THE ORIGIN AND NATURE OF THE PEATY SOILS OF TRAVANCORE.

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The *Kari* soils occur in patches among the taluks of Ambalapuzhay, Sherthalay and Vaikom of Central Travancore, and cover an aggregate area of over 20,000 acres. They are essentially dark and strongly smelling tracts lying below the sea level, subject to inundation by fresh water during the monsoon months (June–October) and by sea-water during the remaining part of the year. The *Kari* lands of Ambalapuzhay have been partially reclaimed during recent years and are chiefly under paddy cultivation, but the crops often fail partly owing to unfavourable climatic conditions (Pillai and Subrahmanyan, *J. Indian Inst. Sci.*, 1930, **13A**, 1) and partly owing to inadequate drainage, accumulation of decaying vegetation, intense acidity and increasing amounts of chlorides and sulphates. In view of the partial submergence of these lands by sea-water and the etiolation and 'yellowing' of rice plants so frequently observed about a month after sowing, Narayana Aiyar was led to conclude that the soils contain considerable quantities of the chloride and the sulphate of sodium, which inhibit the absorption of requisite amounts of the essential mineral nutrients as well as iron by the plants (Travancore Agric. Dept., 1923, Leaflet No. 126). He therefore suggested a system of drainage and liming for the amelioration of these lands.

Owing to the reasons stated above and their general inaccessibility, the major part of the *Kari* lands still remain wild and marshy regions with scarcely any vegetation except a coarse aquatic grass, the *Kathira*, which alone appears to flourish on it. The botanical identity of *Kathira* is still obscure. The grass is characterised by its small, submerged stem, profuse system of roots and prolific tillering: its leaves are hollow and rod-like, with thin, white internodes. It is used locally as a fodder.

There is no reliable record with regard to the origin and the early history of the *Kari* soils. Folklore points to the identity of these regions with the *Kandawa Vana* of Mahabaratha and there is increasing evidence to show that the area was once covered by forest. In different parts of the *Kari* tracts, partially decomposed wood as well as stumps of huge forest trees are still to be found. Stout stems of such trees together with the adhering roots have also been dug out, from time to time, from depths of six feet and over. It is, however, hardly probable that the original forest would have flourished under the present soil conditions of *Kari* lands. There is a suggestion that the region was once more elevated, and owing perhaps to an upheaval became depressed below sea-level. This view is supported by recent evidence that the *Kari* lands and surrounding areas of *Kuttanad* were once a part of the Arabian Sea (K. Parameswaran Pillai, *Dept. of Agr. Travancore, Bull.*, 1924, **9**). It may be presumed, from the above, that the lands were reclaimed from the sea partly by natural silting of rivers and partly by the efforts of man.

As already observed by Pillai and Subrahmanyan (*loc. cit.*), the *Kari* lands are characterised by the presence of (*a*) large quantities of partially decomposed organic matter and (*b*) abnormal amounts of soluble iron and aluminium salts. The physical properties and, to some extent, the chemical composition of the soils point to their being allied to the low-moor (Fen) peats (Waksman and Stevens, *Soil Sci.*, 1928, **26**, 113) of the temperate regions. The high temperature and the heavy rainfall of Travancore, the alternate inundation of the soils with fresh and salt water and the occurrence of considerable amounts of iron and aluminium salts suggest, however, that the conditions prevailing in the *Kari* lands are different from those in the low-moor peats. The present investigation was undertaken to determine (*a*) the conditions leading to formation of the *Kari* lands, (*b*) the relation between the organic matter of the soils and their vegetation, and (*c*) the agencies responsible for the solution of abnormal amounts of iron and aluminium.

EXPERIMENTAL.

The *Kari* soils examined in the present investigation were those from Ambalapuzhay. One of the authors (T.R.N.P.) toured the area and collected representative specimens to a depth of about 3 feet from different parts of the unreclaimed and the partially reclaimed tracts. It was found that the soil occurred in two distinct layers, the upper corresponding to the first foot, and the lower to the next 1½-2 feet. Specimens of the upper layer were more or less uniform; those of the sub-soil were more variable, being sometimes darker and more sticky, sometimes lighter and more sandy than those of the upper layer.

The mechanical composition, the available nutrients, the water-soluble constituents, the lime and other mineral requirements of the *Kari* soils have already been studied by Narayana Aiyar (*loc. cit.*) and by Pillai and Subrahmanyan (*loc. cit.*). To determine the nature and the extent of association between the mineral constituents of the soil and those of the existing vegetation, representative air-dried specimens of the soil and *Kathira* from different parts of the area were analysed by the A. O. A. C. (1925) methods. Table I presents the range of values thus obtained.

TABLE I.

Chemical constituent	Percentage			
	Kari soil		*Kathira*	
	From	To	From	To
Moisture	12·5	13·7	7·15	7·20
Loss on ignition...	38·0	45·0	78·7	80·5
Ash	41·5	48·0	12·1	14·1
Silica	26·5	32·2	5·3	7·1
Iron (Fe_2O_3)	3·5	4·0	1·3	1·5
Aluminium (Al_2O_3)	6·8	8·8		
Calcium (CaO)	0·6	0·8	0·7	1·1
Phosphoric acid (P_2O_5)	0·03	0·04	0·20	0·37
Potash (K_2O)	0·15	0·17	1·18	1·30
Sulphate (SO_4)	1·75	2·30	0·61	0·77
Chloride (Cl)	0·04	0·06	2·01	2·50

The moisture of the soil samples varied considerably with the period of air-drying. If the specimens were dried for only two or three days as in the case of ordinary soils, the moisture was in some cases as high as 30 per cent. On prolonged drying and storage the moisture diminished steadily, becoming constant at about 13 per cent., as observed above.

