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# Clay Research

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# Study of Dispersion Characteristic of Clays Used in Traditional Ceramics

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***Abstract–**This study is concerned with the dispersion characteristics of ceramic clay minerals used in tile making, and also effect of ageing on Rheological behavior, pH of clay Suspensions. The effect of dehydrated sodium phosphates on dispersion was also investigated. For this reason, four types of ceramic clay samples, of different characteristics were chosen and four commercial dispersants namely, sodium hexametaphosphate (SHMP) marked as D1, sodium Tripolyphosphate (STPP) as D2 and two anionic dispersants (sourced from elsewhere) marked as $B_1$ & $B_2$ were used for clay suspensions. Each dispersant was studied to determine its effect on dispersion characteristics of different clay-water system utilized in the experiments. The deflocculates varied in dispersion efficiency depending upon the interaction of the clay-water-phosphate system. But before the studies on ageing, rheological behavior of clay samples were studied systematically, depending on the type and amount of dispersants. Suspensions with four different dispersant concentrations were prepared for rheological and ageing studies. These suspensions were aged for 24 hours to observe the changing of their rheological behavior. The result indicated that the rheological and ageing behavior of suspensions changed for different clay samples with the changes in concentration of water and dispersant. It was also found that at lower pH the viscosity of clay suspension were more and vice versa. The suspensions prepared by using an optimum amount of dispersant showed a non-Newtonian flow character independent of the type and amount of dispersant present.*

***Key words :*** Clay, pH, Rheology behavior, Dispersant, Mineralogy

## Introduction

Kaolinite, a hydrated aluminum silicate of composition $Al_2O_3.2SiO_2.2H_2O$, occurs in the form of thin, generally hexagonal platelets, of length-to-thickness ratio of about 10. Kaolinite layers have amphoteric properties. The faces or surfaces bear a permanent negatives charge and depending on the pH, there is positive or negative charge on the edges. Kaolinite platelets can connect in edge-edge (E-E), edge-face (E-F), and face-face (F-F) configurations.[1-2] The

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easy formation of the different types of connection depends on the balance of electrostatic contacts (attractive or repulsive), which are controlled by the dispersions chemistry, and the attractive Vander Waals forces between the particles.[2] In acidic environments alumino groups exposed on the edges of the particles actually attach hydrogen ions in water consequently generating positive charge. Hence, edges and faces of particles will equally attract giving rise to face-edge attraction and coagulation of kaolinite dispersions referred as "card-house" arrangement. Under alkaline situation, the edge charge is either missing (neutral charge) or negative and the particles are deflocculated, provided the dispersion concentration in solution is low. At high dispersant concentrations, electrostatic repulsion (or attraction) between the particles is compact because of electrical double layers compression or ion protecting of the surface charges. Thus, the particles adhere to one another along their basal surfaces, forming "card-pack" arrangement.[2-3] Clays are typically used in the manufacture of numerous traditional clay-based ceramics. The mineralogical and chemical compositions of clays determine the ceramic behavior and properties of the clays, i.e. their plasticity, drying and firing characteristics.[4]

The fluidity of a ceramic suspension alters in time through storage. Usually, viscosity changes irreversibly with ageing period. These changes may occur according to the nature of raw materials as well as the characteristics and amount of dispersant agents in suspension w.r.t. ageing period like as a few hours or few days or few months. This method is referred to as the ageing effect and is usually observed in cases of ceramic suspensions with high solid content that contains 40% or more clay. Although, the ageing effect depends upon the nature and solubility of raw materials (particularly of clay), particle size distribution, organic impurities present, quality of water (must not contain excess $Na^{+}$, $K^{+}$, $Fe^{+2}$, $Ca^{+2}$, $Mg^{+2}$ , $Cl^{-}$, $SO_4^{-2}$, $PO_4^{-2}$ and $CO_3^{-2}$ ions) and the pH value of the medium. It may also be influenced by the type, amount and stabilizing mechanism of the dispersant used in the preparation of a suspension.[5] For this reason, ceramic producers wish to minimize the ageing effects arising from characteristics of raw materials by combination of clays of different properties.[6] Some of alkaline silicates such as sodium silicate ($Na_2SiO_3$) or calcium silicate, ($CaSiO_3$) and carbonates, such as sodium carbonate ($Na_2CO_3$) or calcium carbonates ($CaCO_3$) are used as dispersant to give the fluidity of both ceramic clays and suspensions. Along with these common dispersants, sodium silicate ($Na_2SiO_3$) is well-known to show fine performance on dispersing clays in ceramic processing. The proper defloculant is helpful to reduce the viscosity of clay suspensions.[7-8]

In ceramic industry, chemical additives are usually used to reduce viscosity of suspension to maintain the higher dry clay concentration as possible. Inorganic substances such as silicates, phosphates and carbonates sodium salts or organic additives, generally polyacrylates salts with different molecular structures, are generally used. They are added in a percentage between 0.1 wt% and 0.6 wt%, to reduce the viscosity characteristically around 200-400 mPa.s.[9-10]

The mechanism of the sodium silicate consists adsorption of negatively charged anions by positively charged edges of the clay platelets w.r.t. pH of the suspension. The phosphates with more significant defloculent are sodium hexametaphosphate $(NaPO_3)_6$ and sodium tripolyphosphate $(Na_5P_3O_{10})$. The phosphate_anion is adsorbed on top of clay particle edges, increasing their negative charge.[10-11] Polyacrylates: sodium or ammonium salts, are defloculants with good efficiency, their anions are easily adsorbed on the clay particles, increasing the negatives charges and determine an electrostatic repulsion between particles.[12] Rheology and properties of final fired clay body that consist of these clays will depend on the composition and the homogeneity of the clay mineral mixture.[13] The control of the rheological properties and constancy of concentrated clay suspensions is determined in the ceramic industry and quite a few efforts have been made to this scope.[14] Though, there are less studies on the effect of clay mineralogy on the rheological behavior of clay mixture. Lot of scientific papers related to the rheological characterization of ceramic clay suspensions have been studied. Thus, the purpose of this work is to compare the dispersion characteristics of ceramic clay minerals used in tile making, and also effect of ageing on Rheological behavior, pH of clay Suspensions and the effect of dehydrated sodium phosphates on dispersion characteristics.

## Materials and Methods

### *Raw materials*

Morbi and Thangadh in Gujarat, India is a hub for the ceramic industries, where different kinds of clays are used. During the processing of ceramic product, clay suspensions are required to pass through the spray drier. Further, to study rheological characteristics w.r.t, different dispersants , various clays samples were collected from different places of Morbi and Thangadh.

For this study, four different types of clays were used, three white clays marked as C1, C2 & C3 and one black clay marked as C4.

Clays C1, C2 & C3 were collected from Morbi, Gujarat and Clay C4 was collected from Thangadh, Gujarat

### *Preparation of clay samples*

Big lumps of clay were crushed up to

~1 inch size, mixed thoroughly and then pulverized. The pulverized clay samples were again ground up to 75 microns particles size and dried up to constant mass in an oven at 110°C.

### *Dispersive agents used*

Four commercial dispersants, sodium hexameta phosphate (SHMP) marked as D1, sodium tripolyphosphate as D2 and two unknown anionic dispersant marked as $B_1$ & $B_2$ were used as an electrolyzing agent for clay suspensions.

### *General Characteristics of clay samples*

The properties of the clay samples (C1, C2, C3 & C4) were determined by using various techniques. Grit contents were determined by passing the sample through 300 mesh sieve. All the clay samples were visually observed for physical appearance. Particle Size Distribution (PSD) in the range of 0.3 to 400 micron was determined by laser based particle size analyzer, model 920L of CILAS, France. All the samples were characterized for complete chemical analysis by standard laboratory methods.

### *Mineralogical Characterization of clay samples*

The rheological measurements of clay suspensions were done using a Brookfield "R/S pPus Rheometer" at 25 $s^{-1}$ and 300 $s^{-1}$ shear rates. The optimization experiments previously carried out indicated that the best measurements would be obtained between these shear rates. Thus, viscosities with shear rate less than 25$s^{-1}$ & higher than 300 $s^{-1}$ could not be detected. In all the measurements CC40 spindle of the device was used. The effect of pH was measured by pH meter model Systronic India: μ pH SYS 361. The mineralogical composition of the raw materials as well as qualitative and quantitative phase analysis of multiphase mixtures were determined by using X-ray diffraction model Phillips PW-1710 equipment with Ni filter and CuKα. Different vibration spectra such as stretching / bending vibrations present in clay samples were identified by using FTIR spectrometer model Spectrum-100 of Perkin Elmer in the range of 400 to 4000 $cm^{-1}$. To determine the physico-chemical characteristics, the unfired clay samples were subjected to thermo gravimetric and differential thermal analyses (TG/DTA) using TG/DTA6300 model instrument of Sieko Instruments Ltd, Japan on 200 mesh fine powder of the sample by heating them up to 1200° C at a heating rate of 10°C.$min^{-1}$ and using calcined alumina powder as reference inert material.

### *Preparation of Clay suspensions*

Depending upon the flow characteristic, various clay suspensions were prepared by using 100 gms of dried clay samples for rheological test. Clay suspensions were prepared using 45%, 50%, 55% and 60 % of water content with four types of dispersants. Each dispersant was added in the range from 0.1% to 0.6% in the suspension of each water concentration.

These suspensions were stirred in magnetic stirrer for 30 min. The rheological properties were determined by measuring viscosity, pH, shear rate and shear stress.

These suspensions were then allowed to age for a period of 24 hrs and after that the rheological changes that took place were evaluated as a function of the type of dispersant. The results are furnished from figures 5-12.

## Results and Discussion

The general characteristics of clays as shown in Table 1 indicated that the water plasticity of clay C2 & C4 was less than that of clay C1 & C3. The residue (retained mass) on 300 mesh sieve was observed and found that clay C3 contains about 30 % coarser materials indicating presence of impurities as contamination.

From fig.1, it was found that mean diameter of the particles for all the clay samples falls in the range of 10 to 17 micron. This confirms the presence of fine particles in the clay samples and this indicates that no further grinding of the material would be required for its future use in ceramic wall tile making. Thus, it can be used directly followed by proper blunging in ceramic wall tile body preparation.

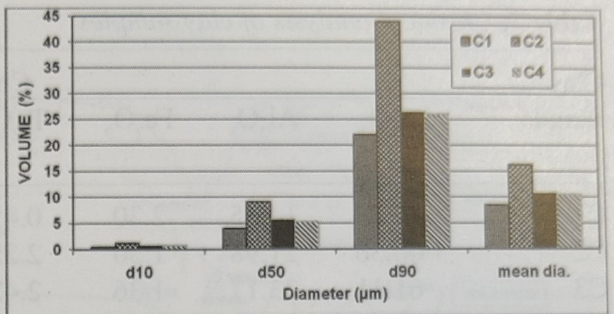


**Fig. 1.** *Particle Size distribution of clay samples.*

Table 2 showed that all clays contained $SiO_2$ in the range of 60 to 70 wt % as a major constituent and $Al_2O_3$ present in the range of 14 to 24 wt.%. MgO content falls in the range of 0.1 to 1 wt. % which indicated less contamination. The coloring impurities like $Fe_2O_3$ and $TiO_2$ were found in the range of 1.0 to 2.5 wt. Percent which indicated that the clay samples contain goethitic iron impurities that which converted to hematite during calcinations & are leached more efficiently. Table

**Table 1.** *General characteristics of clay samples*

| Clay samples marked | C1 | C2 | C3 | C4 |
|---|---|---|---|---|
| Residue on 300 mesh (% by mass) | 5.56 | 4.22 | 29.84 | 6.19 |
| Water of Plasticity (% by mass) | 30.40 | 22.80 | 26.40 | 24.70 |
| Dry Shrinkage (% wet basis) | 2.56 | 5.88 | 5.92 | 5.63 |
| Fired Shrinkage (% wet basis) | 6.96 | 5.07 | 4.43 | 3.66 |
| Dry Strength ($kg.cm^{-2}$) | 6.36 | 20.72 | 49.14 | 35.42 |
| MOR ($kg.cm^{-2}$) | 315.42 | 269.69 | 252.49 | 236.30 |

**Table 2.** *Chemical analysis of clay samples*

| Clay sample | Chemical content, % | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $Ti_2O_3$ | CaO | MgO | $Na_2O$ | $K_2O$ | Loss on ignition |
| C1 | 70.30 | 14.65 | 2.30 | 0.45 | 2.09 | 1.20 | 0.40 | 3.70 | 4.62 |
| C2 | 60.56 | 21.98 | 1.50 | 2.25 | 3.08 | 0.08 | 0.18 | 0.88 | 9.371 |
| C3 | 61.11 | 23.17 | 1.36 | 2.42 | 1.43 | 0.48 | 0.17 | 0.36 | 9.47 |
| C4 | 62.88 | 23.76 | 0.81 | 1.45 | 0.99 | 0.16 | 0.24 | 0.48 | 9.23 |

showed LOI in the range of 5 to 9.5 wt. % due to oxidation of organic mass.

### *XRD Characterization*

XRD is used to determine the mineralogical composition of the raw material components as well as qualitative and quantitative phase analysis of multiphase mixtures. XRD patterns of the clay samples as furnished in fig. 2 indicates the presence of quartz, and kaolinite as the major phases.[7] Further the presence of quartz and kaoline in the clay samples were substantiated also in FTIR study.

### *FTIR analysis of clay*

FTIR studies help in the identification of various forms of the minerals present in the clay. In the IR studies of unfired clay samples furnished in fig.3, the Si–O stretching vibrations were observed in all four clays at 798 -797 cm–1, 539-538 cm–1 and 437-470 cm–1 showing the presence of quartz.[15] , a strong band at 3652-3653

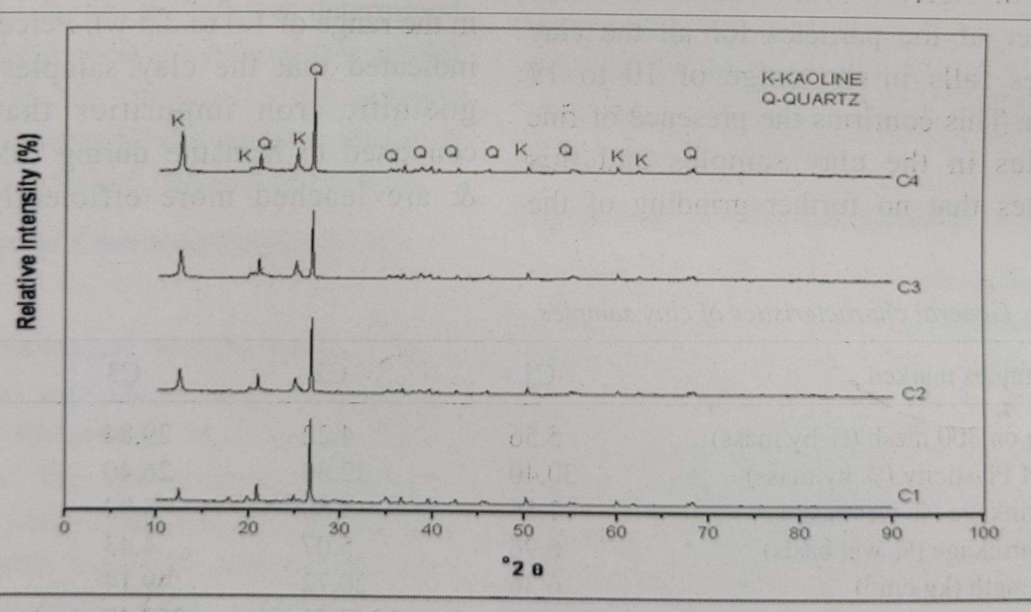


**Fig. 2.** *XRD Pattern of clay samples*

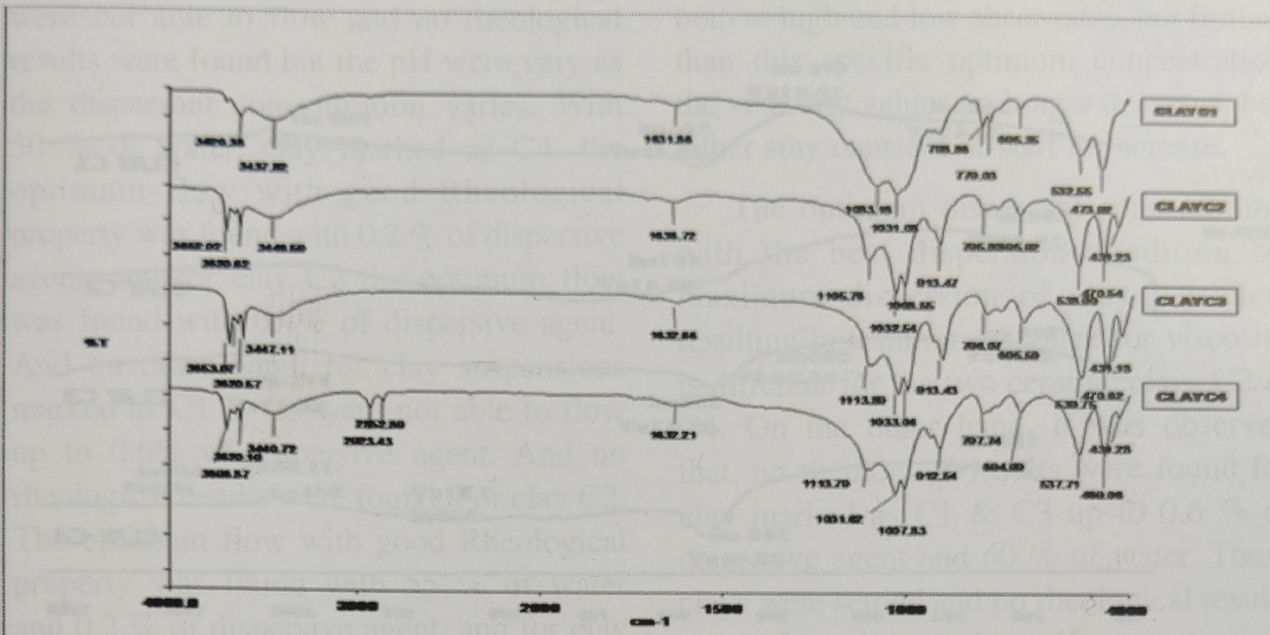

**Fig. 3.** *FTIR analysis of clay samples*

cm–1 and 3620 cm–1 indicate the possibility of the hydroxyl linkage. However, a broad band at 3620 cm–1 and a band at 1631-1632 cm–1 in the spectrum of clays suggest the possibility of water.

Most of the bands such as 1031-1032 cm–1, 914-910 cm–1, 798-789 cm–1, 695cm–1, 539-532 cm–1, 470 cm–1 show the presence of kaolinite.[16] The vibrations observed at 910-914 cm–1 indicate the possibility of the presence of hematite.[17] Absence of Carbon (such as C-C Aliphatic) could be seen very clearly in the clays C1, C2, & C3. Also, stretching spectra for O-H of free hydroxyl & O-H Stretching were absent in clay C1, resulted in decrease in wt. loss which is clearly shown in chemical analysis result (table II), thus the results of IR are quite helpful in the identification of various forms of minerals present.[17]

### *TG/DTA Analysis*

Thermo Gravimetric / Differential Thermal Analysis (TG/DTA) were used to determine phase changes like transition, decomposition simultaneously with change in mass of the sample that occur on heating.

