98.

FORMS, DISTRIBUTION AND AVAILABILITY OF SULPHUR IN REPRESENTATIVE SOIL PROFILES OF KERALA STATE

BY

K. LEELA, B Sc (Ag)

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INTRODUCTION

Sulphur is an element which is essential for all forms of life, as it is a common constituent of proteins, with the sulphur in amino acids like Cysteine and methionine. Furthermore it is contained in many other important cell compounds such as vitamins, thiamine and biotin. Sulphur serves as a regulatory element in the synthesis of chlorophyll and the acceleration of root development. It is important as a redox system in respiration and in activities of certain enzymes. Hence the importance of sulphur in agriculture.

Though sulphur was recognised as an essential plant nutrient since the days of Liebig, this nutrient received only very little attention in the hands of agricultural scientists in the past. That sulphur as a plant nutrient has not been given proper importance in agricultural research was emphasised by Alway in his review of 1940. Since then sporadically various aspects of sulphur economy of plants has received increasing attention to advance scientific aims at one hand and to solve soil fertility problems on the other. In the past, sulphur received little attention, because it was supplied in fertilizers, insecticides and fungicides inadvertently. With the trend towards high analysis fertilizers, which are either low in sulphur or even sulphur free, and with the use of less sulphur in insecticides and fungicides, the incidental addition of sulphur to soils has been decreased. These developments are responsible for the recent interest shown in the study pertaining to sulphur as a plant nutrient.

Sulphur deficiency has been reported in arid, semi-arid and humid regions. In the United States, shortage of sulphur for alfalfa was reported from Washington, Idaho and Oregon. Deficiencies of this element have occurred on cotton and tobacco on the sandy coastal plain soils of Alabama, Georgia, Florida and North Carolina. It has been reported that sulphur increased the yield of clover in the sandy soils of Florida. In India, sulphur deficiency is reported only in the tea soils of Punjab.

Sulphur is present in soils in both organic and inorganic forms. In mineral soils it is associated with pyrite (FeS_2). Sphalerite (ZnS), Chalcopyrite (Cu_2FeS_2), gypsum ($CaSO_4 \cdot 2H_2O$) and epsomite ($MgSO_4 \cdot 7H_2O$). In humid regions the organic form is predominant, as the sulphur ion is readily leached from the soil.

The transformation that sulphur undergoes in soils is of importance as it affects soil conditions and plant growth. The completely oxidised and reduced substances, sulphuric acid and hydrogen sulphide respectively are the microbial products that have the maximum effect on soils.

The effects are more dramatic under condition where the soil has been reclaimed from the sea or where it is periodically flooded with brackish water.

The fluctuating moisture regime in most of the water-logged soils of Kerala may lead to the formation of reduction products like sulphides or oxidation products like sulphuric acid, the accumulation of both affecting plant growth. Some of the portions are subjected to periodical inundation with sea water also. Subramoney (1965) observed that the symptoms of the physiological disease in rice known as "Kuttipachal" found in Kerala, and symptoms similar to those seen in hydrogen sulphide injury. The fact that causes and symptoms of hydrogen sulphide injury in rice deserve more attention at this juncture need not be emphasised. The water-logged condition under which the rice is grown and the use of ammonium sulphate in plenty, in the acid soils of Kerala are conducive to the production of either hydrogen sulphide or sulphuric acid.

In view of the transformation that sulphur undergoes in the soil it is essential that the forms in which it exists in the soil are thoroughly studied. Hence it is thought that a detailed study of the different forms of sulphur present in the soil and their distribution and nature of availability will be of use in further investigation of the cause of hydrogen sulphide injury to rice plants in Kerala soils.

Considering the above points, the present study is undertaken with the following objectives.

1) To determine the different forms of sulphur and their distribution in representative profile soils of Kerala.

2) To study the relationship of sulphur with other general constituents of the soils.

3) To assess the sulphur availability by different methods.

Soil samples were collected from three different depths viz., 0-20 cm, 20-40 cm and 40-60 cm respectively from seven soil profiles representing different soil groups of Kerala. They were analysed for different forms of sulphur and also for their general and related properties. Available sulphur was estimated using different extractants. Neubauer test was also conducted employing *ragi* seedlings to find out the plant available sulphur.

REVIEW OF LITERATURE

CHAPTER II

REVIEW OF LITERATURE

A. Forms of Sulphur in Soil

Sulphur occurs in soils in two broad categories, organic and inorganic. In the surface horizons of most well drained acid soils nearly all of the sulphur is present in organic forms and only small amounts (usually only a few parts per million) of sulphates are present. In sub-soil horizons, however, appreciable amounts of sulphate may accumulate and inorganic sulphur compounds may make up a major proportion of the total sulphur.

Studies on sulphate sulphur have been reported by Brown and Kellogg (1915) for Iowa soils, by Ames and Boltz (1916), for Ohio soils and by McAuliffe for Minnesota soils. Other investigations of this nature have been conducted at various agricultural experiment stations. Alway, Marsh and Methley (1937) undertook studies on the atmospheric sulphur in Minnesota. The results of all these investigations have shown that the amounts of sulphate sulphur in soils and atmospheric sulphur are extremely variable.

The occurrence of sulphates as soluble salts of sodium, magnesium and calcium in soils is well known, but except under arid or poorly drained conditions the presence of appreciable amounts of soluble sulphates is likely only in sub-soil horizons. Insoluble sulphates like barium sulphate may also occur, although precise knowledge of their true chemical nature is somewhat limited.

Beattie and Haldane (1958) however have identified barytes occurring as small concretions in certain New South Wales soils. Williams, Williams and Scott (1960) have reported the presence of insoluble sulphate associated with calcium carbonate in calcareous soils in Scotland. This too could be a common form of insoluble sulphate in soils.

Freney *et al.* (1962) reviewing certain aspects of sulphur as a soil constituent and plant nutrient, found that most of the sulphur in humid regions was in organic form. They also noted that in most soils the inorganic fraction contained only a small portion of forms other than sulphates.

Williams and Steinbergs (1962) studying the chemical nature of sulphate in some Australian soils observed that in the surface horizons of most of the well drained acid soils nearly all the sulphur was present in organic form. It was also established that except under anaerobic conditions, when reduced form of sulphur, particularly sulphides, might predominate most of the inorganic sulphur in soils occurred as sulphates.

Williams and Steinbergs (1965) also reported that sulphur occurred in soils mainly in organic form or as sulphate. They concluded that important categories of sulphate in Australian soils included water soluble sulphate, adsorbed sulphate and insoluble sulphate associated with calcium carbonate.

b. Distribution of different Forms of Sulphur

1. Total Sulphur:

Investigating the total sulphur content of a wide range of lowveld soils, Goldschmit (1951) reported a variation from 40 to 1800 lb/ac. ft. It was also observed that sandy granite soils contained much lower amounts than loams or heavy loams of fairly high organic matter.

According to Shkondo (1957) the sulphur content of Zoi-Burya soils of Russia varied from 0.05 to 0.10 per cent or less.

Walker and Adams (1958) determining the sulphur content of the grassland soils of New Zealand for 3 horizons, found mean values of 700, 410 and 230 lbs/acre for the A, B and C horizons respectively. Soils in strongly weathered sequence had higher sulphur content in all the three horizons studied as reported by Walker and Adams (1959). Investigations in a chronosequence at Taupe (New Zealand) by Walker, Thapa and Adams (1959) showed that the percentage of sulphur increased steadily with time. Comparing the virgin soils and 35 year old pastures in chronosequence, they observed that average annual increase was 14 lbs sulphur per acre.

Jordan and Baker (1959) reported that the total sulphur content of north Idaho soils varied from 0.020 to 0.039 per cent.

Purokshi (1959) presented data on the distribution and acreage of high sulphur soils of the Finnish coast. While greater part of these soils contained 1000-5000 or 5000-10000 kg/hr. in some regions sulphur amounted to 10,000 to 20,000 kg or more.

Kotor, Grazesiuk and Chodan (1963) determined the sulphur content of some soils in Olsztyn province. Total sulphur in 12 profiles and 28 top soils varied from 8.4 to 638 mg/kg mineral soil and from 2031.3 to 4406.2 mg/kg peat soil (both dry weight). The sulphur content decreased with depth in mineral soils and increased in peat soils. There was a linear relationship between carbon levels and total sulphur contents of soil.

Aidinyan (1964) studied the content and forms of compounds of sulphur in various soils of the U.S.S.R. In non-saline soils the distribution of sulphur in the profile depends on the distribution of humus carbon. Sulphur accumulation is greatest in humus accumulated horizon and decreases gradually towards the parent material. In non-saline soils the distribution of sulphur in the profile depends on the distribution of humus carbon. Sulphur accumulation is greatest in humus accumulated horizon and decreases gradually towards the parent material. In non-saline soils 70-90 per cent of the total sulphur was bound to the organic matter and sulphur occurred in all the main fractions of the humus.

Nikolov (1964) reported total sulphur content in 17 main soil types of Bulgaria. The sulphur content was 14.9 - 37.2 mg/100 g. in top horizon and 9.1 - 20.4 mg in the C horizons. The sulphur content depended mainly on organic matter content. Chernozem smonitzas and chernozem contained the higher amounts of sulphur, gray forest soils contained less and cinnamon forest soils contained the least sulphur.

Kanwar and Takkar (1964) examined a large number of soil samples from tea gardens of Punjab for sulphur. The total sulphur content varied from 130 to 279 ppm (average 158.8 ppm) in the top layer, and decreased with increasing depth in the profiles. Sulphur content were higher in soils at high altitudes than at lower altitudes.

Massoumi and Cornfield (1964) analysed 58 samples of mineral soils and found that total sulphur ranged from 112 to 1775 ppm. Calcareous soils were richer in total sulphur (average 858 ppm) than non calcareous soils (average

485 ppm). Total sulphur was significantly correlated with sulphate, but its variation accounted for only 15% of the variation in sulphate. Davidesco and Palovski (1968) observed that the sulphur content in the arable layer varied from 16 mg/100 g. in reddish brown forest soil to 44 mg/100 g. in leached chernozem soils of the Rumania. There was no correlation between sulphur and humus content of the soils. In the reddish brown forest soils, the fulvic acid fraction of humus contained more sulphur (10-12 mg/100 g.) than the humic acid fraction did (6-8 mg/100 g.).

Jacob (1966) studying the sulphur status of Kerala soils found that wetland soils contained more sulphur than dryland soils. Maximum reserves of sulphur were found in Kari soil of Kuttanad. In general the total sulphur decreased with an increase in the depth of the profile. The reverse was found in the case of Kari soils. Total sulphur was significantly and positively correlated with organic carbon.

2. Organic sulphur:-

Evans and Post (1945) determined total sulphur, total organic sulphur, the humus fraction of organic sulphur and sulphate sulphur in number of Minnesota soils. Both humus and total organic sulphur were higher in the chernozems and the black prairie soils than in the podzols.

Madnov (1946) determining sulphur content of a number of chernozem and chestnut soils, found that in chernozem the organic sulphur constituted about 75 per cent and in chestnut soils about 50 per cent of the total sulphur.

Shkonde (1957) working on Russian soils found that about 90 per cent of the sulphur in the ploughed layer of meadow dark brown soil was represented by organic sulphur and stable minerals and in sod-podsolic soils these forms represented 80 per cent of the total sulphur.

Estimating different forms of sulphur in the calcareous and non-calcareous soils of Italy, Oliver (1960) found that the content of organic sulphur varied from 77 to 2300 ppm.

Parson and Tinsley (1961) suggested that the organic compounds in the soil organic matter to which a considerable fraction of the soil sulphur was covalently bound, could be sulphated polysaccharides or sulphate esters of phenols and they showed that polysaccharides might constitute upto 30 per cent of the organic sulphur.

Kanwar and Surinder Mohan (1962) while studying the distribution of different forms of sulphur in Punjab soils, found that organic sulphur formed 72 per cent of the total sulphur in acid soils, while it was only 10 per cent in alkaline soils.

Kanwar and Mohan (1964) studying the distribution of forms of sulphur in Punjab soils found that organic forms abounded in acid soils. There was a close relationship between carbon, nitrogen and organic sulphur.

Kanwar and Takkar (1964) examining the soil samples from tea gardens of Punjab observed that, of the total sulphur 72 per cent was in organic form. There was a close correlation between organic sulphur and levels of carbon, nitrogen and organic phosphorus.

Lowe (1965) studied sulphur fractions of selected Alberta soil profiles of the chernozemic and podzolic orders. Organic forms of sulphur predominated in all surface and B horizons, although inorganic sulphate reached high levels in C horizons of some chernozemic profiles.

Jacob (1966) studying the sulphur status of Kerala soils also observed that organic sulphur constituted the major portion of the total sulphur.

3. <u>Sulphide Sulphur:</u>

Rost (1922) reported occurrence of sulphides in samples of peat and muck from Golden valley peat experiment of Minnesota. Sulphides were present at all levels in the peat. Sulphide content expressed as hydrogen sulphide was found to vary from 0.016 to 0.06 per cent for the lower most layers of peat and 0.002 to 0.013 per cent for the muck substratum immediately below.

Tszyun and Tszin (1967) determined micro-quantities of hydrogen sulphide in Chinese soils by isotopic dilution using radio active isotope S^{35}. Under ordinary conditions rice soils contained only a few mg. hydrogen sulphide per 100 g.

Jacob (1956) studying Kerala soils observed that appreciable quantities of sulphides were found only in paddy soils. The lower layers contained considerably lesser amounts of total sulphides than the upper horizon.

4. Sulphate sulphur and other extractable forms of sulphur:

The sulphur content of soils in the humid areas of the United States was listed by Miller (1951). The total sulphate in some soils varied from 2.8 per cent in chernozems to 7.9 per cent in podsols.

Jordan and Bardsley (1958) reported only 3 ppm or less of sulphur extractable by Morgan's acetate acetic acid buffer from the surface horizons of red yellow podsolic soils of South eastern parts of United States, and it tended to accumulate 6-30 inches below the surface.

Neller (1959) reported that the sulphate extracted with sodium acetate (pH 4.8) from various profiles of uncropped soils in Florida was generally absent from surface soils and accumulated in the subsurface layers where clay was present. The increase in sulphate with increasing clay content was highly significant and the extractable sulphate tended to be higher in soils with predominantly kaolinitic and illitic clay than with montmorillionitic clay.

In a group of 24 soils studied by Freney (1961) only about one per cent of the total sulphur occurred in inorganic compounds less oxidised than sulphates.

The values for available sulphur in 105 different Polish soils estimated by Nowosielski (1961) varied from 0.3 to 33 mg/100 g. in the arable layers and from traces to about 15 mg/200 g. in the deeper horizons. The values were lowest in light loamy soils and highest in peats.

Comparing the nutrient status of a peaty soil and a red loam laterite soil of Kerala, Money (1962) found that sulphate content of the peaty soil was 2.3 per cent while it was only in traces in red loam soil.

Lowe and DeLong (1963) observed that organic soils of Quebec contained substantially more carbon bonded sulphur than did mineral soils and 47-58% of the sulphur was in this form in organic soils whereas in mineral soils only 10-35 per cent of the sulphur was bonded to carbon. Recovery of carbon bonded sulphur in acid extractable fractions was higher in organic soils but only 52-84 per cent in 3 mineral surface soils. The acid extractable fraction was usually largest and the non-extractable fraction was very small.

Koter, Grzesiuk and Chodan (1963) determining the sulphur content of some soils in Olsztyn province found that the sulphate content varied from traces to 67.5 mg/kg soil and decreased with depth in profile.

Kanwar and Mohan (1964) studying distribution of forms of sulphur in Punjab soils observed that sulphate form predominated in calcareous soils of pH 7. Kanwar and Tarkar (1964) examining soil samples from tea gardens of Punjab also reported that sulphate occurred only in small amounts.

Massoumi and Cornfield (1964) analysing samples of mineral soils found that water soluble sulphate sulphur varied from 6 to 190 ppm. Jacob (1966) studied Kerala soils and reported that in well aerated soil sulphate sulphur accounted for the major portion of inorganic sulphur.

C. Sulphate Adsorption by Soil

All the inorganic sulphate is not extractable with water. Solutions containing displacing anions may extract a fraction which is considered to be adsorbed.

Mattson (1927) found that an appreciable quantity of sulphate was adsorbed by some soil colloids and that the adsorption capacity of a Norfolk soil colloid increased with increasing acidity.

Lysimeter studies of MacIntire et al (1945) show that liming increases the out go of sulphates.

Ensminger (1954) studying Alabama soil found that most surface horizons and light textured soils had only low capacity to adsorb sulphate but that appreciable adsorption was possible in B and C horizons. The capacity of soils to adsorb sulphate was affected by certain soil treatments. Increasing amounts of superphosphate applied to a Cecil sandy clay loam resulted in decreasing amounts of soluble sulphate. Liming also resulted in a decrease in the retention of sulphate. The sulphate adsorption capacity of a number of materials was determined in an attempt to show what fraction of soils might be responsible for the retention of sulphate. The data show that dehydrated aluminium oxide adsorbed much more sulphate than any of the other materials. The iron minerals adsorbed rather small amounts of the sulphate while the Davidson colloid, kaolinite and bauxite were intermediate.

