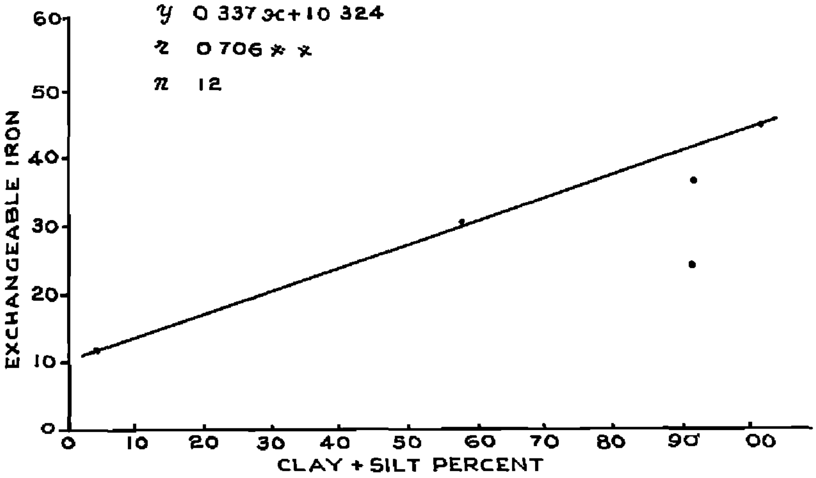
* Significant at 5% level
** Significant at 1% level
*** Significant at 0.1% level

RELATIONSHIP BETWEEN WATER SOLUBLE Fe
AND pH IN DRY SOILS



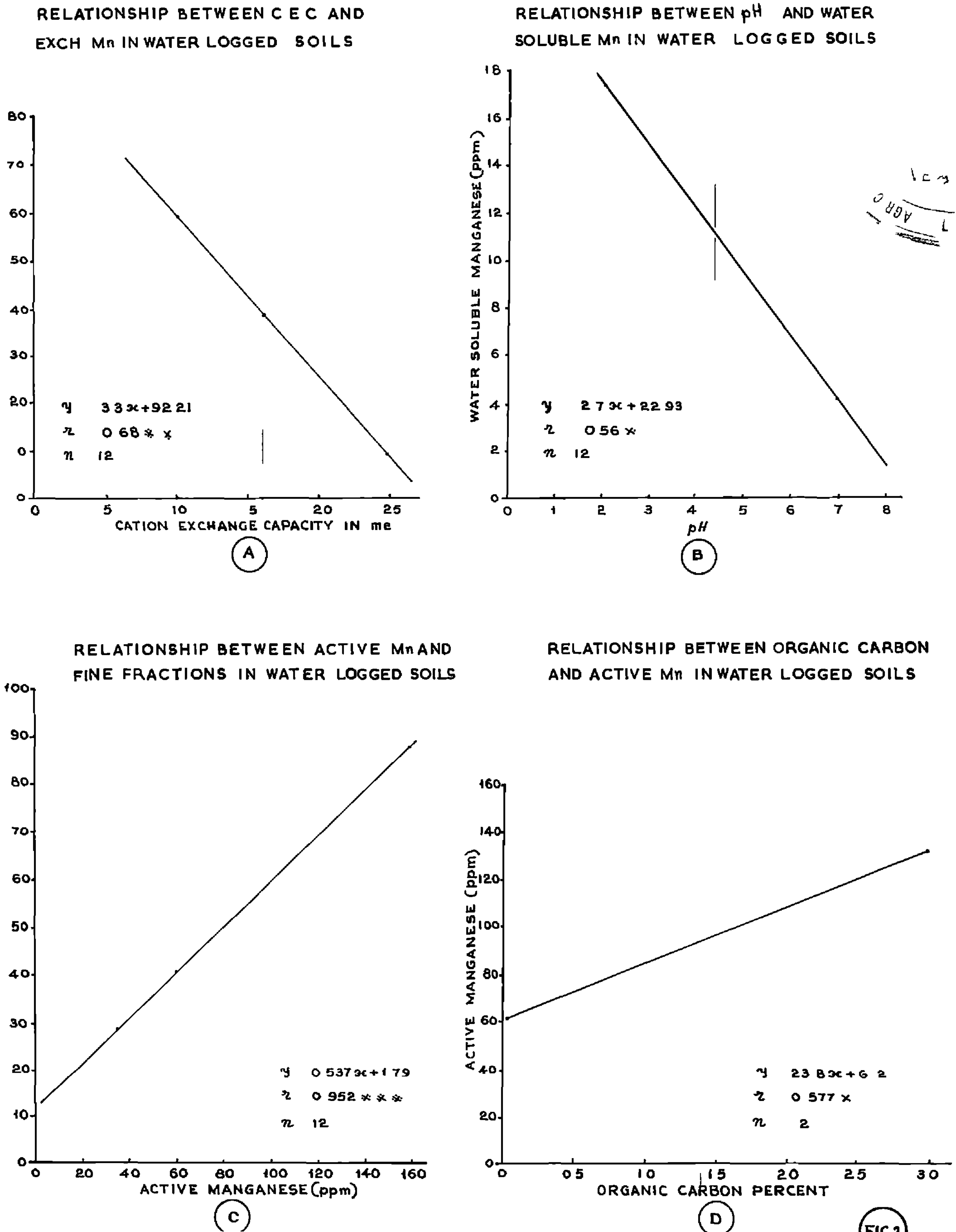
(A)

