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3rd Professor S K Mukherjee CMSI Foundation Lecture

Molecular Orientations in Mica and its Implication on Potassium Fertility of Soil

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Abstract–*In sixties the work of Radoslovich and Norrish established distortions from the previously accepted ideal structures of mica. The main distortions was that the surface oxygen triads (the oxygens forming the bases of the tetrahedra) are rotated about c alternatively clockwise and anti-clockwise through an angle α from their positions in the ideal hexagonal arrangement. The cavities in the surface oxygen array are deformed from the hexagonal arrangement of the ideal model to a ditrigonal array, so the interlayer cations in micas have six nearest neighbours. Formerly the interlayer cations were thought to be in twelve-fold co-ordination, situated in the hole formed between two vertically opposed hexagonal rings of oxygens. Later on this theory was slightly modified showing that interlayer K—O distance was a variable in mica structures and was not the constant 2.81Å as assumed earlier . These along with the interlayer K-H(of octahedral OH) distance due to different orientations of octahedral OH group vary with mica composition and hence leads to different K release threshold levels. This in turn has implications on observation of two threshold levels, viz., Release threshold level and fixation threshold levels in soil which vary from soil to soil depending on the ratio of trioctahedral and dioctaheral components of mica. The range of labile K between these two threshold levels was termed Plateau of Labile K. If soil available K remain within in this range neither release nor fixation takes place. The difference between these two levels was found to be due to hysteresis effect between adsorption and desorption. High contribution of non exchangeable K to plant uptake, even in the presence of high available K was due to the fact that in the rhizosphere the available K went below the threshold level of K release. Simulation model showed that the response to applied potassium was found to be dependent on the release threshold levels of potassium.*

Introduction

Honourable Chairman, Co Chairman, esteemed delegates, ladies and gentlemen, I feel greatly honoured to pay homage to a great scientist, a teacher and a visionary, Professor S.K Mukherjee through my deliberation He was a man of colloid science. In my student days I had a chance to listen to his lecture on "Thermodynamics of ion exchange" and I knew what is teaching. I was spirited to enter into the wonder world of soil science.

Potassium release and fixation is now a text book topic. I would like to give emphasis on some mineralogical features at the molecular level governing release and fixation characteristics of soil, which have been paid relatively less attention than what should have been. A considerable part of Indian soils, particularly the alluvial soils of Indo-Ganjetic plain is rich in micaceous mineral and has large amount of potassium in the non exchangeable phase. Even in other soils, appreciable micaceous minerals are present. But the nature of these micaceous minerals is not same in all these soils with respect to their rate of release of potassium from non exchangeable form to exchangeable form

Starting with the classical work of Scott and Smith (1966) on K release from different micaceous clay minerals in presence of sodium chloride(1N), it has been shown (Fig. 1) that until and unless potassium concentration in the bathing solution was reduced below a particular level, which varied from mineral to mineral, potassium from non exchangeable source could not be released appreciably.

These levels called as critical K concentration or threshold level of K release were found to be as follows

Phlogopite	30 mg/l=	7.69×10^{-4}M ,
Biotite	15 mg/l=	3.84×10^{-4}M
Illite	7 mg/l=	1.79×10^{-4}M,
Muscovite	0.3 mg/l =	7.69×10^{-6}M

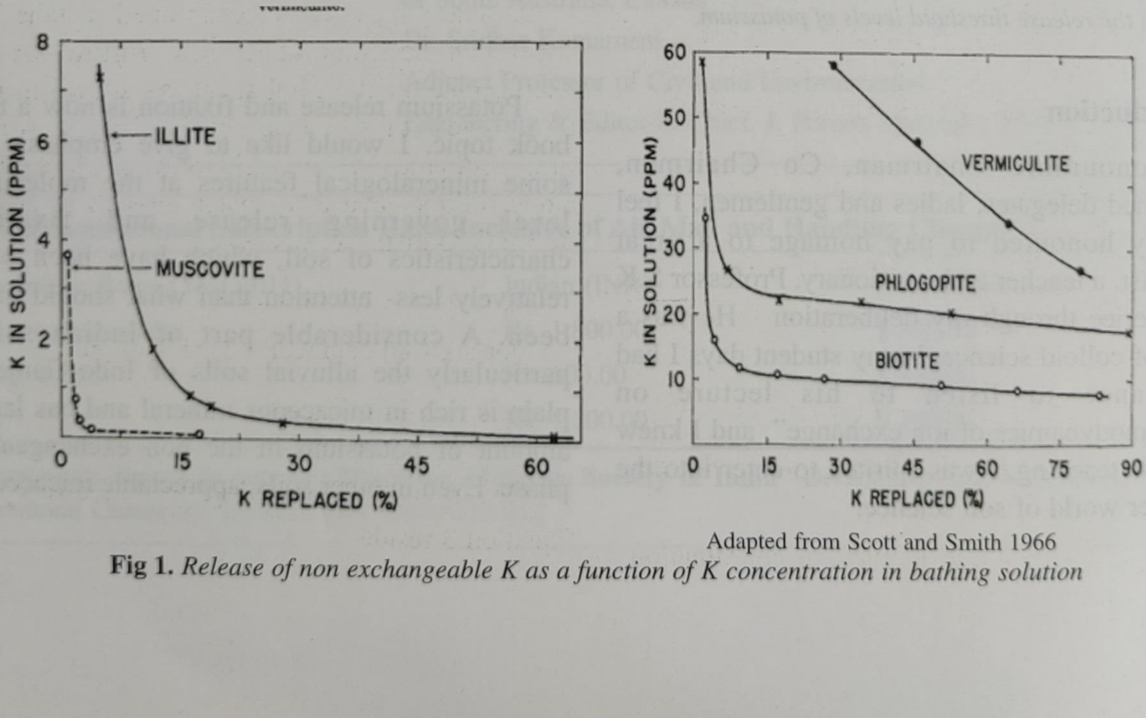
Assuming an equilibrium state between mineral K and solution K at these concentrations, chemical potential or more correctly relative chemical potential of potassium in solution with respect to sodium, which was used as the replacing ion, should be equal to bonding energy of potassium in the mineral.

Free energy change of solution K relative to sodium ion in the bathing solution at this threshold level can be calculated as $\Delta G = \mu_K - \mu_{Na} = RT \ln\frac{a_K}{a_{Na}} + \text{constant } (\mu^o_K - \mu^o_{Na})$. Assuming that potassium will be released when its free energy in the interlayer sites is more than that in the bathing solution, these calculated ΔG values could be equated to K-bonding energy in the interlayer sites. Following this hypothesis and taking activity of sodium ion as 0.77, the K bonding energy of different minerals are calculated and shown as follows:

Calculated relative K-bonding energy

Phlogopite =	-17.1kJ/mole
Biotite =	-18.8 kJ/mole
Illite =	-20.7 kJ/mole
Muscovite =	- 28.5 kJ/mole

Although different mica minerals have different K bonding energies, these cannot be distinguished by X-ray diffraction analysis, because all these minerals shows d(001) ≅ 10 Å,



Adapted from Scott and Smith 1966

Fig 1. *Release of non exchangeable K as a function of K concentration in bathing solution* indicating no opening of the interlayer space. To find out the reason behind the different K bonding energies in different mica minerals, one has to go a little detail in the structure of micaceous minerals.

Structural details of layer silicate vis -a--vis micaceous minerals

These differences in K bonding energy in the interlayers of different mica are due to variations of K-O bond length which occurred as a result of adjustment of the 'misfit 'between unequal tetrahedral and octahedral sheet.

'Misfit' between unequal tetrahedral and octahedral sheet in ideal structure

Around 1930 the classical studies of Bragg and his collaborators, and of Pauling, established the general geometrical features of layer silicate structures. The general description of the structural classes of layer silicate minerals was given based on geometrical simplification that the highly symmetric tetrahedral sheet with regular hexagonal network and octahedral sheets described superimpose exactly at the apical oxygen atoms. Octahedra and tetrahedra were considered to be regular and no account was taken of the effect of the size of the central cation on the size of the group.

b dimension, b_t, of an unconstrained tertrahedral sheet with hexagonal symmetry and containing only Si in the tetrahedra can be calculated from simple trigonometry (Fig. 2) as shown below

$$\cos 30^\circ = \frac{\frac{1}{2}b_t}{2D_B}$$

$$\frac{\sqrt{3}}{2} = \frac{b_t}{4D_B}$$

or $b_t = 2\sqrt{3} \times D_B$,,........(Equation 1)

where D_B is the distance between adjacent basal oxygen atoms.

Since for four fold tetrahedral coordination, it can be shown that Si-O bond length, D_t which is equal to $r_{Si} + r_O$ (radius of cation plus radius of anion)

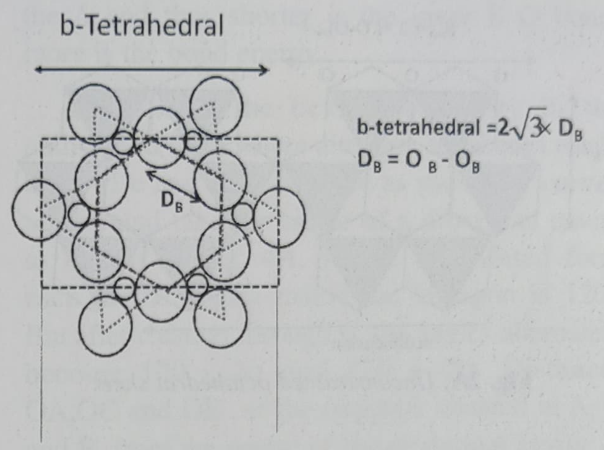


Fig. 2. *Calculation of tetrahedral b in ideal structure*

$$D_t = \frac{\sqrt{3}}{\sqrt{2}} \times r_O = \frac{\sqrt{3}}{\sqrt{2}}\frac{D_B}{2}$$

$$\text{Therefore}, D_B = 2 \times \frac{\sqrt{2}}{\sqrt{3}} \times D_t$$

Substituting this value of D_B in equation 1, we get tetrahedral b_t in terms bond length D_t of tetrahedral cation and oxygen,

$$b_t = 2\sqrt{3} \times 2 \times \frac{\sqrt{2}}{\sqrt{3}} \times D_t = 4\sqrt{2} \times D_t$$

.........(Equation 2)

Similarly b_o, of an unconstrained octahedral sheet can be calculated from figure 2A of unconstrained octahedral sheet. As shown in the figure every third octahedron is different (trans form) from the other two (cis form) i.e., repetition along b dimension takes place after three edges or 3 × O-O distance. Therefore

$b_o = 3 \times 2 \times r_a$ (Equation 3)

For six fold octahedral coordination

$D_o = r_c + r_a = \sqrt{2} \times r_a$

Or $r_a = \frac{D_o}{\sqrt{2}}$. Substituting this value of r_a in Equation 3 results

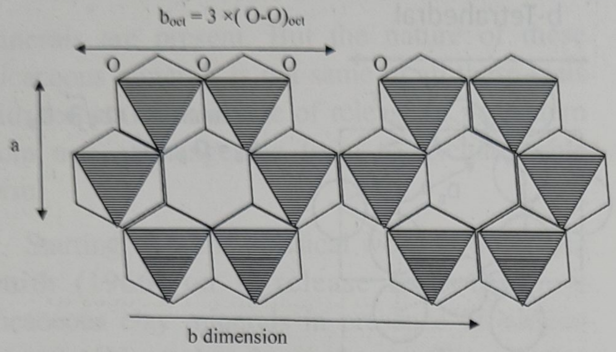


Fig. 2A. *Unconstrained octahedral sheet*

$$b_o = 3\times 2 \times \frac{D_o}{\sqrt{2}} = 3\times\sqrt{2} \times Do$$

where D_o is the octahedral cation-oxygen bond length. Values of D_t and D_o, obtained from International Tables are Si^{IV} –O 0.161, Al^{IV} – O 0.179, Al^{VI}-O .191, Mg ^{IV} - O 0.216, Fe^{2+IV} – O 0.214, Fe^{3+IV} –O 0.186 nm. With these values of tetrahedral and octahedral bond length , b value of undistorted tetrahedral and octahedral sheet can be calculated. It shows that a tetrahedral sheet (only Si) with hexagonal symmetry has a calculated 'b' dimension =0.916nm. As the Al^{IV} -O bond length is longer, substitution of Al for Si increases further the b dimension of an unconstrained tetrahedral sheet. On the other hand calculated 'b' for Al octahedral sheet = 0.81nm and calculated 'b' for Mg-octahedral sheet=0.891. Thus it is quite evident that unconstrained tetrahedral sheet is larger than octahedral sheet , particularly dioctahedral sheet and the ratio of b_t/b_o is a measure of ' Misfit'

Adjustment for linking tetrahedral sheet with octahedral sheet

To link larger tetrahedral sheet with a smaller octahedral sheet, either the tetrahedral sheet has to reduce its dimension or octahedral sheet has to increase its dimension or both. In fact both the processes take place, though reduction of tetrahedral dimension dominates. Single crystal structure determination by X-ray diffraction provides the basis of much of the current knowledge of the crystal chemistry minerals. Positions of individual atoms can be found with an error of less than 0.001nm. Since 1954, Fourier and least squares methods have been used by several research workers (Brown 1965) to determine atomic co-ordinates of layer silicates with much greater precision than before. All these studies showed considerable distortions from the previously accepted ideal structures. The main distortions (Fig. 3 and Fig. 4) are: *(i)* The surface oxygen triads (the oxygens forming the bases of the tetrahedra) are rotated about c alternatively clockwise and anti-clockwise through an angle α from their positions in the ideal hexagonal arrangement and thus reducing the b dimension of the tetrahedral sheet. Because of the effect of the vacant octahedral site, the tetrahedra are also slightly tilted in di octahedral structures. *(ii)* The octahedra are flattened in the direction normal to the layers and thus enlarging the b dimension to some extent. The octahedral layers are between 1.95 and 2.25 A thick; thicknesses from 2.2 to 2.5 A would be expected for regular octahedra.

Radoslovich (1961) showed that the angle through which the tetrahedra are twisted can be calculated from a knowledge of the structural formula and the observed b axis of the mineral. It is easily shown that

$$\cos \alpha = b_{observed} / b_{calculated}$$

$b_{observed}$ is obtained from the position of the 060 reflection or 06 band in the x-ray diffraction pattern of a layer silicate. $b_{calculated}$ is obtained from the length that the b axis would have in an undistorted tetrahedral layer (b tetrahedral) and can be calculated (Equation 2) (Radoslovich & Nortish, 1962) from the average length of the bond between the tetrahedral cation and the surrounding oxygen atoms which can be calculated from the structural formula. For micas Radoslovich considered an invariant interlayer cation to surface oxygen distance for each cation species so that the tetrahedral twisted until the surface oxygen locked on to the interlayer cation.

Later work showed that this conclusion was not justified. From detailed structure determinations on iron micas by Steinfink (1962) and Donnay *et al* (1964) and that calculated from Gatineau's work (1963) on Muscovites coordinate showed that K-O distance was a variable in mica structure and not constant as assumed by Radislovich and Norrish (1962) In fact this variability was one of the reasons why micas differ in the ease with which mica released potassium (Raussel-Colom *et al.,* 1965)

Consequences of tetrahedral rotation

As a consequence of tetrahedral rotation hexagonal cavity created by basal oxygen in the ideal structure becomes ditrigonal cavity (Fig. 3 and 4). In ideal structure K is surrounded by twelve oxygens equidistant from K. But after rotation three oxygen in one layer and three oxygen from adjacent layer come closer to potassium and other six oxygen move away from K. Potassium is now surrounded by two shells of six oxygen, instead of one shell of twelve oxygen, practically K becomes six fold coordinated. It can be shown that the angle of rotation, α is proportional to Δ (difference in K-O bond length in two shells). Thus more the rotation more is the Δ and thus shorter is the inner K-O bond, more is the bond energy.