The mineral composition of the soil and its vegetation are not in any way related to each other. The distribution of soil-constituents points to a laterite origin, and shows a preponderance of iron, aluminium and sulphate over the others. The composition of *Kathira*, on the other hand, resembles those of the commoner flora of arable or grassland except that its silica content is a little too low and the chloride somewhat high. Since the grass is aquatic and since the surface-water of the *Kari* regions contains fairly large quantities of chlorides, particularly when there are tidal rises, it would appear from the above that the grass is independent of the soil for its mineral nutrition. During the dry months of the year, however, the concentration of sulphates and of iron and aluminium salts in the surface water tends to increase, owing to continuous solution of those salts from the soil. Since such salts are toxic to the commoner forms of vegetation, the growth of *Kathira* under such conditions, together with the foregoing observations regarding the distribution of its inorganic constituents, suggest that the grass is (*a*) tolerant of iron and aluminium salts in high concentration and (*b*) selective in its absorption of minerals.

It has already been mentioned that *Kathira* is used as a fodder, but only a part is so used; quite a considerable proportion of the *Kari* area is under deep water and hence inaccessible. The abundant grass in such tracts is not cut, but merely allowed to decay in the water-logged soil, and decomposition products of the grass would tend to accumulate. *Kathira* contains about 80 per cent. of organic matter and this accumulating in the soil would modify its composition. To ascertain the nature and the extent of the foregoing change a comparative study of the distribution of organic matter in the soil and in *Kathira* was conducted.

Distribution of organic matter.

In view of the indeterminate nature of the constituents affected by either fractional alkali extraction or partial oxidation, methods involving the use of such treatment were not attempted. Since the *Kari* soil contains considerable quantities of undecomposed plant residues and since *Kathira* is the principal form of vegetation, the nature of the association between the two was studied by comparing the amounts of the different plant constituents in each. The determinations were carried out on oven-dried specimens by the method of Waksman and Stevens (*loc. cit.*) and the results are shown in Table II.

TABLE II.

Fraction	Percentage			
	Kari soil		*Kathira*	
	From	To	From	To
Ether soluble	1·5	1·7	3·1	3·7
Alcohol (95 per cent.) soluble	0·8	0·9	1·2	1·3
Reducing sugars as glucose	*Nil*	*Nil*	2·5	3·0
Water soluble	2·3	2·5	10·2	14·6
HCl (2 per cent.) soluble	5·1	7·2	22·1	25·5
Pentosans as xylose	*Nil*	*Nil*	11·4	12·2
Celluloses	*Nil*	*Nil*	1·8	2·7
Lignin	21·7	30·5	27·5	34·5
Crude protein (N × 6·25)	3·2	3·5	5·6	6·1

The material extracted from the soil by (ethyl) ether was a dark-brown, sticky mass, about 7 per cent. of which dissolved in petroleum ether. The extract gave on evaporation a brown, oily liquid which had a peculiar and persistent aromatic smell and was readily inflammable. The liquid was soluble in alcohol, dilute alkali and concentrated sulphuric acid, but not in water or any of the dilute mineral acids. The yield of oil was too low to permit of systematic study. The petroleum ether extract of *Kathira* did not contain even traces of the oily liquid obtained from the soil.

To ascertain whether the oil arose from the woody material occurring in the soil, chips of the wood were freed from adhering earth, dried in the oven and extracted as before; on evaporating the extract an oily liquid with the properties described above was obtained. It may be inferred, therefore, that the oily liquid was derived from the woody material probably surviving from the previous forest age, and not from the present vegetation.

The residue from the petroleum ether extract was an amorphous, yellowish brown powder insoluble in water, but partially soluble in dilute alkali. It melted at 70-75° with some decomposition into a dark, viscous liquid which, on cooling, set to a glassy and brittle solid. The substance burnt with a smoky flame, and analysis showed it to contain carbon, hydrogen and sulphur, but no nitrogen. The composition and properties suggested that the substance was probably a mixture of resins. The same resinous substance formed the major part of the ether extract of *Kathira* while practically absent from the woody materials occurring in the soil. It thus follows that the ether-extractives of the soil were derived principally from *Kathira*, and from woody residues to a small extent only.

Russell (Soil conditions and plant growth, 1927, 178) observed that certain substances dissolving in volatile solvents and possessing wax-like properties tend to accumulate in soils rich in organic matter, and interfere with the wetting of the soil and the movement of water. The previous observations of the present authors (*loc. cit.*) have shown that the ether-extractives of the *Kari* lands form thin, oily coatings around the soil particles and are responsible for (*a*) the retention of high percentages of moisture for long periods and (*b*) the non-wetting of the dry soil even after prolonged standing with water. These and the present observations suggest that the wax-like constituents referred to by Russell are probably resins derived from undecomposed plant residues, tending to accumulate in soils which contain large amounts of organic matter and are not provided with adequate drainage or aeration.

It is a common observation on the *Kari* lands that dry weather within the first fortnight after broadcasting the seeds causes the seedlings to wilt, though the soil, as a whole, may still contain a high percentage of moisture ; in many cases the wilting continues for several days even after showers. Probably the resins form thin, impenetrable coats around the soil particles and thus prevent the ready movement of water from within as well as from without.

With a view to estimating the extent to which the resins increase the moisture-holding capacity of the soil, a specimen (30 g.) of air-dried *Kari* soil was extracted with ether and while one portion (10 g.) of the residual soil was left in the resin-free condition, another (10 g.) was mixed thoroughly with the ether extract, and the solvent allowed to volatilise. The two specimens were then saturated with water, spread out to dry in air for two days, then dried in the oven and their moisture contents compared. It was observed that the specimen treated with resin contained 38·3 per cent. of moisture and that from which the resin had been extracted, 5·4 per cent. Thus the retention of high percentages of moisture by the *Kari* soil is due more to the minute quantities of resin than to the large amounts of other organic substances present in it. The previous observation of Pillai and Subrahmanyan (*loc. cit.*) that it is the nature of the organic matter rather than the total amount lost on ignition that determines the moisture-holding capacity of a soil, is also confirmed.

To obtain an idea of the extent to which the resins affect the solution of organic as well as inorganic substances from the soil, equal weights (20 g.) of air-dried and ether-extracted specimens respectively were treated with 50 c. c. portions of cold water and, after being shaken for 30 minutes, the extracts were passed through a Buchner filter with frequent washings until about 250 c. c. of the filtrate collected in each case. The soil sediments on the funnel were then washed repeatedly with hot water (60°) and the filtrates amounting to another 250 c. c. in each case collected. The different extracts, thus obtained, were evaporated to dryness on the water bath and their ash contents determined (Table III).