Kamprath, Nelson and Fitts (1956) showed that soil containing a relatively large amount of 1:1 type clay minerals adsorbed more sulphate from calcium sulphate solution than did soils in which 2:1 type clay minerals predominated. Sulphate adsorption decreased as the pH increased from 4 to 6 and was directly related to sulphate concentration. Increasing PO_4 content of the solution reduced sulphate adsorption.

Tikhova (1953) indicated that in a range of soils, sulphate adsorption was greatest in soils of the most sub-tropics; less in sod-podsolised soils and least in chernozems, chestnut soils and solonetsec.

Schell and Jordan (1959) observed that the sulphate adsorption capacity of several clay minerals was related to total surface area. They suggested three mechanisms of sulphate adsorption viz. i) adsorption at the exchange sites ii) occlusion between lattice sheets, and iii) substitution for aluminium and silica in the lattice.

Equilibrium experiments with sulphate-chloride mixtures and potassium sulphate conducted by Chang and Thomas (1963) showed that the amount of anions held by anion retaining materials (B_2 horizon of loams, iron coated kaolinite) increased with time. This together with other observations suggest that sulphate ions were exchanged for OH and the H ions formed by the hydrolysis of aluminium in the presence of salt neutralized the OH ions, thus carrying the reaction towards completion.

Chao (1964) studied the effects of 26 inorganic and organic anions on sulphate adsorption by soil suspensions. Of the anions tried 18 reduced sulphate adsorption to varying degrees. The anionic effects could be explained by competition for anion exchange sites or anion replacement, ability of anions to form chelate complexes with iron and aluminium and precipitation reactions. Hydroxyl and bicarbonate ions decreased sulphate adsorption by increasing the equilibrium pH of soil suspension.

Chao, Harward and Fang (1965) demonstrated that an increase in the content of hydroxy components (iron coating) resulted in an increase in sulphate adsorption and in pH of the solution phase. The data were consistent with the view that sulphate was retained through an anion exchange reaction with OH groups in soils. Hydroxyl groups involved with the reaction were predominantly associated with the hydroxy iron and aluminium oxides in soils.

Koter *et al* (1966) conducted studies using S^{35} on sulphate adsorption by some humic soil substances. It was found that with increasing acidity of the soil environment of the rate of sulphur adsorption increased in fulvic acids and decreased in humic acids.

D. Sulphate Mobility in Soil

Sulphate added or released in the soil by decomposition is subject to loss by leaching. Data reported by Erdman and Bollen (1927) showed that Iowa soils lose over 50 pounds of sulphur per acre annually from the surface layers.

McKell and Williams (1960) have shown that 12 inches of percolate removed 77 per cent of the sulphur contained in 100 lbs of gypsum applied to a sandy soil.

Tikhova (1962) observed that the mobilisation of sulphate originating from organic sulphur in humic substances increased with increasing moisture contents and at temperatures ranging from 0 to 100°C the sulphate content varied between 1.66 and 5.8 mg/100 kg dry soil. The sulphate was fixed by

Ba, Cl and NO_3 and sulphate mobilisation was decreased by Ca and promoted by K and Na. Highest mobilisation of sulphate occurred on decreasing pH from 6.00 to 1.82 or increasing it from 7.00 to 9.35.

Swokoda and Thomas (1965) showed that the desorption by hydrolysis of adsorbed sulphate ions influenced the distribution of other ions in the columns of calcium saturated Cecil soil.

Yaalon (1965) studied the downward movement of chloride and sulphate together with their redistribution in the profile as affected by soil, and hydrologic factors Dispersion increased with column length or in the field, with depth of moisture penetration, it increased also as the pore size decreased.

E. Sulphur Transformations

1. Oxidation and Reduction:

Stephenson and Powers (1924) observed that the oxidation of sulphur applied to two widely different soils one representative of arid and the other of humid condition caused a decided increase in the water soluble calcium and potassium but reduced the amount of water soluble phosphorus. Even the lighter application produced an increase in acidity. The flocculating effect of oxidised sulphur may be of considerable value under certain conditions.

Hesse (1957) found that biological oxidation of organic sulphur was extremely slow compared with that of carbon and nitrogen. Incubation with sulphur containing amino acids or calcium sulphate increased the rate of oxidation of soil sulphur.

Lloyd, Frederic, Starkey and Segal (1957) studied the decomposability of some organic compounds in soil. Sulphate was the major product when cysteine was added to the soil and allowed to react. Their study on the degradation of methionine in soil showed that sulphur of methionine was released as methyl mercaptan, part of which was oxidised to dimethyl disulphide. Sulphate was not an end product of methionine decomposition.

Koves and Vamos (1960) showed that the intensity of sulphate reduction by both the facultative sulphate reducing bacteria and obligatory anaerobic autotropic sulphate reducers (*Desulfovibro desulfuricans*) is closely related to the Hydrogen sulphide formed. Sanden (1962) studying the alkalinization of soils cultivated to rice in the Danube plain concluded that under the influence of intense anaerobic processes, sulphur reducing bacteria decomposed sulphate to sulphides and these reacted with carbonic acid produced by the bacteria to give sodium carbonate and bicarbonate. The soils having a less dense granulometric structure and less salinization undergo most pronounced alkalinization in the hottest months.

Hart (1962) demonstrated the formation of elemental sulphur as an intermediate in poly-sulphide oxidation in mangrove soils. Vanos (1964) observed that damage due to Hydrogen sulphide occurring in some acidic heavy paddy soils and peaty fish ponds was usually preceded by falls in temperature and atmospheric pressure. The oxygen content of the water layer increased with the fall in temperature and as the redox level sunk in the mud, the superficial layer of the mud was oxidised and sulphuric acid formed which released hydrogen sulphide from the sulphide in its environment. The decrease of atmospheric pressure lifted the gases including hydrogen sulphide from the hollows of the mud into the water layer and thence into the atmosphere. The gases carried colloidal particles and rendered the water turbid. The released hydrogen sulphide might result in root rot and deficiency diseases in the rice plants and algal bloom and fish death in ponds.

Nelson (1964) while studying the status and transformation of sulphur in Mississippi soils found that the average amounts of sulphate sulphur released after 1, 2, 3 and 6 month incubation were, 2.1, 3.0, 5.4 and 8.9 lbs/acre respectively. The total amount of sulphur mineralised was related to the level of organic sulphur in the soil. The ratios of N to sulphur mineralised for the 2-3 and 6 month samples were 4.8, 6.5 and 5.8 respectively.

Timar and Szabolcs (1964) conducted laboratory experiment to find out the effect of organic matter on sulphate reduction in alkali soils. Measurements of redox and pH values and amounts of hydrogen sulphide evolved at the end of the experiment period showed that marked evolution of hydrogen sulphide occurred only in the presence of organic matter.

Ogata and Brower(1965) studied the effect of native and applied organic matter on sulphate reduction under anaerobic conditions in arid zone soils. The results indicated that appreciable reduction of the sulphate did not occur in poorly drained saline soils unless undecomposed plant residue was present or soil organic matter was greater than 5 per cent.

2. Microbial transformations of Sulphur:-

Verner and Orlovsky (1948) detected sulphate reducing bacteria in saline soils and particularly in peaty and bog solonchaks, where anaerobic conditions prevailed. Their activity was demonstrated by a decrease in the quantity of sulphate and increase in the quantity of sulphides and bicarbonates in the culture solution inoculated with the soils.

Starkey (1950) also indicated that microorganisms that transformed sulphur and its compounds were present in soils. The transformation of any one organism was marked by the reaction of others and the material that accumulated was either the completely oxidised product sulphate under aerobic conditions, or the reduced product, sulphide under anaerobic conditions.

Bromfield (1953) noticed that after treatment with volatile antiseptic some soils evolved hydrogen sulphide when moistened with sucrose and ammonium sulphate and incubated aerobically. He identified the bacterium producing hydrogen sulphide as _Bacillus megatherium_.

Koyama and Sugarwase (1950) observed that all submerged situations were not reducing. Several lake muds contained more of their inorganic sulphur as sulphate than as sulphides.

Satyanarayana and Datta (1953) noted sulphate reducing organisms in all the profiles in the soils of Rann area of Cutch. Their activity varied throughout the profile independently of the horizon. The organism was a rod-shaped motile spore former.

Starkey _et al_ (1953) showed that end products of the decomposition of cystine by microorganisms isolated from soil may be sulphate, sulphide or polythionates depending on the experimental conditions. Picci (1954) reported that the ratio of sulphur oxidation was highest at 15 to 20 per cent moisture content and in samples with a sand-clay ratio of 3:1. Addition of peptone and glucose increased sulphur oxidation more than mineral nitrogen and complex carbohydrates.

Freny (1958) followed the aerobic transformation of cysteine to sulphate in soil and established a sequence in the following order.

Cysteine → Cystine → Cystine di sulphoxide →
→ cysteine sulphinic acid → sulphate.

Studying the fixation of sulphur in the muck of Lake Victoria, Hesse (1958) pointed out that in the presence of large amounts of organic sulphur sulphates were found more than sulphides. Sperker (1954) suggested that production of hydrogen sulphide by several strains of *Bacillus megatherium* might transform ferric phosphate to black forms of sulphide with release of available phosphate. Hurt (1959) concluded that sulphide accumulation was fairly common under strongly reducing conditions such as at depth in tidal swamps or in poorly drained soils.

Subramoney (1960) studied the sulphur bacterial cycle and the probable mechanism of toxicity in acid soils of Kerala and worked out the sulphur microbial cycle in the following reversible sequence. Sulphuric acid ⇌ sulphates ⇌ sulphides ⇌ organic and elemental sulphur ⇌ sulphuric acid.

According to Stevenson (1964) the sulphur cycle in soil is divided into four distinct phases viz. mineralisation, immobilisation, oxidation and reduction.

F. Soil Reaction and Sulphur

Hart (1959) studied the sulphur oxidation in tidal mangrove soils and observed that when the soil was dried its pH value fell to 3.0 to 2.4 due to the activity of sulphur oxidising bacteria. When the pH value of the soil fell below 3 a rapid decline in the number of the organisms present occurred and it was suggested that this was due to the increase in the availability of ferric iron which also occurred below this pH value. Calcium carbonate had two main effects on sulphur oxidation; one on the sulphur oxidising bacteria, increasing or decreasing sulphur oxidation according to whether the pH value was moved into or out of the range of activity, and an inhibitory effect on pyrites oxidation. The results indicate that the pyrites fraction was not oxidised above pH 3 anthat it was not involved in acid formation.

Purokoshi (1959) working on the effect of liming on the sulphate soils of the Finnish coast showed that up to 32 tons of calcium carbonate were required for the improvement throughout the profile and for maximum yields of oats, barley and hay.

Nelson (1964) studied the effect of pH on the acetate soluble sulphur content of a Mayhew soil in Mississipoi before and after incubation. On incubating acid soil (pH 4.3) for three months, acetate soluble sulphate greatly increased in samples limed to pH 5-7, with maximum increase of 27 lbs per acre at pH 6.8.

Massoumi and Cornfield (1965) observed that differences in the extent of mobilisation or immobilisation due to pH were small or inconsistent except during incubation with straw when maximum immobilisation increased with pH.

G. Available Sulphur Evaluation

Diagnostic methods for sulphur status have followed the general approaches used for other elements such as nitrogen and phosphorus, which included oxidation by various solvents, incubation, microbial growth, plant growth and composition.

As total sulphur content has shown little promise as an index of available sulphur, several workers have attempted to measure a labile fraction of organic sulphur.

Williams and Steinbergs (1959) found that a fraction designated "heat soluble sulphur" (which may contain the most labile portion of the organic sulphur) was better correlated with sulphur uptake of plants than were other measures of readily available sulphur such as sulphate sulphur.

Kilmer and Nearpass (1960) preferred extraction with 0.5 M sodium bi carbonate at pH 8.5 as an indicator of available sulphur. Sulphur extracted by this reagent which may include a labile fraction of the organic sulphur as well as inorganic sulphate was strongly correlated with sulphur 'A' values.

A measure of readily available sulphur was obtained from the uptake over a period of 8 days by turnip roots. Uptake was closely related to sulphate extracted by the ammonium acetate solution of Bardsley and Lancaster.

Aspergillus niger was suggested as a test organism for sulphur by Malavolta and Galli (1951), and Picci (1952) and its growth was found to be closely correlated with sulphur status of some Australian soils.

Gorski, Nowosielski and Urbanska (1963) indicated that for low soil contents of available sulphur the *Aspergillus niger* method was more sensitive than the Chesnin yien nephelometric method. Incubation changed the available sulphur content of some but not all soils. In 20 soils studied there was no close relationship between total sulphur and available sulphur, but in fertilised soils the correlation was closer.

Naik and Das (1964) working on Indian soils found that the recovery of added sulphur by *Aspergillus* method was approximately 80 per cent.

H. Uptake of Sulphur by Plants

Anderson and Webster (1950) showed sharp contrast between the sulphur supplying power of two cotton growing soils in Georgia by growing cotton for 5 years on soils which received 0, 4, 8, 16 and 32 pounds of sulphur per acre applied annually. The heavier soil, a Leadvale silt loam contained a high sulphate content in the upper 12 inches. On this soil no response to added sulphur was obtained. The lighter soil, Norfolk loamy sand contained less than 1 ppm extractable sulphate sulphur in the upper 12 inches but from that point downwards sulphur accumulated reaching a maximum at the 30 to 36 inch layer. On this soil no measurable yield reduction occurred for four years when cotton was grown without applied sulphur but fifth year yields were drastically reduced.

Pawlk and Bentley (1964) studied the uptake of sulphur by crops using S^{35}. It was found that the uptake was much greater from the top soil than from greater depths, regardless of the availability of sulphur in the lower horizons.

I. Effect of Sulphur on the availability of other elements

Garey and Barber (1952) demonstrated that oxidation of sulphur or acid production was apparently important for releasing manganese from unavailable form and acidity maintained the equilibrium conditions favourable to the existence in soil of the manganous form.

Spek (1952) observed that the oxidation of sulphides present in the clay deposits removed the calcium carbonate from this deposit. In fine silt deposits this loss resulted in the formation of impermeable 'Knik soils' with a high exchangeable magnesium content and particles flocculated by calcium sulphate.

Investigations using the perfusion technique conducted by Vavra and Frederick (1952) showed that sulphur or sodium thiosulphate applied at rates equivalent to 5 tons per acre of sulphur greatly reduced pH and released considerable amounts of soluble manganese from soils in which no soluble manganese was found before treatment.

Reisenauer (1963) found that the uptake of soil and fertiliser molybdenum was markedly reduced by application of sulphate. Higher rates of sulphur fertilization also reduced the apparent efficiency with which molybdenum was used by the plant.

EXPERIMENTAL DETAILS

TABLE I

DETAILS REGARDING SOIL SAMPLES

Profile No.	Soil type	Name of place	District in Kerala State
1.	Lakebed soil	Vellayini	Trivandrum
2.	Peaty soil	Vaikom	Kottayam
3.	✓Forest soil	Devicolam	Kottayam
4.	Alluvial soil	Moncompu	Alleppy
5.	✓Laterite soil	Pattambi	Palghat
6.	Swamp soil	Kattampalli	Cannanore
7.	✓Sandy soil	Tellicherry	Cannanore

CHAPTER III

EXPERIMENTAL DETAILS

A. Details Regarding Soil Samples

Soil samples collected from seven soil profiles, representing different soil types of Kerala, constituted the material for the present study. From each profile, samples were collected from three different depths viz. 0-20 cm, 20-40 cm and 40-60 cm respectively. Details regarding the samples are presented in Table I.

B. Methods of Analysis

1. Preparation of Soil Samples:

The soil samples were air dried, powdered gently and passed through a 2 mm. sieve. The material which passed through the sieve was taken up for subsequent analysis and examination.

2. Physical Properties:

Using Keen-Raczkowski Brass cup method (Piper, 1950) the following physical properties were determined.

a. Pore space

b. Water holding capacity

c. Volume expansion

d. Apparent density or bulk density and

e. Absolute or real specific gravity.

