FORMS AND DISTRIBUTION OF ORGANIC MATTER IN SOME FOREST SOILS OF WEST BENGAL

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This is to certify that the thesis entitled " Forms and distribution of Organic Matter in some Forest Soils of West Bengal" submitted to the Bidhan Chandra Krishi Viswavidyalaya for the Degree of Doctor of Philosophy in Agriculture (Agricultural Chemistry and Soil Science) embodies a piece of bonafide research work carried out by Sri Purna Chandra Bishayee under our supervision and guidance and no part of the thesis has been submitted for any other diploma or degree. It is further certified that any help or source of information availed of in this connection has duly been acknowledged.

(S.K.Banerjee) (N.C.Debnath)

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Purna Chandra Bishayee
(Purna Chandra Bishayee).

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CHAPTER - I

INTRODUCTION

The term forest derived from the latin root 'foris' meaning out of door is a large uncultivated tract of lands covered with trees and under wood. Forest controls agroclimatic conditions like flood, drought, erosion etc and also checks air pollutions and maintains the oxygen level of the environment. Plant species have a great effect on the physical and physico-chemical properties of soil through roots and leaves (litter, humus and organic matter). The effect varies from plant to plant and also from species to species of the vegetations.

In the forest land organic matter derived from leaf fall and decomposition of root has a role on the pedogenic process of the soils. Although the different vegetations contain the same group of substances, their amounts are extremely variable and as the rate of decomposition of the individual component is not the same, the nature and composition of the humus substances produced from them vary and as a result the effect of organic matter derived from different types of vegetations has differential effect on soil formation and horizon development. Impact of organic matter on soil development and horizon differentiation becomes more effective when the movement of organic constituents takes place with sesquioxide constituents. The downward movements i.e., leaching of humus depend upon the types of vegetation, soil and topography of land. So the quantity and nature of humus in different horizons in a particular profile is a product of type of vegetation, soil, topography and climatic conditions.

In India forest covers 74,5890 sq.kms. out of the total geographical area of 32,80480 sq.kms.(i.e.,22.74% of the total geographical area). West Bengal, with a geographical area of 87,850 sq.kms.,has nearly 11,837 sq.kms.of forest area,which constitutes about 13.5% of the total geographical area of the state (Anonymous, 1977), and displays extreme variation in physiography, soil characteristics and types of vegetations. As because the nature of vegetation plays an important role in characterising the soil organic matter the present investigation was undertaken to study the forms and distribution of organic matter in some forest soils of West Bengal under different types of vegetations.

CHAPTER - II

REVIEW OF LITERATURE

2.1 Soil Humus and its formation

Soil organic matter and in particular, the soil humus is nodoubt one of the most complex materials existing in nature. Its composition has exercised the minds of chemists from the very begining, but inspite of the prolonged and painstaking research, the task of identifying and characterising all of the components present in soil organic matter is formidable.

Hunus formation can be regarded as a case of arrested or interrupted decomposition in which partially metabolised aromatic residues from the parent vegetation and newly synthesised microbial products undergo free radical polymerisation reaction to produce either yellow or brown to black coloured acidic, polydispersed substance of biologically inert-high molecular weight compounds. Humus is essentially a mixture of several groups of chemical complexes of individual characteristic properties. The existing knowledge about the composition of humic substances supports the view that reactions between phenols derived from lignin or synthesised by microorganisms and nitrogeneous compounds derived from proteins are important in the formation of these substances.

The theory that humic acids are formed by condensation of phenolic and nitrogeneous compounds has developed from (i) the isolation of different phenolic compounds from the degradation of humic acids (Flaig and Beutelspacher, 1951, 1954; Flaig and Breyhan, 1956; Haider and Martin, 1967; Khan and Schnitzer, 1971; Riffaldi and Schnitzer, 1973; Chakrabarty *et al.*, 1974; Schnitzer, 1977) and (ii) experiments imitating the synthesis of humic acids under artificially imposed physiological conditions performed in test tubes or in cultures of microorganisms (Martin and Haider, 1969; Grabbe and Haider, 1971; Bondietti *et al.*, 1972; Martin *et al.*, 1972).

Among the identified phenols that are formed either by oxidative or reductive cleavage of humic acids, or isolated from soils or synthesised by microorganisms, there are two types of phenolic compounds, that are of interest in studies of the structure and, therefore, also of the chemical and physical properties of humic acids. Phenols have been found possessing either two or several hydroxyl groups in *ortho* position or two or three hydroxyl groups in *meta* position. Both types of compounds differ widely in their reactivity. The differences in reactivity are important with regard to the function of nitrogen in the molecules of humic acids.

Phenols of mainly resorcinol and phloroglucinol type that are synthesised by microorganisms, contribute to the composition of humic acids. These substances are altered by transformation to phenols that can be oxidised to quinones and by reactions with nitrogenous compounds or oxidative coupling with quinones.

The formation of phenols from lignins occurs mainly by microbial degradation in which the cleavage of the aromatic ring plays an important role and the structure of the lignin molecule is disrupted. Large or small degradation products are formed which contribute to the composition of humic substances by reaction with nitrogeneous compounds in all phases of the degradation. In the course of the above mentioned reactions the heterocyclic compounds contributing to the colour of humic substances, are also formed.

Thus the humification process of plant and animal residues as a whole can be explained only by considering the activity of the various representatives of the microflora possessing differential enzymatic fermentation mechanisms.

2.2 State of Humus in the soil

The formation and nature of humus are influenced by the nature of organic residues of vegetation and animal origin. In evergreen forests, the largely organic surface layer are usually not mixed with inorganic soil layers, the former are referred to as " raw humus " or " duff ". In deciduous forests, the organic residues and their decomposition products are well mixed with inorganic part of the soil giving rise to a type of humus known as " Mull " . In forest area 3 types of humus layer are found, (i) Litter (L), (ii) Fermentation (F), (iii) Humus (H). Beside these **there** is a mineral humus horizon (A_h) in which organic as well as mineral constituents or even organic substance as pigment of the mineral, are present.

According to a new proposal of Babel (1971,1972), these horizons can be subdivided further into L_n (n:new), L_v (V:Garman "verandert" analogous C_v); F_r (r:plant residue),F_m (m:medium ratio plant residue:fine substance),H_r (r:plant residue), H_f (f:fine substance), A_{hh} (hh:rich in humus), A_{hu} (part of A_h under A_{hh}). These horizons were defined by their plant residue/fine substance ratio (except for L_n with L_v and the A_h horizons). The sequence of L,F,H and A_h horizon is not developed in all humus profiles. Any of these four horizons may be missing.

The organic matter content of soils may range from less than 0.1% in desert soils to as high as 20% in prairie soil. It may be even higher in peat bogs, say upto 50-80% to close to 100% in organic soils. Light textured soil usually contain less humus than heavy textured soils. Only a small part of the humus substances in the soil is in a free state, a large part is variously linked to the mineral part of the soil through complex or chelate formation. Khanna and Stevenson (1962) and Whitehead and Tinsley (1964) reported that some of it is bound to the clay through polyvalent cations, such as Ca or Al, on the humus. Some is bound to positively charged surface of Fe and Al hydrated oxides, either through electrostatic bonding or by specific anion absorption and some is held on clay surfaces through hydrogen bonding or by vander-Wall forces.

2.3 Distribution of organic matter in soil

The organic matter content of a soil increases with the rate at which plant residues are added to the soil. Forest soils have the bulk of their organic matter close to the soil surface. Prairie soils, by contrast, have a considerable proportion of their organic matter in the deeper horizons for not only do they receive grass and other debris on the surface, but also many of the grasses produce a deep extensive root system which annually may add a greater weight of organic matter to the body of the soil than the leaves added to the surface. The humus, which the decomposition of these roots yield, is thus produced in the deeper layer of the soil.

The rate of decomposition of the organic matter depends on the soil aeration, calcium supply and temperature. The more favourable a soil is for animal life, by being well aerated and adequately supplied with calcium, the more rapid in general, is the decomposition. Poorly drained or very acid soils which can only carry a small animal population nearly always have a higher organic matter content in their surface layers than well-drained neutral soils. Higher temperatures also encourage higher rates of organic matter decomposition, the soil microorganisms being more vigorously active at high (optimum) temperature (Russel, 1961).

In a soil humus is not distributed evenly through the profile depth. It is largely concentrated in the upper 10-20" or the surface soil layer and decreases rapidly in the subsoil. In brown forest soil and in the red and yellow soils there is a rapid drop in the organic matter content below the upper 6". In prairie soil, chernozems and chestnut brown soils there is a gradual decrease of organic matter with depth. Podzolic soils have a zone at the junction of the surface litter layer and mineral soil layer, very rich in humic material. A well marked humus podzol may also have an accumulation of humus matter in the B_1 horizon. Hence the total organic matter may be up to 5 to 6 per cent by weight and 75 - 80 per cent of this can be extracted as humic acid.

The total amount of humus and its composition change the soil chemical properties. Cernescu and Cicotti (1964) showed that the humic/fulvic acid ratio in humus depends on the soil pH and increases with an increase of the degree of soil saturation by bases. The higher percentage of humus in soils under forest plantations was determined by several investigators (Tumin, 1930; Usov, 1938; Baiko and Gobulenko, 1949; Glotova, 1950,1952; Zonn and Sokolar,1960). In the soils of the forest regions approximately 50 per cent of the total humus content of the 0 - 100 cm layer is concentrated in the 20 cm, below 20 cm, the humus content decreases rapidly (Kononova, 1966).

2.4 Extraction, fractionation and purification of humus of soil

2.4.1 Extraction of humus

Although the classical method of extracting soil organic matter with dilute aquous NaOH (eigher 0.1 N or 0.5 N) still remins quantitatively the most efficient amongst the available methods, there is evidence that the materials extracted may have undergone considerable modification in the process by aerial oxidation and hydrolysis. But Welte (1952) showed that humic acid extracted with 0.5 per cent NaOH solution had similar light absorbance characteristics as the same humic acid extracted with 1 per cent NaF solution. Smith and Lorimer (1964) reported that humic acids extracted with dilute $Na_4P_2O_7$ from peat soils resembled in all respects the humic acids extracted with dilute NaOH solution.

The concentration of NaOH solution affects the yield of the humic material extracted as well as its ash content (Schnitzer, 1978). Levesque et al. (1966) and Ponomareva and Plotnikova (1968) found 0.1(N) NaOH to be more efficient extractant than higher NaOH concentrations. However, the most suitable extractant for isolating humic material low in ash was either 0.4(N) or 0.5(N)NaOH solution (Levesque et al.,1966).

Extraction of organic matter by neutral solution is generally slight but Simon (1929) found NaF to be an efficient extractant. Subsequently, Bremner and Lees (1949) showed that neutral solutions of anions which precipitated or formed chelates or coordination complexes with calcium and trivalent metal cations which prevented the ready deflocculation of much of the organic matter in soils were very efficient in the extraction of humus. Bremner and Lees (1949) suggested the use of 0.1 M Na-pyrophosphate solution of pH 7 as the most efficients extractant. Goh and Williams (1979) opined that for studing a large number of soil samples reasonable information on pedogenic changes of soil organic matter may be obtained by using only the pyrophosphate extracts. According to Aleksandrova (1960) $Na_4P_2O_7$ solution extracts not only humic substances but also organo-mineral complexes without destroying non-silicate forms of sesquioxides. Kononova (1966) suggested that the efficiency of extraction by $Na_4P_2O_7$ could be improved by raising the pH from 7.0 to 9.0.

Several attempts were made to extract the organic matter by using chelating resins (Levesque and Schnitzer, 1967; Dormarr, 1972), and organic solvents (Martin and Reeve, 1957; Parson and Tinsley, 1960; Hayes <u>et al</u>.,1975) but the extraction was poor. Another technique that has been used by a number of worker is ultrasonic dispersion (Anderson <u>et al</u>., 1974; Watson and Parson,,1974).

2.4.2 Fractionation of humus

Mineral acids are generally used for the separation of fulvic acid and humic acid fractions in the soil extract. The humic acid being soluble in alkali and insoluble in acid is precipitated upon the addition of acid, while the fulvic acid being soluble both in alkali and acid remains in solution. The fraction not extracted from soil and insoluble in acid and alkali is called humin. Some workers further subdivided humic acids by adding of salt to give gray and brown humic acids or by extraction of alcohol soluble hymatomelanic acids. The same nomenclature is used for the three main fractions even when the extraction is carried out using neutral salts, complexing agents or organic solvents in place of the traditional alkali. The fractionation scheme is depicted as follows:

Humic substances
fractionation on the basis
of solubility

Soluble in acid Soluble in alkali	Insoluble in acid Soluble in alkali	Insoluble in acid Insoluble in alkali
Fulvic acid	Humic acid	Humin

←—— Decreasing molecular weight ——

←—— Decreasing carbon content ——

←—— Decreasing nitrogen content ——

←—— Decreasing resemblance to lignin ——

←—— Increasing oxygen content ——

←—— Increasing acidity and C.E.C. ——

Many investigator have used paper electrophoresis (Coulson et al., 1959; Singh and Singh, 1960) for the separation of humus substances. They observed several fluorescent areas on paper chromatograms. Kononova and Belchikova (1960) used the circular partition paper chromatography for comparing humus substances from various soils.

Humus substances may also be fractionated on activated charcoal column (Forsyth, 1947) and on starch column (Kononova et al., 1958).

In recent years, gel filtration has been widely used for the fractionation of soil humic material (Ferrari et al., 1963; Ferrari et al., 1967; Swift and Posner, 1971; Goh and Raid, 1975; Goh and Williams, 1979). It is a simple, relatively inexpensive and very effective technique for studying polymers. It can be used for the separation, purification and fractionation as well as for the determination of molecular weight distribution.

2.4.3 Purification of humus

Humic acid extracts from mineral soils are generally contaminated with silicates i.e., clay, sesquioxides and salts etc. Silicates can be removed efieciently with dilute solutions of HCl-HF. The solutions is then neutralised and dialysed. Dubach and Mehta (1963) have reviewed how preparations with very low ash contents can be obtained by repeated solutions - centrifugation - precipitation techniques, or by treatment with complexing agents and ion exchange resins. Most of the non-polymeric organic materials as well as salts are removed during dialysis. Fulvic acids are radily purified by passage over Amberlite IR-120 or Dowex-50 exchange resins in H-forms (Schnitzer and Skinner, 1968).

2.5 Chemical properties

2.5.1 Elementary analysis

Humus is not a single substance and does not possess a definite composition. The composition of humic substances depends naturally on the soil from which it was extracted and the method of extraction, purification and fractionation followed.

Humic substances are built up of carbon (C), oxygen (O), hydrogen (H), nitrogen (N), sulphur (S) and phosphorus (P), no other element forms an integral part of humic substances (Russell, 1961). Carbon and hydrogen content of the fulvic acids are always lower than that of humic acids. Whereas, oxygen contain of fulvic acids is higher but hydrogen contain remain more or less same in both the cases (Kononova, 1966 ; Singh and Ganghwar, 1971; Riffaldi and Schnitzer, 1973). For some Russian soils Kononova (1966) found mean carbon,oxygen, hydrogen and nitrogen contents of 61.0, 31.0, 3.7 and 4.1 per cent for the humic acid and 46.0, 48.0, 3.5 and 2.4 per cent for the fulvic acid. Schnitzer (1977) estimated the elemental composition of humic and fulvic acids extracted from soils formed under widely differing geographic and pedologic conditions such as those prevailing in the Arctic, the cool temperate subtropical and tropical climatic zones. The carbon content of humic acids ranges from 53.8 to 58.7%, the oxygen content from 32.8 to 38.3%, percentages of hydrogen and nitrogen vary from 3.2 to 6.2% and 0.8 to 4.3% respectively. The sulphur content ranges from 0.1 to 1.5%. The carbon content of fulvic acids ranges from 40.7 to 50.6% that of oxygen from 39.7 to 49.8%, nitrogen from 0.9 to 3.3% and hydrogen from 3.8 to 7.0%.

With increasing molecular weight of the substances, the carbon content increases generally. The change in elementary composition can be explained on the basis of the decreasing number of oxygen containing groups (e.g. -COOH) with increasing molecular weight. Gillam (1940) found no essential differences between the elementary composition of humic acids isolated from forest soil, meadow soil and manured soil. Tishenks and Rydalevskaya (1936), however, were able to show regular changes in the elementary composition of humic acids, reflecting the natural conditions under which the humus was formed in a series of soil ranging from podzolic to chernozems and further, to chestnut soils. The C/H ratio has been taken as a measure of either the degree of condensation of aromatic rings or the state of oxidation (Kononova,1966; Schnitzer and Khan, 1972; Flaig et al., 1975).

Based on C/H ratio, the Russian Scientist Kononova (1966) concludes that there is an increasing degree of aromatization of humic acids in a series of podzolic soil to chernogem and a decrease in the degree of aromatization in chestnut soil to serozem. The humic/fulvic acid ratio also varies from soil to soil. The variation is mainly due to the presence of different type of vegetation, different moisture and climatic conditions and different parent material. Kumada and Matsui (1970) estimated the amount of aromatic carbon in humic acids by permanganate oxidation method, according to him it increases in the order :

$$A - \text{type} > B - \text{type} = P - \text{type} > R_p - \text{type}.$$

2.5.2 Functional groups of humus

Humic acids comprise both colloidal and true acids containing functional groups such as carboxyl, hydroxyl (both - phenolic and alcoholic), free amino and imino groups and methoxyl groups. Fulvic acids having structural units similar to those in humic acids, may be considered the least mature representatives of the humic acid groups (Kononova,1966).

2.5.2.1 Methods of determining Oxygen containing functional groups

The numbers and the types of oxygen-containing functional groups greatly influence the reactivities of humic substances in the soil environment. The principal active groups are carboxyl and phenolic hydroxyls, which give the colloids acidic properties, and ketone and aliphatic hydroxyls.

In practice, to determine, the total acidity an excess of $Ba(OH)_2$ is reacted with the humic materials and unreacted base is back-titrated with standard acids. It is assumed that all of the exchangeable hydrogen ions are replaced by Ba^{+2}.

However, Schnitzer and Gupta (1965) found that some substituted phenols did not quantitatively replace acidic hydrogen with barium ions. Total acidity determination can also be possible directly by titration of H^+-humic materials with strong base. It is necessary to carryout titrations to higher pH values in order to estimate the total acidity of the sample being investigated. The total acidity and specially the -COOH content of fulvic acids are considerably higher than those of humic acids.

Carboxyl groups are the major contributors to the acidic properties of humic substances. The amounts of carboxyl present in humic substances are generally determined by the calcium acetate method, described by Schnitzer and Gupta (1965) in which the acid released by calcium acetate is measured by titration.

The carboxyl contents of humic substances can be estimated by determining the increases in nitrogen content of humate derivatives formed by reactions with hydroxylamine phenyl hydrazine or 2,4 di-nitrophenyl hydrazine (Flaig et al., 1955; Schnitzer and Skinner, 1965). The carboxyl content can be estimated from the amount of unreacted reagent which can be measured from the polarographic reduction of nitrogen (Schnitzer and Skinner, 1966).

2.5.2.2 Methods of determining Nitrogen containing functional groups

The forms and distributions of nitrogen in soil environment have been reviewed by Bremner (1967). Acid hydrolysis of soil organic matter releases between 20 and 50 percent of the soil nitrogen as amino acids and over 30 different amino acids have been identified though only 14 are usually present in appreciable amount (Bremner, 1967). 5-10% of nitrogen is held as amino sugars. An appreciable part of the nitrogen in soil organic matter is released as ammonium on acid hydrolysis. This is often called amide nitrogen because many amides released ammonium on acid hydrolysis (Stevenson and Goh, 1971). A considerable percentage of the total nitrogen in humic materials is neither protein like nor amino sugars nor ammonia. This unknown nitrogen is not released by acid and base hydrolysis. It has commonly been assumed that much of the unhydrolysable nitrogen is present in heterocyclic rings or binds heterocyclic or aromatic rings together.

2.5.3 Ion Exchange properties

The major oxygen containing functional groups in humic substances are carboxyls, hydroxyls and carbonyls. The proportion of these groups varies depending upon the degree of humification of the carbonaceous materials. The total acidity equals to sum of -COOH and phenolic -OH groups. The acidity specially the -COOH content of fulvic acids are considerably higher than those of humic acids (Dutta and Mukherjee, 1968; Banerjee and Mukherjee, 1971, 1975; Banerjee *et al*., 1979; Chakrabarty *et al*., 1980; Mukhopadhyay *et al*., 1982).

Potentiometric (Chatterjee and Bose, 1952 ; Pommer and Breger, 1960; Wright and Schnitzer, 1960, Schnitzer and Desjardins, 1962; Posner, 1964; Dutta and Mukherjee, 1968; Banerjee and Mukherjee, 1971, 1975; Banerjee, 1974; Banerjee *et al*., 1979; Bishayee *et al*., 1981; Mukhopadhyay *et al*.,1982) and conductometric (Dutta and Mukherjee, 1968; Gamble, 1970; Banerjee and Mukherjee, 1971, 1975; Bishayee *et al*., 1981) titrations have been employed for the determination of acidic functional groups in humic substances. Potentiometric titration curves are usually sigmoidal suggesting an appearent monobasic character. Multiple inflexious in the potentiometric titration curves have been reported by Chatterjee and Bose (1952), Marshall and Patnaik (1953), Banerjee and Mukherjee (1971) and Banerjee *et al*. (1979). Their appearence and distinctness vary with the nature of the base used.

Zadmard (1939), found that HA titrated with alkali hydroxides showed a much more rapid rise in pH in the titration curves than in the case with alkaline earth hydroxide. The base exchange capacity calculated at pH 7.0 was found to be in the order :

$$Ba(OH)_2 > Ca(OH)_2 > KOH > LiOH > NaOH$$

Khanna and Stevenson (1962) have reported the apparent pK_{av} values for the pyrophosphate and alkali extracted humic acid as 4.5 and 4.8 respectively, while the average value reported by Martin and Reeve (1968) for Al free organic matter from some podzol B horizons is 3.9. Dawson et al. (1950) have reported a pK values of 5.2 for acid washed peat neutralised with lime. The calculated pK_{av} values for the titration curves published by Puri and Sarup (1938), Gillam (1940), Marshall and Patnaik (1953) range from 5.4 to 6.1 whereas the reported value of Merck's humic acid varies from 6.8 to 7.0. The variation of the titration curves with changes in ionic strength (KCl) has recently been studied by Posner (1964). The shape of titration curves conforms to a Gaussian distribution of acid pK values with a deviation of 1.7 units about a mean (pK_o).

Conductometric and specially high frequency titration in non aquous media have been carried out by van Dijk (1960). Which enable one to distinguish clearly and determine exactly carboxyl and phenolic hydroxyl acidities from the maxima and minima in the titration curves. Gamble (1970) assumed that fulvic acids have two types of -COOH groups : type-I which is ortho to phenolic hydroxyl group, and type-II which is not adjacent to phenolic hydroxyl group. Banerjee (1974) observed that the minima in the conductometric titration curves of humic acids disappeared when the acid was hydrolysed with 6(N) hydrochloric acid. From this he concluded that the initial lowering may be due to -COOH groups of amino acids present in humic acid moiety.

Schnitzer (1977) extimated the different acidic functional groups of humic and fulvic acids extracted from widely differing soils. More systematic and careful study on the humic and fulvic acids of different soils under different vegetation will throw light on the degree of humifications of organic residues.

Singh and Ganhgwar (1971) reported that low land humic acid was more humified than upland humic acid. They concluded that topography and drainage were important in the humification process.

2.5.4 Complex formation with clay and metal

Certain aspects of the interactions between humic substances and metal ions are well documented (Beckwith, 1955; Khanna and Stevenson, 1962; Schnitzer and Skinner, 1963, 1965; Banerjee and Mukherjee, 1972a, 1972b). The interactions have been described variously as ion exchange, salt formation, complexation, surface absorption, chelation, coagulation and peptisation through -COOH, -OH and amide functional groups (Mortensen, 1963). The magnitude of pH drop on the addition metal ions to aquous solutions of humic and fulvic acids may be taken as an indicator of complex formation. Beckwith (1955) concluded that metals of the first transition series formed complexes with humic substances and the order of stabilities of different metal complexes followed that of the Irving - Williams series. The principal reaction between metals and humic substances involves both -COOH and phenolic -OH groups.

Joshi and Ghonsikar (1979) studied the infra-red characteristics of humus in soils of Rajasthan and found that fulvic acid was present in the form of salts as was evident from the preponderance of ionised COO^- groups.

Since humic and fulvic acids are heterogenious mixtures of substances varying in charge densities (Banerjee, 1971), molecular weights (Kononova, 1966; Orlov _et_ _al_., 1971; Cameron _et_ _al_., 1972; Goh and Raid, 1975; Schnitzer and Khan, 1972, 1978) and acidities (Butler and Ladd, 1969; Rashid,1971) the complex formation will be influenced by these properties. A better understanding of the chemistry of the complexes would provide us with useful information on the role of humic substances in soil-forming processes, soil structure formation, nutrient availability and specially micro and toxic elements and their mobilisation, transport in aquatic environment.

The ratio of humic and fulvic acids varied from 0.4 to 2.0 and their ability to form complexes with metal and clay varied widely depending upon the active functional groups available for each interactions. Similar variation were reported between cultivated and forested soils by Srivastava and Raman (1981).

2.5.5 Thermal Degradation

TG, DTG and DTA and isothermal heating have been used for investigating the mechanism of thermal decomposition of humic materials. Schnitzer and Hoffman (1964) heated a humic acid and a fulvic acid at constant rate under air from room temperature to 540°C; samples were withdrawn at regular intervals and analyzed by chemical and IR methods. The carbon content of the chars increased with temperature accompanied by a simultaneous decreased in oxygen. Chars of humic acid and fulvic acid heated to 540°C contained identical percentages of carbon and hydrogen but no oxygen. Phenolic -OH groups were more stable than $-CO_2H$ groups but both were degraded between 250° and 400°C. The two types of functional groups were more heat resistant in the fulvic acid than in humic acid. The main reactions governing the pyrolysis of humic acid are

(a) degradation (upto 200°C), (b) a combination of decarboxylation and dehydrogenation (between 200° and 250°C) and (c) further dehydrogenation (upto the highest temperature). The main reaction governing the pyrolysis of fulvic acid is dehydration.

According to Shurygina et al. (1971) DTA and TG data as well as infra-red spectra and analytical data for humus substances extracted from a chernozem and a podzolic soil showed that aromatic structures predominated in the humic acid fraction particularly those of the chernozems, and that aliphatic structures predominated in the fulvic acid fractions particularly those of the podzol in soil.

2.5.6 Coagulation Threshold

From the data at present available it has been established that the humic acid molecule consists of (a) an aromatic ring, (b) nitrogen containing compounds in cyclic forms and in the form of peripheral chains and (c) possible reducing substances. The aromatic part of humic acid molecule has hydrophobic properties, whereas the side chains contain groupings with hydrophilic properties. The predominence of one or the other part determines the hydrophilic nature of the humic acid as a whole. This supposition is confirmed by determining the coagulation threshold of humic acids which also characteris the nature and properties of this group of substances. Depending upon the behaviour of humus substances towards electrolytes ($CaCl_2$), Kononova (1966) observed that the degree of condensation of the aromatic ring of humic acid increased on passing from podzolic soils to chernozems. Banerjee and Mukherjee (1972) observed that the low molecular weight compound is more hydrophilic than their high molecular weight one. Therefore, fulvic acids are most stable towards electrolyties.

Vil'k (1962) found that humic acid containing narrow C/N ratio is more resistance to coagulation by $CaCl_2$ and has low optical density.

The behaviour of humic substances with respect to coagulation by electrolytes is of great importance in soil processes. The detailed and systematic study of the substances extracted from different types of soils towards electrolytes will help in determining the translocation of humus substances and their organomineral compounds in the soil profile, the formation of soil structure and also the intensity of the action of humic acids on the mineral constituents of the soil.

2.6 Physical and physico-chemical properties of humic matter and methods of their determination

Work done in the recent past on the physical and physico-chemical properties of the humic substances and methods of their determination have been reviewed in this section.

