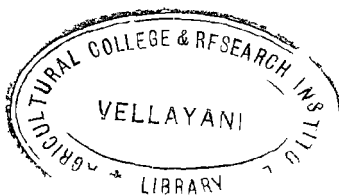# STUDIES ON
EXTRACTABLE ALUMINIUM IN RICE SOILS OF KERALA

By

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THESIS

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE IN AGRICULTURE (AGRICULTURAL CHEMISTRY) OF THE UNIVERSITY OF KERALA

DIVISION OF AGRICULTURAL CHEMISTRY
AGRICULTURAL COLLEGE AND RESEARCH INSTITUTE
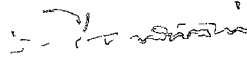VELLAYANI, TRIVANDRUM

1967

CERTIFICATE

This is to certify that the thesis herewith submitted contains the results of bonafide research work carried out by Kumari H. Karthikakutty Amma 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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Shri. E.J. Thomas, Junior Professor of
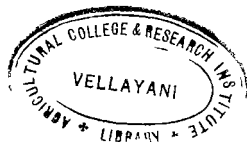Agricultural Statistics, for the guidance in the
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INTRODUCTION

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INTRODUCTION

Rice is the major food crop of Kerala and it
covers an area of about 2 million acres. Most of the
work carried out so far on the chemical and agronomic
problems of rice soils of this State relate to the
availability of the major plant nutrients and response
to added fertilizers. More than 80 percent of the rice
soils of Kerala are acidic in reaction. Consequently,
large amounts of soluble and exchangeable aluminium are
likely to be present in these soils causing direct and
indirect harmful effects on plants.

Plant species differ widely in their tolerance of
aluminium in nutrient solutions and acid soils containing
high levels of soluble or exchangeable aluminium, as
reported by Burgess and Pember (1923). The nature of
this differential aluminium tolerance has not been fully
clarified. There may be direct effects such as phosphorus
fixation or indirect effects such as increasing soil
acidity.

Though some workers have reported that aluminium
in traces is beneficial to certain plants it is not
usually considered as one of the essential elements. The

more frequently reported condition is that of aluminium toxicity.

An explanation regarding the toxicity mechanism is that soluble aluminium greatly reduces the degree of activation of isocitric dehydrogenase and malic enzyme by manganese even if manganese is supplied adequately or in excess. Aluminium injury has been associated with the decrease in the uptake and utilisation of P as reported by Burgess (1923) and decrease in the uptake and utilisation of calcium as suggested by Foy and Brown (1962). A decrease in the overall permeability of plant roots has also been recorded.

although much is known regarding the aluminium content of plants, relatively little data are available on the aluminium status of rice soils. Very little work has been done on the distribution of aluminium in Kerala soils and the available information on this subject is very meagre.

The present investigation was, therefore, undertaken with the following main objectives viz.,

3

1.   To characterise the rice soils of Kerala on the basis of the amounts of aluminium removed by various extracting solutions.

2.   To study the relationship of soil pH to extractable aluminium.

3.   To determine the aluminium content in rice plants grown on these soils.

4.   To investigate the seasonal variations in potassium chloride extractable aluminium with special reference to the cropping period.

REVIEW OF LITERATURE

REVIEW OF LITERATURE

Extractable aluminium

Mirasol (1922) citing an unpublished work of
Knight reported that more aluminium was extracted from
potassium saturated soils than from those saturated
with calcium.

Burgess (1923) suggested that aluminium can be
extracted with a weak acid viz., 0.5 N acetic acid.

Pierre et al (1932) suggested that the presence
of soluble salts is required for maximum extraction of
aluminium.

Hoglstad (1933) showed that the decrease in
extractable aluminium with increased base saturation
was due to the amphoteric properties of aluminium.

Chernov and Kislitsyana (1955) showed that the
ratio of hydrogen ions to aluminium ions in the potassium
chloride extracts of acid soils depended on the type of
soil, on the horizon sampled, and on the time interval
between extractions.

Mclean et al (1958) found that ammonium acetate
at pH 4.8 to be the most satisfactory extractant for
aluminium for Ohio soils. For soils below pH 4.8 they
found barium chloride to be a more suitable extractant.

Rixon and Sherman (1962) found that liming the
surface soils reduced the amount of aluminium extract-
able with 1N ammonium acetate. Similar results were
obtained by Plucknett and Sherman (1963) on sub soils.

McLean et al (1962) have shown that single
leaching is as good an index as multiple leaching for
indicating the relative amounts of extractable aluminium.

Exchangeable aluminium

Paver and Marshall (1934) demonstrated that the
liberation of aluminium from unsaturated clays by
neutral salts was due to direct exchange of the
aluminium by the cations.

Ayres (1943) showed that most of hawaii's highly
leached soils are extremely acidic. H ion saturation
in many of them were above 95 percent.

But Limy and Yu (1957) showed that the acidity of
Krasnozems and Zheltozems is almost exclusively due to

exchangeable aluminium. The maximum content of exchangeable hydrogen is only 4 percent of the total exchange acidity.

Yarusov (1948) found that while exchangeable hydrogen ions contribute acidity in top soils, the acidity in lower horizons was mainly due to the preponderence of aluminium ions.

Chatterjee (1949) showed that aluminium present in the surface of clays may be liberated by neutral salts (inorganic fertilisers) in amounts toxic to crop plants.

Russel (1950) considered mineral soils to be aluminium soils and not hydrogen soils. He found that exchangeable aluminium contributed markedly to exchange acidity in such soils.

Nikistikina (1951) showed that exchangeable aluminium content can be decreased by application of organic matter in the form of Farm Yard Manure.

Harward and Coleman (1954) found that aluminium predominated in H - Al clays prepared by electrodialysis or dilute acid leaching.

Paver and Marshall (1955) showed that acid clays are really H – Al clays.

Chernov and Belyaeva (1956) showed that exchangeable acidity of acid podzolised and chernozem is mainly due to the presence of adsorbed hydrogen ions.

Fiskell and Gamman (1958) suggested that ammonium acetate was an extractant for exchangeable aluminium for Florida soils.

Holowaychuk (1958) showed that even though all the extractable aluminium was not completely exchangeable, a definite relationship exists between extractable aluminium and cation exchange capacity of soils.

Low (1958) used barium chloride as an extractant for replaceable aluminium on bentonite clays.

Moskal (1959) showed that the appearance of mobile aluminium was counteracted with corresponding reduction in soil acidity by the annual application of 20 tons per hectare of Farm Yard Manure. Balev et al (1957) also showed that Farm Yard Manure decreased soil acidity and mobile aluminium content.

Hattovi and Kawaguchi (1959) showed that on acid soils exchangeable aluminium can be supplied by both the clay minerals and by free alumina.

Coleman et al (1960) showed that the removal of exchangeable aluminium by 1N potassium chloride reduced phosphorus sorption by soils except in those which contained low exchangeable aluminium and high amounts of iron and aluminium oxides.

Sokolov (1960) showed that exchange acidity of Kraznozem and sod podzolic soil is mainly due to exchangeable aluminium. Appreciable quantities of exchangeable hydrogen occurred in peat soil, but not in Krasnozem or sod podzolic soils.

Avdomin et al (1960) showed that application of cow dung decreased the hydrolytic acidity of the soil, increased the total exchangeable bases and decreased the available aluminium content.

Pratt and Blair (1961) showed that extraction with 1N potassium chloride allowing a minimum time of contact with the first portion of the extractant probably gives the most reliable estimate of exchangeable aluminium.
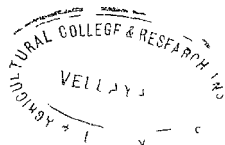
McLean et al (1962) showed that 1N potassium
chloride solution removed only about a sixth to a
quarter of the acidity from soils with a base unsatura-
tion of more than 80 percent.