In this brief, clays is measured and evaluated with TG/DTA and result furnished in fig. 4 showed endothermic peak of quartz inversion at 588-566°C in all clay samples. An endothermic peak present in clay C1, C3 & C4 at 496-503 °C indicating dehydroxylation of kaolinite, where reaction (a) takes place.[10-11]

$$Al_2Si_2O_5(OH) \rightarrow Al_2SiO_7 + 2H_2O \quad ...(a)$$

Pre mullite formation showed by an exothermic peak at 971-963°C in Clays C1, C3 & C4.[12]

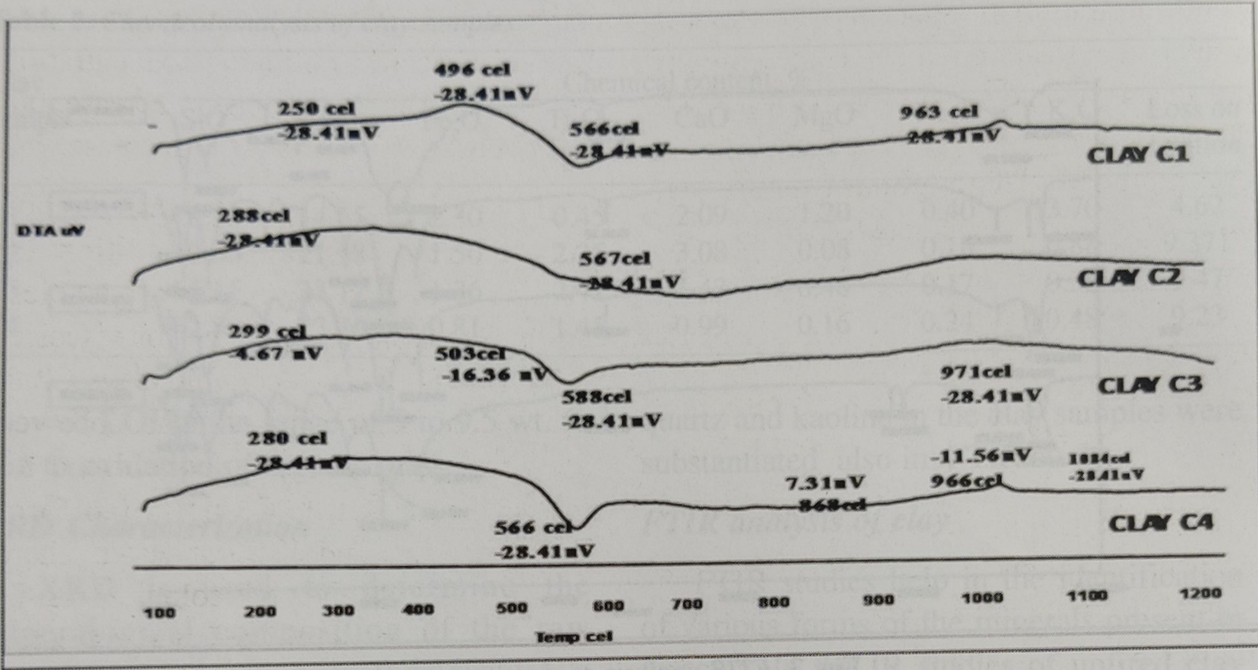


**Fig. 4.** TG/DTA of clay samples.

## *Rheological Studies*

The results of rheological studies are given in figs. 5-10, based on the type of dispersant. The water of plasticity result shown in table no. I, indicate that clay marked as C2 & C4 has lower of as compared to C1 & C3. On the other hand, residue on 300 mesh result indicated the presence of more grit content for clay C3. From the experiments it was observed that with 45% of water and dispersant up to in range of 0.6% used, all the clay suspensions

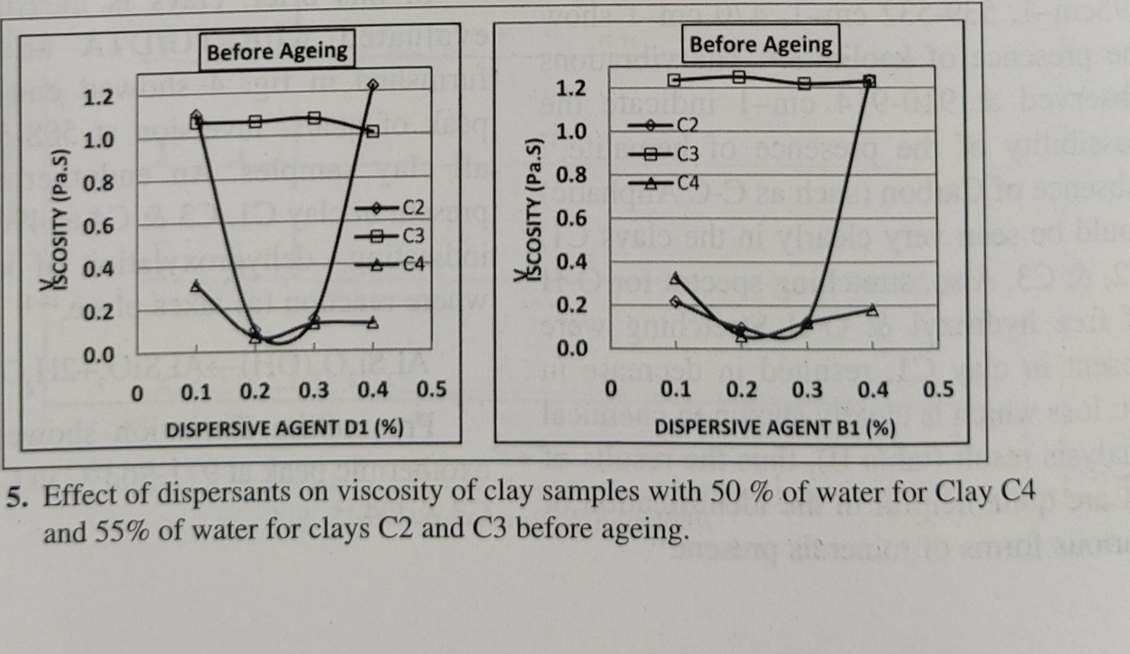


**Fig. 5.** Effect of dispersants on viscosity of clay samples with 50 % of water for Clay C4 and 55% of water for clays C2 and C3 before ageing.

were not able to flow and no rheological results were found but the pH were vary as the dispersant concentration varies. With 50 % of water, clay marked as C4, the optimum flow with good Rheological property was found with 0.2 % of dispersive agent, and for clay C2 the optimum flow was found with 0.4% of dispersive agent. And on other hand, for clay suspensions marked as C1 & C3 were not able to flow up to 0.6% of dispersive agent. And no rheological results were found, For clay C2, The optimum flow with good Rheological property was found with 55 % of water and 0.2 % of dispersive agent, and for clay C1 & C3 , no rheological results were found for clay C1 & C3 up to 0.7 % of dispersive agent and were settled down with 60% of water content.

As is observed in related figures, dispersant concentrations up to a specific optimum value lower the viscosities of suspensions prepared from clays C2 & C4, both at high and low shear rates, but further than this specific optimum concentration the viscosity values no longer decrease, but either stay constant or start to increase.

The optimum dispersant concentration with the best dispersion condition by maximum dispersion of clay particles, resulting in a minimum value for viscosity is different for the two ceramic clays C2 & C4. On the other hand, it was observed that, no rheological results were found for clay marked as C1 & C3 up to 0.6 % of dispersive agent and 60 % of water. These clays were settled and no rheological results were found but the pH varies as a concentration of dispersive varies.

Similarly, after ageing of 24 hrs, it can be observed from the fig.6, the minimum amount of dispersant required for complete dispersion of C2 & C4 clays suspension. The amount of all dispersive agent are 0.2 %(wt/wt) for Clay suspensions C2 & C4,

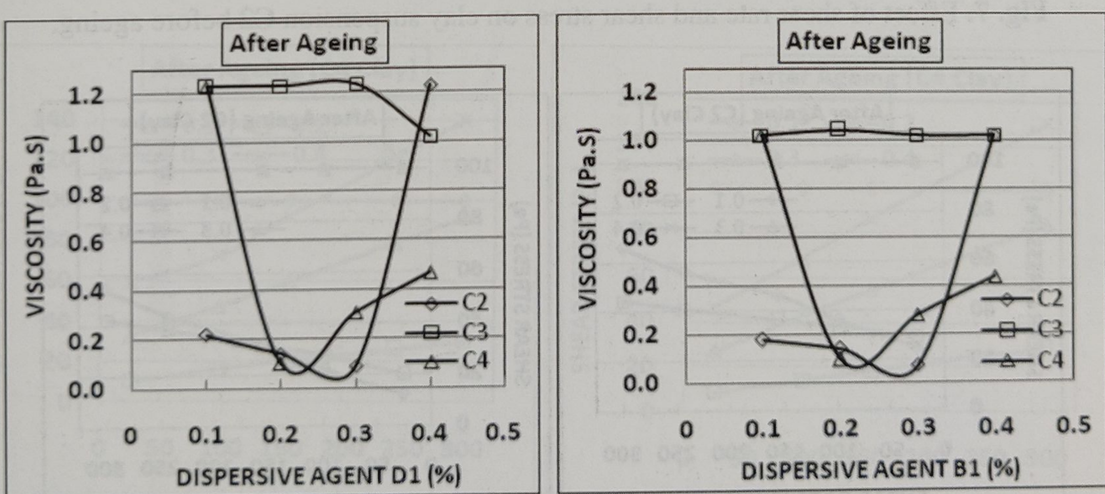


**Fig. 6.** Effect of dispersants on viscosity of clay samples with 50 % of water for Clay C4 and 55% of water for clays C2 and C3 after ageing.

but only difference in that, for clay suspension C4, the optimum flow with good rheological behavior can be obtained in 50% water (wt/wt) and for Clay suspension C2, 55 % of water required to achieve the optimum flow. The evaluation of figures (5-6) indicates that in all suspensions, independent of the type of dispersant present, as it can be seen in related figure (5-6), dispersive agent D1 are quite effective in case of suspension with C2 (55% of water), but for C4, dispersant D2 are quite effective with 50% of water. On the other hand, these four dispersive agents with a range of 0.1 – 0.6 % (wt/wt) are ineffective for clays C1 & C3. The shear stress values increase in a non-linear manner with increasing shear rates, this indicate that the ceramic clay suspensions prepared with all dispersants used shows a non- Newtonian fluid behavior. For clay C2 & C4 with 0.2% of all four dispersive agents, viscosities were decreased, this is resulted from the difference of dispersing

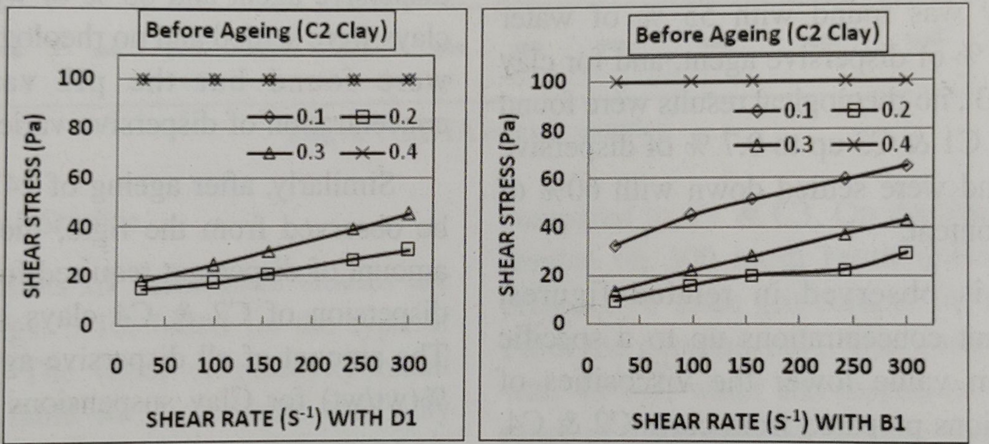


**Fig. 7.** Effect of shear rate and shear stress on clay suspension C2 before ageing.

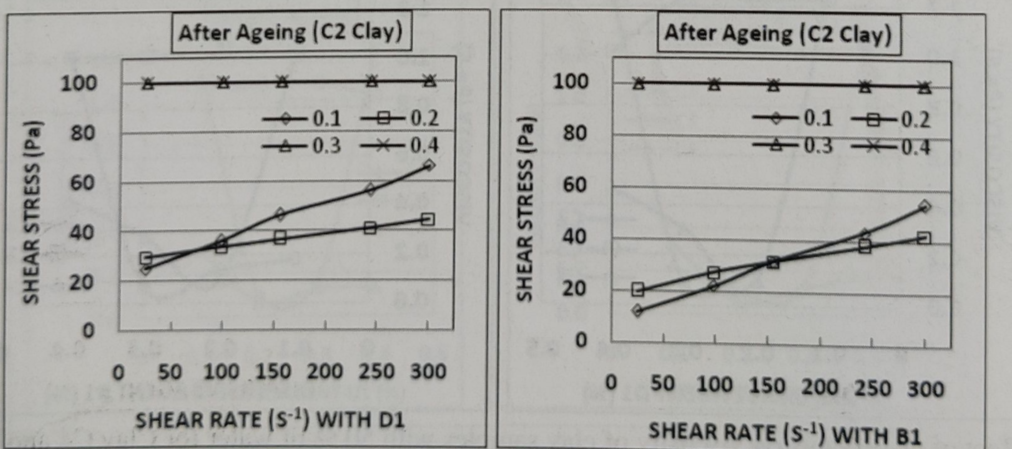


**Fig. 8.** Effect of shear rate and shear stress on clay suspension C2 after ageing.

mechanism for those two phosphates deflocculates was selected for the investigation. Each was studied to determine its effect on the control of dispersion in the different clay-water system utilized in the experiments.

The various phosphates have some common properties, but differ in efficiency as to specific reactions.[7] The Results of this investigation indicate only the relative capabilities of phosphate reagents, all of which were dehydrated sodium phosphates in dispersing different types of clay minerals. The prevail sources of negative charge on clay mineral is unfulfilled chemical bonds at the broken edges, or from dissociation of $H^{-1}$ showing $OH^{-1}$ group or the octahedral (alumina) sheet the Negative

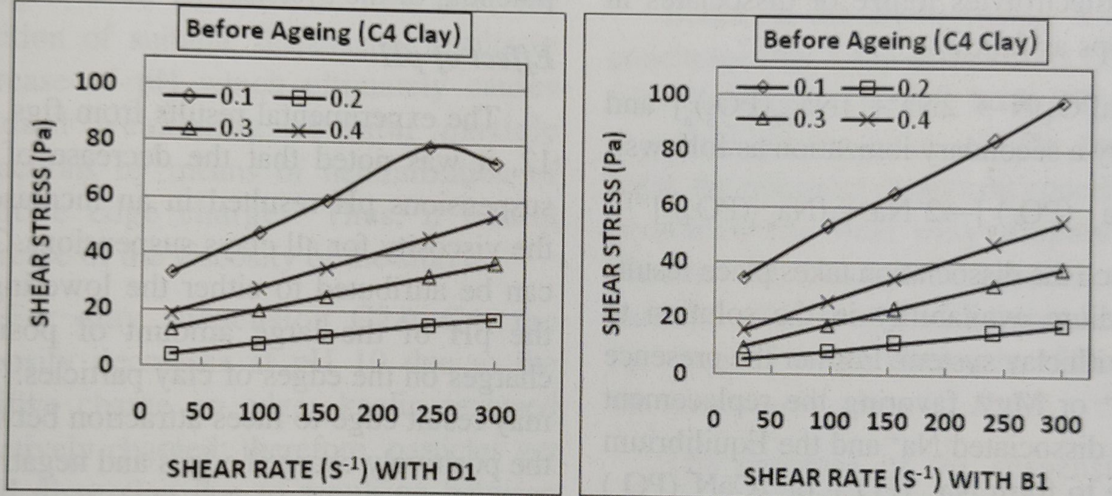


**Fig. 9.** Effect of shear rate and shear stress on clay suspension C4 before ageing.

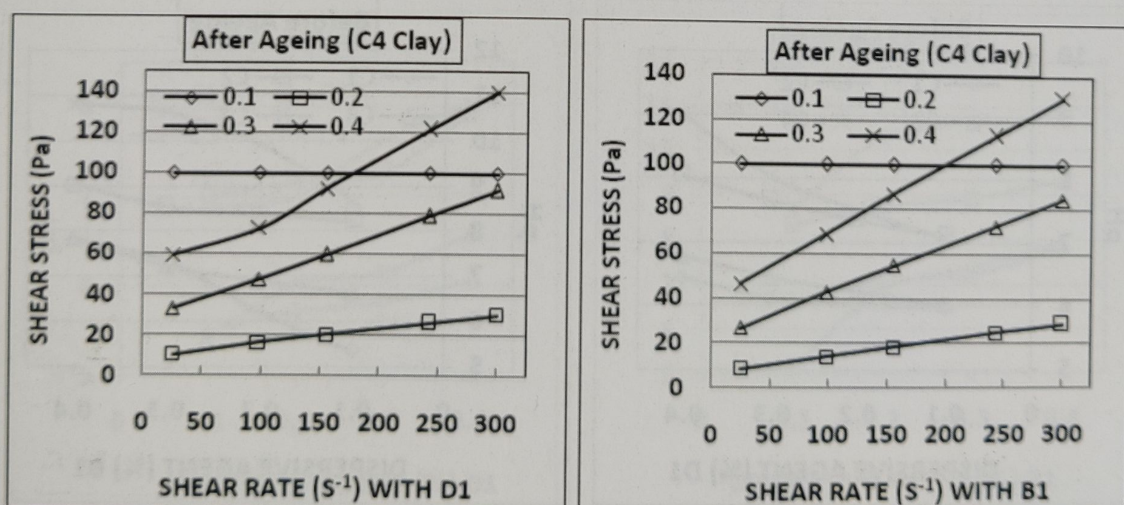


**Fig. 10.** Effect of shear rate and shear stress on clay suspension C4 after ageing.

charge may also be increased through the adsorption of high valence negative ions to positive ions showing at the broken edges Since the anion exchange capacity of clay participle is equivalent to the cation exchange capacity. It is reasonable that the dispersibility of clay could readily be partial by the valance of the anions injected into the clay-water system. A clay particle contains some charged ions. Phosphate based Electrolytes ionize or dissociates in two steps as fallows.

$(NaPO_3)N \rightarrow 2Na^{+} + [Na_{n-2}(PO_3)_n]$ and possibly a secondary ionization as follows:-

$[Na_{n-2}(PO_3)_n] \rightarrow 2\ Na^{+} + [Na_{n-4}(PO_3)_n]$[14]

Once the dissociation takes place results in sodium availability in the solution to react with clay system. Further the presence of $Ca^{++}$ or $Mg^{++}$ favoring the replacement of the dissociated $Na^{+}$ and the Equilibrium reverse to form $Na_{n-2}(PO_3)_n$ or $2CaN_{4.}(PO_3)_n$. Thus possible complex salt formed is a function of the concentration of ca++ and mg++ in the system. Ca++ and mg++ as a part of complex anions, affecting the total negative charge on the clay particles in clay, water, ionized salt system. Anions may be attracted to partly neutralize positive ions showing at the broken edges of clay particles. The net result could be the addition of strong negative charges to the clay particles, thus increasing the dispersion potential of the system.[7]

### *Effect of pH*

The experimental results from figs. 11-12, it was noted that the decrease of the suspensions pH resulted in an increase in the viscosity for all clays suspensions. This can be attributed to either the lowering of the pH of the large amount of positive charges on the edges of clay particles. This may result edge-to faces attraction between the positively charged edges and negatively charged basal surfaces in a "house of cards"

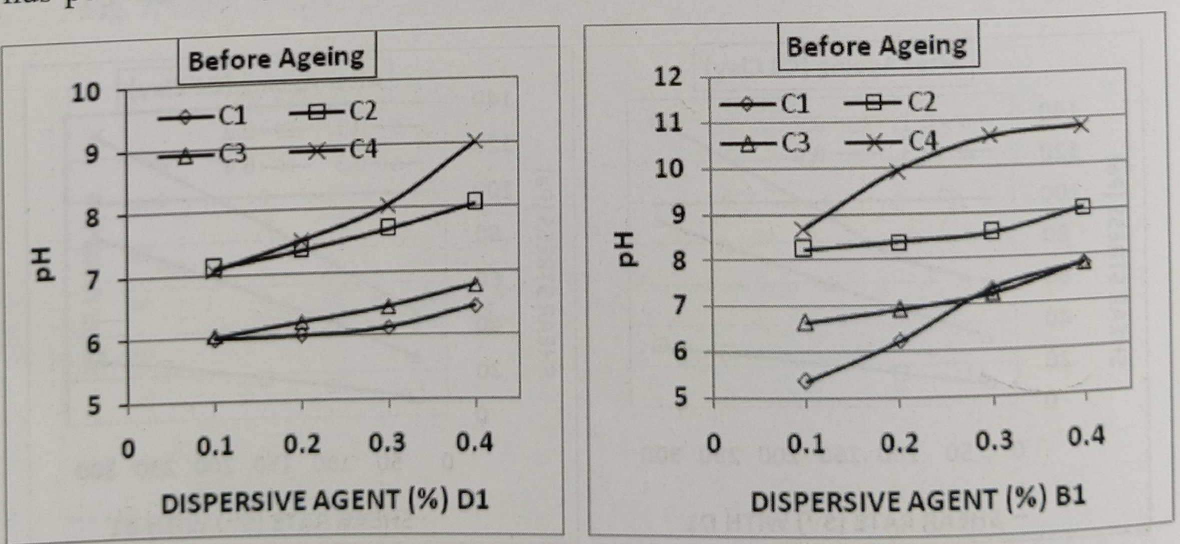


**Fig. 11.** Effect of dispersants on pH of clay suspension before ageing.

conformation. On the other hand, increase in pH resulting large amount of negative charges on the edges of clay particles. Therefore, the repulsion between the same negatively charged particles increases.[16] The high viscosity and pseudo plasticity of acidic kaolinite suspensions are a consequence of strong electrostatic interaction between particles due to the coexistence of negatively and positively charged basal surfaces. In this case, the addition of suitable dispersants results in increase of pH which ultimately causes gradual weakening of inter particle attractions by means of neutralization of positive edge charges. Thus, it finally decrease of the viscosity of the slurry.