TABLE III.

Treatment of soil	Percentage			
	Cold water soluble		Hot water soluble	
	Loss on ignition	Ash	Loss on ignition	Ash
Air dried	1·95	3·93	0·35	0·33
Air dried and extracted with ether	2·15	4·33	0·50	0·53

The results show that in spite of the prolonged extraction, the soil containing the resinous matter still retains appreciable amounts of soluble substances. The retention will, no doubt, be very much more pronounced on the field, where the conditions for solution are much less favourable than in the above experiment so that the resins will interfere with the solution of organic as well as inorganic substances to a very much greater extent than that indicated by Table III.

The alcohol-soluble portions of the soil as well as *Kathira* resembled the corresponding ether extractives in their physical properties. They differed from the latter in elementary composition, containing nitrogen in addition to carbon, hydrogen and sulphur.

The foregoing observations indicate that *Kathira* is the chief form of organic matter undergoing decomposition in the *Kari* soil. The resins present in the grass tend to accumulate in the soil as they offer more resistance to decomposition than most other plant constituents. Absence of reducing sugars, pentosans and celluloses from the soil (vide Table II) suggests that these plant constituents undergo ready decomposition. The occurrence of small quantities of materials soluble in water and hydrochloric acid, respectively, indicates that (*a*) such substances undergo only partial decomposition in the soil, or (*b*) the water and acid soluble constituents of the soil are different from those of the decaying vegetation. The latter view is supported by the fact that the soil contains considerable quantities of soluble iron and aluminium salts. The presence of a high proportion of lignin in the soil indicates that this constituent offers considerable resistance to decomposition by the soil organisms. The nitrogen contents of the soil and the grass run in parallel, and allowing for the larger proportion of minerals in the former, it would follow that none of the plant nitrogen is lost from the soil by either leaching or denitrification.

From the above, it may be seen that the transformations in organic matter leading to the formation of the *Kari* soils are of the same type as those prevailing in the peaty soils of the temperate regions. The rapid decomposition of hemicelluloses and celluloses and the accumulation of lignins lend support to the general theory of Fischer and Schrader (cited from *Soil Sci.*, 1928, **26**, 117) regarding the origin of peat. The persistence of the ether-soluble constituents is not in accordance with the observations of Waksman and Stevens (*loc. cit.*) for low-moor peats, but is explained by the difference in climatic conditions and nature of the vegetation.

Distribution of Nitrogen.

This was determined to ascertain the nature and extent of the transformations undergone by the different forms of nitrogen present in *Kathira* while decomposing in the *Kari* soil. The nitrogen contents of the different fractions were estimated by the method of Waksman and Stevens (*loc. cit.*) and that of free and saline ammonia by the method of Maclean and Robinson (*J. Agric. Sci.*, 1924, **14**, 548), the results being shown in Table IV.

TABLE IV.

Fraction	Percentage of nitrogen			
	Kari soil		*Kathira*	
	From	To	From	To
Ether-soluble	*Nil.*		*Nil.*	
Water-soluble	0·005	0·041	0·170	0·172
Free and saline NH_3	0·017		*Nil.*	
HCl (2 per cent.) soluble	0·061	0·064	0·302	0·351
H_2SO_4 (80 per cent.) soluble	0·047	0·050	0·177	0·190
Humin	0·382	0·401	0·310	0·321
Total (as calculated)	0·512	0·573	0·959	1·034
Total (as estimated)	0·540	0·572	0·909	1·071

The water-soluble fraction of the soil never contained more than 8 per cent. of the total nitrogen, but varied considerably within that limit. The corresponding figures for *Kathira* were very much higher, but did not vary appreciably with the specimen. The percentage of the acid-soluble fractions of the soil was much lower than that of the grass, suggesting that such fractions, together with the water-soluble forms, underwent ready decomposition in the *Kari* soil conditions. Ammonia was obviously one of the products of such decomposition, but the quantities present in that form do not account for more than 4 per cent. The percentage of humin nitrogen in the soil is higher than that of *Kathira*: this observation when considered together with the fact that the grass undergoing decomposition in the soil mixes with the large amounts of mineral matter which the latter contains, would suggest that the total amount of humin nitrogen in the soil very much exceeds that indicated by the percentage. Since the organic matter of the soil is derived chiefly from *Kathira*, it follows that the water and acid-soluble nitrogenous constituents of the grass are not lost from the soil, but are merely transformed into the more resistant humin. The above observations also help to account for those of Dachnowsk (*J.*

Agric. Res., 1924, **29**, 72) who noted that on continued submergence by water, the proteins of peat do not undergo ready ammonification. The accumulation of humin nitrogen in the soil does not, however, mean that it will ultimately become unavailable to plant nutrition: indeed, as observed by several workers in Europe and in America, one of the problems relating to a reclaimed peat soil is the prevention of the too rapid decomposition of organic matter and unaccountable loss of nitrogen which follows the introduction of drainage and application of lime. The difference between the quantities of total nitrogen shown by summation of the different forms, and that estimated experimentally, is not considerable. Allowing for the experimental error, it is hardly probable that anything more than traces of the soil or plant-nitrogen existed in forms other than those described above.

Distribution of minerals in the Kari soils.

It has already been observed that the *Kari* soils (*a*) are rich in calcium, iron and aluminium sulphates and other salts, but (*b*) contain only limited amounts of potassium chloride and other salts. Iron and aluminium salts are not, however, known to be present in such large quantities in any of the peats or peaty soils so far examined. In view of the above and the well-known toxic effects of high concentrations of soluble iron and aluminium salts on plant life, the extent to which the salts mentioned under (*a*) were present in the water-soluble form was determined and the quantities compared with those present in the ash (Table V).

TABLE V.