McLean et al (1964) found that titrable but non-
exchangeable component of acidity was largely due to
hydroxy aluminium.

Aluminium toxicity in acid soil

Donison (1922) and Line (1926) reported that
aluminium compounds are so insoluble that they cannot
occur in solution in concentrations sufficient to cause
injury to plant growth. They are the major toxic factor
in acid soils.

Magistad (1925) determined the solubility of
aluminium in water and soil solution at different pH
values. At pH 5.0 water as well as soil solution could
hold 1-2 ppm of soluble aluminium. Solubility was found
to decrease with increasing pH values. In the pH range
3.0 to 4.5 the solubility of aluminium increased
progressively. At lower pH values solubility of alumi-
nium rapidly increased. He found that the decrease in

acidity due to liming of soils with pH below 5.0 was
mostly due to the decrease in aluminium solubility.

McLean (1927) reported that in the absence of
phosphate considerable amount of aluminium may be
maintained in soil solution between pH 4.0 and 4.5.
Plants differed in their sensitivity to aluminium
toxicity. Aluminium in minute quantities is a growth
stimulant and in large quantities is toxic.

According to Blair and Prince (1927) acids and
acid forming materials such as aluminium sulphate,
aluminium nitrate and aluminium phosphate reduce pH of
the soil and increased the amount of active aluminium
in solution. They found basic slag to be effective in
reducing the active aluminium in soil solution.

Pierre et al (1932) stated that soils of relatively
high percent base saturation at low pH values yielded in
general less aluminium in solution than soils of low
percentage base saturation. They also observed that
aluminium solubility was markedly increased by a high
concentration of soluble salts.

From a study on eighteen very acid soils
Pohlman (1933) concluded that nitrification and sulphur

oxidation were effective in bringing aluminium into the
soil solution.

Pierre and Stuart (1933) affirmed that the
problem of aluminium toxicity and phosphorus availability
were closely interrelated. Direct root injury and inter-
ference with the translocation and assimilation of
phosphate due to precipitation of phosphorus within the
plant by the absorbed aluminium are the two probable
causes of aluminium toxicity.

Lockard and Mewalter (1956) attempted a review of
the work of three different soil investigators and showed
that aluminium toxicity occurs at concentration between
6.7 to 40.5 ppm. They also observed that addition of
200 ppm of aluminium sulphate had a slight stimulating
effect. Upto 600 ppm no adverse effect was found. The
heavier doses were toxic.

Tomlinson (1957) observed that an aluminium level
higher than 250 ppm might be harmful to plants. He also
showed that a concentration of 1000 ppm of soluble iron
would adversely affect the crop.

Moorman (1961) stated that in some rice soils of
Indochina aluminium concentration was as high as 800 ppm

and it seriously affected the production of rice.

Cate and Sukhai (1964) concluded that a concentration of water soluble aluminium as low as 1-2 ppm markedly inhibited rice roots in the absence of nutrient cations. Higher concentrations prevented root growth and produced mottlings on the leaves. Concentrations of neutral salts greater than 1800 ppm affected plant growth both by salt injury and by displacing aluminium with the soil solution. They advised leaching the soil with sea water to improve acid soils.

Aluminium in soils at different periods of the year

pH plays an important role in the amount of extractable aluminium in soils. pH of soils fluctuate in water-logged soils. Submergence of a soil leads to gradual increase in pH. The magnitude of the change appears to depend on the initial pH, the organic matter content and duration of submergence.

Gillespie (1920) noted a decrease in hydrogen ion concentration when a soil was submerged.

Subramonian (1928) demonstrated the reality of the decrease in hydrogen in concentration due to submergence.

He attributed the increase in pH to the increased concentration of ammonia. But Schollen berger (1929) showed that the increase in pH was due to increased concentration of manganese.

A decrease in hydrogen ion concentration under water-logged condition causes a decrease in extractable aluminium also.

Burgess (1923) showed a direct correlation between pH and active aluminium. He also noted a possible relationship between active aluminium and rainfall.

Magistad (1925) found that aluminium solubility seemed to increase with increasing acidity.

Yuan and Fiskell (1959) used 1N ammonium acetate at six pH levels and found that as acidity increased, extractable aluminium increased.

Plucknett and Sherman (1963) found a decrease in extractable aluminium with increase in pH of the soil and attributed this to the formation of less soluble forms of aluminium hydroxides.

McLean et al (1964) showed that at higher pH values hydroxy aluminium ions polymerise and form inter layers or surface coatings in the clays and other colloidal systems and since the polymerised hydroxy aluminium is not extractable with potassium chloride, the titrable but non-exchangeable component of acidity was largely due such hydroxy aluminium.

But more recently McLean et al (1965) examined the comparative roles of organic and inorganic components of acidity and found that hydroxy aluminium have only a smaller role than was originally thought.

Ayres et al (1965) showed that as soil acidity increases, aluminium soluble in both potassium chloride and ammonium acetate also increases. Therefore in these soils continued and extensive use of ammonium fertilisers might produce soils so acid that aluminium toxicity would become a problem in the sugarcane soils of Hawaii.

MATERIALS AND METHODS
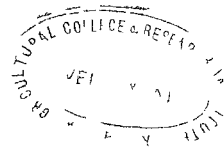
MATERIALS AND METHODS

Collection of Soil Sample

Twenty surface soil samples (0 to 15 cm) were collected from different representative rice tracts of Kerala State. The soils include <u>Kari</u>, <u>Karapadam</u>, <u>Kayal</u> and low level laterites. The samples were collected in cotton bags lined inside with polythene and transported to the laboratory for analysis. Soils were collected at monthly intervals from December 1966 to April 1967 from two selected sites, one from a double crop field near Vellayani and the other from the bed of the Vellayani <u>kayal</u> for periodical analysis of aluminium

Collection and preparation of plant samples

Rice plants were collected from fields, the soils of which were already collected for the present investigation. The plants were washed well in tap water, followed by distilled water and then taken to the laboratory in polythene bags for analysis. The root portion was discarded. The plant tops were air dried, cut into small pieces and further dried in an

air oven at 70°C. The prepared samples were kept in labelled bottles.

Treatment of samples

A. Soils

The soils were air dried, ground and allowed to pass through a 2 mm seive.

Treatment of air dried soils using different extractants

Extractants used

1. 1N potassium chloride (Ayres et al, 1965)
2. 1N ammonium acetate (Ayres et al, 1965)
3. Distilled water (Ayres et al, 1965)

10 g of air dried soil sample was shaken for one and a half hours using 1N potassium chloride at different ratios namely 1:10, 1:20 and 1:40. The solution was filtered and used for determination of aluminium. Three successive extractions were carried out using 1N potassium chloride in the ratio 1:10. For determination of extractable aluminium, air-dried samples were shaken with 1N ammonium acetate at different pH values (4.8, 6 and 8). Successive extractions were carried out three times in
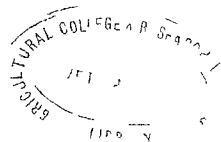
the ratio 1:10 with ammonium acetate of pH 4.8. The
solutions were filtered and the concentration of
aluminium in the filtrate determined. For water soluble
aluminium, the air-dried soils were thoroughly wetted
with distilled water and drained for approximately
twenty hours. Suction was then applied and aluminium
determined in the filtrate colorimetrically with
aluminon reagent as suggested by Yuan and Fiskell (1959).

B. Plant samples

The plant samples were prepared for analysis of
aluminium according to the method described by Piper
(1949). Two grams of oven-dried samples were dry ashed
in a platinum crucible. The ash was dissolved in dilute
hydrochloric acid. The silica was separated out and
destroyed using hydrofluoric acid.

Determinations

1. Mechanical analysis

Mechanical analysis was carried out by the
International Pipette method (Piper, 1950).

2. pH

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

3. Organic carbon

Organic carbon was estimated by Walkley and Black's method as described in Piper (1950).