RELATIONSHIP BETWEEN FINE FRACTIONS AND EXCH Fe
IN WATER LOGGED SOILS



(B)

FIG I



RELATIONSHIP BETWEEN C E C AND EXCH Mn IN WATER LOGGED SOILS

RELATIONSHIP BETWEEN pH AND WATER SOLUBLE Mn IN WATER LOGGED SOILS

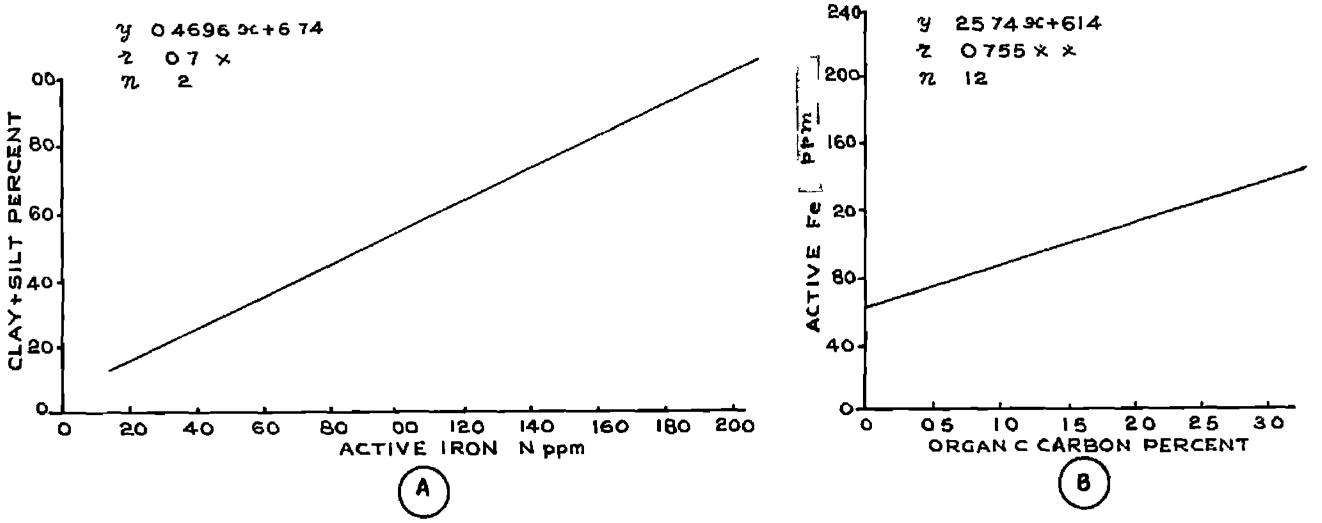
RELATIONSHIP BETWEEN ACTIVE Mn AND FINE FRACTIONS IN WATER LOGGED SOILS

RELATIONSHIP BETWEEN ORGANIC CARBON AND ACTIVE Mn IN WATER LOGGED SOILS