Description	Percentage in the unreclaimed area			
	Iron (Fe_2O_3)	Aluminium (Al_2O_3)	Calcium (CaO)	Sulphate (SO_4)
In ash	4·00	8·50	0·80	2·30
Water-soluble	0·10	0·50	0·54	2·73

The quantities of iron and aluminium salts extractable from the soil by cold water were less than 3 and 6 per cent. respectively of those present in the ash. The figures should not, however, be taken to represent quantities originally present in the soluble form, since the addition of large quantities of water would have (*a*) altered the reaction of the soil suspension and thereby reduced the solubility of the salts, and (*b*) brought about the hydrolysis of the iron and aluminium salts, resulting in the release of free acids and formation of sparingly soluble basic salts. The above inference was supported by the fact that the water-extract contained free sulphuric acid (0·3–0·4 per cent.) and that its sulphate content (2·73 per cent.) was disproportionately higher than those of the associated metallic radicles. About 70 per cent. of the calcium present in the soil occurred in the soluble form: subsequent analysis showed that the latter consisted mostly of the sulphate, the quantity of surface water having been more than sufficient to dissolve it completely.

Considerable difficulty was experienced in determining the forms and mode of distribution of iron in the *Kari* soil. Owing to the instability of the ferrous salts and the readiness with which ferric as well as ferrous salts undergo hydrolysis, it was not possible to obtain any useful data from the analyses of cold and hot water extracts of air-dried specimens of the soils. Extraction with 1, 3, 5 and 7 per cent. solutions of hydrochloric, sulphuric and acetic acids respectively also led to no definite results. Estimation of iron in presence of soil organic matter also presented some difficulties. Titrating aliquot parts of soil extract against standard dichromate with diphenylamine as internal indicator was found to be unsatisfactory since the colour change was not sharp: with ferricyanide as external indicator, the end-point was partially masked by the colour of the extract. Direct titration against permanganate was unsatisfactory because of action by that reagent on the organic matter of the extract. A number of trials carried out with soil extracts to which known quantities of ferrous salts had been added showed, however, that in presence of acid and minute quantities of manganous sulphate the permanganate reacted first with the ferrous salt and then with the organic matter. The reaction with the ferrous salt was instantaneous while that with the humic matter was rather slow, so that the latter remained unaffected until all the ferrous salt had been oxidised to the ferric condition. Advantage was taken of this observation and by titrating with the ferricyanide as the external indicator it was possible to obtain fairly concordant results for soil extracts containing known quantities of ferrous salts. Ferric iron was estimated by the above method after reduction to the ferrous condition. For the latter purpose zinc was found to be more useful than stannous chloride. Analysis of many aqueous and acid extracts showed, however, that no ferrous iron was present in the air-dried soil and that the quantities of ferric salts present in the different specimens were small and variable. It would appear from the above that although, under the field conditions, *Kari* soils contain considerable quantities of ferrous iron in the water-soluble form, yet hydrolysis followed by air-drying converts them into basic ferric salts which are insoluble even in dilute mineral acids.

To trace the changes leading to solution of iron under field conditions, specimens of soil were submerged by varying quantities of water