4. Cation exchange capacity

10 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 of standard acid followed by titration with standard alkali (Piper, 1950).

5. Sesquioxides

10 g soil was digested with 1:1 hydrochloric acid and filtered. The filtrate was made upto a known volume. Sesquioxides were precipitated in an aliquot of the hydrochloric acid extract. They were filtered, ignited and weighed as combined oxides (Piper, 1950).

6. Iron oxide

Iron was then determined in a separate aliquot
of the hydrochloric acid extract by reduction with zinc
and dilute sulphuric acid and the ferrous solution thus
obtained was then tirated with standard potassium
permanganate solution (A.O.A.C., 1960).

7. Aluminium oxide

Aluminium oxide was estimated by noting the
difference between the sesquioxides and iron oxide as
determined earlier.

8. Exchangeable, extractable and water soluble aluminium

The filtrate for the determination of aluminium
was prepared as described earlier. The aluminium present
in the filtrate was determined by aluminon method. In
all cases interference of iron was eliminated using
thioglycollic acid. The interference of organic carbon
was avoided by destroying it with hydrogen peroxide.
The transmittancy of the solution was read on the Klett-
Summerson photoelectric colorimeter using a green filter.

9. Aluminium in plant

Chenery's colorimetric analysis of aluminium using thioglycollic acid as inhibitor for iron (Chenery, 1948) was used. The transmittancy of the solution was read on the Klett-Summerson photoelectric colorimeter using a green filter.

RESULTS

R E S U L T S

The details of soil samples used in this study are given in Table I. The soil pH varies from 3.1 for Kari soils of Kuttanad to 6.5 for kayal soils. For Kari soils pH ranges from 3.1 to 4.6, for kayal soils the range is 5.1 to 6.5. pH of Karapadam soils lies between 4.3 and 5.5 while for low level laterite the range is from 4.8 to 5.3.

Table II presents data on some properties of the soils which have a bearing on the present investigation. The cation exchange capacity varies from 58.0 to 5.8, the maximum values being shown by Kari soils and the minimum values by laterite soils. The variation in the range of values for organic carbon is more conspicuous. It varies from 17.57 for Kari soils to 1.37 for laterite soils. With respect to alumina (Al_2O_3), the variation is not so marked, the Kari soils showing comparatively lower values. Iron oxide content varies from 4.8 percent to 17.0 percent.

The mechanical composition of soils is given in Table III. The data show that clay content varies from
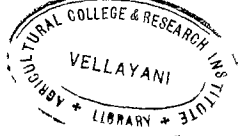
TABLE I

Details of soil samples used for study

Sl. No.	Soil type	Soil pH	Location	Soil condition
1	Kari	3.1	Vaikom	Wet land paddy
2	..	4.1	Vadayar	,,
3	..	4.3	Karumadi	,,
4	..	4.0	Ampalapuzha	,,
5	..	4.3	Ellichira	,,
6	..	4.6	Nilamperoor	,,
7	..	4.9	Thakazhi	,,
8	..	4.3	Kavalam	,,
9	Kayal	5.1	Vellayani	,,
10	..	6.5	Vechoor	,,
11	..	6.4	Mundar	,,
12	..	5.3	Trichur kole	,,
13	Karapadam	4.3	Madirampally	,,
14	..	5.5	Mundar	,,
15	..	5.4	Nedumudi	,,
16	..	4.3	Purakad	,,
17	Low level laterite	5.2	Pattambi	,,
18	..	5.2	Vellayani	,,
19	..	4.8	Mavelikara	,,
20	..	5.3	Trichur	,,

TABLE II

Analysis of soil

Sl. No.	Soil Type	CEC (m.e./100 g)	Organic carbon (%)	Fe_2O_3 (%)	Al_2O_3 (%)
1	Kari	58.0	13.29	9.8	6.8
2	..	38.0	12.58	9.3	6.1
3	..	35.0	9.11	4.8	5.5
4	..	45.0	9.44	10.5	8.5
5	..	35.1	11.00	7.0	10.5
6	..	34.0	17.57	9.9	12.1
7	..	31.0	15.72	9.0	10.5
8	..	35.00	16.50	14.1	10.5
9	Kayal	28.0	2.80	9.8	13.0
10	..	20.1	5.25	10.4	8.0
11	..	14.0	5.50	5.5	8.5
12	..	35.6	11.40	5.9	16.9
13	Karapadam	36.4	2.38	10.5	19.5
14	..	25.1	2.77	9.5	10.5
15	..	30.0	1.37	8.5	12.5
16	..	35.0	4.87	10.5	16.5
17	Low level laterite	5.8	1.69	9.5	17.5
18	..	5.8	1.20	19.6	12.6
19	..	15.8	4.45	10.5	13.6
20	..	23.0	1.66	12.3	15.9

TABLE III

Mechanical composition of soils

Sl. No.	Soil type	Coarse sand (%)	Fine sand (%)	Silt (%)	Clay (%)
1	Kari	1.35	3.2	21.0	67.5
2	..	0.95	12.0	17.2	59.5
3	..	1.10	4.0	19.0	60.6
4	..	2.00	9.5	21.0	69.0
5	..	1.56	10.0	26.0	61.0
6	..	2.05	12.1	25.5	59.0
7	..	1.95	6.0	30.0	60.9
8	..	1.75	9.8	19.0	65.0
9	Kayal	3.50	14.0	21.0	51.0
10	..	5.00	16.0	16.5	49.0
11	..	4.00	15.5	20.0	50.5
12	..	3.50	17.1	18.0	55.0
13	Karapadam	3.00	14.0	12.0	45.0
14	..	9.10	15.8	11.0	40.0
15	..	6.10	11.0	17.0	39.5
16	..	8.90	15.5	15.8	46.0
17	Low level laterite	48.00	19.0	11.0	25.0
18	..	35.10	16.0	10.0	30.0
19	..	30.25	17.5	5.0	25.5
20	..	25.16	18.5	7.5	20.0

20 to 69 percent. Almost all soils selected are clayey in nature.

Table IV presents data on aluminium extracted by different extractants viz., ammonium acetate, potassium chloride and water. The maximum quantity of aluminium (7000 ppm) was extracted by ammonium acetate from _Kari_ soils. The minimum quantity of aluminium extracted was 275 ppm from kayal soils. With regard to the amount of aluminium extracted by 1N potassium chloride the general trend was as in the case of ammonium acetate extraction. But the quantity extracted by 1N potassium chloride was less than that extracted by ammonium acetate. In the case of extraction with water, the quantity extracted was much less, the range of variation being from 1-16 ppm.

Aluminium extracted by ammonium acetate at various pH values is shown in Table V. The maximum quantity of aluminium was extracted at pH 4.8. At pH 6.0, the maximum quantity extracted was 1225 ppm the minimum quantity being 40 ppm. At pH 8.0 the amount of aluminium ranges from 250 to 5 ppm.

TABLE IV

Aluminium extractable by various extractants

Cl. No.	Soll type	Normal ammonium acetate (pH 4.8)	Normal potassium chloride	Water
			ppm	
1	Karl	7000	3700	16
2	..	3005	1800	10
3	..	2015	1471	8
4	..	2550	1810	10
5	..	3000	1300	8
6	..	1500	685	7
7	..	750	750	7
8	..	2015	975	5
9	Kayal	676	202	5
10	..	275	85	1
11	..	525	95	1
12	..	670	150	4
13	Karapadam	2550	2000	2
14	..	575	200	3
15	..	580	216	4
16	..	2750	738	8
17	Low level laterite	600	143	5
18.	..	675	152	5
19	..	1000	925	6
20	..	700	1180	5

TABLE V

Aluminium extractable by 1N ammonium acetate at different pH values

Sl. No.	Soil type	Soil pH	pH 4.8	pH 6.0	pH 8.0
				ppm	
1	Sari	3.1	7000	1225	250
2	..	4.1	3005	600	120
3	..	4.3	2015	400	80
4	..	4.0	2550	980	125
5	..	4.3	3000	400	78
6	..	4.6	1500	301	50
7	..	4.9	750	250	35
8	..	4.3	2015	404	82
9	Kayal	5.1	676	225	40
10	..	6.5	275	40	5
11	..	6.4	525	45	6
12	..	5.3	670	201	35
13	Karapadam	4.3	2550	395	81
14	..	5.5	575	200	40
15	..	5.4	530	176	42
16	..	4.3	2750	385	75
17	Low level laterite	5.2	600	201	39
18	..	5.2	675	196	40
19	..	4.8	1000	266	40
20	..	5.3	700	201	36

Table VI presents data on successive extraction of soil with 1N ammonium acetate.