For clay suspension C2& C4, the viscosity decreases at pH 10 due to the positive charge on edges kaolin reversed negatively charged; therefore, particles get good dispersion due to repulsion between negatively charged on both edge and surface of particles, it was found that the decrease of the suspensions pH resulted in an increase in the thixotropy which is noted for C1 & C3. clay suspensions .Here , the edge-to face hetero coagulated network can form because of the attraction of oppositely charged edges and surface of kaolin-platelets and vice versa.

## Conclusions

Based on the above studies it may be concluded that, Clay suspensions C1 & C3 with dispersant (D1, D2, B1& B2) display a pseudo plastic behavior .On the other hand, the optimum dispersant concentration produces the best clay dispersion in presence of maximum percent of clay particles. This results in a minimum value for viscosity which obviously different for the two ceramic clays C2 & C4.

The decrease of the suspension pH results in an increase in thixotropy. From the experiments with sample code 2 & 4

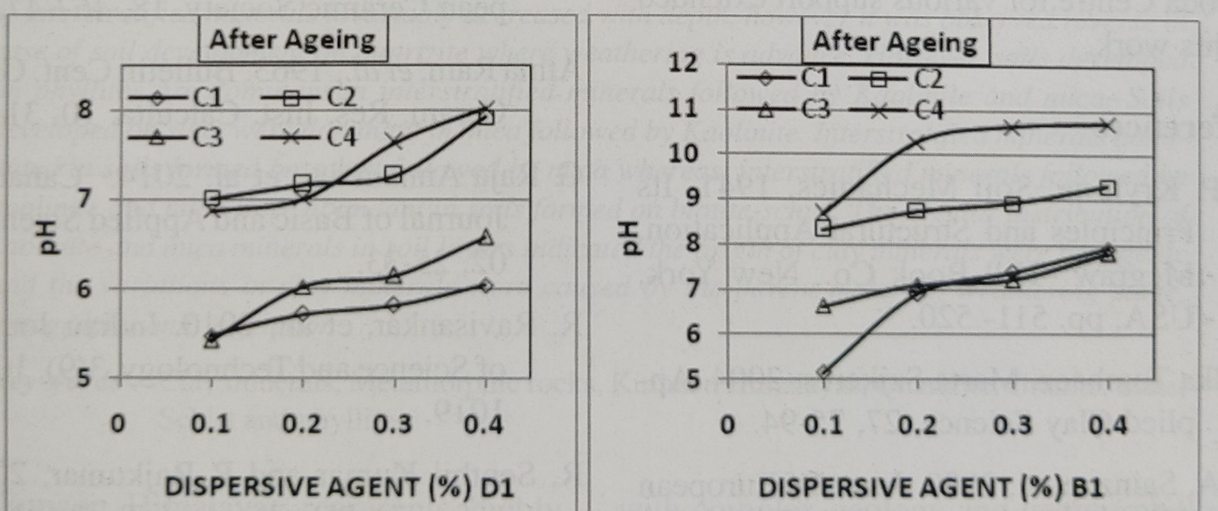


**Fig. 12.** Effect of dispersants on pH of clay suspension after ageing.

containing clay suspension, the viscosity decreases at pH 10 due to good dispersion. This may be attributed to the repulsion between negatively charged on both edge and surface of particles. Similar observation has been made for clay suspensions C1 & C3. where, the decrease of the suspensions pH resulted in an increase in thixotropy may be due to the formation of edge-to face hetero coagulated network. This results in attraction of oppositely charged edges and surface of kaolin-platelets and vice versa. Thus, type and concentration of dispersants has a significant influence in reducing the viscosity of the clay suspension suitable for ceramic body making.

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# Characterization and Clay Minerals Composition of Soils Derived from Metamorphic Formation of Kumaon Himalayas

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***Abstract*****–***Mineralogical compositions of soils developed over metamorphic formation were carried out to know the physio-chemical bahaviour and mineralogical composition of clay fractions in soils of Kumaon Himalayas and their genesis. Soils vary greatly in their properties due to complex geology and geomorphology. Soils are mostly sandy loam to sandy clay loam in texture, strongly acidic to slightly acidic in reaction with pH varies from 4.8 to 6.3, rich in organic carbon, low in CEC. Clay mineralogical studies based on XRD analysis of surface and subsurface layers of selected pedons developed over Quartzite, granite, phyllites, schist and slate in soils of Kumaon hills of Uttarakhand were conducted and exposed to X-ray diffraction analysis. The x-ray diffraction pattern indicated that soils developed on quartzite contained highest amount of mica followed by interstratified and Kaolinite minerals. The content of kaolinite increased with soil formed through mixed layer phase. Kaolinite was the dominant mineral in soil-clay fraction of granite followed by interstratified minerals and micas. The content of interstratified minerals invariably decreased with depth, however it was observed reverse in case of soil development on quartzite where weathering is advance. However, soils developed on phyllites are dominant in interstratified minerals followed by Kaolinite and mica. Soils developed on slate were dominant in mica followed by Kaolinite. Interstratified minerals dominated in soils formed on schist followed by mica whereas, interstratified minerals followed by kaolinite and mica were abundant in soils formed on biotite-schist. The regular distribution of kaolinite and mica minerals in soil layers indicated the origin of clay minerals were pedogenic and the variations in clay minerals were caused by the parent material, weathering stage, topography and vegetation*

***Key words :*** Clay minerals, Metamorphic rocks, Kumaon Himalayas, Quartzite, Granite, Slate, Schist and phyllites

Kumaon Himalayas represents highly folded and faulted chain of Kumaon hills with complex geology and geomorphology leading to micro-level variation in soils.

Detailed studies on morphological, physical and chemical properties soils of Kumaon Himalayas have been reported by Sidhu *et al.,* (1997); and Singh *et al.,* (2004). But the information on occurrence of clay minerals in these soils and their impact on soil development are very scanty. Clay mineralogical make up of soils is necessary for soil classification at lower categorical lever and physico-chemical bahaviour .The nature of clay minerals help us to know about genesis of soils and their relation with the parent material (Surya, *et al.*, 2005). Thus, an attempt has been made in the present investigation to elucidate the mineralogy of clay fractions in soils to ascertain mineralogical composition and genesis of soils.

## Materials and Methods

The study area, Khulgad watershed (29°34'31'' to 29°41' N latitudes & 79°32'15'' to 79°37' E longitudes) covering about 3278 ha, representing highly folded and faulted chain of Kumaon hills of Almora district of Uttrakhand (Fig. 1). Topography is extremely hilly and rolling with general elevation ranges from 900 to 2200 m above msl. The relief is excessive except in piedmont slopes and valley where it is somewhat excessive to flat. General slope of watershed is from west to east and slope gradient ranges from 1 to 74 per cent. The drainage pattern is dominantly trelis and rectangular in quartzite while angular in granite-gneiss. However, parallel and dendritic pattern was found on phyllites and schist (Walia *et al.,* 2013). The geology of the area composed of pre-cambrian metamorphic rocks such as gneiss, schist, quartzite, slate and phyllites (Wadia, 1975, Krishnan 1982). The Almora group that constitutes the Almora neppe is made up of predominantly granitiferreous mica-schist interbedded with micaceous quartzites intimately associated with augen gneisses and subordinate phyllites as metagreywackes (Valdiya, 1980, and Valdiya, 1988).Climatically, the area represents humid, sub-temperate and monsoonal type with annual rainfall of 950mm and annual temperature of 19.8 °C.

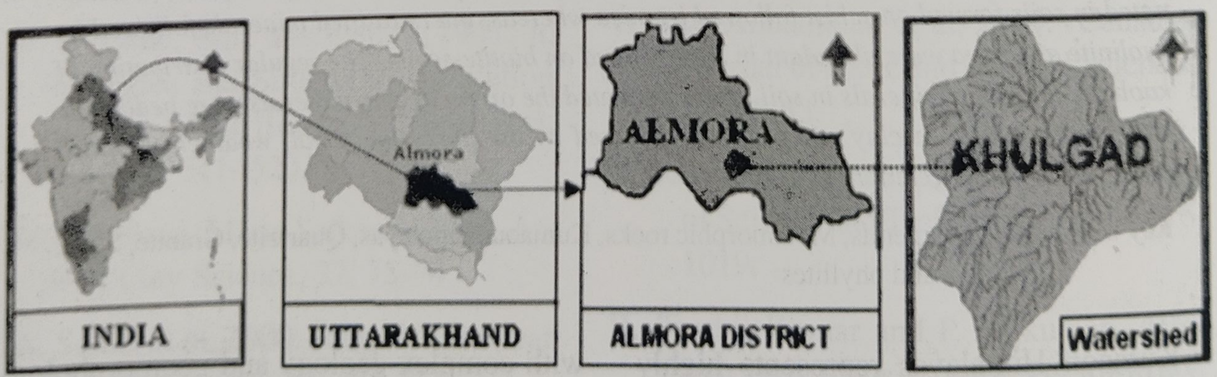


**Fig. 1.** Location map of Study area, Khulgad watershed, Almora

The area qualifies for *'thermic'* temperature and *'Udic'* moisture regime. The present land use is pasture, moderately dense to dense forest and under cultivation on mid hill and lower terraces.

Based on detailed soil survey, nine representative Pedons, (two developed over Biotite schist, two over Sitlakhet schist, one each over slate, phyllites and granite and two over quatrzite) were selected for studying morphological and physic-chemical and mineralogical properties. Soil samples were analyzed for Physico-chemical properties such as pH, EC, CEC and organic carbon as per the standard laboratory procedures (Black, C.A, 1965, Sarma *et. al* 1987). Particle size fractions were estimated by International pipette method. The clay fractions (2- 0.2 μm and < 0.2 μm) were separated from soil samples (< 2mm size) after dispersion using size segregation procedure of Jackson (1979). The selected soil samples developed different parent were exposed to X-ray diffraction analysis for their identification after giving various treatments. X-ray diffraction (XRD) analysis of clays of selected samples pertaining to representative pedons was done.

The parallel oriented Ca/K saturated clay samples were subjected to x-ray analysis with Philips diffractometer using Ni - filtered Cu-k alpha radiation at a scanning speed of $2^0$ 2 Ø per minute. Clay minerals were identified according to the procedure outlined by Jackson (1979); Semi-quantitative estimation of clay minerals was also computed based on the principles outlined by Gjems (1967).

## Results and Discussion

### *Soil morphological and physio-chemical properties*

The detailed information about morphological and physio-chemical properties of soil developed over different parent material presented in Table 1. It reveals that the soils developed on quartzite are deep, well drained, dark yellowish brown to brown, sandy loam to sandy clay loam, rich in organic carbon, moderately acidic soils very high AWC and low CEC., occurred on mid hill terraces and classified as *fine-loamy, Ultic Hapludalfs* (Walia, et.al., 2013) . However, deep, sandy loam, slightly acidic soils high in AWC found in lower hill terraces (coarse-loamy, Dystric Eutrudepts).soil developed on gneissic parent material occurred on Hill Slopes are moderately shallow, somewhat excessively drained, sandy loam to sandy clay loam, and classified as *Fine-loamy, Humic Dystrudepts*, These soils are rich in organic carbon, very strongly acidic in reaction (pH 4.7-5.5), and low in CEC, AWC. soils developed on schist (garnetiferous) landscape are shallow to moderately shallow, somewhat excessively drained, dark yellowish brown, sandy loam, medium in organic carbon, slightly to strongly acidic in reaction, low AWC and CEC and classified as *Loamy/Coarse Loamy, Lithic*

**Table 1.** *Morphological and Physio-chemical properties of soils formed on different parent materials*

| Parent material | Soil layers/ | Depth (cm) Horizon | colour | Texture | Clay (%) | pH | OC (%) | CEC (Cmol (P+)kg-¹) | Base saturation (%) |
|---|---|---|---|---|---|---|---|---|---|
| | | | Salla Rautela series - *Fine-loamy, Dystric Eutrudepts* | | | | | | |
| Deolikhan | Ap | 0-16 | 10YR4/3M | sl | 13.60 | 5.27 | 1.78 | 15.1 | 72 |
| Quartzite | Bw | 16-63 | 10YR4/4M | sl-scl | 20.40 | 5.46 | 0.46 | 7.8 | 67 |
| | | | Dhamas Series - *Fine-loamy, Ultic Hapludalfs* | | | | | | |
| Damas | Ap | 0-19 | 10YR4/3M | sl | 14.80 | 4.98 | 1.01 | 7.2 | 57 |
| Quartzite | Bw/Bt | 19-110 | 10YR4/4M | scl | 23.50 | 5.80 | 0.30 | 8.5 | 65 |
| | | | Sitlakhet series - *Fine loamy, Humic Dystrudepts* | | | | | | |
| Granite | Ap | 0-12 | 10YR 3/1M | sl | 10.80 | 5.13 | 2.69 | 17.7 | 53 |
| | Bw | 12-40 | 10YR5/4; 7.5YR4/4M | sl-scl | 20.20 | 4.82 | 0.42 | 8.4 | 47 |
| | | | Kaphalkot Series – Coarse-loamy, Typic Dystrudepts | | | | | | |
| Biotite schist | Ap | 0-16 | 10YR 5/4D | Scl | 25.20 | 5.00 | 0.71 | 5.9 | 56 |
| | Bw | 16-92 | 10YR4/4M | sl | 12.00 | 5.05 | 0.55 | 5.4 | 55 |
| | | | Kharkhunna series – loamy, *Lithic Udorthents* | | | | | | |
| Biotite schist | Ap | 0-13 | 2.5Y 4/2M | sl | 10.80 | 6.03 | 0.37 | 4.3 | 63 |
| | $A_{12}$ | 13-26 | 2.5Y 4/2 M | sl | 8.80 | 5.90 | 0.17 | 4.6 | 63 |
| | | | Bhargal Rautela series - *Lithic Udorthents* | | | | | | |
| Sitlakhetschist | Ap | 0-15 | 10YR 4/4M | sl | 16.80 | 5.22 | 0.62 | 6.2 | 53 |
| | | | Champa series - *Dystric Eutrudepts* | | | | | | |
| Sitlakhetschist | Ap | 0-17 | 10YR 4/3M | sl | 8.40 | 6.14 | 1.67 | 12.7 | 77 |
| | Bw | 17-35 | 10YR 4/3M | sl | 10.40 | 6.22 | 0.50 | 7.1 | 77 |
| | | | Kurchaun series (P85)- Coarse-loamy, *Dystric Eutrudepts* | | | | | | |
| Slate | Ap | 0-12 | 10YR 4/3M | sl | 9.20 | 5.99 | 0.44 | 3.9 | 62 |
| | Bw | 12-64 | 10YR 4/4M | sl | 11.60 | 6.30 | 0.18 | 4.01 | 64 |
| | | | Kathpuriya series (P73)- Fine loamy, *Humic Dystrudepts* | | | | | | |
| Phyllites | Ap | 0-10 | 10YR 4/2M | l | 24.40 | 5.26 | 3.45 | 11.9 | 63 |
| | Bw | 10-44 | 10YR 4/4M | scl | 22.40 | 5.55 | 0.63 | 6.8 | 58 |

*Udorthents/ Dystric Eutrudepts.* Soils developed on schist (Biotite) landscape are shallow, excessively drained, dark grayish brown, sandy loam, moderately acidic in reaction, low in organic carbon, AWC and CEC and classified as *loamy, Lithic Udorthents* whereas, soils developed on shitlaket schist landscape are deep, somewhat excessively drained, dark yellowish brown, sandy loam to sandy clay loam, strongly to very strongly acidic in reaction, high in organic carbon, low in CEC and high in AWC and classified as fine loamy over *Coarse-Loamy, Typic Dystrudepts*. Soils developed over phyllites and slate are moderately shallow, somewhat excessively drained, dark grayish brown, gravelly sandy clay loam to loam, strongly acidic, high in organic carbon, low in AWC and CEC, classified as Fine-*loamy, Humic Dystrudepts.* Soils developed over slate are moderately deep, somewhat excessively drained, dark yellowish brown, sandy loam, moderately to slightly acidic, medium in organic carbon, AWC and low in CEC, classified as Coarse-*loamy, Dystric Eutrudepts.* The three pedogenic stages of soil evolution varying from Entisols, Inceptisols and Alfisols were observed in the study area. (Walia *et al.,* 2013)

### *Mineralogical Composition of the Total and Fine Clay Fractions*

Soils of selected soil profiles developed on different parent materials were processed by standard methodology and were exposed to X-ray diffraction analysis for their identification after giving various treatments. The XRD of fine and total clay fractions of soil derived from different parent materials were dipcted in fig. 2a and 2b.

### *Semi - quantitative estimates of clay minerals*

The distribution of clay minerals in the soils developed on different parent materials is presented in Table 2. Based on the X-ray diffraction pattern revealed that soil developed on granite are dominated by Kaolinite followed by interstratified minerals and mica. However, the mineralogical composition of soils developed on quartzite contained highest amount of mica followed by interstratified and kaolnite minerals. The content of kaolinite increases with soil development formed through mixed layer phase. Soils developed on phyllites are dominant in interstratified minerals followed by kaolinite and mica. Soils developed on slate were dominant in mica followed by kaolinite. Interstratified minerals dominated in soils formed on Sitlakhet schist followed by mica. However, interstratified minerals followed by kaolinite and mica were abundant in biotite-schist. Abundance of mica decreased in Ap horizon and increased in Bw horizon except in soils developed on Sitlakhet schist. The variations in kaolinite content were smaller except Sitlakhet and biotite-schist where it increased with depth. The content of interstratified minerals invariably decreased with depth, however it was observed reverse in case of soils developed on quartzite where the weathering is in advance. This trend was also observed in the soils developed on phyllites under dense forest conditions. Smaller amount of vermiculite were found almost in all the soils. Similarly, traces of smectite were found in soils developed on Deolikhan quartzite, slate, phyllites and granite. Traces of chlorite minerals were also found in the soils formed in granite, biotite-schist, and Sitlakhet schist. The clay mineralogical composition of these soils by and large was observed to be mixed in soils derived from quartzite and granite. Interstratified minerals were dominant in soils formed from phyllites, biotite schist and Sitlakhet schist though nature of interstratifications showed some variations. Mica was dominant in soils developed on slate. The variations were mostly caused by the parent material, weathering stage, vegetation and topography.