3. Study of General and Related Properties: Chemical Properties:

a. Moisture:- A known weight of the soil was dried in an air oven at 105°C to constant weight and moisture content calculated (A.O.A.C. 1950).

b. Loss on ignition:- A known weight of the soil was ignited for 8 hours at dull red heat. The difference between the weights before and after ignition was used for calculating loss on ignition on moisture free basis (A.O.A.C. 1950).

c. Iron and Alumina:- The ignited soil was extracted with constant boiling hydrochloric acid for 8 hours. In an aliquot of the extract the hydroxides of iron and alumina were precipitated by adding ammonium hydroxide and estimated gravimetrically as oxides (A.O.A.C. 1950).

d. Iron:- Iron was estimated by reducing it to ferrous form with nascent hydrogen obtained from Zinc and sulphuric acid and titrating it against decinormal potassium permanganate (A.O.A.C. 1950).

e. Alumina:- The alumina present in the soil was calculated by subtracting the value of independently estimated iron oxide from the total sesquioxide value (A.O.A.C. 1950).

f. Calcium:- Calcium was estimated in the filtrate from iron and alumina by precipitating it as calcium oxalate and titrating against decinormal potassium permanganate after dissolving in dilute sulphuric acid (A.O.A.C. 1950).

g. Total Phosphorus:- An aliquot of hydrochloric acid was evaporated and silica dehydrated. It was extracted with nitric acid and phosphorus was precipitated in the extract as ammonium phosphomolybdate. It was dissolved in excess of 0.1619 potassium hydroxide and excess alkali titrated back with 0.1619 nitric acid. From the amount of alkali utilised phosphorus content was calculated.

h. Total Nitrogen:- Nitrogen was estimated by Kjeldahl method (Piper, 1950). The nitrogen in the sample was converted to ammonium sulphate by digesting it with concentrated sulphuric acid, copper sulphate and potassium sulphate. The ammonia was distilled off by treating the digested material with 40 per cent alkali and heating it in a distillation flask. The ammonia evolved was absorbed in a known excess of decinormal sulphuric acid. The excess acid was titrated back with 0.1 N alkali. The nitrogen content of the soil was calculated from the amount of acid consumed.

i. Organic Carbon:- The wet oxidation method of Walkley and Black was followed. About 0.5 gm. of powdered soil was treated with potassium dichromate and sulphuric acid. Excess of potassium dichromate was titrated back with standard ferrous ammonium sulphate solution. From the volume of potassium dichromate used the organic carbon was calculated (Piper, 1950).

j. pH:- pH was determined with the Beckman pH meter using a 1:2.5 soil-water suspension (Jackson, 1950).

k. Exchangeable Calcium:- A known quantity of the soil was leached successively with neutral normal ammonium acetate solution. Exchangeable calcium was determined in the leachate by versenate method (Jackson, 1962).

l. Available phosphorus:- Available phosphorus was determined colorimetrically by Bray and Kurtz No.2 method described by Jackson (1962) employing fluoride ion to displace phosphate ion.

m. Available nitrogen: Available nitrogen was estimated by alkaline permanganate method (Subbiah and Asija, 1956).

n. Redox Potential:- Redox potential was determined with the potentiometer using a 1:3 soil water suspension.

o. Anion Exchange Capacity:- Total anion exchange capacity was determined according to Piper's method (Piper, 1947).

Five grams of the soil were weighed accurately, transferred to a narrow mouthed bottle and 22.5 ml of normal ammonium phosphate solution were added. The bottle was stoppered tightly and shaken vigorously for a few seconds. It was placed in a water bath kept at a temperature of 50 to 60°C, shaking vigorously at intervals of fifteen minutes. After one and a half hours the bottle was removed from the bath and allowed to stand overnight.

The contents were filtered through Whatman No.50 filter paper. The bottle and stopper were rinsed with about 10 ml of normal ammonium phosphate solution and then with a jet of the same solution from a wash bottle. When the soil had been transferred quantitatively to the filter paper the leaching was continued with 5 to 10 ml portions of ammonium phosphate, draining the soil completely between successive additions, until the volume of the leachate was about 100 ml.

The excess of ammonium salts remaining in the soil in the funnel was removed by leaching with 5 to 10 ml portions of 80% alcohol. The soil was washed with two lots each of 5 ml of absolute alcohol to facilitate the drying of the soil and assist in its removal from the funnel.

When sufficiently dry the soil and filter paper were transferred to a small beaker and the funnel washed with water to remove the last traces of soil. The contents were diluted to 200 ml, 80 ml of normal sodium hydroxide added and boiled for 5 minutes. The suspension was transferred to a 250 ml volumetric flask, rinsing the beaker with hot water. When cooled, the suspension was diluted to the graduation mark, stoppered and mixed well.

The residual colour of the aliquot was removed by heating with bromine water. To a 50 ml aliquot 5 ml of saturated bromine water were added and if not sufficiently alkaline, a few drops of normal sodium hydroxide until the colour of the bromine disappeared. The solution was stirred and normal hydrochloric acid added drop by drop until the solution was just acid. The excess of bromine was removed by the addition of 5 ml of sodium sulphate solution and the solution boiled to remove most of the excess of sulphurous acid.

Phosphorus was determined in the aliquot by vanado-molybdophosphoric yellow colour method described by Jackson (1962).

4. <u>Different forms of Sulphur</u>:

a. <u>Total Sulphur</u>:- Total sulphur was determined by the procedure given by Jackson (1958).

About 2 gm. of finely ground and well mixed soil was fused with 5 times its weight of Sodium carbonate and 0.3 gm. of sodium nitrate in a platinum crucible. The fusion was done in an electric furnace. After fusion the melt was thoroughly disintegrated in water on the steam bath. The solution was then filtered and enough Hydrochloric acid added to make the solution about 0.3 N Hydrochloric acid in excess.

The solution was neutralised with ammonium hydroxide to remove the silica remaining in the filtrate which gels at this time. Solution was again filtered and hydrochloric acid added.

The solution was brought to boiling and 10 ml of 10 per cent barium chloride was added to precipitate sulphur as barium sulphate. The precipitate was washed free of chloride, ignited and weighed. From the weight of barium sulphate percentage of sulphur was calculated.

D. Humus Sulphur:- The method suggested by C.A.Evans and Rost (1945) was followed.

About 50 gm. of soil were taken and leached successively with 500 ml of distilled water, 500 ml of 1% hydrochloric acid and again with 500 ml of distilled water. The soil was then transferred to bottles and shaken several times over a period of 3 days with 1 litre of 4% ammonium hydroxide, to peptize the humic material. After standing the supernatant liquid containing the humic material was siphoned off and centrifuged to remove the suspended clay.

An aliquot of 500 ml was taken, evaporated to dryness and fused with magnesium nitrate solution. The residue was extracted with hot water and sulphur estimated gravimetrically in the extract.

c. <u>Organic Sulphur:</u> Total organic sulphur was estimated by the method described by C.A.Evans and Rost (1945).

Depending on the amount of organic matter 5 or 10 gm. of soil was leached with water, then with 1% hydrochloric acid and finally with distilled water till free of chloride. The soil was transferred to a beaker and oxidised with 30% hydrogen peroxide. When the oxidation was completed it was filtered and sulphur estimated in the filtrate gravimetrically, precipitating as barium sulphate.

d. <u>Sulphate Sulphur:</u>- The leachate from 50 gm. of soil used for humus sulphur estimation was concentrated to a small bulk, filtered and the sulphate estimated in the filtrate gravimetrically.

e. <u>Morgan's extractant Extractable Sulphur:</u>- The Turbidimetric method described by Chesnin and Yien (1951) was adopted.

Twenty gm. of air dried soil was shaken with 100 ml of Morgan's extracting solution for half an hour in a 250 ml conical flask. The contents were filtered through Whatman

No.42 filter paper. Depending on the sulphur content 10 to 20 ml aliquot of the extract was transferred to a 25 ml volumetric flask. One gram of 30 to 60 mesh barium chloride crystals was added to this and shaken for one minute. One to 2 ml of gum acacia solution depending on the sulphur content was added to this and the solution made up to volume. Turbidity readings were taken, from 5 to 30 minutes after the precipitation had occurred, in a photoelectric colorimeter using a blue filter. The readings obtained were compared with the values on a prepared standard curve to obtain the sulphur content of the sample.

f. Neutral ammonium acetate extractable sulphur:- Twenty gm. of soil were extracted with 100 ml of neutral ammonium acetate solution after shaking for half an hour. The sulphur content of the filtrate was estimated turbidimetrically (Chesnin and Yien, 1951).

g. Normal Hydrochloric Acid Soluble Sulphur:- Twenty gm. of soil were extracted with 100 ml of normal hydrochloric acid. Sulphur was estimated in the filtrate turbidimetrically (Chesnin and Yien, 1951).

h. Potassium di hydrogen phosphate extractable Sulphur: This fraction included adsorbed sulphite also. The method was described by Ensminger (1954). Twenty gm. of soil were shaken with 100 ml of potassium dihydrogen phosphate solution

solution containing 500 ppm phosphorus. The contents were filtered through Whatman No.42 filter paper and the sulphur content of the filtrate determined turbidimetrically (Chesnin and Yien, 1951).

1. *Sulphate adsorption capacity*:- Ten grams of soil were shaken with 100 ml calcium sulphate solution containing 40 ppm sulphur. The sulphur content of the filtrate was determined turbidimetrically and the quantity of sulphur adsorbed from the solution by soil calculated. The sum of soluble sulphate (sulphate sulphur extracted by sodium acetate of pH 4.8) plus sulphate sulphur adsorbed from calcium sulphate solution gives the adsorption capacity of the soil (Ensminger, 1954).

C. Neubauer Test

1. Details of Experiment:

Twenty one soil samples collected at three different depths from seven soil profiles were utilised for the study.

One hundred grams of soil from each sample were mixed with 50 gm. of quartz sand and placed in petri dishes of 11 cm. diameter and 7 cm. depth.

One hundred *ragi* (Co.7) seedlings were grown on these soils for a period of 17 days. At the end of this period they were removed, and the plant material weighed, dried and analysed for sulphur content.

This technique is based on the high rate of uptake of nutrients by a large number of plants grown on a limited quantity of soil. The amount of nutrients present in the plant was taken to represent the available nutrient in the soil (Neubauer and Schneider, 1923).

2. Analysis of plant material for sulphur:

The dried sample was weighed and digested with magnesium nitrate solution till all the liquid was evaporated and the evolution of brown fumes ceased. The residue was then heated in a muffle furnace at 350°C until a completely white residue was obtained. Water and hydrochloric acid in excess were added, boiled, filtered into 250 ml volumetric flask, the residues washed thoroughly with water and filtrate made up to volume.

The versenate method of Jackson was followed for the estimation of sulphate in the extract. Sulphate in an aliquot of the solution was precipitated by the addition of an excess of standard barium chloride solution and the excess barium remaining after the precipitation of barium sulphate was determined by titration with versenate.

Statistical analysis of the data

Scatter diagrams were drawn to determine possible relationships that sulphur content bears to other chemical constituents viz., the content of iron, alumina, phosphorus, total nitrogen and organic carbon. The existence of inter-relationships, if any, among different forms of sulphur was also examined. In specific cases, where the relationships were seen to be close on plotting the data on graph paper correlation coefficients were worked out and tested for significance. In significant cases, the regression equation was calculated and the regression line fitted.

OBSERVATIONS

CHAPTER IV

OBSERVATIONS

The results obtained from the analysis of the soil samples and the general observations made are presented in this chapter.

A. General

1. Physical Properties (Table II)

Apparent density ranged between 1.06 and 1.51.

Maximum pore space of 60 per cent was noted for forest soil. Lower depth of lake soil had the lowest pore space of 29 per cent. Except in peat in all profiles pore space decreased with depth.

Volume expansion on wetting ranged from 6.4 to 24.0 per cent. Maximum water holding capacity ranged between 29.8 and 62.3 per cent. It was maximum in forest peat and alluvial soil medium in the case of lake swamp and laterite soil and low in sandy soil.

2. Chemical Constituents (Table III)

a. Moisture:- The moisture content of the soil ranged from 0.2 per cent in sandy soil to a maximum of 6.2 in peat soil. In individual profiles moisture content decreased with increase in depth except for the peat profile which showed an increase.

TABLE II

PHYSICAL PROPERTIES

Particulars of soil sample: Profile No.	Particulars of soil sample: Depth of sampling (in cm.)	Water holding capacity (Per cent)	Pore Space (Per cent)	Volume expansion on wetting (Per cent)	Apparent Density	True Specific Gravity
1. Lake soil Vellayini	0-20	55.4	37	17.9	1.13	1.50
	20-40	54.1	36	17.1	1.12	1.52
	40-60	35.7	29	14.0	1.25	1.60
2. Laterite soil Pattambi	0-20	40.4	49	17.0	1.31	0.92
	20-40	43.2	49	13.2	1.35	2.36
	40-60	43.8	48	15.5	1.68	2.52
3. Swampy soil Kattampalli	0-20	47.0	54	15.8	1.30	2.45
	20-40	49.5	52	23.8	1.35	2.20
	40-60	43.4	50	15.8	1.34	2.30
4. Sandy soil Tellicherry	0-20	30.5	43	5.5	1.62	2.08
	20-40	31.3	43	6.4	1.51	2.60
	40-60	25.8	37	8.6	1.61	2.37
5. Peat soil Vaikom	0-20	59.5	51	24.6	1.19	2.10
	20-40	57.9	54	16.9	1.22	2.09
	40-60	60.8	58	15.6	1.13	2.31
6. Alluvial soil Mancompu	0-20	60.8	55	22.7	1.18	1.96
	20-40	43.8	55	16.8	1.35	2.40
	40-60	38.3	47	16.0	1.16	2.01
7. Forest soil Devicolam	0-20	62.8	60	21.4	1.15	2.30
	20-40	62.3	59	20.5	1.11	2.28
	40-60	55.6	57	14.6	1.21	2.40

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TABLE III

CHEMICAL CONSTITUENTS
(Percentage, Moisture free basis)

Particulars of soil sample Profile No.	 Depth of sampling (in cm.)	Moisture %	Loss on ignition	Sesquioxides (R_2O_3)	Iron oxide (Fe_2O_3)	Alumina (Al_2O_3)
1. Lake soil Vellayini	0-20	2.3	8.7	22.25	6.35	10.0
	20-40	2.2	4.7	14.21	4.61	9.60
	40-60	0.4	2.9	6.93	1.50	5.43
2. Laterite soil Pattambi	0-20	1.6	6.2	19.93	8.43	11.50
	20-40	2.7	6.9	19.83	7.96	11.87
	40-60	1.5	6.4	19.84	7.25	12.59
3. Swamp soil Kattampalli	0-20	2.9	5.0	17.10	5.82	11.28
	20-40	1.9	4.1	14.37	4.52	9.85
	40-60	2.2	3.6	11.96	3.62	8.34
4. Sandy soil Tellicherry	0-20	0.4	1.83	2.78	1.96	0.82
	20-40	0.3	1.12	2.49	1.77	0.72
	40-60	0.2	0.63	1.62	0.95	0.67
5. Peat soil Vaikom	0-20	3.6	10.2	3.89	1.91	1.98
	20-40	5.2	11.6	1.46	1.00	0.46
	40-60	6.2	11.8	1.04	0.74	0.30
6. Alluvial soil Moncompu	0-20	4.5	10.4	16.50	4.02	12.48
	20-40	4.1	9.8	12.76	3.35	9.51
	40-60	3.0	8.2	10.57	4.32	6.25
7. Forest soil Devicolam	0-20	4.8	9.8	14.39	8.86	5.53
	20-40	4.1	7.6	11.94	7.50	4.44
	40-60	4.0	6.3	7.05	3.08	3.97

b. Loss on Ignition:- The loss on ignition was found to vary widely. The values ranged from 0.62 to 14.8 per cent. The sandy soil gave the lowest value and peat soil the highest. Except for peat the profiles showed a decreasing tendency with increase in depth.

c. Sesquioxides:- The total amount of iron and aluminium oxides varied considerably, the values ranging from 1.04 per cent for the lower depth of sandy soil to 22.25 in the surface lake soil. In all profiles the iron and aluminium content decreased with increase in depth. The content was low in the case of peat and sandy soil.

(1) Iron Oxide:-

The iron content varied between 0.74 and 8.86 per cent. Iron content decreased with increase in depth in all the profiles. Peat and sandy soil profiles gave the minimum value. A close relationship was observed between the iron oxide and total sulphur contents (r = 0.683).

(2) Alumina:-

Alumina content was found to be very low in sandy and peat profiles. No statistically significant correlation was observed between this constituent and total sulphur content.