2.6.1 Molecular weight

A wide variety of methods have been used for measuring molecular weights of humic substances. Vapour pressure osmometry method is the most suitable methods for measuring number average ($\overline{M}_n$) molecular weights of water soluble humic substances. Flaig and Beutelspacher (1968) have used the ultracentrifuge to measure sedimentation and diffusion constants, molecular weight, radius and friction coefficient of humic acid at different pH levels in the absence and presence of NaCl. Posner and Creeth (1972) estimated weight average molecular weight of humic acids by equilibrium ultracentrifugation. Cameron and Posner (1974) determined the molecular weight distribution of four humic acids by density gradient ultracentrifugation. $\overline{M}_{n's}$ of humic acids range from 5,900 to 13,500, $\overline{M}_{w's}$ from 49,000 to 2,16,000 and $\overline{M}_{z's}$ from 3,00,000 to 11,00,000 .

There is a wide variation in the equivalent weights of different humic acids (Pommer and Breger, 1960; Schnitzer and Desjardins, 1962). Using the freezing point depression method, Schnitzer and Desjardins (1962) found the molecular weight of organic matter to be 1684 and 669 for podzol A_o and B_h horizons respectively, the equivalent weights being 165 for A_o and 76 for B_h. So the ratio of molecular weight to equivalent weight was 10 for organic matter from the A_0 horizon and 9 for the horizon B_h. These ratios were equal to the sum of carboxylic and phenolic groups.

Because viscometric measurement can provide important information about particle shapes and sizes, particle weights and polyelectrolytic behaviour of macromolecules, this method was applied to characterisation of humic acids by several authors whose contributions have been summarised by Flaig et al. (1975). Flaig and Beutelspacher (1954) investigated the viscometric properties of natural and synthetic humic acids and concluded that the particles were globular. Orlov and Gorshkova (1965) from viscosity measurement of soil humic acid reported that the particles were spherical while Piret et al. (1960) assumed strongly hydrated forming elongated elliptic molecules. Khan (1971) states that HA's consist of mixtures of spherical and linear particles; on the otherhand, Kumada and Kawamura (1968) conclude that viscometric measurements can not tell whether humic acid particles are spherical or linear, the only information that the literature contains a lot of contradictory information of humic acid characteristics that can be measured by viscometry.

Roy et al. (1973) from viscosity and diffusion studies of synthetic humic acids proposed a coiled confreguration in a medium of high ionic strength, which would reasonably be approximated by rigid spherical or ellipsoidal models. Kumada and Kawamura (1968) tried to find relationship between the types of humic acids determined by electronic spectra and viscometric properties. They investigated the pH dependent viscosity changes of humic acid of various origins. According to the differences in viscosity Kumada (1965) distinguished three groups of humic acids.

Molecular weight for humic substances determined from viscosity measurement can only be regarded as relative and not as absolute value because the materials used are highly polydisperse. The average molecular weight data from viscosity measurements on humic acids by Piret et al. (1960) and Visser (1964) were calculated from equations designed from synthetic polymers of known structures and conformations. Thus the values of 5×10^4 and 36×10^4 quoted by the authors were only regarded as order of magnitude because of the constraints implicit in the equation used. The values for synthetic humic acids are much lower (Roy et al., 1974).

2.6.2 Ultracentrifuge

Flaig and Beutelspacher (1968) used the ultracentrifugation technique to measure sedimentation and diffusion constants, molecular weight, radii and friction coefficients of a humic acid at different pH levels in the absence and presence of NaCl. When sedimentation and diffusion coefficients were measured in water, a mean molecular weight of 2050 was obtained. Addition of 0.2M NaCl suppressed the charge effects and the same humic material than gave the mean molecular weight of 77,000. Posner and Creeth (1972) using equilibrium ultracentrifugation technique obtained the $\overline{M}_n$ and $\overline{M}_w$ values for unfractionated humic acids and were able to estimate polydispersity from the $\overline{M}_n / \overline{M}_w$ ratio. Ultracentrifugation can also be used to determine molecular weight distribution by using a density gradient technique. In applying the technique Cameron and Posner (1974) used a D_2O / H_2O density gradient to determine $\overline{M}_n$, $\overline{M}_w$ and $\overline{M}_z$ values for a number of extracts. $\overline{M}_n$'s of the HA's ranged from 5,900 to 13,500, $\overline{M}_w$'s from 49,000 to $>$2,16,000 and $\overline{M}_z$ from 3,00,000 to$>$11,00,000 .

2.6.3 Osmometry

This is the only effective technique which can be used to determine the number average molecular weight of high polymer systems. By applying this technique to a solution of dialysed humic acid extract obtained from a podsol B horizon Wright et al. (1958) reported a mean molecular weight of 508000. Wake and Posner (1967) measured the molecular weight of humic acid fractionated by ultrafiltration. The values obtained varied from 2000 upto approximately 34,000 . Swift et al. (1970) using similar fractionation technique determined $\overline{M}_n$ values ranging from 1500 to 65,000 .

2.6.4 Sephadex gel filtration

Recently, sephadex gel filtration is being extensively used for the fractionation of humic substances into homogenious molecular weight fractions (Ferrari and Dell'Agnola, 1963; Raishid and King, 1969; Anderson and Hepburn, 1977; Banerjee and Sengupta, 1977). This is experimentally the simplest and most convenient method and for these reasons it has been widely used. Weight average molecular weight of the order of 300 to >2,00,000 have been reported for soil humic acids (Posner, 1963; Dubach et al., 1964; Bailly and Margulis, 1968). For HA's and FA's extracted from marine sediments $\bar{M}_{w's}$ ranging from 700 to 72,000,000 (Rashid and King, 1969; Rashid, 1971) and for humic substances extracted from natural waters $\bar{M}_{w's}$ ranging from <700 to >50,000 have been proposed (Gieseking, 1976).

2.6.5 X-ray

Attempts have been made to characterise humic acids by X-ray (Kasatochkin and Zilberbrand, 1965; Kasatochkin et al., 1964; Tokudome and Kanno, 1965; Kodama and Schnitzer, 1967) and electron microscopic (Flaig and Beutelspacher, 1951; Khan, 1971; Schnitzer and Kodama, 1975; Chen and Schnitzer, 1976) studies, but they have yielded very little useful information. Kasatochkin et al. (1964) concluded from X-ray studies that humic substances contain flat condensed aromatic net work to which side chains and functional groups are attached. Flaig and Beutelespacher (1951, 1954) from electron microscopic studies suggested that humic acids consist of tiny spherical particles capable of uniting into chains and forming recemose aggregates.

2.6.6 Electron Spin Resonance (ESR)

Steelink and Tollin (1967) outlined the principles and application of electron spin resonance for detecting and estimating stable free radicals in humic substances and discussed their roles in polymerisation-depolymerisation reactions, in reactions other organic molecules including pesticides and toxic pollutants. They concluded that a polymer containing ortho- and para- quinhydrones might account for some of the observed properties of its e.s.r. sepctra. ESR spectra of aquous HA and FA solutions usually consist of single line devoid of hyperfine splitting, with g-values ranging from 2.0031 to 2.0045, line widths from 2.0 to 3.6 G and free radical concentrations from 1.4 x 10^{17} to 37.4 x 10^{17} spin/g (Senesi and Schnitzer, 1977). Senesi and Schnitzer (1977) also investigated the effects of pH, reaction time chemical reduction and irradiation on the spectra of FA . Atherton <u>et al</u>. (1967) reported hyperfine splitting of ESR signals of HA's when these were dissolved in 0.1(N) NaOH.

Riffaldi and Schnitzer (1972a, 1972b) quoted free radical contents of the order of $10^{17} - 10^{18}$ spin/g of humic substances which decreased in the following order :

Humine $>$ Humic acid $>$ Fulvic acid

Hayes et al. (1975) found that the relative amounts of the radicals in humic and fulvic acids depended on the solvent used for extraction.

2.6.7 Electron Microscopy and Electron Diffraction

For observing shapes and sizes of HA and FA particles, electron microscope has been used by several workers (Flaig and Beutelspacher, 1951,1954; Visser, 1964; Khan,1971; Schnitzer and Kodama, 1975; Chen and Schnitzer, 1976). Flaig and Beutelspacher (1951, 1954) studied the morphological features of humic acids by electron microscope and showed that humic acids are tiny spherical particles capable of uniting into chains and of forming recemose aggregates, through hydrogen bonding at low pH. Electron micrographs of humic acids published by Khan (1971) showed a loose spongy structure with many internal spaces.

Schnitzer and Kodama (1975) examined fulvic acid under electron microscope and reported that the crystallinity, shapes, dimensions and extent of aggregations of the particles depended on pH.

Chen and Schnitzer (1976) used a scanning electron microscope to explore the effect of pH on the shape, size and degree of aggregation of humic and fulvic acid particles. There was a gradual transition from fibrous structure at low pH to a more sheet-like one at higher pH. Simultaneously, the particles become smaller as the pH increased.

2.6.8 Fluorescence

Humic substances when excited by light of proper frequency exhibit visible fluorescence and this property, has been used by a number of workers (Sowden and Parker, 1953; Coulson et al., 1959; Sowden and Deuel, 1961; Kononova, 1966; Banerjee and Mukherjee, 1972b) to study the different fractions of humus substances. More recently attempts have been made to obtain structural information from fluorescence excitation spectra of humic materials (Ghosh and Mukherjee, 1972; Ghosh and Schnitzer, 1980). These workers noted that humic substances, irrespective of their origin exhibited characteristic bands near 470 m /u which they attributed to the presence of aromatic fluorophores with electron donating functional groups. Fluorescence intensities decreased with decreasing pH and increasing ionic strength. This is due to decreasing ionization, increasing particle association, and to coiling of macromolecular structure. The fluorescence characteristics of FA and HA were obtained to be related to the free radical content, colour and phenolic structures. Muller-Wegener (1977) showed that maximum fluorescence of a model humic acid prepared by alkaline autooxidation of hydroquinone, of the methylated derivative of this model acid, and of a humic acid from a moor soil occurred at different acid concentrations. He showed that the effect of pH of fluorescence also varied with the acid. On a relative basis, fluorescence intensities of FA were always greater than those of HA. This suggests that not only do HA contain more absorbing centers but also the possible involvement of fluorophore groups in the cross linking of HA structure. Statistically significant correlations have been found between the free radical content of humic substances and absorbance at 465 mμ (Kleist and Mucke, 1966).

2.6.9 Infra-red Spectroscopy (IR)

A number of authors have described the use of IR spectroscopy for studying soil humus substances and synthesised humus like substances (Schnitzer et al., 1959; Farmer and Morrison, 1960; Flaig, 1960; Mortensen and Schewendinger, 1963; Ziechmann, 1964; Goh and Stevenson, 1971; Banerjee et al., 1975; Banerjee et al., 1976; Majumder et al., 1976). IR spectra of humic substances shows band at the following frequences : 3400 cm^{-1} (hydrogen bonded OH), 2900 cm^{-1} (aliphatic C-H stretch), 1725 cm^{-1} (C=O of CO_2H, C=O stretch of ketonic C=O), 1630 cm^{-1} (aromatic C=C hydrogen bonded C=O of carboxyl or quinone,COO^-), 1450 cm^{-1} (aliphatic C-H), 1400 cm^{-1} (COO^-, aliphatic C-H), 1200 cm^{-1} (C-O stretch of OH deformation CO_2H) and 1050 cm^{-1} (Si-O or silicate impurities) (Schnitzer and Khan, 1972). The IR spectra in the fingerprint regin ($<$1000 cm^{-1}) appeared almost featureless both for original humic acids and their interaction products (Senesi and Testini, 1983). The spectra of the brown soil fractions appear much less structured in the fingerprint region ($<$1300 cm^{-1}).

Stevenson and Goh (1971) classified the IR spectra of humic substances into three general types as follows:

Type-1 : Spectra of this type are typical of those generally shown for humic acids. Strong bonds are evident near 3400, 2900, 1600 and 1200 cm^{-1}. The 1600 cm^{-1} band is about equal in intensity to the one at 1720 cm^{-1}.

Type-II : These spectra shown by the low molecular weight fulvic acids are characterised by very strong absorption near 1720 cm^{-1}. A second unique feature is that absorption in the 1600 cm^{-1} region is weak and centred near 1640 cm^{-1}.

Type-III: In addition to the major absorption bands shown by types I and II, relatively strong bands are evident near 1540 cm^{-1} and 1050 cm^{-1}. Absorption near 2900 cm^{-1} (aliphatic C-H absorption) is also more pronounced. A unique feature of these spectra is the presence of bands indicative of proteins and carbohydrates.

A more elaborate classification of humic acid according to IR characteristic was made by Kumada and Aizawa (1958), who classified humic acids into major types (A, B, R_p and P) based on the relative intensities of specific absorption bands.

2.6.10 Nuclear Magnetic Resonance (NMR)

Well differentiated N.M.R. spectra were obtained by Ludeman et al. (1973) for lignins and synthetic and natural humic acids. They estimated the percentages of aromatic protons in the different spectra. Later, Lentz et al. (1977) used pulsed N.M.R. (100 MHZ) and the technique to compare the spectra of humic acid isolated at pH 4.5, 7.0 and 14.0 from the A and B horizons of podzol. Spectra (run, in 0.1N NaOH) recorded the same percentage (34-35) of aromatic protons in the pH 4.5 extract from the two horizons. Results of Sciacovelli et al. (1977) illustrated how elementary composition and N.M.R. chemical shift data of soil humic materials were influenced by the extractant used.

For determination of structure of humic substances a relatively new technique ^{13}C Nuclear Magnetic Resonance(NMR) spectrascopy have been applied by so many scientist (Ogner, 1973, Wilson and Goh, 1977; Hatcher et al., 1980a; Hatcher et al.,1980b; Newman et al., 1980; Hatcher et al.,1981a; Hatcher et al., 1981b; Preston and Ripmeester, 1982).

2.6.11 Absorption Spectra (UV and Visible)

Both the ultraviolet and visible absorption spectra of humic acids are featureless and monotonic in character showing no maxima or minima; the optical density usually decreases as the wave length increases and gives a little structural information (Schefier and Welte, 1950). With most samples, however, a shoulder in the region of 250 - 270 m/u, possibly due to a quinonid moiety is observed. In spite of their diverse origins, HA and FA molecules appear to contain similar π electron distributions and these are such that the absorptions overlap (Ghosh and Schnitzer, 1979). The optical density of alkaline solutions of humic acids with equal carbon content characterises the ratio of the carbon in the aromatic part to the carbon in the side radical. When there is a predominance of the aromatic net work, the optical density of the humic acid molecule is higher and there is a steepness of the curves. The reverse is the case when there is a predominance in the aliphatic groupings (Kononova, 1966).

The light absorption of humic acids appears to increase with increase in (i) the degree of condensation of aromatic rings (Kononova, 1966), (ii) the ratio of carbon in aromatic nuclei to carbon in aliphatic side chains (Kasatochkin et al., 1964), (iii) total carbon content and (iv) molecular weight (Chen et al., 1977). All of these factors are likely to effect the E_4/E_6 ratio. As no rigorous experimental evidence was available to confirm these suggestions, Chen et al. (1977) made detailed studies in the field. Though they reaffirmed the fact that E_4/E_6 ratio was independent of the sample concentration, they were unable to obtain evidence that the ratio was directly related to the concentration of condansed aromatic structures. They also concluded that the E_4/E_6 ratio was (a) governed by particle size or molecular weight (b) affected by pH and (c) related to free radical concentrations, contents of oxygen, carbon, carboxyl and total acidity. They considered that particle size was a direct function of molecular weight, so that the molecular weight was of the greatest consequence whereas, the other parameters were secondary.

Kumada (1965) from spectrometric investigation classified humic acids from different soils types into three types which denoted as A-, B- and R_p-types.

The ratio of optical densities of dilute aquous humic acid (Na form) and fulvic acid solutions at 465 and 665 m/u (the so called E_4/E_6 ratio or $Q_{4/6}$) is widely used for characterisation of these substances. The ratio is independent of the concentration of carbon in solution (Kononova, 1966; Schnitzer and Khan, 1972). Kononova (1966) believes that the magnitude of E_4/E_6 ratio is related to the degree of condensation in the aromatic nets of carbon atoms. A low ratio indicates relatively high degree of condensation of aromatic humic constituents. On the otherhand, a high E_4/E_6 ratio reflects a low degree of aromatic condensation and infers the presence of relatively large proportions of aliphatic groupings. But Chen et al. (1977) reported that E_4/E_6 values were not directly related to the degree of humification.

Pospisil and Drozdova (1976) reported that gray humic acids have the lowest and fulvic acids the highest colour quotient, but E_4/E_6 values are affected by the method of extraction and by prepative methods, for a give type of humic acid, the value of E_4/E_6 ratio is determined by the proportion of low molecular weight to high molecular weight fractions.

Tan and Giddens (1972) by gel filtration of humic acids and fulvic acids with sephadex G-50 obtained low and high molecular weight fractions with different chemical and spectral characteristics. The high molecular weight humic acid was insoluble in water and had a strong infra-red C-H absorption at 2900 cm^{-1}. Both humic fractions had low E_4/E_6 values than fulvic acids and no correlation could be found between the partition coefficients (K_α) and the E_4/E_6 ratios. The low molecular weight fulvic acid had higher k_α and E_4/E_6 values than the higher moleculars weight fulvic acid. In this case, a positive correlation was observed between k_α and E_4/E_6.

Petrovic and Vitorovic (1981) showed that the optical density of humic acid isolated from Kosovolignite was proportional to the carbon content and the C/N ratio and inversely proportional to the H/C ratio. The E_4/E_6 ratio was inversely proportional to the carbon content and the C/N ratio.

The optical properties of humic acids (HA) were determined by Klinka and Lowe (1976) from forest humus layers of eight forest ecosystems, representing xeric, mesic, hygric and subhydric hydrotopes in both dry and wet subzones of Coastal western hemlock biogeoclimatic zone. $E^{1\%}_{400}$ m/u (index of colour intensity of HA solutions) was found to increase, in general, with an increasing moisture status for both subzones, and in the wetter subzone optical properties of HA showed relatively less variation. Higher values of $E^{1\%}_{400}$ m/u were attributed to the development of mature HA of high aromaticity and degree of decomposition, which in turn is an index of microbiological activity. $E^{1\%}_{400}$ m/u showed some relationship to humus forms and to the compositions of tree layers in forest stands from which litter HA develop. Significant correlations were found between optical properties of HA and pH, total calcium contents, C/N ratio and both total and exchangeable K levels.

CHAPTER - III

SCOPE AND OBJECT OF THE PRESENT INVESTIGATION

The formation, nature and abundance of humus in the soil are influenced by a number of factors of which the nature of plant residues incorporated in the soil plays a very vital role. Although the plant materials generally contain the same groups of substances (waxes, fats, resins, proteins, simple and complex sugars), proportion of these substances in different plants is extremely variable and this materially affects the humification rate which in turn brings variation in the forms and distribution of humus in soil. As humus has a positive role in the pedogenic process of soil, its nature and distribution will in turn influence the soil characteristics. Adequate information regarding the nature, composition and properties of humus in relation to the types of vegetation in the forests of West Bengal is lacking. In view of that the present investigation was undertaken to study the distribution and nature of organic matter in the forest soils of West Bengal. During this study, attempts have been made to look at humus from different angles and combine the results from a variety of measurements to arrive at a consistent understanding of it.

In the present investigation for identification, characterisation and distribution of humus in soils under different forest vegetations the following programmes were undertaken :

i) Characterisation of different forest soils of West Bengal.

ii) Study of vegetation at different agroclimatic regions.

iii) Extraction, fractionation and purification of humic and fulvic acids from the soils.

iv) Characterisation of humic substances by,

  a) Elemental analysis,

  b) Electromatritic studies.

v) Viscomentric analysis.

vi) Spectral analysis:

  a) Absorption spectra,

  b) Fluorescence excitation spectra,

  c) Infra-red spectra.

CHAPTER - IV

TRACT DEALT WITH

4.1 Situation

West Bengal situated in north eastern part of India lies between 21°32' and 27°14' north latitude and 85°51' and 89°53' east longitude and is bounded with the Himalayas on the north, the Bay of Bengal on the south and the tropic of Cancer running across the middle and it covers an area of 87,882 sq.kms. having 50 subdivisions under 16 districts. The ombrothermic data of different places are given in Table-IB.

4.2 Soils

According to the physiography, the area of West Bengal is divided into 4 parts (1) mountain region in the north, (2) colluovial or gravelly soil undulating area in the west, (3) central alluvial plain and (4) low laying coastal area in the south.

On the four regions of West Bengal eight types of soils are found **viz.** (i) Gangetic alluvial (22%), (ii) Vindhya alluvial (18%), (iii) Terai and Tista alluvial (9%), (iv) Coastal alluvial (16%), (v) Laterite (8%), (vi) Red (7%), (vii) Gravelly (18%), (viii) Brown forest (2%).

4.3 Forest

In these soils different types of forests are found. The forest of West Bengal have been divided mainly into the following four groups (Anonymous, 1964) :

1) Mangrove Forest (37%)
    - a) Salt water (18%), (b) Low Mangrove (2%),
    - c) Chars and water areas (17%);

2) Lateritic and Alluvial Forest (38%)
    - a) Coppies sal (33%), (b) Miscellaneous (5%);

3) Terai and Duars Forest (18%)
    - a) Miscellaneous (7%), (b) Riverain (2%),
    - c) Plain sal (9%);

4) Hill Forest (7%)
    - a) Lower hill (2%), (b) Middle hill (1%), (c) Upper hill (3%), (d) Sub-alpine (1%).

4.4 Vegetation Community

4.4.1 Mangrove forests

Mangrove forest is found in the Sundarban area, the southern part of 24-Parganas district. The principal vegetation are Sundri (Heritiera minor), Garjan (Rhizophora conjugata), Goran (Ceriops roxburghiana), Gengwa (Excaecaria agallocha), Khalsi (Aegiceras majus), Hantal (Phoenix paludosa), Golpatta (Nipa fruticans).

4.4.2 Alluvial forests

The major portion of alluvial area is under cultivation. In some pockets Eucalyptus spp., Tectona grandis , Shorea robusta and Terminalia arjuna etc are planted by Forest Department but their growth are not satisfactory. However, in some pockets of Nadia district Tectona grandis grows well. The plantation of Eucalyptus spp. and Acacia auriculiformis has also been tried.

4.4.3 Lateritic forests

The forest under lateritic area consists predominantly of sal but miscellaneous species are also found here and there. The forests in general conform to 4B/C2 of Champions Forest types and the sal forests comes under category A3 of his sal types - Dry peninsular type of sal or called ' Northern tropical Dry-Deciduous - Dry Sal ' according to the standard classification of the Forest types of India. In some area Jhanti Forest are also found and seems to belong to Champions secondary seral type 2S/2 Dry - decidous scrb forest of Dry tropical zone (Anonymous, 1964).

The common associates of sal are Mohua (*Madhuca latifolia*), Kend (*Diospyros melanoxylon*), Sidha (*Iages tracmiaprarviflora*), Parasi (*Cleistan collinus*), Gulguli (*Cochlopesmum gospypium*), Peasal (*Pterocarpus marsupium*), Rahara (*Soymida febrifuge*), Kusum (*Schlicehera friguga*), Palas (*Butea monosperma*), Seuli (*Nyetanthes arbortristes*), Arjun (*Terminalia arjuna*), Haritaki (*Terminalia chebula*), Asan (*Terminalia tomentosa*), Bahera (*Terminalia belerica*), Chakalfa (*Adina cordifolia*), Semul (*Salmalia malababarica*), Gamar (*Gmelina arborea*), Bhela (*Semecarpus aracardium*), Pial (*Buchanania latifolia*) etc.

Because of peculiar dry nature of the climate and poor soil, the growth of trees is generally poor. Due to heavy biotic interference in the forest land, the probability of formation of humus layer has been remote. Even the leaf, litter are swept away for the house hold consumption. This type of forest covers a considerable area of the districts of Bankura, Birbhum, Bardwan, Midnapore and Purulia.

4.4.4 Terai and Hill Forests

Although the area of Terai and Duars forest is 18% and Hill forest is only 7%, the hill forest area is much more important than any other area as because only a limited work has been done in this area.

The variation in altitude aspect, climate have influenced the forest type in this area. The following types of forests can be distinguished in the area.

(i) Riverain forests, (ii) Hill forests.

(i) Riverain forests

These are found in sandy soils near river bed of the great Rangit river in the Tista vally Range and correspond to Champions seral type 1S/2 of tropical dry evergreen forest. The main species found are Siris (Albizzia procera and Albizzia odoratissima), Dabdaba (Garuga pinnata), Sal (Shorea robusta), Teak (Tectona grandis). The undergrowth consist of herbeceous annuals, shurbs and grasses the commonest species being Eupatorium odoratum and Saccharum spontaneum.

(ii) Hill forests

The forests are divided into the following four classes :

a) Lower hill forest (300 - 900 m)
b) Middle hill forest(900 - 1800 m)
c) Upper hill forest (1800 - 2700 m)
d) Sub-alpine forest (2700 m and above).

a) Lower-hill forests

The main type of forest within this altitude ranged is Shorea - Terminalia - Schima community. The species Dendrocalmus hamiltonii is generally present throughout the forests. The plant species in these area is (i) 3b/C2/D1 (a)- East Himalayan Well Hill Sal of Northern Tropical Moist Deciduous Forests, (ii) 3b/E6 East Himalayan Moist Deciduous Forest, (iii) 3b/2S/4 East Subhimalayan Wet Mixed Forest of Northern Tropical Moist Deciduous Forest according to Champions. The species found in this region are Shorea robusta, Teminalia nudiflora, Schima wallichii, Lagerstroemia parviflora, Ailanthus grandis, Salmalia malbarica, Antnocephalus cadamba.

b) Middle-hill forests

The major portion of the forests area within these altitude is under plantation of Cryptomeria japonica. The main type of forests within this altitude range is Castanopsis-Quercus-Alcimandra community. The composition of the crop is more or less similar to Champions type 7b/C1 Bengal Sub-tropical Hill forest of Northern Sub-tropical well Hill Group. The most dominant species Castanopsis tribuloides, Quercus lamellosa, Machilus edulis, Beilschmiedia spp., Alcimandra cathcartii etc are found between this altitude.

c) Upper-hill forests

The main type of natural forest within this altitude range belongs to *Quercus* - *Acer* - *Castanopsis* community. The floristics are evergreen in nature. Deciduous species occur particularly at higher elevation. Major part in this area is under the coniferous species *Cryptomeria japonica*. In some places *Pinous patula* was planted. The most cospicus trees are Oaks, Laurets, Magnolias, Alder, Maples, Birches, Bucklandias etc. The forests by an large is of mixed type and corresponds to Champions type 10b/C1-East Himalayan Wet Temperate Forest of Northern Wet Temperate Group. The dominant species of natural forests are *Quercus lamellosa*, *Acer campbellii*, *Michelia doltsopa* etc.

With the variation in altitude (1800 - 2400 m), rainfall and the composition of plants species vary. Oak - Hemlock forests are met within upper portions of Singalila Range (between 2400 - 3000 m) and correspond to Champions type 11/C1 (c) - Eastern Oak - Hemlock forests of Himalayan Moist Temperate group. The Hemlock (*Tsuga brunnoniana*) gradually gives away to Silver fir (*Abies densa*) at the higher altitude of the wet temperate forest.

d) Sub-alpine forests

The forests of this area may be classified as Champions type - 13/C2 - East Himalayan Sub-alpine forests. These comprise mainly evergreen conifers (viz. Silver fir) admixed with some broad-leaved species (viz. Rhododendron). Silver fir (Abies densa) is the dominant species characterised by it low branching habit. Broad-leaved species of Birch also grow in the vicinity of Silver fir at places. Though few trees of Rhododendron occur sporadically, it is mainly a consociation of Silver fir in this zone.

Pure consociations of Silver fir are distributed between 3000 m to 4000 m altitude in the Singalila Range. Above 4000 m altitude the forests lose their quality and join the alpine scrub type of vegetation.