Results of multiple extraction is given in Table VII together with the corresponding equilibrium pH values. With Kari, Karapadam and laterite soils extractable aluminium dropped off sharply with successive treatments. In the case of kayal soil considerable decrease is not found. A rise in equilibrium pH values can also be noted with increasing number of extractions. In kayal soils where the third extraction produced no less aluminium than the second, there was no change in equilibrium pH.

Table VIII shows the effect of soil solution ratio on the quantity of aluminium. With the Kari soils, 400 ml potassium chloride solution extracted on an average nearly three times as much aluminium as the 100 ml solution. With the kayal soils, the change was not so intense as in the case of Kari soils. In Karapadam soils also the general trend was like that of Kari soils. With one exception the laterite soils also behaved like kayal soil with regard to the amount of aluminium extracted and shift in equilibrium pH values.
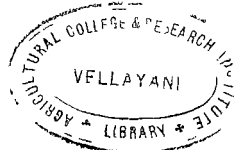
TABLE VI

Aluminium in successive 1N ammonium acetate (pH 4.8)
extracts of soils

Sl. No.	Soil type	I extraction	II extraction	III extraction
			ppm	
1	Kari	7000	2115	1015
2	..	3005	1109	835
3	..	2015	900	326
4	..	2550	1108	795
5	..	3000	980	600
6	..	1500	425	225
7	..	750	205	155
8	..	2015	700	300
9	Kayal	676	150	75
10	..	275	102	70
11	..	525	270	250
12	..	670	105	80
13	Karappadam	2550	825	602
14	..	575	602	150
15	..	580	125	88
16	..	2750	725	515
17	Low level laterite	600	150	5)
18	..	675	150	61
19	..	1000	650	420
20	..	700	350	250

TABLE VII

Aluminium in successive 1N potassium chloride
extracts of soils

Sl. No.	Soil pH	I extraction	Eq. pH	II extraction	Eq. pH	III extraction	Eq. pH
1	3.1	3700	2.9	2500	3.4	1200	3.5
2	4.1	1800	3.9	1020	4.2	720	4.5
3	4.3	1471	4.0	1005	4.3	800	4.8
4	4.0	1810	3.8	925	4.1	625	4.3
5	4.3	1300	4.2	825	4.4	500	4.5
6	4.6	685	4.3	420	4.5	200	4.8
7	4.9	750	4.7	525	4.9	220	5.1
8	4.3	975	4.1	625	4.3	300	4.5
9	5.1	202	4.9	182	5.2	100	5.2
10	6.5	85	6.3	85	6.5	67	6.5
11	6.4	95	6.1	86	6.3	40	6.4
12	5.3	150	5.0	120	5.0	100	5.3
13	4.3	2000	4.0	1200	4.3	600	4.3
14	5.3	200	5.1	150	5.3	75	5.5
15	5.4	216	5.2	136	5.5	120	5.6
16	4.3	738	4.1	520	4.3	300	4.4
17	5.2	143	5.0	105	5.2	62	5.2
18	5.2	152	5.0	100	5.2	44	5.3
19	4.8	925	4.6	525	4.9	405	4.9
20	5.3	1180	5.0	730	5.2	300	5.2

TABLE VIII

Effect of soil solution ratio on aluminium
extractable by 1N KCl

| Sl. No.	Soil solution ratio	Aluminium in soil ppm	Sl. No.	Soil solution ratio	Aluminium in soil ppm
1	10:100	3700	11	10:100	95
	10:200	6065		10:200	125
	10:400	11000		10:400	140
2	10:100	1800	12	10:100	150
	10:200	3800		10:200	250
	10:400	8640		10:400	375
3	10:100	1471	13	10:100	2000
	10:200	2750		10:200	3010
	10:400	3953		10:400	3750
4	10:100	1810	14	10:100	200
	10:200	3806		10:200	350
	10:400	5706		10:400	475
5	10:100	1300	15	10:100	216
	10:200	2710		10:200	375
	10:400	3708		10:400	480
6	10:100	685	16	10:100	738
	10:200	895		10:200	890
	10:400	1915		10:400	980
7	10:100	750	17	10:100	143
	10:200	975		10:200	156
	10:400	1050		10:400	175
8	10:100	975	18	10:100	152
	10:200	1050		10:200	175
	10:400	2700		10:400	189
9	10:100	202	19	10:100	925
	10:200	216		10:200	1050
	10:400	275		10:400	1375
10	10:100	85	20	10:100	1180
	10:200	95		10:200	1275
	10:400	115		10:400	1300
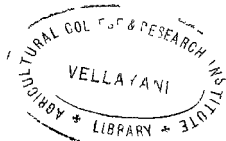
Table IX shows data on the amount of aluminium extracted with corresponding pH of extract. An increase in the pH of extract can be noted with increasing pH of soil.

The results of plant analysis for aluminium are given on Table X. The values range from 0.16 to 0.015 percent.

Table XI shows the variation in extractable aluminium with period at two locations in Vellayani. For the low level laterite the amount of aluminium ranges from 1795 ppm in December to 900 ppm in April. In Vellayani kayal the corresponding values were 810 ppm and 250 ppm respectively.

TABLE IX

Aluminium extracted by water with corresponding
equilibrium pH values

Sl. No.	Soil type	Soil pH	pH of extract	Aluminium in extract
				ppm
1	Kari	3.1	3.4	16
2	..	4.1	4.5	10
3	..	4.3	4.7	8
4	..	4.0	4.2	10
5	..	4.3	4.6	8
6	..	4.6	4.3	7
7	..	4.9	5.4	7
8	..	4.3	4.7	9
9	Kayal	5.1	5.4	5
10	..	6.5	6.6	1
11	..	6.4	6.7	1
12	..	5.3	5.5	4
13	Karopadam	4.3	4.5	2
14	..	5.5	5.6	3
15	..	5.4	5.8	4
16	..	4.3	4.7	8
17	Low level la'erite	5.2	5.5	5
18	..	5.2	5.6	5
19	..	4.8	4.9	6
20	..	5.3	5.5	5

TABLE X

Analysis of plant (paddy)

Soil No.	Soil pH	Aluminium in plant (%)
1	3.1	0.150
4	4.0	0.120
9	5.1	0.065
16	4.3	0.100
18	5.2	0.075
19	4.8	0.089
20	5.3	0.080

TABLE XI

Seasonal variation in extractable aluminium at two locations in Vellayani

Month	KCl extractable aluminium	
	Double crop land	Kayal
	ppm	
December	1795	810
January	1510	700
February	1390	556
March	1180	515
April	900	250

DISCUSSION

DISCUSSION

The results of the present investigation on
extractable aluminium in the various rice soils of
Kerala State as adjudged by different extractants viz.,
water, normal ammonium acetate and 1N potassium
chloride in relation to the uptake of aluminium by rice
plants are discussed hereunder.

The study on extractable aluminium in the
various soil types shows that the amount extracted
depends not only on the nature of the extractants but
also on soil characteristics such as pH, cation exchange
capacity, texture (Table II and III), soil to solution
ratio (Table VII) employed for the extraction and the pH
of the extractant (Table V).