3. Total and Exchangeable Calcium (Table IV)

a. Total calcium:- The calcium content varied between 0.035 and 0.234 per cent. Except in the case of swamp soil

TABLE IV

TOTAL & EXCHANGEABLE CALCIUM
(Moisture-free basis)

Particulars of soil sample		Total Calcium (CaO) (Per cent)	Exchangeable Calcium m.e. %
Profile Number	Depth of sampling (in cm.)		
1. Lake soil Vellayini	0-20	0.21	2.8
	20-40	0.16	1.7
	40-60	0.15	1.4
2. Laterite soil Pattambi	0-20	0.11	1.6
	20-40	0.10	1.2
	40-60	0.07	0.8
3. Swamp soil Kattampalli	0-20	0.15	1.4
	20-40	0.09	1.2
	40-60	0.23	1.6
4. Sandy soil Tellicherry	0-20	0.07	0.90
	20-40	0.06	0.40
	40-60	0.07	0.40
5. Peat soil Vaikom	0-20	0.11	1.1
	20-40	0.10	1.1
	40-60	0.07	1.9
6. Alluvial soil Moncompu	0-20	0.12	1.7
	20-40	0.10	1.3
	40-60	0.06	2.3
7. Forest soil Devicolam	0-20	0.06	1.4
	20-40	0.04	0.8
	40-60	0.04	0.6

TABLE V

TOTAL AND AVAILABLE PHOSPHORUS
(Percentage, moisture free basis)

Particulars of soil sample		Total Phosphorus P_2O_5	Available P_2O_5 (Bray & Kurtz No.2)
Profile Number	Depth of sampling (in cm.)		
1. Lake soil Vellayini	0-20	0.0450	0.0048
	20-40	0.0340	0.0020
	40-60	0.0160	0.0036
2. Laterite soil Pattambi	0-20	0.2692	0.0106
	20-40	0.2610	0.0076
	40-60	0.2513	0.0064
3. Swamp soil Kattampalli	0-20	0.0710	0.0076
	20-40	0.0580	0.0086
	40-60	0.0460	0.0100
4. Sandy soil Tellichery	0-20	0.0276	0.0184
	20-40	0.0240	0.0210
	40-60	0.0256	0.0072
5. Peat soil Vallom	0-20	0.0760	0.0040
	20-40	0.0649	0.0036
	40-60	0.0448	0.0026
6. Alluvial Soil Moncompu	0-20	0.0395	0.0036
	20-40	0.0182	0.0036
	40-60	0.0176	0.0038
7. Forest soil Devicolum	0-20	0.0814	0.0026
	20-40	0.0795	0.0028
	40-60	0.0468	0.0026

TABLE VI

TOTAL AND AVAILABLE NITROGEN
(Percentage, moisture free basis)

Particulars of soil sample Profile Number	 Depth of sampling (in cm.)	Total Nitrogen	Available Nitrogen
1. Lake soil Vellayini	0-20	0.2310	0.0193
	20-40	0.2040	0.0171
	40-60	0.0615	0.0088
2. Laterite soil Pattambi	0-20	0.0868	0.0143
	20-40	0.0791	0.0077
	40-60	0.0[illegible]02	0.0053
3. Swamp soil Kattampalli	0-20	0.1106	0.0182
	20-40	0.0725	0.0141
	40-60	0.0532	0.0100
4. Sandy soil Tellichery	0-20	0.0304	0.0088
	20-40	0.0364	0.0052
	40-60	0.0282	0.0045
5. Peat soil Vaikom	0-20	0.1372	0.0163
	20-40	0.1424	0.0168
	40-60	0.1512	0.0179
6. Alluvial soil Moncompu	0-20	0.1372	0.01[illegible]8
	20-40	0.1358	0.0082
	40-60	0.1330	0.0069
7. Forest soil Devicolam	0-20	0.0883	0.0073
	20-40	0.0756	0.0064
	40-60	0.0673	0.0061

in all soils there was a decrease in calcium content with increase in depth. No statistically significant relationship was observed between this constituent and total sulphur.

b. Exchangeable calcium:- The exchangeable calcium content varied with individual profiles. Sandy soil gave the lowest values, these being 0.60 m.e. per cent for surface soil and 0.40 for lower depths. The surface layer of the lake soil recorded the maximum value of 2.6, followed by the lowest depth of alluvial soil, which recorded the value of 2.3 m.e. per cent.

4. Total and Available Phosphorus (Table V)

a. Total phosphoric acid:- Maximum phosphoric acid content was recorded in laterite soil (0.27%). The minimum content of 0.016 per cent was observed in the case of sub soil layer of lake soil. There was no significant correlation between total phosphoric acid and total sulphur contents.

b. Available phosphoric acid:- The availability varied from 0.0020 per cent in the case of lake soil to 0.0210 in the case of sandy soil. Maximum availability was observed in sandy soils.

5. Total and Available Nitrogen (Table VI)

a. Total Nitrogen:- Except for peat in all profiles total nitrogen decreased with increase in depth. Highest value was observed in the case of lake soil (0.231%) and

TABLE VII

ORGANIC CARBON AND ORGANIC MATTER CONTENT
(Percentage, moisture free basis)

Particulars of soil sample Profile Number	 Depth of sampling (in cm.)	Organic Carbon	Organic matter content (organic carbon x 1.732)
1. Lake soil Vellayini	0-20	2.980	5.160
	20-40	2.690	4.659
	40-60	1.580	2.736
2. Laterite soil Pattambi	0-20	1.020	1.700
	20-40	0.594	1.029
	40-60	0.413	0.716
3. Swamp soil Kattampalli	0-20	0.885	1.533
	20-40	0.592	1.025
	40-60	0.415	0.718
4. Sandy soil Kollichery,	0-20	0.240	0.415
	20-40	0.120	0.208
	40-60	0.060	0.104
5. Peat soil Vaikom	0-20	2.280	3.949
	20-40	3.060	5.299
	40-60	3.060	5.299
6. Alluvial soil Moncompu	0-20	2.94	5.091
	20-40	2.28	3.949
	40-60	2.28	3.949
7. Forest soil Devicolam	0-20	1.68	2.909
	20-40	0.72	0.1247
	40-60	0.60	0.1040

TABLE VIII

pH AND REDOX POTENTIAL

Particulars of soil sample		pH 1:2.5 soil water suspension	Redox potential 1:3 soil water suspension Millivolts
Profile number	Depth of sampling (in cm.)		
1. Lake soil Vellayani	0-20	4.9	400
	20-40	4.8	414
	40-60	4.7	428
2. Laterite soil Pattambi	0-20	4.6	438
	20-40	5.0	436
	40-60	5.2	426
3. Swamp soil Kattampalli	0-20	5.2	446
	20-40	5.4	436
	40-60	6.0	426
4. Sandy soil Tellicherry	0-20	4.2	420
	20-40	5.6	386
	40-60	5.8	406
5. Peat soil Vaikom	0-20	5.7	434
	20-40	5.0	461
	40-60	4.9	459
6. Alluvial soil Moncompu	0-20	5.4	433
	20-40	5.2	435
	40-60	5.2	453
7. Forest soil Devicolam	0-20	6.0	422
	20-40	5.9	310
	40-60	6.3	431

the lowest value in sandy soil (0.025%). Highly significant correlation was observed between the total nitrogen and total sulphur content (r = 0.531).

b. Available nitrogen:- The values ranged from 0.0045 in sandy soil to 0.0103 in lake soil. Decrease in content was observed with the increase in depth, except in peat profile.

6. Organic Carbon and Organic Matter Content (Table VII)

a. Organic carbon:- High organic carbon values were recorded for peat, lake and alluvial soil profiles, the highest value being 3.06 per cent. The value obtained for the sandy soil was the minimum viz. 0.06 per cent. Close correlation was observed between total sulphur and organic carbon values (r = 0.940).

b. Organic matter:- Organic matter content varied from 0.203 to 5.299 per cent.

7. pH and Redox Potential (Table VIII)

a. pH:- The pH of all the soils was on the acid side, with values ranging from 4.2 to 6.3. The laterite, swamp, sandy and forest soils showed an increase in pH with depth whereas lake, peat and alluvial soils showed decrease in pH with depth.

b. Redox potential:- The values ranged between 310 and 401 millivolts

TABLE IX

TOTAL ANION EXCHANGE CAPACITY AND SULPHATE ADSORPTION CAPACITY

Particulars of soil sample		Anion exchange capacity m.e.percentage	Sulphate adsorption capacity m.e. percentage
Profile number	Depth of sampling (in cm.)		
1. Lake soil Vollayini	0-20	1.32	0.036
	20-40	0.63	0.037
	40-60	0.27	0.041
2. Laterite soil Pattambi	0-20	0.43	0.027
	20-40	0.33	0.026
	40-60	0.35	0.035
3. Swamp soil Kattampalli	0-20	0.35	0.031
	20-40	0.36	0.037
	40-60	0.28	0.033
4. Sandy soil Tellicherry	0-20	0.81	0.014
	20-40	0.19	0.016
	40-60	0.23	0.018
5. Peat soil Vaikom	0-20	0.66	0.042
	20-40	0.81	0.043
	40-60	1.12	0.045
6. Alluvial soil Moncompu	0-20	1.23	0.041
	20-40	1.14	0.040
	40-60	1.39	0.046
7. Forest soil Devicolam	0-20	2.46	0.034
	20-40	2.05	0.034
	40-60	2.15	0.037

TABLE X

TOTAL SULPHUR AND NITROGEN/SULPHUR RATIO

Particulars of soil sample		Total sulphur per cent	Nitrogen/sulphur ratio
Profile number	Depth of sampling (in cm.)		
1. Lake soil Velleyini	0-20	0.1230	1.67
	20-40	0.1164	1.74
	40-60	0.0274	2.24
2. Laterite soil ✓ Pattambi	0-20	0.1027 ✓	0.64
	20-40	0.0860	0.89
	40-60	0.0315	1.91
3. Swamp soil Kattampalli	0-20	0.1962	0.71
	20-40	0.1027	0.71
	40-60	0.0685	0.78
4. Sandy soil Tollicherry ✓	0-20	0.0671 ✓	0.75
	20-40	0.0436	0.83
	40-60	0.0219	1.15
5. Peat soil Vaikom	0-20	0.4247	0.32
	20-40	0.3206	0.20
	40-60	0.3246	0.20
6. Alluvial soil Moncompu	0-20	0.2466	0.56
	20-40	0.2055	0.66
	40-60	0.1022	1.30
7. Forest soil ✓ Devicolam	0-20	0.1058 ✓	0.80
	20-40	0.0685	1.10
	40-60	0.0648	1.23

8. <u>Total anion exchange capacity and sulphate absorption capacity</u> (Table Ia)

a. <u>Anion exchange capacity</u>:- Maximum anion exchange capacity was observed in the case of forest profile. The values for the three different depths were 2.46, 2.05 and 2.15 respectively. In general the anion exchange capacity decreased with increase in depth. In peat profile it increased with increase in depth.

b. <u>Sulphate absorption capacity</u>:- The general tendency shown was to increase with increase in depth. The values ranged between 0.024 and 0.046.

B. Forms of Sulphur

1. <u>Total Sulphur and Nitrogen/Sulphur ratio</u> (Table 4)

a. <u>Total sulphur</u>:- Total sulphur content varied from 0.3246 to 0.0219 per cent. Maximum quantity was observed in peat profile, which showed an increase in content with increase in depth. In all the other profiles the content decreased with depth. Minimum was observed in sandy soil profile.

Highly significant relationships were observed between total sulphur and other forms of sulphur such as organic sulphur (r = 0.[illegible]), humus sulphur (r = 0.832), water soluble sulphur (r = 0.876), sulphate sulphur (r = 0.877),

TABLE XI

TOTAL ORGANIC AND HUMUS SULPHUR

Particulars of soil sample		Organic sulphur		Humus sulphur	
Profile number	Depth of sampling (in cm.)	Total content per cent	Percentage to total sulphur	Total content per cent	Percentage to total sulphur
1. Lake soil Vellayini	0-20	0.1162	94.3	0.0218	18.8
	20-40	0.1062	91.3	0.0152	11.3
	40-60	0.0187	86.2	0.0024	11.2
2. Laterite soil Pattambi ✓	0-20	0.0575 ✓	87.6	0.0176	17.9
	20-40	0.0833	82.0	0.0156	18.7
	40-60	0.0284	90.2	0.0022	7.8
3. Swamp soil Muttampalli	0-20	0.1535	95.5	0.0165	10.7
	20-40	0.0957	98.5	0.0137	13.9
	40-60	0.0641	93.6	0.0044	6.5
4. Sandy soil ✓ Tellicherry	0-20	0.0605 ✓	80.2	0.0065	10.1
	20-40	0.0371	84.7	0.0024	6.5
	40-60	0.0174	78.5	0.0012	5.9
5. Peat soil Vaikom	0-20	0.4173	98.2	0.0508	12.2
	20-40	0.3019	96.4	0.0390	11.8
	40-60	0.5123	97.7	0.0621	12.1
6. Alluvial soil Moncompu	0-20	0.2343	95.6	0.0312	13.3
	20-40	0.1907	93.3	0.0241	12.6
	40-60	0.0546	92.6	0.0152	16.1
7. Forest soil Devicolam ✓	0-20	0.1001 ✓	91.3	0.0086	8.6
	20-40	0.0620 ✓	90.5	0.0034	5.5
	40-60	0.0400	73.0	0.0012	3.00

HCl soluble sulphur (r = 0.942), neutral ammonium acetate extracted sulphur (r = 0.721), available sulphur (r = 0.935) and Neubauer test value for sulphur (r = 0.856).

b. Nitrogen/sulphur ratio:- Nitrogen/sulphur ratio was found to vary from 0.29 to 2.34. The ratio was low in the case of peat soil profile and high in lake soil profile.

2. Organic and humus sulphur (Table XI)

a. Organic sulphur:- Organic sulphur constituted the major portion of total sulphur in all the soils. The value ranged between 0.174 and 0.312 per cent. Their percentage to total sulphur varied from 68.2 to 98.2. A decrease with increase in depth was noted except for the peat profile. There was a close relationship between organic sulphur and other constituents viz. organic carbon (r = 0.919), total sulphur (r = 0.995), humus sulphur (r = 0.566), water soluble sulphur (r = 0.846) and sulphate sulphur (r = 0.   ).

b. Humus sulphur:- Humus sulphur content was found to vary between 0.0012 and 0.0321 per cent. The content decreased with increase in depth. Expressed as percentage of organic sulphur the values varied from 6.8 to 10.7

3. Water soluble and sulphate sulphur (Table XII)

a. Water soluble sulphur:- The content was low for all soils, and ranged from 0.0012 to 0.0036 per cent. Values for this form as percentage of total sulphur varied from 0.83 to

TABLE XII

WATER SOLUBLE AND SULPHATE SULPHUR

Particulars of soil sample		Water soluble sulphur		Sulphate sulphur	
Profile number	Depth of sampling (in cm.)	Content per cent	Percentage to total sulphur	Content per cent	Percentage to total sulphur
1. Lake soil Vellayani	0-20	0.0035	2.5	0.0068	5.5
	20-40	0.0028	2.4	0.0057	4.9
	40-60	0.0025	6.5	0.0042	15.3
2. Laterite soil Pattambi	0-20	0.0027	2.5	0.0046	4.5
	20-40	0.0021	2.7	0.0032	5.8
	40-60	0.0018	5.7	0.0046	14.6
3. Swamp soil Kuttanpalli	0-20	0.0016	1.0	0.0021	1.4
	20-40	0.0018	1.5	0.0036	3.5
	40-60	0.0020	2.5	0.0032	5.6
4. Sandy soil Tellicherry	0-20	0.0012	1.8	0.0024	3.6
	20-40	0.0016	3.7	0.0036	8.2
	40-60	0.0024	11.6	0.0013	11.6
5. Peat soil Vaikom	0-20	0.0036	0.8	0.0058	1.4
	20-40	0.0036	0.9	0.0074	1.4
	40-60	0.0030	1.0	0.0033	1.6
6. Alluvial soil [illegible]	0-20	0.0048	1.9	0.0054	3.8
	20-40	0.0045	2.1	0.0086	4.2
	40-60	0.0034	3.5	0.0070	6.5
7. Forest soil Devicolam	0-20	0.0036	3.3	0.0065	5.5
	20-40	0.0016	3.2	0.0058	6.5
	40-60	0.0018	3.3	0.0041	7.3

TABLE XIII

MORGAN'S EXTRACTANT EXTRACTABLE AND KH_2PO_4 EXTRACTABLE SULPHUR

Particulars of soil sample		Morgan's extractant		KH_2PO_4 extractant	
Profile number	Depth of sampling (in cm.)	Content per cent	Percentage to total sulphur	Content per cent	Percentage to total sulphur
1. Lake soil Vellayini	0-20	0.0250	20.3	0.0375	30.4
	20-40	0.0187	16.1	0.0280	24.1
	40-60	0.0125	45.6	0.0177	63.9
2. Laterite soil Pattambi	0-20	0.0057	8.0	0.0120	11.7 ✓
	20-40	0.0050	5.6	0.0090	10.1 ✓
	40-60	0.0038	12.1	0.0080	25.4
3. Swamp soil Kattampalli	0-20	0.0212	13.6	0.0321	20.6
	20-40	0.0130	14.6	0.0330	37.0
	40-60	0.0112	16.4	0.0385	56.2
4. Sandy soil Tellicherry	0-20	0.0037	5.5	0.0075	11.2 ✓
	20-40	0.0037	8.5	0.0125	28.6 ✓
	40-60	0.0037	16.9	0.0125	57.1
5. Peat soil Vaikom	0-20	0.0600	14.1	0.0950	22.4
	20-40	0.0612	11.8	0.0850	16.3
	40-60	0.0612	11.9	0.0700	13.4
6. Alluvial soil Moncompu	0-20	0.0473	16.3	0.0560	23.3
	20-40	0.0470	21.9	0.0600	27.3
	40-60	0.0420	41.1	0.0550	53.8
7. Forest soil Devicolam	0-20	0.0212	19.3	0.0275	25.1 ✓
	20-40	0.0182	23.6	0.0180	26.3 ✓
	40-60	0.0056	8.1	0.0090	16.4

10.96. The highest percentage to total sulphur was observed in the lower depth of sandy soil profile. It was lowest in the peat profile. Percentage to total sulphur increased with increase in depth in all profiles.

b. <u>Sulphate sulphur</u>:- The total content varied from 0.0021 to 0.0064 per cent. Percentage to total sulphur varied between 1.35 and 15.68. The percentage to total sulphur was high in the case of sandy soil and low in the case of peat profile. The percentage showed a general tendency to increase with increase in depth. Close relationship was observed with other fractions.