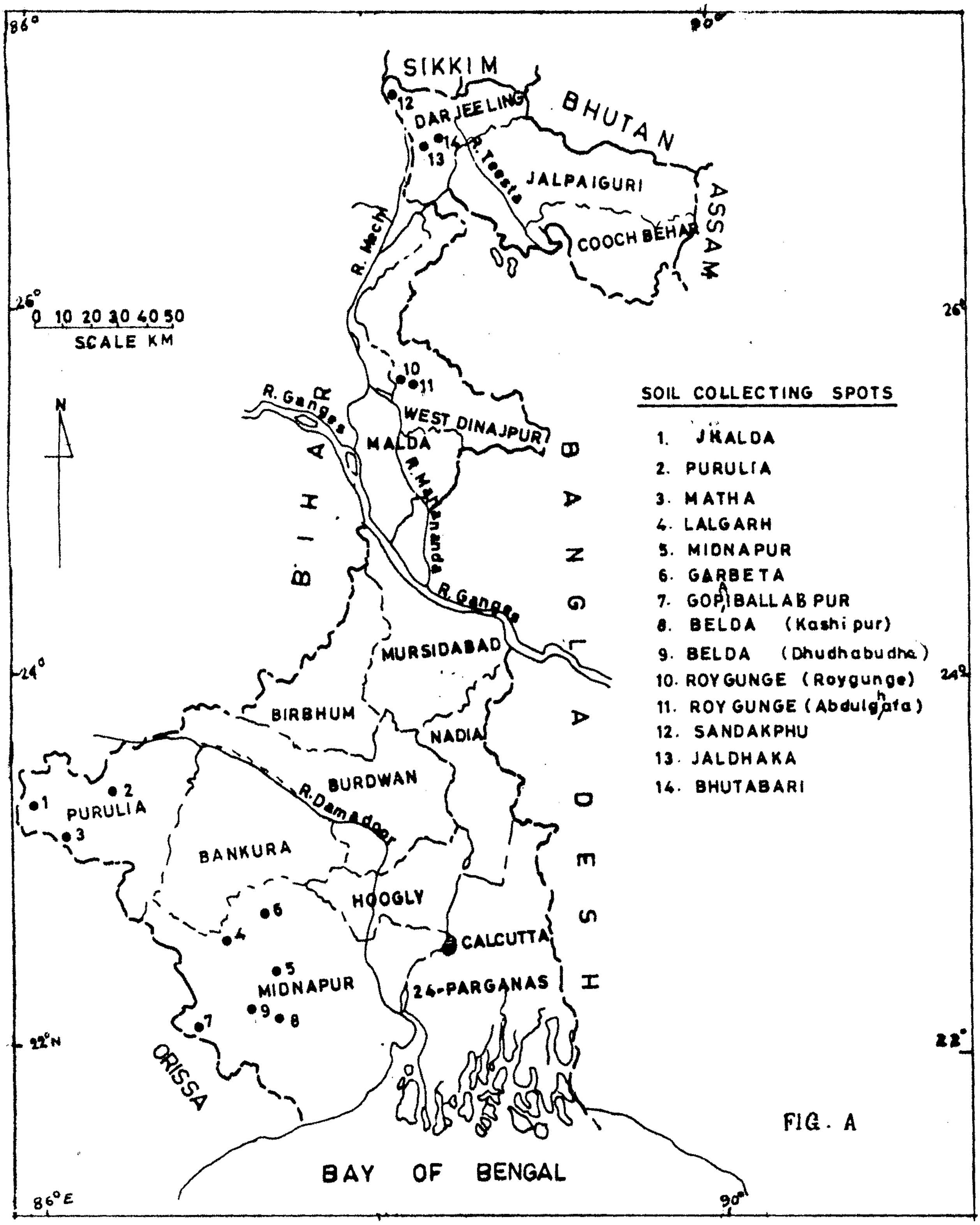
This community is a consociation of Abies densa. In the second storey scattered trees of Rhododendron companulatum and Betula alnoids can be noticed. The third storey comprises Arundinaria aristate, Rosa sericea etc. under a moderately open canopy, whereas under a closed one practically there is no growth other than few scattered grass like Agropyron bromus etc. There is an appreciable amount of epiphytic moss and lichens on the stems.

The hilly soil under Darjeeling district is called as brown forest soil. But the demarcation line of brown forest soils is not clearly established at present. The soils of

Darjeeling District occur at diverse bioclimatic conditions and on various soil forming rocks under deciduous and coniferous forests.

The common features of typical brown forest soil are high humus content, predominance of fulvic acids and relatively low degree of condensation of aromatic ring in humic acids.

CHAPTER - V


86°
90°
26°
24°
22°N
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SIKKIM
BHUTAN
ASSAM
DARJEELING
JALPAIGURI
COOCH BEHAR
R. Teesta
R. Mechi
R. Ganges
R. Mahananda
WEST DINAJPUR
MALDA
BIHAR
BANGLADESH
MURSIDABAD
BIRBHUM
NADIA
BURDWAN
R. Damadoar
PURULIA
BANKURA
HOOGLY
CALCUTTA
MIDNAPUR
24-PARGANAS
ORISSA
BAY OF BENGAL
0 10 20 30 40 50
SCALE KM
N
1
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4
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11
12
13
14
SOIL COLLECTING SPOTS
1. JHALDA
2. PURULIA
3. MATHA
4. LALGARH
5. MIDNAPUR
6. GARBETA
7. GOPIBALLAB PUR
8. BELDA (Kashi pur)
9. BELDA (Dhudhabudha)
10. ROYGUNGE (Roygunge)
11. ROY GUNGE (Abdulghata)
12. SANDAKPHU
13. JALDHAKA
14. BHUTABARI

FIG. A

Studies on the Soils and Vegetations of some Forest areas of West Bengal

In the present investigation soils under different forest types of West Bengal covering the districts of Purulia, Bankura, Midnapore, West Dinajpur and Darjeeling and their corresponding vegetation parameters were investigated. The vegetation parameters and morphological features of soils were studied in the field and soil samples were collected from different genetic horizons and studied in the laboratory.

5.1 Materials and Methods

5.1.1 Methodology of Vegetation Survey

The vegetation data were collected through sampling representative sites and of quadrat analysis.

100 sq.m. (10 m x 10 m) was found optimum as the minimal area and, hence, quadrats of this size were used to study tree (tree quadrat), 25 sq.m. (5 m x 5 m) for shrubs (shrub quadrat), 1 sq.m. (1 m x 1 m) quadrats (regeneration quadrat) for regeneration study.

In each stand, 12 tree quadrats were laid out continuously and all the tree species were recorded storeywise.

Girth at breast highest and total height of each tree were also recorded.

5.1.2 Methodology of Soil Survey

Soil samples were collected from the genetic horizons of all the profiles of the study area. The soil collecting spots were shown in the Fig. A. Morphological characteristics of different profiles in the field were studied according to the soil Survey Staff (1966).

5.1.3 Methods of Soil Analysis

The soil samples collected during field survey work were dried in diffused sunlight and after being separated from undecomposed plant residues ground in an wooden mortor and passed through 1 mm sieve and preserved in polythene containers.

Physico-chemical Analysis

pH of the soils

The pH of the soil samples was measured by Elico pH meter after suspending in distilled water and 1(N) KCl solution separately in the ratio 1:2.5 . Before estimation, the pH meter was standarised by standard buffer solutions.

Organic Carbon

Organic carbon in each sample was estimated by wet digestion method as suggested by Walkley and Black (Black, 1965).

Total Nitrogen

The total nitrogen in the soil sample was determined by modified Kjeldahl method (Jackson, 1967).

Cation Exchange Capacity (C.E.C.)

Cation exchange capacity of the soil samples was estimated by the method proposed by Schollenberger and Simon (1945) using neutral normal ammonium acetate solution (Jackson, 1967).

Exchangeable Cations (Ca^{+2}, Mg^{+2}, K^{+} , Na^{+})

Taking ammonium acetate leachate the exchangeable cations were determined.

Calcium (Ca^{+2})

Exchangeable calcium was determined by titrating against EDTA using murexide as indicator and 4(N) NaOH was used for maintaining pH - 11 (Black, 1965).

Magnesium (Mg^{+2})

Exchangeable magnesium (Mg^{+2}) was determined by titrating the ammonium acetate extract by EDTA solution in presence of Erichrome Black T as an indicator (Black, 1965).

Potassium (K^+) and Sodium (Na^+)

Exchangeable Na^+ and K^+ were determined by Flame photometer (Black, 1965).

Determination of Total Exchangeable acidity

Total exchangeable acidity was determined first by leaching of soil with 1(N) KCl then titrating this solution with NaOH using phenolphthalein as indicator.

Exchangeable Al^{+3} and H^+ were estimated from 1(N) KCl extract by titrating with standard alkali in presence of phenolphthalein (Black, 1965).

Determination of mobile form of sesquioxides

Mobile form of sesquioxides were determined gravimetrically (Dhir, 1967).

Fusion analysis of soils

Total analysis of the soils was performed after fusing the soil (1 g) with Na_2CO_3 in a muffle furnace at 700°C.

5.2. Results and Discussion of Soil and Vegetation Parameters

The study areas of the present investigation were classified mainly into three different zones according to soil and climatic conditions.

The study sites no - 1 to 9 were situated under low rainfall and dry hot climatic zones and the soils were mainly lateritic of which three sites were under *Tectona grandis* (site - 1 to 3), one under *Eucalyptus* spp. (site - 6) and five under *Shorea robusta* (site-4, 5 and 7 to 9).

The site no - 10 and 11 were situated in alluvial region having sub-tropical climatic zone and the species found were *Terminalia arjuna* and mixed broad leaves respectively.

The site no - 13 and 14 were situated under cool climatic zone in hilly area with heavy precipitation containing *Ailanthus grandis* and mixed vegetation respectively. The site no - 12 was situated under sub-alpine region containing vegetation *Abies densa* mixed with *Rhododendron* spp.

5.2.1 Vegetation

The vegetation parameters of different sites have been represented in Table - IA. From the Table - IA it is observed that the basal area of top storey and the total basal area of both the top storey and second storey were maximum in site -10 situated in the alluvial area which were 146.66 m^2/ha (Terminalia arjuna - 122.04 m^2/ha and Lagerstroemia flos-reginae - 24.62 m^2/ha) and 150.044 m^2/ha respectively.

In the lateritic zone the maximum and minimum number of trees per hectare in case of top storey were 3300 (site - 5) and 200 (site - 7) respectively, and in both the cases the plant species was Shorea robusta. In site - 5 although the total number of trees per hectare was maximum, its total basal area was minimum (8.505 m^2/ha). The average height of the trees in this zone varied from 3.5 m (site - 5) to 13.82 m (site - 4). The average height of the top storey in site - 10 was maximum (19.92 m) and the species were Terminalia arjuna and Lagerstroemia flos-reginae.

From simple statistical analysis it is observed that the surface soil organic carbon bears a significant positive correlation ($r = + 0.725$) with total basal area of the different plants under lateritic and alluvial areas (Table - XI).

5.2.2 Description of the soil profiles

The morphological description of soil pedons are given below:

PEDON - 1

(i) Location- Purulia Division, Jhalda Range and Beat.
(ii) Physiography - Flat land.
(iii) Slope - 0 - 1%
(iv) Drainage - Poorly drained.
(v) Erosion - Slight.

Horizon	Depth (cm)	Description
A_1	0-18	Brownish yellow (10 YR 6/6, D) to dark yellowish brown (10 YR 4/4, M) sandy loam, medium moderate subangular blocky, slightly hard, friable, slightly sticky, few fine iron concretions, few coarse and few fine roots, gradual smooth boundary.
B_{21t}	18-41	Dark yellowish brown (10 YR 4/4,M) sandy clay loam, strong subangular blocky hard, firm, sticky, coarse iron concretions few with few decomposed parent materials, few coarse and few fine roots, clear smooth boundary.

Horizon	Depth (cm)	Description
B_{22t}	41-64	Dark yellowish brown (10 YR 4/4,M) sandy clay loam, strong subangular blocky, hard, firm, sticky, fine discontinuous clay skins common on the ped surface, iron concretions common with few decomposed parent material, few coarse roots, clear smooth boundary.
B_{23tcn}	64-72	Yellowish brown (10 YR 5/6) 20%, yellowish brown (10 YR 5/4) 80%, mottle yellow (10 YR 7/6) sandy clay loam, medium moderate angular blocky, many clay skins on the ped surfaces, hard, firm, plastic, soft iron concretions common, few roots, clear smooth boundary.
B_{24tcn}	72 -121	Yellowish brown (10 YR 5/4,M), mottle pale brown (10 YR 6/3) sandy clay, medium moderate angular blocky, hard, firm, plastic, many clay skins on the ped surfaces, soft iron concretions common, few roots.

PEDON - 2

(i) Location - Purulia Division and Range, Keshargarh Beat,
Domkadi Village.

(ii) Physiography - Flat land.

(iii) Slope - 0 - 2%.

(iv) Drainage - Well drained.

(v) Erosion - Slight.

Horizon	Depth (cm)	Description
A_{11}	0-9	Brownish yellow (10 YR 6/6, D) to yellowish brown (10 YR 5/6, M) loamy sand, weak fine subangular blocky, hard, friable, nonsticky, many roots, clear smooth boundary.
A_{12}	9-26	Yellowish brown (10 YR 5/8, M) loamy sand, medium subangular blocky, hard, friable, nonsticky, few coarse roots, gradual smooth boundary.
B_{11}	26-50	Yellowish brown (10 YR 5/8,M) mottle, pale yellow (2.5 Y 7/4) loamy sand, hard, friable, nonsticky, **medium** subangular blocky, medium to coarse iron concretions few, few fine roots, clear smooth boundary.
B_{12}	50-67	Yellowish brown (10 YR 5/6, M) 80%, dark yellowish brown (10 YR 4/4, M) 20%, mottle pale yellow (2.5 Y 7/4) sandy loam, medium subangular blocky, friable, sticky, medium to coarse iron concretions few, roots common, clear smooth boundary.

Horizon	Depth (cm)	Description
B_{21t}	67-80	Light red (2.5 YR 6/6, M) 50%,yellowish brown (10 YR 5/6, M) 20% and dark yellowish brown (10 YR 4/4, M) 30% sandy clay loam, strong subangular blocky, friable, sticky, fine discontinuous clay skins common on the ped surfaces, coarse iron concretions common, roots common, clear smooth boundary.
B_{22t}	80-150+	Compact layer of iron concretion and quartz particles.

PEDON- 3

i) Location - Purulia Division, Matha Range, Bagmundi Beat, Kudna Village.
ii) Physiography - Low land.
iii) **Slope** - 0 - 2%
iv) Drainage - Well drained.
v) Erosion - Slight.

Horizon	Depth (cm)	Description
A_{11}	0 - 22	Dark yellowish brown (10 YR 4/4,M) loamy sand, weak subangular blocky, roots common, clear smooth boundary.
A_{12}	22 - 49	Dark yellowish brown (10 YR 4/6,M) sandy loam, medium subangular blocky, one medium and two large krotovenous, roots common, gradual smooth boundary.
B_1	49 - 75	Strong brown (7.5 YR 5/6,M), sandy loam, medium subangular blocky, few fine iron concretions, one large and one medium krotovenous, roots common, gradual smooth boundary.
B_2	75 - 101	Dark brown (7.5 YR 4/4,M) sandy loam, strong subangular blocky, few fine iron concretions, one very large krotovenous, roots common, clear smooth boundary.
BC	101 - 145	Dark brown (7.5 YR 4/4, M) sandy loam, strong subangular blocky, few fine iron concretions with few quartz particles, one large krotovenous, few roots.

PEDON - 4

i) Location - East Midnapore Division, Lalgarh Range, Bhimpur Beat and Mouza.

ii) Physiography - Low land.

iii) Slope - 0 - 2%.

iv) Drainage - Well drained.

v) Erosion - Slight.

Horizon	Depth (cm)	Description
A_{11}	0 - 7	Light yellowish brown (10 YR 6/4,D) to dark yellowish brown (10 YR 4/4, M) loamy sand, strong subangular blocky, slightly hard, friable, medium to coarse roots common with few fine, clear smooth boundary.
A_{12}	7 - 26	Strong brown (7.5 YR 5/6,D) to strong brown (7.5 YR 4/6,M) sandy loam, strong subangular blocky, slightly hard, friable, slightly sticky, medium to coarse roots common with few fine, gradual smooth boundary.
B_1	26 - 52	Strong brown (7.5 YR 4/6, D) to dark brown (7.5 YR 3/4,M) sandy clay loam, strong subangular blocky,

Horizon	Depth (cm)	Description
		slightly hard, firm, sticky, medium to coarse iron concretions few with few quartz particles,few roots, gradual smooth boundary.
B_{21t}	52 - 85	Strong brown (7.5 YR 5/6,D) to strong brown (7.5 YR 4/6, M) sandy clay loam, medium moderate subangular blocky, hard, firm,sticky, fine discontinuous clay skins on the ped surfaces, medium to coarse iron concretions with many quartz particles common, few roots, clear smooth boundary.
B_{22tcn}	85 - 127	Strong brown (7.5 YR 4/6, M) sandy clay loam, medium moderate subangular blocky, hard, firm, sticky, many clay skins on the ped surfaces, medium to coarse iron concretions with many quartz particles, clear smooth boundary.
B_{23tcn}	127 - 141	Strong brown (7.5 YR 4/6,M) sandy clay loam ,strong subangular blocky, hard, many clay skins on the ped

surfaces, coarse iron concretions and medium to coarse quartz particles many.

PEDON - 5

i) Location - East Midnapore Division, Midnapore Range, Bhadutala Beat and Mouza.
ii) Physiography - Flat land.
iii) Slope - 0 - 1%.
iv) Drainage - Poorly drained.
v) Erosion - Slight.

Horizon	Depth (cm)	Description
A_{11}	0 - 15	Pale yellow (2.5 Y 7/4,D) to olive yellow (2.5 Y 6/6,M) sandy loam, weak fine subangular blocky, slightly hard, friable, sticky, medium to fine iron concretions common, medium to coarse roots common, clear smooth boundary.
A_{12}	15 - 44	Pale yellow (2.5 Y 7/4,D) to olive yellow (2.5 Y 6/6,M) loam, weak subangular blocky, slightly hard, friable, sticky, medium to coarse iron concretions common, many medium

Horizon	Depth (cm)	DESCRIPTION
		to fine roots, clear smooth boundary.
B_{21}	44 - 65	Pale yellow (2.5 Y 7/4, M) 80%, light yellowish brown (2.5 Y 6/4,M) 20%, mottle brownish yellow (10 YR 6/6) sandy clay loam, medium moderate subangular blocky, slightly hard, friable, sticky, medium to coarse roots many with few fine, medium to coarse iron concretions with rusty-speaks, quartz particles present, clear smooth boundary.
B_{22t}	65 - 77	Pale yellow (2.5 Y 7/4,M) 80%,olive yellow (2.5 Y 6/6, M) 20%, mottle brownish yellow (10 YR 6/6) sandy clay loam, medium moderate subangular blocky, slightly hard, friable, sticky, fine discontinuous clay skins common on the ped surfaces, many iron concretions and quartz particles, roots common, clear smooth boundary.
B_{23t}	77 - 124+	Light gray (2.5 Y 7/2, D) to yellowish brown (10 YR 5/6, M) sandy clay loam, medium moderate angular blocky, slightly hard, friable, sticky, many

Horizon	Depth (cm)	Description
		clay skins common on the ped surfaces, medium to coarse iron concretions common, quartz common, roots common, clear smooth boundary.

PEDON - 6

i) Location - East Midnapore Division, Garbeta Range and Beat, Dhabani - 1 Mouza.

ii) Physiography - Flat land.

iii) Slope - 0 - 2%.

iv) Drainage - Poorly drained.

v) Erosion - Slight.

Horizon	Depth (cm)	Description
A_1	0 - 11	Brownish yellow (10 YR 6/6, D) to yellowish brown (10 YR 5/6, M) sandy loam, medium subangular blocky, slightly hard, friable, slightly sticky, fine to medium iron concretions, quartz many, medium to coarse common with few fine roots, clear smooth boundary.
B_1	11 - 48	Dark yellowish brown (10 YR 4/6,M) sandy clay loam, medium subangular

Horizon	Depth (cm)	Description
		blocky, hard, friable, sticky, medium to coarse few with many fine iron concretions, quartz many, few fine roots, gradual smooth boundary.
B_{21tcn}	48-98	Yellowish brown (10 YR 5/8, M), mottle yellowish red (5 YR 5/8) 5% sandy clay loam, medium moderate subangular blocky, hard, friable, sticky, many clay skins on the ped surfaces, medium to coarse few with many fine iron concretions, quartz many, few fine roots, clear smooth boundary.
B_{22tcn}	98-120+	Light yellowish brown (10 YR 6/4,D) to yellowish brown (10 YR 5/4,M) sandy clay loam, strong subangular blocky, slightly hard, friable, slightly sticky, many clay skins on the ped surface, medium to coarse iron concretions, quartz few, few fine roots, clear smooth boundary.

PEDON - 7

i) Location - West Midnapore Division, Gopaiballabpur Range and Beat, Kendugari Mouza.

ii) Physiography - Flat land.

iii) Slope - 0 - 1%.

iv) Drainage - Well drained.

v) Erosion - Slight.

Horizon	Depth (cm)	Description
A_{11}	0 - 17	Yellowish brown (10 YR 5/6, M) loamy sand, weak subangular blocky, friable, nonsticky, fine iron concretion with few fine quartz, fine to medium roots many with few coarse, few krotovenous, gradual smooth boundary.
A_{12}	17 - 40	Brownish yellow (10 YR 6/8, M) loamy sand, weak subangular blocky, friable, nonsticky, few fine iron concretions with fine quartz few, many roots, few krotovenous, gradual smooth boundary.
B_1	40 - 60	Yellow (10 YR 7/8, M) sandy loam, weak subangular blocky, friable, slightly sticky, red speaks present,

Horizon	Depth (cm)	Description
		medium iron concretions, many roots, few krotovenous, gradual smooth boundary.
B_{21}	60 - 116	Brownish yellow (10 YR 6/6, M) 90% loam, medium subangular blocky, friable, sticky, medium to coarse many with few fine iron concretions, medium to coarse many with few fine quartz, many roots, gradual smooth boundary.
B_{22t}	116 - 150+	White (7.5 YR 8/0, M) 50%, red (2.5 YR 4/6, M), 50% sandy clay loam, medium subangular blocky, many clay skins present, hard, friable, very sticky, medium to coarse iron concretions many with medium to coarse quartz many, few roots.

Plinthitic horizon wetness of the soil increase down the profile, because of the shallow water table.

PEDON - 8

i) Location - West Midnapore Division, Belda Range, Kashipur Beat and Mouza.

ii) Physiography - Flat land.

iii) Slope - 0 - 1%.

iv) Drainage - Well drained.

v) Erosion - Slight.

Horizon	Depth (cm)	Description
A_1	0 - 16	Yellow (2.5 Y 8/6,D) to light olive brown (2.5 Y 5/4, M) sandy loam, weak subangular blocky, many fine iron concretions, fine to medium with plenty quartz particles many, medium to coarse roots common with many fine, gradual smooth boundary.
B_1	16 - 40	Yellow (2.5 Y 7/6, D) to olive yellow (2.5 Y 6/6, M) sandy clay loam, slight hard, medium subangular blocky, few fine iron concretions, many quartz particles, medium to coarse roots common with many fine, gradual smooth boundary.

Horizon	Depth (cm)	Description
B_{21t}	40 - 63	Yellow (2.5 Y 7/6, D) to olive yellow (2.5 Y 6/6, M) sandy clay loam, slight hard, medium moderate subangular blocky, fine discontinuous clay skins common on the ped surface, many iron concretions, fine to medium quartz particles common, few roots, gradual smooth boundary.
B_{22t}	63 - 82	Yellow (2.5 Y 7/6, D) to light olive brown (2.5 Y 5/6, M) sandy clay loam, slight hard, fine discontinuous clay skins common on the ped surfaces, medium moderate subangular blocky, few iron concretions, quartz particles common, few roots, clear smooth boundary.
B_{23t}	82 - 132+	Dark yellowish brown (10 YR 4/6,D) to light gray (10 YR 7/2, M) sandy clay loam, fine discontinuous clay skins common on the ped surfaces, slight hard, medium moderate subangular blocky, many iron concretions, quartz particles common,few roots.

PEDON - 9

i) Location - West Midnapore Division, Belda Range, Keshari Beat, Dhudhebudha Mouza.

ii) Physiography - Flat land.

iii) Slope - 0 - 1%.

iv) Drainage - Well drained.

v) Erosion - Slight.

Horizon	Depth (cm)	Description
A_1	0 - 25	Pale yellow (2.5 Y 8/4, D) to olive yellow (2.5 Y 6/6, M), sandy loam, slight hard, prismatic, fine plenty quartz particles, many roots, gradual smooth boundary.
B_1	22 - 53	Yellow (2.5 Y 7/6, D) to olive yellow (2.5 Y 6/6, M) sandy clay loam, slight hard, prismatic, few fine iron concretions, many fine quartz particles, many roots, gradual smooth boundary.
B_{21t}	53 - 80	Yellow (2.5 Y 8/6,D) to olive yellow (2.5 Y 6/6, M) sandy clay

Horizon	Depth (cm)	Description
		loam, slight hard, prismatic, fine discontinuous clay skins common on the ped surfaces, many fine quartz particles, many roots, gradual smooth boundary.
B_{22t}	80 - 102	Pale yellow (2.5 Y 7/4, D) to light yellowish brown (2.5 Y 6/4, M) silty clay loam, hard, prismatic, fine discontinuous clay skins common on the ped surface, medium to coarse iron concretions few with few quartz particles, many fine roots, clear smooth boundary.
B_{23tcn}	102 - 147+	Light brownish gray (2.5 YR 6/2,D) to grayish brown (2.5 Y 5/2, M) sandy clay, prismatic, many clay skins on the ped surfaces, medium to coarse quartz particles.

PEDON - 10

i) Location - Malda West Dinajpur Division, Roygunge Range, Beat and Mouza.

ii) Physiography - Flat land.

iii) Slope - 0 - 1%.

iv) Drainage - Well drained.

v) Erosion - Slight.

Horizon	Depth (cm)	Description
A_{11}	0 - 30	Light yellowish brown (10 YR 6/4, M) to brown (10 YR 5/3, M), mottle strong brown (7.5 YR 5/6) 25% clay loam, medium subangular blocky, hard, friable, moderately sticky, fine common with common rustyspeaks, five big and eight small krotovenous, roots common, gradual smooth boundary.
A_{12}	30 - 45	Brown (10 YR 5/3, D) to brown (10 YR 5/3, M), mottle strong brown (7.5 YR 5/6) 50% sandy clay loam, medium subangular blocky, slight hard, moderately sticky, firm, very sticky, fine common with rustyspeaks iron concretions, one very big and three small krotovenous, roots common, gradual smooth boundary.

Horizon	Depth (cm)	Description
B_1	45 - 80	Brown (10 YR 5/3, D) to brown (10 YR 5/3, M), mottle strong brown (7.5 YR 5/6) 50% sandy clay loam, medium subangular blocky, slightly hard, firm, very sticky, fine common with rustyspeaks iron concretions, four small krotovenous, roots common, gradual smooth boundary.
B_{2t}	80 - 103	Brown (10 YR 5/3, D) to brown (10 YR 5/3, M) mottle strong brown (7.5 YR 5/6) 50% clay loam, medium subangular blocky, hard, firm, very sticky, fine discontinuous clay skins common on the ped surfaces, few iron concretions, few small krotovenous, few roots, clear weavy boundary.
B_3	103 - 140	Light brownish gray (10 YR 6/2,D) to brown (10 YR 5/3,M), mottle strong brown (7.5 YR 5/6) 50% sandy clay loam, hard, friable, very sticky and very plastic, coarse iron nodule present, few roots, gradual smooth boundary.

Horizon	Depth (cm)	Description
BC	140 - 173+	Pale brown (10 YR 6/3, D) to pale brown (10 YR 6/3, M) loam, soft, loose, nonsticky, weak subangular blocky, iron nodule present, few roots.

PEDON - 11

i) Location - Malda West Dinajpur Division, Roygunge Range and Beat, Abdulghata Mouza.
ii) Physiography - Flat land.
iii) Slope - 0 - 1%.
iv) Drainage - Well drained.
v) Erosion - Slight.