The pH of the soil influences the amount of
aluminium extracted by the three different extractants
and this is revealed by the significant negative
correlation between pH of the soil on the one hand and
the amount of aluminium extracted by the extractants on
the other. The correlation coefficients and the
regression equations are given below:-

No.	y	Corre-lation	x	r	Regression equation
1	Extractable aluminium (ammonium acetate) (pH 4.8)	Vs	Soil pH	− 0.7	$y = 1012.6 + 187x - 9212x^2$
2	Extractable aluminium (potassium chloride)	Vs	Soil pH	− 0.8	$y = 6312.0 + 84x - 1860x^2$
3	water soluble aluminium	Vs	Soil pH	− 0.8	$y = -3.69x + 24.08$

From Table IV as well as from the sign of the correlation coefficients, it is clear that the amount of extractable aluminium increases as the pH decreases. This is to be expected since aluminium is more soluble under acid conditions. A similar correlation between pH and extractable aluminium has been demonstrated by Yuan and Fiskell (1959). In general, the extractable aluminium in soils tends to reach a minimum value near neutral pH which corresponds to nearly 100 percent base saturation. This result is in conformity with amphoteric properties of aluminium and has been amply demonstrated by Magistad (1925).

Figures 1, 2 and 4 show graphically the results obtained on extraction with 1N ammonium acetate (pH 4.8) and 1N potassium chloride and water of twenty different rice soils with pH values ranging from 3.1 to 6.5. Appreciable amounts of aluminium are not extracted till the soil pH is below 5.0. Below this pH approximate leniarity with decrease in pH value is maintained. A similar, but slightly different, relationship was obtained by Ayres et al (1965) with only ammonium acetate extract in the sugarcane soils of Hawaii.

Correlations between the clay fraction and the amount of aluminium extracted by 1N ammonium acetate extract pH 4.8 ($r = +0.51$) and between the clay fraction and the aluminium extracted by normal potassium chloride ($r = +0.49$) are significant. This is in confirmity with the results obtained by Lin and Coleman (1960). Since the clay fraction contributes considerably towards the cation exchange capacity of the soil, this relationship suggests that part of the aluminium extracted is exchangeable in nature. In fact, a significant correlation exists between the cation exchange capacity of the soil and the aluminium extracted by 1N potassium chloride, while there is no significant correlation for the

aluminium extracted by the normal ammonium acetate.
This suggests that the normal ammonium acetate extracts
larger amounts of aluminium from forms other than
exchangerble.

A significant correlation exists between the
aluminium extracted and the organic carbon content.
This suggests a close relationship between aluminium and
organic matter. The work of McLean et al (1965) suggests
that aluminium bound with organic matter is non-
extractable with normal potassium chloride.