It was also indicated that clay mineralogical – suite of soils developed over quartzite and slate were similar except that the little amount of smectite was more pronounced in soil developed over slate. While granite, phyllites shows similar

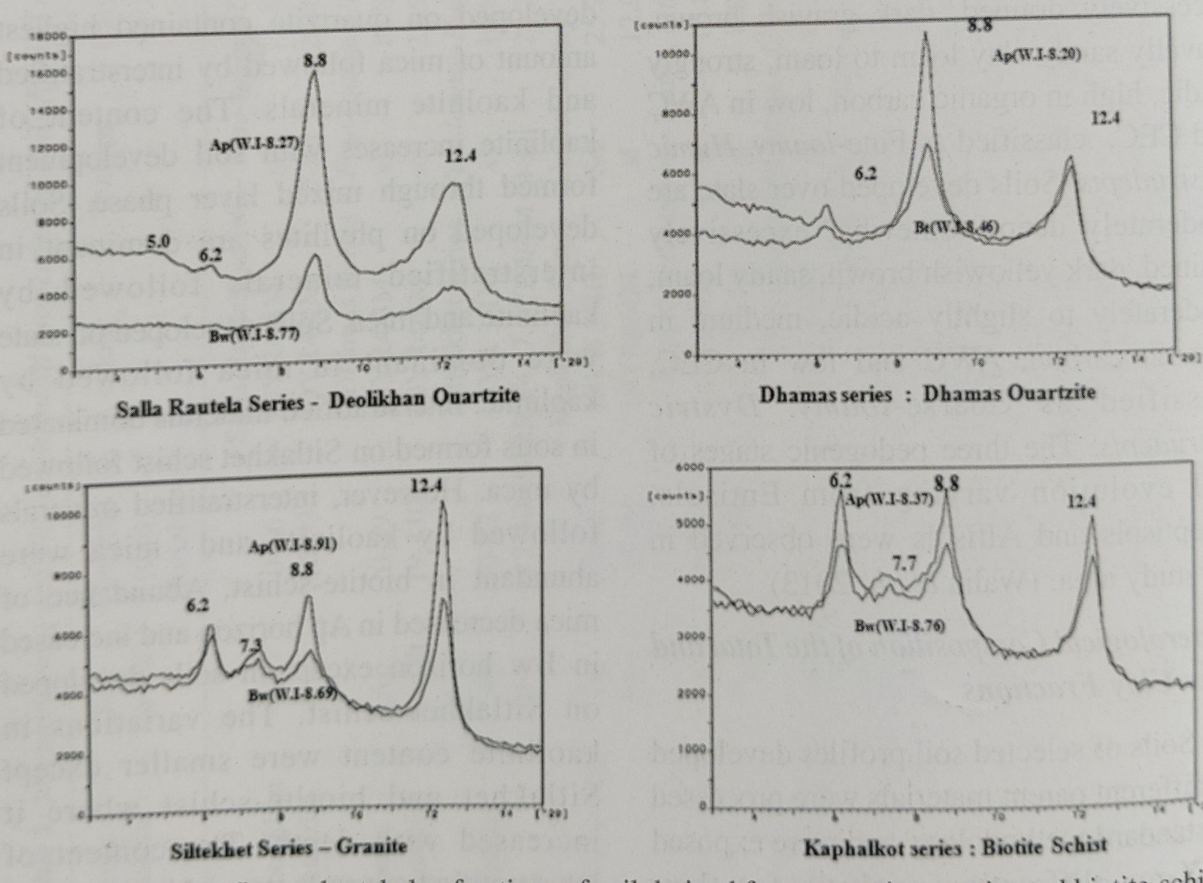


**Fig. 2a.** XRD of fine and total clay fractions of soil derived from quartzite, granite and biotite-schist

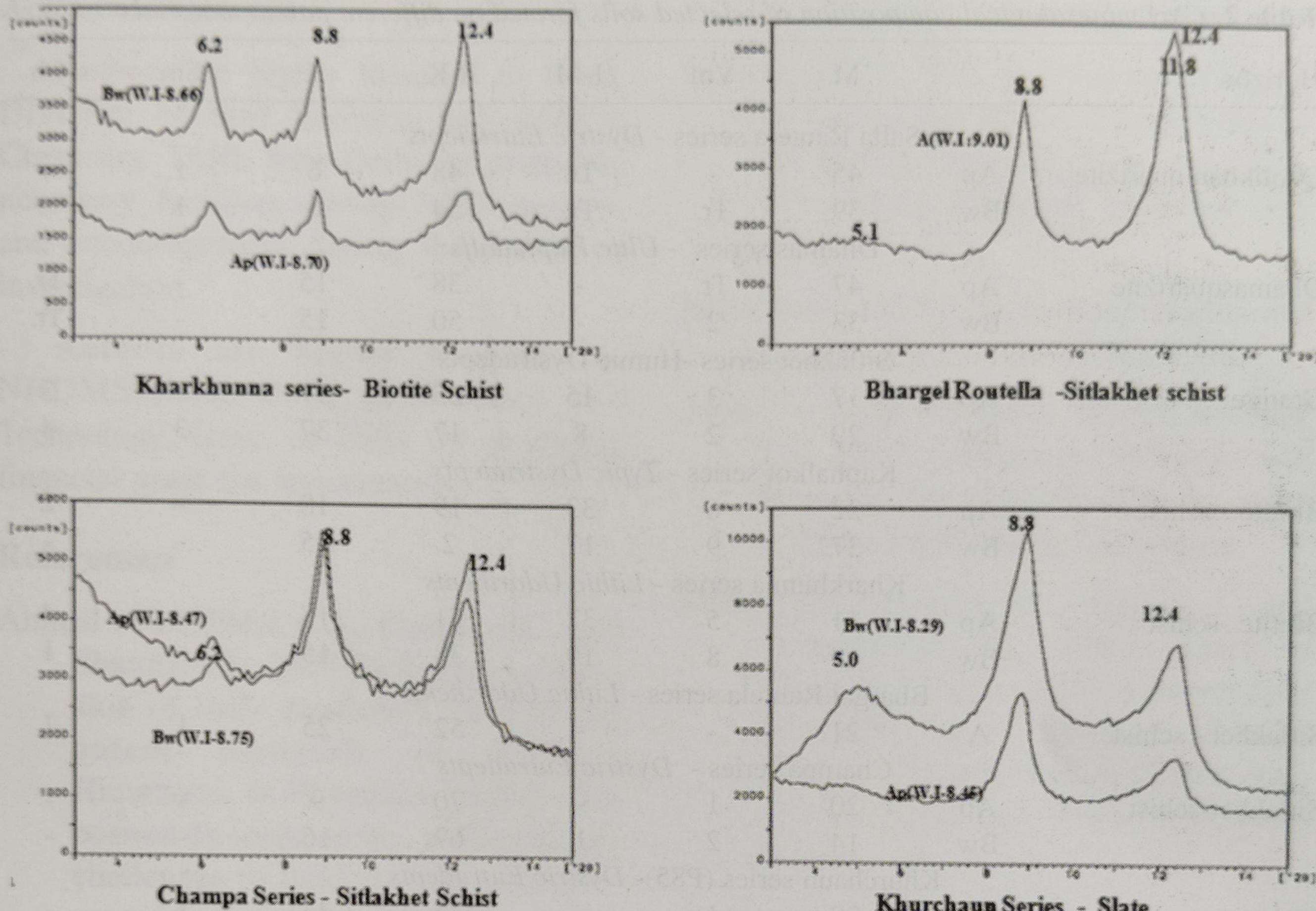


**Fig. 2 b.** XRD of fine and total clay fractions of soil derived from Sitlakhet-schist and slate

mineralogical composition with dominance of Kaolinite and traces of smectite in lower horizons. Gorai, T. (2010) also observed the similar findings that the soils derived from quartzite contained mica as dominant mineral while kaolinite was subdominant mineral with traces of smectite in clay fractions of soils of Kumaon region of Almora district. Surya *et al.,* (2005) reported clay mineralogical studies based XRD analysis described that kaolinite was the dominant clay minerals in soil-clay fraction dominance of quartzite schist and mica was dominant in murrum-clay fractions. Presence of kaolinite, mica and quartz shows the nature of parent material. The presence of negligible amounts of the smectite in the subsurface soils indicated that smectite may be of detriatal origin and moved to lower layer by lessivage in light textured soils. The clay mineralogical analysis of soils developed at different toposequence in Kumaon Himalayas reported soils developed over very steep hill slope with schist as parent material and mostly under garazing and scrub lands, had

**Table 2.** *Clay mineralogical composition of selected soils formed on different parent materials*

| Horizon | | M | Vm | I-M | I-K | K | Sm | Ch |
|---|---|---|---|---|---|---|---|---|
| | | Salla Rautela series - *Dystric Eutrudepts* | | | | | | |
| Deolikhan quartzite | Ap | 45 | - | Tr. | 48 | 6 | 1 | - |
| | Bw | 39 | Tr. | Tr. | 54 | 6 | 1 | - |
| | | Dhamas series - *Ultic Hapludalfs* | | | | | | |
| Dhamasquartzite | Ap | 47 | Tr. | - | 38 | 15 | - | Tr. |
| | Bw | 33 | 2 | - | 50 | 15 | - | Tr. |
| | | Sitlakhet series -Humic Dystrudepts | | | | | | |
| Granite | Ap | 17 | 3 | 15 | 25 | 37 | - | 3 |
| | Bw | 29 | 2 | 8 | 17 | 37 | 3 | 4 |
| | | Kaphalkot series - *Typic Dystrudepts* | | | | | | |
| Biotite - schist | Ap | 22 | 6 | 33 | 19 | 18 | - | 2 |
| | Bw | 37 | 9 | 17 | 2 | 35 | - | - |
| | | Kharkhunna series - *Lithic Udorthents* | | | | | | |
| Biotite -schist | Ap | 11 | 5 | 32 | 31 | 17 | - | 4 |
| | Bw | 19 | 8 | 19 | 38 | 15 | - | 1 |
| | | Bhargal Rautela series - *Lithic Udorthents* | | | | | | |
| Sitlakhet - schist | A | 21 | - | - | 52 | 25 | 1 | 1 |
| | | Champa series - *Dystric Eutrudepts* | | | | | | |
| Sitlakhet-schist | Ap | 20 | 1 | - | 70 | 9 | - | - |
| | Bw | 14 | 2 | 1 | 67 | 16 | - | - |
| | | Khurchaun series (P85)- *Dystric Eutrudepts* | | | | | | |
| Slate | Ap | 50 | 1 | - | 25 | 23 | 1 | - |
| | Bw | 56 | - | Tr. | 19 | 21 | 4 | - |
| | | Kathpuriya series (P73)- *Humic Dystrudepts* | | | | | | |
| Phyllites | Ap | 19 | 4 | 28 | 16 | 31 | 2 | - |
| | Bw | 12 | 1 | 36 | 24 | 26 | - | 1 |

M: Montmorillonite; Vm: Vermiculite; I-M: Interstratified mica; I-K: Interstratified kaolinite; K: Kaolinite; Sm: Smectite and Ch: Chlorite

relative abundance of Kaolinite followed by interstratified kaolonite and mica (Ahmad *et al.* (2009). Hills soils are intensively leached resulting in fall of base status of ionic environment. In such conditions illite became unstable and weather to Kaolinite type minerals. Hence the genesis of soils formed in various physiographic units reveled that the soils developed in the region were influenced primarily by their parent material. The clay mineralogical composition of soils by and large was observed to be mixed in soils and the variations were mostly caused by the parent material, weathering stage, vegetation and topography.

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# Monitoring of soil $CO_2$ evolution and dehydrogenase activity under the influence of *Trichoderma harzianum* encapsulated nanoclay polymer composite

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**Abstract**–*Monitoring of soil respiration and dehydrogenase activity (DHA) under the influence of* Trichoderma harzianum *encapsulated nanoclay polymer composite (TENCPC) was done to investigate the impact of TENCPC on soil $CO_2$ evolution and the enzymatic activity, particularly dehydrogenase, which is an important indicator of soil health. Soil samples were collected from a long term fertilizer trial under dryland agriculture. The treatments were control (no nutrient supplemented)-$T_1$, 100% recommended dose of fertilizer (RDF) i.e. 80-40-30 kg $ha^{-1}$ N: P: K-$T_2$, 100% N through farm yard manure (FYM)-$T_3$, 50% N through FYM-$T_4$, 50% RDF + 50% N through FYM-$T_5$ and farmer's general practice (20 kg N $ha^{-1}$)-$T_6$. At 4$^{th}$ hour, the average $CO_2$ release from soil through microbial respiration was highest for $T_2$ (100 % RDF) i.e. 1.5 mg $CO_2$-C/g soil/hr whereas, for control ($T_1$), it was 0.6. At 4$^{th}$ hr, $CO_2$-C evolution rate was highest at 2.40 $CO_2$-C (mg/ g soil/ hr) for $T_3$ treated with TENCPC @ 1 mg/ 100 g soil, incubated up to 168$^{th}$ hour, and lowest was under $T_1$ i.e. 0.97. The application of TENCPC in soil also increased the soil DHA during both the years. After the application of TENCPC in soil, the maximum DHA was for $T_3$ i.e. 70.4 TPF µg/ g soil/ day and minimum was for $T_1$ i.e. 26.61, whereas, the corresponding value before the application of TENCPC was 64.2 and 25.7, respectively after 7 days of incubation.*

## Introduction

Wilt-nematode disease complex, caused by *Fusarium oxysporum* and *Meloidogyne incognita*, has been identified as one of the major yield limiting factors for pulses in rainfed *rabi* cropping system in India (De *et al.*, 2000). It was found that moist soil condition was an effective measure in controlling *Fusarium* wilt in *Cicer* in rainfed areas from a long term experiment

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in Pakistan (Haq *et al.*, 2009). On the other hand, *Trichoderma harzianum* is a potential biological control agent to control wilt causing fungi like *Fusarium oxysporum* (Sharma, 2011). Nanoclay polymer composite is a superabsorbent and showed a significant slow release property for both water and nutrient (Sarkar *et al.*, 2013). So, combination of nanoclay polymer composite along with *Trichoderma harzianum* could be a promising strategy to control this serious disease under rainfed condition. Nanomaterials are ultimately remain in soils ecosysytem (Nowack and Bucheli, 2007) and soil microorganisms could be significantly affected when exposed to nanomaterials (Navarro *et al.*, 2008). It was also found that direct contact with highly purified carbon nano tubes aggregates can lead to bacterial cell death, and incubation of bacterial cells with 5 µg/mL carbon nano tubes for 1 hr induced a significant loss in bacterial viability (Kang *et al.*, 2007). Thus, change in activity of soil microorganisms that play an important role in nutrient cycling has been a sensitive indicator of soils' response to environmental stressors. The impact of manufactured nanomaterials on soil microbial community was estimated using soil respiration as it is an established method to determine the effects of anthropogenic chemicals on aerobic soil activity (Jones and Ananyeva, 2001). When soils were incubated in the presences of nanomaterials like fullerene ($C_{60}$) as a granular, as an aqueous suspension (nC60) and tetrahydrofuran (THF) residues, and control up to 180 days, a reduction in the rate of respiration and soil enzymatic activity compared to the control would be expected if soil populations were subjected to a highly toxic material (Tong *et al.*, 2007; Johansen *et al.*, 2008). In addition, fullerenes applied to biosolids did not alter cumulative $CO_2$ and $CH_4$ formation or community composition of microorganisms inhabiting anaerobic environments (Nyberg *et al.*, 2008). Influence of *Trichoderma harzianum* encapsulated nanoclay polymer composite (TENCPC) on the soil $CO_2$ evolution and dehydrogenase activity is a little explored area of research. Hence, the effect of manufactured nanomaterials on soil must be pointed out so that awareness can be created about the environmental consequences of nanotechnology. In view of the above, the present experiment was formulated to study the soil $CO_2$ evolution and dehydrogenase activity under the influence of *Trichoderma harzianum* encapsulated nanoclay polymer (TENCPC) composite on soils from a 30 years long term fertilizer trial under dryland agriculture. In this study, the impact of TENCPC on soil microbial respiration through $CO_2$ evolution was determined. On the other hand, the enzyme activities are excellent indicators of soil microbial function, and have been applied in studies to assess the changes in microbial function caused by soil contamination. So, dehydrogenase enzyme activity was taken as another key parameter for microbial activity after the application of TENCPC in soil.

## Materials and Methods

### *Soil sampling and characterization*

The experimental soil sample (0-15) cm depth, was collected from experimental site at research farm (25⁰ 18' N, 83⁰ 03' E, altitude 129 m above mean sea level) of Banaras Hindu University, Varanasi in the year 2012-2013 and 2013- 2014, growing lentil in rice-lentil cropping system under rainfed condition. This experiment has been under the network of the All India Coordinated Research Project on Dryland Agriculture (AICRP-DLA) of the Indian Council of Agricultural Research continuing since 1985. Varanasi falls under the transect 4 of IGP region having semi-arid to sub-humid climate with average rainfall of 1081.4 mm and annual potential evapotranspiration of 1525.2 mm. About 87% of the total rainfall is received during monsoon season (June to September). The experimental soil was classified as fine loamy, mixed, hyperthermic *Udic Haplustepts.* Plant nutrients were supplied only in rainfed rice through organic and inorganic sources of nutrients and second crop lentil cultivated with the residual fertilizer i.e. no external application of organic and inorganic fertilizer in lentil. The six treatments comprising combinations of organic and inorganic sources were tested in 100 g soils arranged in a completely randomized design with three replications under laboratory condition. The treatments were: control (no nutrient supplemented)-$T_1$, 100% recommended dose of fertilizer (RDF) i.e. 80-40-30 kg $ha^{-1}$ N: P: K-$T_2$, 100% N through farm yard manure (FYM)-$T_3$, 50% N through FYM-$T_4$, 50% RDF + 50% N through FYM-$T_5$ and farmer's general practice (20 kg N $ha^{-1}$)-$T_6$. Some of the initial soil chemical characteristics such as pH (1:2.5), electrical conductivity (dS/m), cation exchange capacity (cmol($p^+$) / kg soil), organic carbon (%) of each treatment (Table 1) were measured through standard procedures (Jackson, 1973).

### *Preparation of Trichoderma harzianum encapsulated nanoclay polymer composite (TENCPC)*

Nanoclay polymer composite was prepared from commercially available nano-bentonite through the process described by Liang and Liu, 2007. The conidial pellet of *T. harzianum* was suspended in 100 mL of clay monomer suspension and mixed thoroughly to give a conidial concentration of 2.7 X $10^8$ colony forming units per milliliter (cfu/ mL). The whole polymerization reaction was carried out in a controlled temperature i.e., 30±2°C, otherwise higher temperature may cause the death of *Trichoderma harzianum* cells after encapsulating in the polymer matrix.

### *Soil incubation*

Soil from each treatment was taken in conical flasks, moisture of each soil was maintained at field capacity and TENCPC

**Table 1.** *Chemical characteristics of soil*

| Treatments | pH (1:2.5) | EC (dS/m) | Organic carbon (%) | Cation exchange capacity (cmol(P$^+$)/kg soil) |
|---|---|---|---|---|
| $T_1$ | 7.63 | 0.18 | 0.26 | 12.5 |
| $T_2$ | 7.54 | 0.25 | 0.28 | 13.7 |
| $T_3$ | 7.46 | 0.21 | 0.36 | 15.3 |
| $T_4$ | 7.48 | 0.22 | 0.29 | 14.1 |
| $T_5$ | 7.49 | 0.20 | 0.33 | 14.7 |
| $T_6$ | 7.68 | 0.20 | 0.27 | 11.7 |

was applied @ 1 mg/100g soil. The incubation study was carried out in controlled temperature of 30±2 °C to study the effect of TENCPC on soil respiration and dehydrogenase activity.

### *Soil $CO_2$ evolution*

Soil respiration was estimated by alkali trap method proposed by Anderson 2003. The rate of $CO_2$ evolution from each soil was observed before and after the application of TENCPC at 4$^{th}$, 24$^{th}$, 48$^{th}$, 72$^{nd}$, 120$^{th}$ and 168$^{th}$ hour of incubation.

### *Dehydrogenase activity (DHA)*

DHA was measured by the method proposed by Klein *et al.,* 1971. Soil from each treatment was incubated with and without TENCPC at controlled temperature for 7 days. DHA was measured through the TPF (2, 3, 5-triphenyl formazon) formation, which was expressed as μg TPF $h^{-1}$ $g^{-1}$ soil.