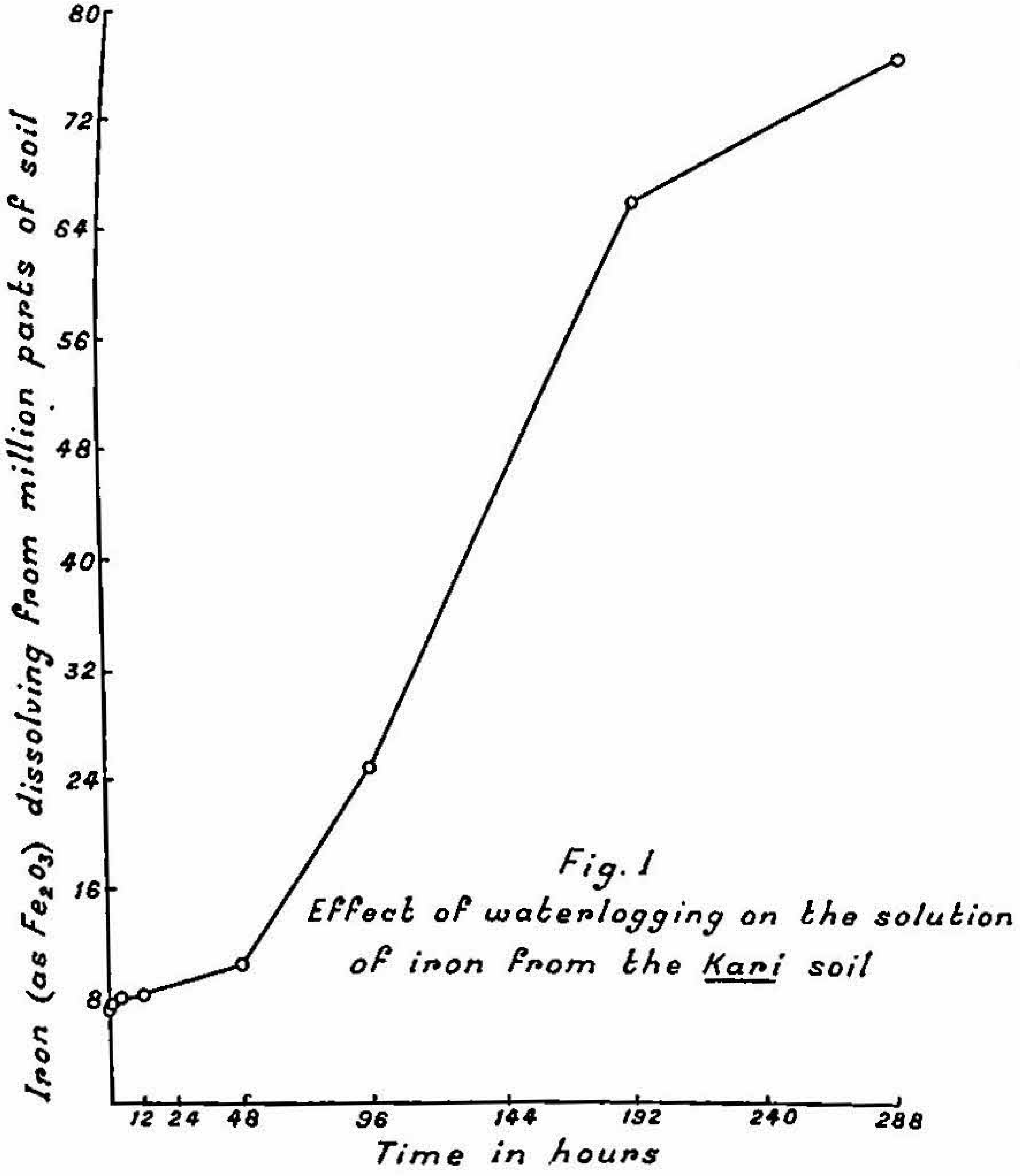

Fig. I
Effect of waterlogging on the solution of iron from the *Kari* soil

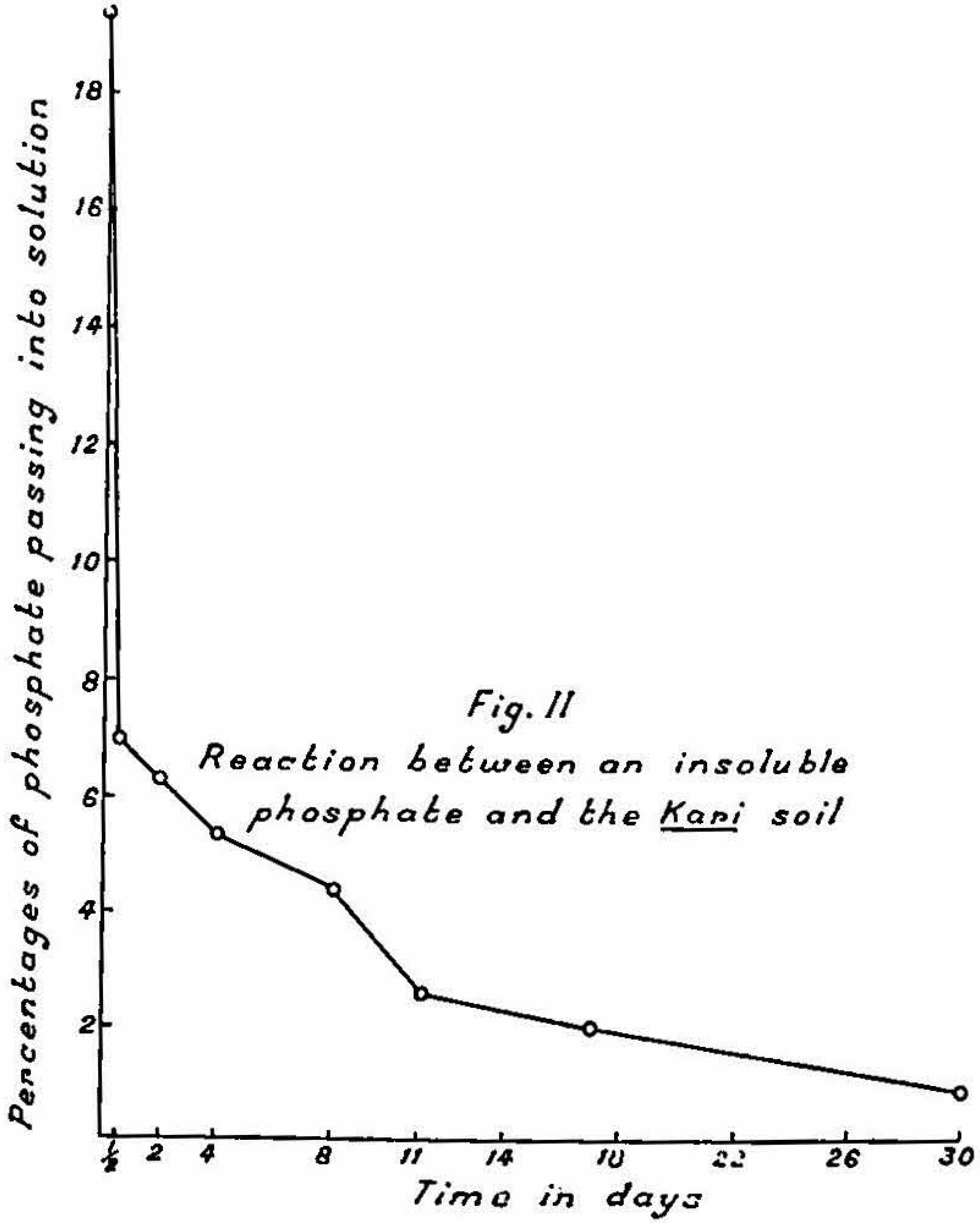

Fig. II
Reaction between an insoluble phosphate and the *Kari* soil

and the attendant reactions followed at 37° as well as at the room temperature (25–30°). It was noted in all the cases that the surface water became first acid owing to increasing quantities of sulphuric acid passing into solution. This was followed by evolution of minute quantities of hydrogen sulphide and solution of increasing amounts of ferrous iron. The reactions were more prominent in the case of specimens submerged by relatively small amounts of water (2 parts of water to 1 part of soil) and maintained at 37°, rather than in those standing under larger quantities of water or maintained at the lower temperature.

To estimate the iron dissolving under the field conditions, specimens (20 g.) of the soil were submerged by water (60 c.c.) at the laboratory temperature (25–30°) and the total quantities of iron passing into solution at different stages determined. The results (Fig. I) show that although only minute quantities of iron were present in the initial stages, increasing amounts passed into solution on continued standing under water. The rate of solution was highest between the fourth and the eighth days when quantities corresponding to over 4,000 parts per million of soil passed from the soil into the surface water. Solution of further quantities continued throughout the period of observation though the rate slackened, to some extent, after the eighth day. The above observations accord with those of Robinson (*Soil Sci.*, 1930, **30**, 197), who noted that considerable quantities of ferrous salts and sulphides were formed from submerged soils. Minute quantities of iron are necessary for plant development, but recent investigations have shown that high concentrations, particularly of ferrous salts, are toxic to plant life. The foregoing observations suggest that one cause of the crop failure so frequently experienced on the *Kari* lands, is the solution of iron in abnormal amount.