4. <u>Morgan's Extractant-extractable and Potassium dihydrogen phosphate extractable sulphur</u> (Table XIII)

a. <u>Morgan's extractant-extractable sulphur</u>:- Values for sulphur extracted by Morgan's extractant expressed as percentage of total sulphur varied from 8.2 to 45.6. With increase in depth the percentage extracted also increased. Close correlation was obtained between this fraction and other fractions viz. HCl soluble sulphur ($r = 0.903$), neutral ammonium acetate soluble sulphur ($r = 0.967$), total sulphur ($r = 0.935$) and Neubauer test values ($r = 0.943$).

b. <u>Potassium dihydrogen phosphate-extractable sulphur</u>:- Potassium dihydrogen phosphate solution containing 500 ppm P extracted one fraction of sulphur which included adsorbed sulphur. The quantity extracted varied considerably in

TABLE XIV

NEUTRAL AMMONIUM ACETATE AND NORMAL HYDROCHLORIC ACID EXTRACTABLE SULPHUR

Particulars of soil sample		Neutral ammonium acetate extracted sulphur		Normal hydrochloric acid soluble sulphur	
Profile number	Depth of sampling (in cm.)	Content per cent	Percentage to total sulphur	Content per cent	Percentage to total sulphur
1. Lake soil Vellayini	0-20	0.0175	11.8	0.0225	56.9
	20-40	0.0137	11.5	0.0662	50.9
	40-60	0.0025	9.1	0.0062	22.6
2. Laterite soil Pattambi	0-20	0.0057	6.5	0.0500	46.7
	20-40	0.0077	8.7	0.0350	35.3
	40-60	0.0062	10.7	0.0125	31.7
3. Swamp soil [illegible]	0-20	0.0225	14.3	0.0687	[illegible]
	20-40	0.0200	16.5	0.0512	34.7
	40-60	0.0169	23.6	0.0612	89.4
4. Sandy soil [illegible]	0-20	0.0052	9.2	0.0350	52.3
	20-40	0.0062	14.2	0.0337	51.1
	40-60	0.0050	22.6	0.0057	39.7
5. Peat soil Vaikom	0-20	0.1475	34.7	0.1030	24.7
	20-40	0.1600	30.7	0.1225	23.5
	40-60	0.1650	31.5	0.1525	[illegible]
6. Alluvial soil [illegible]	0-20	0.1200	[illegible]	0.1200	48.7
	20-40	0.0875	47.4	0.1050	51.2
	40-60	0.0800	78.0	0.0715	70.0
7. Forest soil Devicolam	0-20	0.0250	22.8	0.0687	63.7
	20-40	0.0225	32.1	0.0400	56.4
	40-60	0.0087	13.8	0.0225	41.1

TABLE XV

RESULTS OF THE NEUBAUER TEST

Particulars of soil sample: Profile number	Particulars of soil sample: Depth of sampling (in cm.)	Total green weight of 100 seedlings weight in gms.	Total dry weight of 100 seedlings weight in gms.	Percentage of sulphur in plants moisture free basis
1. Lake soil Vellayini	0-20	1.846	0.1078	0.0084
	20-40	1.229	0.1400	0.0072
	40-60	1.203	0.1391	0.0036
2. Laterite soil Pattambi	0-20	1.622 ✓	0.1565	0.0060
	20-40	1.324	0.0565	0.0048
	40-60	1.352	0.0545	0.0024
3. Swamp soil Kattampalli	0-20	2.159	0.1205	0.0084
	20-40	2.125	0.1410	0.0024
	40-60	1.410	0.0685	0.0015
4. Sandy soil Tellicherry	0-20	1.523 ✓	0.1235	0.0012
	20-40	1.368	0.1298	0.0009
	40-60	1.927	0.0650	0.0156
5. Peat soil Vaikom	0-20	2.211	0.1565	0.0120
	20-40	1.505	0.1335	0.0144
	40-60	1.927	0.0553	0.0156
6. Alluvial soil Moncompu	0-20	2.028	0.1957	0.0132
	20-40	1.912	0.1685	0.0108
	40-60	1.695	0.1460	0.0072
7. Forest soil Devicolam	0-20	1.841 ✓	0.1137	0.0048
	20-40	1.497	0.1475	0.0036
	40-60	1.365	0.1430	0.0031

different soils. Percentage of extraction varied between 10.1 and 63.8. There was a general tendency to increase with depth.

5. Neutral ammonium acetate and normal hydrochloric acid extractable sulphur (Table XIV)

a. Neutral ammonium acetate extractable sulphur:- The quantity extracted from different soils varied considerably. The values ranged from 0.0025 to 0.1650 per cent. Maximum quantity was extracted from peat and alluvial soil profiles. Percentage to total sulphur varied between 3.47 and 78.29. Significant correlation was obtained with total sulphur (r = 0.714), Morgan's extractant extractable sulphur (r = 0.587) and Neubauer test values (r = 0.656).

b. Normal Hydrochloric acid extractable sulphur:- The quantity extracted was variable. Percentage to total sulphur varied between 22.6 and 89.3. These percentages were generally low in the case of peat profile. However the minimum value was recorded in the case of the 40-60 cm layer of the lake profile.

C. Neubauer Test

The seedlings of the Neubauer test were analysed for sulphur content. The data are presented in Table XV.

The total green weight of the seedlings varied from 1.080 gm in the case of sandy soil to 2.21 gm in the case of peat soil for 100 seedlings.

TABLE XVI

RESULTS OF STATISTICAL ANALYSIS

S. No.	Relationship between	Correlation coefficient	Regression equation	No. of pairs of values
1.	Total sulphur vs iron oxide	0.602**	Y = 0.0409 + 0.00[illegible]X	13
2.	Total sulphur vs total nitrogen	0.931***	Y = -0.0518 + 1.9[illegible]X	15
3.	Total sulphur vs organic carbon	0.840***	Y = 0.0763X + 0.0032	28
4.	Organic sulphur vs organic carbon	0.919*	Y = 0.0002 + 0.0727X	18
5.	Total sulphur vs organic sulphur	0.995***	Y = -0.0125 + 1.00X	21
6.	Total sulphur vs humus sulphur	0.982***	Y = -0.0005 + 0.1[illegible]X	21
7.	Total sulphur vs Neubauer test values for sulphur	0.889***	Y = 0.0017 + 0.03X	21
8.	Organic sulphur vs Neubauer test values for sulphur	0.900***	Y = 0.0021 + 0.03X	21
9.	Humus sulphur vs Neubauer test values for sulphur	0.918***	Y = 0.0008 + 0.37X	18
10.	Total sulphur vs Water soluble sulphur	0.876***	Y = 0.0011 + 0.016X	16
11.	Total sulphur vs hydrochloric acid soluble sulphur	0.942***	Y = 0.0027 + 0.51X	16
12.	Total sulphur vs neutral ammonium acetate extractable sulphur	0.714**	Y = 0.0023 + 0.13X	15
13.	Total sulphur vs available sulphur extracted by Morgan's extractant	0.935***	Y = 0.0051 + 0.12X	16

CONTD.

TABLE XVI (CONTD.)

S. No.	Relationship between	Correlation coefficient	Regression equation	No. of pairs of values
14.	Morgan's extractant extractable sulphur vs. neutral ammonium acetate extractable sulphur	0.967^{***}	$Y = -0.0169 + 2.66X$	21
15.	Morgan's extractant extractable sulphur vs hydrochloric acid soluble sulphur	0.902^{***}	$Y = 0.0199 + 1.22X$	19
16.	Total sulphur vs sulphate sulphur	0.877^{***}	$Y = 0.0036 + 0.02X$	16
17.	Hydrochloric acidsoluble sulphur vs water soluble sulphur	0.917^{***}	$Y = 0.0010 + 0.03X$	19
18.	Hydrochloric acid soluble sulphur vs Neubauer test values for sulphur	0.919^{***}	$Y = 0.1087X - 0.0005$	21
19.	Sulphate sulphur vs Morgan's extractant extractable sulphur	0.888^{***}	$Y = 0.0205 + 7.13X$	17
20.	Morgan's extractant extractable sulphur vs Neubauer test values for sulphur	0.945^{***}	$Y = 0.0014 + 0.21X$	21
21.	Organic sulphur vs hydrochloric acid soluble sulphur	0.940^{***}	$Y = 0.0056 + 0.52X$	18
22.	Organic sulphur vs water soluble sulphur	0.846^{***}	$Y = 0.0013 + 0.015X$	17
23. ✓	Sulphate sulphur vs Neubauer test values for sulphur	0.904^{***}	$Y = 0.0046 + 1.78X$	17
24.	Sulphate sulphur vs water soluble sulphur	0.943^{***}	$Y = 0.0002 + 0.56X$	21
25.	Sulphate sulphur vs Hydrochloric acid soluble sulphur	0.805^{***}	$Y = -0.0237 + 14.08$	17
26.	Organic sulphur vs humus sulphur	0.996^{***}	$Y = -0.0063 + 0.23X$	21
27. ✓	Neutral ammonium acetate sulphur vs Neubauer test values for sulphur	0.986^{***}	$Y = 0.0016 + 0.08X$	16

Significance: *** : 0.1 per cent
** : 1 per cent

The maximum dry weight obtained was 0.1965 gm in the case of the laterite soil (surface layer).

Sulphur content in seedlings varied between 0.0006 to 0.0156 per cent. Low values were obtained in the case of seedlings grown in sandy soil. Seedlings grown in peat soil gave the maximum values. The values were significantly correlated with total sulphur (r = 0.869), available sulphur (r = 0.946), neutral ammonium acetate extractable sulphur (r = 0.714) and organic sulphur (r = 0.660).

L. Statistical Analysis

The results of statistical analysis of the data obtained are presented in Table XVI. The individual correlations have been mentioned in the relevant sections presented above.

DISCUSSION

CHAPTER V

DISCUSSION

The observations made during the study of the distribution of different forms of sulphur in representative soil profiles of Kerala are discussed in the following sections.

A. Variation of the Several Fractions with Depth

1. Total Sulphur:

The total sulphur content of different soil types varied considerably (Table X) In all profiles except the peat profile the surface soil contained the maximum amount of total sulphur and it decreased with increasing depth. In the case of peat profile the quantity increased with depth.

The pattern of variation of total sulphur content in the various profiles studied was generally in conformity with the reports of previous workers. Walker and Adams (1958) reported mean values of 700, 410 and 230 lbs/acre for the A, B and C horizons respectively in grassland soils of New Zealand. Kanwar and Takkar (1964) found that total sulphur decreased with an increase in depth of the profile in the tea soils of Punjab. Jacob (1966) working on Kerala soils also reported the same tendency.

The reverse tendency shown by the peat profile is also in accordance with the findings of other workers. Subramoney (1960) recorded 18200 and 31000 ppm total sulphur in the surface soils and sub-soils, respectively, for Kari soils of Kerala. Kotor, Grazesuik and Chodan (1963) reported that the sulphur content decreased with depth in mineral soils and increased in peat soils. Jacob (1956) also reported the same tendency in Kari soils of Kerala.

The total sulphur content is dependent mainly on the organic matter content of the soil. As the organic matter generally decreases with the depth of profile, the total sulphur content also decreases accordingly. But in the case of peat soil it has been found that the organic matter itself increased with depth. This explains the increase in total sulphur content with depth in peat soils. The total sulphur content was maximum in peat profile and minimum in sandy soil.

2. Organic Sulphur and Humus Sulphur (Table XI)

The organic sulphur constituted more than 60 per cent of the total sulphur. In all the surface soils 80 per cent of the sulphur was in the organic form. A decrease with increase in depth was noted in all profiles except the peat profile. Previous workers have also indicated that organic form is the most dominant form of sulphur present in soils. Madnov (1946) reported that in chernozems the organic sulphur constituted about 75 per cent and in chestnut soils about

50 per cent of the total sulphur. Kanwar and Surindermohan (1962) found that organic sulphur formed 73 per cent of the total sulphur in acid soils of Punjab. Atoinyan (1964) reported that 70 to 90 per cent of the total sulphur in non-saline soils of U.S.S.R. was bound in the organic matter. Kanwar and Takkar (1964) found that the organic sulphur varied from 42 to 96 per cent of the total sulphur in the tea soils of Punjab. Jacob (1966) also indicated that the organic form was predominant in the soils of Kerala.

The sulphate ion is one of the most mobile ions present in the soil. The intense leaching due to heavy rainfall in the area and the consequent depletion of inorganic sulphur would be expected to result in the accumulation of the organic form of sulphur, thus rendering it the predominant form.

Humus sulphur content decreased with increase in depth. Expressed as percentage of organic sulphur the value varied from 6.8 to 16.7. Evans and Rost (1945) reported that humus sulphur was contained in that portion of the organic matter which is in an advanced stage of mineralisation. They also reported that both humus and total organic sulphur were higher in the chernozems and the black prairie soils than in the podzols. Maximum quantity was observed in peat profile and the minimum in sandy soil profile. Organic matter content of the peat profile was high, whereas sandy soil contained very little organic matter. Accordingly organic sulphur and humus sulphur contents were also low.

3. <u>Sulphate Sulphur</u> (Table XII)

The total content varied from 0.0021 to 0.0604 per cent. The maximum amount of sulphates were found in alluvial and peat soils. There was an increase in content with depth in the case of peat, swamp and sandy soil profile. The other profiles indicated a decrease with depth. Expressed as percentage of total sulphur the maximum value was observed in the case of lower depths of sandy soil profile and the general tendency was to increase with depth.

Money (1962) working on Kerala soils found that sulphate content of the peaty soil was 2.3 per cent, while it was only in traces in the red loam soil. Later, Grazesuik and Chouan (1963) reported that the sulphate content varied from traces to 37.5 mg/kg. soil and decreased with depth in the profile.

The findings obtained hitherto have established that the lowest rates of movement of sulphate occurs in acid, fine textured soils that are high in hydrous oxides. Under these conditions retardation of sulphate from both physical factors and adsorption is at a maximum. Chao, Harward and Fang (1964) indicated that adsorption of sulphate by soils increased with decreasing pH. So it is quite likely that these factors would have come into play in the mobilization of sulphate and its translocation down the profile. This may account for the fact that some of the profiles showed increase in content with depth and the others indicated decrease with depth.

4. Water soluble sulphur (Table XII)

Water extracted a small fraction of the total sulphur. The content ranged from 0.0012 to 0.0050 per cent. Maximum quantity was extracted from the peat soil and minimum from sandy soil. Percentage of water soluble sulphur to total sulphur showed an increase with increase in depth. Water being a weak extractant understandably only very low quantities were extracted.

5. Morgan's extractant extractable sulphur (Table XII.

Values for sulphur extracted by Morgan's extractant expressed as percentage of total sulphur varied from 5.6 to 45.6. With increase in depth percentage extracted also increased. Under well drained conditions the presence of appreciable amounts of soluble sulphates is likely only in sub-soil horizons. This accounts for the increase in extraction with depth. Keller (1950) reported that the sulphate extracted with sodium acetate (pH 4.8) from various profiles of uncropped soils in Florida was generally absent from surface soils and accumulated in the sub-surface layers where clay was present. The extractable sulphate tended to be higher in soils with predominantly kaolinitic and illitic clay than with montmorillonite clay.

6. Potassium dihydrogen phosphate (Table XIII)

The quantity extracted varied considerably. Adsorbed sulphate was also extracted in this case as the phosphorus replaced sulphate. Percentage of extraction varied between

10.1 and 63.8. There was a general tendency to increase with depth. Spencer and Freney (1960) indicated that this reagent might also release a part of the organic sulphur. In the present study also it was found that the fraction extracted some portion of the organic sulphur too.

7. Neutral normal ammonium acetate extractable sulphur (Table XIV)

Previous workers have indicated that extraction with neutral normal ammonium acetate extracted the sulphate sulphur in addition to a labile fraction of organic sulphur from the soil. This extraction was suggested by McClung *et al.* (1959) and was found to be satisfactory for some soils by Spencer and Freney (1960).

In the present study the quantity extracted varied
25 from 0.0025 to 0.1650 per cent. Maximum quantity was
1650 extracted from peat and alluvial soil profiles. Percentage to total sulphur varied between 5.5 and 78.3.

62
1325

8. Normal hydrochloric acid soluble sulphur (Table XIV)

The quantity of sulphur extracted by normal hydrochloric acid varied between 0.0062 and 0.1325 per cent. Maximum quantities were extracted from peat and alluvial soils. Williams and Steinbergs (1958) reported that up to 80 per cent of the total sulphur was extracted by normal hydrochloric acid from a range of calcareous and alkaline soils. The soils under present study are all acidic and contain very little calcium. Lowe and DeLong (1963) observed that organic soils of Quebec contained substantially more carbon-bonded sulphur and the recovery of carbon-bonded sulphur in acid extractable fraction was higher in organic soils. This fact may be responsible for the increase in extraction from soils containing high organic matter content.

1. Relationship of Sulphur Forms with other General Properties of the Soil

From the data obtained it was found that the iron oxide content bears a close relationship to total sulphur (r = 0.662). However, the peat profile and the top horizons of alluvial soil stood apart from the regression line. The iron oxide content was very low in these soils and the sulphur content high. Starkey (1966) indicated that in the oxidation and reduction that sulphur undergoes in soils iron plays an important role. Therefore it may be quite possible that the high content of sulphur coupled with low iron oxide content may affect the reaction of the sulphur in these soils.

The total sulphur did not show any relationship with alumina, calcium and phosphorus content. The total sulphur content was significantly correlated with organic carbon (r = 0.940) and total nitrogen (r = 0.931). All the three constituents decreased with increase in depth of the profile. The positive correlation obtained here was in accordance with the findings of Kanwar and Mohan (1964) and Kanwar and

Takkar (1964) for Punjab soils. High organic matter content indicated high total nitrogen and total sulphur. This indicates that sulphur content of the soil is mainly derived from the decomposition of plant tissue.