### *Statistical analyses*

The significant differences among the treatments were judged by analysis of variance (ANOVA) in completely randomized design (CRD).

## Results and discussion

### *Soil $CO_2$ evolution*

The average $CO_2$ release from soil through microbial respiration during the study period was highest for $T_2$ i.e. 1.5 mg $CO_2$-C/g soil/hr at 4$^{th}$ hr due to initial faster rate of decomposition of organic matter by microbes for release of nutrients. Initially, at 4$^{th}$ hr release of $CO_2$ under $T_3$ and $T_4$ treatments was found statistically at par (Fig 1). $T_3$ containing 100 % N through FYM having much higher amount of soil microorganisms that involved in significantly faster decomposition rate over the control where no organic or inorganic sources of nutrients were added. At 168$^{th}$ hr, all the treatments showed a decrease trend of release rate of $CO_2$ probably due to lower down of C: N of the soil (Gilani *et al.*, 2008). However, $CO_2$ evolution rates of rest of the treatments were fluctuating between 0.3 to 0.6 mg $CO_2$-C/g soil/hr.

The average soil respiration $CO_2$-C was measured from 4[th] hr to 168[th] hr after the application of TENCPC in soil. TENCPC was added to soil with an objective to increase its metabolic activity as well as to control wilt causing fungi because parasitic fungi were controlled through combined application of FYM and *Trichoderma harzianum* (Goswami *et al*., 2007, Sharma, 2011). This was an attempt to investigate the microbial community structure through respiration as well as dehydrogenase activity in soil as affected by TENCPC. The rate of evolved $CO_2$ after the application of TENCPC is shown graphically (Fig. 1) and results were found statistically significant at LSD (P=0.05), indicating that $CO_2$ evolution underwent an increasing trend after the initiation of the incubation followed by a decreasing trend after 24 hrs. Initially at 4[th] hr, the maximum evolution of $CO_2$ was 2.40 $CO_2$-C (mg/g soil/hr) for $T_3$ treated with TENCPC and lowest was found under control 0.97 $CO_2$-C (mg/g soil/hr) at LSD (P=0.05) treated with TENCPC. It had been reported that NCPC act as a slow release carrier. Soon after its application to the soil, living cells of *Trichoderma harzianum* were released to the soil environment. *Trichoderma harzianum* being a saprophyte fungi, it also released some organic acids, polysaccharides, *etc.* into the soil, which might have enhanced the microbial population as well as the soil aggregation. Ultimately, this had added higher microbial

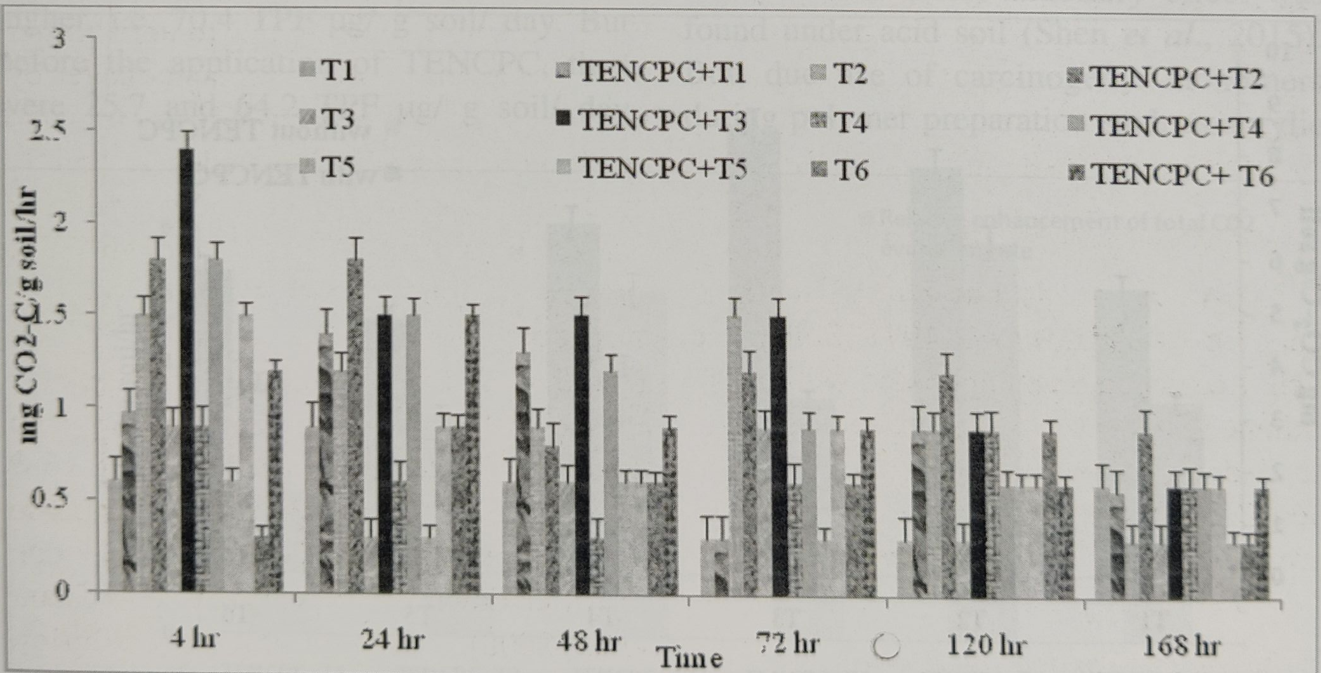


**Fig. 1.** Average $CO_2$ evolution rate during 2012-2013 and 2013-2014 in long-term fertilizer trial under AICRP-DLA with and without TENCPC up to 168[th] hr of incubation period, the vertical bar represent LSD (p = 0.05) values

biomass and more $CO_2$ evolution rate due to faster decomposition rate. Thus, TENCPC positively modified overall microbial community structure of soil, which is a good indicator of soil health. Although, with increase in time, the rate of $CO_2$ evolution decreased in all the six treatments may be due to highly toxic effect of nanomaterials and its poor biodegradable property in soil (Tong *et al.*, 2007; Johansen *et al.*, 2008). *Trichoderma harzianum* encapsulated nanoclay polymer composite found most suitable for $T_3$ because both *Trichoderma harzianum* cells and FYM energized the soil microbes for faster decomposition rate. But overall respiration rate increased initially after the application of TENCPC in each treatment.

The average cumulative $CO_2$ evolution rate, in (Fig. 2), after the application of TENCPC, was highest for $T_3$ i.e. 8.4 $CO_2$-C (mg/g soil/hr) over control i.e. 5.44 and 6.4 $CO_2$-C (mg/g soil/hr) for $T_4$. But, before application, the cumulative $CO_2$ evolution rate was naturally highest for $T_2$ i.e. 6.3 $CO_2$-C (mg/g soil/hr) probably because of presence of full recommended dose of fertilizer application and lowest for control i.e. 3.3 $CO_2$-C (mg/g soil/hr) during the whole study period.

The relative rate of $CO_2$ evolution, in (Fig 3), was significantly higher for $T_3$ i.e. 5.1 $CO_2$-C (mg/g soil/hr) as $T_3$, treated with FYM, enhanced the soil microorganisms activity when combined with TENCPC and lowest for $T_2$ i.e. 1.4 $CO_2$-C (mg/g soil/hr).

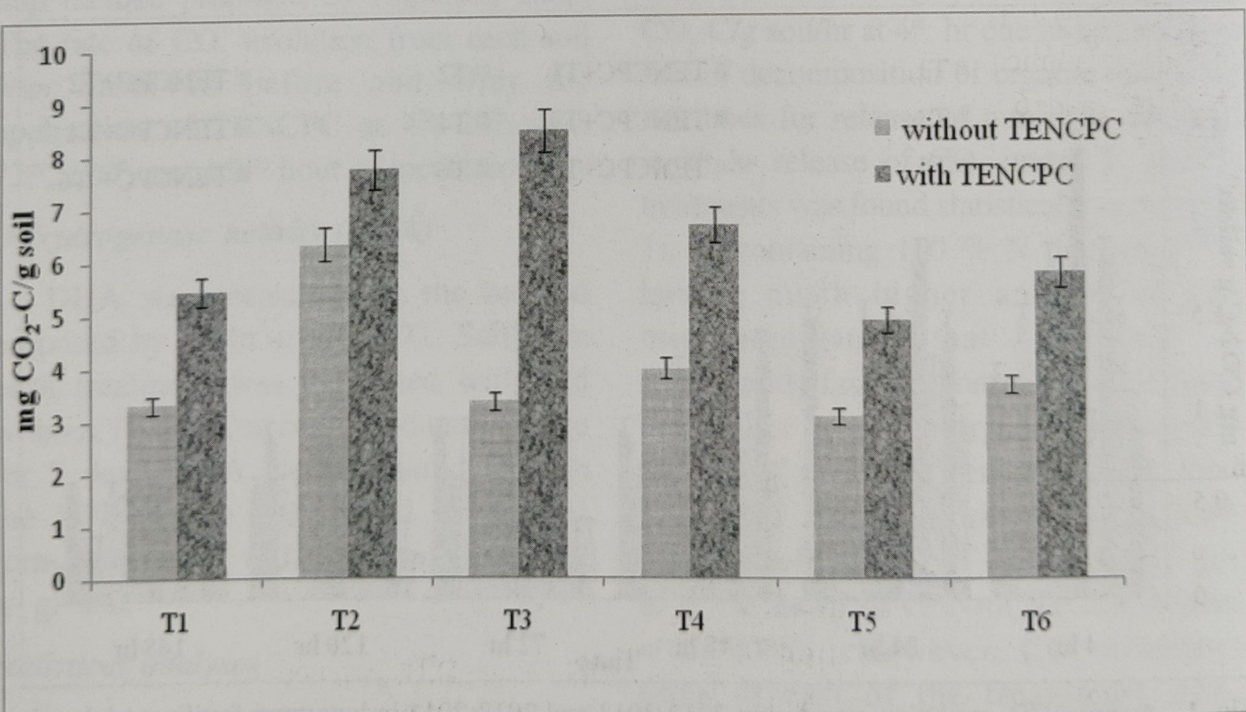


**Fig. 2.** Cumulative $CO_2$ evolution rate of soil with and without TENCPC application during 2012-2013 and 2013-2014, the vertical bar represent error bar at 5 %

$T_2$ recorded highest cumulative $CO_2$ evolution without TENCPC but application with TENCPC reduced the CO2 evolution. This suggested that TENCPC was not degraded easily for $T_2$ due to presence of more residual inorganic fertilizer or may be due to absence of organic matter during both the years.

***Dehydrogenase activity (DHA)***

Dehydrogenase enzyme activity, was used as a biological indicator of soil quality, is closely related to average activity of microbial population. It cannot be accumulated on complex form present in soil. The average TPF (µg/ g soil/day) content (Fig. 4), after the application of TENCPC, under control was found 26.61 whereas, for $T_3$, it was found significantly higher, i.e. 70.4 TPF µg/ g soil/ day. But before the application of TENCPC, they were 25.7 and 64.2 TPF µg/ g soil/ day respectively after 7 days of incubation. The overall increment of soil DHA was highest for $T_3$ due to combination of FYM (Liu *et al.*, 2010) and biomass of *Trichoderma harzianum* through TENCPC. The initial build up of soil microorganisms was more due to accumulation of *Trichoderma harzianum* cells. Being a long chained polymer, TENCPC would take longer time to be degraded. The degradation process of course involved both enzymatic activity and microbial population. Naturally, the DHA enhanced in a much better way during long chain polymer degradation in soil. FYM, on the other hand, acted synergistically in this degradation process during 7 days of incubation period. Besides this, neutral soil pH may be another reason for increased DHA because DHA inhibitory effect was found under acid soil (Shen *et al.*, 2015). But, due use of carcinogenic monomers during polymer preparation such as acrylic

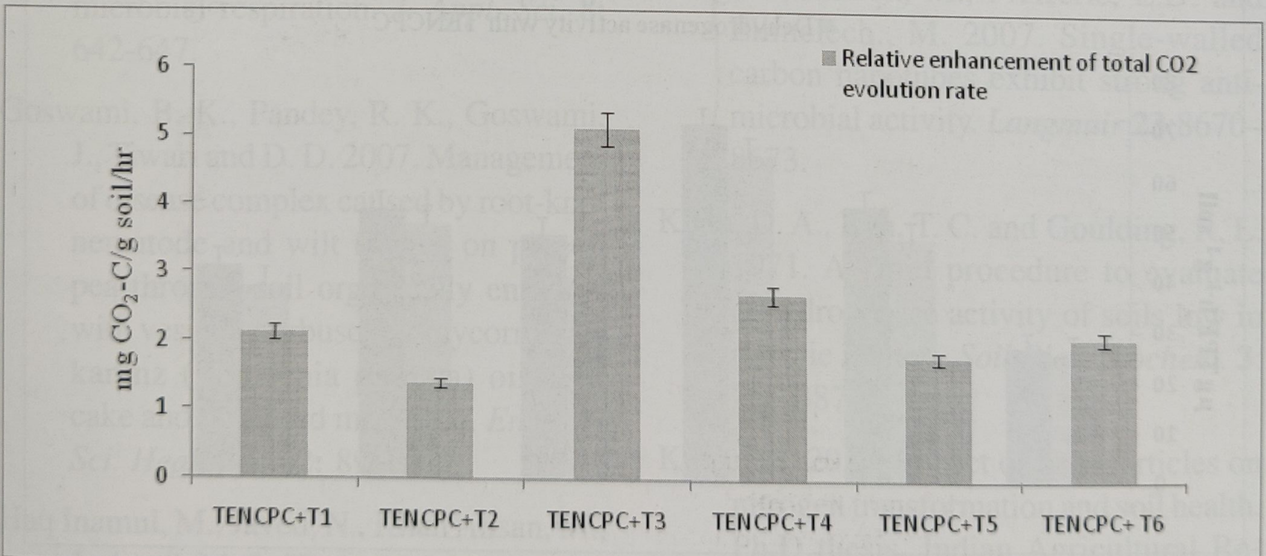


**Fig. 3.** Effect of TENCPC on relative enhancement of total $CO_2$ evolution rate during 2012-2013 and 2013-2014, the vertical bar represent error bar at 5 %

acid, acrylamide had detrimental and toxic effect on soil health and microbial community. Moreover, these toxic nanomaterials might alter the bacterial viability and generated reactive oxygen species in soil Shen *et al.*, 2015; Yadav *et al.*, 2014; Kumar, 2012; Kang *et al.*, 2007). This is the reason why, the DHA in soil might go down day by day in a long term incubation study. Nevertheless, this was a clear indication of biological active soil soon after application of TENCPC in FYM amended soil.

From the continuous monitoring of $CO_2$ evolution and dehydrogenase activity though incubation study, it is inferred that *Trichoderma harzianum* encapsulated nano clay polymer composite has no negative effects on soil respiration properties rather than it has strong positive result observed when is applied with organic matter or manures. The rate of fall of $CO_2$ evolution at 168th hr was due to lower down of C: N of soil and exposure of soil to poorly degradable and toxic nanomaterials. The concomitant effect of FYM and increased microbial population due to slow release of *Trichoderma harzianum* cells enhanced rate of $CO_2$ evolution and dehydrogenase activity in soil. It can be finally concluded that initial application of lower dose (1 mg/ 100 g soil) of TENCPC along with organic input has no negative impact on soil biological environment rather it could increase the soil respiration rate and DHA within the 7 days of incubation.

## Acknowledgement

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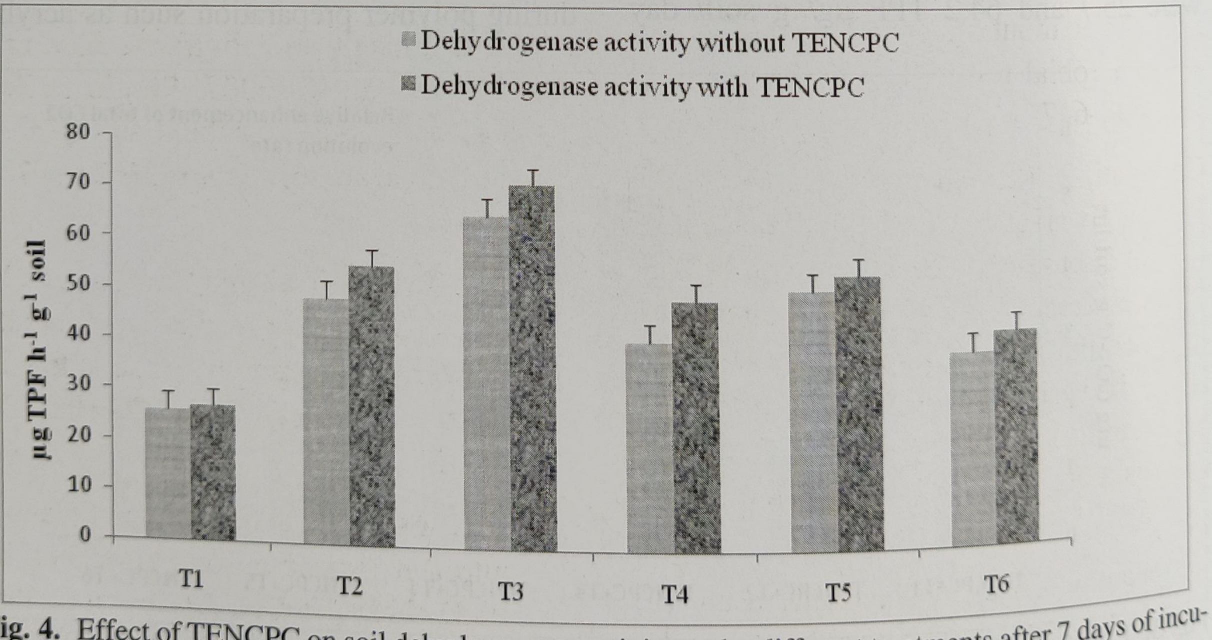


**Fig. 4.** Effect of TENCPC on soil dehydrogenase activity under different treatments after 7 days of incubation period during 2012-2013 and 2013-2014, the vertical bar represent LSD (p = 0.05) values

Principal Scientist, Indian Agricultural Research Institute, New Delhi. The senior author is indebted to the University Grant Commission, New Delhi, for granting funds in a major research project on nanotechnology in agriculture (BHU project code-P-01/683).