Horizon	Depth (cm)	Description
A_1	0 - 36	Grayish brown (10 YR 5/2, D) to dark grayish brown (10 YR 4/2,M) sandy clay loam, strong subangular blocky, hard, firm, very sticky, krotovenous many, many roots, gradual smooth boundary.
B_{11}	36 - 83	Pale brown (10 YR 6/3, D) to brown (10 YR 5/3, M) loamy sand, weak subangular blocky, soft, friable, nonsticky, few rustyspeaks,roots common, gradual smooth boundary.

Horizon	Depth (cm)	Description
B_{12}	83 - 118	Light gray (10 YR 7/2) 30%, dark reddish brown (5 YR 3/3) 50%, yellowish red (5 YR 5/8) 20% loamy sand, loose, friable, nonsticky, few iron concretions, few roots, gradual smooth boundary.
C_1	118 - 153	Dark reddish brown (5 YR 3/4) 50%, light brownish gray (10 YR 6/2)50% loamy sand, weak subangular blocky, slightly hard, friable, sticky,fine many with coarse common iron concretions, few roots, gradual smooth boundary.
C_2	153 - 185	Sandy layer.

PEDON - 12

i) Location - Darjeeling (special) Division, Singalila Range, Sandakphu Block.
ii) Physiography - Low land.
iii) Slope - 10%.
iv) Drainage - Good.
v) Erosion - Slight.
vi) Altitude - 3530 m.

Horizon	Depth (cm)	Description
A_o	0 - 20	Very dark brown (10 YR 2/2, M) loam, granular, friable, slightly sticky, many fine quartz particles, many roots, many krotovenous, clear weavy boundary.
B_{21t}	20 - 38	Dark yellowish brown (10 YR 3/6, M) clay loam, granular, friable, moderately sticky, fine discontinuous clay skins common on the ped surfaces, fine iron concretions with many fine quartz particles, krotovenous many, many roots, clear weavy boundary.
B_{22t}	38 - 56	Dark yellowish brown (10 YR 4/6, M) sandy clay loam, granular, firm, moderately sticky, fine discontinuous clay skins common on the ped surfaces, medium to coarse quartz particles many with few iron concretions, krotovenous many, roots common, clear weavy boundary.

Horizon	Depth (cm)	Description
B_{23t}	56 - 74	Dark yellowish brown (10 YR 4/6,M) sandy clay loam, medium subangular blocky, firm, moderately sticky, fine discontinuous clay skins common on the ped surfaces, fine to medium many with coarse common quartz particles with very few iron concretions, many krotovenous, few roots, clear weavy boundary.
BC	74 _ 120+	Brown (10 YR 5/3, M) sandy loam, structureless, gravely, friable, nonsticky, medium to coarse quartz particles many with many iron concretion.

PEDON - 13

i) Location - Kalimpong Division, Jaldhaka Range,
No.13 Block.
ii) Physiography - Gently sloping land.
iii) Slope - 0 - 3%.
iv) Drainage - Well drained.
v) Erosion - Slight.
vi) Altitude - 745 m.

Horizon	Depth (cm)	Description
A_1	0 - 8	Black (5 YR 2.5/1, M) sandy loam, loose, one krotovenous, many fine roots, gradual smooth boundary.
B_1	8 - 52	Black (5 YR 2.5/1, M) sandy loam, loose, two krotovenous, many fine roots, gradual smooth boundary.
B_2	52 - 60	Dark reddish brown (5 YR 2.5/2, M) sandy loam, loose, few fine roots.

PEDON - 14

i) Location - Kalimpong Division, Neora Range, Meenglers Block, Bhutabari Mouza.

ii) Physiography - Plain land.

iii) **Slope** - 0 - 1%.

iv) Drainage - Well drained.

v) Erosion - Slight.

vi) Altitude - 460 m.

Horizon	Depth (cm)	Description
A_1	0 - 14	Dark brown (10 YR 4/3, M) clay loam, weak subangular blocky, medium to coarse common with many fine roots, clear smooth boundary.

Horizon	Depth (cm)	Description
B_1	14 - 35	Dark brown (7.5 YR 3/4, M) sandy clay, loose, few spots of decomposed parent materials, medium to coarse common with many fine roots, gradual smooth boundary.
B_2	35 - 140	Dark brown (7.5 YR 3/4, M) sandy clay, loose, medium to coarse few with few fine roots.

5.2.3 Soil

5.2.3.1 Physico-chemical properties of soils

Tables-IIA and IIB represented some physico-chemical properties of soils collected from different horizons of the profiles.

The soils of all the horizons of all the **profiles** were acidic to neutral in reaction. The pH ranged from 5.0 to 6.3 for the lateritic soils (pedon - 1 to 9), from 4.9 to 6.7 for alluvial soils (pedon - 10 and 11) and from 3.8 to 5.6 for the hilly soils (pedon- 12 to 14). The highest acidity in case of hilly soils was due to their highest elevated occurence as evidenced by Roychoudhuri and Sukhla (1966).

The difference of pH at different sites may be due to the different types of parent materials, different vegetations and different agroclimatic conditions. The lowest pH was noted at the surface soil of Sandakphu under Abies densa in pedon-12 having heighest amount of organic carbon. This may be due to the production of organic acids during the process of litter decomposition which abet the leaching of the base ions out of root zone escalated by the failure on the part of the existing plant species to recycle the bases adequately.

It was observed that with the increase of altitude the acidity of surface soil under hilly area (pedon- 12 to 14) increased. The results are in agreement with the findings of Roychoudhuri and Sukhla (1966) and Roychoudhuri *et al.* (1983).

It is interesting to note that vegetative cover had a remarkable effect upon pH of the surface soils. Comparing the results presented in Table - IA and Table-IIA it may be inferred that in lateritic area where *Tectona grandis* was the principal vegetation, the pH of the surface soils were more or less increased with increasing the basal area of the plants. However, the effect of the species on the pH values of the soils can be best understood if we keep other soil forming factors constant except vegetation. But this type of study has not been performed in the present case. Nevertheless it may be stated that as a calcicolous plant *Tectona grandis* consumes more calcium and some part of it was returned to the soil through litter fall which increased the soil pH. *Shorea robusta* also in some cases increased the soil pH.

The data in Table-IIA suggest that the soils of pedon - 2,5 to 7, 9,10 and 12 to 14 may be called as acid soils according to the taxonomic system as the pH values of surface soils were less than 5.5 .

The accumulation of organic matter was observed in the top soil due to litter fall and superficial nature of forest tree roots. Among the study sites particularly in lateritic and alluvial areas neither the litter layer (A_{00})

nor the humus layer (A_0) was found. The content of organic matter found in the Sandakphu soil (pedon - 12) was maximum as compared to other study sites.

Compared to hilly soils the lower amount of organic matter was observed in the lateritic and alluvial soils probably due to the oxidation of organic matter by high temperature and relatively low moisture level. The organic matter content in most of the cases was maximum in the surface soils and it decreased down the profile.

In lateritic soils the amounts of organic matter and total nitrogen were very less. In the soils under lower hill area (pedon-13 and 14) the total nitrogen content was fairly high and as a result the C/N ratio was narrow. The results are in agreement with the finding of Yadav et al. (1968). In most cases the C/N ratio more or less decreased down the profile. The high C/N ratio both in the surface and in the sub-surface soils of Sandakphu (pedon-12) indicated that the organic matter was in the **partially** decomposed state. Similar observation was also reported by Nath and Deori (1976) and Roychoudhuri et al. (1983) in some hilly soils of Arunachal Pradesh.

Organic carbon bears a significant positive correlation (r = + 0.793) with nitrogen content of the soils (Table - XI).

In most of the soils under lateritic (pedon - 1 to 9) and hilly (pedon - 12 to 14) areas show a definite increase in clay content with increase in depth and had well developed argillic sub-surface diagnostic horizon while in pedon - 11 under alluvial soil the clay content decreased with depth of the profile.

Cation exchange capacity (C.E.C.) of the lateritic soils was much less than that of hilly soils and generally increased down the profile with increasing clay content. The C.E.C. of soil strongly depended on the quantity and quality of organic matter and on the pH of the soil. It was seen from Table - IIA that the surface soil of hilly area under Abies densa had maximum C.E.C. (38.36 me/100g) followed by Ailanthus grandis (18.22 me/100g) and mixed vegetations (14.79 me/100g). The highest C.E.C. under Abies densa may be due to the nature and composition of humus present in the soil. Considering the clay and organic matter content of these soils, the C.E.C. values were rather low and obviously indicated the dominance of low C.E.C. clay minerals.

The amount of exchangeable calcium increase downwards in all pedons. Among the exchangeable bases calcium was the dominant one followed by magnesium, potassium and sodium. In Sandakphu soil (pedon - 12) the amount of exchangeable calcium decreased downwards. In pedon - 13 and 14 the exchangeable calcium in the sub-surface soil was lower in comparison to the surface soil. The exchangeable potassium increased downwards in pedon - 5 to 7, 9 and 10, and decreased in pedon - 14. The exchangeable sodium increased downwards in pedon - 3 to 7, 9 to 11 and 14. In pedon - 2 and 8 sub-surface soil had maximum exchangeable sodium than that of its surface soils. The exchangeable sodium was minimum in hilly soil (pedon - 12 to 14).

In the lateritic area (pedon - 1 to 7), the exchangeable calcium and potassium (Table - IIA) was maximum in surface soil under Tectona grandis (pedon - 1 to 3) followed by Shorea robusta (pedon - 4, 5 and 7) and Eucalyptus (pedon - 6). Yadav (1963) and Yadav et al. (1968) observed the same thing. Considering the total amount of exchangeable bases in the surface soils under three different vegetations, the soil under Tectona grandis had maximum amount of exchangeable bases (2.372 - 4.584 me/100g) where major part was contributed by calcium alone (1.948 - 3.89 me/100 g). Eucalyptus (2.058 me/100g) stood second and Shorea robusta (0.687-1.91 me/100g) contributes the least.

The relatively higher concentration of exchangeable calcium and magnesium under Tectona grandis acts to elevate the soil pH values. The results show that there is an increase of soil pH with the increase of total exchangeable bases in surface soil under particular type of vegetation.

Although the surface soil under pedon - 7 and 9 had same pH values but in case of pedon - 9 total exchangeable bases and exchangeable calcium, magnesium and potassium were minimum. Although the total basal area under site - 9 was higher than that of site - 7, the lesser amount or organic matter was observed in site -9. This may be due to the higher amount of exchangeable bases (Yadav, 1968) favouring rapid decomposition of organic matter.

In pedon - 7 to 9, under Shorea robusta the exchangeable calcium, magnesium and total exchangeable bases, C.E.C. and base saturation of the surface soil increased as the total area of the vegetative cover increased.

From the above results it may be inferred that the physico-chemical properties of soils were partly influenced by the tree species, their numbers and basal areas.

The total exchangeable bases increased downwards in case of most of the pedons under lateritic area except in pedon - 12. In pedon - 13 and 14 the total exchangeable bases in the sub-surface soil were lower than that of its surface. The total exchangeable bases were minimum in pedon - 7. Base saturation of the three types of soils increases in the following order:

Lateritic & Alluvial soil	$>$	Lower hill forest soil	$>$	High altitude hilly forest soil (Sub-alpine)
(pedon - 1 to 11)		(pedon -13 & 14)		(pedon - 12)

The percentage **base** saturation was maximum in lateritic soils and minimum in hilly soils. The low base saturation values in hilly soils are in agreement with the values obtained by Pal et al. (1984).

It is observed from Table -IIB that exchangeable Al^{+3} contributed to the soil acidity in major instances.

The ΔpH (difference between pH in water and 1(N) KCl) of Sandakphu soils was fairly wide suggesting that the pH of these soils were not near their zero point charge.

The distribution of mobile form of Fe_2O_3 and Al_2O_3 along the profile of the hilly soils (pedon - 12) indicated the absence of any zone of accumulation (Table -IIB). Moreover, the greater amount of sesquioxides present in surface soil precluded the process of podzolization in operation.

5.2.3.2 Elemental analysis of soil

The results of elemental analysis (Table - III) revealed that silica as **expected** was the major constituent of soil mass (71.63-95.58 percent in lateritic soils, 71.35 -84.45 percent in alluvial soils and 60.035 - 74.06 percent for hilly soils).

In case of pedon - 3, 6, 7, 9 and 14 , the amount of SiO_2 decreased as the depth of the profile increased and reverse was the case in pedon - 11 to 13. In other pedons there was no well defined sequence of its distribution along the profiles. The surface horizons of almost all the lateritic soils were more silicious as indicated by higher SiO_2/Al_2O_3 ratio. Next to silica, sesquioxides (R_2O_3) dominated where alumina contributed higher proportion than iron oxides. The amount of R_2O_3 and Al_2O_3 in pedon - 12 and 14 were high in **comparison** to other pedons. In pedon - 13 and 14 both R_2O_3 and Al_2O_3 increased downwards.

In pedon - 4, 6 and 9 the amount of R_2O_3 in the sub-surface soil was high as compared to surface and sub-soils. In lateritic soil (pedon - 1 to 9), the amount of Fe_2O_3 increased downwards in a profile. This observations are in agreement with the findings obtained by Dolui et al. (1985) in some soils of lateritic area.

The highest amount of CaO and MgO was observed in hilly soils (pedon - 12 to 14) and lateritic soils of pedon - 5 respectively. The maximum amount of K_2O was found in pedon - 10 and 12 to 14 which might be due to the presence of maximum amount of illite and/or mica like minerals.

In West Bengal, climate, latitude, longitude, soil etc show a great range of variation and the resulting reaction ultimately create distinct environment for the growth and development of different forest types.

Among the soil forming factors parent material, topography, climate and time do not change much within a short period and as a result their effect on soil properties within a limited period is negligible, but changes in composition and density of vegetation have bearing on soil properties. Hence, differences in vegetation type will reflect difference in soil properties.

From the foregoing results it is evident that for some nutrients most notably calcium, large species differences existed in the mineral soil, forest floor as well as vegetation. This site - related differences may be accounted for by the transfer of calcium from the surface mineral soil horizons to the vegetations and to the forest floor via litter fall.

Forest soil acidity is strongly affected by the decomposition processes occurring in the forest floor, which are in turn, strongly species - dependent. It ia slso known that soil acidity is determined at least in part by vegetation uptake of calcium. In Tectona grandis the effect is very much pronounced.

The study brings out that soil properties determine the species that become established on a site, and many of the properties studied reflect the site - species/ community relationship. The study of the nutrient accumulation in the mineral soil might only give part of the interpretations of the impact of species on sites and as such the study leaves many intricate questions and various interactions unanswered.

CHAPTER - VI

SOIL ORGANIC MATTER

6.1 Nature and characteristics of soil organic matter under different vegetations

Hundeshagen (1830) was the first forester who recognized the importance of organic matter decomposition and the development of different forms of humus. Emeis (1875) classified forest humus into three types, the first one of well decomposed organic matter incorporated with the mineral soil and containing nitrogen in the form of ' nitric acid', and the other two of ' raw ' organic remains.

The simple concept of superficial organic matter was at one time or another referred to as 'mor', 'mar', 'moor', 'torf', 'dry peat', 'raw humus', 'surface humus', 'duff' and 'holorganic layer', (Wilde, 1957).

Mull and mor humus are not synonymous with 'sweet' and 'sour', humus as was believed originally. The reaction of humus layers varies within the very wide limits of pH 4.8 to pH 8.5 for mull humus and pH 3.0 to pH 8.0 for mor humus. However, within each of these morphological groups the pH value determines the compositions of the microbiological populations and the nature of metabolic by products (Wilde, 1957).

The nature, composition and characteristics of organic components or humus vary from soil to soil. In a series of soils ranging from podzolic to chernozems humus appears to increase in complexity. In such circumstances, it is always advantageous to try to look at humus from different angles and combine the results from a veriety of measurements to arrive at a consistent understanding of it. This is the general basis on which the investigations reported in the thesis were planned and carried out.

6.2 Experimentals

6.2.1 Extraction, fractionation and purification

For extraction of humus materials the soil was shaken with 0.5(N) NaOH solution (maintaining soil : solution = 1 : 10) for 2 hours in a mechanical shaker and then kept over night. The supernatant obtained was centrifuged and then acidified with 2(N) HCl to pH 2.0 and allowed to stand at room temperature for 24 hours. The soluble material (Fulvic acid) yellow in colour was separated from the coagulant (Humic acid) by centrifugation. The humic acid which was brown to black in colour was again brought into solution by adding 0.5(N) Na_2CO_3 solution and reprecipited. The process was repeated. During the process of precipitation and dissolution ash was removed as froth formed on the surface. The process was repeated until froth became white in colour.

Humic acid (HA) was then further purified by shaking at room temperature with dilute solutions of HCl - HF (0.5 ml con. HCl + 0.5 ml of 48% HF + 99 ml of water). The material was kept overnight and the residue was washed with distilled water. The humic acid suspension was then dialysed against distilled water until free of chloride ion.

The yellow colour supernatant containing fulvic acid (FA) was then precipitated by adding small amount of $BaCl_2$ solution and dilute NaOH drop by drop until pH of the solution raised to 8.0, when a brown colour precipitate of Ba-fulvate was obtained. Ba-fulvate was converted into fulvic acid again by treatment with HCl and again converted into Ba-fulvate. This process was repeated thrice and Ba-fulvate was then dialysed against distilled water. Fulvic acid was prepared fresh by passing the aquous suspension of Ba-fulvate through a column packed with Amberlite IR - 120 resin in the H-form.

6.2.2 Determination of Humic and Fulvic components

Carbon content of humic and fulvic acids **were** determined by the rapid method of Kononova and Belchikova (Kononova, 1966).

6.2.3 Determination of Ash

Ash contents of humic and fulvic acids were determined by igniting samples in Pt-crucibles at 750°C for 4 hours

(Schnitzer and Preston, 1983).

6.2.4 Elementary analysis

Elemental carbon (C) and nitrogen (N) of humic and fulvic acids were determined by dry combustion method and micro Kjeldahl method respectively.

6.2.5 Conductometric and Potentiometric studies

The fulvic and humic acid components of each sample were titrated conductometrically (using Toshniwal conductivity bridge) at 30° ± 0.1°C and potentiometrically (using Elico-electric pH meter) at 30° ± 0.1°C with 0.06 (N) NaOH solution.

6.2.6 Determination of Acidity

a) Total acidity and Carboxyl acidity

Total acidity and carboxyl acidity of humic and fulvic acids were determined separately potentiometrically and Ca-acetate method (Schnitzer and Gupta, 1965) respectively.

b) Phenolic hydroxyl acidity

Phenolic hydroxyl acidity of humic and fulvic acids was determined by substracting carboxyl acidity from total acidity.

6.2.7 Determination of Coagulation threshold

The 0.02% solution of Na-humate (pH 8.0) was used for the determination of coagulation threshold values with $CaCl_2$ as the electrolyte. The concentration of $CaCl_2$ solution was such that its final concentration in the humate solution varied from 1 to 20 me/liter. Increasing volumes of this solution from 0.05 to 1 ml were added to a series of test tubes with the help of a microburette and the volume of liquid in each tube was made upto 1 ml with distilled water. 5 ml of Na-humate solution was added to each tube so that the total volume in each tube was 6 ml.

After adding the humate solution the tubes were stoppered and shaken. The time in hours and the corresponding amounts of electrolytes (me/liter) were recorded for (i) the beginning of coagulation as indicated by the appearence of turbidity in the original transparent solutions and (ii) complete coagulation when the solution above the coagulum become transparent. The nature of change in each tube after two hours was recorded (Banerjee and Mukherjee, 1972).

6.2.8 Optical studies

i) Visible spectra

The light absorption properties of humic and fulvic acids were investigated over the visible region of the spectrum Na-salt of humic acid was used for this purpose. Fulvic acid was used as such. The absorption measurement was made with Carl-Zeiss spectrophotometer using quartz and corex cell of

1 cm thickness. For the comparative study of the degree of polymerisation of Na-humates and fulvic acid of different soils, a constant concentration of the components was maintained. The ratio of optical density at 465 m/u to that at 665 m/u was determined (Griffith and Schnitzer, 1975; Chen <u>et</u> <u>al</u>., 1977).

ii) Fluorescence excitation spectra

The fluorescence measurement was made in a Hitachi-Perkin Elmer Fluorescence Spectrophotometer equipped with an automatic recorder. All measurements were made at $25^{\circ} \pm 0.3^{\circ}C$ with a constant light path 1 cm thickness (emission slit, 5 nm, excitation slit, 15.3 nm). The emitting radiation wave length was fixed at 520 m/u and the wave length of excitation radiation was varied automatically from 300 - 500 m/u. The fluorescent attachment consisted of a high pressure Xenon lamp which served as the source of ultra-violet and visible energy imaged on to the entrance site (1 nm) of an exciting monochramoter. Energy of any selected wave length was directed from the monochromator into a sample. The resultant fluorescence of the sample at right angles to the exciting beam entered an analysing monochromator. It fed into a photomultiplier producing a signal which was directly recorded on paper.

The humic acids of different soils in Na-form (pH 8.0), were used for fluorescence measurement. The concentration of the solution in each case was 0.0018%. Fulvic acids (0.001%) were used as such (Spiteller and Schnitzer, 1983).

6.2.9 Infra-red Spectra (IR)

The Infra-red spectra were recorded on KBr pellets prepared by 1 mg dried sample ground with 400 mg KBr for 2 minutes in a ball and the mixture pressed into disks which were dried thoroughly in vacuum over 48 hours before taking the spectra. A Perkin Elmer IR Spectrophotometer (double beam) model 283 fitted with a NaCl prism was used to determine the spectra. The spectra were recorded over the region 2.5 to 14 μ .

6.2.10 Viscosity

The viscosity measurement was done by using Ostwald viscometer (Cannon-Fenske) having flow time for 5 ml of distilled water 224.3 seconds at 25°C.

The relative and specific viscosities were calculated from the relation as shown below :

The relative viscosity (η_r) is defined as :

$$\eta_r = \frac{\eta}{\eta_0} = \frac{\rho . t}{\rho_0 . t_0} \approx \frac{t}{t_0} \qquad ....(1)$$

where η and η_0 are the viscosities, ρ and ρ_0 the densities and t and t_0 the time of flow for the solution and solvent(water) respectively. Since the densities of solution and water are more or less identical, η/η_0 is simply equal to t/t_0.

Now, the specific viscosity (η_{sp}) is

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \eta_r - 1 \qquad \text{........(2)}$$

The reduced viscosity (η_{red}) is

$$\eta_{red} = \frac{\eta_{sp}}{C} = \frac{\eta_r - 1}{C} \qquad \text{........(3)}$$

Where, C is the concentration (wt/vol %) of the solute.

The intrinsic viscosity $[\eta]$ is

$$[\eta] = \left(\frac{\eta_r - 1}{C}\right)_{C \to 0} \qquad \text{........(4)}$$

Therefore, intrinsic viscosity can be obtained by extrapolating the curve of reduced viscosity against concentration to zero concentration.

Sodium humate was prepared by treating a concentrated suspension of dialysed humic acid (low in ash) with a dilute solution of NaOH to pH between 8.0 to 9.0. The solution was then concentrated and the Na-salt was precipitated by the addition of alcohol-acetone mixture. The precipitate was then centrifuged and freed from any excess of alkali after washing several times with 95% neutral alcohol. The salt was finally dried on water bath at 85°C and preserved in a desicator.

6.3 Results and Discussion

6.3.1 Humus and its components present in soil

The results presented in Table -IV show that the amount of organic matter extracted by alkali treatment varied with the nature of the soil. In general, more humic substances were extracted from hilly soils (Pedon - 12 to 14) than from lateritic and alluvial soils. But relatively high amount of humic substances was also extracted from the soils of pedon - 6 of the lateritic areas under Eucalyptus spp. Minimum quantity of humic substances was extracted from the lateritic soil samples of pedon - 2 and 3 under Tectona grandis and pedon - 7 under Shorea robusta. The extractable humus content in pedons - 2, 3, 6, 8, 12 and 14 increased downwards with depth. The amount of humus extracted from the hilly soils of pedon - 12 was the highest.

The humic acid C : fulvic acid C ratio (C_h/C_f) of surface soil of pedon - 1 and 2 under Tectona grandis were 1.0186 and 0.937 respectively and that of pedon - 5, 7 and 9 under Shorea robusta were 0.837, 0.809 and 0.815 respectively. The narrow C_h/C_f ratio in some soils indicates the low degree of humification of organic matter. It may be noted that the extent humification in the surface soil under Tectona grandis (pedon - 1 and 2) was higher than that under Shorea robusta (pedon - 5, 7, and 9). The C_h/C_f ratio of surface soils of pedon-13 under mixed vegetation and pedon-14 under <u>Ailanthus</u> <u>grandis</u> were 0.606 and 0.356 respectively and that of pedon-12 under <u>Abies</u> <u>densa</u> (Sandakphu soil, Sub-alpine) was 0.735. The ratio of humic to fulvic acids (C_h/C_f) of surface and sub-surface soils of lateritic and alluvial soils were found to be higher than that of hilly soils.

According to Gieseking (1975) the C_h/C_f ratio lying between 0.4 to 0.8 was characterised mainly by aliphatic groups. Therefore, it may be inferred that the humus of the surface soils of pedon-3,12 to 14 were more aliphatic in nature than that of the soils of rest of the pedons.

In most of the cases the downwards translocation of humic acid was not very pronounced yielding no zone of accumulation. Humus as a whole was not very mobile and accumulated in or near the surface horizon.

From the statistical analysis it was found that total soil organic carbon showed a significant positive correlation with humus carbon ($r = + 0.995$), humic acid carbon ($r = + 0.889$) and fulvic acid carbon ($r = + 0.991$) The correlation coefficients between humus carbon and humic acid carbon ($r = + 0.887$) and between humus carbon and fulvic acid carbon ($r = + 0.996$) were also positive and significant (Table - XI).

6.3.2 Elementary analysis

The carbon (C) and nitrogen (N) contents of different humic and fulvic acids have been presented in Table - VA. The results show that the percentage of carbon in different fulvic acids under Tectona grandis, Shorea robusta and Eucalyptus spp. varies from 46.57 to 50.36, 46.2 to 49.45 and 46.5 to 46.95 respectively. Their corresponding nitrogen percentages varied from 2.12 to 3.41, 1.79 to 3.65 and 2.23 to 2.54 respectively. The amount of fulvic acid carbon of alluvial and hilly soils varied from 44.83 to 49.47 percent and 40.09 to 48.35 percent respectively, while the corresponding nitrogen percentages varied from 1.68 to 2.56 and 1.26 to 2.51 respectively.

The elemental carbon percentage of different humic acids under Tectona grandis, Shorea robusta and Eucalyptus spp. varied from 53.92 to 61.29, 50.4 to 62.07 and 57.63 to 58.96 respectively. The humic acids under Tectona grandis showed the highest percentage of elemental nitrogen (2.95 - 4.53%) followed by Eucalyptus spp.(2.35 - 2.66%) and Shorea robusta (1.55 - 2.8%). The highest amount of elemental C and N in humic acid was observed in the surface soil of pedon - 12 under Abies densa (C = 65.97%, N = 6.2%). The results of the elemental analysis of the humic components are in accordance with the findings of Rogzyk (1963), Kononova (1966), Schnitzer (1977) and Hatcher et al. (1981a, 1981b). It is also observed from Table - VA that with increasing the depth of the profile the percentage of elemental C and N of humic acid more or less decreased with a few exceptions (pedon - 4 and 7).

The C/N ratio of different surface and sub-surface soil humic acid under *Tectona grandis* (pedon - 1 to 3), *Shorea robusta* (pedon - 4, 5 and 7 to 9), *Eucalyptus* (pedon - 6), *Terminalia arjuna* (pedon - 10), mixed vegetation (pedon - 11) and *Abies densa* (pedon - 12) varied from 13.53 to 18.28, 18.0 to 39.06, 21.67 to 25.09, 22.19 to 28.79, 22.29 to 27.43 and 10.47 to 10.62 respectively. The highest content of nitrogen in surface and sub-surface soils of Sandakphu humic acid were due to the highest C/N ratio in these soils. Humic acid of surface soil under *Abies densa* showed low C/N ratio in comparison to that under *Tectona grandis*, *Eucalyptus* spp., *Shorea robusta*, *Terminalia arjuna* and mixed vegetation.