It was observed that the peat soil profile stood apart in many of the regressions. This profile presented a different picture from the others in that the organic matter content, total nitrogen and total sulphur increased with increase in depth. Iron oxide content was comparatively very low. The sulphur content was very high in these soils. This difference in pattern may be responsible for the observed deviation from general trend for the majority of the soils studied.

C. Forms of Sulphur and their Interrelationships

Sulphur was present mainly in the organic form in all the profiles studied. High mobility of the sulphate ion and the intensity of leaching due to heavy rainfall accounts for this.

A very highly significant correlation was observed between total sulphur and organic sulphur ($r = 0.962$). A very close relationship existed between organic sulphur and humus sulphur content ($r = 0.986$). Very highly significant relationships were also observed between total sulphur on one hand and other forms of sulphur on the other viz. water soluble sulphur (r = 0.876), sulphate sulphur (r = 0.877), hydrochloric acid soluble sulphur (r = 0.842), neutral ammonium acetate extractable sulphur (r = 0.714), Morgan's extractant extractable sulphur (r = 0.935) and Neubauer test values for sulphur (r = 0.859).

Koter, Grazesuik and Chodan (1963) observed a linear relationship between total sulphur and sulphate sulphur contents of soil. Inter-correlations worked out by Spencer and Freney (1960) between sulphur fractions and plant growth indicated that the amounts of sulphur extracted by all procedures showed a fairly close association with plant growth and uptake of sulphur.

The very close relationship observed among various forms of sulphur simplifies very much the study of these forms, because even from the estimation of the most easily determined form all the other forms can be predicted. Water soluble sulphur itself showed close relationship with total sulphur sulphate sulphur and other extractable forms of sulphur. This form can be easily estimated either turbidimetrically by the method of Chesnin and Yien or volumetrically employing the versenate method described by Jackson

D. Available Sulphur:- Determination: Comparison of Efficiency of Various Extractants

The soil was extracted with Morgan's extractant, potassium dihydrogen phosphate solution containing 500 ppm phosphorus and neutral normal ammonium acetate solution to find out the quantity of sulphate extracted by each. These extractants were utilised by previous workers to find out the plant available sulphur. It is generally known that the inorganic sulphate is available to plants, and that they generally take up sulphur in the form of sulphate ion. As most of the soil sulphur is in the organic form and very little sulphate is present in the surface layers it is evident that organic sulphur is converted to inorganic sulphate before it becomes available to plants.

Jordan and Bardsley (1958) and Williams and Steinberg (1959) indicated that adsorbed as well as barium and calcium sulphates were available to plants. Spencer and Freney (1960) found that the best correlation with sulphur uptake or percentage yield were obtained for cold water extractable sulphate, hot water extractable sulphate, Aspergillus sulphur and 'heat soluble' sulphur. Correlation with other fractions were appreciably poorer, the weakest correlation being with total sulphur and its derivative, reserve sulphur. Neutral ammonium acetate extraction was found to be satisfactory for some soils.

Out of the extractants tried neutral ammonium acetate solution extracted the maximum quantity. The quantity extracted from the peat and alluvial soils was the highest. It was quite evident that the extractants were capable of extracting a fraction of the organic sulphur too, as the content in very many cases was more than the sulphate sulphur estimated.

Neubauer test was conducted employing *ragi* (Co.7) seedlings to find out the plant-available sulphur. Neubauer test values for sulphur were found to be low when compared to the quantity extracted by the above extractants. However, significant relationships were observed between Neubauer test values for sulphur and other available forms of sulphur extracted by Morgan's extractant and neutral normal ammonium acetate solution.

6. General considerations regarding Sulphur Content and Availability in Kerala Soils

In the study now undertaken it has been found that the soils are generally well supplied with sulphur. Peat soils contain the maximum quantity of sulphur. The organic matter content of these soils is also high and its tendency is to increase with depth. As the organic matter content increases sulphur content also increases, which indicates that the sulphur content is mainly derived from the decomposition of plant tissues.

Regarding the availability of sulphur as measured by various extractants and Neubauer Test it was found that the maximum availability was found in peat soil and alluvial soil, though the content was varying depending upon the extractants. Therefore in general there is no deficiency in the soil for this element. The relatively higher content of sulphur observed in some cases may prove harmful, depending upon the environmental conditions and other related properties of the soil.

The iron oxide content of the Kerala soils are generally high but in the present study it has been observed that the peat soil contained very little iron oxide. Sulphur content of these soils was the highest. Since iron plays an important role in the oxidation and reduction of sulphur compounds it is quite possible that this will affect the reaction of the sulphur in these soils.

The study has brought to light that very close relationships exist among organic carbon, total nitrogen and total sulphur, and the total sulphur itself is highly correlated with other sulphur forms. Hence it is suggested that even the estimation of nitrogen which is done as a routine analysis in all soils can be used for drawing a very good idea regarding sulphur and its various forms by prediction from nitrogen.

SUMMARY AND CONCLUSIONS

CHAPTER VI

SUMMARY AND CONCLUSIONS

A detailed study was undertaken to determine the distribution of different forms of sulphur, its availability and its relationship to other general constituents, in soils of Kerala. Soil samples collected from three different depths viz., 0-20 cm, 20-40 cm and 40-60 cm respectively from seven soil profiles, representing different soil groups of Kerala, constituted the material for the study. They were analysed for different forms of sulphur and also for their general and related properties. Neubauer test was conducted employing *ragi* seedlings to find out the plant available sulphur. Available sulphur was estimated by different extractants also.

The data obtained were studied and analysed statistically. Scatter diagrams were drawn to determine possible relationships that sulphur content bears to those of other chemical constituents viz., the contents of iron, alumina, phosphorus, total nitrogen and organic carbon. The existence of interrelationships, if any, among different forms of sulphur was also examined. In specific cases, where the relationships were seen to be close, correlation coefficients were worked out and tested for significance.

Conclusions

The study brought to light the following conclusions.

The content of different forms of sulphur varied considerably from soil to soil. In general the soils were not deficient in this element. Peat and alluvial soils had relatively higher content of sulphur.

In all profiles, except the peat profile, the surface soil contained the maximum amount of total sulphur and it decreased with increasing depth. The reverse was observed in the case of peat profile.

The organic sulphur constituted more than 60 per cent of the total sulphur considering all depths together. In all the surface soils 90 per cent of the total sulphur was in the organic form. A decrease in sulphur content with increase in depth was observed except for the peat profile. Sulphate sulphur content values were generally low. Percentage of sulphate sulphur to total sulphur was maximum in the case of lower depths of sandy soil profile.

Very close correlations were obtained among organic carbon, total nitrogen and total sulphur. All the three constituents decreased with increase in depth of the profile. High organic matter content indicated high total nitrogen and total sulphur. This indicates that sulphur content of the soil is mainly derived from the decomposition of plant tissue.

The total sulphur content itself was highly correlated with other sulphur forms viz. organic sulphur, sulphate sulphur, water soluble sulphur, Morgan's extractant extractable sulphur, Neutral ammonium acetate extractable sulphur and Neubauer test values for sulphur. Hence it is suggested that even the estimation of nitrogen which is done as a routine analysis in most soils will give a very good estimate of sulphur and its various forms in Kerala soils.

The total sulphur content was positively correlated with iron oxide content. However, the peat profile and the top horizons of the alluvial soil stood apart from the general relationship pattern. The iron oxide content was very low in these soils and the sulphur content high. Since iron plays an important role in the oxidation and reduction of sulphur compounds it is possible that this will affect the reaction of sulphur compounds in these soils.

Significant relationships were observed between Neubauer test value for sulphur and other available forms of sulphur, viz., those estimated by Morgan's extractant and Neutral normal ammonium acetate solution. Neubauer test values for sulphur were found to be low when compared to the quantity extracted by the other extractants. Significant relationship was also observed among Neutral normal ammonium acetate extractable sulphur and Morgan's extractant extractable sulphur. Out of the extractants tried Neutral normal ammonium acetate extracted the maximum quantity of sulphur. It was quite evident that the extractants were capable of extracting a fraction of the organic sulphur too, as the content in very many cases were more than the sulphate sulphur estimated. These available forms of sulphur showed close relationship with sulphate sulphur and water soluble sulphur too.

In spite of the heterogeneous nature of the soil collection, the relationships obtained among total sulphur and other constituents and sulphur forms were close.