FIG 2

RELATIONSHIP BETWEEN ACTIVE Fe AND FINE FRACTIONS IN WATER LOGGED SOILS

RELATIONSHIP BETWEEN ORG CARBON AND ACTIVE Fe IN WATER LOGGED SOILS



RELATIONSHIP BETWEEN WATER SOLUBLE Mn AND EXCH Mn IN DRY SOILS

RELATIONSHIP BETWEEN FINE FRACTIONS AND EXCH Mn IN DRY SOILS

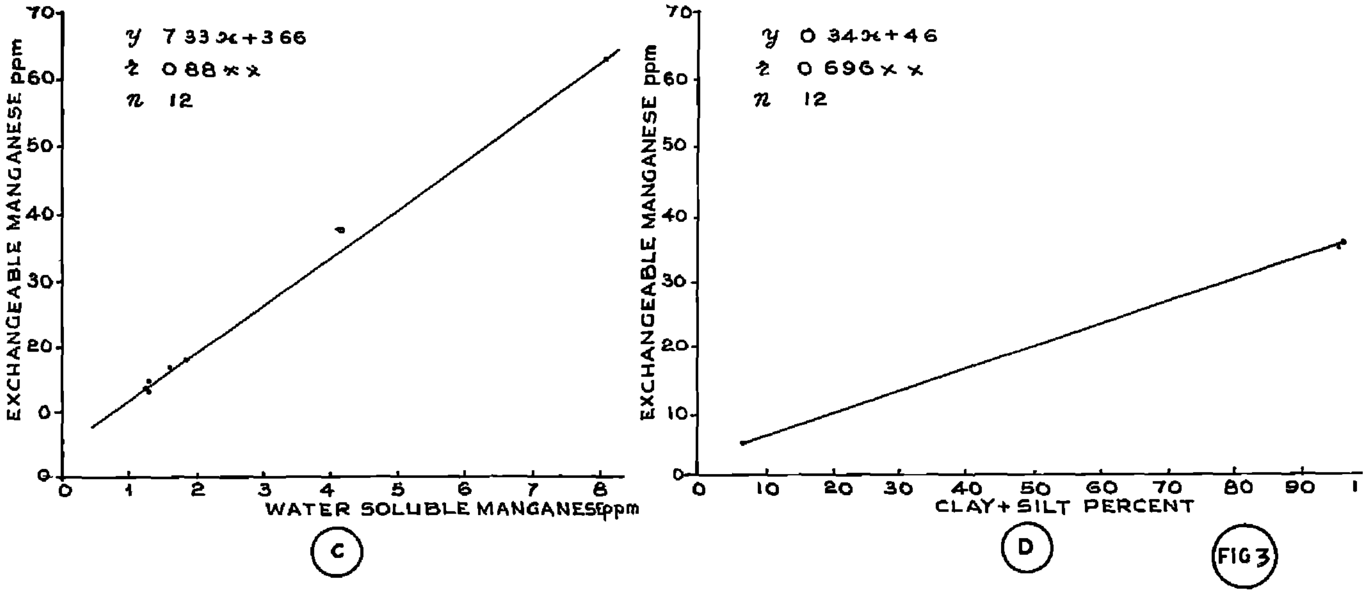
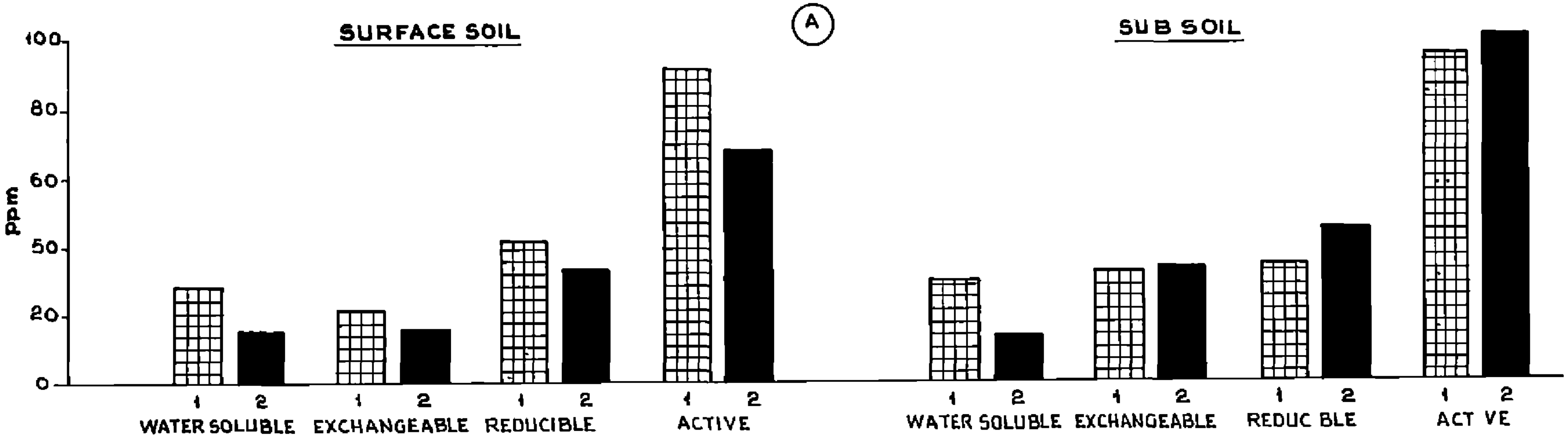