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# Spatial Variability of Soil Fertility Parameters in Jirang Block of Ri-Bhoi District, Meghalaya

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**Abstract**–*Spatial variability of soil fertility parameters is important to know the distribution of fertility status in a particular area. Surface soil samples from Jirang block, Ri-bhoi district of Meghalaya were analysed for soil reaction, organic carbon, available macro- and micronutrients status. The spatial variability maps were generated for soil parameters by regularised spline technique in ArcGIS 10.0. Soil pH varied from extremely acidic to moderately acidic. The maximum area of soil was under moderately acid (59.3% area) followed by extremely acid (27% area), very strongly acid (6.9% area) and strongly acid (6.9 % area). Soil organic carbon content varied from medium (40% area) to high (60% area). The available nitrogen content was high in 54.5 % area where as available phosphorus was medium in 67.8 % area. Available potassium content was low in 67.5 % area. The micronutrients status was sufficient. The multi-macronutrient map (N, P and K) showed 25.4% area was deficient in either all or more than one macronutrient which was classified as high prioritized zone. The multi-micronutrient map (Fe, Mn, Zn and Cu) showed maximum area under low prioritized zone (80.5% area).*

***Key words :*** Spatial variability, Soil fertility parameters, Interpolation, Spline method, multinutrient deficient zone

## Introduction

Soil characteristics are the outcome of the interplay of pedogenic factors and processes prevailing in a particular area. The hilly and mountainous regions are endowed with a wide range of environmental factors that exert an influence on spatial variability of soils. A review of those factors and processes that have contributed to soil formation is necessary for a better understanding of the soils of a particular area. In India, harsh climatic conditions, population pressure, land constraints, and the decline of

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traditional soil management practices have often reduced soil fertility (Stoorvogel and Smaling, 1990; Tandon, 1998; Henao and Baanante, 1999; Bumb and Baanante, 1996).The north eastern hilly region of india is characterised by heavy soil erosion, loss of soil fertility and deforestation causing acute environmental degradation and severe ecological imbalance (Sachchidananda, 1989). Shifting cultivation or slash & burn agriculture, locally known as *Jhum* cultivation, is the main form of agriculture in this region. In north east India, the average annual loss of top soil, organic carbon, $P_2O_5$ and $K_2O$ due to shifting cultivation is to the extent of 40900, 702.9, 0.15 and 7.5 kgha$^{-1}$, respectively (ICAR, 1983). The repeated use of land with short *Jhum* cycle finally converts the *Jhum* fallows into degraded wastelands. In cultivated areas the imbalanced and indiscriminate use of fertilizers in intensive cropping system without adequate restorative practices may pose threats to sustainability of system, as high yielding varieties draw heavy amount of plant nutrients from soil and nutrient uptake often exceeds replenishment through fertilizers causing soil fertility deterioration at many places (Singh and Lal, 2011). Farmers usually apply fertilizers without considering the information on soil fertility status and nutrient requirement of the crop, which leads to either nutrient toxicity or deficiency (Ray *et al.*, 2000). In order to apply nutrients, based on soil fertility, it is necessary to know the location specific variability in nutrient supply to provide optimum doses of fertilizers as per the crop nutrient demand (Dobermann and Cassman, 2002). Geographic Information System (GIS) helps to generate such spatial variability maps (Sood *et al*., 2009). Information on spatial variability of soil fertility parameters for the Meghalaya Plateau is lacking. Therefore, the present study was undertaken with the objectives (1) to assess the nutritional status of the soils of Jirang block in Ri-Bhoi district of Meghalaya and (2) to map the spatial variability of soil fertility parameters for delineating the multi-nutrient deficient zones.

## Materials and Methods

The present study was conducted in the Jirang (Community and Rural Development) block lies in the north west direction of the Ri-Bhoi district of Meghalaya between 25° 47’17.16” N to 26 °5’ 22.56” N latitude and 91° 20’40.56” E to 91 °51’ 41.4” E longitude. The total geographical area (TGA) of the block is 714 km$^2$ (71400 ha). The geology of the study area comprises mostly of (i) Gneiss with old inliers of Sela group and (ii) Granite rocks. The block occupies around 648.42 km$^2$ (90.8 % of TGA) under Gneiss with old inliers, sela group and 65.58 km$^2$ (9.2 % of TGA) under granite rocks on 1:600000 scale. The study area represents two agro-ecological sub-regions (AESR) of middle Brahamaputra plain, hot humid eco-subregion (15.2) with an area of 553.5 km$^2$

(77.5% of TGA) and under Meghalaya Plateau and Nagaland hill, warm to hot moist, humid to perhumid eco-subregion (17.1) with an area of 160.5 km$^2$ (22.5% of TGA). It is characterised by hot and moist summers and cool winters belonging to subtropical climate. The mean summer and winter temperatures are 26.4 °C and 13.8 °C, respectively. The average annual rainfall of the area is about 2395 mm.

Geo-referenced surface soil samples (0-15 cm) were collected from 248 locations in the study area representing different terrain situations. The collected soil samples were processed, passed through 2mm sieve and stored for laboratory analysis. Soil reaction was determined by using pH meter with glass electrode from soil:water in the ratio 1:2.5 (Jackson, 1973). Organic carbon was determined by chromic acid wet digestion method (Walkley and Black, 1934). The available nitrogen was estimated by alkaline $KMnO_4$ method (Subbiah and Asija, 1956). Available phosphorus and potassium were estimated by 0.03 N $NH_4F$ and 0.025 N HCl reagents (Bray and Kurtz, 1945) and neutral normal ammonium acetate method (Jackson, 1973), respectively. Cationic micronutrients namely Zn, Fe, Cu and Mn were determined using the DTPA (diethylenetriaminepenta acetic acid) extraction method (Lindsay and Norvell, 1978).

Regularised spline interpolation technique for point data was used to create different layers for pH, organic carbon, available N, P, K, Fe, Mn, Zn and Cu in a GIS environment (Arc GIS 10.0 software) (Collins and Bolstad, 1996; Hutchinson, 1995).

The layers generated for macronutrients (N, P and K) and micronutrients (Fe, Mn, Zn and Cu) were used to define the priority areas for multinutrient management intervention. Initially the surfaces were classified into three classes *viz*., low, medium and high depending on their nutrient status. The low category was given

**Table 1.** *Categorization for the soils parameters studied*

| Parameter | Categories | | |
|---|---|---|---|
| | Low (1) | Medium (2) | High (3) |
| OC (%) | <0.4 | 0.4 – 0.75 | >0.75 |
| N (kg ha$^{-1}$) | <280 | 280-560 | >560 |
| $P_2O_5$ (kg ha$^{-1}$) | <34 | 34-68 | >68 |
| $K_2O$ (kg ha$^{-1}$) | <135 | 135-335 | >335 |
| Fe (mg kg$^{-1}$) | <4.5 | 4.5-9.0 | >9.0 |
| Mn (mg kg$^{-1}$) | <3.5 | 3.5-7.0 | >7.0 |
| Zn (mg kg$^{-1}$) | <0.6 | 0.6-1.2 | >1.2 |
| Cu (mg kg$^{-1}$) | <0.2 | 0.2-0.4 | >0.4 |

a value 1 and similarly the medium and high categories were given a value of 2 and 3, respectively (Table 1) (Takkar, 2009; Brays and Kurtz, 1945).

After reclassification, two layers were generated by using the decision tree. Multi-macronutrient layer was generated by combining all the macronutrient layers (available N, P and K), whereas multi-micronutrient layer was generated by combining all the cationic micronutrient layers (Fe, Mn, Zn and Cu). All the macro- and micronutrient surface layers were combined into one using the decision tree given (Table 2, 3). All the layers were given equal weightage in the operation and the

**Table 2.** *Decision tree for multi macronutrient map (N, P and K).*

| | | |
|---|---|---|
| IF | All the layers have value 1 | High priority area |
| ELSE IF | Two layers have value 1 and one layer has value 2 | High priority area |
| ELSE IF | Two layers have value 2 and one layer has value 1 | High priority area |
| ELSE IF | All the layers have value 2 | Medium priority area |
| ELSE IF | One layer has value 1, other layer has value 2 and another layer has value 3 | Medium priority area |
| ELSE IF | Two layers have value 2 and one layer has value 3 | Medium priority area |
| ELSE IF | All the layers have value 3 | Low priority area |
| ELSE IF | Two layers have value 3 and one layer has value 2 | Low priority area |

**Table 3.** *Decision tree for multi micronutrient map (Fe, Mn, Zn and Cu).*

| | | |
|---|---|---|
| IF | All the layers have value 1 | High priority area |
| ELSE IF | Three layers have value 1 and one layer has value 2 | High priority area |
| ELSE IF | Three layers have value 1 and one layer has value 3 | High priority area |
| ELSE IF | Two layers have value 1 and other two layers have value 2 | High priority area |
| ELSE IF | All the layers have value 2 | Medium priority area |
| ELSE IF | Three layers have value 2 and one layer has value 1 | Medium priority area |
| ELSE IF | Three layers have value 2 and one layer has value 3 | Medium priority area |
| ELSE IF | Two layers have value 2, third layer has value 1 and fourth layer has value 3 | Medium priority area |
| ELSE IF | One layer has value 2 and two layers have value 1 and fourth layer has value 3 | Medium priority area |
| ELSE IF | Two layers have value 1 and other two layers have value 3 | Medium priority area |
| ELSE IF | All the layers have value 3 | Low priority area |
| ELSE IF | Three layers have value 3 and one layer has value 1 | Low priority area |
| ELSE IF | Three layers have value 3 and one layer has value 2 | Low priority area |
| ELSE IF | Two layers have value 3 and other two layers have value 2 | Low priority area |

value for each surface was evaluated in a raster environment.

## Results and Discussion

### *Fertility status and their spatial distribution*

The surface soils of the study area were extremely acid to moderately acid which ranged from 4.2 to 6 (Tables 4, 5, Fig.1a). The area under extremely acid (< 4.5) was 19207 ha (29.6 % of TGA) and under moderately acid was 42279 ha (59.3 % of TGA). The organic carbon in these soils ranged between 0.49 percent and 3.01 percent with an average value of 1.47% (Fig.1b). About 60 % of TGA was under high organic carbon content followed by medium organic carbon content (40 % of TGA). The soil available nitrogen content varied from 121 to 744 kg $ha^{-1}$ with an average value of 351 kg $ha^{-1}$ (Fig.1c). The area under low, medium and high available nitrogen content was 8.8 %, 36.7 % and 54.5 % of TGA, respectively. The mean available P (Bray's P) and K contents were 65 kg $ha^{-1}$ and 190 kg $ha^{-1}$, respectively (Fig.1d). In case of available P majority of the area was under medium nutrient status (67.8 % of TGA) followed by high nutrient status (32.2 % of TGA) whereas available potassium status was low to high (Fig.1e). The area under low potassium content was the highest (67.5 % of TGA) followed by high (21.7 % of TGA) and medium available potassium (10.8 % of TGA). The mean available Fe, Mn, Zn and Cu contents were 105.1, 26.5, 2.03 and 4.7 mg $kg^{-1}$, respectively (Table 4) which indicated sufficient status of these micronutrients in

**Table 5.** *Spatial distribution of soil reaction.*

| Soil reaction (pH) | Area (ha.) | % of TGA |
|---|---|---|
| Extremely acid (<4.5) | 19207 | 26.9 |
| Very strongly acid (4.5-5.0) | 4969 | 6.9 |
| Strongly acid (5.1-5.5) | 4945 | 6.9 |
| Moderately acid (5.6-6.0) | 42279 | 59.3 |
| Total area | 71400 | 100 |

**Table 4.** *Descriptive statistics of soil parameters.*

| Parameter | Mean | Range | SD |
|---|---|---|---|
| pH | 5.01 | 4.2-6.0 | 0.33 |
| OC (%) | 1.47 | 0.49 – 3.01 | 0.46 |
| N (kg $ha^{-1}$) | 350.6 | 121.4 – 744.4 | 90.1 |
| $P_2O_5$ (kg $ha^{-1}$) | 65.05 | 44.9 – 234.8 | 26.9 |
| $K_2O$ (kg $ha^{-1}$) | 190.01 | 53.8 – 954.2 | 116.4 |
| Fe (mg $kg^{-1}$) | 105.1 | 4.7– 154.42 | 25.8 |
| Mn (mg $kg^{-1}$) | 26.5 | 3.55 – 91.48 | 17.4 |
| Zn (mg $kg^{-1}$) | 2.03 | 0.60 –7.52 | 0.98 |
| Cu (mg $kg^{-1}$) | 4.7 | 0.34 – 16.79 | 2.23 |

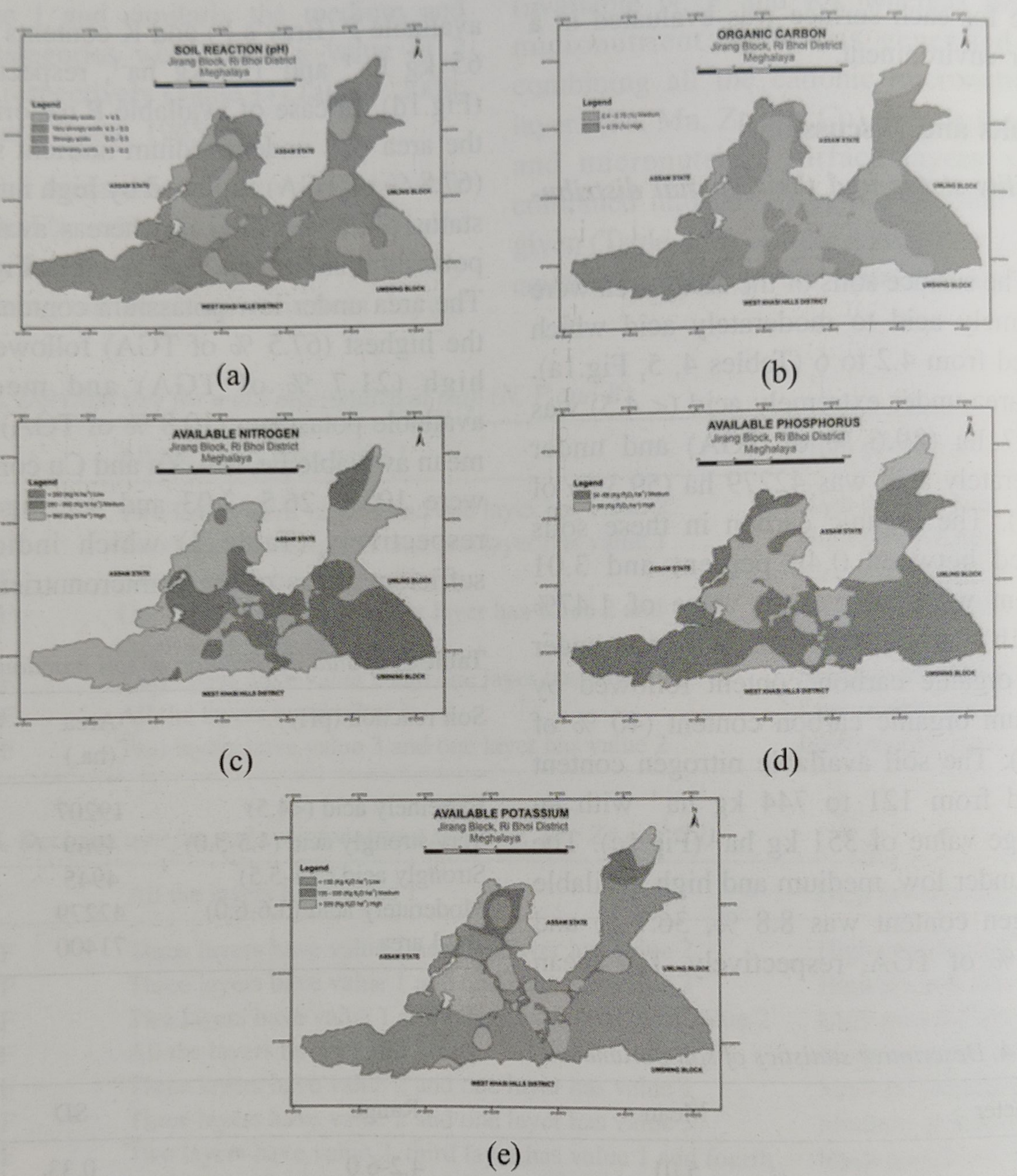


**Fig. 1.** *Spatial distribution of (a) soil reaction (pH), (b) organic carbon, (c) available nitrogen, (d) phosphorus and (e) potassium in Jirang block, Ri-Bhoi district.*

the study area (Fig. 2). Higher amounts of Zn and Cu may be due to high organic carbon content (Venkatesh *et al.*, 2003).

It is observed that available N and K varied widely with standard deviation (SD) of 90.1 and 116.4, respectively from the mean value. In the high hills, due to abundant vegetation, high amount of N and K were present, whereas in valley areas the status was low to medium because of uptake of N and K by crops (Table 5, 6) which are not replenished by the addition of fertilizers.

*Multi-nutrient deficiencies*

The multi-nutrient map was generated by considering the macro- and micro-nutrients. As majority of the study area was high or medium in organic carbon content, it was not considered in multi-nutrient mapping. The multi-macronutrient map (Fig. 3) indicated that about 25.4 % of total geographical area (TGA) of the block had deficiency in either or all the macronutrients (N, P and K). This area needs to be given immediate attention in terms of nutrient management decision as the soils are already exhausted in terms of nutrient supplying capacity either due to intensive cropping or due to leaching (Havlin *et al.*, 1999). Whereas 55.3% of TGA was under medium prioritized zone which need proper attention to reverse the trend of decline in soil fertility for crop production by judicious management of the resources, inspite of the fact that fertility status under this category was better compared to the areas under high priority class. The

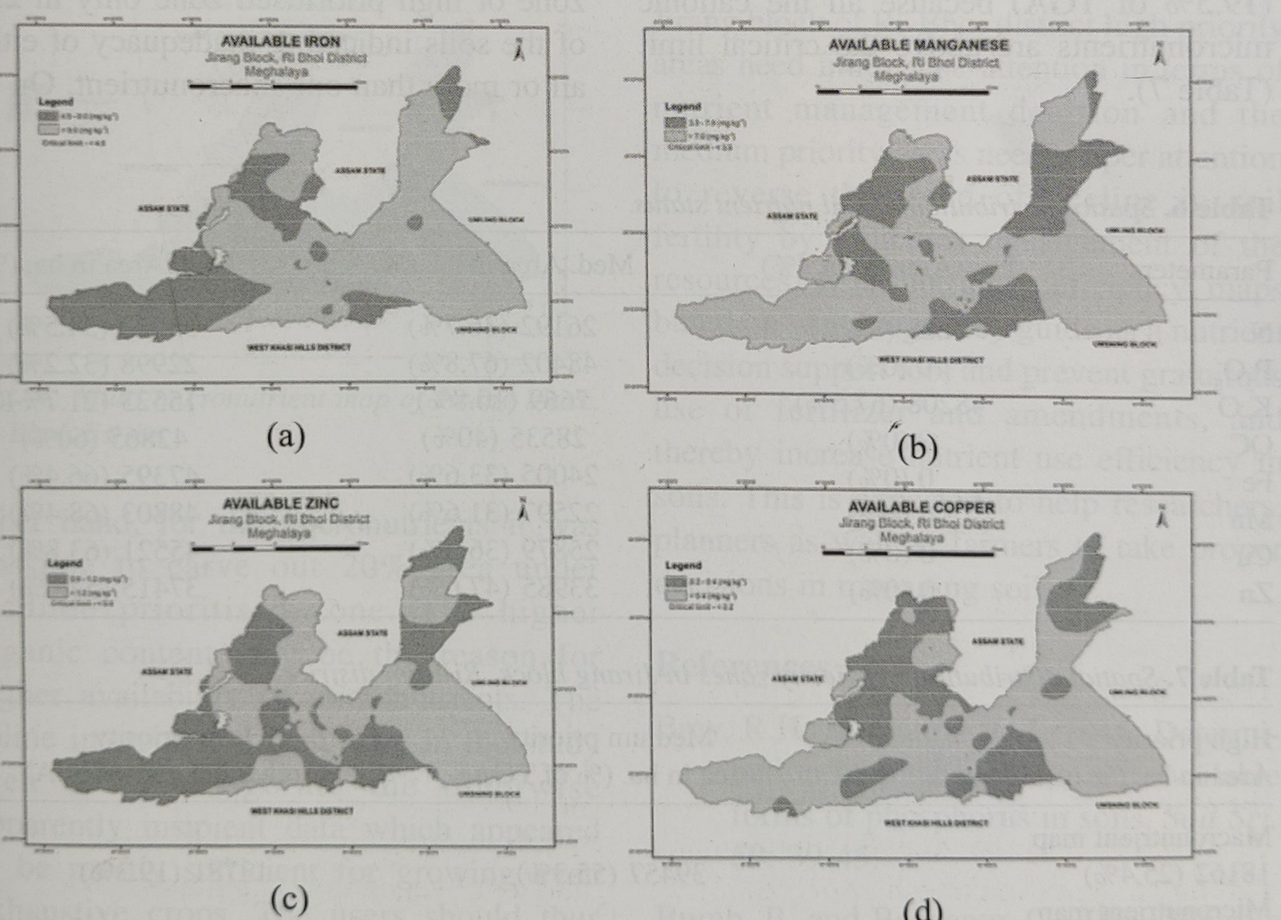


**Fig. 2.** *Spatial distribution of available (a) Fe, (b) Mn, (c) Zn and (d) Cu in Jirang block, Ri-Bhoi district.*

remaining area of the block was under high nutrient status category with regard to available N, P and K. The area under low prioritized zone was 19.3 % where excess application of fertilizers should be avoided, because over application of fertilizers induces neither substantially greater crop nutrient uptake nor significantly higher yields (Smaling and Braun, 1996). The multi-micronutrient map (Fig. 4) of the study area showed that around 80.5% of TGA was under low prioritized zone due to high content of cationic micronutrients followed by medium prioritized zone (19.5% of TGA) because all the cationic micronutrients are above the critical limit (Table 7).