The influence of the pH of the extractants on the
quantity of aluminium brought into solution has been
studied in the case of normal ammonium acetate (Table V,
Figure 3). This reveals that the amount of aluminium
brought into solution varies widely among the four
different soil types. In the case of Kari and Karapadam
soils it rose sharply as the pH decreases. The high
level of extractable aluminium in the poorly drained
Kari and Karapadam soils seems to substantiate the work
of England and Coleman (1959) who found the percentage
base saturation of aluminium to increase with decreased
drainage. More over, these soils are of very low pH
values and the high acidity is responsible for the
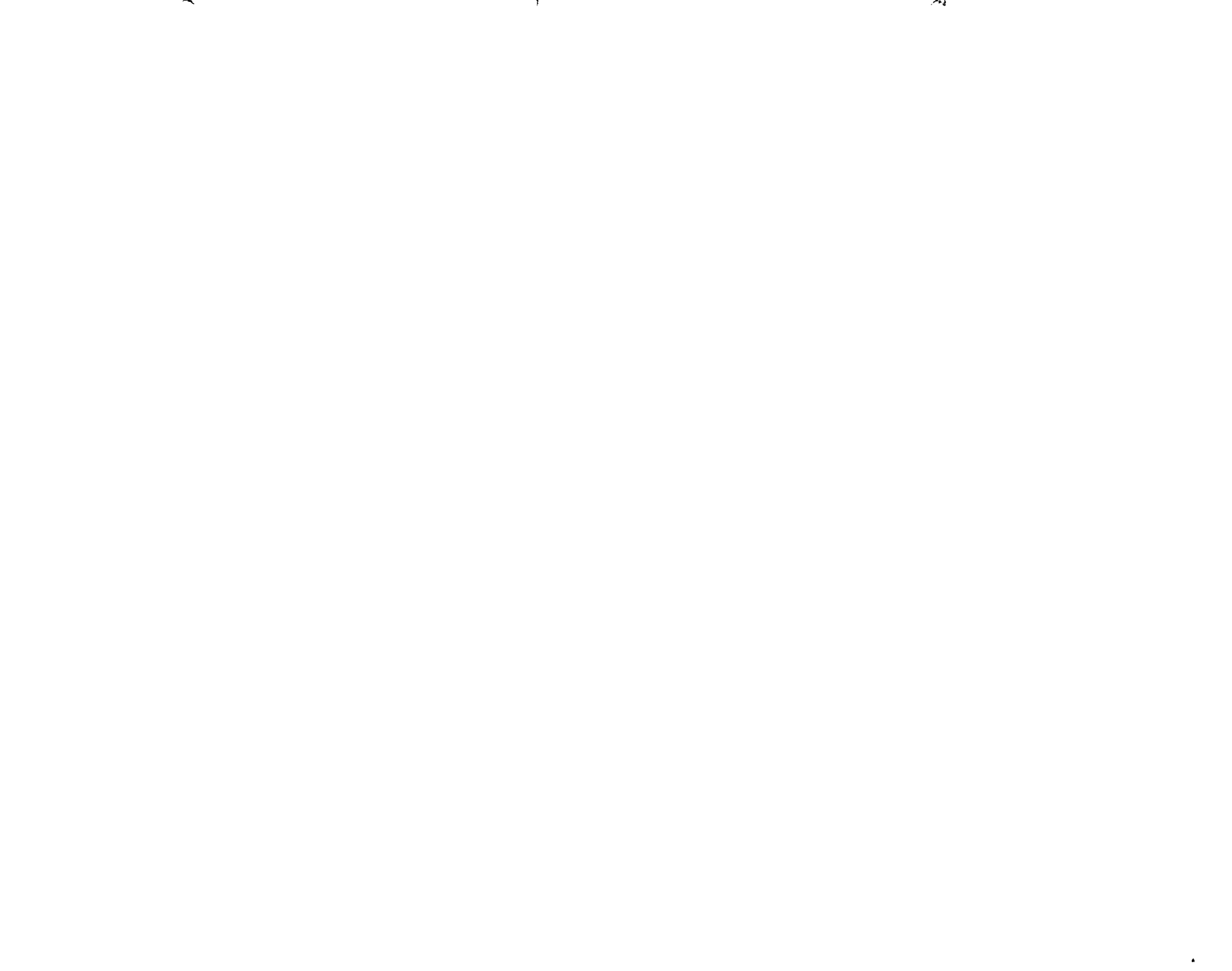dissolution of the aluminosilicate minerals present in
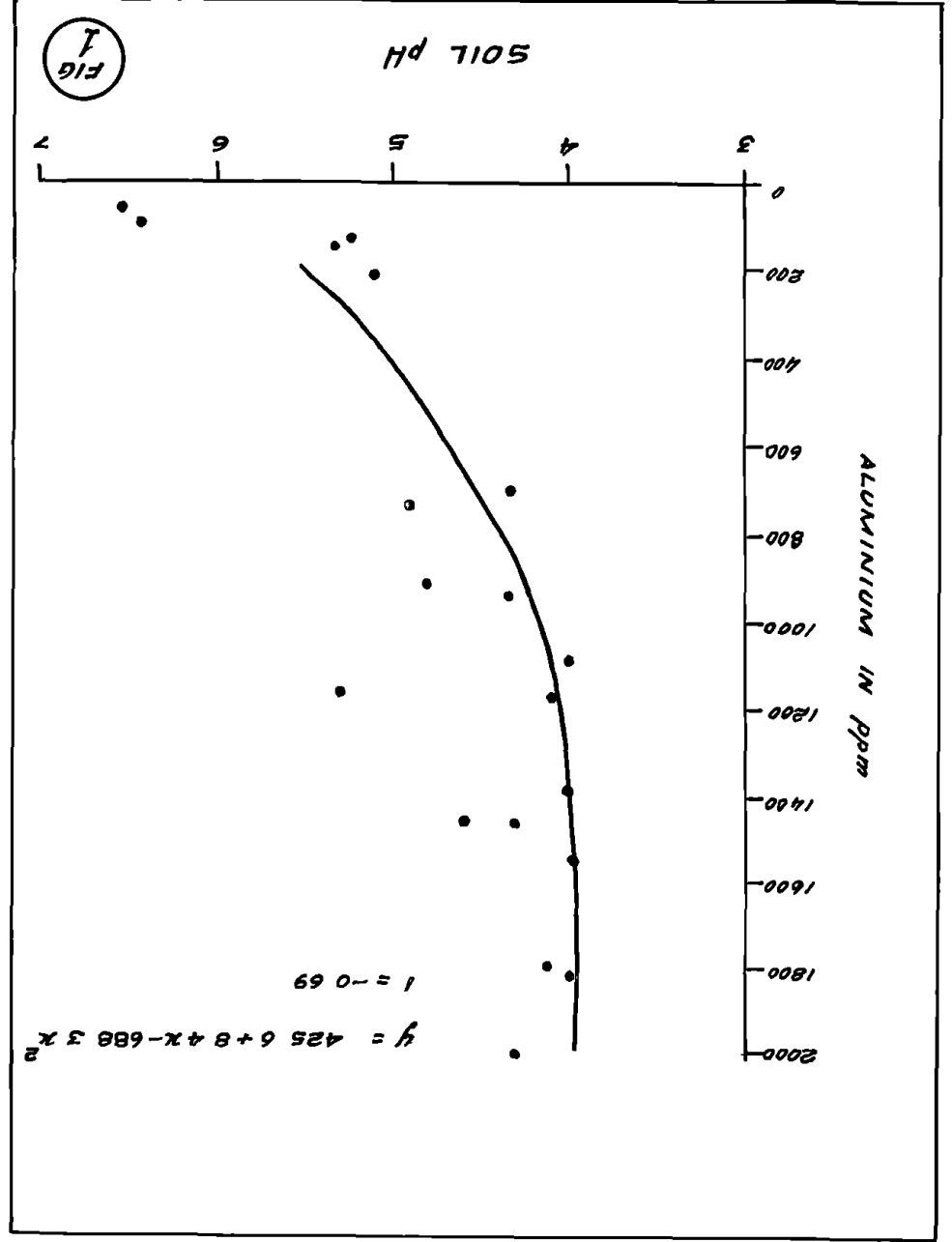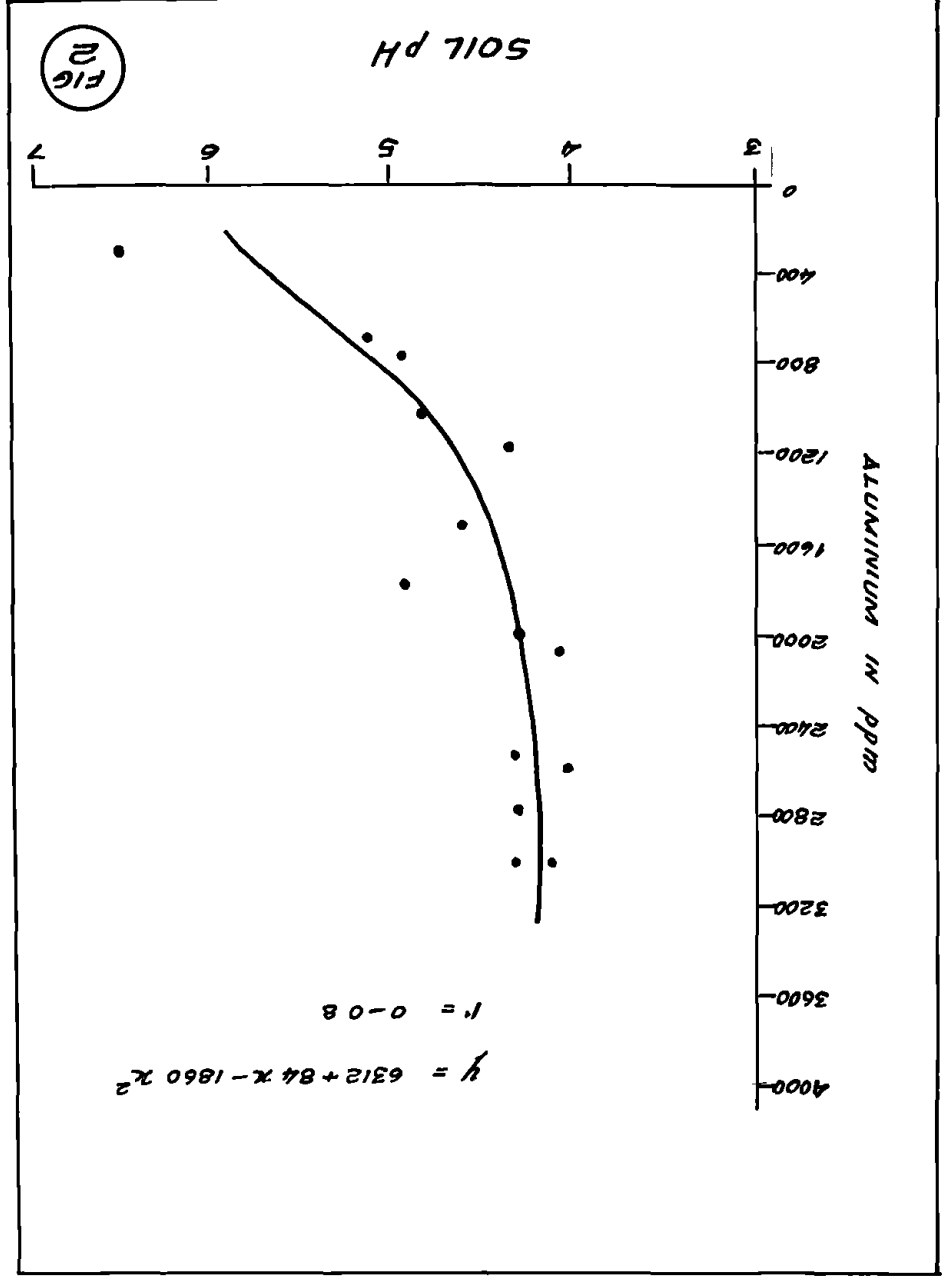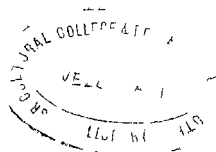
Fig. 2.   Graphical representation of aluminium
           extracted by ammonium acetate (pH 4.8)
           from different soils types of Kerala.

Fig. 1   Graphical representation of aluminium
          extracted by potassium chloride from
          different soil types of Kerala

them. Relatively lower values for extractable aluminium
in the laterite soils are probably due to the high iron
oxide concretionary fractions present in the surface
horizons. In the kayal soils the presence of deposits
of lime shells has been reported by Kurup (1966). This
together with the comparatively higher pH values observed
for these soils may account for the low extractable
aluminium. Similar results have been obtained by Tyvoa
et al (1965).