6.3.3 Ash content of humic and fulvic acids

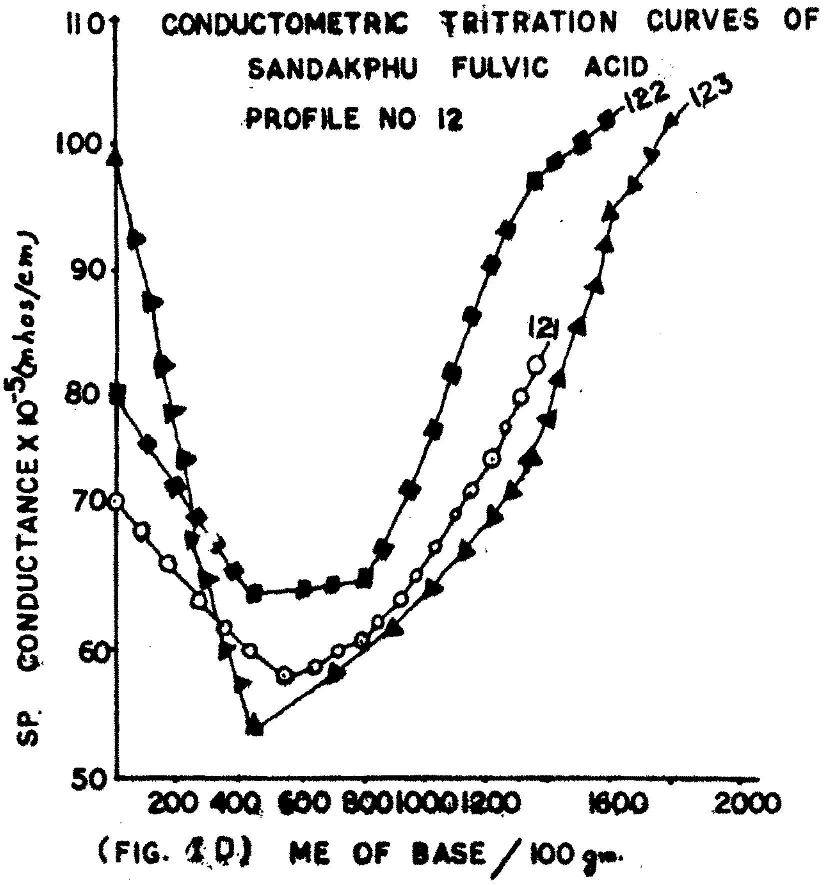
From the results presented in Table - VB it was found that the ash content of dialysed humic acid varied from 0.2 to 9.6 percent. The amount of ash in humic acids (HA) was minimum in case of lateritic soils and maximum in case of hilly soils (pedon - 12). In fulvic acids (FA), the ash content varied from 8.21 to 25.5 percent. It was also evident from the results that humic and fulvic acids of sub-surface soils had higher ash content than those of surface soils.

6.3.4 Conductometric and Potentiometric tritration

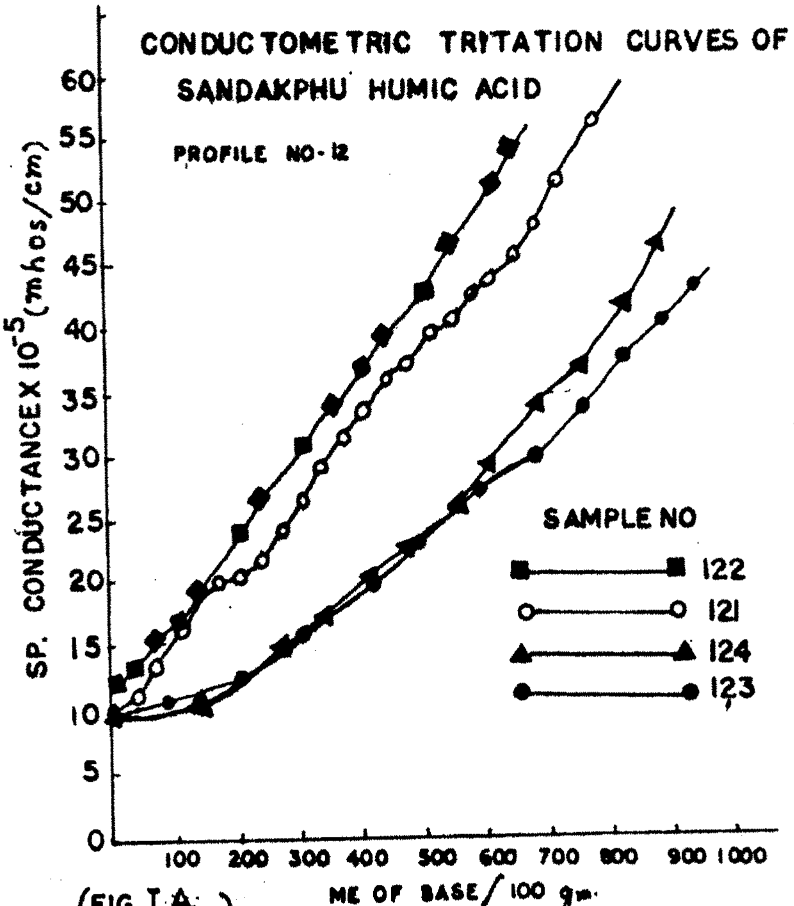
The conductometric titration curves of some humic and fulvic acids have been shown in Figs. IA, IB, IC and ID, IE, IF respectively. The conductometric titration curves of humic acids of lateritic (pedon - 1 to 9) and alluvial (pedon - 10 and 11) soils showed single break, indicating their monobasic behaviour, but hilly soils of pedon - 13 and 14 and only the sub-surface and the sub-soils of Sandakphu (Sub-alpine forest, pedon- 12, i.e., sample No - 122 and 123) showed two breaks and only the surface soil of Sandakphu showed three breaks in the titration curves.

Conductometric titration curves of fulvic acids showed three breaks in most of the samples. The three breakes indicate the presence of three acid functions (Banerjee and Mukherjee, 1975).

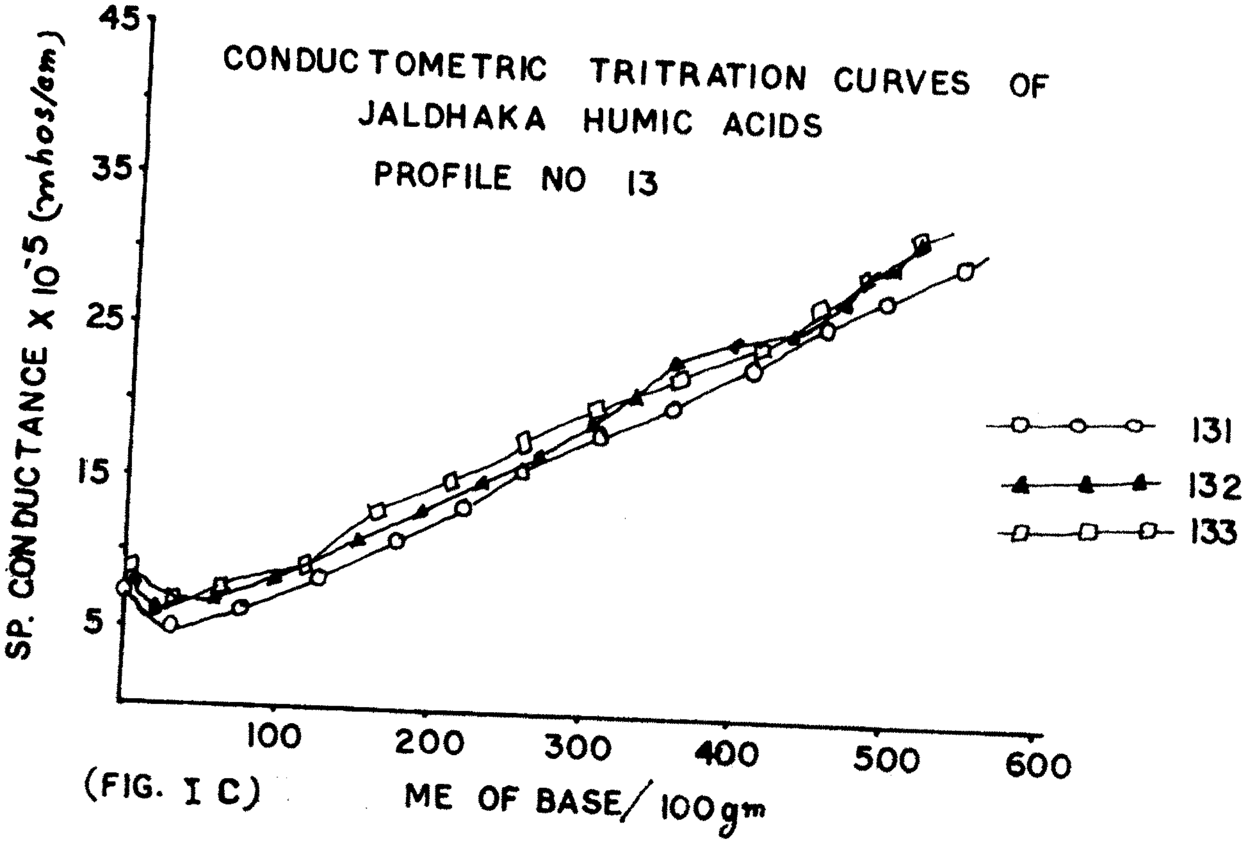
Under the comparable concentrations (40 mg/100 ml) the initial specific conductances of humic acid solutions were different and the values ranged from 3.5×10^{-5} to 6.5×10^{-5} mhos/cm for lateritic and alluvial soils (pedon - 1 to 11) and 5.5×10^{-5} to 12.5×10^{-5} mhos/cm for hilly soils (pedon - 12 to 14). The specific conductance at


CONDUCTOMETRIC TRITRATION CURVES OF
SANDAKPHU FULVIC ACID
PROFILE NO 12
SP. CONDUCTANCE X 10^{-5} (mhos/cm)
110
100
90
80
70
60
50
200 400 600 800 1000 1200 1600 2000
ME OF BASE / 100 gm.
122
123
121

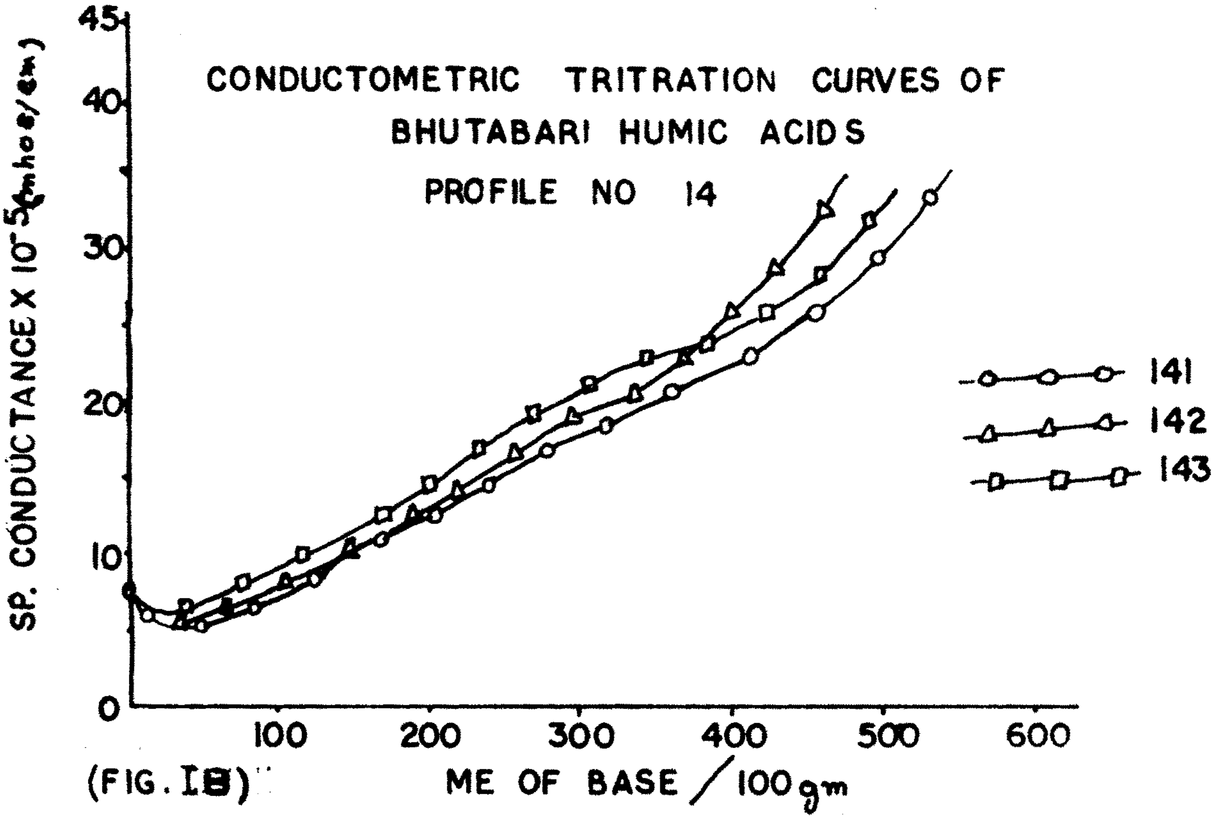
(FIG. 1D)


CONDUCTOMETRIC TRITATION CURVES OF
SANDAKPHU HUMIC ACID
PROFILE NO-12
SP. CONDUCTANCE X 10^{-5} (mhos/cm)
60
55
50
45
40
35
30
25
20
15
10
5
0
100 200 300 400 500 600 700 800 900 1000
ME OF BASE / 100 gm.
SAMPLE NO
122
121
124
123

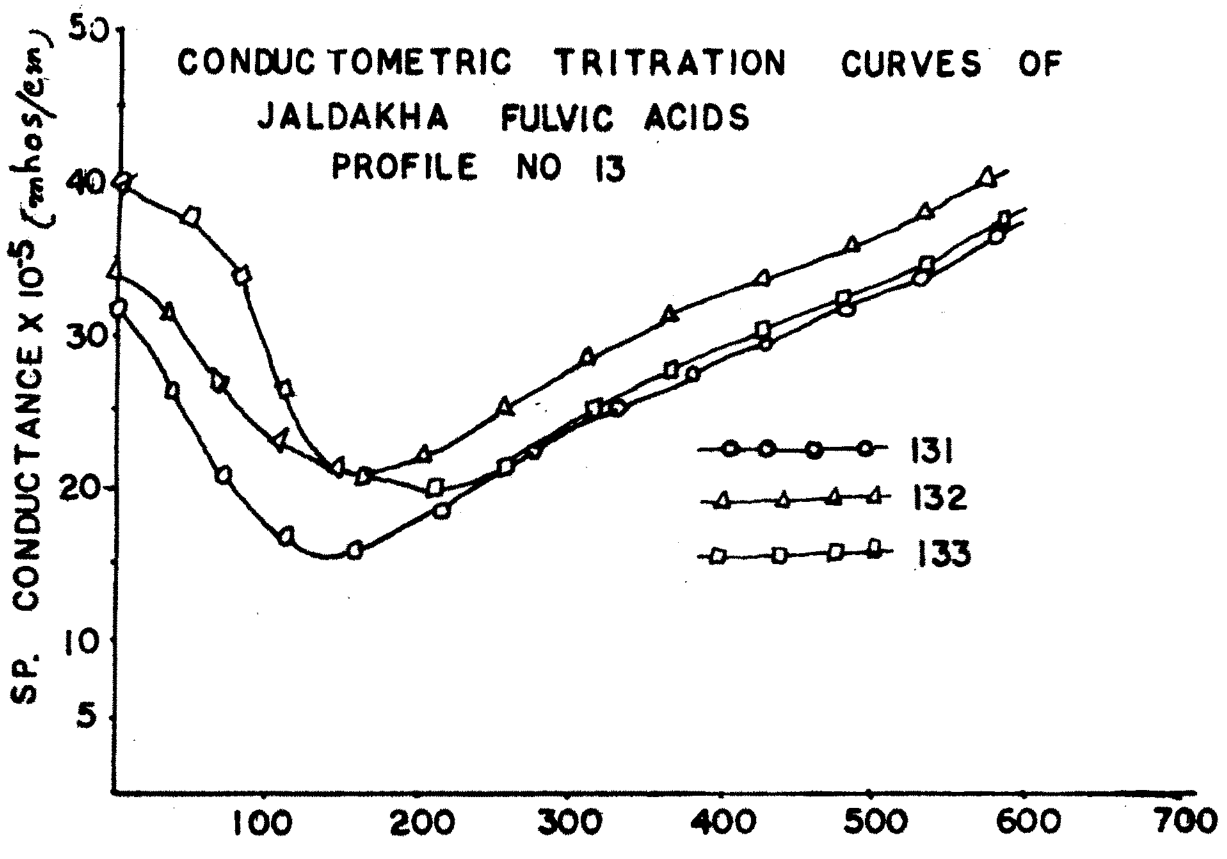
(FIG. I A)


CONDUCTOMETRIC TRITRATION CURVES OF
JALDHAKA HUMIC ACIDS
PROFILE NO 13
SP. CONDUCTANCE X 10⁻⁵ (mhos/cm)
45
35
25
15
5
100
200
300
400
500
600
ME OF BASE/100gm
131
132
133

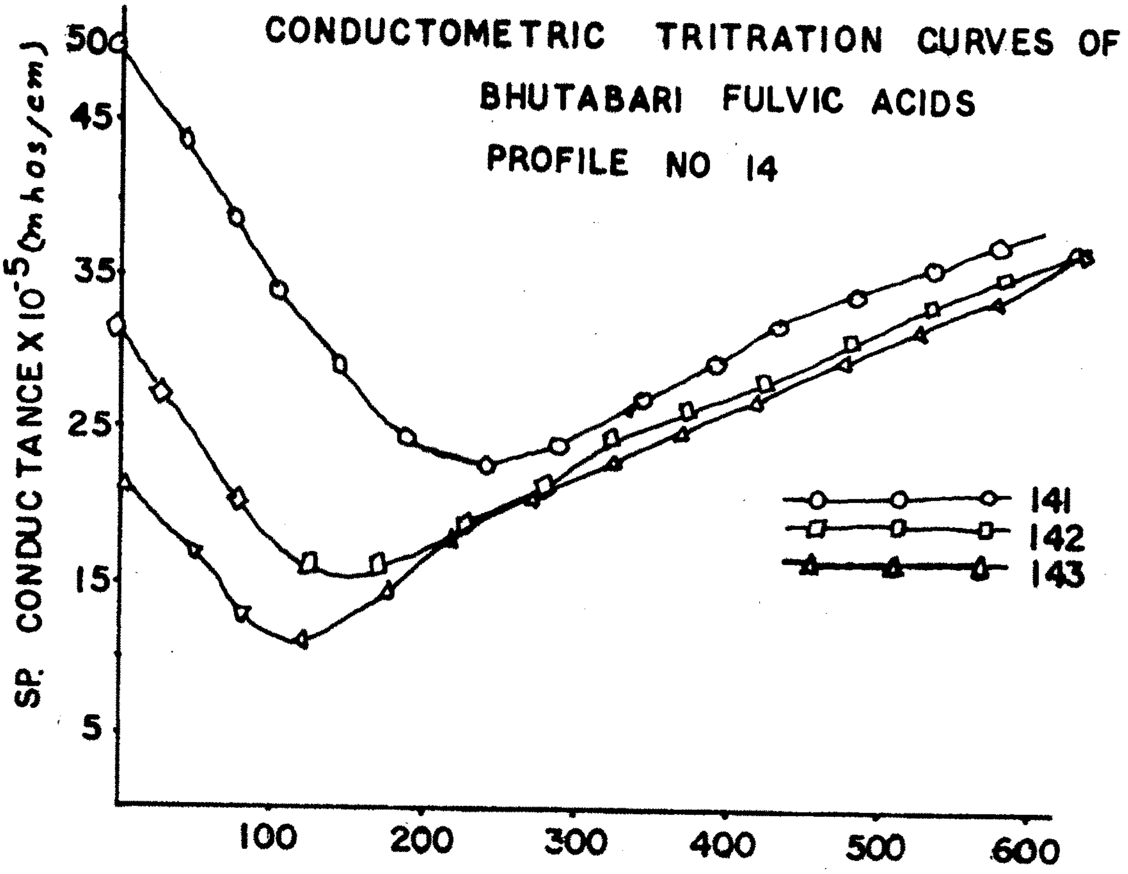
(FIG. I C)


CONDUCTOMETRIC TRITRATION CURVES OF
BHUTABARI HUMIC ACIDS
PROFILE NO 14
SP. CONDUCTANCE X 10⁻⁵ (mhos/cm)
45
40
30
20
10
0
100
200
300
400
500
600
ME OF BASE / 100gm
141
142
143

(FIG. IB)


CONDUCTOMETRIC TRITRATION CURVES OF
JALDAKHA FULVIC ACIDS
PROFILE NO 13
SP. CONDUCTANCE X 10-5 (mhos/cm)
50
40
30
20
10
5
100
200
300
400
500
600
700
131
132
133
ME OF BASE / 100 gm

(FIG. I F)


CONDUCTOMETRIC TRITRATION CURVES OF
BHUTABARI FULVIC ACIDS
PROFILE NO 14
SP. CONDUCTANCE X 10-5 (mhos/cm)
50
45
35
25
15
5
100
200
300
400
500
600
141
142
143
ME OF BASE / 100 gm

(FIG. I E)

the equivalence points in the conductometric titration curves of different humic acids were found to lie in the region 19.5 x 10^{-5} to 44.5 x 10^{-5} mhos/cm. The initial specific conductance of fulvic acids under the same concentration (40 mg/100 ml) ranged from 21.0 x 10^{-5} to 32.0 x 10^{-5} mhos/cm for lateritic and alluvial soils and 21.5 x 10^{-5} to 99.0 x10^{-5} mohs/cm for hilly soils. The specific conductance at the equivalence points in the conductometric titration curves of different fulvic acids of hilly soils, except Sandakphu soil (Sub-alpine forest), ranged from 24.8 x 10^{-5} to 35.5 x 10^{-5} mhos/cm and for Sandakphu soils (pedon - 12) the values lay between 85.0 x 10^{-5} to 97.0 x 10^{-5} mhos/cm.

The initial conductance appeared to be almost entirely due to hydrogen counter ions produced by the dissociation of carboxyl and phenolic hydroxyl groups of these acids. It is to be noted that the initial conductance of fulvic acids was nearly three to nine times greater than that of humic acids indicating that fulvic acids were some what stronger acids.

All the conductometric titration curves of humic acids showed a drop in specific conductance at the low values of α . The minima most probably represented the amount of free hydrogen ion produced by the dissociation of carboxyl groups.

The exchange capacities were calculated from the final breaks of the different humic acids of surface and sub-surface soils under lateritic, alluvial and hilly soils (pedon - 1 to 14). The C.E.C. of humic acids of different horizons of Sandakphu soil (Sub-alpine forest soil, pedon - 12) decreased downwards.

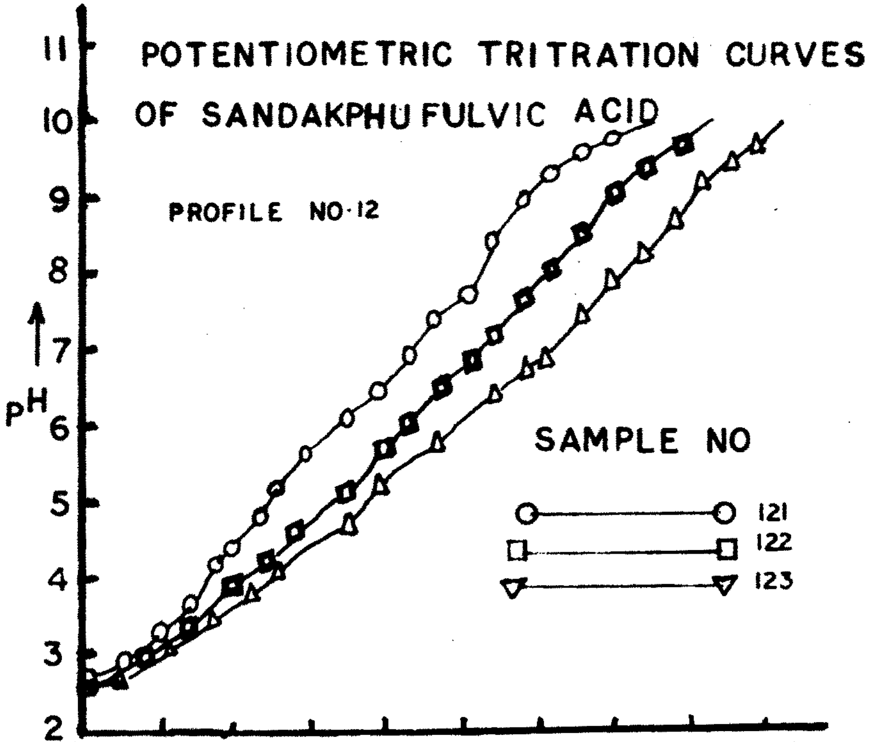
All the conductometric titration curves of fulvic acids showed a pronounced initial drop in specific conductance and a sharp break corresponding to 40-60 percent neutralization. The sharp break was due to the neutralization of the carboxyl groups associated with aromatic ring (Dutta and Mukherjee, 1968 ; Banerjee and Mukherjee, 1975; Banerjee et. al., 1979). The third break in the titration curves of fulvic acid was perhaps due to the neutralization of phenolic -OH groups strongly attached to the benzene rings.

The exchange capacities determined conductometrically from the final breaks of different fulvic acids under alluvial and lateritic soils ranged from 462.0 to 862 me/100g, the highest values 1536.0 me/100g being recorded by the soils of pedon - 12 collected from Sandakphu. For lower hill soils (pedon - 13 and 14) the values ranged from 372.0 to 526.5 me/100g. The C.E.C. of fulvic acids increased with the depth of the profile.

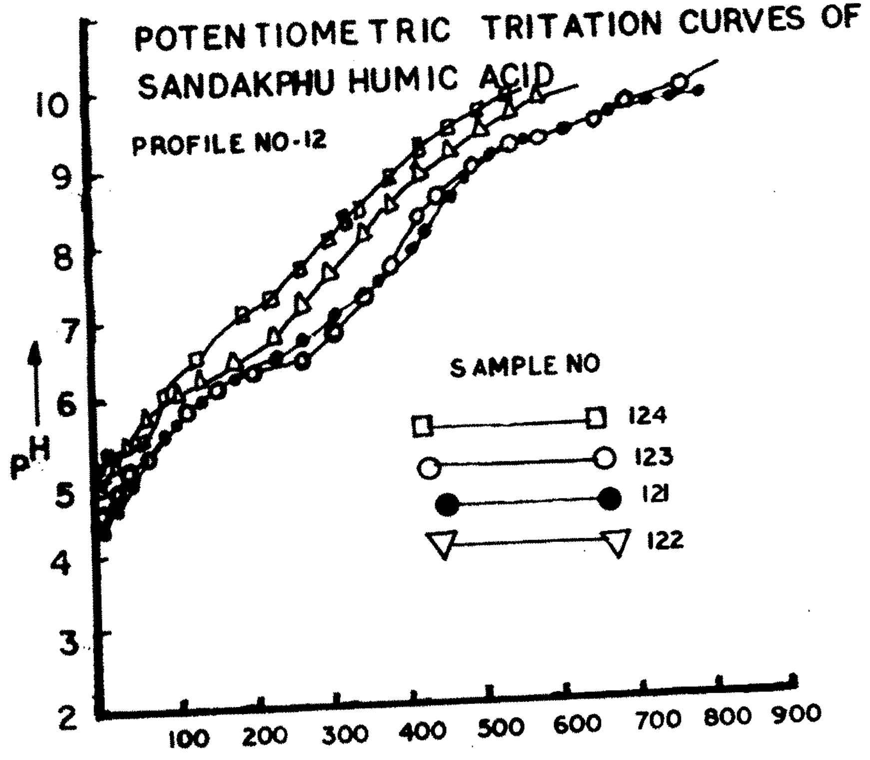
The potentiometric titration curves of some humic and fulvic acids were shown in Figs. IIA, IIB, IIC and IID, IIE, IIF respectively. The potentiometric titration curves of humic acids in most cases showed single break, with an exception in the soils of pedon - 12 to 14 where two breaks were obtained. But in case of fulvic acids in most of the samples two breaks were obtained.