The dataset developed in this study indicated that the major soils are extremely to moderately acid and the organic carbon content is generally not meagre. Slightly more than half of the soils are sufficient in available nitrogen and about two thirds of the soils are adequate in available phosphorus, whereas only one third of the soils are adequate in available potassium. The available micronutrients (Fe, Mn, Zn and Cu) are also in the sufficient range. Under such circumstances, the multi-macronutrient map developed using spline interpolation method resulted in a deficient zone or high prioritised zone only in 25% of the soils indicating inadequacy of either all or more than one macronutrient. On the

**Table 6.** *Spatial distribution of soil nutrient status.*

| Parameters | Low Area in ha. (%) | Med. Area in ha. (%) | High Area in ha. (%) |
|---|---|---|---|
| N | 6288 (8.8%) | 26192 (36.7%) | 38920 (54.5%) |
| $P_2O_5$ | 0 (0%) | 48402 (67.8%) | 22998 (32.2%) |
| $K_2O$ | 48208 (67.5%) | 7669 (10.8%) | 15523 (21.7%) |
| OC | 0 (0%) | 28535 (40%) | 42865 (60%) |
| Fe | 0 (0%) | 24005 (33.6%) | 47395 (66.4%) |
| Mn | 0 (0%) | 22597 (31.6%) | 48803 (68.4%) |
| Cu | 0 (0%) | 25879 (36.2%) | 45521 (63.8%) |
| Zn | 0 (0%) | 33985 (47.6%) | 37415 (52.4%) |

**Table 7.** *Spatial distribution of priority zones in Jirang block, Ri-Bhoi district.*

| High priority Area in ha. (% of TGA) | Medium priority Area in ha. (% of TGA) | Low priority Area in ha. (% of TGA) |
|---|---|---|
| Macronutrient map | | |
| 18162 (25.4%) | 39457 (55.3%) | 13781 (19.3%) |
| Micronutrient map | | |
| 0 (0%) | 13918 (19.5%) | 57482 (80.5%) |

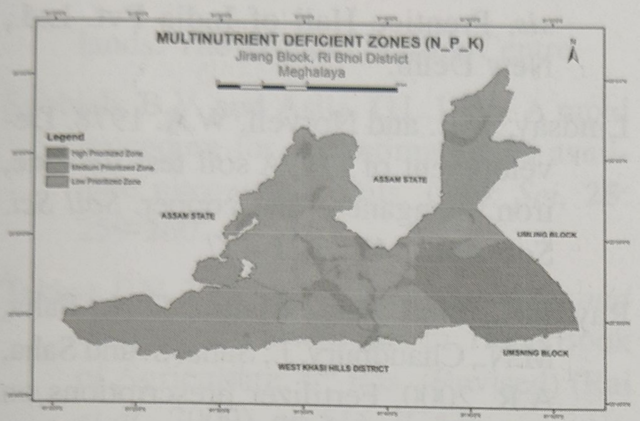


**Fig. 3.** *Spatial distribution of available (a) Fe, (b) Mn, (c) Zn and (d) Cu in Jirang block, Ri-Bhoi district.*

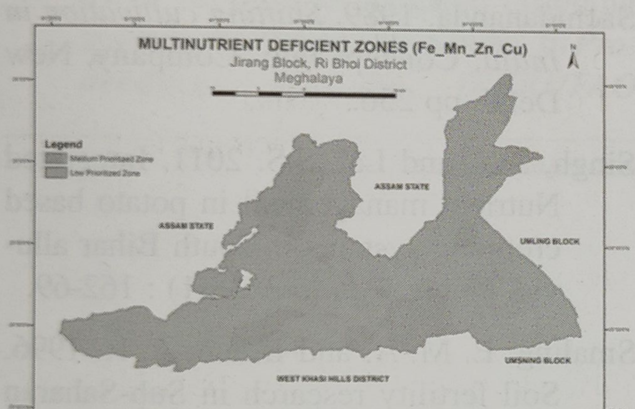


**Fig. 4.** *Multi-micronutrient map of Jirang block, Ri-Bhoi district*

other hand, for the micronutrients it was possible to carve out 20% area under medium prioritised zone. The higher organic content may be the reason for higher availability of micronutrients. The spline interpolation technique in the study area could invigorate the otherwise apparently insipient data which appeared to be mostly sufficient for growing even exhaustive crops. The users should thus ponder upon the results of the study, especially the high prioritised areas for monitoring purpose which would be much easier due to the development of minimum dataset instead of the difficulty of handling multiple data.

## Conclusions

Spline interpolation technique can be effectively used to represent spatially the various soil fertility parameters namely pH, organic carbon, available N, P, K, Fe, Zn, Cu and Mn. The decision tree used in the methodology of this study is very simple and flexible. The study showed that in Jirang block of Ri-Bhoi district high priority areas need immediate attention in terms of nutrient management decision and the medium priority areas need proper attention to reverse the trend of decline in soil fertility by judicious management of the resources. Multinutrient deficiency maps based on weightage may guide as a nutrient decision support tool and prevent gratuitous use of fertilizer and amendments, and thereby increase nutrient use efficiency in soils. This is expected to help researchers, planners as well as farmers to take proper decisions in managing soils.

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# Role of Clay in Recovery of Organic Matter in Arable Black Soils of India: An Inverse Pyramid Relation

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***Abstract–*** *We studied the logic of blanket recommendation of Walkley Black Recovery Factor (WBRF) with a set of ~1000 shrink-swell soil samples with varying clay content, representing two important food growing zones namely the Indo-Gangetic Plains and the Black Soil Region (BSR). Since clay and organic matter form strong clay complexes, we investigated how quantity of clay can influence recovery of organic matter from soils analyzed following standard procedure. Increase in clay content, soil depth and aridity (low rainfall) have similar effect in increasing WBRF due to decreased organic matter recovery. While the relation is a straightforward in low clay soils, the study showed that recovery of organic matter remains unaffected for BSR soil clays > 60% warranting a new initiative for an inter facial research to link pedology and edaphology.*

***Key words :*** WBRF, Soil, Clay, Recovery, Organic matter.

## Introduction

There are various methods available to determine soil organic carbon (SOC), which includes wet oxidation method. In this method soil organic matter which contains about 48-58% of organic carbon, is oxidized by chromic acid utilizing the heat of reaction as well as dilution of sulphuric acid (Walkley and Black, 1934; Jackson, 1973). The method claims to estimate organic carbon to an extent of 77% and so as to make it 100%, the determined value is multiplied with the correction factor of 1.29 to get a near true estimate. This factor is known as the Walkley Black Recovery factor (WBRF) which varies among soils, their management regimes and even soil horizon (Tabatabai, 1996).

The qualitative nature of the soil substrate and their quantitative proportion of surface reactivity, referred to as surface charge density (SCD), control the rate of accumulation of organic carbon (OC). The knowledge of its decomposition and recovery while carrying out its determination in the laboratory is important.

Increase in organic C enhances SCD of the soil and the ratio of internal/external exchange sites (Poonia and Niederbudde, 1990). It may be mentioned that in the black soil regions (BSR), the dominant soils in semi-arid tropics (SAT) are black soils (Vertisols and their intergrades, with some inclusions of Entisols in the hills) and associated Alfisols. All these soils are dominated by smectites (Bhattacharyya *et al.*, 1993). The presence of smectites increases SCD, which offers greater potential for carbon sequestration in these soils. Black soils, therefore, may reach a quasi-equilibrium value (QEV) of more than 2% as reported in the representative soils developed in the basaltic alluvium (Bhattacharyya *et al.*, 2014).

While discussing the role of soil colloids in carbon accumulation in soils, Bhattacharyya and Pal (2003) estimated that the total proportion of soil organic pools (i.e., moderately oxidized, strongly oxidized, physically, and chemically sequestered) are controlled by clay minerals to the extent of 18, 20, 20, and 20%, respectively. This suggests that a minimum 78% of the total organic matter in soil is controlled by inorganic substrate (precisely phyllosilicate minerals with higher surface area in the finer fractions). Relatively more (2-3%) SOC content in Indian Mollisols and Australian Vertisols is not uncommon (Bhattacharyya *et al.*, 2006; Dalal and Conter, 2000). The importance of SCD, rainfall, and their combined influence indicates an inverse pyramid relation of content of SOC with US taxonomic soil

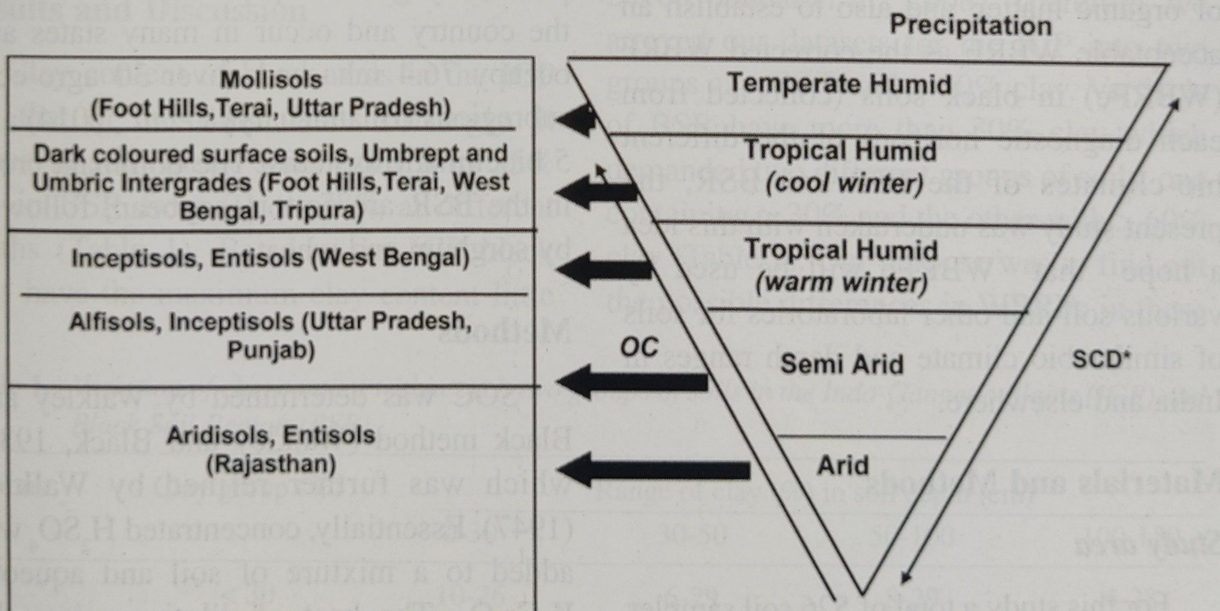


**Fig. 1.** *Inverse pyramid relation with accumulation of organic carbon (OC) in soils grouped following U.S. Soil Taxonomy as influenced by precipitation, temperature, and substrate quality (* SCD, surface charge density) (source: Bhattacharyya et al., 2014).*

orders (Fig. 1) (Bhattacharyya *et al.*, 2015a).

Recent observations indicate the occurrence of Vertisols and their intergrades (Soil Survey Staff, 2006) in the Indo-Gangetic plains (IGP) (Bhattacharyya *et al.* 2013). These deep to very deep and smectite dominated soils are commonly known as black soils (black cotton soils), which, are characterized by the presence of either slickensides or wedge-shaped peds, ≤ 30% clay and cracks that open or close periodically. Occurrences of vertic intergrades in the IGP are more common than that of the Vertisols (Bhattacharyya *et al.*, 2009).

In order to find out a relation between clay content (in terms of surface areas and SCD of the clay mineral) and the recovery of organic matter, and also to establish an acceptable WBRF as the corrected WBRF (WBRFc) in black soils (collected from each diagnostic horizon) of the different bio-climates of the IGP and BSR, the present study was undertaken with this idea a hope that WBRFc will be used by various soil and other laboratories for soils of similar bio climate and depth ranges in India and elsewhere.

## Materials and Methods

### *Study area*

For this study a total of 526 soil samples (303 of IGP and 223 of BSR) were selected in different bioclimatic zones. The IGP covers about 52.01 mha and represents 8 agro-ecological regions (AERs), 14 agro-ecological sub regions (AESRs) (Mandal *et al.*, 2014) and 7 bioclimatic systems. The nature and properties of the alluvium vary in texture from sandy to clayey, calcareous to non-calcareous and acidic to alkaline. In the IGP, rice-wheat cropping system is dominant followed by cotton-wheat, bajra-wheat and maize-wheat.

The BSR is mainly occupied by black soils in the Indian SAT; although their presence has also been reported in the humid and arid bioclimatic systems (Bhattacharyya *et al.,* 1993, 2008, 2009). These soils are spatially associated with red soils and form a major soil group of India and developed in basaltic alluvium under different climates. These soils are potentially good crop production zones in the country and occur in many states and occupy 76.4 mha and cover 30 agro-eco-subregions (Bhattacharyya *et al.*, 2014) and 5 bioclimatic systems. The dominant crops in the BSR are cotton, soybean, followed by sorghum and wheat.

### Methods

SOC was determined by Walkley and Black method (Walkley and Black, 1934) which was further refined by Walkley (1947). Essentially, concentrated $H_2SO_4$ was added to a mixture of soil and aqueous $K_2Cr_2O_7$. The heat of dilution raises the temperature sufficiently to induce a substantial, but not complete oxidation by the acidified dichromate. Residual dichromate was titrated using ferrous sulphate solution. The difference between the sample titrated by ferrous ammonium sulphate [Fe $(NH_4)_2(SO_4)_2 \cdot 6H_2O$] (FAS) and that of the blank titration determined the amount of easily oxidizable organic carbon. The corrected Walkley-Black recovery factor ($WBRF_c$) was estimated using wet (Walkley-Black method) and dry combustion (C/N analyzer) methods as detailed by Bhattacharyya *et al.*, (2015b). Calcium carbonate equivalent in soils was determined following the standard method (Jackson, 1973) to estimate soil inorganic carbon (SIC) which constitutes twelve percent of $CaCO_3$. Prior to analysis, the soil samples were air dried and ground to 100 mesh size.

## Results and Discussion

Clay content of black soils in the IGP and that of the BSR varies strikingly. It varies in IGP black soils from 6 to 55% and in BSR from 21 to 78% at different depths (Table 1). Besides, the IGP black soils have the maximum clay content little less than 60% and thus is not falling under fine and very fine at the family level of soil classification (Soil Survey Staff, 2014).

It is known that SCD (determined by nature of clay, surface area, charge characteristics and cation exchange capacity), controls the organic carbon sequestration in soils (Bhattacharyya *et al.*, 2015b). Logically, therefore, the IGP soils with > 30% clay (with vertic properties due to more smectite), and the BSR soils with < 60% and/or > 60% clay, would influence WBRFc. Conversely, these smectites with more clay and SCD should influence the recovery of organic matter. Ideally more organo-clay mineral complexes are formed in the black soils which are stabilized and remain more in the recalcitrant pool than the IGP soils (Chivane and Bhattacharyya 2010; Mandal *et al.*, 2008). Therefore, we arrayed our datasets for the IGP into two groups as < 30% and > 30% clay. Vertisols of BSR have more than 30% clay which demanded two different groups of soils, one containing > 30% and the other with > 60% clay (Table 1). Our purpose was to find out the possible differences in WBRFc in these

**Table 1.** *Variation of clay content within each two groups of soils in the Indo-Gangetic Plains (IGP) and Black Soil Region (BSR)*

| Regions | Clay group (%) | Range of clay (%) in soil depth (cm) | | | |
|---|---|---|---|---|---|
| | | 0-30 | 30-50 | 50-100 | 100-150 |
| IGP | < 30 | 10-26 | 6-29 | 8-29 | 4-28 |
| | >30 | 30-51 | 33-51 | 34-55 | 30-51 |
| BSR | <60 | 22-59 | 22-59 | 23-59 | 21-59 |
| | >60 | 61-73 | 61-75 | 61-78 | 60-75 |

4 different soils grouped according to their clay content. The other variable we introduced was the bioclimatic system which has a major role to play in arriving at the WBRFc.

The trend of graphs (Figs 2- 5) indicate a relatively lower recovery of organic carbon in soils of both the IGP and BSR with high clay content. This trend is more pronounced in black soils and the soils of IGP with > 30% clay. A similar observation was reported from Venezuelan soils (Chacon *et al.*, 2002). However, the correction factors reported earlier show an increasing trend with increase in clay content (Velmurugan *et al.*, 2009). A closer look at the datasets (Fig. 2 in Velmurugan *et al.*, 2009) indicates Y axis as OC recovery percentage which, as a matter of fact, should be Walkley Black recovery factor. Observations of these authors were made with clays with different nature, and SCD that formed clay- organic complex, which may not be identical to soils under our study.

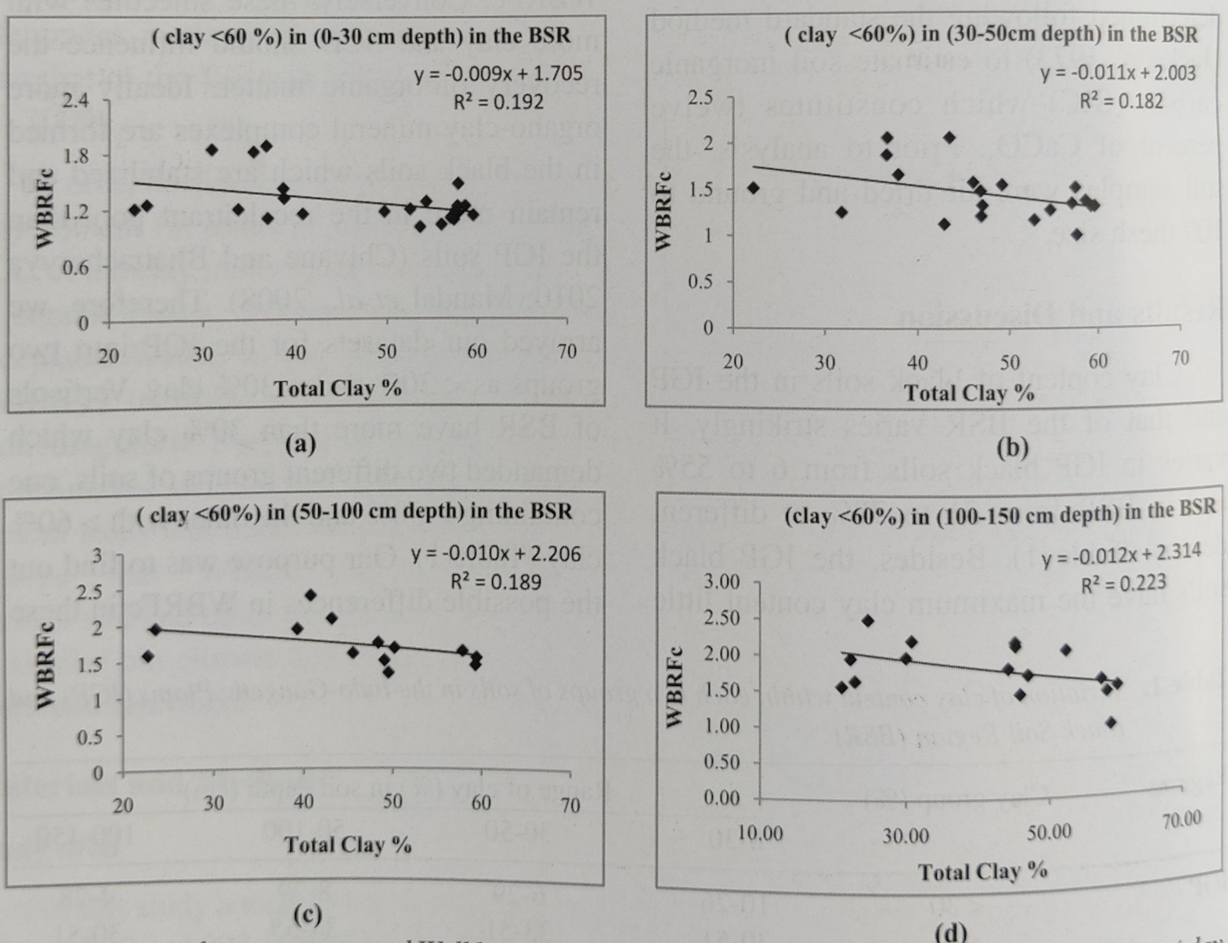


**Fig. 2.** *Relation between corrected Walkley Black Recovery Factor ($WBRF_c$) and total clay % where (clay 30-60%) in a) 0-30 cm, b) 30-50 cm, c)50-100 cm, d) 100-150 cm soil depth in the black soil regions (BSR)*

We studied soils representing three bioclimatic systems in the IGP (Table 2). Influence of bio-climate in organic matter recovery and WBRFc has been detailed elsewhere (Bhattacharyya *et al.*, 2015b). We discuss in this paper the effect of clay in controlling these two parameters namely organic matter recovery and WBRFc. A general tendency of increased WBRFc with the increase in clay content in IGP black soils is observed (Table 2) with soils low and high clay content with some exceptions. Interestingly, for the black soils an opposite trend was observed. Clay generally increases with pedon depth of black soils due to clay illuviation. Therefore, with the increase in depth increase in WBRFc can also be explained by increased clay content; notwithstanding with the fact of decreased microbial counts in the lower layers ((Bhattacharyya *et al.*, 2015b). Increase in clay content, soil depth and aridity (low rainfall) have therefore similar effect in increased WBRFc due to decreased organic matter recovery (Table 2) (Figures 3, 4).