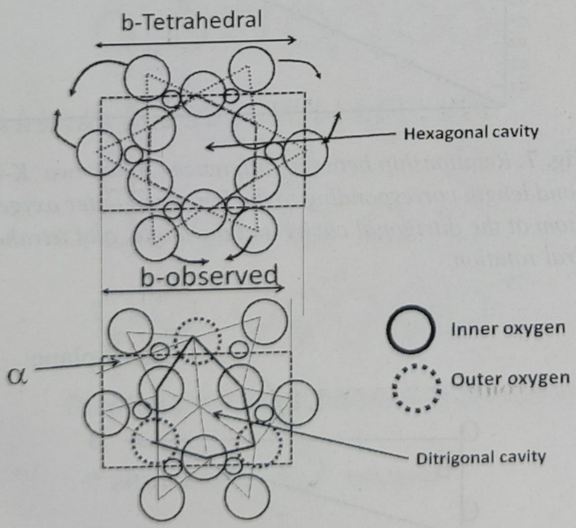


Fig. 3. *Distortion of ideal hexagonal structure due to tetrahedral rotation and reduction of b dimension*

Fig. 4B is the hexagonal cavity in the undistorted form where alternate tetrahedra rotate clockwise and anticlockwise as shown by curved arrows and take the shape of a ditrigonal cavity as shown in Fig. 4A. In the undistorted form each of the angles inside the hexagon is 120°. But after rotation through α, the angles alternately become 120 - 2α and 120 + 2α. Distances OA,OC and OE of the oxygens situated at A, C and E from the centre of the ditrigonal cavity ,O are equal to L1(say) but greater than the distances OB, OD and OF of the oxygen situated at B, D and F from O which are equal to L2. To calculate L1 and L2, let us take the triangle ΔKBC (Fig. 5) in which BC is the O_B-O_B distance which remain unchanged during rotation= x, OC =L1and and OB=L2, angle OBC = 60 + α and angle OCB= 60-α

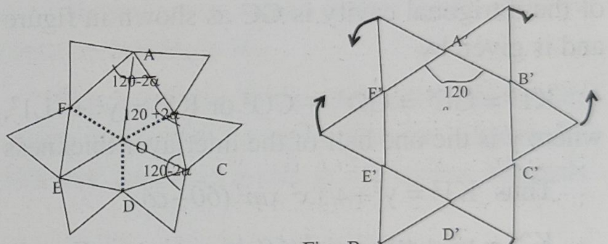


Fig. A Fig. B

Fig. 4. *a, b Angular changes of the hexagonal cavity due to tetrahedral rotation*

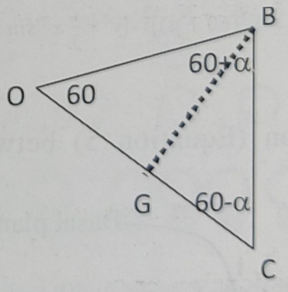


Fig. 5. *Geometrical representation of distance of oxygen atoms, B and C from the centre, O of ditrigonal cavity*

Drawing BG perpendicular to OC, BG = BC sin(60-α)= x sin(60-α)

Also BG=OB sin 60, therefore OB sin 60 = x sin(60-α)

Or, L2= OB $=\frac{2}{\sqrt{3}} x sin\ (60-\alpha)$

Similarly it can be shown L1=$\frac{2}{\sqrt{3}} x sin\ (60+\alpha)$

Now the bond length between inter layer K situated directly below O and the oxygen atoms situated at B and C on the basal plane will be different because of the different length of L1 and L2 in the ditrigonal cavity. Let interlayer K is situated at G (Figure 6) of the right angled triangle ΔGOC, where O is the centre of the ditrigonal cavity and C is the position of oxygen at distance L1 from the O in the basal plane. Thus GC is the interlayer K-O bond length (K1) for the outer oxygen. Similarly GB of the right angled triangle ΔGOB is the interlayer K-O bond length (K2) for the inner oxygen

K-O bond length (K1) corresponding to oxygen atom at C at a distance L1 from centre of the ditrigonal cavity is GC as shown in figure and is given by

$K1^2 = GC^2 = GO^2 + CO^2$ or $K1^2 = y^2 + L1^2$, where y is the one half of the interlayer thickness

Thus $K1^2 = y^2 + 4/3\, x^2\, xin^2\, (60+\alpha)$

$$K2^2 = y^2 + 4/3\, x^2 \sin^2 (60-\alpha) \quad \text{.. (Eqn 4)}$$

Therefore, the difference in K-O bond length between outer and inner oxygen is given by

$$\Delta = K1\text{-}K2 = [y^2 + \tfrac{4}{3} x^2 \sin^2(60+\alpha)]^{\frac{1}{2}} - [y^2 + \tfrac{4}{3} x^2 \sin^2(60-\alpha)]^{\frac{1}{2}} \quad \text{.. (Eqn 5)}$$

This relation (Equation 5) between the ditrigonal parameters, Δ and α depends mostly on x, the tetrahedral O-O distance and also depends on y, one-half the interlayer thickness, which is a insensitive parameter. By taking typical values of x= 2.64Å and y=1.50Å, several values were calculated by McCauley and Newnham (1971) from equation (3) and were found to be in good agreement with the experimental points. At small values of α, Equation (5) reduces to

$$\Delta = \left(\frac{360}{\pi\sqrt{3}}\right)\left(\frac{x^2}{\sqrt{x^2+y^2}}\right)(\alpha^o) = K_{calc}\,\alpha^{\circ}, \text{.....(Eqn 6)}$$

which is a linear relationship showing Δ proportional to α°. This has been verified in fig 1

In addition to tetrahedral-octahedral sheet misfit, the nature of interlayer cation was also found to be another cause of ditrigonal distortion. Field strength or ionic potential (ionic size/ionic radius) was used to characterize the effect of interlayer cation on ditrigonal distortion. A multiple regression analysis was done by McCaule and Newnham 1971 on a number of

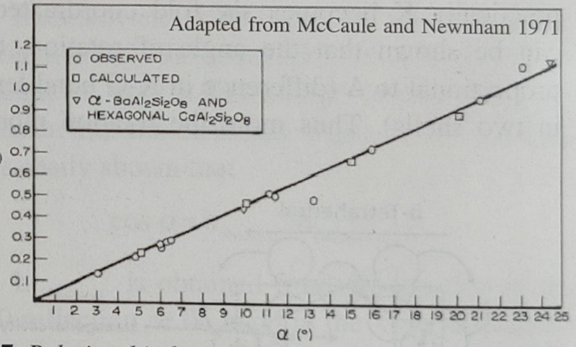


Fig. 7. *Relationship between difference (Δ) of two K-O bond length corresponding to the inner and outer oxygen atom at the ditrigonal cavity and the angle a of tetrahedral rotation*

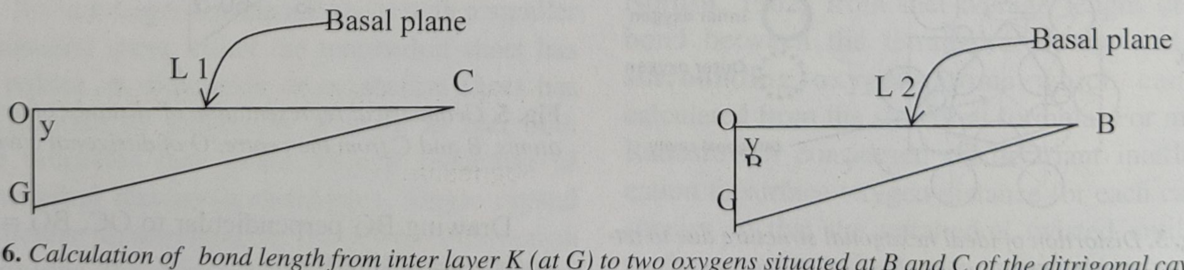


Fig. 6. *Calculation of bond length from inter layer K (at G) to two oxygens situated at B and C of the ditrigonal cavity*

dioctahedral and trioctahedral micas to quantify the effect of misfit as measured by b_t/b_o and field strength of interlayer cation as measured by ionic potential and obtained the following equations:

$$\alpha^o = 218.0(b_t/b_o) - 1.5(\text{field strength}) -221.5 \quad \text{.....(Eqn 7)}$$

The standard regression coefficients of this analysis revealed that the interlayer cation has an average contribution of about 10 % to the amount of rotation. The primary control of the ditrigonal distortion, was therefore the tetrahedral-octahedral sheet misfit. This equation may be used to predict the amount of tetrahedral rotation in micas from chemical composition data (b_t and b_o and field strength can be calculated from chemical composition). Once rotation, α, is calculated, Δ, which is the difference between outer and inner K-O length, can be obtained from equation 3 or equation 4. Thus the bonding behaviour of interlayer K in micas can be ascertained. Since dioctahedral b dimension is shorter than trioctahedral b, tetrahedral rotation has to be more in dioctahedral mica and more will be the value of (Equation 5) Δ and thus K-O bond length corresponding to inner oxygen will be shorter and stronger in dioctahedral (K2, Equation 4) mica.

OH group orientation

Bassett (1960) realized first that the octahedral hydroxyl group at the interface of tetrahedral and octahedral sheet could influence the strength of interlayer potassium bonding, As shown in the figure 8, the OH bonds in the octahedral sheet of dioctahedral mica, muscovite are directed in a slanting way, at an angle of 74° with the normal to the basal plane towards vacant octahedral site in both the layers which have been confirmed by neutron diffraction study by Rothbauer, 1971. This increased the distance between interlayer K and H of OH group (0.40 nm) and thus reduced the repulsive force . Since in trioctahedral mica there is no vacant octahedral site, OH bond has to remain perpendicular as has been confirmed by Rayner, 1974. In other words, K-H distance is less (0.31 nm) in case of trioctahedral mica which create more repulsive force on interlayer K .

Thus variations in the tetrahedral rotation and orientation of OH group in different mica lead to different threshold levels in micaceous minerals.

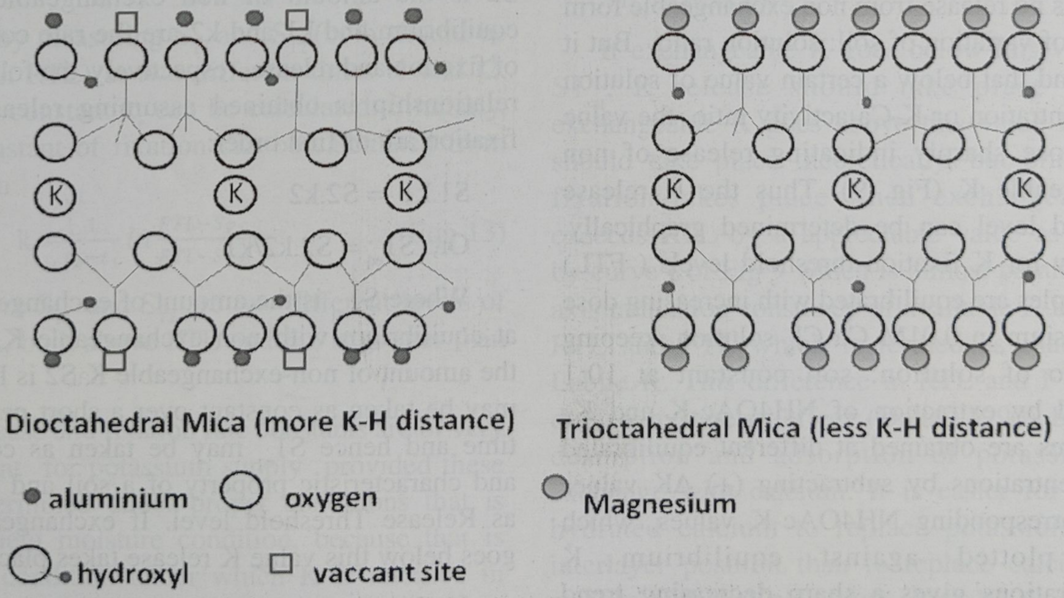


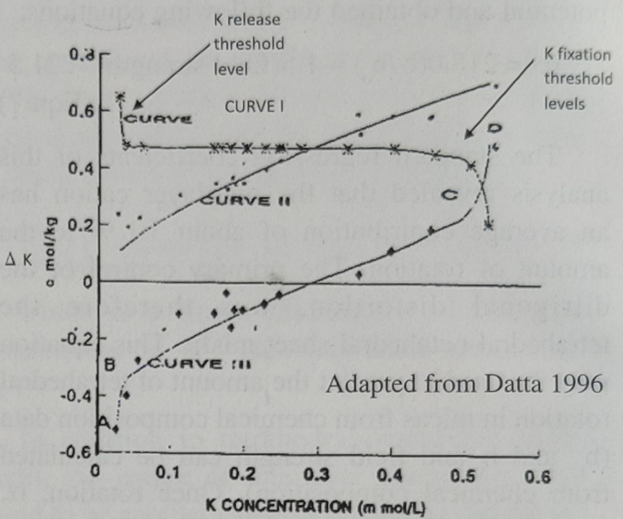
Fig. 8. *OH group orientation in dioctahedral and trioctahedral mica*

K release and fixation threshold levels in soils

Since different micaceous minerals have different K release threshold levels due to the variation of K-bonding energy of the interlayer K, their effect will be reflected in soil also depending on the relative quantity of different micaceous minerals present in soil.

Determination of threshold levels in soil

K release threshold levels (RTL) in soils can be determined from methods of determination of K-Ca Q/I relationship extending it to very high solution: soil ratio and simultaneously estimating exchangeable K by ammonium acetate (Datta and Sastry 1988, 1989, Datta 1996). The method consists of desorbing solid phase K by lowering K concentration in soil solution to different levels by shaking 2 g soil with different volumes of 0.01 M $CaCl_2$, ranging from 10 ml to 800 ml, so that K release starts from non exchangeable form. After desorption, the soil samples are extracted by ammonium acetate to determine the amount of exchangeable K remained after desorption. The amount (ΔK) desorbed in 0.01 M $CaCl_2$ solution and the amount extracted by ammonium acetate (NH4OAc-K) after desorption when added together will expected to give constant value (K_T) if there is no release from non exchangeable form in spite of variation of soil: solution ratio. But it was found that below a certain value of solution K concentration or K-Ca activity ratio, the value of K_T rose sharply indicating release of non exchangeable K (Fig. 9). Thus the K release threshold level can be determined graphically. Similarly for K fixation threshold levels (FTL) soil samples are equilibrated with increasing dose of potassium in 0.01M Ca Cl_2 solution, keeping the ratio of solution: soil constant at 10:1 followed by extraction of NH4OAc-K and K_T are values are obtained at different equilibrated K concentrations by subtracting (+) ΔK values from corresponding NH4OAc-K values, which when plotted against equilibrium K concentrations gives a sharp decreasing trend after a particular value of K concentration which is termed as Fixation Threshold Level (FTL). (Fig. 9)



Adapted from Datta 1996

Curve III is K Vs K concentration, Curve II is NH4OAC-K Vs K concentration
Curve I is K_T Vs K concentration

Fig. 9. *Graphical determination of threshold levels of K release and fixation*

Rate of K release and fixation in terms of RTL and FTL

If S1 is the amount of exchangeable K and S2 is the amount of non exchangeable K at equilibrium and k1 and k2 are the rate constants of fixation and release, respectively, the following relationship is obtained assuming release and fixation are of first order:

$$S1.k1 = S2.k2$$

$$\text{Or, } S1_{eq} = S2.k2/k1$$

Where $S1_{eq}$ is the amount of exchangeable K at equilibrium with non exchangeable K. Since the amount of non-exchangeable K S2 is large, it may be taken as constant over a short period of time and hence $S1_{eq}$ may be taken as constant and characteristic property of a soil and termed as Release Threshold level. If exchangeable K goes below this value K release takes place

Under non equilibrium condition, the rate of release of total labile K (S_T) should be proportional to how much it is below the RTL and thus the rate is given by (Datta, 2005)

$$\frac{dS_T}{dt} = k_r(RTL\text{-}S1) \quad \text{… (Eqn 8)}$$

Where, k_r is the release rate constant and (RTL-S1) is the deviation of exchangeable K from equilibrium value

Under unsaturated moisture condition the amount of K present in solution is very small relative to total labile K. Thus exchangeable K , S1 can well be approximated as total labile K, S_T and equation 8 can be written as

$$\frac{dS_T}{dt} = k_r(RTL\text{-}S_T) \quad \text{.. (Eqn 9)}$$

Since RTL is assumed to be constant for short period of time, so $\frac{dS_T}{dt}$ can be written as $\frac{d(RLT-S_T)}{dt}$ and thus equation 9 can be written as

$$\frac{d(RLT-S_T)}{dt} - k_r(RTL\text{-}S_T) \quad \text{…. (Eqn 10)}$$

$$-\int_{t1}^{t2} \frac{d(RTL-S_T)}{RTL-S_T} = k_r \int_{t1}^{t2} dt \quad \text{….(Eqn 11)}$$

Arranging equation 10 we obtain equation 11 which when integrated from t =t1 to t2, and arranged we get equation 12.

$$k_r = \frac{1}{t_2-t_1} ln \frac{RTL-S_{T1}}{RTL-S_{T2}} \quad \text{... (Eqn 12)}$$

So by measuring S_{T1} and S_{T2} (both should be less than RTL) at two different times t1 and t2, the rate constant k_r can be calculated. Similarly, rate constant of fixation can be calculated from equation

$$k_f = \frac{1}{t_2-t_1} ln \frac{FTL-S_{T1}}{FTL-S_{T2}}. \quad \text{... (Eqn 13)}$$

where S_{T1} and S_{T2} are two different levels of labile K, both above FTL and S_{T2} is greater than S_{T1}

Release and fixation rate constants are of very important for potassium supply provided these are determined under proper conditions that is under field moisture condition, because that is natural condition under which K is released in the soil. Most of the rate constant values published in literature are determined in a very high solution : soil ratio using different extractants which may not simulate the natural condition of soil which release potassium below RTL

Determination of rate constant of K release and fixation soils under field capacity moisture condition

In this method (Datta 2005), an amount of soil (say 500 g) is first leached with 2 litres of 1M $CaCl_2$ solution to reduce the level of exchangeable K below RTL and then kept undisturbed with polythene cover at a particular temperature. Available K of this soil is then determined after two time intervals, say 10 (t1) and 20 (t2) days and then release rate constant k_r is calculated by equation 12. Similarly rate constant of fixation, k_f can be calculated by equation (13) from data of available K determined after two time intervals, t1 and t2 from soils incubated at field moisture condition after adding a high dose of potassium, say 100 mg/kg soil. Rate constants of release and fixation determined in this way gives most realistic values

Diffeence between FTL and RTL values

As shown above

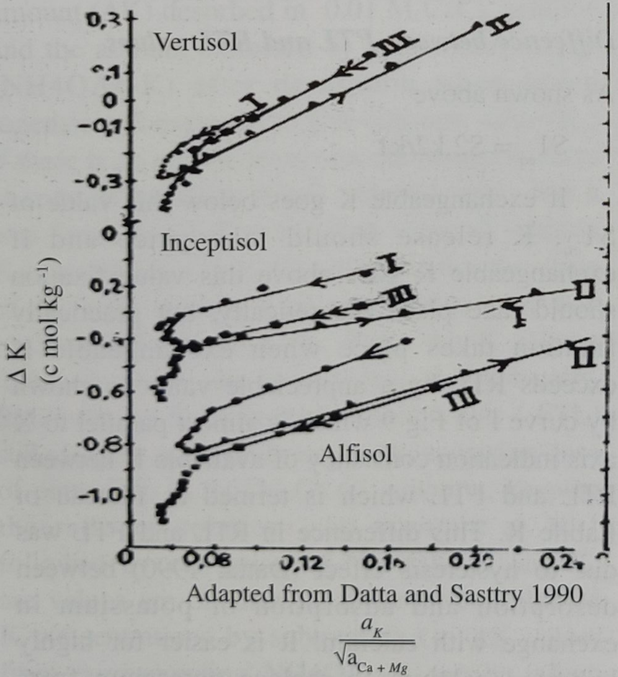
$S1_{eq} = S2.k2/k1$

If exchangeable K goes below this value of $S1_{eq}$, K release should take place and if exchangeable K goes above this value fixation should take place theoretically, but practically fixation takes place when exchangeable K exceeds RTL by a appreciable value as shown by curve I of Fig 9 which is almost parallel to X axis indication constancy of available K between RTL and FTL which is termed as Plateau of Labile K. This difference in RTL and FTL was due to hysteresis effect (Datta, 1990) between desorption and adsorption of potassium in exchange with calcium. It is easier for highly hydrated calcium to replace potassium from interlayer position than to replace calcium by weakly hydrated potassium. Fig. 10 shows that

K adsorption after desorption did follow the same path as desorption. During adsorption process, K could not enter the specific inter layer sites (curved line) but occupied planer sites (linear line).