The pH at initial and at the equivalence point in the potentiometric titration curves of humic acid under comparable concentrations (40 mg/100 ml) were different, the values ranged respectively from (i) 4.0 - 4.7 and 8.9 - 9.4 for Tectona grandis (pedon - 1 to 3), (ii) 3.9 - 5.5 and 8.5 - 9.9 for Shorea robusta (pedon - 4,5 and 7 to 9), (iii) 4.75 - 5.0 and 9.7 - 9.9 for Eucalyptus (pedon - 6), (iv) 4.1 - 5.3 and 8.9 - 9.6 for Terminalia arjuna (pedon - 10) and mixed vegetation (pedon - 11), (v) 3.6 - 5.0 and 8.05 - 9.35 for hilly soils (pedon - 12 to 14). The corresponding values for fulvic acids were (i) 2.6 - 2.9 and 9.1 - 9.4, (ii) 2.5 - 2.8 and 8.65 - 9.0, (iii) 2.5 and 8.7 - 8.85, (iv) 2.5 - 3.0 and 9.0 - 9.55, (v) 2.65 - 3.35 and 7.9 - 8.65.

From the Table - VI it is observed that the exchange capacities (C.E.C.) of humic acids determined potentiometrically varied from 315.0 - 440.5 for Tectona grandis (pedon - 1 to 3), 364.5 - 374.5 for Eucalyptus (pedon - 6), 264.0 - 388.0 for Shorea robusta (pedon-4,5



(FIG. II D)



(FIG. II A)

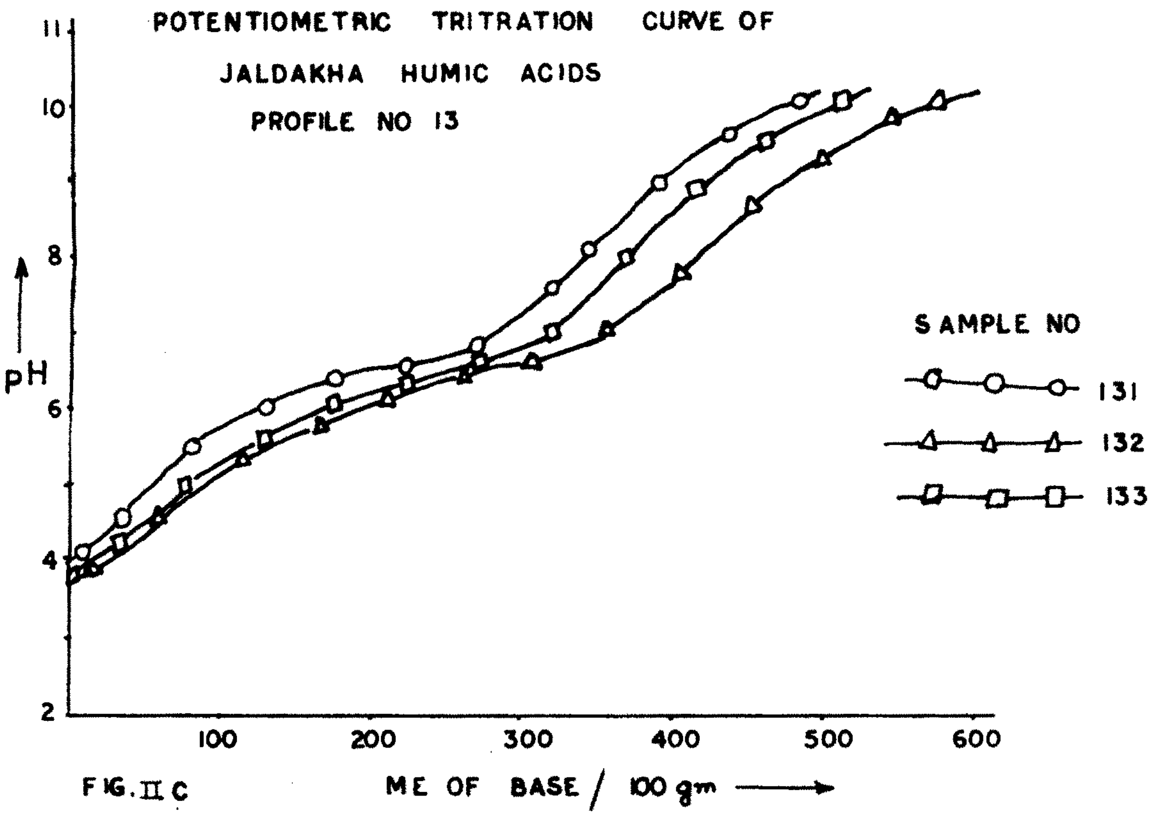

POTENTIOMETRIC TRITRATION CURVE OF JALDAKHA HUMIC ACIDS PROFILE NO 13

FIG. II C

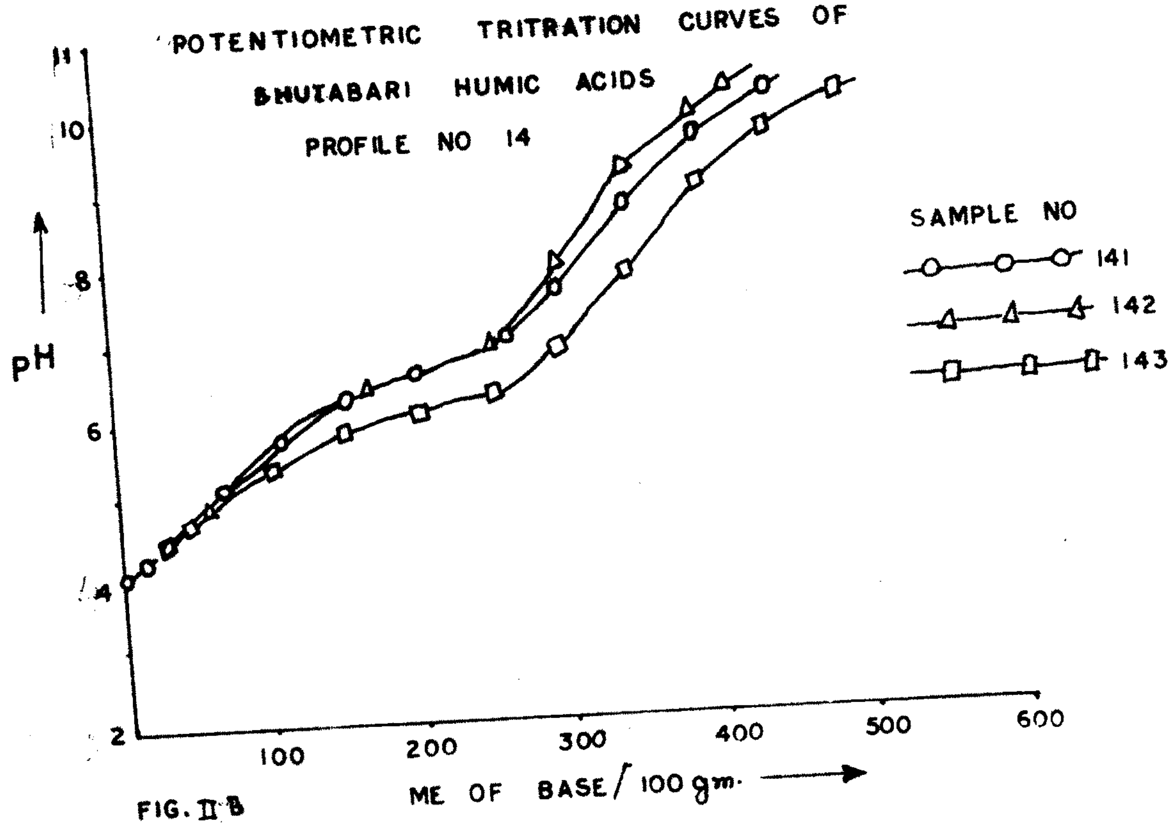

POTENTIOMETRIC TRITRATION CURVES OF BHUTABARI HUMIC ACIDS PROFILE NO 14

FIG. II B

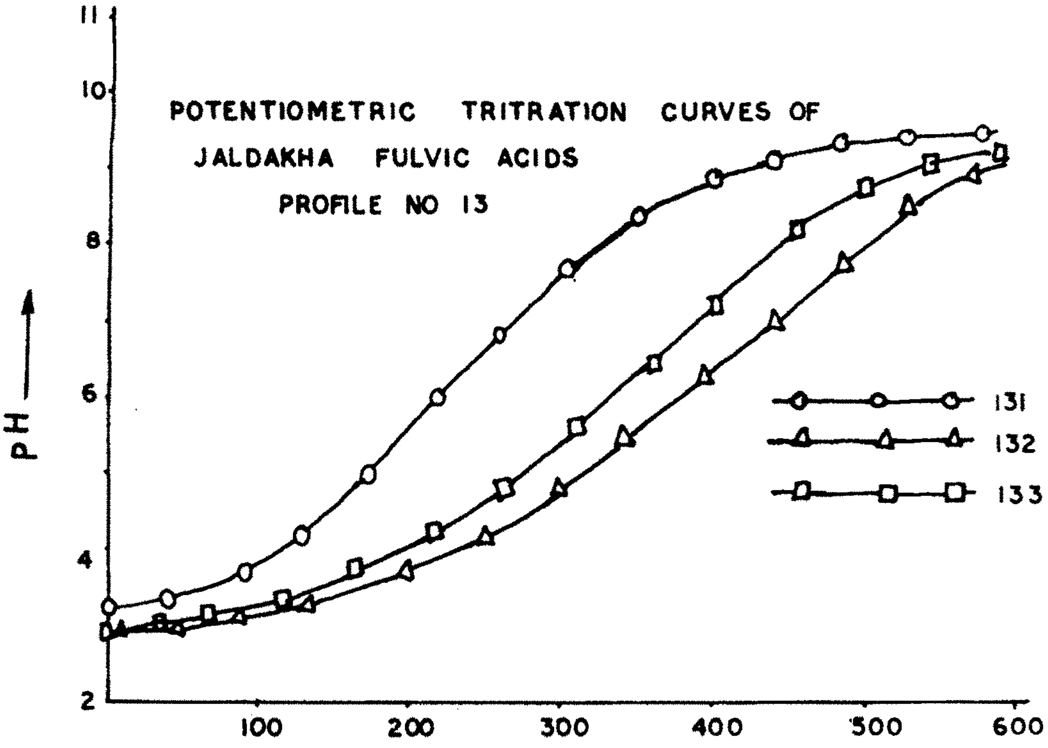


FIG. II F

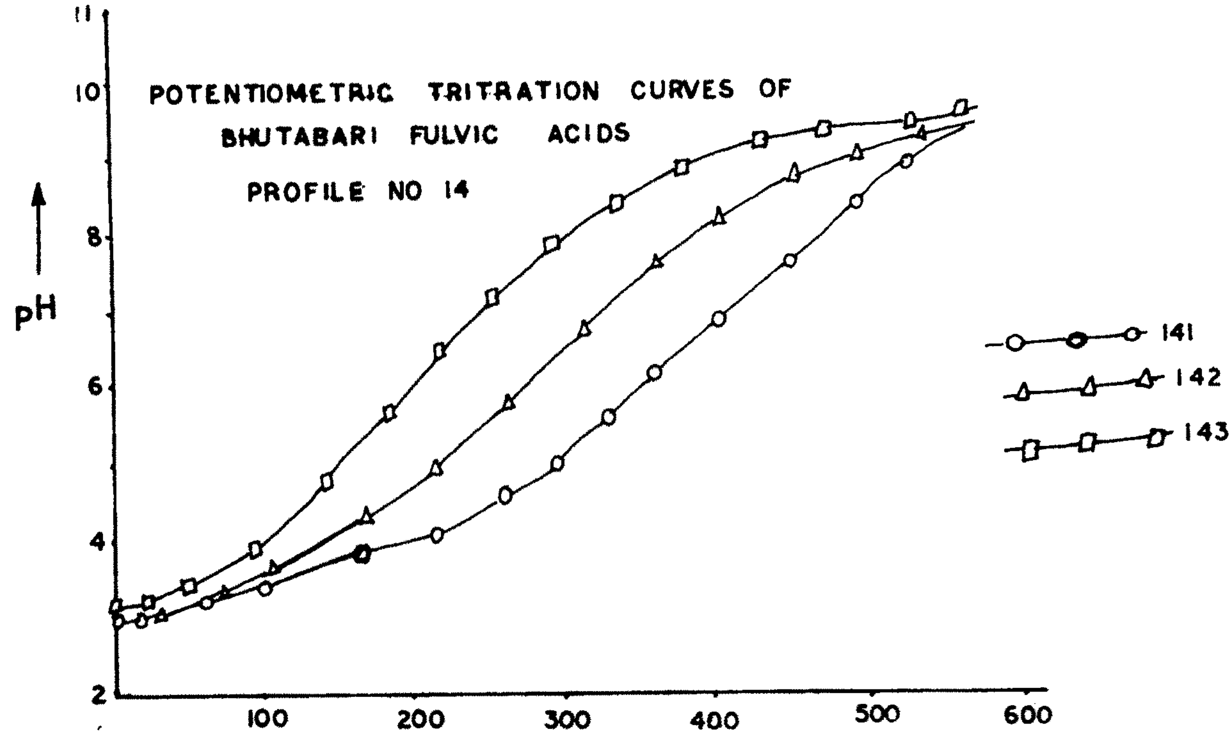


FIG. II E

and 7 to 9) and 256.0 - 289.0 for Terminalia arjuna (pedon - 10), 245.0 - 265.5 for mixed vegetation (pedon-11) and 371.0 - 545.0 for Abies densa, Ailanthus grandis and mixed vegetation (pedon - 12 to 14).

The exchange capacities (C.E.C.) of fulvic acids determined potentiometrically varied from 565.0 - 850.0 for Tectona grandis (pedon - 1 to 3), 655.0 - 798.0 for Eucalyptus (pedon - 6), 445.0 - 702.0 for Shorea robusta (pedon - 4, 5 and 7 to 9), 663.0 - 806.4 for Terminalia arjuna and mixed vegetation (pedon - 10 and 11) and 290.0 - 1557.5 for hilly soils (pedon - 12 to 14).

The total acidity at the equivalence point of humic and fulvic acids of different soils determined from potentiometric titration curves were more or less the same as that obtained from conductometric titrations.

The pK_{av} values of hilly soils (pedon - 12 to 14) were determined from the pH titration curves at 50% neutralization (Table - VII). The appearent pK_{av} values for humic and fulvic acids in absence of electrolytes ranged from 5.99 to 7.2 and 4.09 to 5.9 respectively.

The lack of break at the first equivalence point makes it difficult to decide whether an acid is monoprotic or diprotic. Sturrock (1968) suggested that if the change in pH i.e., △ pH between the 1/4th and 3/4th titration points is about 0.954 pH unit, then the acid is said to be polyprotic. The values of △pH were given in Table - VII. The values indicate that all the acids were polyprotic.

6.3.5 Acidity of humic and fulvic acids

The C.E.C. (total acidity) of humic and fulvic acids is equals to the sum of carboxyl ($-CO_2H$) and phenolic hydroxyl (-OH) groups.

From Table - VA it is found that in most cases carboxyl acidity had accounted for the major acidity in both humic and fulvic acids. Only a few exceptions had been observed in case of humic acids (sample no - 62, 101, 123, 124 and 125) and fulvic acids (sample no - 102and 123) where acidity due to phenolic -OH groups predominated over carboxyl groups. Carboxyl groups were more in fulvic acids than in humic acids.

It has been noticed that in case of sub-alpine forest soil (pedon - 12) as the depth of the profile increased the total acidity and also the carboxyl acidity of humic acid decreased but the acidity due to phenolic -OH groups increased. In case of fulvic acid both the carboxyl and phenolic hydroxyl acidities increased down the profile.

In most cases the acidity of fulvic acid was greater in sub-surface soil than in surface soil (pedon - 1 to 12). Acidity of fulvic acids under Tectona grandis (pedon - 2 and 3) was higher than that under Shorea robusta (pedon - 8 and 9).

Humic acids under Tectona grandis (pedon - 1 and 3) recorded higher C.E.C. values than that under Shorea robusta (pedon - 7, 8 and 9). Humic acids under Terminalia arjuna and mixed vegetation in alluvial soil (pedon - 10 and 11) had the lowest C.E.C. On the other hand humic acids under Eucalyptus (pedon - 6) showed C.E.C. values intermediate between Tectona grandis and Shorea robusta.

Humic acids of Sandakphu soil (pedon -12) recorded the highest C.E.C. From the results presented in Table - VA it was observed that the C.E.C. of humic acid of surface and sub-surface lateritic soils under different vegetations (pedon - 1 to 9) were as follows:

Tectona grandis $>$ Eucalyptus $>$ Shorea robusta

The carboxyl and total acidity of humic acids of a particular type of vegetation increased with the increase of its nitrogen content. The surface soil humic acid under Abies densa (pedon - 12) recorded the highest C.E.C. (545.0 me/100g) and also the highest nitrogen content (6.2%)

followed by that of Tectona grandis, Shorea robusta, Eucalyptus, Terminalia arjuna and mixed vegetations. This is in accordance with the findings of Senesi and Testini (1982).

The C.E.C. of humic acid of surface soil under pedon - 4 (sample no - 41) was lower than that of its sub-surface soil (sample no - 42). This may be due to the effect of vegetation where Diospyros melanoxylon as a second storey and Shorea robusta as a top storey were plantated together, but the reverse was observed in case of pedon - 5, 7 to 9 where total vegetative cover was Shorea robusta. Again the C.E.C. of surface soil humic acid under Terminalia arjuna (pedon - 10) was lower than that of sub-surface but the reverse was the case in pedon - 11 under mixed vegetation.

6.3.6 Spectral studies

a) Visible spectra

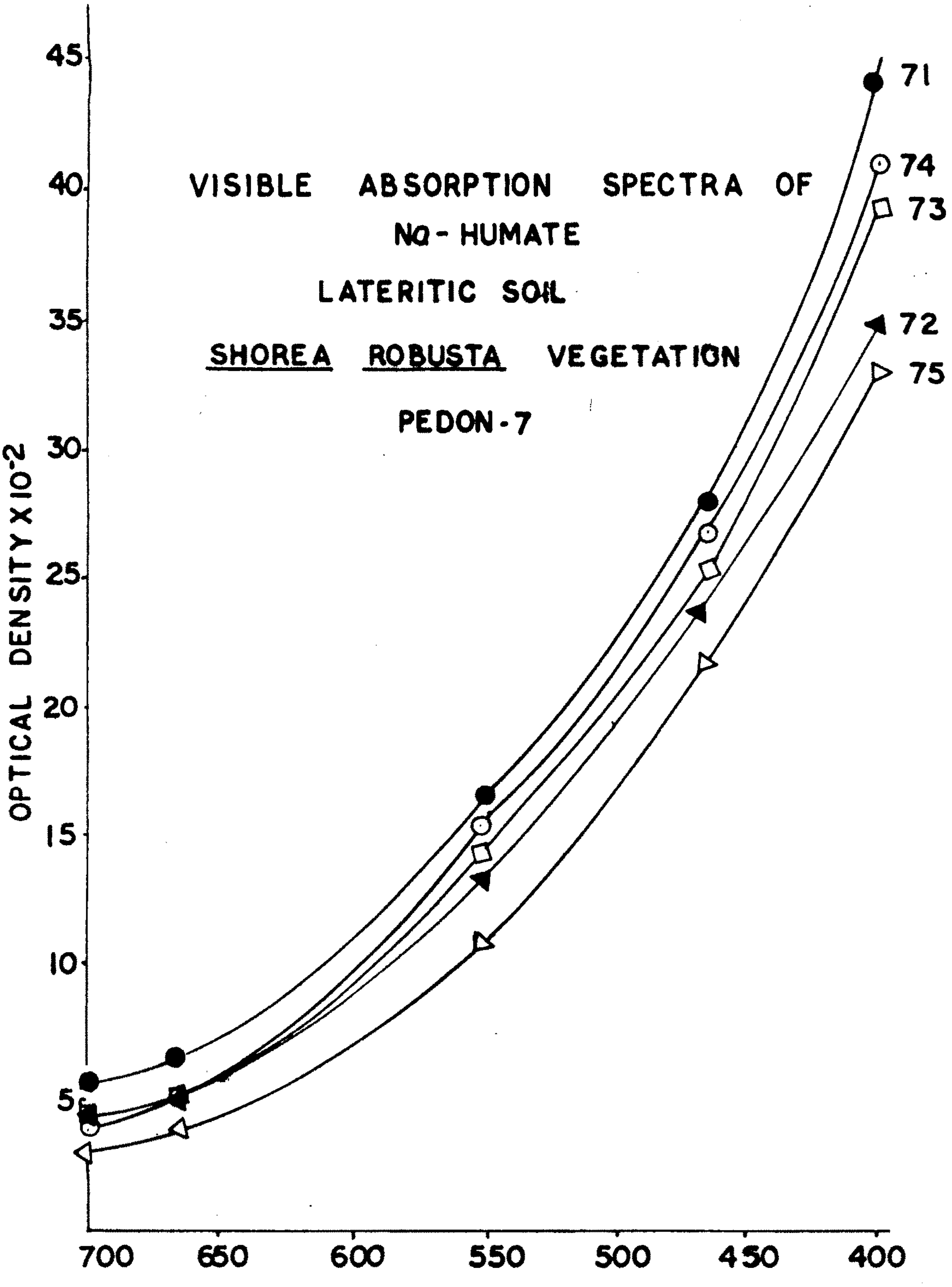
The optical density of humic substances indicates the degree of condensation of aromatic nets or the carbon atoms (Kononova, 1966). It was found that the humic acids had higher optical densities than the fulvic acids. The spectrophotometric titration curves of humic and fulvic acids were shown in Figs. IIIA, IIIB, IIIC and IIID.

The E_4/E_6 values of humic and fulvic acids extracted from the lateritic soils (pedon - 1 to 9) and alluvial soils (pedon - 10 and 11) were found to lie between 3.81 to 5.83 and 7.08 to 12.4 respectively (Table - VB). In hilly soils of pedon - 13 and 14 the E_4/E_6 values for humic acids were between 2.94 to 4.25 and that of fulvic acid 8.42 to 9.62. For sub-alpine forest soil (Sandakphu) the E_4/E_6 values for humic acids ranged from 3.12 to 3.83, whereas in case of fulvic acids the values ranged from 7.45 to 12.08.

It may be noted that the E_4/E_6 values for humic acids were much lower than those of fulvic acids. The E_4/E_6 values of humic and fulvic acids observed in the present investigation were very close to those obtained by Kononova (1966), Schnitzer and Khan (1972), Pospisil and Drozdova (1976), Valkoff and Cerri (1978).

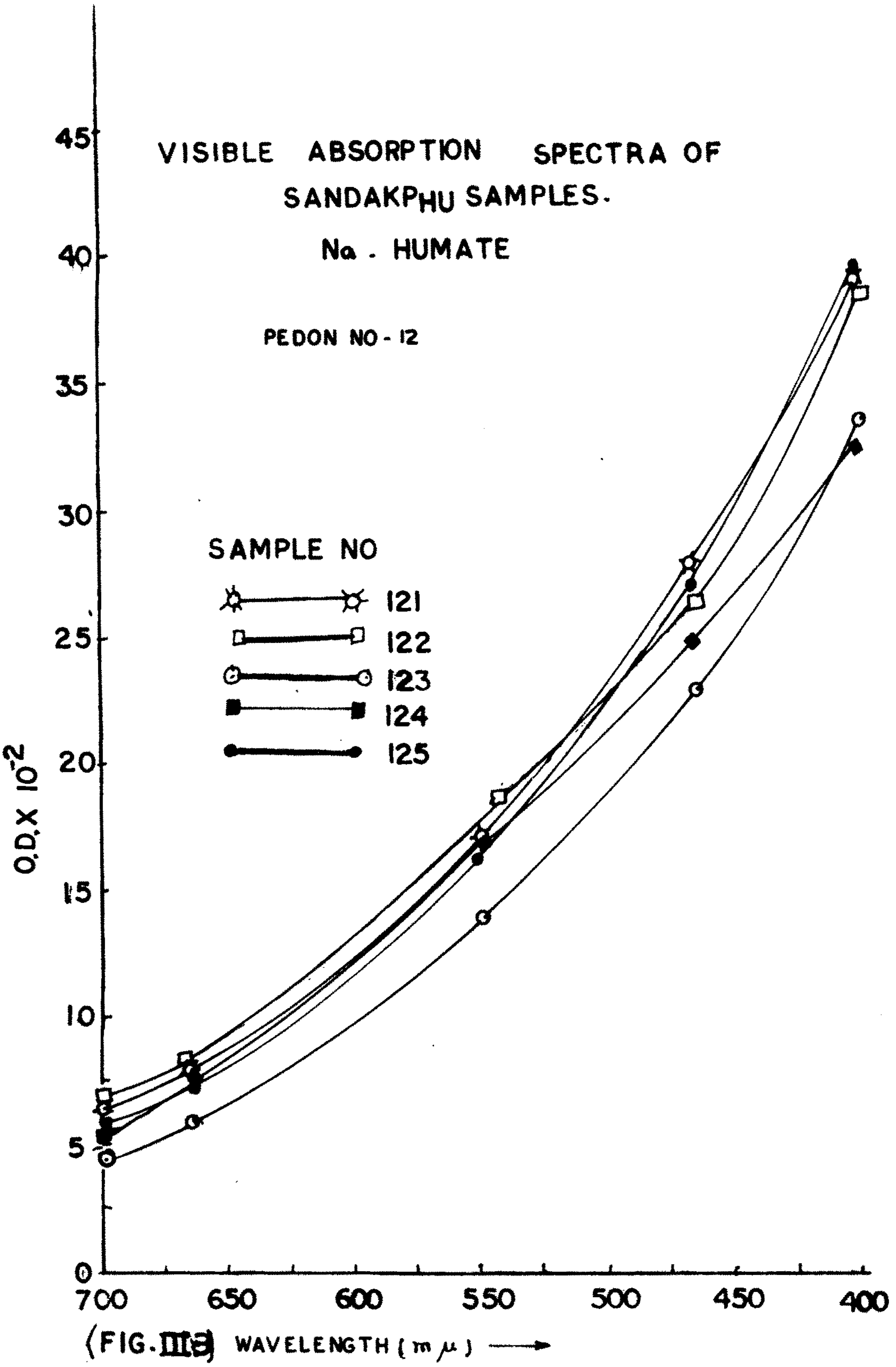
Fulvic acid fractions are more mobile than humic acids because of the less complexity in their structure. The results of the present investigations show that the E_4/E_6 values of fulvic acid of pedon - 13 and 14 decreased downwards with depth. The E_4/E_6 values of humic acids, of pedon - 3, 5 and 7 was found to increase downwards.

It may be observed that, although the E_4/E_6 values of Sandakphu (Sub-alpine) humic acids were lower, its C.E.C.