The effect of soil solution ratio on the aluminium
extracted with 1N potassium chloride was also studied.
A given weight of the soil was extracted with increasing
volumes of normal potassium chloride. If solubility is
involved greater quantities of aluminium should be
extracted with increasing volumes of solution. If
exchangeable aluminium alone is extracted larger volumes
of solution should extract only a little more aluminium
than smaller volumes. In the case of the Kari soil the
400 ml potassium chloride solution extracted on the
average more than three times as much aluminium as the
100 ml solution. In Karapadam soils the 400 ml potassium
chloride solution extracted 1.5 to 2 times as much
aluminium as the 100 ml solution. In the kayal soils

and in the low level laterite soils only slight increases were observed. These results could be interpreted as lending weight to the view that exchangeable aluminium is not the principal source of aluminium in the Kari and Karapadam soils while it is a dominant source of aluminium in the kayal and low level laterites. The low pH values of the Kari and Karapadam soils, together with the poor drainage conditions require that these soils contain larger amounts of soluble aluminium.

The amount of water soluble aluminium ranged from 1 to 16 ppm. Concentration of aluminium in the water extracts did not exceed 5 ppm in soils having pH above 5.0. These results are at variance with that of Lindsay et al (1959) who observed a water soluble aluminium concentration of only 0.1 ppm for Hawaiian soils. Within each soil group the amount of water soluble aluminium generally diminished with increasing soil pH (Fig. 4). The Kari and Karapadam soils contain higher amounts of water soluble aluminium than the kayal soils and low level laterites (Table IV).

Studies on the extractability of aluminium provide evidence that dissolution rather than exchange mechanics accounts for much of the aluminium appearing in the highly
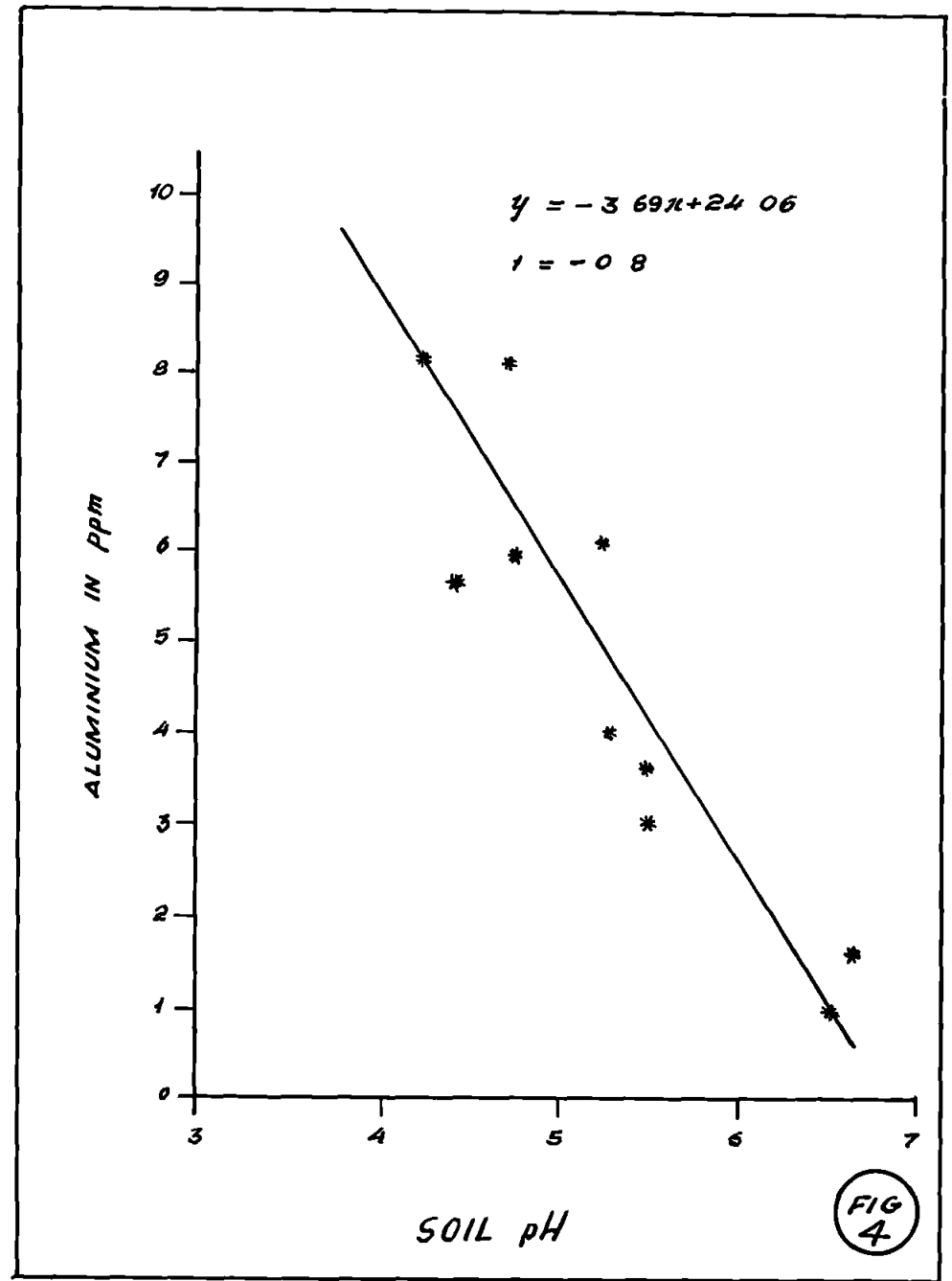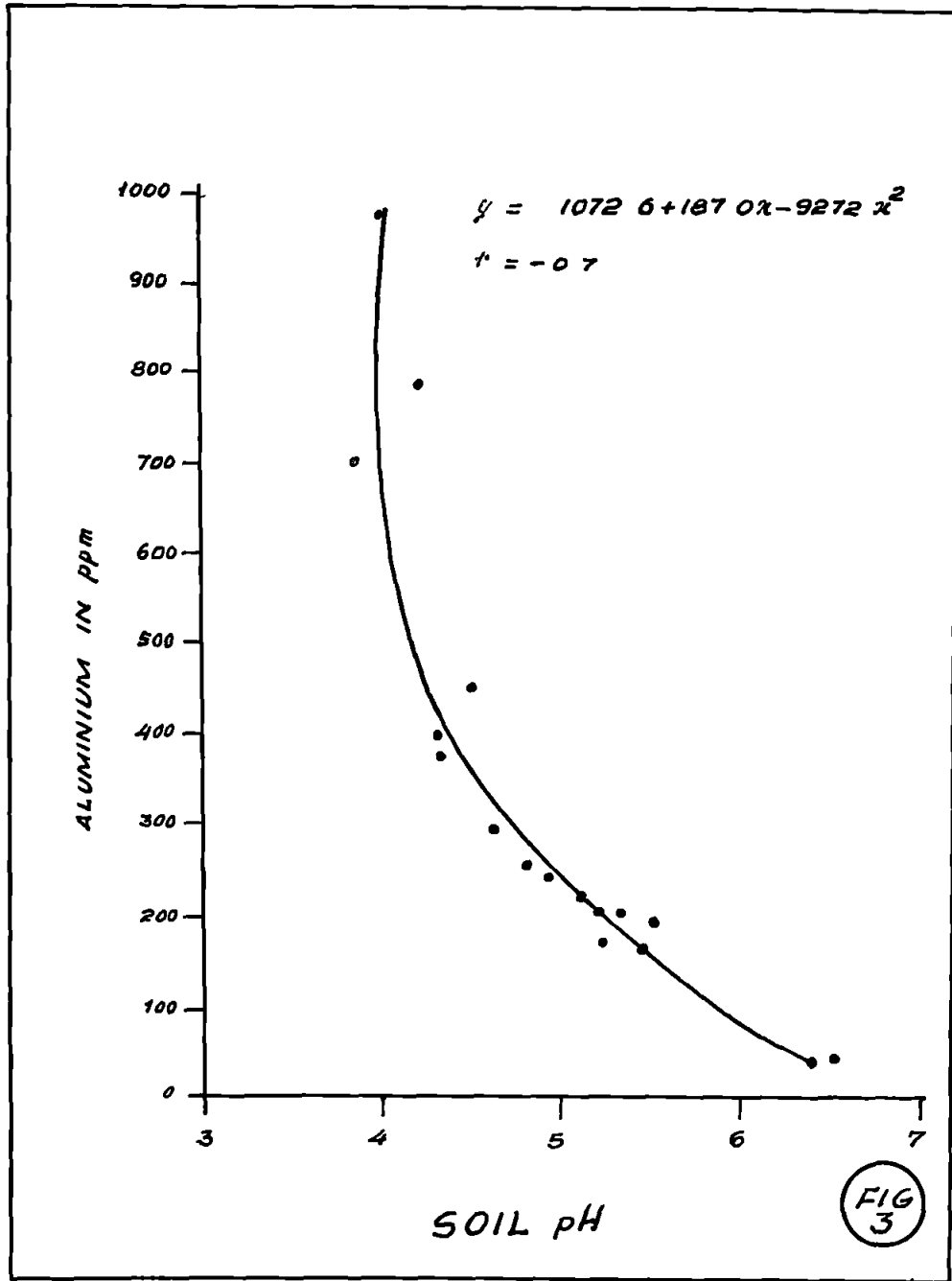
acid Kari and Karapadam soils. Water soluble aluminium concentrations above 2 ppm is considered to markedly affect, the rice roots and thus diminish the final yields. (Cate and Sukhai, 1964). Some of the soils recording high amounts of water soluble aluminium in the State are notorious for the low productivity of rice. Kurup (1966) observed that application of lime at twice the lime requirement levels is able to decrease the aluminium contents of <u>Kari</u> soils below toxic concentrations. Inundation of these soils with salt water during 6 months of the year prior to the cropping period helps to replace exchangeable aluminium and wash the soil free of aluminium.