Importance and practical implication of RTL and FTL

The threshold levels are very important for potassium dynamics as these are the gateways of K release and fixation and are important parameters for status of potassium supply from soil to crops. It has been shown that the threshold levels of K release are mineral specific viz., RTL of muscovite, illite, biotite and phlogopite were found to be 0.3, 7.0, 15.0 and 30 mg/L, respectively in terms of solution K concentration (Scott and Smith, 1966). Thus by determining the RTL of soil one can find the nature of potassium bearing mineral controlling potassium release. A high value indicates the presence of trioctahedral minerals rich in potentially available K and a very low value indicates highly depleted soil having only dioctahedral mica. Thus it is not only available and nonexchangeable K reserve which show actual K status of soils but it is RTL also which gives true status of potential K reserve of soil.



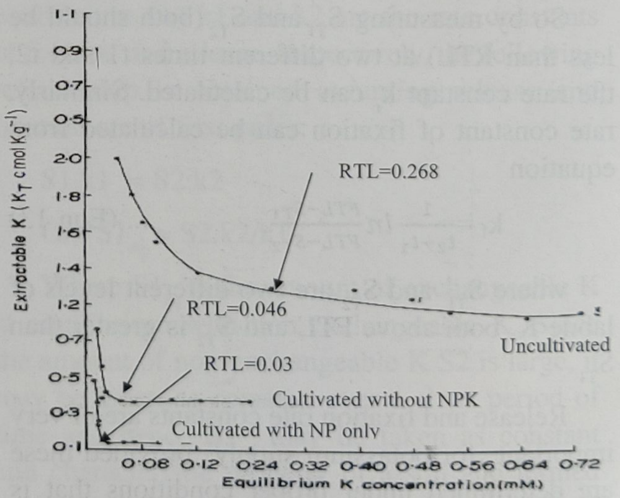
Adapted from Datta and Sastry 1990

Fig. 10. *K-Ca Q/I Curves of three soils. Curve I shows K desorption, curve II shows K adsorption after desorption, curve III shows K redesorption after drying for two months*

Figure 11 shows how RTL changes with fertilizer management. Soil from an uncultivated plot shows highest value of RTL indicating presence of trioctahedral minerals which had been confirmed by IR spectra (Datta and Sastry 1988), whereas continuous intensive cultivation with NP fertilizer only and excluding potassium fertilizer leads to depletion of trioctahedral mica causing RTL to decrease to a very low value. Although it is the fertilizer management history which largely determines the RTL and FTL, usually Vertisols are having low RTL values. Table 1 shows RTL and FTL of some Indian soils.

Sensitivity of threshold level parameters, RTL, FTL, k_r and k_f

The effect of threshold level parameters, RTL, FTL, k_r and k_f on K uptake, release, fixation and plants response to fertilizer application have been simulated through a semi mechanistic model duly modified by incorporating threshold level parameters



Adapted from Datta and Sastry 1989

Fig. 11. *Threshold levels of K release of an Inceptisol as affected by different fertilizer use*

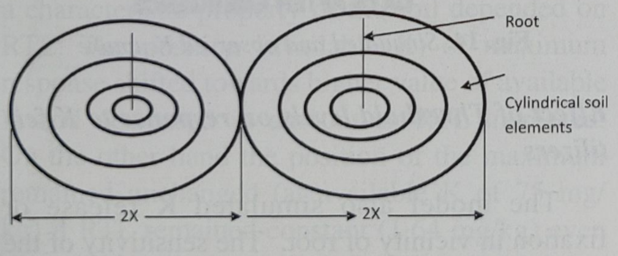
Table 1. Threshold level of K release and fixation of some Indian soils

Soils/Clay minerals	Release Threshold Level mM/L	Fixation Threshold levelmg/L
IARI (Typic Haplustept)		
0-15 cm	0.138	0.864
30-45	0.097	0.8
Coimbatore (Vertic Ustochrept)		
0-15	0.313	0.608
30-45	0.148	0.544
Palampur (Typic Haplustalf)		
0-15	0.167	0.551
30-45	0.230	0.892
Vijaypura (Typic Kandustalf)		
0-11	0.132	1.040
11-35	0.091	0.897
Sarol (Typic Haplustert)		
0-15	0.059	0.595
15-46	0.068	0.550

Description of the Model

Based on the assumption that nutrient flux from soil to root proceeds by mass flow and diffusion and influx into roots follows Michaelis – Menten kinetics, Nye and Marriot(1969) developed a mechanistic model for the transfer of nutrients from soil into plants. This model was based on conservation of solute and water in a series of small hollow cylindrical soil elements around the root (Fig 12).

Accordingly the difference between influx and outflux of solute and water from each soil cylindrical element has to be equal to the change in concentration in it. This model has been used by several authors for modifications to include the effect of root hair (Itoh and Barber 1983), inter root competition (Cushman 1979), and age dependent parameter of root (Cushman 1984). In the model considering inter root competition each one cm of root can absorb nutrients from a soil cylinder extending up to a radial distance of X cm, where X is equal to $1/\sqrt{\pi \times RLD}$, where RLD is root length density. This is because RLD is defined as length per unit volume, so that volume per unit length will be 1/RLD.



2X = the diameter of the soil cylinder containing one cm of root

$X = \frac{1}{\sqrt{\pi \times RLD}}$, RLD = Root Length Density (cm/cm^3)

Fig. 12. *Schematic diagram showing two segments of root of one cm each surrounded by series of cylindrical soil elements extending up to a radial distance X envisaged in a model of inter root competition.*

Datta (2005) has used this model to include a source and a sink function to account for K release and K fixation, respectively, in the rhizosphere by applying the threshold level concept. K release in the rhizosphere is a frequent phenomenon. It has been observed that in spite of high values of available K in the bulk soil, there had been an appreciable portion of non exchangeable K taken up by crop. This is due to the fact that due to higher demand of K created on the root surface and lower diffusive K supply to root surface owing to several constraints , such as low moisture and low impedance factor, a steep gradient is created around root surface (Fig 13) resulting K concentration below RTL resulting release of non exchangeable K .

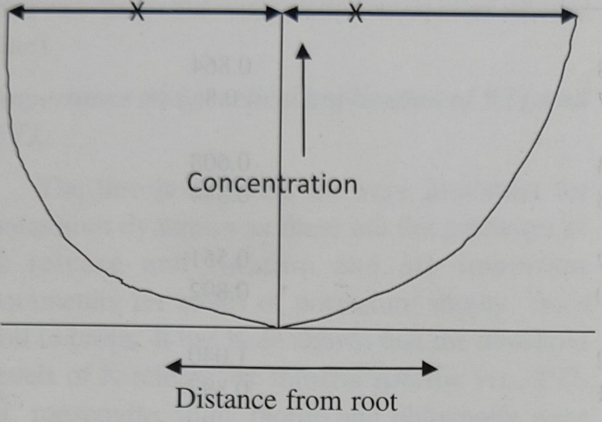


Fig. 13. *Creation of nutrient gradient around root surface*

The opposite process may also take place when supply of nutrient is more than the root demand. In that case potassium fixation may take place in the root zone.

According to this modified model the change of concentration (C_l) of a less mobile nutrient with time around a root segment is described by the following equation:

$$\frac{dC_l}{dt} = \frac{1}{r}\frac{d}{dr}\left(r.D_e\frac{dC_l}{dr} + \frac{v_o r_o C_l}{b}\right) + \frac{\rho_b}{b}\left(\frac{dS_r}{dt} - \frac{dS_f}{dt}\right) \quad \text{...(Eqn 14)}$$

In which $\frac{\rho_b}{b}\left(\frac{dS_r}{dt} - \frac{dS_f}{dt}\right)$, is incorporated as source /release ($\frac{dS_r}{dt}$) and sink/fixation ($\frac{dS_f}{dt}$) function, where, C_l = concentration of the soil solution, r = radial distance from the root axis, r_o = root radius, D_e = effective diffusion coefficient = $D_{1.}$ f .θ/b, D_1 = diffusion coefficient of K in pure solution, f=impedance factor as function of θ and bulk density, θ = volumetric moisture content, b= buffer power= ρ_b.dS1/dCl, ρ_b= bulk density v_o = rate of water uptake, t=time. dS_r/dt = rate of K release = k_r(RTL-Cl) and dS_f/dt = rate of K fixation = k_f(Cl-FTL), k_r and k_f are rate constant of release and fixation, respectively.

This differential equation (Eqn 14) has been solved numerically to simulate K concentration in all the cylindrical soil segments around a root as well as in the central zone on the root surface and then crop uptake is simulated by using Michaelis - Menten equation as follows:

Uptake per unit volume of soil =

$$2\pi r_o * RLD * V_{max} (C_{lo})/(K_m + C_{lo}) * \Delta t,$$

where, C_{lo} is solution concentration in the innermost compartment and Δt is a time step. Total uptake is obtained by summing up all these uptakes. Inter root competition has been simulated by equating flux is equal to zero at $r = 1/\sqrt{(\pi.RLD)}$. Fig 14 shows reasonably good agreements between simulated and observed uptake of potassium under field condition

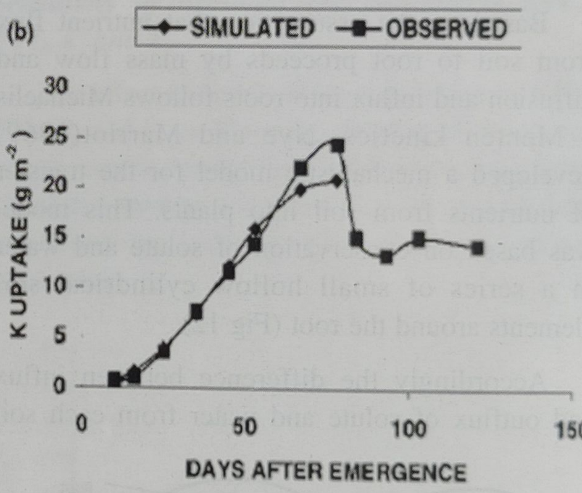


Fig. 14. *Simulated and observed K uptake*

Effect of Threshold levels on response to K fertilizers

The model also simulated K release or fixation in vicinity of root. The sensitivity of the threshold level parameters such as RTL and FTL in terms of plants response has been shown in Fig 22 Response to fertilizer application has been defined here as increase in K uptake over control by application of a certain dose of fertilizer. Figure 15a shows simulated effect of three different values of RTL viz., 0, 1.64 and 5 mg/kg and two values of FTL, viz., 10 and 31 mg/kg on plants response towards application of potassium fertilizer of 45 mg/kg as a function of available K in soil

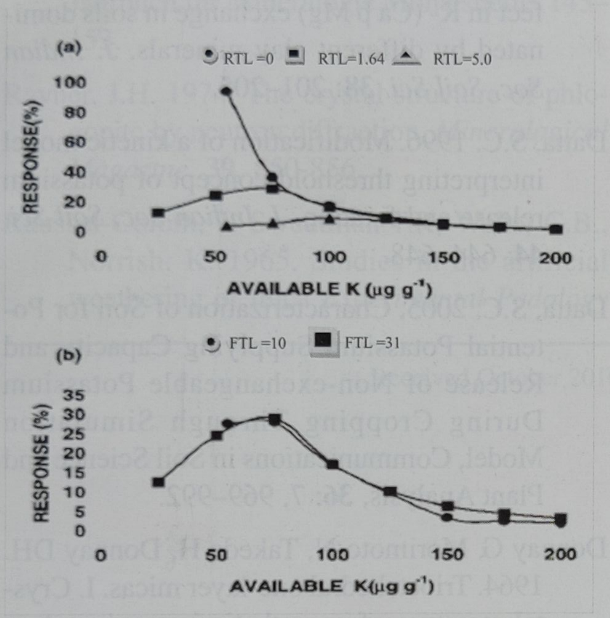


Fig. 15. *Simulated effect of (a) release threshold level (RTL) and (b) fixation threshold level (FTL on response (increase in K uptake over control).*

It was observed that response increased with available K, attained a maximum and then decreased. The value of the available K at which maximum response occurred is important for economic use of fertilizer. This maximum being a characteristic property of the soil depended on RTL. The position (available K) of maximum response shifted towards higher value of available K and decreased in amount as RTL increased. On the other hand the position of the maximum remained unchanged (at available K of 75 mg/kg) if RTL remained constant (1.64 mg/kg) even though dose of applied fertilizer had been changed to (a) 25mg/kg; (b) 45 mg/kg; and (c) 68 mg/kg. (Figure 16)

Similarly, Figure 15b showed simulated effect of two different values of FTL on response towards a single dose of 45 mg/kg K as a function of available K of surface soil (0–0.15 m). The effect of FTL was found to be significant at very high value of available K (150 mg/kg), otherwise this is insensitive parameter.

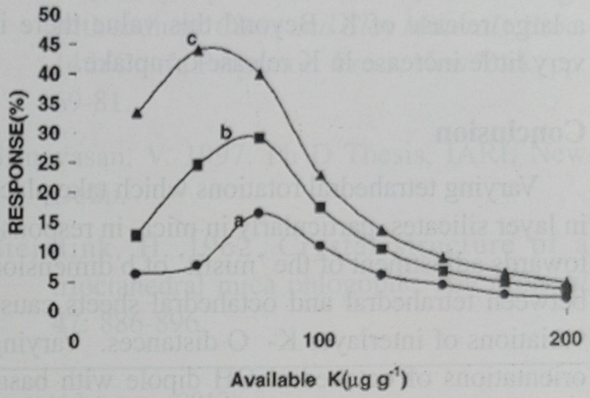


Fig. 16. *Simulated response (percent increase in K uptake over control) to applied potassium fertilizers. (a) 25mg/kg; (b) 45 mg/kg; and (c) 68 mg/kg*

Effect of rate constant of release and fixation on K release/fixation and uptake

Figure 17a shows the effect of release rate constants on K uptake and K release during cropping. To see the effect of release rate constant, a high value of RTL (5 mg/kg) and a

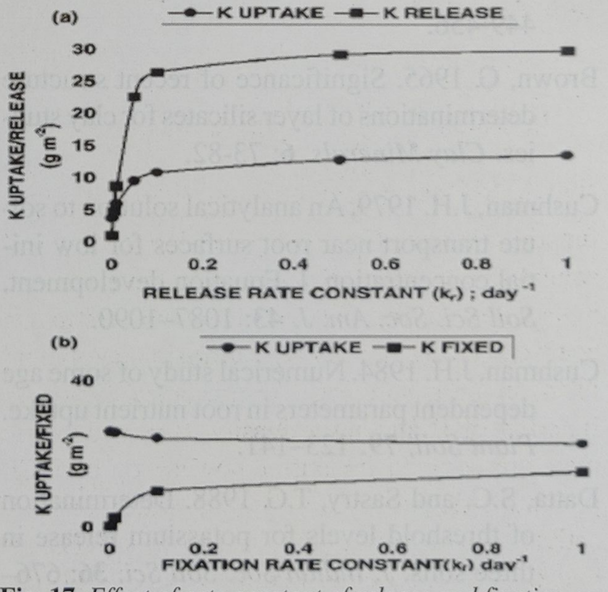


Fig. 17. *Effect of rate constant of release and fixation on K release/fixation and uptake*

low value of available K (55 mg /kg) were chosen to simulate appreciable release during cropping. The rate constant of release (kr) was found to be very sensitive up to a value of 0.1 mg/kg below which a small increase in rate constant produces a large release of K. Beyond this value there is very little increase in K release or uptake.

Conclusion

Varying tetrahedral rotations which take place in layer silicates, particularly in mica, in response towards adjustment of the 'misfit' of b dimension between tetrahedral and octahedral sheets cause variations of interlayer K- O distances. Varying orientations of octahedral OH dipole with basal plane cause variations of interlayer K-H distances. Both of these orientations result variation of K release threshold levels of micaceous minerals in soils. Simulation model duly modified by incorporating threshold level parameters indicate that these parameters play a very important role in determining plants response of K uptake to applied K fertilizer as a function available K.