To determine the toxic action of dissolved salts on the rice plant the following experiment was conducted. The soil (1 part) was submerged by water (2 parts) in glass basins for 4 days when rice seedlings (0·5″–1″ high) were planted; after exposure to air and light it was observed that the seedlings soon became yellow, and within ten days were all dead or dying. Similar observations were made when the seeds were germinated in the *Kari* soil itself; after emergence of the first few leaves, the seedlings became yellow and died. The foregoing observations thus suggest that the yellowing of rice plants so commonly observed on the *Kari* lands is probably due to the presence of abnormal amounts of iron in the surface water. Simultaneously with the yellowing of the seedlings, it was observed that white, needle-like crystals formed incrustations at the sides of the germinating-basins; these were recrystallised from water and found to contain only iron, aluminium, calcium and sulphate.

To identify the principal inorganic salts in the surface water, this was decanted from the soil (200 g.), filtered through the Buchner and concentrated on the water bath. After 24 hours, minute crystals were rapidly filtered, and after washing and recrystallisation were found to consist exclusively of hydrated calcium sulphate. Alcohol of 95 per cent. was added to the mother liquor until precipitation was complete, the recrystallised material consisting solely of calcium sulphate. On allowing the alcohol-treated liquor to stand overnight, silky, fibrous crystals separated containing iron, aluminium and sulphate; they melted on gentle warming, but decomposed on strong heating emitting fumes of sulphur trioxide and leaving oxides of iron and aluminium. These crystals were, on further analysis, identified to be those of ferrous aluminium sulphate, $FeSO_4$, $Al_2(SO_4)_3$, $24H_2,O$, a double salt occurring as the mineral, halotrichite, in Baluchistan, Persia and several other countries. Although known since 1802, Wirth first prepared it in the laboratory (*Z. angew. Chem.*, 1913, **26**, 81) by mixing equimolecular proportions of ferrous and aluminium sulphates in saturated solution out of contact with air. The spontaneous formation of this salt in the submerged *Kari* soils therefore supports the fact that (*a*) ferrous and aluminium sulphates are present in high concentrations in the soil and (*b*) the soil-conditions are anaerobic and hence unsuitable for air-loving plants and micro-organisms.

The investigations of Barber (cited from *Mem. Agric. Dept. India, Chem. Ser.*, 1913, **3**, 93) have shown that although the rice plant requires considerable quantities of water and grows best only under the conditions of the swamp soil, it is not really an aquatic plant. Its root-system resembles in structure and function those of the other cereals, thereby indicating that the plant requires adequate soil aeration. The anaerobic conditions prevailing in the submerged *Kari* soil coupled with high concentration of toxic ferrous and aluminium ions suggests that it is not suitable for the cultivation of rice.

It has already been shown that the total sulphur content of the *Kari* soil is higher than that indicated by the amount of sulphate present in the ash. The low value of the latter is explained by the presence of readily decomposable sulphates such as the ferrous aluminium double salt. The free acid released by hydrolysis on treating the soil with excess of water corresponded to 0·3–0·4 per cent. of sulphuric acid on the dry weight of the soil, but the estimates thus obtained could not indicate the quantities of the bases with which the acid had originally been associated. The total sulphur content of the soil as determined by Benedict's method (*J. Biol. Chem.*, 1909, **6**, 363) was 3·6 per cent. made up of 0·91 per cent. water-soluble sulphates, 0·19 and 0·22 per cent. respectively as sulphates soluble on shaking for 3 minutes with 5 and 7 per cent. hydrochloric acid, 0·29 per cent.

soluble sulphate as determined by Wiley's method (Principles and practice of agricultural analysis, Vol. I, 594): 1·4 per cent. was soluble in 2 per cent. alkali and 1·2 per cent. insoluble in either dilute acid or dilute alkali. Sulphides were absent from the air-dried specimens, but were readily formed on submergence in water.

The foregoing observations provide an outline of the distribution of sulphur in the soil, but do not throw much light on the forms in which it is present. In addition to the sulphates of sodium, calcium, iron and aluminium, the soil appears to contain sulphur in organic combination to the extent of about one-third of the total amount. The insoluble forms of sulphur may be partly organic and partly inorganic.

The high sulphur content of the *Kari* soils and the readiness with which the different forms undergo decomposition suggest that, under favourable conditions, the soils could be used in place of sulphuric acid for increasing the solubility of bones and mineral phosphates which are not otherwise readily available for plant nutrition. If all the combined sulphur is to undergo oxidation to sulphuric acid, or otherwise react directly with the insoluble phosphates, the concentration of active material would correspond to 10·8 per cent. of sulphuric acid on the dry weight of the soil. It would therefore appear possible to prepare a fertiliser similar to superphosphate by allowing suitable proportions of *Kari* soil and insoluble phosphates to either react together or undergo biological decomposition in presence of each other. The plant residues and the fairly large quantities of nitrogenous compounds present in the soil should facilitate the biological decomposition and increase the manurial value of the compost thus prepared. It is possible that the iron and the aluminium salts present in the soil would react with the dissolved phosphates and precipitate them, thereby reducing their solubility in solvents used for measuring the availability of phosphatic manures; but being in a fine state of division they would no doubt be readily available for plant nutrition.

To obtain a preliminary idea of the nature of the reaction between the *Kari* soil and an insoluble phosphate, the following experiment was made:—Small lots of the soil (25 g.) and calcium phosphate (0·355 g.) were weighed together into conical flasks and the mixtures treated with 25 c.c. of water; the suspensions remained at room temperature (25–30°) for varying periods and the water-soluble phosphates determined at different stages.

The results (Fig. II) show that water-soluble forms increased to about 20 per cent. in less than half an hour, but fell off steadily on further standing with the soil, water-solube phosphate being less than 1 per cent. at the end of 30 days. Since the *Kari* soils are rich in iron and aluminium salts which pass steadily into solution on continued standing with water, the above observations suggest that calcium phosphate first dissolved by the sulphuric acid, and after reaction with the dissolved iron and aluminium salts precipitated as the insoluble phosphates of those elements. Precipitation in the soil need not, however, reduce the fertilising value of the phosphates, since they, being in finely divided condition, would still be readily available for plant nutrition. Indeed, a similar reaction is known to take place some time after adding either superphosphate or any of the other soluble forms to the soil. Under such conditions, although the availability of the phosphates, as determined by solution in dilute acids, may be low, the plants may still have abundant supplies of phosphates for their nutrition. In the above experiment, the availability at the end of 30 days as determined by Dyer's citric acid method (*J.C.S.*, 1894, **65**, 115) was 22·0 per cent. of the phosphate originally added. In view of the previous observation, it may be inferred that the quantity actually available for plant nutrition was considerably more than that indicated by the above figure.