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* Originals not seen

ILLUSTRATIONS

FIG. 1 DEPTH FUNCTIONS OF SULPHUR

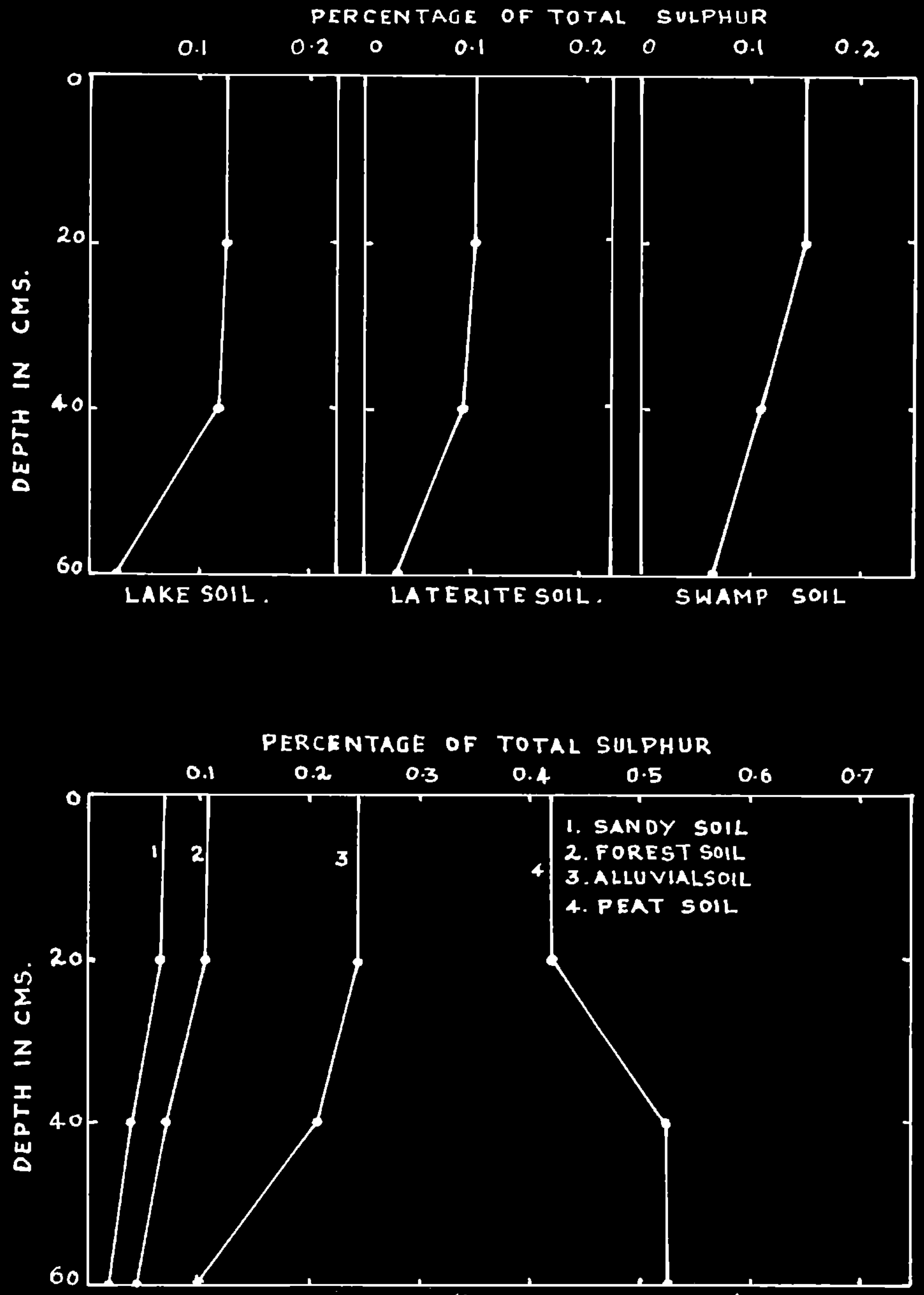

FIG.2 IRON OXIDE-TOTAL SULPHUR RELATIONSHIP

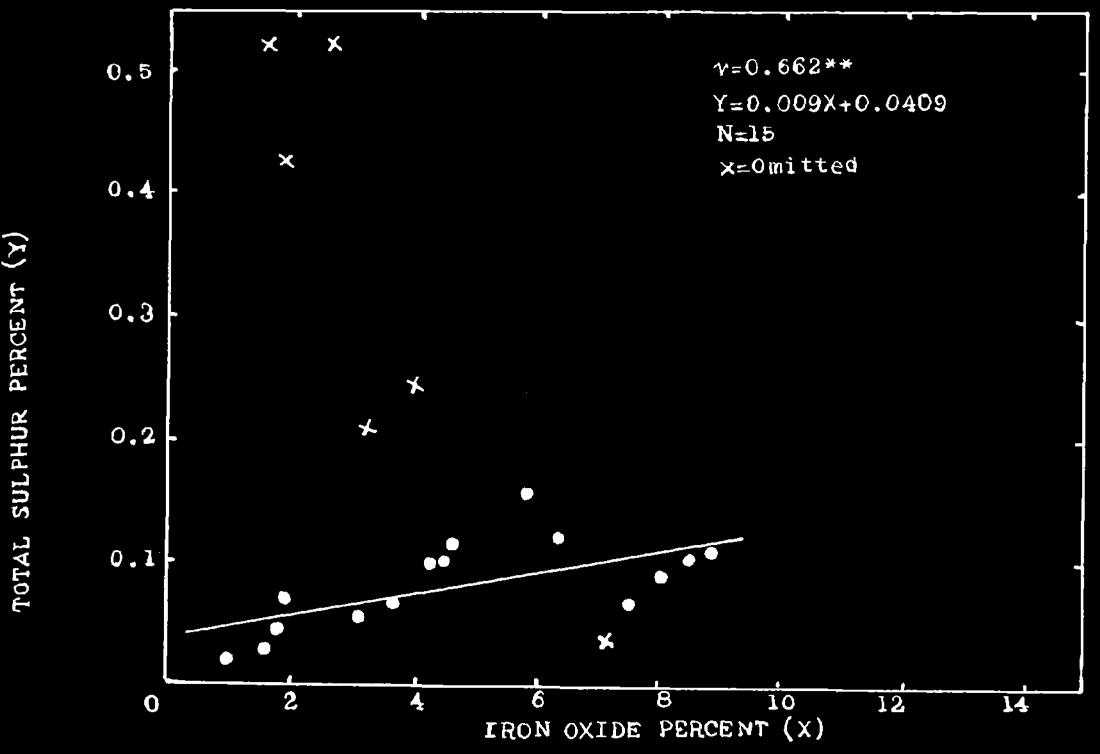

FIG.3 TOTAL NITROGEN-TOTAL SULPHUR RELATIONSHIP

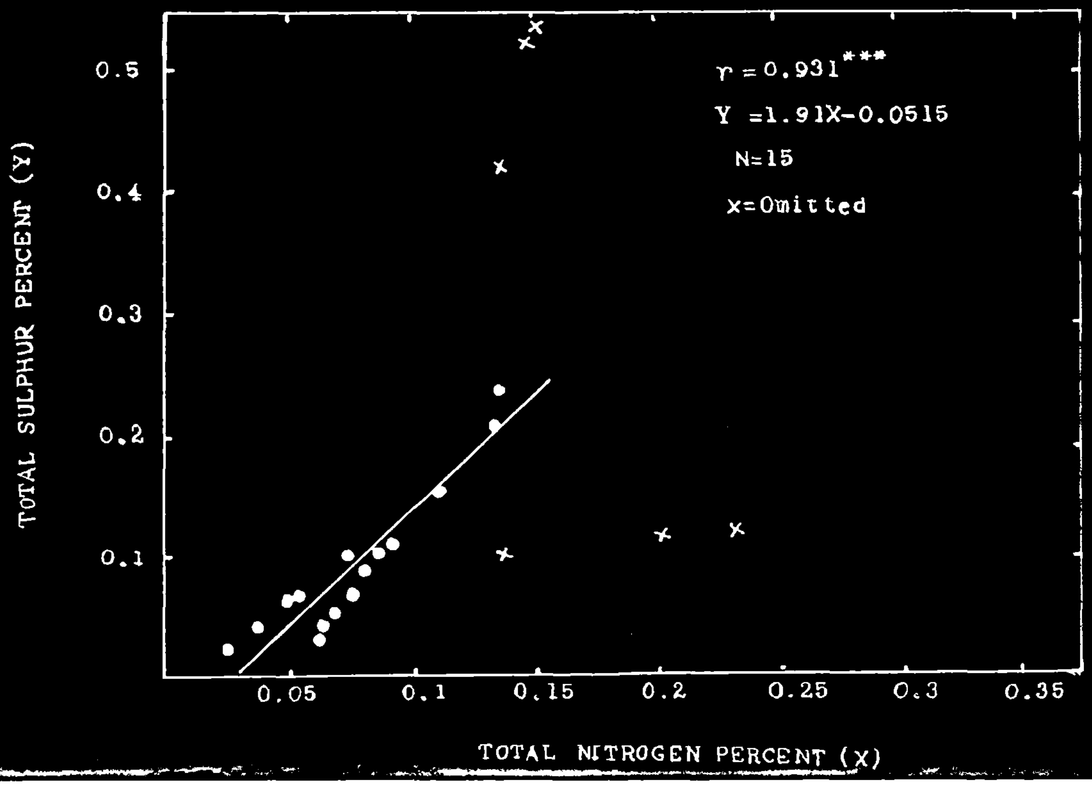

FIG.4 ORGANIC CARBON-TOTAL SULPHUR RELATIONSHIP

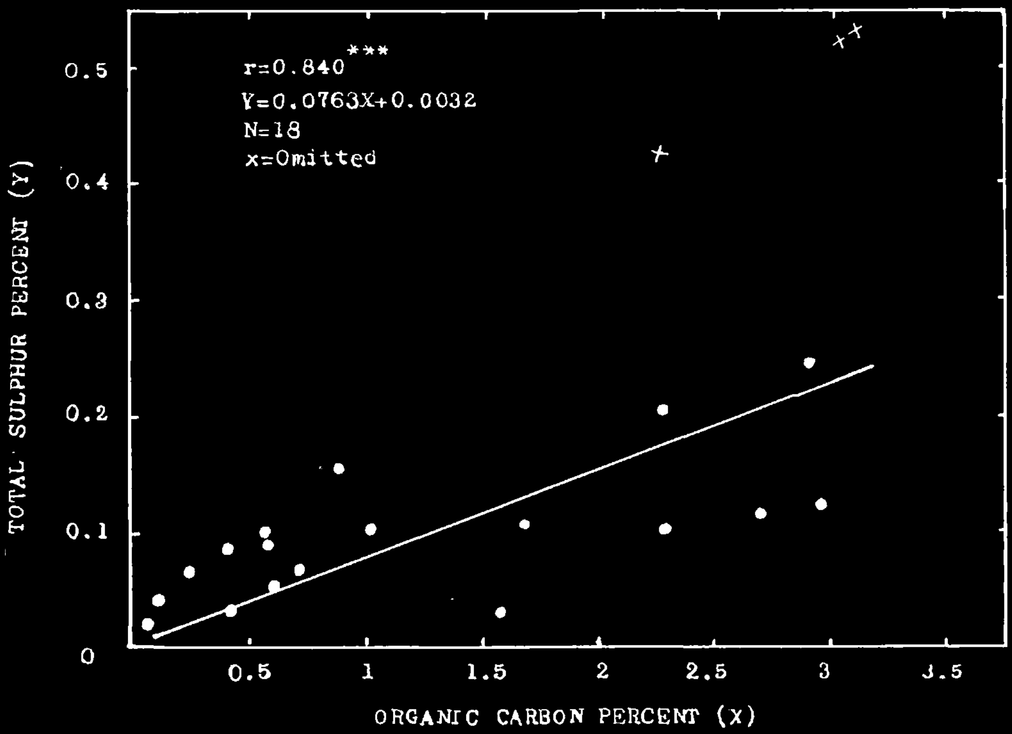

FIG.5 ORGANIC CARBON - ORGANIC SULPHUR RELATIONSHIP

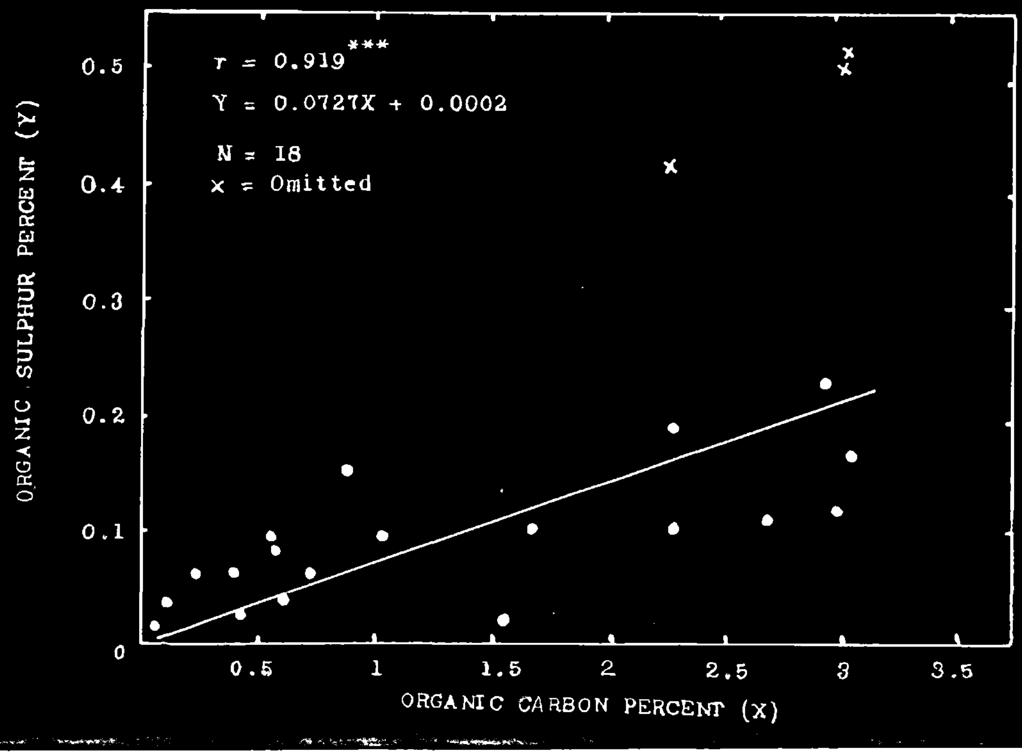

FIG.6. TOTAL SULPHUR - ORGANIC SULPHUR RELATIONSHIP

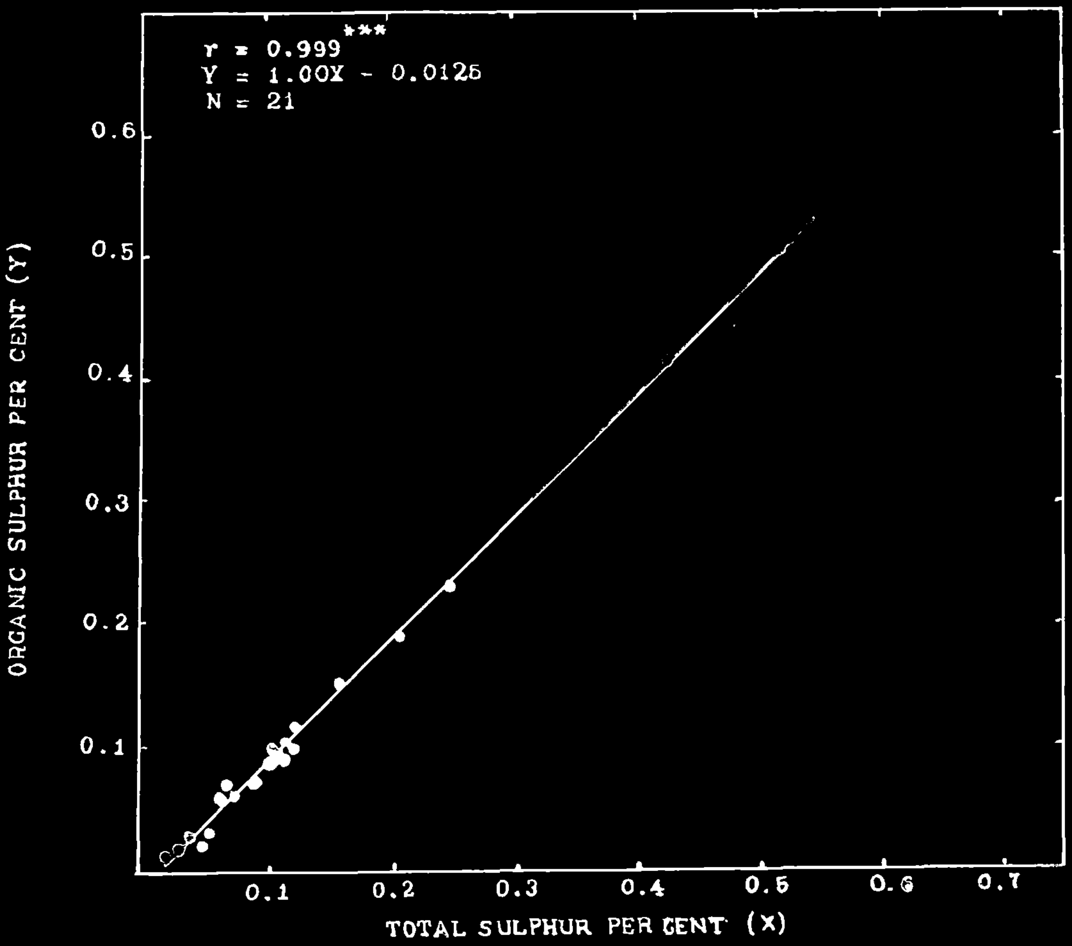

FIG.7. ORGANIC SULPHUR - HUMUS SULPHUR RELATIONSHIP

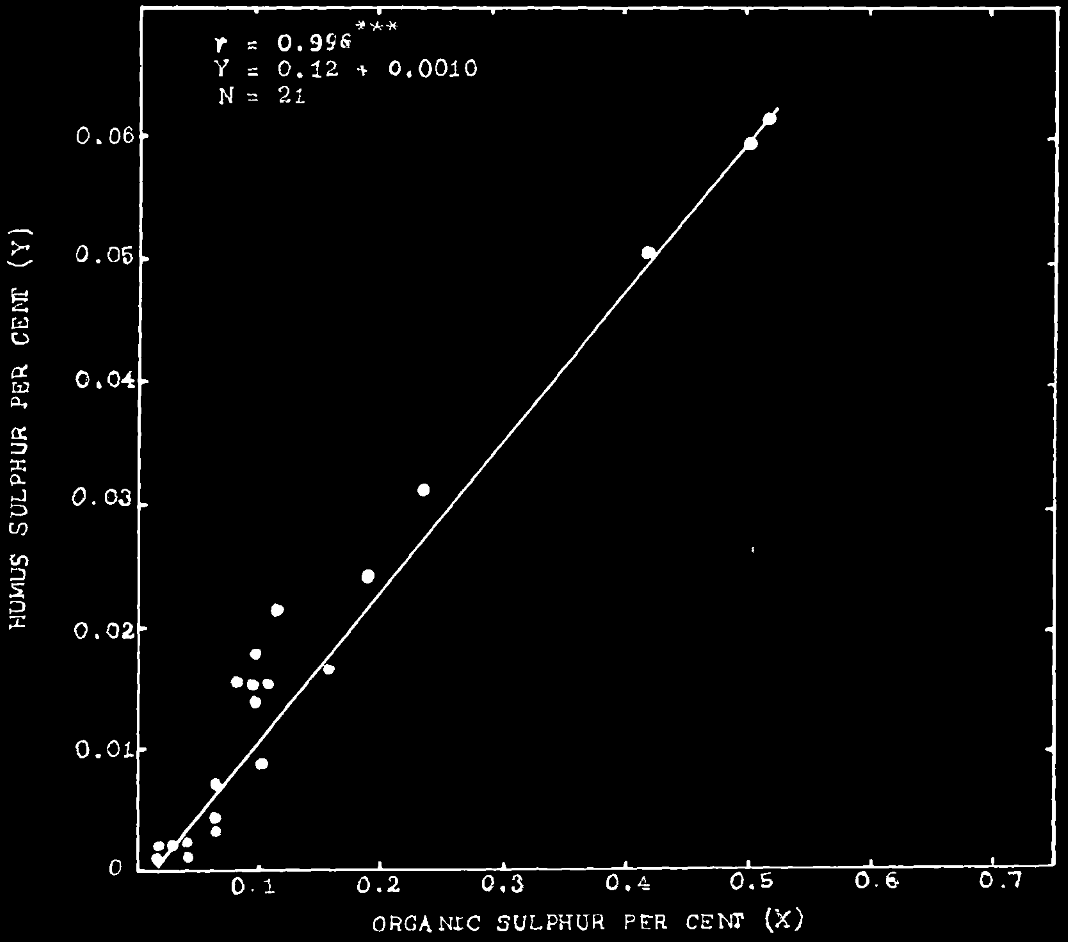

FIG.8. TOTAL SULPHUR - SULPHATE SULPHUR RELATIONSHIP

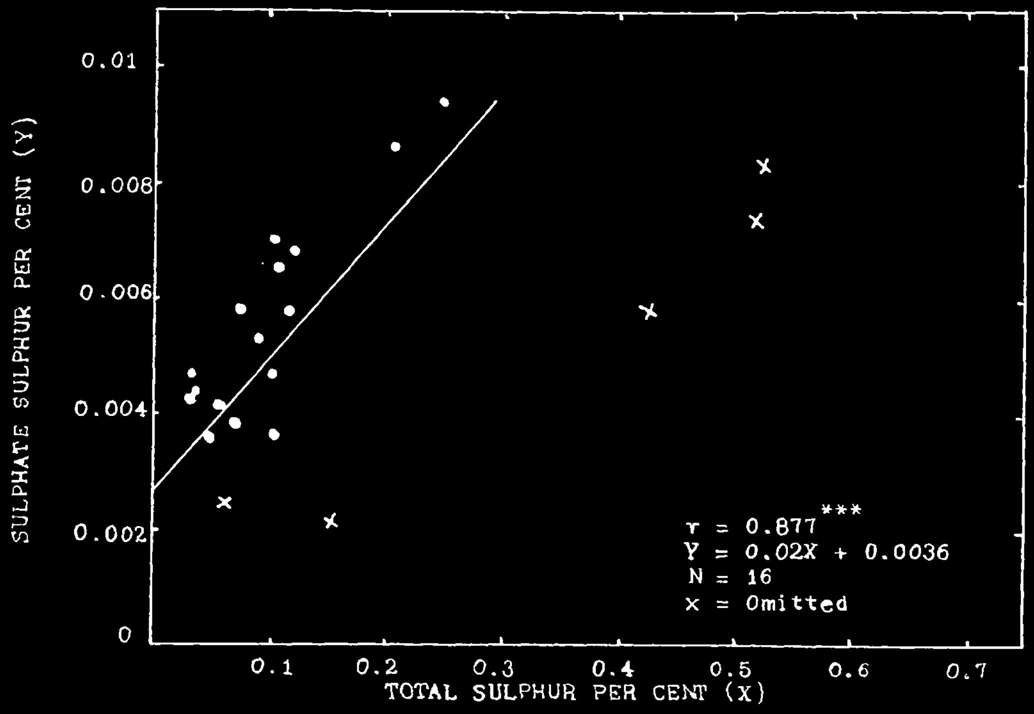

FIG.9. TOTAL SULPHUR - WATER SOLUBLE SULPHUR RELATIONSHIP

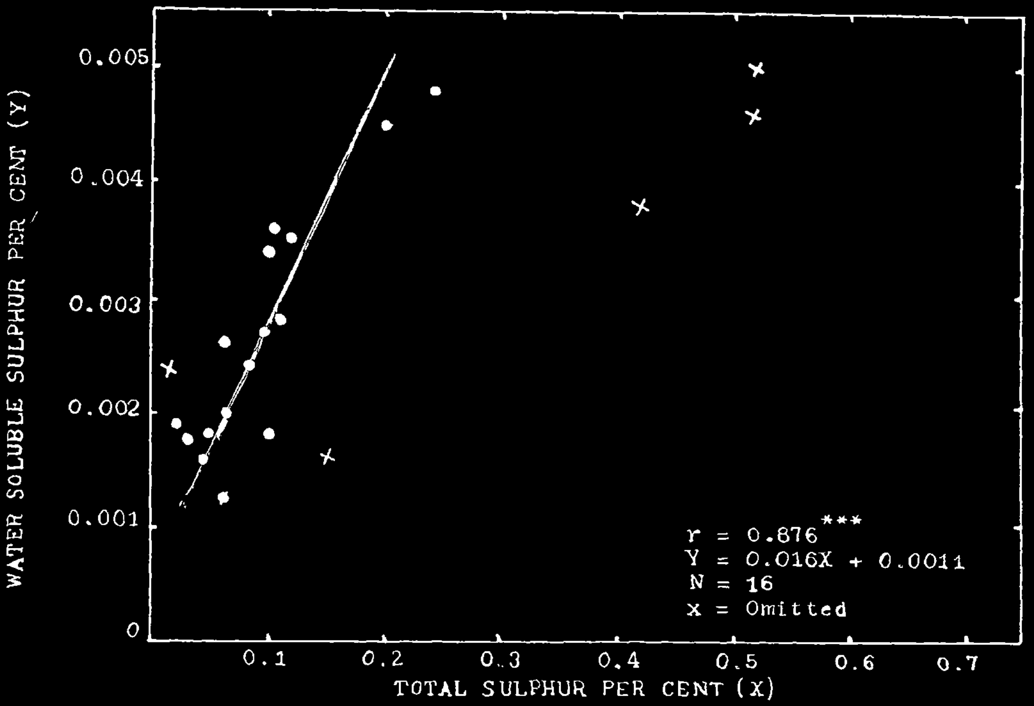