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Polyacrylamide and Starch Grafted Polyacrylamide Based Nanoclay Polymer Composites for Controlled Release of Nitrogen

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Abstract–*Nanoclay polymer composites (NCPCs) based on cross linked polyacrylamide(PAM) and starch grafted polyacrylamide (St-PAM) were prepared with variable clay percentage (6%, 12%, 18% and 24% of monomer). The NCPCs were characterized by FTIR (Fourier transform infrared spectroscopy) and X-ray diffraction (XRD). Increased clay doping above 18% in NCPCs resulted in incomplete dispersion and exfoliation of clay in polymer matrix. Clay doping above 18% did not further decreased the urea release from NCPCs. Both PAM and St-PAM based NCPCs had similar slow urea release property.*

Key words *:* Nanoclay polymer composite, Polyacrylamide, Starch grafted polyacrylamide, Urea

Introduction

Incorporation of layer silicates mostly montmorillonite to composites not only make the composite inexpensive but also improve their mechanical and thermal stability properties (Basak *et al*., 2012). Several materials have been used for preparing NCPCs, but the traditional water absorbing materials are acrylic acid or acrylamide-based products which have poor degradability (Kiatkamjornwong *et al.,* 2002). Because of their unique advantages, natural polymers such as starch, protein, chitosan, etc. are being used for preparing NCPCs (Wu *et al.,* 2008). Apart from the type of polymer used, clay mineral type and its content has significant bearing on properties of NCPCs. The clays are believed to increase the barrier properties by creating tortuous path that retard the progress of gas molecule or diffusion process through polymer matrixes (Sinha Roy and Okomoto, 2003). Therefore, in the present work, we prepared two different types of nanoclay polymer composites with variable clay doping and evaluated for their slow release fertilizer properties.

Material and Methods

Polyacrylamide (PAM) and starch grafted polyacrylamide (St-PAM) NCPCs were prepared using commercially available nano bentonite through the process as described by Liang and Liu, (2007) and Mandal, (2014), respectively with some modifications. PAM NCPC was prepared using acrylic acid (4.75g) and acrylamide (1.15g) neutralizing with ammonia (neutralization degree, 60%) in a four neck reaction vessel equipped with a condenser, a thermometer and a nitrogen line. The vessel was placed on a magnetic stirrer with heating control. Commercial bentonite (6%, 12%, 18% and 24% respectively) was added and dispersed in the partially neutralized monomer solution. Under nitrogen atmosphere, the cross linker N, Ñ-methylenebisacryamide (NNMBA) (57.6 mg) was added to the acrylic acid (AA)/ acrylamide (Am)/clay mixture solution and the mixed solution was stirred on the magnetic stirrer

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at room temperature for 30 min. Then the temperature was increased slowly to 70°C with vigorous stirring after the radical initiator ammonium persulphate (APS) (80.2 mg) was introduced to the mixed solution. After completion of the polymerization reaction the resultant product was washed with distilled water. For St-PAM NCPCs 3 g starch and 0.1141 g APS were dissolved in 100 mL distilled water in four necked reaction vessel and mixed on a magnetic stirrer. The mixture was heated to 90-95 °C for 15 minutes with continuous stirring under nitrogen atmosphere to obtain gelatinized starch. To this mixture partially neutralized (60%) AA (23.04 g) was added followed by Am (4.6 g). Various percentage of bentonite clay (6%, 12%, 18% and 24% of monomer) was added. NNMBA (0.2304 g) was added to the above mixture as cross linking agent and stirred for 30 minutes. As an initiator 0.3204 g APS was added and temperature was gradually increased to 70 °C. After completion of polymerization reaction, the temperature was reduced to room temperature and the resultant St-PAM NCPCs were washed with distilled water and dried at 100 °C to constant weight. The dried NCPCs were ground in a mixer grinder and passed through 2 mm sieve for uniform particle size.

The loading of urea carried out by immersing pre-weighed dry gels into the 50% aqueous solution of urea for 24 h to reach swelling equilibrium. Thereafter, the swollen gels were dried at 60°C until constant weight is achieved. Urea loaded NCPC (0.2 g) dry gels were placed in beakers containing 100 mL distilled water (release medium) without stirring. The content of urea in aqueous solution was determined (Douglas and Bremner, 1970) at 2, 6, 12, 24, 48 and 72 hour interval, since the addition of NCPC, from which the release curves of urea for different NCPCs were obtained. The statistical design followed a completely randomized design (CRD) with three replicates.

The characteristic functional groups of NCPCs, clay and polymers were carried out employing Fourier transform infrared spectrometry (FTIR) in the region 400–600 cm^{-1} using KBr pellets. Wide angle X-ray diffraction patterns of NCPCs and bentonite were recorded using a Philips PW1710 X-ray diffractometer employing Cu-Kα radiation with a Ni filter. The particle size of bentonite was measured with Zetatrac particle size analyzer.

Results and Discussion

From the particle size analysis of the tested commercial bentonite sample it was observed that 80 percentile particles were below 61 nm size by considering the aspect ratio of 1:10 for bentonite clay. The TEM micrograph also revealed that the particles size of bentonite were less than 100 nm (data presented elsewhere). So TEM analysis and particle size analysis confirmed the nanosize of bentonite clay.

Infrared spectroscopy (FTIR)

The FTIR spectra of bentonite, polyacrylamide (PAM) polymer and PAM NCPC doped with 12% clay has been shown in Fig.1. Fig. 1A shows the infrared spectrum of commercial bentonite with a characteristic absorption band at 3698 cm^{-1} and 3621cm^{-1} corresponding to –OH stretching and at 696 cm^{-1} corresponding to stretching vibration of Si-O bond.

FTIR spectrum of PAM polymer showed bands at 3446 cm^{-1} corresponds to N-H stretching of acrylamide unit, 2932 cm^{-1} due to the CH stretching of acrylate unit, 1547cm^{-1} and 1717 cm-$^{-1}$ due to carbonyl moiety of acrylamide unit in polymer (Fig.1 B). In the FTIR spectra of PAM NCPC there was shifting of peak at 3695 cm^{-1} to 3461 cm^{-1} and 2929 cm^{-1} due to the CH stretching of acrylate unit, 1559 cm^{-1} and 1717 cm-$^{-1}$ due to carbonyl moiety of acrylamide unit which are also present in PAM polymer (Fig. 1C).

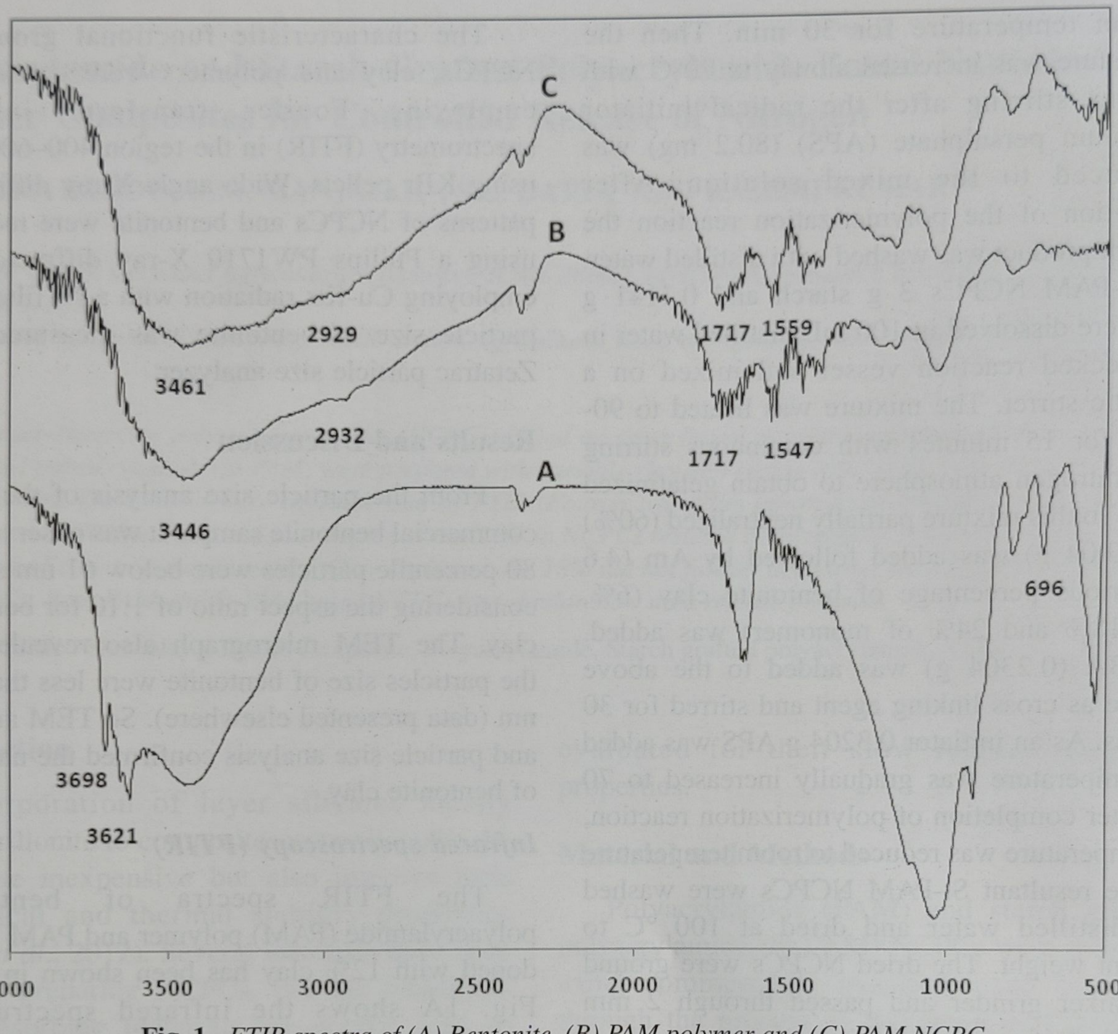

Fig. 1. *FTIR spectra of (A) Bentonite, (B) PAM polymer and (C) PAM NCPC*

The FTIR spectra of pure corn starch, starch grafted PAM polymer (St-PAM) and St-PAM NCPC doped with 12% clay has been shown in Fig.2. The FTIR spectra of pure corn starch (Fig. 2A) showed a broad absorption band at 3446 and 3348 cm^{-1}, characteristic peak of OH stretching of glucosidic ring of starch, 2931 and 2802 cm^{-1} due to CH stretching, peaks for COC stretching at 1152 and 1062 cm^{-1} and a peak at 1684 cm^{-1} for water adsorbed in starch amorphous regions. For the St-PAM (Fig. 2B), the bands at 1648, 1560 and 1460 cm^{-1}, attributed to the C=O stretching, the NH bending and the CN stretching respectively, were observed for the –CONH$_2$ groups. It showed a peak at 3449 cm^{-1} due to glucosidic ring of starch, but its intensity is more than starch. The absorption peak at 560 cm^{-1} attributed to OH group of starch dissipated and a new absorption peak at 1400 cm^{-1} appeared due to CO$_2$ group in St-PAM. The FTIR of St-PAM NCPC (Fig. 2 C) showed similar absorption peaks as St-PAM and the characteristic peak of bentonite at 3695 cm^{-1} and 696 cm^{-1} were absent or shifted.

The peaks at 1717, 1687 and 1542 cm^{-1} due to –CONH$_2$ groups of acrylamide observed in PAM polymer changed in the St-PAM (Fig. 2B) and showed the peaks at 1648, 1560 and 1460 cm^{-1}, which suggested change in –CONH$_2$ group during reaction. In the St-PAM FTIR spectrum peak at 3446 and 3348 cm^{-1} has been shifted to 3449 cm^{-1} due decrease in content of free hydroxyl groups and formation of intermolecular hydrogen bonding between starch and PAM (Jin, *et al.*, 2013). There also is increase in intensity of the peak at 3449 cm^{-1} due to glucosidic ring of starch; it might be due to unutilized OH group of the grafted poly acrylamide (Bai, 2015; Athwale and Rathi, 1999). The absorption peak at 560 cm^{-1} attributed to OH group of starch dissipated which indicated that the OH group on starch has changed during the reaction (Wu *et al.*, 2008) and a new absorption peak at 1400 cm^{-1} corresponding to CO_2 group appeared in St-PAM. The peak observed at about 1111 cm^{-1} corresponds to the asymmetric stretching vibration of COC group implied a successful O-site grafting polymerization reaction. The change in absorption peak for $-CONH_2$ and OH groups in grafted sample suggested that the reaction between OH groups on starch and $CONH_2$ group on acrylamide chain take place during the reaction.

The FTIR spectra of PAM NCPC and St-

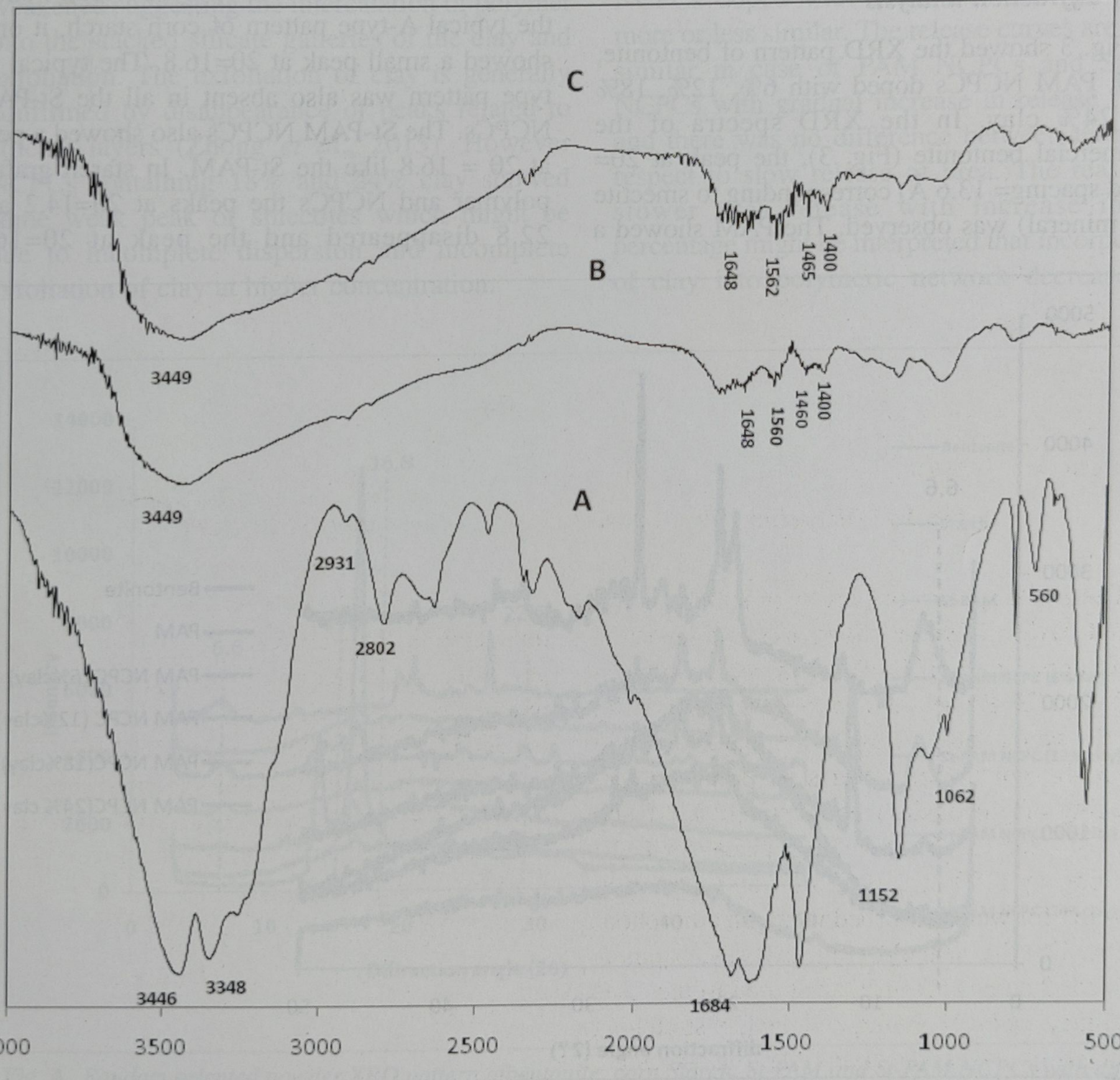

Fig. 2. *FTIR spectra of (A) Corn starch, (B) St-PAM polymer and (C) St-PAM NCPC*

PAM NCPC showed that absorption peaks at 3698 cm^{-1} corresponding to –OH stretching and at 696 cm^{-1} corresponding to stretching vibration of Si-O bond characteristics of bentonite shifted after incorporation of clays into polymer network and showed bands in 3446–3448 cm^{-1} range due to N-H stretching of acrylamide unit. The shift of 3698 cm^{-1} and presence of peaks in 3446–3448 cm^{-1} range suggests copolymerization between –OH groups on clay and monomers and formation of H bond between clay and polymer network (Liang and Liu, 2007).