FIG 3

DISTRIBUTION OF DIFFERENT FORMS OF IRON IN WATER LOGGED AND DRY SOILS



DISTRIBUTION OF DIFFERENT FORMS OF Mn IN WATER LOGGED AND DRY SOILS

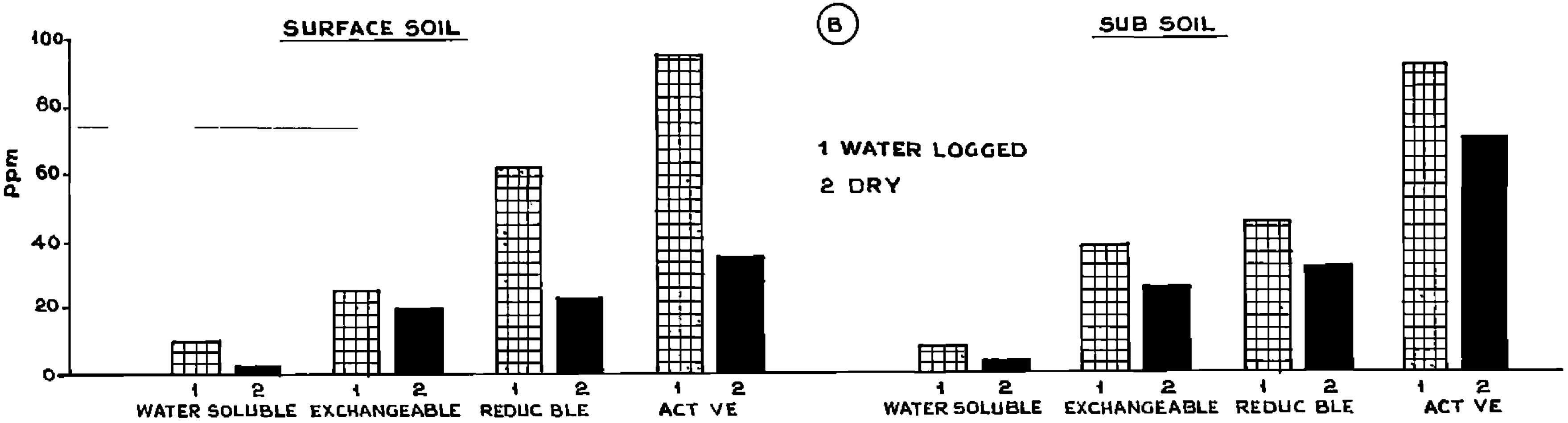


FIG 4