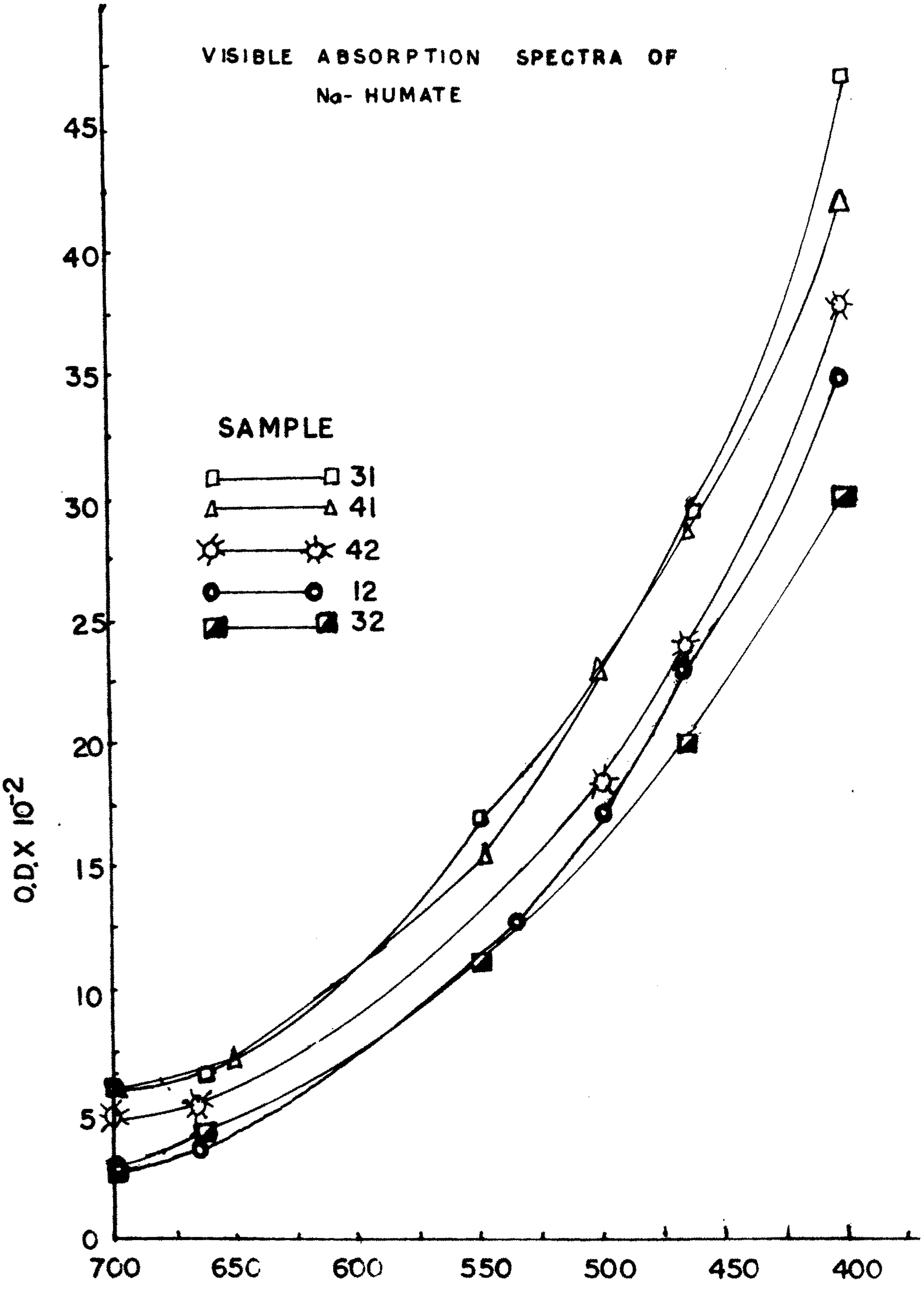


VISIBLE ABSORPTION SPECTRA OF
Na-HUMATE
LATERITIC SOIL
<u>SHOREA</u> <u>ROBUSTA</u> VEGETATION
PEDON-7

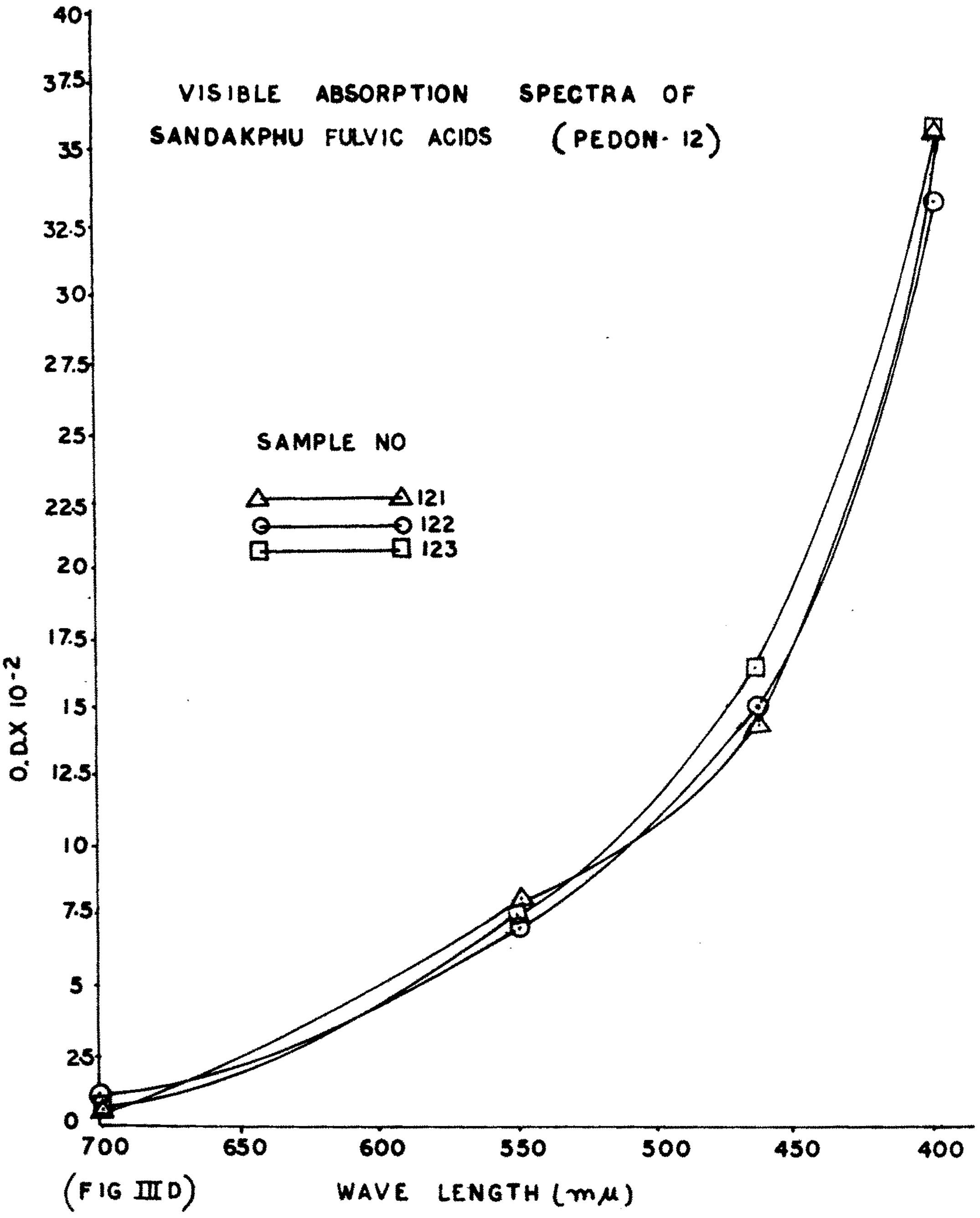
(FIG III A)


VISIBLE ABSORPTION SPECTRA OF
SANDAKPHU SAMPLES.
Na. HUMATE
PEDON NO-12
SAMPLE NO
121
122
123
124
125
O.D. X 10^{-2}
45
40
35
30
25
20
15
10
5
0
700
650
600
550
500
450
400
WAVELENGTH (mμ) →

(FIG. III8)



(FIG. IIIC) WAVELENGTH (mμ) →



VISIBLE ABSORPTION SPECTRA OF SANDAKPHU FULVIC ACIDS (PEDON- 12)
SAMPLE NO
△ 121
⊙ 122
□ 123
O.D.X 10-2
40
37.5
35
32.5
30
27.5
25
22.5
20
17.5
15
12.5
10
7.5
5
2.5
0
700
650
600
550
500
450
400
WAVE LENGTH (mμ)

(FIG III D)

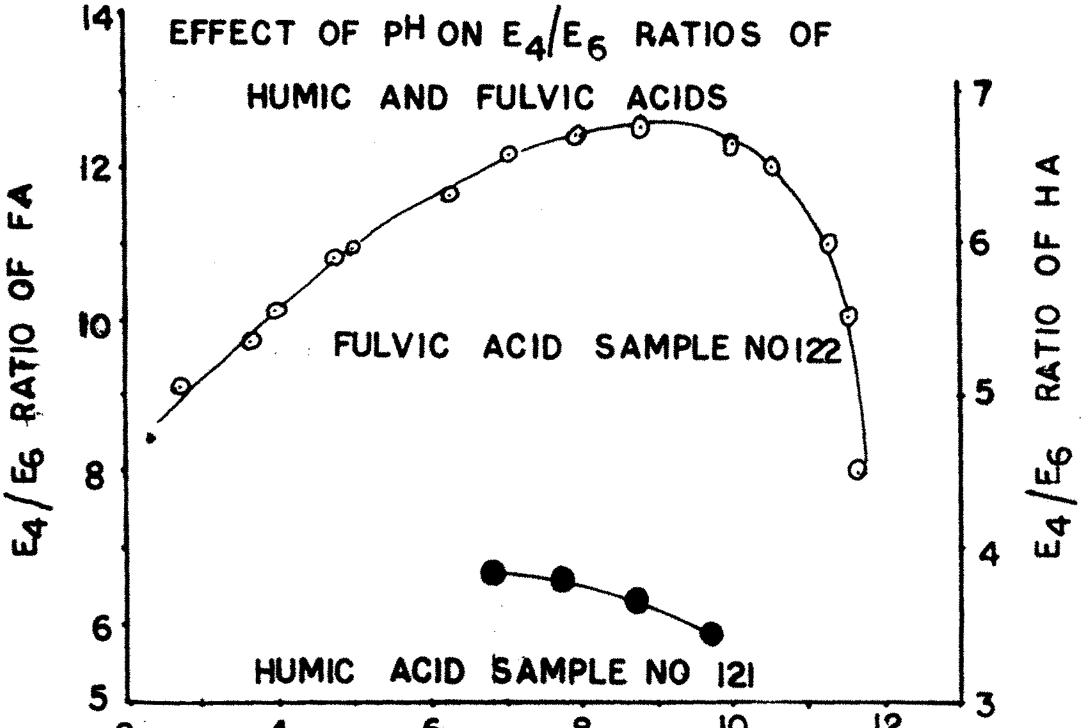
values were greater than that of lateritic and alluvial soils. Bishayee *et al*. (1981) also observed similar results.

The E_4/E_6 values of humic acids of surface and sub-surface lateritic and alluvial soils under different vegetations were in the following order :

Shorea robusts (pedon - 8 & 9) > *Tectona grandis* (pedon - 1 & 3) > *Terminalia arjuna* & Mixed vegetation (pedon - 10 & 11)

The E_4/E_6 values of humic acids of hilly soils (pedon - 12 to 14) were lower as compared to those of lateritic and alluvial soils indicating their higher degree of aromatisation.

Many investigators have shown that humic acid molecules possess an aromatic ring and peripherial chains (aliphatic). The mobility of humic acid down the profile seemed to depend on the ratio between aromatic and aliphatic structure in the molecule. If the aromatic structure predominates, it is less mobile. As the mobility of surface humic acid down the profile is lower in amount so from this point of view it may be concluded that sub-surface humic acid of Sandakphu soil is more aromatic in nature compared to its surface.


EFFECT OF PH ON E4/E6 RATIOS OF
HUMIC AND FULVIC ACIDS
FULVIC ACID SAMPLE NO 122
HUMIC ACID SAMPLE NO 121
E4/E6 RATIO OF FA
E4/E6 RATIO OF HA
14
12
10
8
6
5
7
6
5
4
3
2
4
6
8
10
12

(FIG. III E)

Table -XI lists correlation coefficient between quotient values (E_4/E_6 ratios) and a number of analytical measurements of the humic acids.

In humic acid (HA) the correlation between E_4/E_6 values and the amount of carbon (C) was negative ($r = -0.421$), but between E_4/E_6 and the amount of nitrogen (N) it was positive ($r = + 0.395$). The quotient values bore a positive correlation with total acidity ($r = + 0.418$), and it was so with coagulation threshold ($r = + 0.243$) and even with carboxyl acidity ($r = + 0.325$), but negatively correlated with phenolic hydroxyl acidity ($r = - 0.961$). This observation substantiates the findings of Chen _et_ _al_. (1977) and Chakrabarty _et_ _al_. (1980).

Effect of pH on E_4/E_6 ratio of humic substances

The E_4/E_6 ratios for fulvic acid (sample no - 121) increased as the pH was raised from 1.0 to 7.0, attained **maximum** values between pH 7.5 and 9.5 and then tended to decrease gradually (Fig. IIIE). The changes in E_4/E_6 ratios with pH in humic acid (Fig. IIIE) were small in comparison to that in fulvic acid, although slight decreased at high pH were observed. The insolubility of humic acid in aquous medium at pH 6.5 limited the scope of experiments with these materials. However, the findings are in agreement with those reported by Chen _et_ _al_. (1977).

Relation between E_4/E_6 and ash content

The relation between ash content and E_4/E_6 values of Sandakphu humic acid samples were shown in Table - IX. From the results it is found that in a profile as the depth increased the E_4/E_6 value also increased with increasing ash percentage, when the ash was not removed. But when the ash was removed the values decreased.

(b) Fluorescence excitation spectra

The fluorescence excitation spectra of Na-humates and fulvic acids of different samples in water were shown in Figs. IVA, IVB, IVC and IVD. The fluorescence excitation spectra, which was recorded in terms of microammeter reading, were drawn in terms of intensity of excitation radiation taking it equivalent to the microammeter reading.

Humic and fulvic acids of the different soil samples exhibited fluorescence with excitation maximum at 470 m/u with different intensity. The differences in the intensity of observed fluorescence might be due to the variation of the concentration of the fluorescing groups in these substances.

The fluorescence spectra of lateritic soil humic acids under Shorea robusta (pedon - 7) showed hyperchromic effect i.e., as the depth of the profile increased the fluorescence intensity also increased. This was also found to be true in case of Sandakphu soil humic acids (pedon - 12). The fluorescence spectra of humic acids of pedon - 7 and 12 presented in Figs. IVA and IV B respectively. Figs. IVA and IVB indicate that the density of the fluorophore groups were minimum at the surface soil and maximum in the lower horizons.

It is interesting to note that humic acid of some lower horizons (sample no - 75 of pedon - 7 and sample no - 125 of pedon - 12) showed a very weak band near about 400 m/u. This band was comparatively more pronounced in the sample of the lowest horizon (Figs. IVA and IVB).

According to Goldschmidt (1954) 360 m/u band was found in case of fulvic acid sample due to its phenolic structure in which hydroxyl (OH) group conjugated through the ring with a carboxyl (COOH) group at para position which was either absent or found in a very low concentrations only. This para hydroxyl benzoic acid structure was generally absent in humic acid and therefore, only FA instead of HA gave two bands. In the present study only a very weak band was observed at or near about 400 m/u (Fig. IVD) which might be due to the presence of lower amount of para-hydroxy benzoic acid.

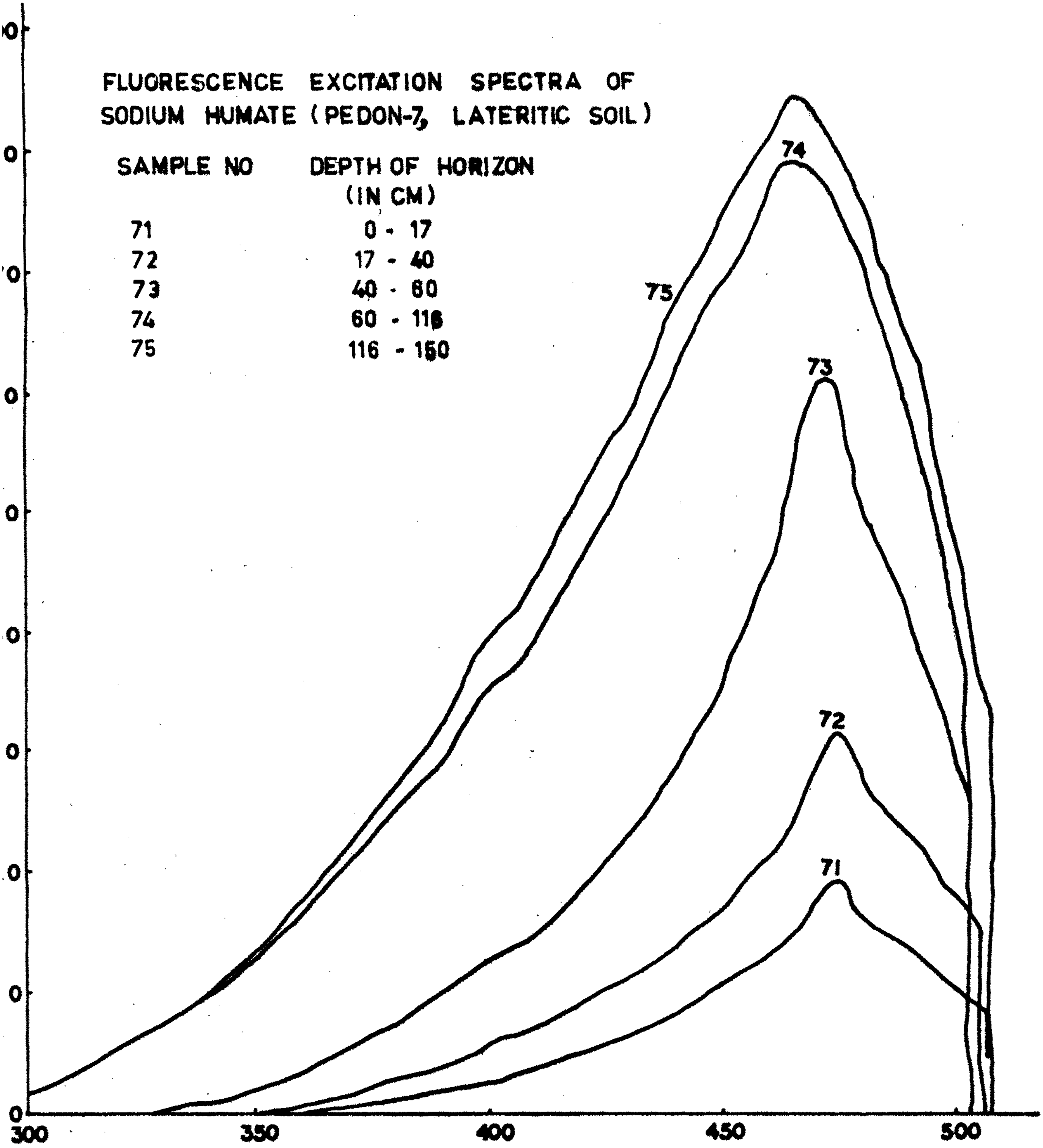
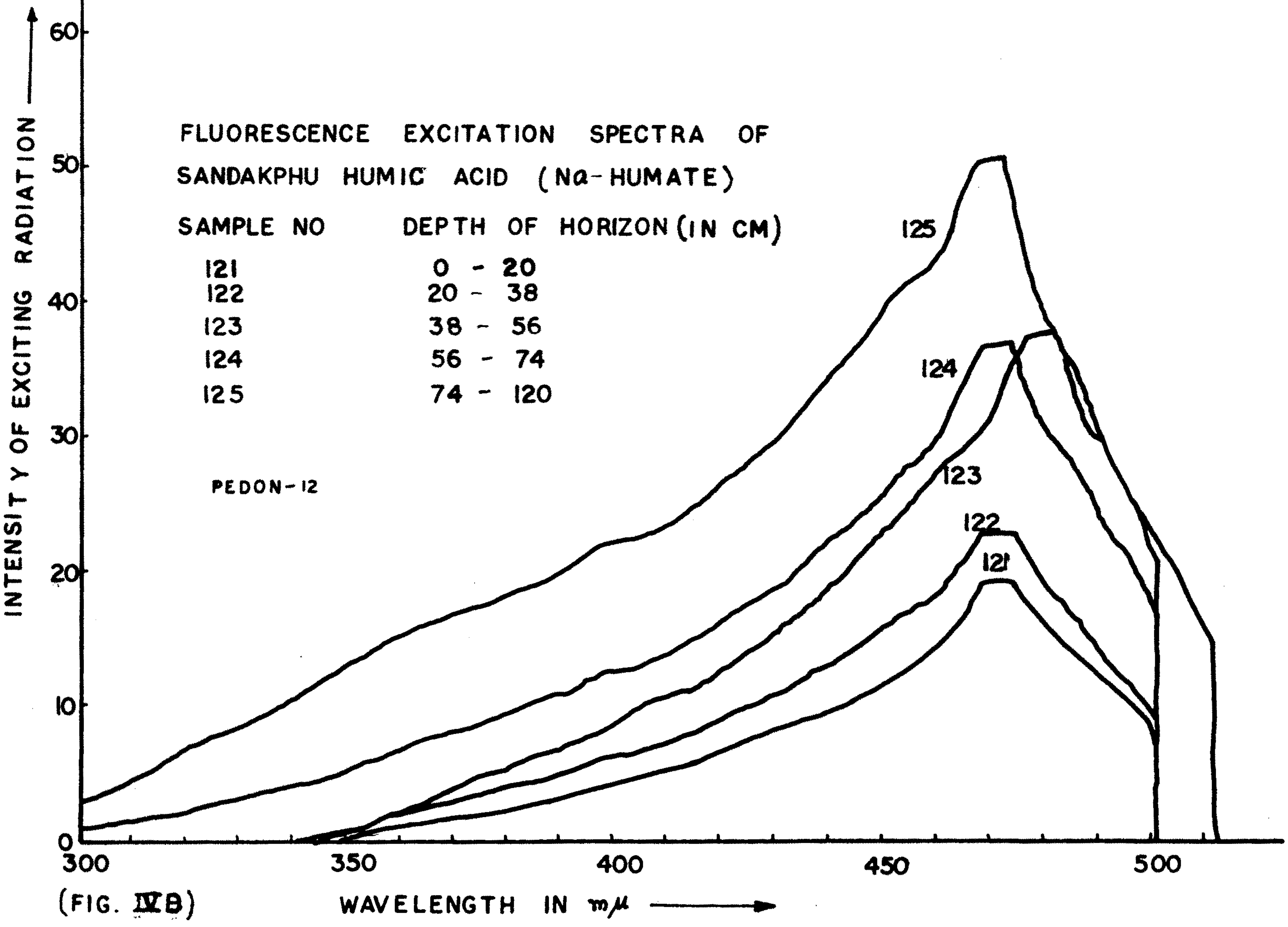
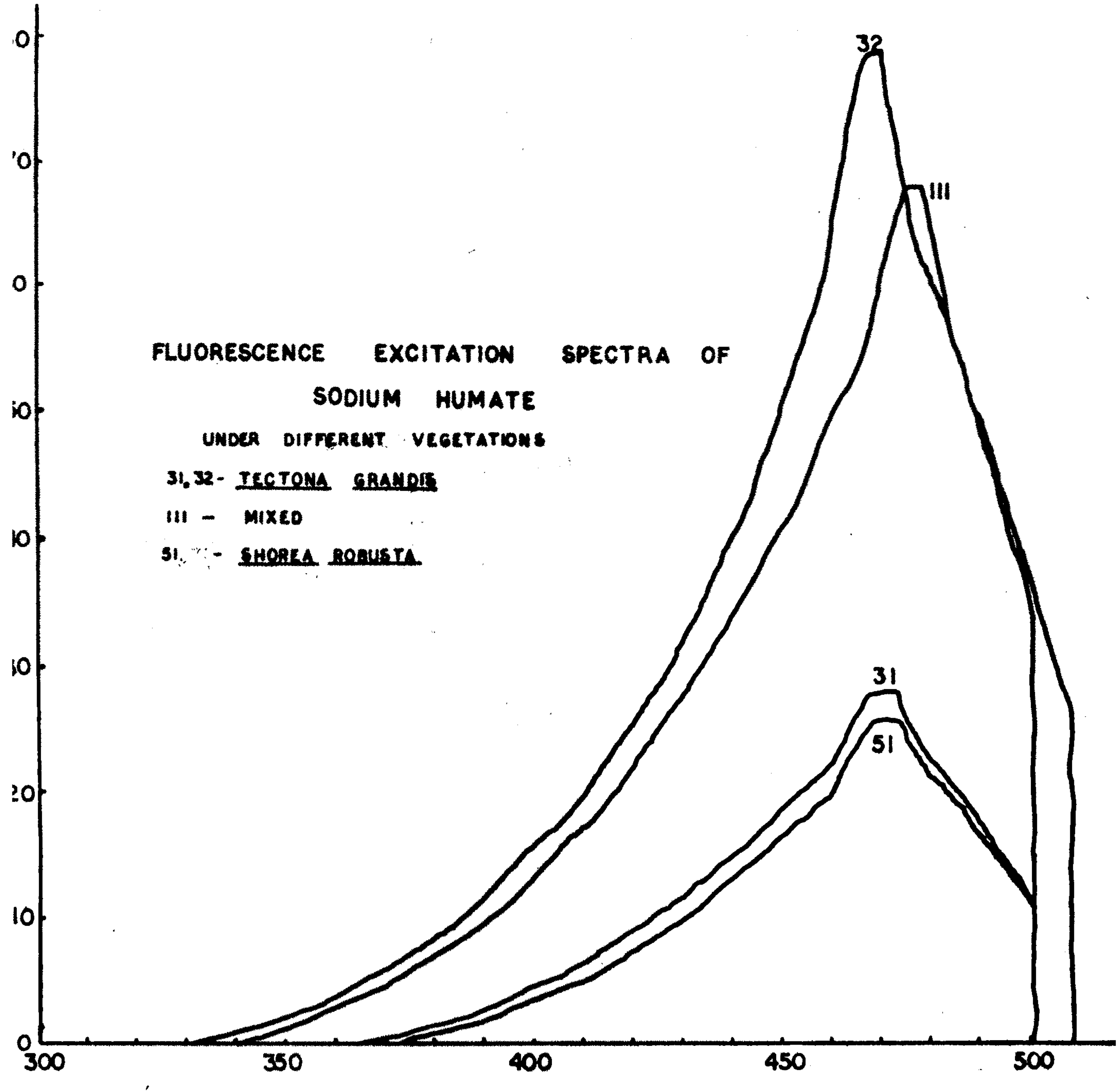

FLUORESCENCE EXCITATION SPECTRA OF SODIUM HUMATE (PEDON-7, LATERITIC SOIL)
SAMPLE NO
DEPTH OF HORIZON (IN CM)
71 0 - 17
72 17 - 40
73 40 - 60
74 60 - 116
75 116 - 150
75
74
73
72
71
0
300
350
400
450
500
WAVELENGTH IN mμ →

FIG. IV A.