X-ray diffraction analysis

Fig. 3 showed the XRD pattern of bentonite, PAM, PAM NCPCs doped with 6%, 12%, 18% and 24% clay. In the XRD spectra of the commercial bentonite (Fig. 3), the peak at $2\theta=6.6$ (d spacing= 13.6 Å) corresponding to smectite (2:1 mineral) was observed. The PAM showed a broad peak in the XRD pattern. In XRD patterns of PAM NCPC doped with 6% and 12% clay the characteristic peak of smectite at $2\theta=6.6$ was absent but the peak started appearing in PAM NCPC doped with 18% clay and clearly visible in PAM NCPC doped with 24% clay. Fig.4 showed the XRD pattern of bentonite, pure corn starch, St-PAM, St-PAM NCPCs doped with 6%, 12%, 18% and 24% clay. The corn starch showed XRD pattern of typical cereal starch i.e. A-type pattern. The A-type pattern of corn starch is due to presence of high amount of amylopectin (Zeng *et al.*, 2011). The St-PAM polymer didn't show the typical A-type pattern of corn starch, it only showed a small peak at $2\theta=16.8$. The typical A-type pattern was also absent in all the St-PAM NCPCs. The St-PAM NCPCs also showed a peak at $2\theta = 16.8$ like the St-PAM. In starch grafted polymer and NCPCs the peaks at $2\theta=14.2$ and 22.8 disappeared and the peak at $2\theta=16.8$

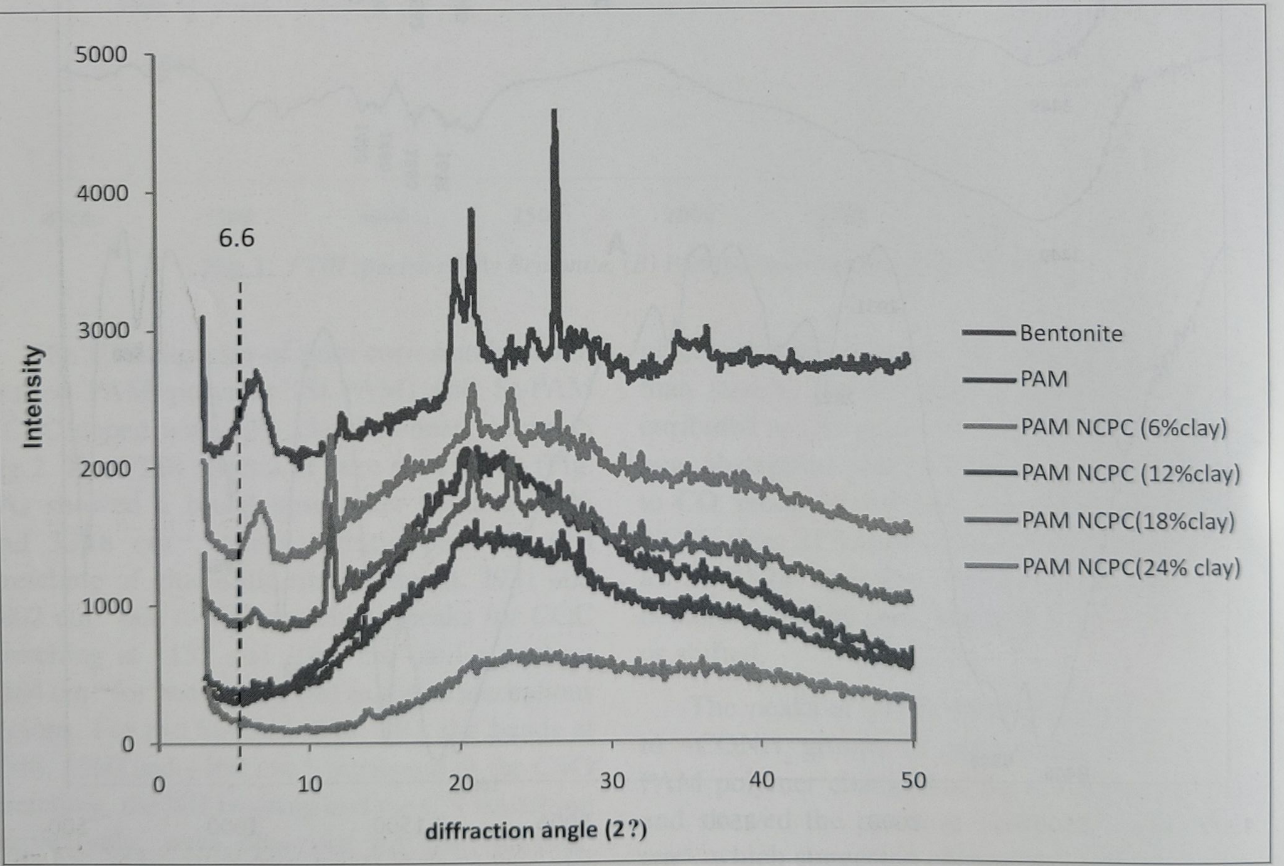

Fig. 3. *Random oriented powder XRD pattern of bentonite, PAM and PAM NCPCs with different concentration of clays*

weakened. This disappearance and weakening of peaks of starch suggested that the crystalline region of starch also participated in the graft polymerization reaction (Gao *et al.*, 1994; Athwale and Rathi, 1999; Zou *et al.*, 2013).

The characteristic peak of smectie at $2\theta=6.6$ was absent in St-PAM NCPC doped with 6% and 12% clay but visible in St-PAM NCPC doped with 18% and 24% clay. As the XRD pattern of all the NCPCs showed that after incorporating bentonite into polymeric network, the typical diffraction peak of smectite clay disappeared or weakened suggesting the intercalation of polymer into the stacked silicate galleries of the clay and exfoliation. The exfoliation of clay is generally confirmed by disappearance of peaks related to silicate layers (Zhong *et al.*, 2013). However NCPCs containing 18% and 24% clay showed some weak peak of smectites which might be due to incomplete dispersion and incomplete exfoliation of clay at higher concentration.

Urea release behavior from NCPCs in water

The periodic release of urea in water from the three NCPCs doped with bentonites at four different concentrations loaded with urea was studied. The Fig. 5 depicts a very rapid release of urea from NCPCs doped with 6% clay in both polymer based NCPCs. In case of NCPCs doped with 6% clay, 80–85% of loaded urea was released within 72 hours of incubation period where as 70–75% loaded urea released in case of NCPCs doped with 12, 18 and 24% clay after 72 hours of incubation. Release of urea from NCPCs doped with 12%, 18% and 24% were more or less similar. The release curves are nearly similar in case of PAM NCPCs and St-PAM NCPCs with gradual increase in release of urea and there was no difference between them with respect to slow release of urea. The reason for slower urea release with increase in clay percentage might be interpreted that incorporation of clay into polymeric network decreased the

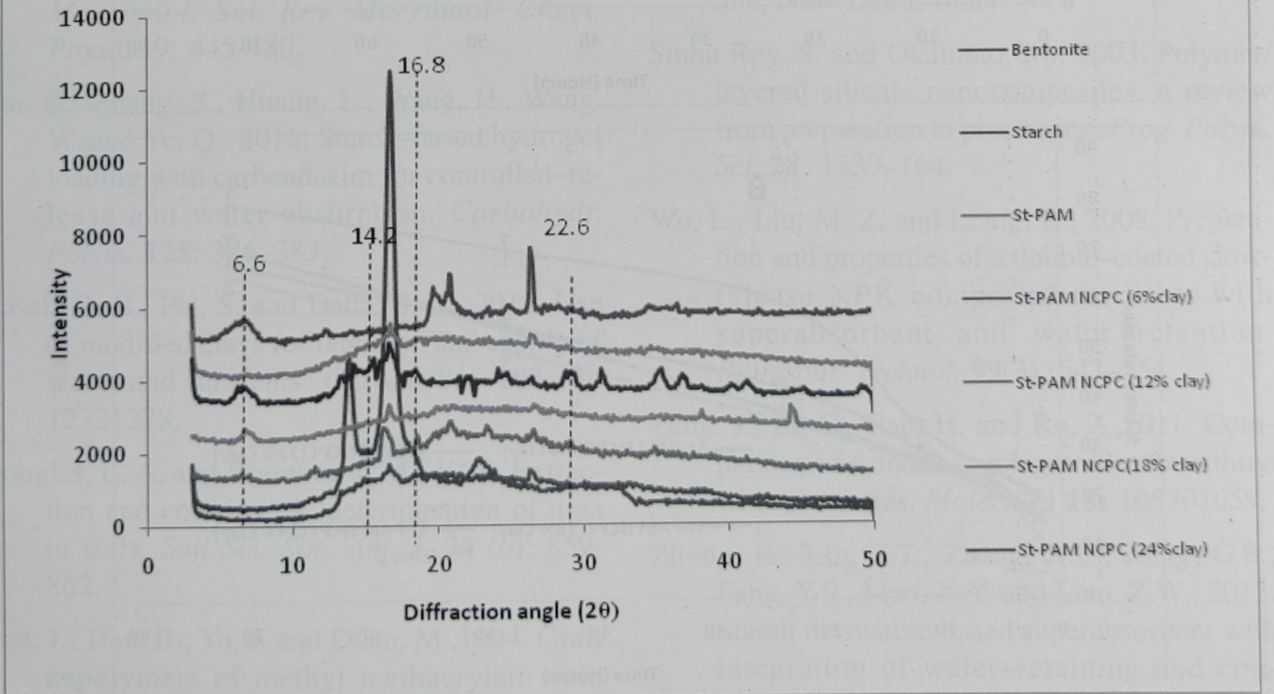

Fig. 4. *Random oriented powder XRD pattern ofbentonite, corn Starch, St-PAM and St-PAM NCPCs with different concentration of clays*

mesh size of polymer composites, which enhanced the barriers for urea diffusion, thereby resulting in slow release pattern. The increased barrier property with incorporation of clay has been described by Sinha Ray and Okamoto (2003) for diffusion of gas. They proposed that clays increases the barrier properties by creating a maze or tortuous path that retard the progress of the gas molecule through polymer matrix. With increment in clay concentration from 6% to 18%, the rate of release from NCPCs was decreased owing to the increased crosslinking density of NCPCs and increased tortuosity of polymer matrix. After 12% clay concentration the release percent did not decreased much, it was due to incomplete exfoliation and dispersion of clay in the polymer matrix above 12% clay, which do not contribute much towards increasing cross linking density of polymer. NCPCs doped with 24% clay were found to release urea at a higher rate compared to NCPCs doped with 12% and 18% clay. In case of 24% clay doped NCPCs

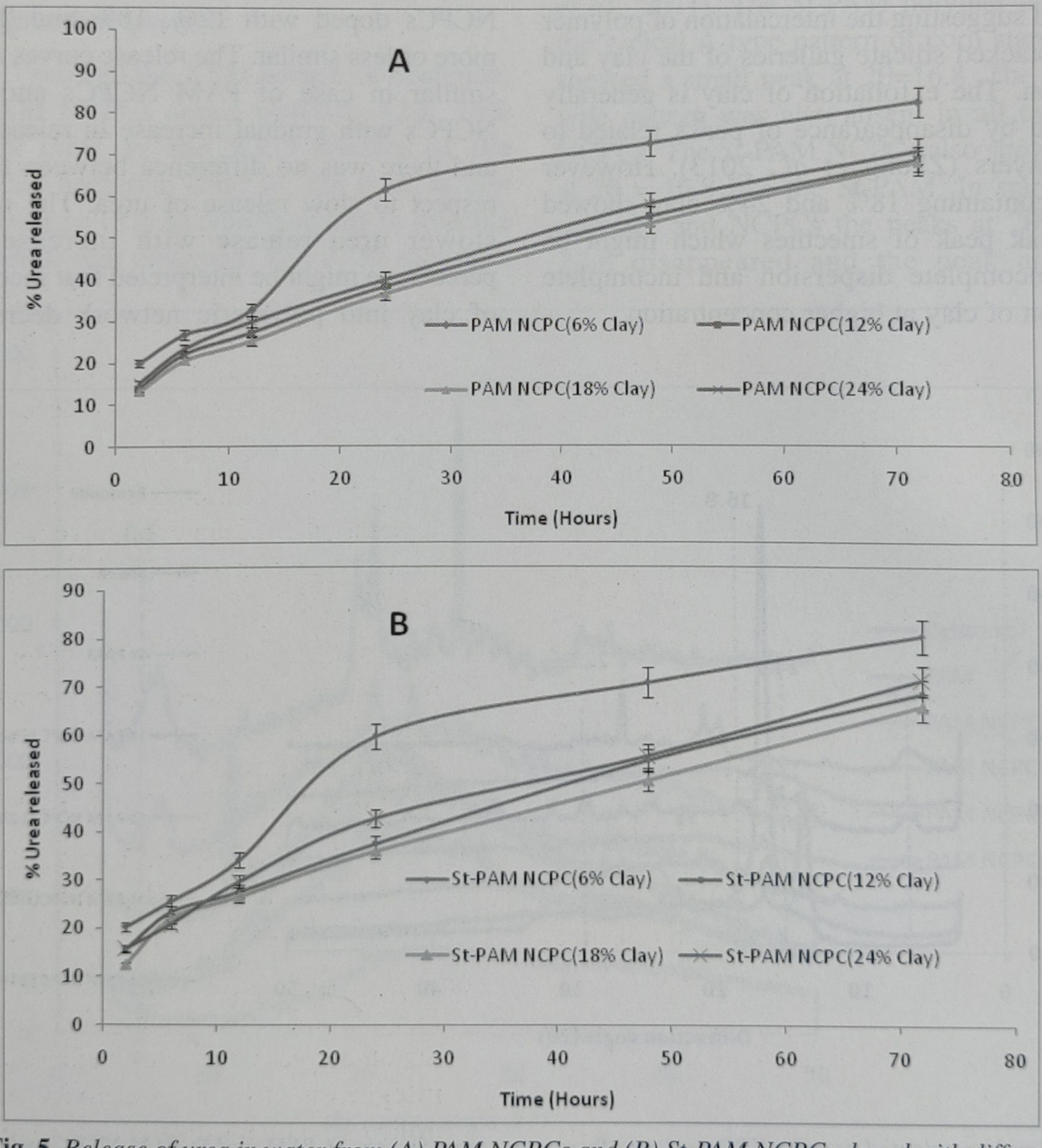

Fig. 5. *Release of urea in water from (A) PAM NCPCs and (B) St-PAM NCPCs doped with different clay concentrations*

some of urea might remain on surface of NCPCs instead of adsorbed inside the polymer matrix as the porosity drastically reduced at 24% clay doping, which was clear from lowest water absorbency of NCPCs doped with 24% clay (data presented elsewhere). So higher clay doping did not resulted in further decrement of urea release.

Conclusions

NCPCs based on PAM and St-PAM with variable clay doping were synthesized. FTIR and XRD study confirmed the successful grafting of starch on PAM and incorporation of bentonite in the polymer matrix. This study revealed that clay doping upto 12% of monomer resulted in uniform dispersion and exfoliation of clay in the polymer gallery. Starch can be used instead of acrylamide for synthesis of NCPCs without affecting its slow release property.

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Impact of Long-Term Manuring and Fertilization on Silt and Clay Protected Carbon in two Alfisols with Varying Texture

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***Abstract–**Fine textured soil have greater potential for physical protection of soil organic matter (SOM) as compared to coarse fraction. One of the principal factor responsible for the association of C with silt and clay fraction is soil texture and clay minerology. Our hypothesis was to study how soils with dissimilar climate texture and duration of manuring and fertilization influence C retention in two Alfisols with similar clay mineralogy (kaolinite dominant). The C carrying capacity of silt+clay fraction was estimated by a mathematical model developed by Hassink (1997). The study revealed that texture plays a significant role in determining C carrying capacity of silt and clay fraction of Alfisols of Bhubaneswar, Odisha and Pattambi, Kerala. The sandy clay loam soils of Pattambi stabilized more silt+clay protected C than sandy loam soil of Bhubaneswar. The application of 100%NPK, 150% NPK and 100% NPK+ FYM promoted stabilization of C in silt and clay fraction compared to 50% NPK and unfertilized control treatment. In general, the C retention potential of subsoil was higher than the surface-soil at both the sites indicating greater C sequestration potential.*

Key words : Silt+clay fraction, C carrying capacity

Chemical stabilization, physical protection and biochemical stabilization are the three main mechanisms of SOM stabilization (Christensen, 1996). Chemical or physiochemical association of SOM with silt and clay particles can result in chemical stabilization of SOM (Feller and Bear, 1997; Hassink, 1997). Existence of the relationship between soil texture and silt and clay associated carbon has been correlated, but no correlation was found between texture and C associated with sand sized fraction (Hassink, 1997). The capacity to protect organic carbon (C) and nitrogen (N) in fine textured soils is higher than coarse textured soils with similar addition of organic inputs (Hassink *et al.*, 1997; Jenkinson, 1988). Association with silt and clay particles can be attributed as one of the main factors responsible for the physical protection of organic C and N in soil (Theng, 1979). In fine soil fractions, the C and N associated is largely affected by soil texture, unlike in large fractions, where it is mainly regulated by organic inputs rather than soil texture (Christensen, 1992, Garwood *et al.,* 1972). Even though stability of organic matter in soil is mainly determined by mechanisms of protection in soil, it is still unclear about the quantification of the capacity of soil to protect SOM and the upper limit to preserve the SOM (Van Veen and Kuikman, 1990). Both soil texture and clay minerology are determinant factor in deciding the capacity of soil to retain C and N. The specific surface area (SSA) of clays

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range from 40 m^2 g^{-1} for kaolinite to 800 m^2 g^{-1} for 2:1 type clay minerals e.g., smectite and montmorrilonite, and the amount of humic substances adsorbed depends on SSA (Tate and Theng, 1980). Contrary to assumptions and predictions by the models, there is loss of native soil C with addition of C inputs under native conditions. There are several lines of study which suggested the existence of upper limit of C saturation in soils. Many long term fertilizer experiment studies show linear relationship between C inputs and total soil carbon content across different treatments (Larsen *et al*, 1972; Paustian *et al*, 1997).

The lower stabilization in 1:1 clay dominant soils could be attributed to different types of clays and also the effect of climate, as these are normally observed in tropical or subtropical regions. The higher temperature and precipitation in these region may contribute to the faster decomposition and hence lower stabilization of C in 1:1 type of clays. However, the type of clay can be considered to play important role as different clays have significant difference in specific surface area and CEC (Greenland, 1965) and hence different adsorption capacities. The loss of silt and clay associated C during cultivation is minimal as the dominance and sensitivity of sand associated C is more (Camberdella and Elliot, 1992) and the transfer of sand associated C to silt and clay associated fraction during decomposition. Climate is considered as one of the important factors which greatly influence the C carrying capacity of soil (Hassink, 1997). Among climate, temperature and rainfall which are considered as driving force for faster cycling of C and other nutrients in soil (Hassink, 1997). It might be possible that soil type with similar clay minerolgy but varying texture and climatic condition might affect the C carrying capacity of soil (Hassink, 1997). Alfisols found in Bhubaneswar and Kerala are similar in minerolgy but differs in texture and the climatic conditions in which these soils are developed, the former location receives an annual rainfall of 1449 mm has perhumid climate and the latter receives an annual rainfall of 2727 mm has humid climate.