FIG.10. SULPHATE SULPHUR - WATER SOLUBLE SULPHUR RELATIONSHIP

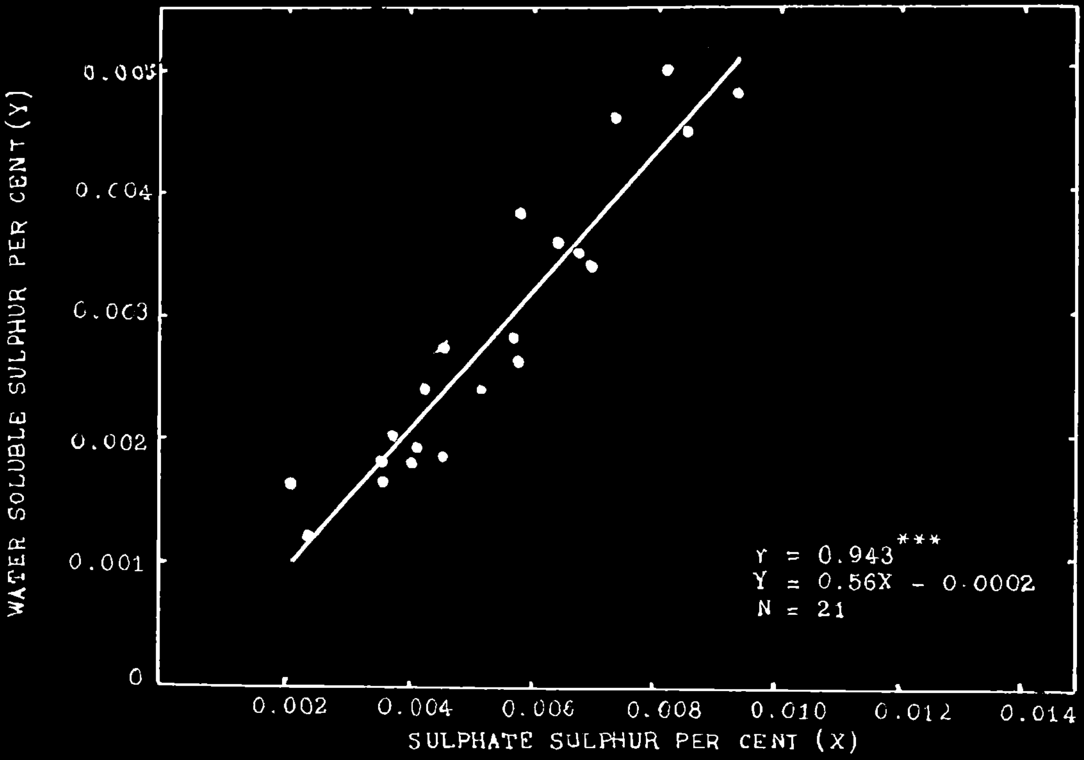

FIG.11. SULPHATE SULPHUR - NEUBAUER TEST VALUE FOR SULPHUR RELATIONSHIP

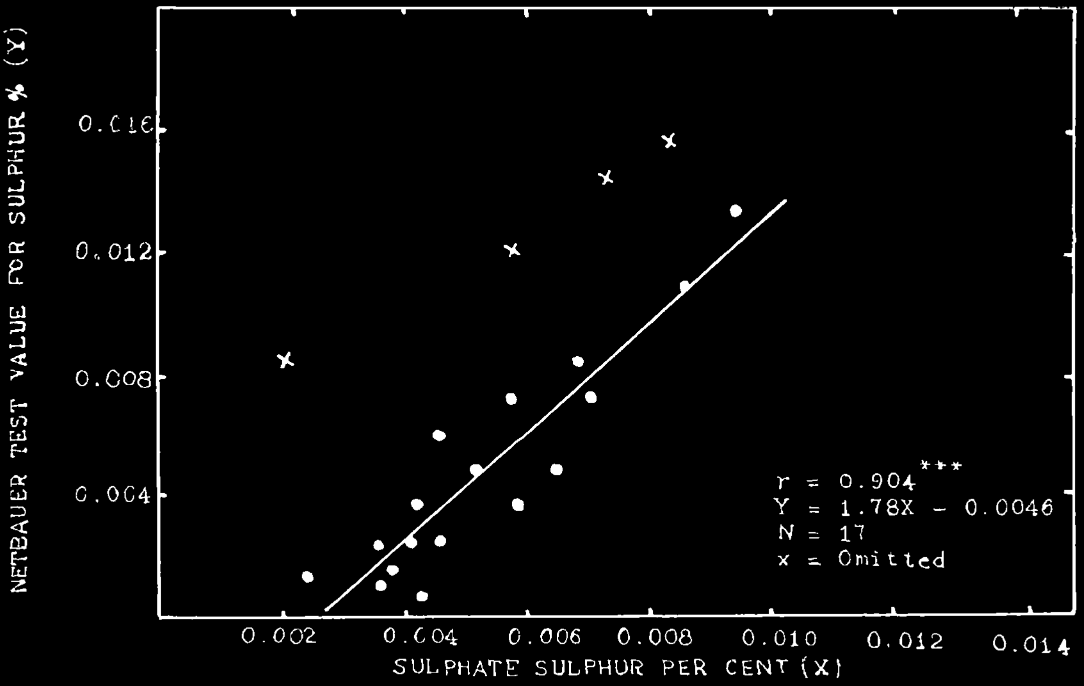

FIG. 12. MORGAN'S EXTRACTANT EXTRACTABLE SULPHUR–NEUBAUER TEST VALUE FOR SULPHUR RELATIONSHIP

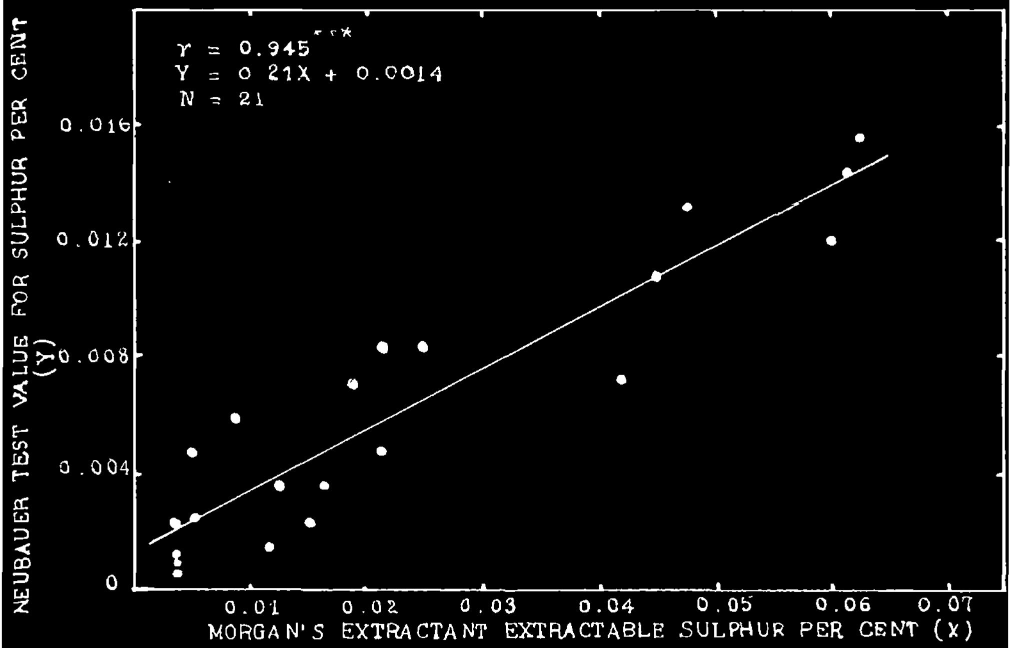

FIG. 13. MORGAN'S EXTRACTANT EXTRACTABLE SULPHUR–NEUTRAL AMMONIUM ACETATE EXTRACTABLE SULPHUR RELATIONSHIP

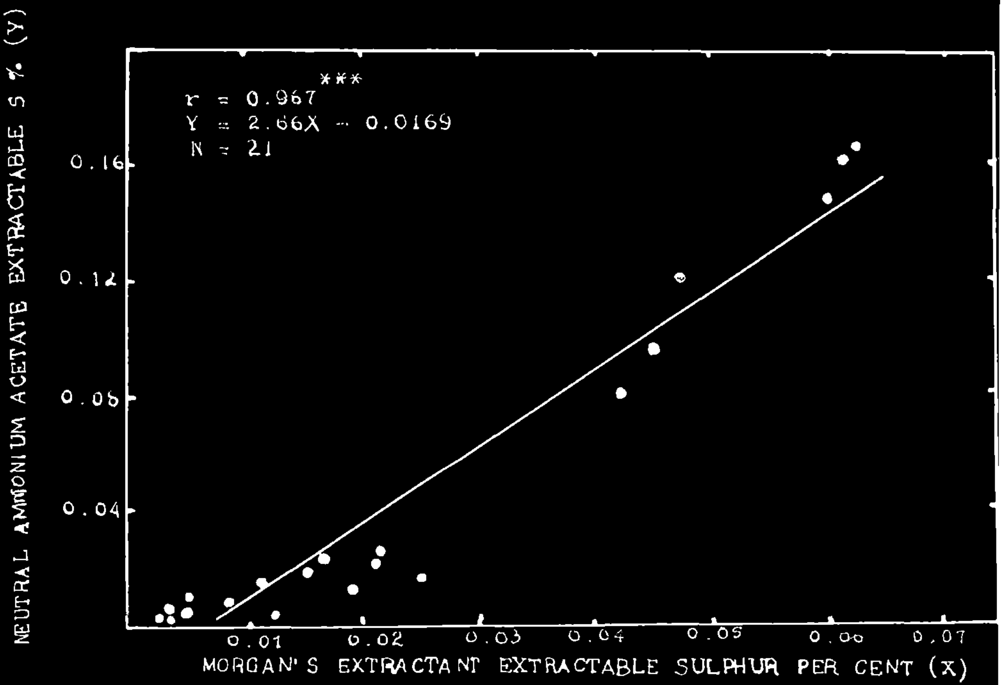

FIG. 14. TOTAL SULPHUR - HYDROCHLORIC ACID SOLUBLE SULPHUR RELATIONSHIP

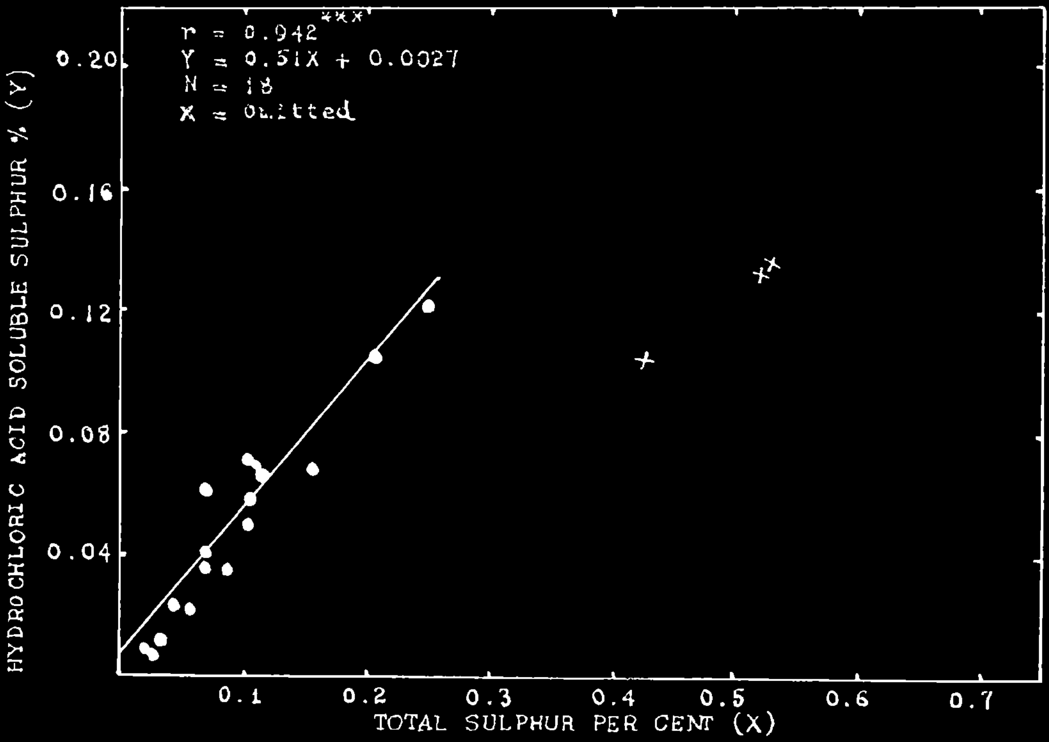

FIG. 15. MORGAN'S EXTRACTANT EXTRACTABLE SULPHUR - HYDROCHLORIC ACID SOLUBLE SULPHUR RELATIONSHIP

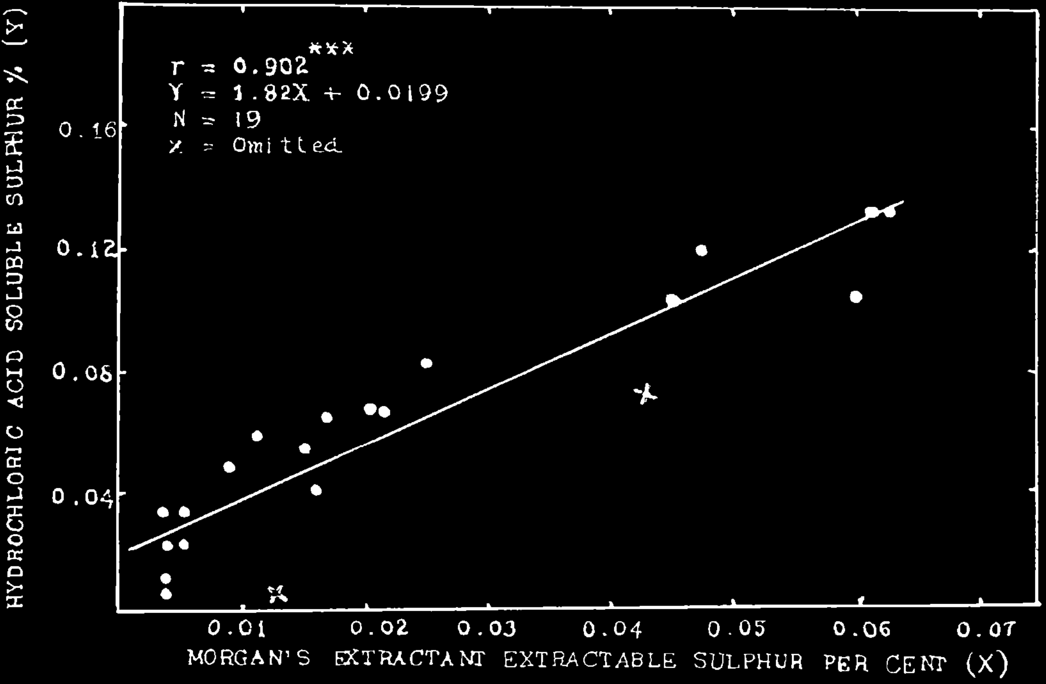

FIG. 16. HYDROCHLORIC ACID SOLUBLE SULPHUR – WATER SOLUBLE SULPHUR RELATIONSHIP

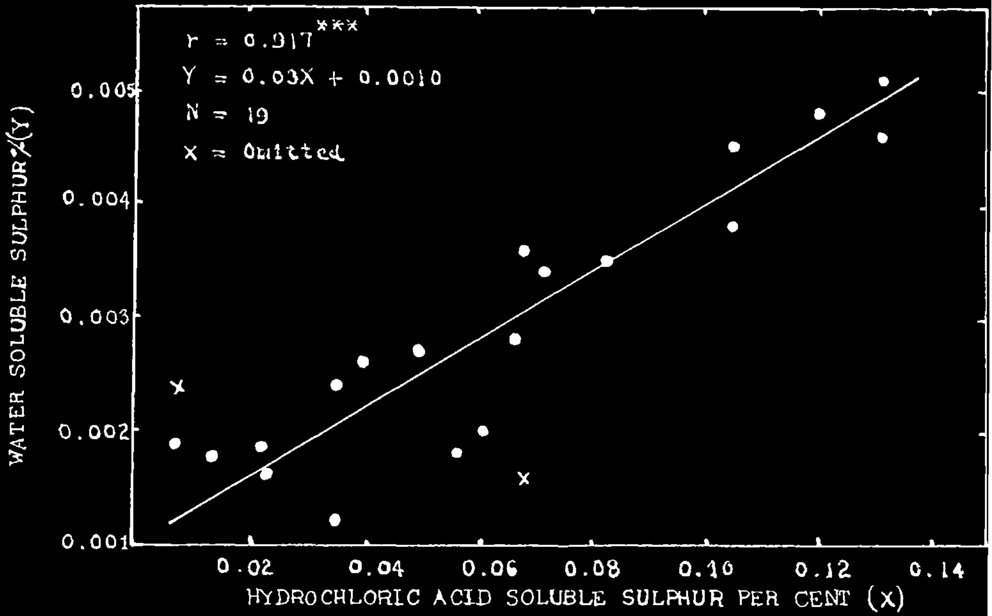

FIG. 17. HYDROCHLORIC ACID SOLUBLE SULPHUR – NEUBAUER TEST VALUE FOR SULPHUR RELATIONSHIP