Further experiments to determine the optimum conditions for the treatment of different insoluble phosphates so as to secure the maximum availability for plant nutrition are in progress and will form the subject of a later communication.

DISCUSSION.

From their geographical situation and seasonal conditions, it might appear that the *Kari* soils form a separate class. The results of the present investigation show, however, that the chemical and biological changes leading to the transformation of organic matter in the *Kari* soils are of the same type as those in the commoner peat soils. The accumulation of resins and ligniferous materials, retention of high percentages of moisture and conversion of the simpler forms of nitrogen into the more resistant humin are all characteristic of soils containing large amounts of organic matter without adequate drainage or aeration.

The *Kari* soils do, however, differ from peat soils in containing large amounts of (*a*) soluble iron and aluminium salts and (*b*) sulphur compounds, principally mineral sulphates. Whereas the occurrence of large amounts of organic matter is explained by the existence of the woody residues of the forest age and the decaying aquatic vegetation, the abnormal amount of the above-mentioned inorganic constituents is not easily explained. Though the West Coast soils are generally of laterite origin and are rich in iron and alumina, the conversion of those insoluble compounds into soluble forms, particularly such readily oxidisable compounds as ferrous aluminium sulphate, are features of the *Kari* soil which could be explained only by a careful biochemical study of the changes occurring therein.

It has already been observed by Pillai and Subrahmanyan (*loc. cit.*) that, during the monsoon months, a large part of the clay and the fine salt fractions of the single and double crop paddy lands respectively situated immediately above the *Kari* lands are washed down into the lower regions. Since the above-mentioned soil fractions are rich in iron and alumina, it may be inferred that considerable amounts of those minerals thus tend to accumulate in the low-lying areas. A part of the minerals would, no doubt, pass into the backwaters and be carried by the flowing tide into the sea: a part may also be mixed with the waters of the adjoining Vembanad lake: but a considerable portion would collect in the stagnant waters of the *Kari* land and settle in the soil on prolonged standing.

It has been shown by Subrahmanyan (*J. Agric. Sci.*, 1929, **19**, 627) that, in waterlogged soils containing large quantities of organic matter in readily decomposable forms, the dissolved oxygen of the surface water is rapidly engaged and considerable amounts of organic acids, chiefly lactic, acetic and butyric, are produced. A similar observation has been made by Subrahmanyan and Desikachar (unpublished data) in the course of their studies on the decomposition of plant-residues in waterlogged soils. It may be expected that the acids thus produced will react with the minerals of the soil and bring them, in increasing quantities, into solution in the surface water.

Gillespie (*Soil Sci.*, 1920, **9**, 199) has noted that on submerging a soil a reduction potential is set up. The observations of the present authors have shown that appreciable quantities of hydrogen sulphide are formed within the first few days after submergence of the *Kari* soils. Since the mineral sulphates were the chief sulphur-containing compounds present in the soils prior to their submergence, it may be inferred that the hydrogen sulphide was largely formed by the reduction of sulphuric acid released from the soils by hydrolysis. Under such conditions, it may be expected that (*a*) appreciable quantities of iron and aluminium would pass into solution and (*b*) ferric iron would be reduced to the ferrous condition. The different reactions described above may be represented by the following equations.—

(1) $A\ C_nH_{2n}O_n \longrightarrow B\ CH_3 \cdot CH\ (OH) \cdot COOH + C\ CH_3 \cdot COOH + D\ CH_3 \cdot (CH_2)_2 \cdot COOH$ etc.

(carbohydrates of plant residues)

(2) $\left.\begin{matrix} Fe_2O_3 \\ Al_2O_3 \end{matrix}\right\} + 6\ HX \longrightarrow FeX_3 + AlX_3$

(X represents the negative radicle of a monobasic organic acid)

(3) $FeX_3 + (H) \longrightarrow FeX_2 + HX$

It has already been mentioned that the *Kari* lands are subject to inundation by sea-water whenever there are tidal rises. It may, therefore, be expected that the salts of the sea-water would react with the iron and aluminium salts rendered soluble by the biological reaction progressing in the soil. Since sea-water contains chiefly the chlorides and sulphates of sodium, magnesium and calcium and since the total amount of such salts brought in with every tide, would be proportionately much greater than the soluble iron and aluminium salts present in the soil, it would follow from the law of mass action that the major part of the iron and aluminium salts would be converted into the corresponding chlorides and sulphates. The chlorides are not, however, stable in presence of water, so it may be expected that they would undergo decomposition resulting in the formation of the corresponding metallic hydroxides and the release of hydrochloric acid, which would then be carried away by the flowing tide. This would account for the water above the *Kari* land containing chlorides and the consequent absorption of fairly large quantities of those salts by *Kathira*, which, as mentioned already, derives its nutrition exclusively from the surface water. Under the same conditions, the sulphates are relatively more stable. A part of them would combine with the organic matter of the soil and form floes from which they could not be readily leached out. In presence of excess of water, a part would undergo partial hydrolysis resulting in the formation of the corresponding stable, basic salts. It may, therefore, be expected that, after a succession of tidal ebbs and flows, the soils would contain only the sulphate of calcium, which is a sparingly soluble salt and the basic sulphates of iron and aluminium which are insoluble in water. On air-drying the soil taken at this stage, the ferrous salt would be readily oxidised to the ferric condition. The above explanation would account for (*a*) the leaching out of only calcium sulphate on first extraction with large amounts of water, (*b*) the absence of ferrous salts from both the aqueous and the acid extracts of the air-dried specimens and (*c*) the presence of only minute quantities of free sulphuric acid in aqueous extracts of the air-dried soil. The various reactions leading to the different transformations may be represented by the following equations.—

$$(4)\quad \left.\begin{matrix} FeX_2 \\ AlX_3 \end{matrix}\right\} + \begin{matrix} Na_2So_4 \\ NaCl \end{matrix} \longrightarrow \begin{matrix} FeSO_4,\ (FeCl_2) \\ Al_2\,(SO_4)_3,\ (AlCl_3) \end{matrix}$$