The hypothesis of the study was that dissimilar texture and climatic conditions might influence the C carrying capacity of two Alfisols with similar mineralogy. The objective of the study was to unravel the long term effect of manuring and fertilization on C carrying capacity of silt+clay size fractions in two Alfisols with similar mineralogy and varying texture cultivated with rice-rice cropping systems located in Bhubaneswar, Odisha and Kerala.

Materials and Methods

Collection of soil samples

The soil samples were collected to a depth of 0 to 15 cm and 15 to 30 cm from two different ongoing long term fertilizer experiments (LTFEs) located in Bhubaneswar, Odisha and, Pattambi, Kerala in the year 2013. The LTFEs at Bhubaneswar was initiated in 2002 and at Pattambi in 1996 with rice-rice cropping system. Bhubaneswar receives an annual rainfall of 1449 mm has tropical and subhumid climate and Pattambi receives an annual rainfall of 2727 mm has perhumid climate. Soils of both the locations belong to Alfisols with acidic in nature. The Alfisols of Bhubaneswar and Pattambi are sandy loam and sandy clay loam in texture, respectively. The physico-chemical properties of two soils are presented in Table 1. The treatments considered for the study were control (no fertilizer or manure input), 50% NPK, 100% NPK, 150% NPK, 100% NPK + FYM (10 t ha^{-1}) and 100% NPK + lime. The recommended dose of fertilizer in Bhubanewsar was 100 kg N, 26 kg P_2O_5 and 50 kg K_2O and in Pattambi was 90 kg N, 20 kg P_2O_5 and 38 kg K_2O per hectare.

Separation of clay and silt protected carbon

Fifty grams of air dry soil (2-mm sieved)

Table 1. *Mechanical and physico-chemical characteristics of soils of the experimental field*

	Alfisol	
Parameter	Bhubaneswar	Pattambi
Mechanical analysis		
Sand (%)	66.24	62.24
Silt (%)	12.28	10.28
Clay (%)	21.48	27.48
Textural class	Sandy loam	Sandy clay loam
Chemical property		
pH	6.36	5.5
EC (dsm^{-1})	0.10	0.04
SC (g/kg)	7.0	15.0
Available N (kg/ha)	150	242
Available P_2O_5 (kg/ha)	7.77	15.3
Available K_2O (kg/ha)	163	80

was suspended in 250 ml water for 24 hrs and ultrasonicated at 6000 rpm for 15 minutes (Cole Parmer, T25 Digital ULTRA TURRAX). The dispersed soil suspension was transferred to a 1 L glass cylinder which was shaken end over end until the whole soil was suspended fully. By applying Stokes' law and a particle density of 2.675 g cm^{-3} the settling time was decided. The particles <20μm were isolated by siphoning the suspension at the appropriate depth and were dried for 4 hours at 105°C, ground and analyzed for total C. Particle size analysis was done after oxidation of organic matter with H_2O_2 and removal of $CaCO_3$ with HCl. The amounts of C associated with the particle size fraction <20 μm were calculated by using the percentage of particles <20 μm obtained after removal of organic matter and $CaCO_3$ and the C content of the fraction <20 μm obtained after sonification (Hassink, 1997).

$$\text{C (in fraction} <20\ \mu\text{m)} = 4.09 + 0.37 \times \%\ \text{particles} <20\ \mu\text{m}$$

The total soil carbon (TSC) and total soil nitrogen (TSN) in < 20 μm was determined (from oven dried fine sieved samples) by dry combustion method in a CHNS analyzer (Eurovector, model Euro EA3000). The soil texture was determined by international pipette method (Piper, 1942) and the dominant clay present was determined using XRD (McGlashen and Hardy, 2005).

Statistical analysis

The effect of different treatments on silt plus clay protected carbon across various treatments in soils was statistically analysed in Randomised Block Design with one way ANOVA by WINDOW based SPSS statistical package (Version 10.0).

Results and Discussion

Carbon (C) carrying capacity of silt+clay fraction

The dominant clay mineral identified in Alfisols at Bhubaneswar and Pattambi was kaolinite with sandy loam and sandy clay loam in texture, respectively. The soils of Bhubaneswar had 34.8 % silt and clay, of which 21.48 % was clay. In soils of Pattambi had 38.48 % silt plus clay of which 27.48 % clay.

The C content in clay+silt fraction in Alfisol of Bhubaneswar at 0–15 cm soil depth varied from 13.7 g kg^{-1} in 50% NPK to 23.1 g kg^{-1} in 100%NPK+FYM treatment (Table 2). The maximum amount of C that can be associated with silt and clay particles as estimated by the formula was 16.8 g kg^{-1}. The difference between the actual and the protective C (max C) ranged from as low as -6.91 g kg^{-1} in control to as high as 6.30 g kg^{-1} in 100% NPK+FYM. This indicates that the further addition of organic carbon limits its association with silt and clay and hence the soil is approaching towards saturation. In sub surface soil depth (15–30 cm), the C content in silt+clay fraction was observed highest in 100%NPK+FYM. The C content in silt+clay fraction under 100%NPK, 150%NPK, 100%NPK+lime was significantly higher than that in 50%NPK or control treatments. The protective C at 15–30 cm soil depth was

Table 2. *Effect of different treatments on silt plus clay protected C in 0-15 cm and 15-30 cm soil under rice-rice cropping system of Bhubaneswar, Odisha*

Treatments	Actual C ($g\ kg^{-1}$)		Protective C ($g\ kg^{-1}$)		N ($g\ kg^{-1}$)		C/N		Difference (Actual-Protective) ($g\ kg^{-1}$)		Silt + clay	Clay (%)	Mineral
	0-15 cm	15-30 cm	0-15 cm	15-30 cm	0-15 cm	15-30 cm	0-15 cm	15-30 cm	0-15 cm	15-30 cm			
50%NPK	13.7d	6.1c	16.8	21.3	3.30b	5.57a	4.20bc	1.09c	-3.05d	-15.2c	34.8	21.48	Kaolinite
100%NPK	16.9b	7.0b	16.8	21.3	3.43b	2.16bc	4.97a	3.25b	0.13b	-14.3b			
150%NPK	15.6c	7.3b	16.8	21.3	3.25b	2.15bc	4.84ab	3.39b	-1.16c	-14.0b			
100%NPK+lime	16.8c	5.5c	16.8	21.3	3.52b	1.74c	4.80ab	3.20b	-0.007b	-15.7c			
100%NPK+FYM	23.1a	11.0a	16.8	21.3	4.31a	2.34b	5.39a	4.72a	6.30a	-10.3a			
CONTROL	9.9e	5.6c	16.8	21.3	2.57c	1.73c	3.88c	3.24b	-6.91e	-15.7c			

estimated to be 21.3 g kg^{-1}. The difference in actual and the estimated protective C in 15–30 cm soil depth was observed lowest in 100%NPK+FYM and it was highest in the control treatment. The C content in clay+silt fraction at 0–15 cm soil depth was almost double than that at 15–30 cm soil depth. In both the soil depths, the optimal (100%NPK) or super optimal (150%NPK) dose of NPK significantly increased the C content in clay+silt fractions over sub-optimal dose of NPK (50%NPK). Amendments of lime with 100%NPK did not have additional benefit in increasing the C content in clay+silt fraction in 0–15 cm, however, the same treatment decreased the C content in 15–30 cm soil depth. The protective C content in sub surface soil was estimated to be higher than that in surface soil. The difference in actual C and protective C content in majority of the treatments excepting 100%NPK and 100%NPK+lime (0 to 15 cm) in both the soil depths was negative. The difference being more negative indicates greater potential for more retention of C by clay+silt fraction. The more C content in clay+silt fraction indicates that especially the clay fraction is approaching towards saturation. The treatments especially where suboptimal dose of NPK was applied or only chemical fertilizers were applied hold greater potential for more C retention by clay+silt fraction. In this respect integrated use of chemical fertilizers along with FYM (100%NPK+FYM) being already enriched with C would have lesser potential for C retention by clay+silt fraction. It has been observed that the sub-surface soils being more deficient in C content (more negative the difference) had greater potential for C retention than surface soils.

The C content in clay+silt fraction in Alfisol of Pattambi at 0–15 cm soil depth varied from 24.7 g kg^{-1} in 50%NPK to 32.6 gkg^{-1} in 100%NPK+FYM (Table 3). The maximum amount of C that can be associated with silt and clay particles as estimated by the formula was 18.3 g kg^{-1}. The difference between the actual

Table 3. *Effect of different treatments on silt plus clay protected C in 0-15 cm and 15-30 cm soil under rice-rice cropping system of Pattambi, Kerala*

Treatments	Actual C (g kg^{-1})		Protective C (g kg^{-1})		N (g kg^{-1})		C/N		Difference (Actual-Protective) (g kg^{-1})		Silt + clay	Clay (%)	Mineral
	0-15 cm	15-30 cm	0-15 cm	15-30 cm	0-15 cm	15-30 cm	0-15 cm	15-30 cm	0-15 cm	15-30 cm			
Pattambi													
50%NPK	24.66b	13.5b	18.3	20.5	4.37ab	2.96b	5.64b	4.59ab	6.33a	-7.02b	38.48	27.48	Kaolinite
100%NPK	25.81b	18.4a	18.3	20.5	4.68a	3.88a	5.51b	4.78ab	7.48a	-2.06a			
150%NPK	26.10b	14.7b	18.3	20.5	4.68a	3.11b	5.60b	4.76b	7.77a	-5.80b			
100%NPK+lime	31.27a	19.8a	18.3	20.5	2.99b	3.85a	10.44a	5.12ab	12.9a	-0.69a			
100%NPK+FYM	32.64a	22.0a	18.3	20.5	3.13ab	4.05a	10.41a	5.48a	14.3a	1.54a			
CONTROL	25.93b	12.5b	18.3	20.5	4.61a	2.85b	5.65b	4.38b	7.60a	-7.96b			

and the protective C (max C) ranged from as low as -6.34 g kg^{-1} in control to as high as 14.3 g kg^{-1} in 100%NPK+FYM. This indicates that the further addition of organic carbon to the soil will not be associated with silt and clay and is hence saturated. In sub surface soil depth the C content was observed highest in 100%NPK+FYM. The C content in 100%NPK, 100%NPK+lime was significantly higher than 50%NPK, 150%NPK or control treatments. The protective C at 15–30 cm soil depth was estimated to be 20.5 g kg^{-1}. The difference in actual and the estimated protective C in 15–30 cm soil depth was observed lowest in the control and it was highest in the 100%NPK+FYM. The C content in clay+silt fraction at 0–15 cm soil depth was almost double than that at 15–30 cm soil depth. In the surface layer, no significant difference was observed in the C content among all the treatments. Amendments of lime with 100%NPK brought similar benefit as to amendment with FYM with 100%NPK in increasing the C content in clay+silt fraction in 0–15 cm. The protective C content in sub surface soil was estimated to be higher than that in surface soil. The difference in actual C and protective C content in all the treatments in the 0–15 cm depth was positive, whereas in the 15–30 cm depth, barring the 100% NPK+FYM treatment, the difference was negative in all the treatments. The C content being more compared to the protective C and the positive difference in the surface layer indicates that the clay and silt fraction in the surface layer is approaching saturation. The negative difference in the sub surface indicates greater potential for more retention of C by clay+silt fraction. The treatments where only chemical fertilizers were applied had greater potential to sequester C in the subsurface soil. In this respect integrated use of chemical fertilizers along with FYM or lime (100%NPK+FYM and 100%NPK+lime) being already enriched with C would have lesser potential for C retention. Hence, the subsurface layer, having greater negative difference have more potential to sequester C. The mathematical expression depicting maximum C carrying capacity in <20 μm size fraction as developed by Hassink (1997) underestimated this in Alfisol of Pattambi. Thus the model predicted protective C was less than the actual C content in clay+silt fraction. This indicates that the model of Hassink (1997) needs to be recalibrated for Alfisol of Pattambi. Soils which are predominant with clays of high surface area adsorb more humic substances than those with lower surface area (Tate and Theng, 1980). The amount of C associated with the clay and silt fraction was less than 10 g kg^{-1} soil in coarse textured soils and up to 37 g kg^{-1} soil in fine-textured soils (Hassink, 1997). Whole-soil organic C concentration was positively related to silt plus clay content at sites with 16–60% clay and 25–50% clay (Plante *et al.*, 2006). With the increase in clay content, the micro-aggregate associated organic C increased from 34 to 18% approximately in Saskatchewan soils. A strong correlation between clay content and organic C content was observed in Southern Great Plains (Nichols,1984). Shang *et al.* (1998) studied the mineral association of SOM with Oxisols and Alfisols and reported that OM associated with coarse fraction of Alfisol accounted for 21 to 30% of soil C and one half of the OC of both the soils were associated with silt sized fraction. This constituted a major portion of micro–aggregates. The association with poorly crystalline oxides and aggregation with the crystalline oxides and clays stabilized the C in silt fractions. About 23% of total soil C was associated with light fraction C from silt sized micro-aggregates (Shang *et al.*, 1998). Six *et al.* (2002) found higher aggregate stability and lower correlation with C content in 1:1 clay dominated soils. They observed higher turnover rates of C associated with micro-aggregates compared to macro-aggregates indicating higher protection of C by micro-aggregates. The average mean residence time of micro-aggregate is 209 ± 95 years. Balesdent *et al.* (2000) also concluded that micro–aggregates protect C more than macro-aggregates. Song *et al.* (2015) reported that application of balanced inorganic fertilizers with FYM significantly increased the SOC content in the micro–aggregate and silt + clay fraction.

Nitrogen (N) and C:N of silt+clay fraction

The nitrogen (N) content in silt+clay fractions ranged from 2.57 g kg^{-1} in control to 4.31g kg^{-1} in 100%NPK+FYM treatment at 0–15 cm depth in Alfisol of Bhubaneswar. The application of graded doses NPK significantly increased N content in silt+clay fraction, while the N content increased dramatically when FYM was superimposed over 100%NPK. In lower soil depth the N content in silt+clay fraction was recorded highest in 50%NPK treatment. The C:N ratio ranged from 3.88 in control to 5.39 in 100%NPK+FYM at 0–15 cm soil depth, while at 15–30 cm soil depth the C:N was observed lowest in 50%NPK and highest in 100% NPK+FYM. It is worth mentioning that 100%NPK+FYM was at par with 100%NPK, 150%NPK and 100% NPK+Lime at 0–15 cm in Alfisol of Bhubaneswar. In 15–30 cm, C:N in silt+clay fraction was significantly higher in 100%NPK+FYM than in other treatments. The 100%NPK, 150%NPK and 100%NPK+lime were at par with each other with respect to C:N in silt+clay fraction. The N content in silt+clay fraction in Alfisol of Pattambi at 0–15 cm depth did not differ significantly across various treatments excepting 100%NPK+Lime which was significantly lower than the other treatments. In 15–30 cm depth the N content in silt+clay fractions in 100%NPK, 100%NPK+Lime and 100%NPK+FYM were significantly higher over other treatments. The C:N ratio in silt+clay fraction at 0–15 cm depth was conspicuously higher in 100%NPK+FYM and 100%NPK+Lime as compared to other treatments. In 15–30 cm, the C:N in silt+clay fraction was significantly higher in 100%NPK+FYM over either 150%NPK or control treatment. Carbon and nitrogen are integral part of SOM and therefore the treatments which were observed enriched with C also were enriched with N. Alfisol of Pattambi being sandy clay loam in texture retained more of C and thereof N than the Alfisol of Bhubaneswar. In general 100%NPK+FYM significantly increased N content in silt+clay fraction. The C:N ratio of soil indicates the stability of SOM, the wider the ratio the higher would be the stability. In general the 100%NPK+FYM showed wider C:N ratio in silt+clay fraction indicating greater stability and this effect was more evident in Alfisol of Pattambi than Alfisol of Bhubaneswar. It is worth mentioning that other treatments comprised of optimal, super-optimal doses could also enhance the stabilization of both C and N in the clay+silt fraction. Christensen (1988) reported that the C:N ratio of silt+organic matter was higher in manured plots, i.e. 14.3:1, and 10.6:1 in clay fraction. The addition of manures increased OM content of silt and clay fraction by 36% compared to only mineral fertilized plots where OM content of silt increased by 21% and clay by 14%. Banger *et al.* (2008) observed that the C:N ratio of clay fraction increased to 8.2:1 and silt fraction to 12.3:1 in FYM treated plots sandy loam soils of Mandya, Karnataka. Hassink (1997) reported that the C and N associated with the clay and silt fraction was lower in the kaolinitic soils of Australia. Close correlation was observed between the C and N content associated with clay and silt fractions. The surface properties of the clay minerals strongly influenced the mineral associated or chemically protected organic carbon.

Conclusions

The C and N carrying capacity in the silt+clay fraction of Alfisol was greatly influenced by soil texture. Alfisol of Pattambi having sandy clay loam in texture stabilized more amount of C and N than Alfisol of Bhubaneswar having sandy loam in texture. The mathematical expression depicting maximum amount of C that can be associated with <20 µm particle size fraction as developed by Hassink (1997) well predicted the C in Alfisol of Bhubaneswar but it needs recalibration for Alfisol of Pattambi. The management strategy involving balanced fertilization with optimal/superoptimal dose of NPK (100% or 150% NPK) or integrated use of optimal dose of NPK (100%NPK) with FYM enhanced the stabilization of C and N in silt+clay fraction. Overall the C retention potential in subsurface soil was greater than surface soil which might be having greater implications on C sequestration.