Results on the multiple extraction of the soils with 1N ammonium acetate (pH 4.8) and 1N potassium chloride show (Table VI and VII) that the quantity of aluminium extracted decreases sharply with successive extractions, t is being greater in the case of normal potassium chloride. This suggests that the dissolution process accounts for greater part of the aluminium extracted by normal ammonium acetate than by normal potassium chloride. The initial decrease in equilibrium pH values is due to the replacement of exchangeable hydrogen ions from the soils by the potassium ions of the extractant. With further extractions the equilibrium

Fig. 4   Graphical representation of aluminium
              extracted by water from different soil
                        types of Kerala

Fig. 3.   Graphical representation of aluminium
              extracted by ammonium acetate (pH 6.0)
              from different soil types of Kerala.

$y = 1072.6 + 187.0x - 9272x^2$

$r = -0.7$

ALUMINIUM IN ppm

SOIL pH

FIG 3

$y = -3.69x + 24.06$

$r = -0.8$

ALUMINIUM IN ppm

SOIL pH

FIG 4

pH values tend to decrease with a concomitant decrease in the amount of aluminium extracted. The fact that these diminishing levels of aluminium were accompanied by increasing equilibrium pH values raises a question as to whether the aluminium was coming from exchange sites. Rising pH values might by themselves account in considerable degree for decreasing levels of aluminium if the source of the element were lattice or oxide aluminium, the solubilities of which are dependent on pH. With the kayal and low level laterite soils the equilibrium pH values are fairly constant with only a slight decrease in the amount of aluminium extracted.

Data on aluminium content in the 1N potassium chloride extract of soils collected from 2 locations viz., a double crop land adjoining the Vellayani lake and the bed of the Vellayani kayal are presented in Table XI.

The results show that in both the locations during the period from December to April there is a gradual decrease in extractable aluminium. The gradual decrease corresponds to the diminishing rainfall and the reduction in the extent of water-logging of the soils.

Lower amounts of extractible aluminium with decrease
in the extent of water-logging may be due to inactiva-
tion of exchange sites due to dehydration. Similar
results have been obtained in Hawaiian soils by
Plucknett and Sherman (1963).

Studies on the uptake of aluminium by the rice
crop (Table X) and correlation of the same with
potassium chloride extractable aluminium (r = +0.95)
ammonium acetate extractable aluminium (r = +0.8) and
water (r = +0.95) suggest that better correlations are
obtained with water and normal potassium chloride.
However, it is seen that water is not a suitable
extractant since the quantities extracted are insufficient
for proper estimation. Between ammonium acetate and
potassium chloride, potassium chloride appears to
extract more of exchangeable aluminium and bears a
closer correlation with aluminium uptake by rice plants.
Hence, for predicting toxic levels of aluminium in rice
soils 1N potassium chloride appears to be a more
suitable extractant.

The results of the present investigation thus
project the need for a very systematic evaluation of

the water and potassium chloride extractable aluminium content of the highly acid rice soils of the state in relation to the existence of toxicity symptoms in rice due to aluminium and how this could be corrected by resorting to a scientific programme of liming.

SUMMARY AND CONCLUSIONS

SUMMARY AND CONCLUSIONS

The distribution of the various forms of aluminium in the samples of soils collected from the major rice tracts of Kerala was assessed using different extracting solutions namely ammonium acetate, potassium chloride and water. Soil characteristics like, texture, organic carbon cation exchange capacity, pH, iron and aluminn content that are likely to influence the amount of aluminium were also studied. Periodical analysis of potassium chloride extractable aluminium was done on two samples collected at monthly intervals, one from Ve leyani lake area and the other from a double crop land adjacent to the Vellayani lake.

The following are the results obtained and conclusions drawn.

1.   Among the 3 different extractants tried for assessing aluminium status, normal potassium chloride was adjudged to be the best.

2.   The pH of the soil influences the amount of aluminium extracted by the different extractants.

3. Appreciable amounts of aluminium are not extracted from soils with pH values above 5.0.

4. Aluminium extracted by normal potassium chloride and normal ammonium acetate is positively and significantly correlated with the clay fraction of the soil.

5. The cation exchange capacity of the soils are well correlated with normal potassium chloride extractable aluminium. The lack of such a correlation for ammonium acetate extractable aluminium suggests that forms other than exchangeable are being extracted to a larger extent by the ammonium acetate.

6. The pH of the extractant has an influence on the amount of aluminium extracted. It increases sharply as the pH of the extractant decreases.

7. Increasing the soil solution ratio, increases by three fold the amount of aluminium extracted from *heri* soils. In the case of *karappadam* soils, there is a two fold increase. In the *kayal* and low level laterite soils, soil solution ratio does not appreciably influence the amount of aluminium extracted. This suggests that exchangeable aluminium is the dominant source of aluminium in *kayal* and low level laterites.

8.   Water soluble aluminium varies from 1-16 ppm.
The Kari and karapadam soils contain higher amounts of
water soluble aluminium.   This suggests the possible
existence of aluminium toxicity in rice grown in those
soils.

9.   Aluminium uptake by rice plants is positively
correlated with extractable aluminium.

10.   A decrease in the amount of extractable aluminium
observed with a decrease in the extent of water logging
and diminishing rainfall suggests inactivation of exchange
sites in the soil by dehydration.

11.   Inundation of Kari and karapadam soils prior to
the cropping period helps to replace exchangeable
aluminium and wash the soils free of aluminium.

        The results of the present investigation thus
project the need for a very systematic evaluation of the
water and potassium chloride extractable aluminium
content of the highly acid rice soils of the State in
relation to the existence of aluminium toxicity symptoms
in rice due to aluminium and how this could be corrected
by resorting to a scientific programme of liming.

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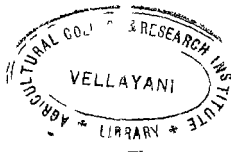
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