For the black soils when all data are

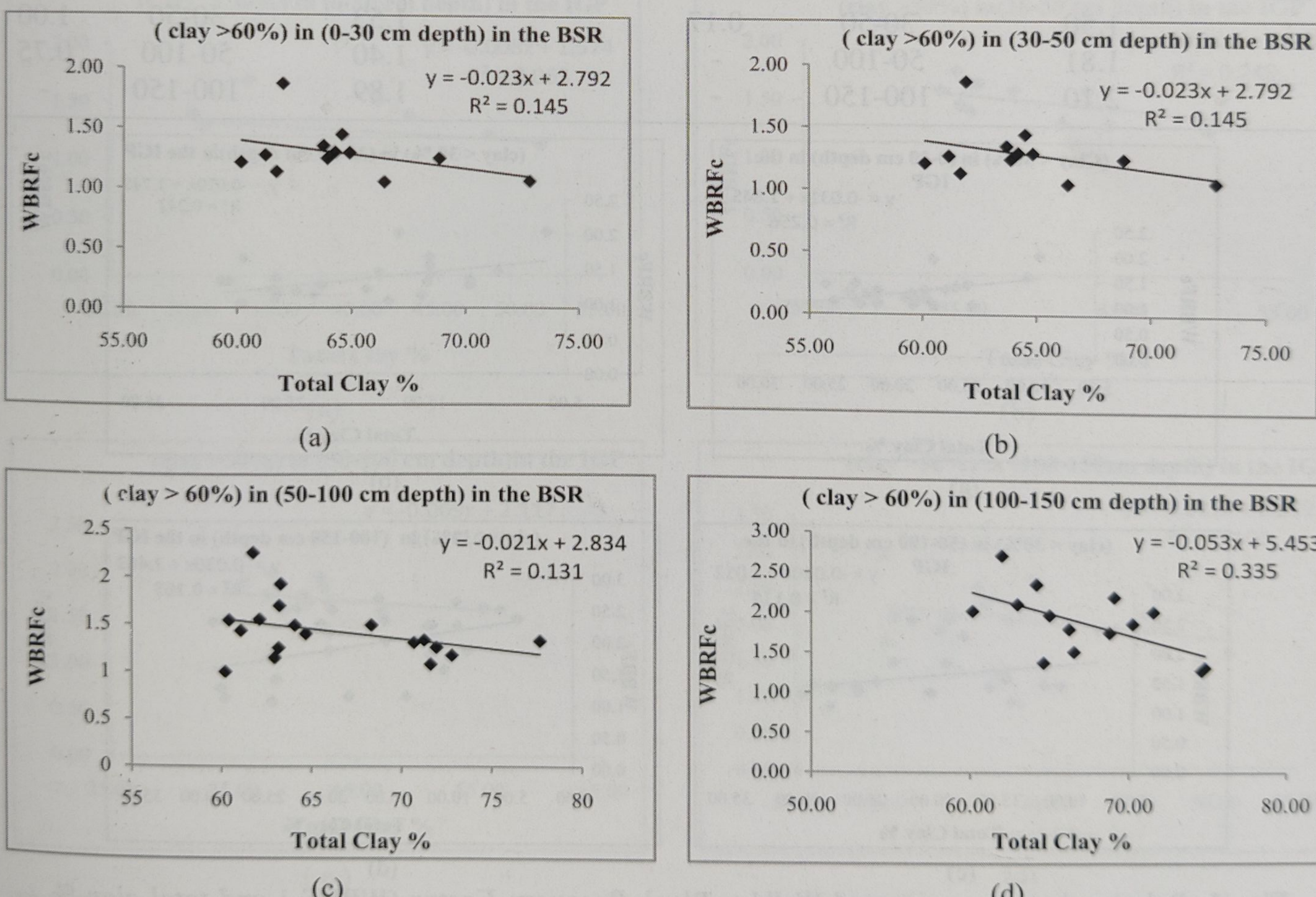


**Fig. 3.** *Relation between Walkley Black Recovery Factor and total clay % where (clay > 60%) in a) 0-30 cm, b) 30-50 cm, c) 50-100 cm, d) 100-150 cm soil depth in the black soil regions (BSR)*

**Table 2.** *Corrected Walkley Black Recovery factor ($WBRF_c$) of the Indo-Gangetic Plains*

| Clay % | WBRFc (mean) | Soil depth cm | $R^2$ | Clay % | WBRFc (mean) | Soil depth cm (clay % ) | $R^2$ |
|---|---|---|---|---|---|---|---|
| | | | Humid to per humid (MAR > 2200 mm) | | | | |
| < 30% | 1.12 | 0-30 | 0.98 | >30% | | No examples | |
| | 1.23 | 30-50 | 0.98 | | - | | |
| | 1.28 | 50-100 | - | | - | | |
| | 1.67 | 100-150 | 0.43 | | - | | |
| | | | Humid to Sub humid (MAR 1000-2200 mm) | | | | |
| <30% | 1.25 | 0-30 | 0.11 | >30% | 1.23 | 0-30 | 0.08 |
| | 1.42 | 30-50 | 0.28 | | 1.46 | 30-50 | - |
| | 1.37 | 50-100 | - | | 1.58 | 50-100 | 0.23 |
| | 1.98 | 100-150 | 0.44 | | 1.89 | 100-150 | 0.29 |
| | | | Semi arid (MAR < 1000 mm) | | | | |
| < 30% | 1.27 | 0-30 | 0.11 | >30% | - | 0-30 | - |
| | 1.50 | 30-50 | 0.17 | | 1.53 | 30-50 | 1.00 |
| | 1.81 | 50-100 | - | | 1.40 | 50-100 | 0.75 |
| | 2.10 | 100-150 | - | | 1.89 | 100-150 | - |

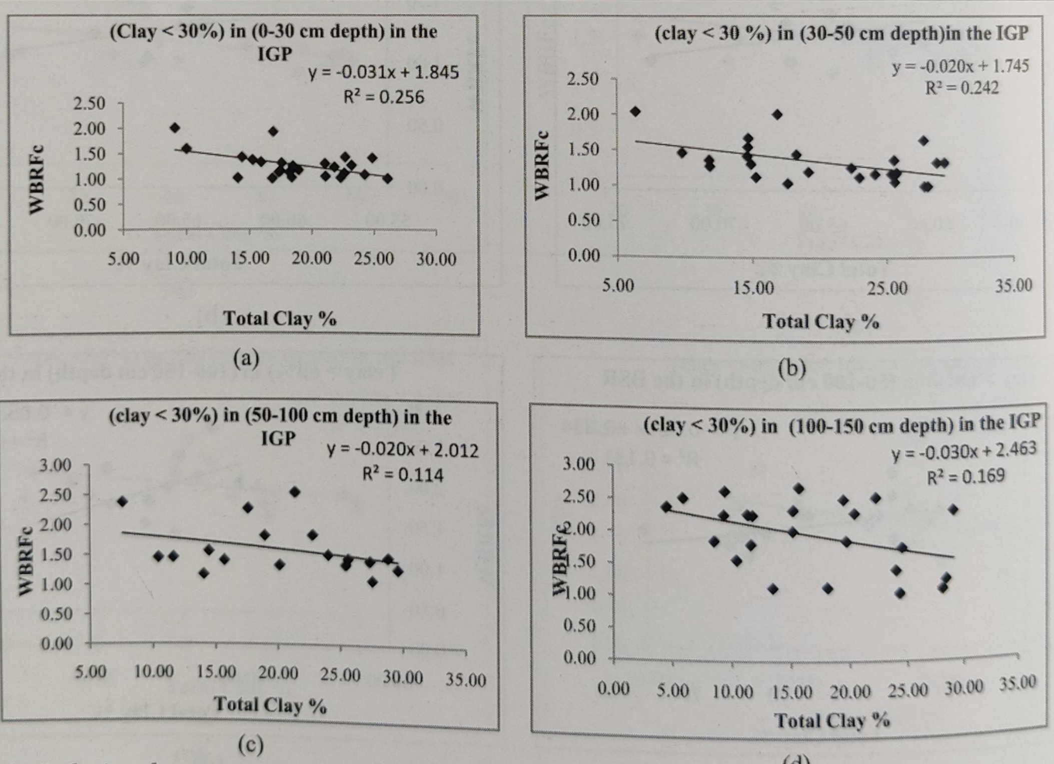


**Fig. 4**. *Relation between corrected Walkley Black Recovery Factor ($WBRF_c$) and total clay % where (clay < 30%) in a) 0-30 cm, b) 30-50 cm, c) 50-100 cm, d) 100-150 cm soil depth in the Indo-Gangetic plains (IGP)*

**Table 3.** *Corrected Walkley Black Recovery factor (WBRF$_c$) of the Black Soil Region*

| | WBRFc (mean) | Soil depth cm | $R^2$ | Clay % | WBRFc (mean) | Soil depth cm | $R^2$ |
|---|---|---|---|---|---|---|---|
| | | | Humid to Sub humid (MAR 1000-2200 mm) | | | | |
| <60% | 1.37 | 0-30 | 0.35 | >60% | 1.06 | 0-30 | - |
| | 1.65 | 30-50 | - | | 1.51 | 30-50 | 0.47 |
| | 1.80 | 50-100 | 0.24 | | 1.38 | 50-100 | - |
| | 1.92 | 100-150 | - | | 1.86 | 100-150 | - |
| | | | Semi arid (MAR < 1000 mm) | | | | |
| < 60% | 1.32 | 0-30 | 0.19 | >60% | 1.30 | 0-30 | 0.29 |
| | 1.48 | 30-50 | 0.18 | | 1.36 | 30-50 | 0.97 |
| | 1.81 | 50-100 | - | | 1.47 | 50-100 | 0.29 |
| | 2.21 | 100-150 | 0.13 | | 1.72 | 100-150 | 0.41 |

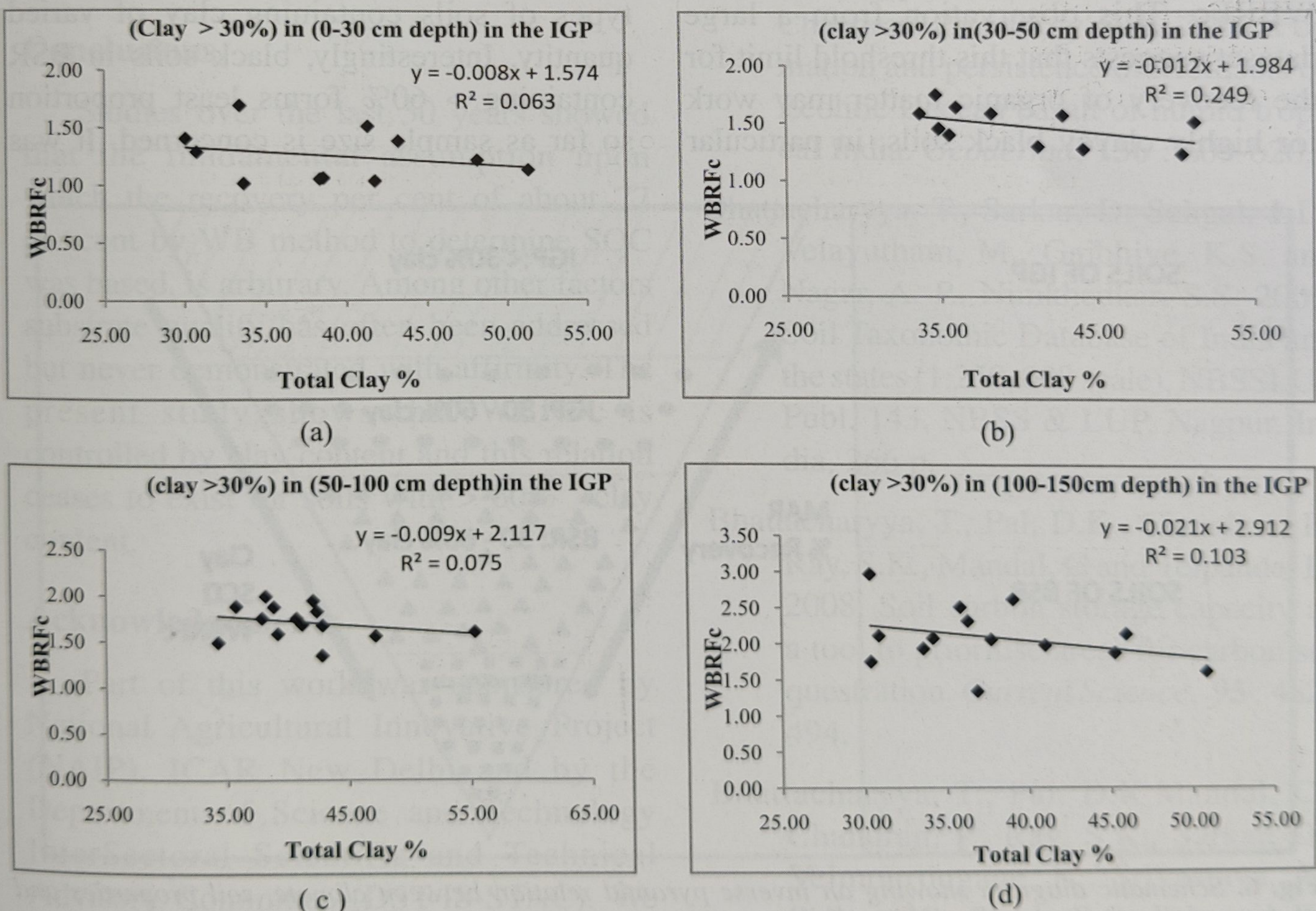


**Fig. 5.** *Relation between corrected Walkley Black Recovery Factor (WBRF$_c$) and total clay % where (clay > 30%) in a) 0-30 cm, b) 30-50 cm, c) 50-100 cm, d) 100-150 cm soil depth in the Indo-Gangetic Plains (IGP)*

pooled, cutting across the bioclimatic systems, a general trend of decrease of WBRFc with increased clay content is observed (Figs 1 and 2). However, when the data are analyzed separately the trend is reversed. It appears that after a threshold clay content (> 60%) in BSR black soils, the clay content may not have any influence in recovery of organic matter because high amount of clay with much higher surface area and SCD are likely to impart resistance to OC decomposition (Mandal *et al.*, 2008) and this causes the stabilization of the WBRFc. This observation from a large dataset suggests that this threshold limit for the recovery of organic matter may work for highly clayey black soils, in particular and other soils, in general. Earlier an inverse pyramid relation was reported for soil taxonomy vis-à-vis bioclimate and surface charge density to comment on both organic and inorganic carbon sequestration (Bhattacharyya *et al.*, 2014) (Fig. 1). The present study shows that climatic parameters (such as rainfall) and percent recovery of organic matter from soils are inversely related to clay content as it (clay) influence WBRFc as well as surface charge density. The figure 6 shows schematically the relative proportion of four different types of soils containing clay of varied quantity. Interestingly, black soils in BSR containing > 60% forms least proportion so far as sample size is concerned. It was

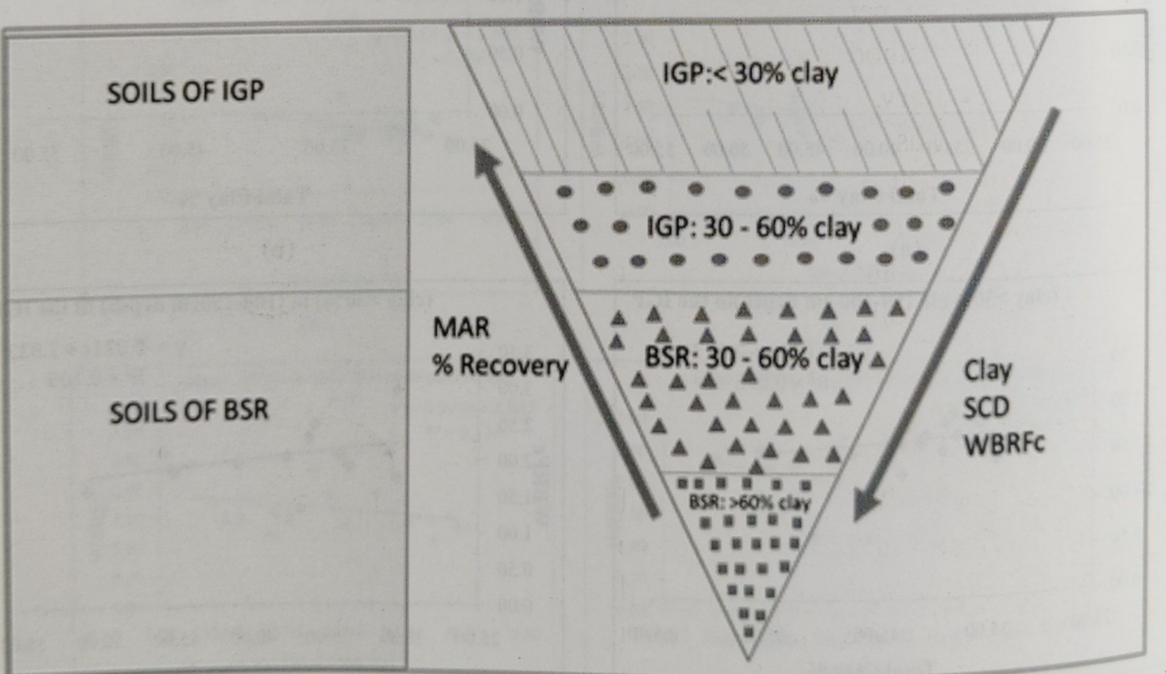


**Fig. 6.** *Schematic diagram showing an inverse pyramid relation between climate, soil properties and Walkley Black Recovery Factor ($WBRF_c$) (Most of the black soils in IGP contain < 30% clay and a little less is occupied by those containing 30-60% clay; for BSR most of the black soils fall within the range of 30-60% clay and few with > 60% clay category)*

noticed that recovery rate in these soils do not follow the trend observed for other types of soils. The quality of clay minerals with smectites as the dominant minerals may be the reason for holding organic matter more tenaciously. The charge characteristics of the smectites of these type of soils and the other soils might open up a new vistas of clay research looking for an interface between pedology (soil taxonomy, mineralogy) and edaphology (soil organic matter estimation and linking it to amount of nitrogen for plant growth).

## Conclusions

Studies over the last 50 years showed that the fundamental assumption upon which the recovery per cent of about 77 per cent by WB method to determine SOC was based, is arbitrary. Among other factors substrate quality has often been addressed but never demonstrated with affirmity. The present study shows that WBRFc is controlled by clay content and this relation ceases to exist for soils with > 60% clay content.

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