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Application of Bentonite and Zeolite to Eliminate the Hazards of Cadmium, Copper and Nickel Metals in Contaminated Soils

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Abstract–*Soil pollution by heavy metals has serious hazards on microorganism, plants, human being and ecological environment. A laboratory experiment has been conducted by adding different doses of bentonite and zeolite to soils contaminated with cadmium, nickel and copper with 200 ppm of each and to the study the kinetics of release of these elements in DTPA extract. The parameters of Hoerl's and Elovich kinetic models were determined to compare the effect of adding zeolite and bentonite on sandy and clay soils. The obtained results indicated that the reaction occurred very fast after adding the remediation material and adsorption attained a constant value. The lower rate of the material was very effective in increasing the adsorption of the heavy metals on the material. The release of elements as a result of adding both zeolite and bentonite followed the order $Cd^{2+} > Cu^{2+} > Ni^{2+}$. The role of zeolite was more pronounced in enhancing the adsorption of the heavy metals more than bentonite due its specific molecular structure and high surface area. Therefore it was recommended to be applied as a remediation material in polluted soils by heavy metals.*

Key words : Zeolite, Bentonite, Heavy metals, Contaminated soils.

Introduction

The industrial wastewaters are considered to be the main source of heavy metal impurities. Mohan *et al.,* (2006) pointed out that mining wastes and acid mine drainage contributed significant quantities of dissolved copper to effluent streams

Removing heavy metals demands high energy or advanced operational requirements. A number of conventional technologies such as coagulation, precipitation, ion-exchange, electrochemical methods, membrane processes, extraction, biosorption, and adsorption have been considered for the treatment of contaminated wastewater (Wang and Peng 2010; Kwon *et al.,* 2010). In the last few years many researchers have studied new techniques to remove contaminants from soils (Saber *et al.,* 2012).

In recent years, attention has focused on the development of in situ immobilization of metals using inexpensive amendments such as minerals (apatite, zeolite, or clay minerals) or waste by-products of steel shot, beringite, iron-rich biosolids, which are promising alternative to conduct remediation methods (Wei-Yu *et al.,* 2009). Ion exchange takes a special place, primarily as inexpensive natural materials, such as zeolite, can be used. Zeolites are widely spread in nature and the costs of their exploiting are low. Exchangeable cations in the zeolite structure, K, Ca, Na, and Mg, are not toxic, which makes the natural zeolite especially suitable for tertiary processes of wastewater treatment (Peri *et al* 2004). Furthermore, Sheta *et al.* (2003) suggested that natural zeolite and bentonite minerals have a high potential for Zn and Fe retention. The availability of the retained Zn was higher than for Fe, and chabazite seems to have the highest ability for Zn sorption and extractability by DTPA. In this point Esmaeilpour *et al.,* (2015) studied the effects of adsorbent minerals (bentonite, zeolite and sepiolite) on transfer of some heavy metals (i.e., Pb, Zn and Cd) from soil to tissues of sunflower.

On the other hand Hasanabadi *et al* (2015) indicated that zeolite was able to decrease the amount of uptake and transmission of lead and cadmium in plant .Marzieh (2014) stressed on the bentonite which play an important role in the adsorbtion of heavy metals.

Marinos *et al* (2007) demonstrated that the removal of Cu(II) using vermiculite reached 67.6%, at ambient temperature and at the agitation speed of 400 rpm, while it was approximately 42.5% at 60°C with no agitation. Mojiri *et al.* (2015) concluded that, for heavy metals removal from landfill leachate and domestic wastewater, employing the powdered zeolite method was more effective than the application of the traditional activated carbon.

The objective of this research work is to reduce or eliminate the hazard of heavy metals through the application of available natural clay mineral and zeolite on contaminated soils.

Materials and Methods

The soil samples from 0–30 cm depth of two cultivated soil types were selected in this study. The first sample collected from village 62, Al Hamool, Kafr El-Shekh governorate was clayey soil and second one was sandy soil from Abou-Rawash, 6 October governorate, Egypt. Table 1 shows some physical and chemical properties of the selected soil samples determined by using standard methods (Black *et al.,* 1982).

Two types of clay minerals remediation materials were used in order to remove the Heavy metals (Cd^{2+}, Cu^{2+} and Ni^{2+}) from the soils studied. Natural zeolite (clinoptilolite) and bentonite were supplied by Company A&O of Trading and Al-Ahram Company respectively. Clinoptilolite and bentonite were ground and then sieved to different fractions of which the fraction of 2.5–5.0 mm were used for this study. The analytical data of the zeolite and bentonite are recorded in table 2 and 3.

Table 1. *Physical and chemical properties of the selected soil samples*

Soil property	Sandy soil	Clay soil
Coarse sand%	80.5	0.6
Fine sand%	13.2	1.0
Silt%	3.8	13.2
Clay%	2.5	85.2
Texture	Sand	Clay
pH 1:5	7.40	7.65
Ec dSm^{-1}	1.65	2.03
Organic matter%	0.78	1.68
$CaCO_3$%	0.33	0.65

The applied materials were added to soils at four doses viz.,. 0, 15, 20 and 25 g/kg.

Three hundred grams of <2 mm air dry soil was taken and 200 ppm of each of metals copper, cadmium and nickel was added to the soil and the samples were then treated with the remediation materials. The treated soils were incubated at 60% of their water holding capacity for 14 days under laboratory conditions. After incubation periods soil samples were extracted to study kinetics of release of potential toxic elements. Release experiments were carried out using Electrical Stirred Flow Unit (ESFU) method for all soil samples and for different incubation times i.e. 2, 8 and 14 days. A Diagram of ESFU used in this paper, the modification of the new set up and mechanism of kinetic working were previously mentioned in more details (Zaghloul, 2002). Exactly 20g from each soil samples was put in the kinetic part of the device with 100 ml of 0.1 N DTPA solutions. The system was vigorously shaken and the solution samples were received after different periods ranging between 1 min to 14 days at 25^0 C ± 2^0 C and analyzed for concentrations of Cd^{2+}, Cu^{2+} and Ni^{2+} using atomic absorption as described by Cottenie, et al (1982). Heavy metals released Data of release

Table 2. Chemical analyses of zeolite mineral used in the study

Zeolite used	CEC (cmol g^{-1})	Surface area (m^2 g^{-1})	pH 1:2.5	Cations %		Major elements (oxides)%			
				$K_2O\%$	$Na_2O\%$	SiO_2	Al_2O_3	Fe_2O_3	CaO
	220	89.82	6.8	3.27	0.78	62.220	11.096	4.033	3.583

Table 3. Particle–size distribution and some chemical properties of bentonite

Bentonite used	Particle size distribution %				Text	pH 1:2.5	EC dS/m	$CaCO_{3\%}$	CEC (kg)
	C.sand% 2000:200u	F.sand% 200:20u	Silt% 20-2u	Clay% > 2u					
	1.1	3.8	5.3	89.8	Clay	8.3	4.10	2.73	53.24

of heavy metals were fitted to the following kinetic models

1- **Hoerl equation** in the form:

$$q=a^{\backslash}t\text{^}b^{\backslash}*e\text{^}(b^{\backslash}*t)$$

2-The **Elovich equation** in the form:

$$q_t = 1/b \ln ab + 1/b \ln t$$

Where:

q = the concentration of metals release in time t

b &b = constant represents desorption rate coefficient (ppm)$^{-1}$.

a &a$^{\backslash}$ = capacity constant in mg metals kg^{-1}soil.

t = time (min).

The kinetic parameters of the tested equations were calculated for different treatments applied. Different statistical parameters such as regression analysis applied to test the conformity of used models to describe HM released from different treated soils, evaluation of significant differences in rate coefficients and cumulative quantity of metals desorbed after remediation were done using SAS software (SAS institute, 1985).

Results and Discussion

The laboratory experiment which was conducted to evaluate the impact of some natural minerals on the adsorption of heavy metals to overcome their hazard on contaminated soils has resulted in valuable data useful in formations.

Regarding the effect of zeolite addition on the adsorption of Cd^{2+} (200ppm) added to soils, the adsorption on sandy soil is obviously lower than clay soil. Fig. 1. illustrate the concentration of element released from soil as affected by three rates of zeolite or bentonite (0.15, 20 and 25g/kg).

As a time factor on the reaction, it starts fast in the first few minutes and continues in a steady state until 14 days. Applying three rates of zeolite or bentonite has insignificant impact on the adsorption of the heavy metal in both sandy and clay soils.

The adsorption process of Cu^{2+} show that the influence of bentonite is slightly higher than zeolite on sandy sample, while in clay sample no differences can be detected (Fig.2).

With respect to the Ni^{2+} element, the release in sandy soil as affected by zeolite and bentonite is more in control than the three rates of mineral, Fig.3. The adsorption of Ni on clay is very high in all treatments; the concentration of released element is ranging between 40 and 80 ppm in both zeolite and bentonite.

The kinetic equations of Elovich and Hoerl models were applied to describe the reaction of adsorption and release of heavy metals through

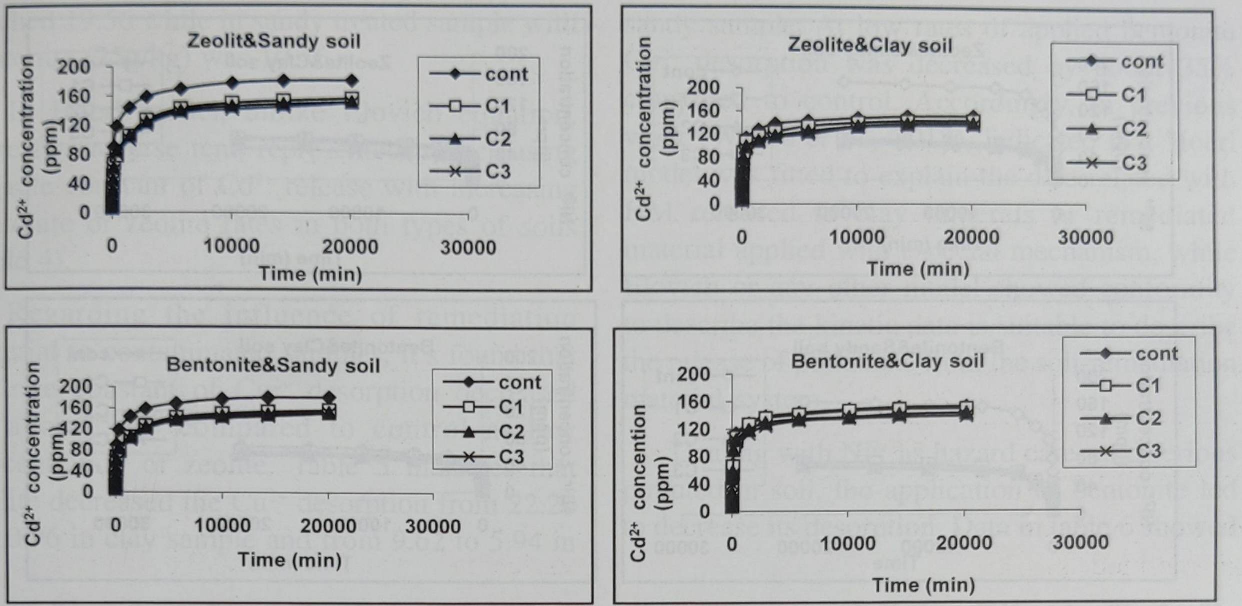

Fig. 1. *Kinetics of Cd^{2+} release from used soils as affected by different rates of Zeolite and Bentonite application.*

the treatment with zeolite and bentonite.

The data in table 4 indicate that R^2 (the coefficient of determination) of Elovich equation ranged between 0.99-0.97, while the respective values of Hoerl equation were 0.97-0.92 in sandy soil indicating the Cd^{2+} release.

The rate of Cd^{2+} desorbed as expressed by the slope values of constant (b) in kinetic equations, were significantly influenced by soil type and slightly by the rate of zeolite or bentonite. In clay sample, the addition of 25g/kg of bentonite led to decrease the rate constant from 23.05 in control to 18.48 in treated sample. The same values in sandy polluted sample decreased from 18.72 in control to 15.50.

The capacity factor (a) in Elovich model

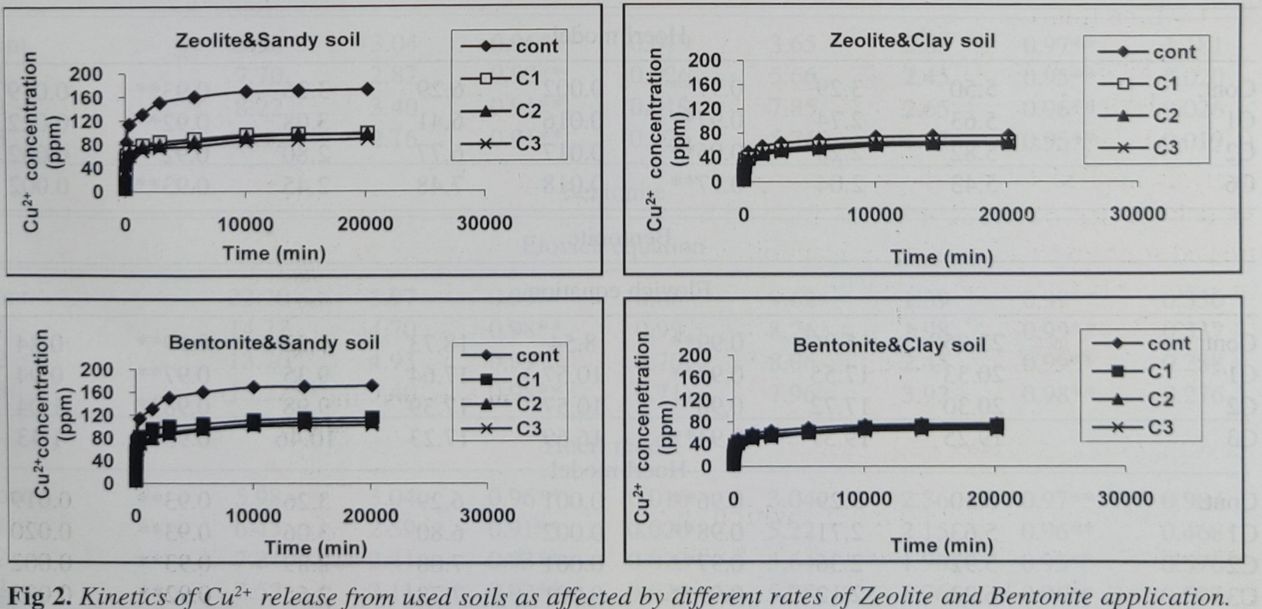

Fig 2. *Kinetics of Cu^{2+} release from used soils as affected by different rates of Zeolite and Bentonite application.*

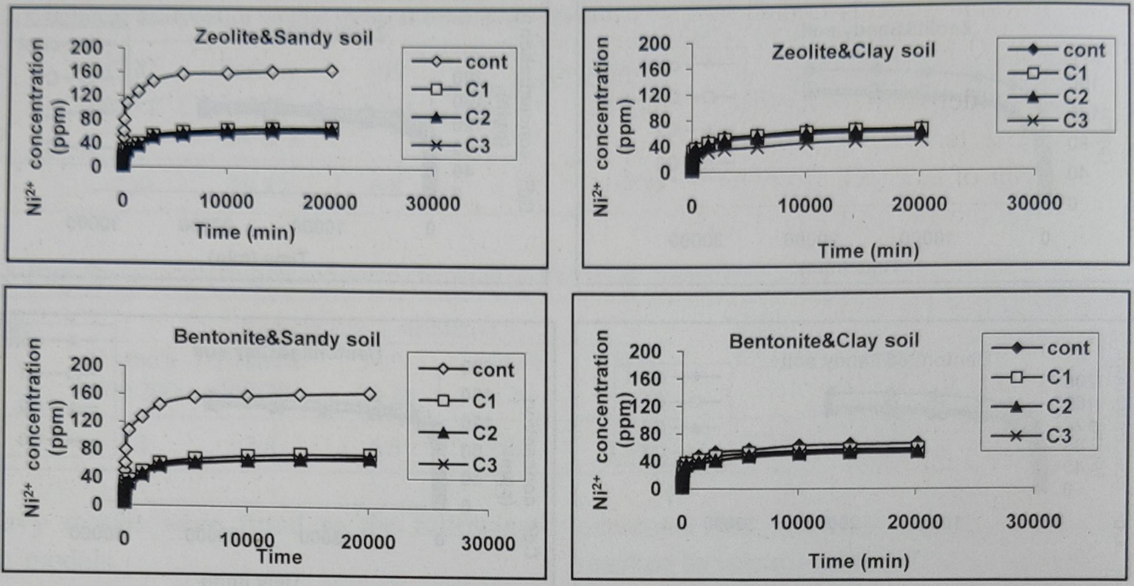

Fig. 3. *Kinetics of Ni^{2+} release from used soils as affected by different rates of Zeolite and Bentonite application.*

Table 4. *Rate constants of Cd^{2+} release from soils treated with zeolite and bentonite*

Treatment	Clay soil				Sandy soil			
	b	a	R^2	SE	b\	a\	R^2	SE
				Zeolite				
				Elovich equation				
Cont.	23.05	15.96	0.99**	8.55	18.73	9.23	0.99**	0.84
C1	20.08	16.03	0.97**	10.37	16.39	9.18	0.98**	0.82
C2	19.32	17.44	0.97**	10.25	15.67	9.79	0.98**	0.70
C3	18.48	17.88	0.97**	10.44	15.50	9.83	0.99**	0.68
				Hoerl model				
Cont.	5.50	3.29	0.97**	0.002	6.29	3.26	0.93**	0.019
C1	5.63	2.74	0.97**	0.016	6.41	3.08	0.92**	0.022
C2	5.82	2.28	0.96**	0.017	6.77	2.80	0.92**	0.002
C6	5.43	2.04	0.97**	0.018	7.48	2.45	0.93**	0.002
				Bentonite				
				Elovich equation				
Cont.	23.05	15.96	0.99**	8.54	18.73	9.23	0.99**	0.84
C1	20.33	17.55	0.97**	10.57	17.64	9.35	0.97**	0.94
C2	20.30	17.72	0.98**	10.57	17.39	9.98	0.98**	1.04
C3	19.25	19.37	0.94**	16.69	17.23	10.46	0.93**	1.43
				Hoerl model				
Cont.	5.50	3.29	0.96**	0.001	6.29	3.26	0.93**	0.019
C1	5.63	2.71	0.98**	0.002	6.80	3.06	0.93**	0.020
C2	5.92	2.36	0.97**	0.001	7.08	2.89	0.93**	0.002
C3	6.23	2.12	0.97**	0.001	7.78	2.65	0.92**	0.002

reached 19.56 while in sandy treated sample with bentonite (25g/kg) was 10.46.