$$+ \ NaX$$

(surface water)

$$(5)\quad \left.\begin{matrix} FeCl_2 \\ AlCl_3 \end{matrix}\right\} + H_2O \longrightarrow \begin{matrix} [Fe\,(OH)_2] & + \ HCl \\ [Al\,(OH)_3] & \text{(Surface water)} \end{matrix}$$

$$(6)\quad \left.\begin{matrix} Al_2\,(SO_4)_3 \\ 2FeSO_4 \end{matrix}\right\} + H_2O \longrightarrow \begin{matrix} 2Al\,(OH)\,SO_4 & + \ H_2SO_4 \\ Fe\,(OH)_2,\ FeSO_4 & \text{(Surface water)} \end{matrix}$$

$$(7)\quad \left.\begin{matrix}[\mathrm{Fe\,(OH)_2}],\ [\mathrm{Al\,(OH)_3}]\\ \mathrm{Al\,(OH)SO_4},\ \mathrm{Fe\,(OH)_2},\ \mathrm{FeSO_4}\end{matrix}\right\} + \xrightarrow[\text{(air-drying)}]{\mathrm{O}} \begin{matrix}\mathrm{Fe_2O_3},\ \mathrm{Al_2O_3}\\ \mathrm{Fe\,(SO_4)_3},\ \mathrm{Al_2\,(SO_4)_3}\end{matrix}$$

(The above equations have not been balanced as the proportions are not known.)

On submerging the air-dried soils, ferric and aluminium sulphates would undergo hydrolysis resulting in the partial release of sulphuric acid and the precipitation of the corresponding basic sulphates. This would explain the presence of fairly large quantities of sulphuric acid, but only traces of iron in the aqueous extract of the soil. On further standing with water, biological decomposition of the plant residues would begin, resulting in anaerobic conditions and the development of organic acids (Subrahmanyan, *loc. cit.*, Subrahmanyan and Desikachar, *loc. cit.*). Increasing quantities of iron and aluminium salts would then pass into solution; ferric iron would be reduced to the ferrous condition. Basic salts of iron and the organic acids would be precipitated, while owing to the favourable reaction increasing quantities of ferrous and aluminium sulphates would be brought into solution.

High concentration of the two sulphates together with the favourable anaerobic conditions would have facilitated the formation of the relatively more stable double salt, as observed already. The different reactions leading to the formation of the ferrous aluminium alum may be represented by the following equations.—

$$(8)\quad \left.\begin{matrix}\mathrm{Fe_2(SO_4)_3}\\ \mathrm{Al_2(SO_4)_3}\end{matrix}\right\} + \mathrm{H_2O} \longrightarrow \begin{matrix}\mathrm{Fe\,(OH)\,SO_4}\\ \mathrm{Al\,(OH)\,SO_4}\end{matrix} + \mathrm{H_2SO_4}$$

$$(9)\quad \left.\begin{matrix}\mathrm{Fe\,(OH)\,SO_4}\\ \mathrm{Al\,(OH)\,SO_4}\end{matrix}\right\} + \mathrm{HX} + \mathrm{H_2O} \longrightarrow \begin{matrix}\mathrm{Fe_2\,(SO_4)_3\ Fe\,(OH)X_2}\\ \mathrm{Al_2\,(SO_4)_3 + Al\,(OH)X_2}\end{matrix}$$

$$(10)\quad \mathrm{Fe_2\,(SO_4)_3} + (2\mathrm{H}) \longrightarrow 2\mathrm{FeSO_4} + \mathrm{H_2SO_4}$$

$$(11)\quad \mathrm{FeSO_4} + \mathrm{Al_2(SO_4)} + 24\mathrm{H_2O} \longrightarrow \mathrm{FeSO_4\ Al_2\,(SO_4)_3\ 24H_2O}$$

(concentrated solution)

(Some of the above equations have not been balanced as the proportions of the products are not known.)

The foregoing reactions were further confirmed by identifying the more important intermediate products on repeating the natural conditions in the laboratory. The organic acids were identified in the manner described by Subrahmanyan (*loc. cit.*). The solution of iron and aluminium salts as well as the reduction of ferric iron to the ferrous condition were also verified. Basic iron salts, largely in the ferric condition, were found to be present either as scum on the surface water or as rings at the sides of the flasks.

The possibilities of utilising the free acid formed from the *Kari* soil for rendering insoluble phosphates available for plant nutrition have already been indicated. That would appear to be a more satisfactory method of utilising the soil than that of burning it as fuel as is usually done in Europe and elsewhere. Although the *Kari* soil burns with a dull flame after prolonged heating, its high moisture and relatively low organic matter contents would detract considerably from its fuel value. Moreover, the acid fumes which will be evolved on heating the soil would poison the air and cause the rapid perishing of the materials which it is intended to heat.

SUMMARY.

The distribution of organic matter in the *Kari* soil suggests that the former is derived mainly from *Kathira*, an aquatic grass which flourishes in the surface water of the soil, and to a small extent, from the remains of a previous forest vegetation. As in other peat soils, lignins left over from the decaying vegetation form the bulk of the organic matter of the *Kari* soil. Nitrogen is present chiefly as humin: there is evidence to show that the soluble and the more readily decomposable plant-constituents are converted into that resistant form in the soil.

The high moisture contents of air-dried specimens of the soil have been shown to be due to the presence of resins which form protective coats around the soil particles and prevent the movement of water and plant-nutrients from within as well as from without.

The minerals present in the *Kari* soil, particularly iron and aluminium sulphates, do not appear to be related to the plant residues which make up its bulk. There is evidence to show that large quantities of iron and alumina are washed down into the *Kari* lands from the higher regions during the monsoon months, and that they are dissolved and further reacted upon in presence of organic acids formed by decomposition of plant materials and the sea salts brought in during the tidal rises. The mechanism of the biological and chemical reactions leading to the formation of the more important mineral constituents, particularly the characteristic ferrous aluminium sulphate [$Fe SO_4 Al_2 (SO_4)_3 24H_2 O$], has been discussed.

The possibility of utilising the free sulphuric acid released from the *Kari* soil for rendering insoluble phosphates available for plant nutrition is indicated.

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