FLUORESCENCE EXCITATION SPECTRA OF
SANDAKPHU HUMIC ACID (Na-HUMATE)
SAMPLE NO DEPTH OF HORIZON (IN CM)
121 0 - 20
122 20 - 38
123 38 - 56
124 56 - 74
125 74 - 120
PEDON-12
125
124
123
122
121
INTENSITY OF EXCITING RADIATION
0
10
20
30
40
50
60
300
350
400
450
500
WAVELENGTH IN mμ

(FIG. IVB)


FLUORESCENCE EXCITATION SPECTRA OF
SODIUM HUMATE
UNDER DIFFERENT VEGETATIONS
31, 32 - TECTONA GRANDIS
111 - MIXED
51 - SHOREA ROBUSTA
32
111
31
51
10
0
300
350
400
450
500
WAVELENGTH IN mμ →

(FIG. IV C)

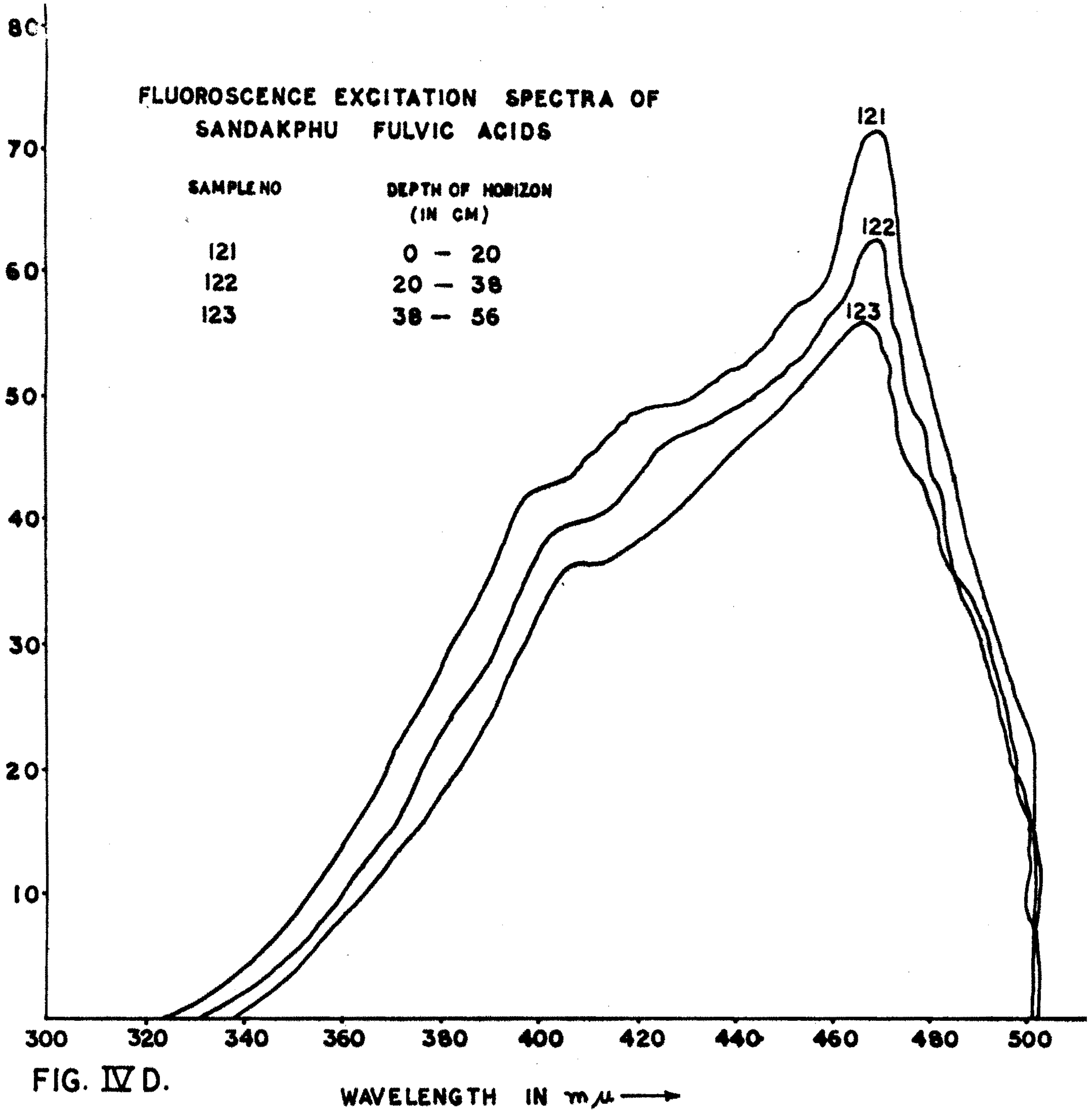

FLUOROSCENCE EXCITATION SPECTRA OF SANDAKPHU FULVIC ACIDS
SAMPLE NO
DEPTH OF HORIZON (IN CM)
121 0 — 20
122 20 — 38
123 38 — 56
121
122
123
80
70
60
50
40
30
20
10
300
320
340
360
380
400
420
440
460
480
500
WAVELENGTH IN mμ ⟶

FIG. IV D.

The intensity of the fluorescence excitation spectra of surface soil humic acid under different vegetations (Fig. IVC) followed the sequence :

Mixed > *Tectona grandis* > *Shorea robusta*
(sample no-H_{111}) (sample no - H_{31}) (sample no - H_{51})

(c) Infra-red spectra (IR)

The IR spectra of humic (Fig.VA) and fulvic (Fig.VB) acids were more or less similar to one another. In the materials of the present investigation the absorption bands were noted in the following regions 2.9 to 3.0 μ, 3.5 μ , 5.8 to 5.9μ , 6.5μ, 7.2 to 7.3μ, 8.7μ, 9.0μ and 9.9μ.

Almost all the humic and fulvic acids studied in the present investigation showed a band approximately 6.25μ (1600 cm^{-1}) which was strong in case of humic acid under *Tectona grandis* and *Shorea robusta* but weak in case of mixed vegetation. The absorption at this wave length may not only be due to stretching vibrations of C = C double bonds (indicating the presence of aromatic groups and conjugated C = O groups) but also to streatching vibration of C = N in heterocyclic nitrogen compounds. Stevenson and Goh (1971) attributed it to the amide absorption of peptides but Schnitzer *et al*. (1959) attributed it to carboxyl structure, whereas

Farmer and Morrison (1960) accounted it for the presence of C=C double bonds. Almost all the humic and fulvic acids of the present investigation showed a strong absorption in the region 2.9 to 3.0/u. Absorption in this region is generally associated with hydroxyl groups which are polymerically bonded through intermolecular hydrogen bonds.

The band in the region 5.8 to 5.9/u (1725 cm^{-1}) which was sharp for all the humic and fulvic acids response to the vibration of the carboxyl and carbonyl (C=O) in aliphatic and aromatic acids (Stevenson and Goh, 1971). The C.E.C. of humic and fulvic acids supported that atleast part of inflextion was due to unionised carboxyl groups, but some other groups for example, aryl, ketones and aldehydes could contribute to this intensity. Stevenson and Goh (1971) showed that this band was greatly reduced in intensity when the humic acid and fulvic acids were converted to the salt form. The humic and fulvic acids under mixed vegetation showed weak bands in the region 2850 cm^{-1} which were caused by C-H stretch frequencies of aliphatic CH_3- , CH_2= groups. A band at 6.5/u (1540 cm^{-1}) was observed in the IR spectra of humic and fulvic acids of lateritic soils. The bands in this region were normally assigned to the peptise linkage of proteines (Stevenson and Goh, 1971). In addition to this broad band, diffused band situated near the region of 8.71/u and 9.9/u were characteristics of C - O stretching vibration or C - H bonding vibration. Moreover, bands in the region 9.0μ and 10.0μ were noticeable in some cases which are probably caused by C-C, C-OH and C-O-C vibration, typical of sugar rings, glucoside linkages and polymeric compounds.

According to the classification of the humic substances by Stevenson and Goh (1971) the humic acids under Shorea robusta resembled Type-I spectra while the spectra of humic acids under Tectona grandis and mixed vegetation resembled Type-II. Fulvic acid under Tectona grandis belonged to Type-III while the same under Shorea robusta and mixed vegetation belonged to Type-II.

6.3.7 Coagulation threshold

The coagulation threshold values of the humate solutions after 2 hours were given in Table -VIII. The amounts of $CaCl_2$ at the beginning of coagulation and for completion of coagulation were different for humic acid from different soils and more or less it followed the sequence as follows :

Alluvial > Lateritic > Hilly

When the vegetation was considered the sequence was as follows:

Mixed (sample no-111) = *Terminalia arjuna* (sample no - 101) > *Shorea robusta* (sample no- 51,71,81 & 91) >
Tectona grandis (sample no-31) > *Abies densa* (sample no -121) > *Ailanthus grandis* (sample no - 141) = *Mixed* (sample n 131)

Humic acid molecules are in general composed of an aromatic part and an aliphatic part. Of these two, the aromatic part is likely to be hydrophobic in aquous medium and hence susceptible to coagulation by electrolytes. The aliphatic part, on the other hand, is hydrophilic and hence is likely to resist coagulation in aquous medium. In accordence with that the extracts which were more resistant to coagulation, may be assumed to consist of larger proportion of the aliphatic part and the extracts which were less resistant to coagulation contained higher proportion of the aromatic part. Therefore, from the results it may be presumed that humic acids under *Terminalia arjuna* (sample no - 101) and mixed vegetation (sample no-111) contain greater amount of aliphatic groupings.

6.3.8 Viscosity

The most interesting property which distinguishes polyelectrolytes from neutral polymer is the way in which the reduced viscosity, η_{sp} / C, is dependent on concentration. The reduced viscosity of a neutral macromolecular solution generally decreases with concentration to its limit, i.e., the intrinsic viscosity, which serves as a measure of the molecular weight. However, for a salt-free polyectrolyte the reduced viscosity increases sharply with decreasing concentration. The sharp increases have been attributed by Fuoss and Straus (1948), partially to molecular dilation of the polyelectrolyte caused by the repulsion of similarly charged ionisable groups which dissociate upon dilution. Thus, in the case of polyelectrolytes, the intrinsic viscosity cannot be evaluated unless salts are added. In the presence of relatively high concentrations of salts, polyelectrolytic behaviour is suppressed and the plot of reduced viscosity vs. concentration is linear and viscosity measurements can then be used to calculate intrinsic viscosity (Fuoss *et al.*, 1948; Mukherjee and Lahiri, 1956).

Fuoss and Strauss (1948), however, have shown that plotting the reciprocal of reduced viscosity against the square root of concentration according to the equation:

$$\eta_{sp} / C = \frac{A}{1 + B\sqrt{C}} \qquad \ldots\ldots\ldots\ldots\ldots(1)$$

gives a straight line which apparently allows the intrinsic viscosity of a salt free polyelectrolyte to be determined by extrapolation.

Determination of Molecular weight

For macromolecules, the intrinsic viscosity, is related to the average molecular weight, $\bar{M}$, by an expression of the form:

$$[\eta] = K\bar{M}^{\alpha} \text{ ....(2)}$$

where K and α are constants whose values depend on the nature of solute and solvent and on temperature. For flexible linear polymers, α varies between 0.5 and 0.8 and for rod shaped molecule α is equal to 1.8. Knowing the values of K, α and the intrinsic viscosity the average molecular weight can be determined from the above equation (Tandford, 1965).

The results of viscosity measurements were graphically represented in the Figs. VIA and VIB. The curves of reduced viscosity vs. concentration of the salt free Na-humates of the different extractions indicated their typical polyelectrolytic behaviour. The reduced viscosity of humic acids extracted from different soil samples in all concentrations increased in the following order:

$$H_{121} > H_{122} > H_{11} > H_{71}$$

The values of intrinsic viscosities obtained by extrapolation to zero concentration of the curves prepared by plotting reciprocal of the reduced viscosity against aquare root of concentration as per Fuoss and Strauss equation of the salt free Na-humate solutions of different samples were in the range of 4.0 to 13.25 ml/g. Dutta and

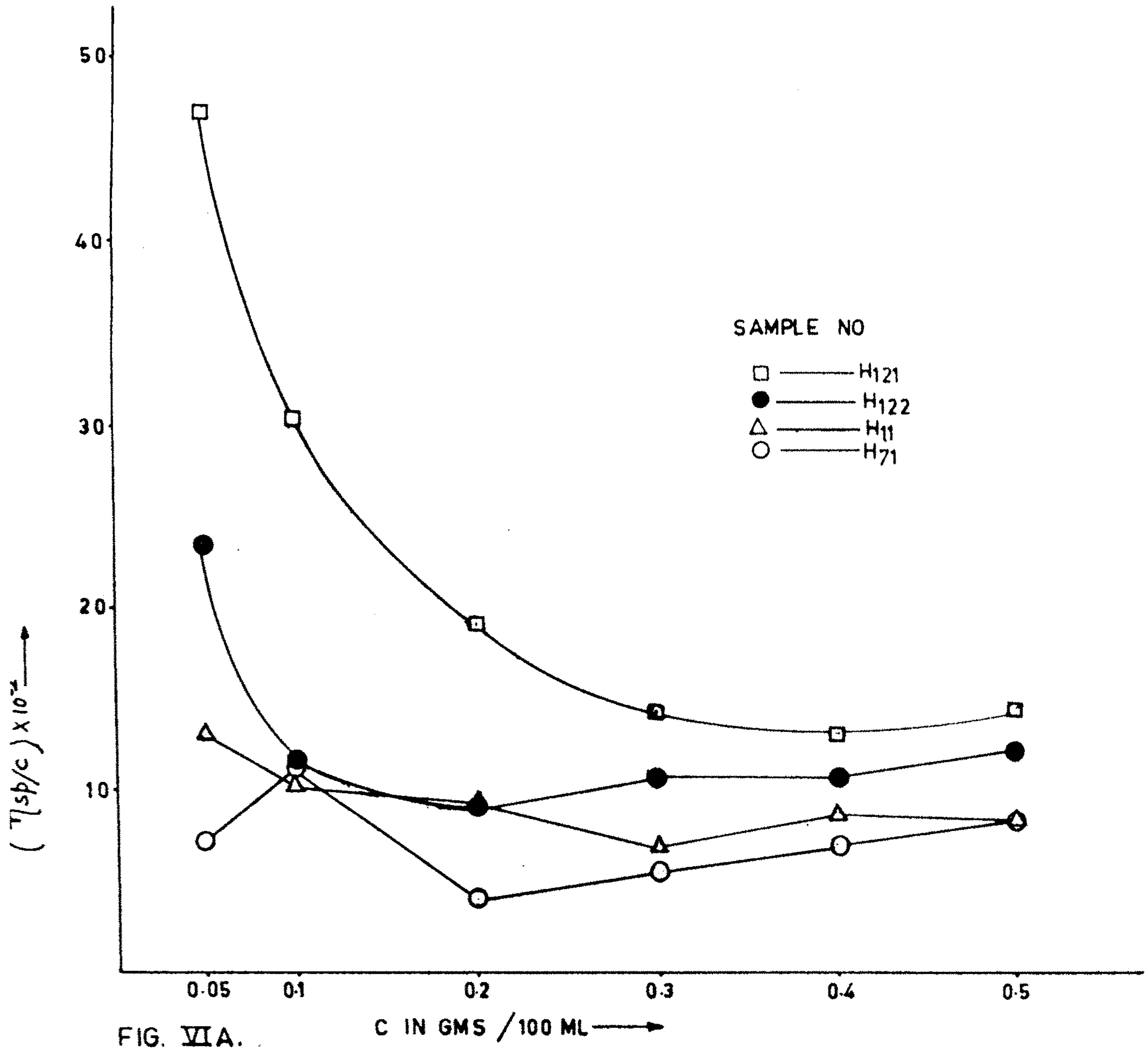


FIG. VIA.

Na- HUMATE

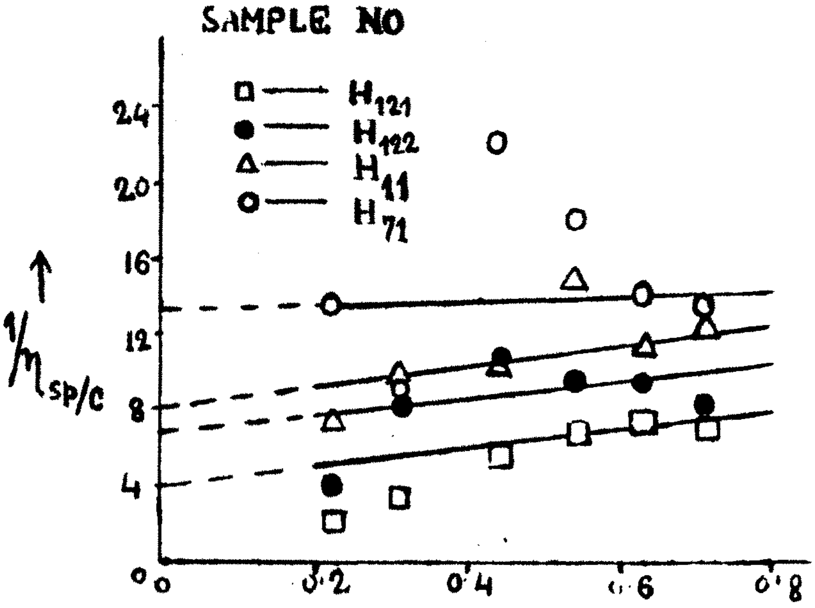

SAMPLE NO
□ —— H_{121}
● —— H_{122}
△ —— H_{11}
○ —— H_{71}
24
20
16
12
8
4
0
$1/\eta_{sp/c}$ ↑
0
0·2
0·4
0·6
0·8
$\sqrt{c}$ →

FIG. VIB.

Mukherjee (1970), working with various types of Indian soils, reported the values in the range 10.36 to 17.86 ml/g.

The values of intrinsic viscosity of different samples of surface humic acid were shown in the Table -X. It is known that the presence of branched structure along the main polymer chain decreased the intrinsic viscosity of the polymer, whereas high molecular weight, high flexibility and long chain increased the intrinsic viscosity of a polymer. In the present case the intrinsic viscosity gradually increased in the following order:

$$H_{71} > H_{11} > H_{122} > H_{121}$$

Therefore, it may be suggested that the flexibility, molecular weight and also the chain length of different humic acids also increased in the same pattern.

From the above discussion it may be concluded that intrinsic viscosities of humic acids under hilly soil (Sandakphu) were lower than that of lateritic soils, and in the lateritic soil Shcrea robusta (sample no- H_{71}) had higher intrinsic viscosity than Tectona grandis (sample no. - H_{11}). In Sandakphu soil the humic acid of sub-surface sample (sample no - H_{122}) had higher intrinsic viscosity than that of surface sample (sample no - H_{121}). Considering vegetation parameters it was observed that intrinsic viscosity increased in the following order:

Shorea robusta > Tectona grandis > Abies densa

TABLE - X

VISCOSITY OF HUMIC ACIDS

Sample No	Vegetation	Soil	$[\eta]_{\text{Salt free}}$ (from Fouss Strauss plot) ml/g.
H_{121}	*Abies densa*	Hilly	4.0
H_{122}	*Abies densa*	Hilly	6.5
H_{11}	*Tectona grandis*	Lateritic	8.0
H_{71}	*Shorea robusta*	Lateritic	13.25

CHAPTER - VII

SUMMARY AND CONCLUSION

The forms and distribution of organic matter in some soils of West Bengal under different forest species (*Shorea robusta*, *Tectona grandis*, *Eucalyptus*, *Terminalia arjuna*, *Ailanths grandis*, *Abies densa* and mixed) have been studie~~s~~d.

From the vegetation data it was found that the total basal area was maximum in *Terminalia arjuna* (150.044m^2/ha) under alluvial soil (site - 10), followed by that in *Shorea robusta* (64.858 m^2/ha) of lateritic area (site - 9). The lowest basal area (8.505 m^2/ha) was obtained in site - 5 containing maximum number (3300 plants) of plants (*Shorea robusta*).

A highly significant positive correlation was observed between surface soil organic matter content and total basal area of different vegetations in lateritic and alluvial zones.

The pH of soils ranged from 5.0 to 6.3 for lateritic soils, from 4.9 to 6.7 for alluvial soils and from 3.8 to 5.6 for hilly soils.

Vegetative cover had an effect upon pH of the surface soil. With increasing total basal area the pH of the surface soil more or less increased under Tectona grandis vegetative cover. Organic matter content of hilly soils was more than that of lateritic and alluvial soils. The differences have been attributed to temperature and moisture variations. The percentage of organic matter decreased down the profile in most cases. Vegetative cover had an effect upon organic matter content of the surface soil (pedon - 1 to 3). The C/N ratio under sub-alpine forest soil (pedon - 12) was higher in comparison to that of the soils of lower hill areas, alluvial and lateritic zones.

The clay content in most of the soils under lateritic and hilly areas showed a definite increase with depth, and had well developed argillic sub-surface diagnostic horizon, while in pedon - 11 under alluvial soil the clay content decreased with depth of the profile. Maximum amount of clay was found in hilly soil under Ailanthus grandis (pedon - 14).

C.E. C. of the lateritic soils were less than that of other soils and generally increased down the profile with increasing clay content. The low C. E. C. values of lateritic soils indicate the dominance of low C. E. C. clay minerals. The maximum C. E. C. was observed in surface soil of hilly area under Abies densa (pedon - 12, 38.36 me/100g) followed by Ailanthus grandis (pedon - 14, 18.22 me/100 g) and mixed vegetation (pedon - 13, 14.79 me/100 g).

Among the exchangeable bases calcium was the dominent one followed by magnesium, potassium and sodium. The exchangeable calcium in the lateritic soil decreased downwards in a pedon but reverse was the case in Sandakphu soil (pedon - 12). Among the pedons - 1 to 7 under lateritic soil the amount of exchangeable calcium and potassium was higher in Tectona grandis (pedon - 1, 2 and 3) followed by Shorea robusta (pedon - 4, 5 and 7) and Eucalyptus hybrid (pedon - 6). Again, the total exchangeable bases was maximum in Tectona grandis (2.372-4.584 me/100 g) followed by in Eucalyptus hybrid (2.058 me/100g) and than in Shorea robusta (0.687 - 1.91 me/100g). Although the surface soil under pedon - 7 and 9 had same pH values but in pedon - 9 total exchangeable bases and exchangeable calcium, megnesium and potassium were lower than that of pedon - 7 and maximum amount of organic matter was observed in pedon - 9.

In pedon - 7 to 9 , under Shorea robusta the exchangeable calcium and magnesium and total exchangeable bases, C.E.C. and base saturation of the surface soil increased as the total basal area of the vegetative cover increased.

The total exchangeable bases increased downwards in most of the pedons under lateritic area, except in pedon - 12. The lowest amount of total exchangeable bases was observed in pedon - 7.

Base saturation of the three types of soils more or less followed the sequence :

Lateritic and Alluvial soil	>	Lower hill soil	>	High altitude hilly soil
(pedon - 1 to 11)		(pedon - 13 and 14)		(pedon - 12)

In Sandakphu soil the exchangeable Al^{+3} contributed to the soil acidity. The Δ pH values of Sandakphu soils were not near their zero point charge and greater amount of sesquioxides present in surface soil precluded the process of podzolization in operation.

From the total analysis of soil it was observed that silica was the major constituent of soil mass and varied from 60.035 - 95.58 per cent. The amount of silica decreased downwards in a profile in most cases, except in pedons - 11 to 13.

Next to silica, Al_2O_3 was the dominant constituent. The amount of Fe_2O_3 increased downwards in the profiles under lateritic area. Soils were low in total bases. Surface soils under lateritic area were more silicious as indicated by high SiO_2/Al_2O_3 ratio. Silica sesquioxides (SiO_2/R_2O_3) ratio and silica alumina (SiO_2/Al_2O_3) ratio were lower in case of hilly soils (pedon - 12 and 14) compared to lateritic and alluvial soils. The K_2O and P_2O_5 percent were higher in hilly and alluvial soils than in lateritic soils.

The maximum amount of humic matter was extracted from hilly soils (pedon - 12 to 14), particularly from Sandakphu soil (pedon - 12). In most cases the ratio of humic acid carbon to fulvic acid carbon (C_h/C_f) were less than unity and the lowest value was observed in case of hilly soil under pedon - 13 and 14, particularly in pedon - 14 under *Ailanthus grandis*. The C_h/C_f ratio of *Tectona grandis* (pedon - 1 and 2) had higher values than *Shorea robusta* (pedon - 7 and 9).

Electrochemical studies of the humic fractions have thrown considerable light on the nature of the acidic functional groups present in them. All the conductometric titration curves of humic acids in lateritic and alluvial soils showed single break, indicating a monobasic behaviour of the respective acids. But the humic acid of hilly soils showed two breaks (pedon - 12 to 14) in the titration curves and in one case (sample no - 121) three breaks was observed.

From the conductometric titration (pedon - 1 to 14) it was found that C.E.C. of humic acids under different vegetations in the lateritic soils followed the sequence :

Tectona grandis > *Eucalyptus* > *Shorea robusta*
(pedon - 1 to 3) (pedon - 6) (pedon - 4,5,7 to 9)

The conductometric titration curves of fulvic acid (FA) showed two breaks in case of (i) surface soil of pedon - 4 and 8 under Shorea robusta and pedon - 11 under mixed vegetation and (ii) both the surface and sub-surface soils of pedon - 5 and 8 under Shorea robusta and in pedon - 14 under Ailanthus grandis. The rest fulvic acid samples showed three breaks.

All the conductometric titration curves of humic acids showed a slight drop in specific conductance at the low value to α. But all the conductometric titration curves of fulvic acids showed a pronounced initial drop in specific conductance.

The total acidity of humic acids determined by potentiometric method was always found to be smaller than those determined conductometrically.

The pH values between the $\frac{1}{4}$th and $\frac{3}{4}$th titration points were found to be greater than 0.954 indicating the polyprotic nature of the acids.

The total acidity of humic and fulvic acids under different soils and different vegetations varied from 245 - 545 me/100g and 290.0 - 1557.5 me/100g respectively.

Carboxyl acidity had a major role in total acidity in humic and fulvic acids. Exception was observed only in a few cases where acidity due to phenolic - OH groups predominated over - CO_2H groups.

In case of Sandakphu humic acid (Sub-alpine, pedon - 12), as the depth of the profile increased acidity due to $-CO_2H$ groups decreased but acidity due to phenolic - OH groups increased. But in case of fulvic acid total acidity, acidity due to $-CO_2H$ groups and phenolic - OH groups increased downwards.

Carboxyl groups were more in fulvic acids compared to humic acid. The carboxyl and total acidity of different humic acids of a particular type of vegetation increased with the increase of its nitrogen content.

From the elementary analysis of humic acid it was found that the amount of carbon and nitrogen were maximum in case of Sandakphu (Sub-alpine) soils under Abies densa (C = 65.97% , N = 6.2%), both the carbon and nitrogen content of humic acid decreased downwards in the profile. The elemental nitrogen content of humic acids under different vegetation followed the sequence :

Tectona grandis > Eucalyptus > Shorea robusta

The E_4/E_6 values of fulvic acid (FA) were higher than that of humic acid (HA).

From the colour quotient (E_4/E_6) of humic substances it was observed that humic acids of Sandakphu soil samples were more humified and polymerised than those of lateritic and alluvial soils.

The E_4/E_6 values of humic acids of pedon - 3, 5 and 7 increased with increasing its depth.

The E_4/E_6 ratio of surface soil humic acids under different vegetations in lateritic and alluvial soils were in the order :

Shorea robusta > *Tectona grandis* > Mixed & *Terminalia arjuna*
(pedon-8 & 9) (pedon - 1 & 3) (pedon - 10 & 11

The E_4/E_6 ratio of both fulvic acid and humic acid was found to be dependent on pH and ash content.

The fluorescence excitation spectra of Na-humate and fulvic acid of different soils under different vegetations indicated that the organic matter of different soils does not consist of independent groups of humic substances but of similar compounds the humic and fulvic acids obtained from them are also similar, probably representing certain stages of a polymer series.

The fluorescence intensity of surface soil humic acid under different vegetations followed the sequence :

Mixed	>	*Tectona grandis*	>	*Shorea robusta*
(Alluvial soil)		(Lateritic soil)		(Lateritic soil)
(sample no -H_{111})		(sample no - H_{31})		(sample no - H_{51})

The coagulation threshold values of humic acid of different vegetations and different soils followed the sequence:

Alluvial > *Lateritic* > *Hilly*

When vegetation was considered the sequence was as follows:

Terminalia arjuna	=	*Mixed*	>	*Shorea robusta*	>	*Tectona grandis*
(sample no -101)		(sample no- 111)		(sample no - 51) 71, 81 & 91).		(sample no -31

Abies densa	>	*Ailanthus grandis*	=	*Mixed*
(sample no-121)		(sample no - 141)		(sample no-131)

The infra-red spectra of humic and fulvic acids were shown in Fig. VA and VB respectively and classified according to Stevenson and Goh (1971).

Humic and fulvic acid samples under different vegetations belong to the following types:

Humic acids

Type - I	*Type - II*
Shorea robusta	*Tectona grandis*
(sample no - H_{41}, H_{81})	(sample no - H_{21},H_{31} & H_{32})
	Mixed vegetation (sample no - H_{112})

Fulvic acids

Type - III	Type - II
Tectona grandis	*Shorea robusta*
(sample no - F_{32},F_{21} & F_{11})	(sample no - F_{81}) & Mixed vegetation (sample no - F_{112})

Hydrodynamic measurements on humic acids showed that the acids are flexible polyelectrolyte with intrinsic viscosity (Fig. VIB) varied from 4.0 to 13.25 ml/g. The intrinsic viscosity of Sandakphu surface soil humic acid (sample no - H_{121}) under *Abies densa* was lower than that of its sub-surface (sample no - H_{122}) and also from *Tectona grandis* (sample no - H_{11}) and *Shorea robusta* (sample no -H_{71}). Therefore, intrinsic viscosity increased in the following order :

$$H_{71} > H_{11} > H_{122} > H_{121}$$

Considering vegetation parameters it was observed that intrinsic viscosity increased in the following order :

Shorea robusta > *Tectona grandis* > *Abies densa*

CHAPTER - VIII

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