In Hoerl model, unlike Elovich equation, there is a reverse tend represented in increasing the rate constant of Cd^{2+} release with increasing bentonite or zeolite rates in both types of soils (table 4).

Regarding the influence of remediation material to contaminated samples, it's found that the rate constant of Cu^{2+} desorption decreased by about 50% compared to control at low concentration of zeolite. Table 5 indicates that zeolite decreased the Cu^{2+} desorption from 22.20 to 10.96 in clay sample and from 9.62 to 5.94 in sandy sample. At low rates of applied bentonite Cu^{2+} desorption was decreased by about 35% compared to control. Accordingly, in previous work (Wahba *et al.*, 2012), indicated that Hoerl model was fitted to explain the data related with HM released to clay minerals or remediated material applied with especial mechanism, while Elovich or any other model showed conformity to describe the kinetic data is suitable to describe the release of pollutants from the soil-remediation material system.

Dealing with Ni^{2+} as hazard cares and serious polluted in soil, the application of bentonite led to decrease its desorption. Data in table 6 showed

Table 5. *Rate constants of Cu^{2+} release from soils treated with Zeolite and Bentonite*

	Clay soil				Sandy soil			
Treatment	b	a	R^2	SE	b\	a\	R^2	SE
				Zeolite				
				Elovich equation				
Cont.	22.20	3.97	0.99**	0.68	9.62	1.39	0.99**	0.336
C1	11.99	4.44	0.97**	0.67	6.97	1.69	0.99**	0.276
C2	11.77	4.74	0.97**	0.65	6.68	1.92	0.98**	0.288
C3	10.96	4.81	0.96**	0.71	5.94	2.04	0.99**	0.276
				Hoerl model				
Cont.	5.98	3.04	0.96**	0.019	3.65	2.83	0.97**	1.181
C1	7.70	2.87	0.92**	0.026	5.66	2.45	0.95**	0.020
C2	8.22	3.40	0.91**	0.019	7.85	2.65	0.96**	0.026
C3	10.52	2.16	0.91**	0.026	5.71	1.55	0.95**	0.019
				Bentonite				
				Elovich equation				
Cont.	22.20	3.97	0.99**	0.68	9.62	1.39	0.99**	0.336
C1	14.77	4.70	0.98**	0.99	8.26	1.98	0.99**	0.337
C2	13.70	4.93	0.99**	0.70	8.06	2.45	0.99**	0.288
C3	13.22	5.40	0.98**	0.71	7.96	3.92	0.98**	0.276
				Hoerl model				
Cont.	5.98	3.04	0.96**	0.016	3.04	2.36	0.97**	0.984
C1	6.43	2.59	0.91**	0.026	5.22	2.15	0.96**	0.468
C2	7.21	2.41	0.93**	0.023	5.64	1.98	0.95**	0.576
C3	7.52	2.11	0.92**	0.025	5.98	1.76	0.96**	0.577

that in Elovich equation, addition of 25g/kg decreased Ni^{2+} desorption from 21.42 to 8.51 in clay sample and from 6.97 to 4.40 in sandy soil. The addition of zeolite at a rate of 25g/kg decreased constant of Elovich equation by about 60%. In this point some researchers found that The selectivity of zeolite species, such as clinoptilolite and chabazite, for heavy metals based on the ionic radius and dissociation constant was as in the followingorder: Pb^{2+}> Ni^{2+}> Cu^{2+}> Cd^{2+}> Zn^{2+}> Cr^{3+}> Co^{2+} (Choi *et al.*, 2001; Ok *et al.*, 2007). Ion exchange of a specific cation is strongly influenced by the presence of competitive cations and complexion reagents such as anions (Inglezakis *et al.* 2003a,b; Inglezakis *et al.*, 2005).

Fig. 4 represented the comparison between Elovich rate constants of Cd^{2+}, Cu^{2+} and Ni^{2+} desorbed from sand and clay soils as affected by zeolite and bentonite application at three rates. According to the standard deviation (SD), it can be concluded that both clay minerals are significantly minimized the rate of heavy metals release in the order Cd^{2+} > Cu^{2+} > Ni^{2+}. It is obvious from the obtained results that the rate of zeolite in reducing the heavy metals release was more pronounced than bentonite.

Table 6. *Rate constants of Ni^{2+} release from soils treated with Zeolite and Bentonite*

	Clay soil				Sandy soil			
Treatment	b	a	R^2	SE	b\	a\	R^2	SE
Zeolite								
Elovich equation								
Cont.	21.42	6.52	0.98**	0.94	6.97	0.81	0.99**	0.276
C1	9.90	8.42	0.97**	0.07	6.84	2.50	0.91**	0.072
C2	8.22	7.93	0.96**	0.50	5.04	3.07	0.93**	0.073
C3	7.92	8.01	0.96**	0.53	4.74	4.38	0.94**	0.036
Hoerl model								
Cont.	6.23	2.14	0.95**	0.019	4.63	2.09	0.96**	0.014
C1	7.63	1.84	0.98**	0.011	5.22	1.68	0.96**	0.016
C2	8.81	1.51	0.98**	0.001	5.75	1.38	0.96**	0.017
C3	9.42	1.22	0.97**	0.002	5.81	1.04	0.95**	0.022
Bentonite								
Elovich equation								
Cont.	21.85	6.52	0.98**	0.94	6.97	0.82	0.99**	0.276
C1	9.13	7.14	0.98**	0.49	6.30	2.29	0.98**	0.264
C2	8.68	8.30	0.98**	0.47	5.92	3.24	0.98**	0.288
C3	8.51	8.33	0.97**	0.50	5.40	4.62	0.97**	0.331
Hoerl model								
Cont.	6.23	2.14	0.95**	0.019	4.63	2.09	0.96**	0.014
C1	2.94	1.94	0.97**	0.011	5.39	1.82	0.96**	0.016
C2	3.41	1.74	0.97**	0.007	6.10	1.46	0.95**	0.019
C3	3.58	1.84	0.97**	0.001	6.44	1.18	0.95**	0.020

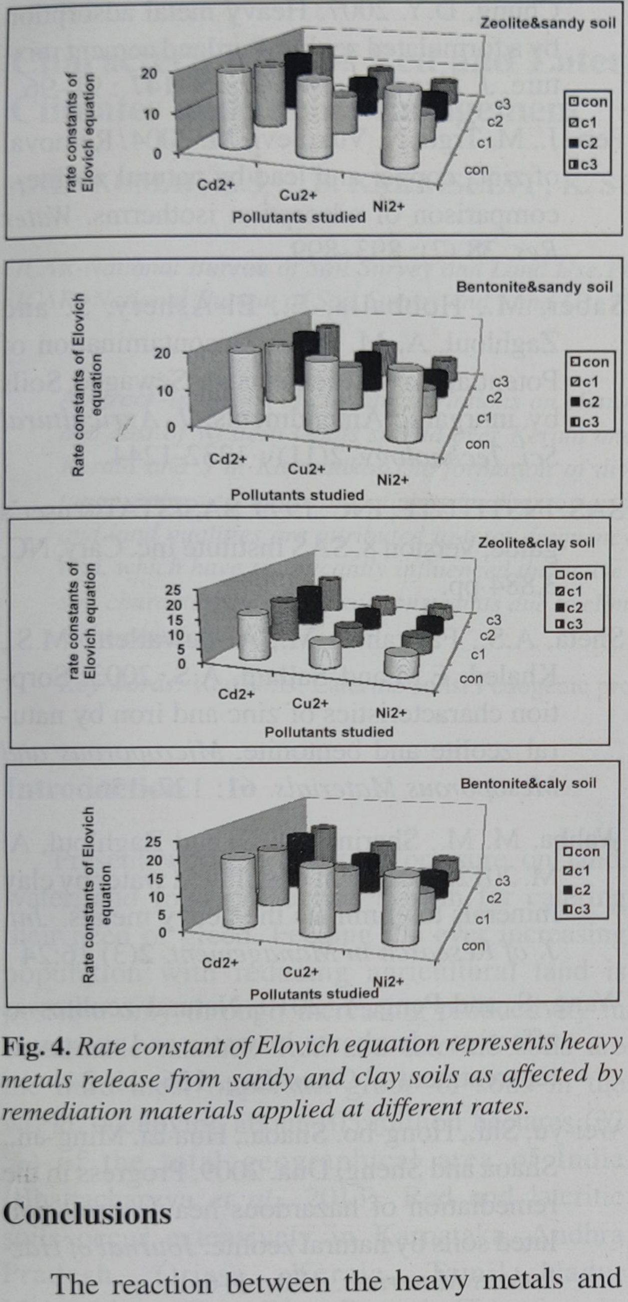

Fig. 4. *Rate constant of Elovich equation represents heavy metals release from sandy and clay soils as affected by remediation materials applied at different rates.*

Conclusions

The reaction between the heavy metals and the clay mineral was very fast. From economic point of view, the low rate of mineral (10 or 15 g/Kg) is quite effective in decreasing the release of heavy metals in both sandy and clay soils.The kinetic models of Elovich and Hoerl were very suitable in expressing the adsorption and release of heavy metals as a result of remediation treatments. Addition of zeolite or bentonite significantly minimized the rate of heavy metals release which was in the order Cd^{2+} > Cu^{2+} > Ni^{2+}. Zeolite, as a remediation material, was more effective on the adsorption of heavy metals than bentonite. This was due to the specific structure of zeolite, high cation exchange capacity and large surface area. However, bentonite has certain properties as its ability to form thixotrophic gels with water and relatively high cation exchange capacity which allowed the adsorption of heavy metals and reduced their release in soils.

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Characterization of Red and Lateritic Soils Formed Under Varied Climates and their Management

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Abstract–*Influence of climatic variations on characteristics of red and lateritic soils formed towards west and east of Western Ghats spread over Kerala and Karnataka was studied by selecting nine pedons, 6 in Kerala and 3 in Karnataka. The formation of diverse group of soils could be attributed to the effect of topography, vegetation and climate leading to various pedogenic processes. Variation in soil characteristics and land qualities are attributed to total, frequency and distribution of rainfall, potential evapo-transpiration, which have significantly influenced the active pedogenic processes and results in profound changes in soil characteristics. The soil constraints due to climatic influence can be reduced through effective management practices.*

Key words: Red soils, Lateritic soils, Pedogenic process, Climate, Soil characteristics and Land use

Introduction

Present world is exerting pressure on land, water, and food production system for catering their need or greed. Feeding the ever increasing population with reducing agricultural land is possible only through increasing productivity in sustainable manner. Red and lateritic soils are the third most important group of soils in the world, occupying about 105 million hectares (32 %) of the total geographical area of India (Bhattacharyya *et al.,* 2013). Red and lateritic soils occur extensively in Karnataka, Andhra Pradesh, Orissa, Kerala, Tamil Nadu, Maharashtra, Goa, West Bengal, Chhattisgarh, Jharkhand, Sikkim, North Eastern states and parts of Andaman and Nicobar and Pondicherry. Laterite soils are typically formed under tropical climate experiencing alternate wet and dry seasons (Srivastava *et al.,* 2000). Red and lateritic soils are generally acidic and have low cation exchange capacity (CEC), low to moderate base saturation (Buol and Cook, 1998). These soils are dominated by kaolinite clay and rich in sesquioxides. Surface crusting, poor inherent fertility, P fixation, aluminium toxicity, low K reserves and soil erosion among others are the major constraints in these soils (Sehgal *et al.,* 1998). Carbonate removal is the pre-requisite for illuviation of clay (Pal *et al.,* 2003). In India, these soils are classified under 5 major soil orders Alfisols, Ultisols, Inceptisols, Mollisols and Entisols and 6 major suborders Ustolls, Ustalfs, Humults, Ustults, Ustepts and Orthents. The distribution of rainfall and length of dry season also plays an important role in soil formation process and influences the soil properties. Soil is one of the most important natural resources and proper understanding of its properties is necessary for judicious, beneficial and optimal use on suitable basis (Jagdish Prasad *et al.,* 2009). The present study has been undertaken to document the changes in soil characteristics of red and lateritic soils under the influence of the present

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semi-arid to per-humid climate and varied topography.

Materials and Methods

Nine pedons were selected and studied having varying climatic settings like total rainfall (mm), frequency and distribution of rainfall, length of dry season, relative humidity (RH), potential evapo transpiration and moisture index. They were selected as a representative of the dominant existing soil of that location in south India (Fig 1). The details of the pedon location and its climate are given in Table 1. Among the studied pedons, Peruva pedon receives the highest rainfall followed by Kanjirappilly and Bangalore receives the lowest rainfall. Due to high average annual rainfall, less dry period, low temperature, high RH, higher elevation and less potential evapotranspiration, Koppa station has highest

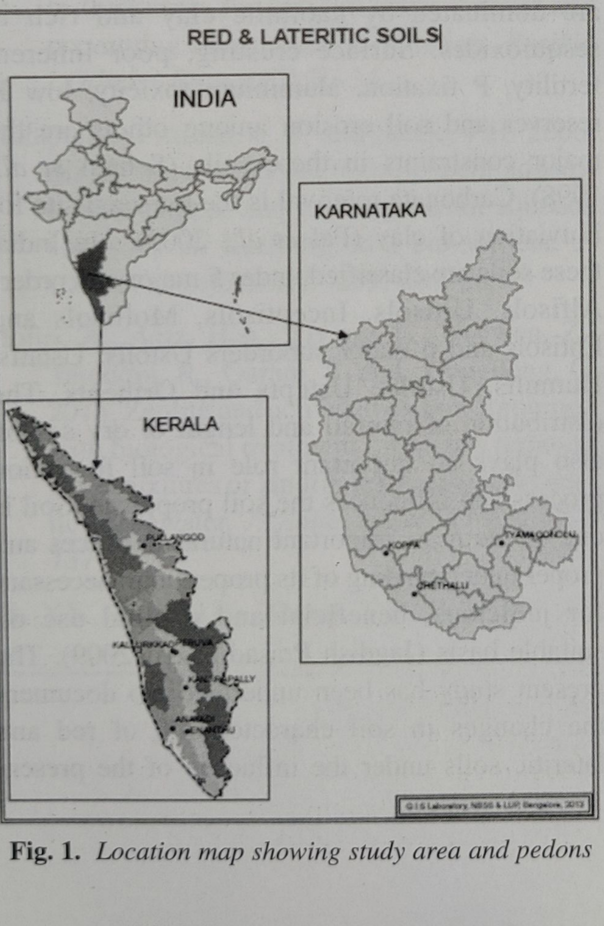

Fig. 1. *Location map showing study area and pedons*

Table 1. *Climatic parameters of studied red and lateritic pedons*

Station	District	Total Rainfall (mm)	Length of dryseason (months)	Temp. (°C)	Relative humidity (%)	Elevation (m) MSL	PET (mm)	Moisture Index (%)	Climatic classes
Koppa	Chikmagalur, Karnataka	3003.1	4.0	22.2	84.6	980	1264	138	Per-humid
Kanjirappilly	Kottayam, Kerala	3627.0	3.0	27.5	72.0	300	1705	81	Hot humid
Kallurkkad	Ernakulam, Kerala	3517.6	3.0	27.7	80.0	200	1703	68	Hot humid
Peruva	Kottayam, Kerala	3985.3	4.5	26.5	79.0	150	1590	60	Hot humid
Enattu	Pathanamthitta, Kerala	2662.8	3.0	27.7	78.0	300	1713	42	Hot humid
Anayadi	Kollam, Kerala	2900.0	4.5	27.0	80.0	50	1717	40	Hot humid
Pullangod	Malappuram, Kerala	2688.0	5.0	26.2	73.0	500	1705	30	Hot humid
Chethalli	Coorg, Karnataka	1607.0	4.0	22.9	69.0	900	1415	14	Moist sub-humid
Tyamagondalu	Bangalore, Karnataka	781.0	5.5	24.0	40.0	920	1553	-34	Semi-arid

moisture index. The climatic variability of the land area has been studied using data received from IMD and other sources. The morphology of the soils was described using standard terminology. Standard analytical procedures were used to characterize the soils in terms of physical and chemical properties. Soil classification was done according to Soil Taxonomy (Soil Survey Staff, 2010). Soil physical and chemical properties have been determined by following standard procedures. Exchangeable acidity ($Al^{3+} + H^{+}$) was determined by using $BaCl_2$-TEA method (Peech *et al.,* 1962). The extractable acidity and total potential acidity were estimated by the method of Baruah and Borthakur (1999). The pH-dependent acidity was determined by subtracting exchangeable acidity from total potential acidity.

Result and Discussion

The studied nine pedons of red and lateritic soils were having different soil physical and chemical characteristics. The significant properties of the soils are presented in Table 2, 3 and 4.

Koppa soils

Soils developed in Koppa area of Chikmagalur district, Karnataka are reddish brown to dark reddish brown (5YR 3/3 /2.5YR 3/4), very deep, gravelly clay, slightly acidic and well drained. The sub soil horizons have well developed argillans. It was having high organic carbon content in the surface and gradually decreased in sub-surface layers. The water pH is little higher than KCl pH. It was moderately to slightly acidic. The total potential acidity of the soils has ranged between 7.0 and 10.7 cmol (p+) kg^{-1} and high KCl-Al with low CEC and base saturation by sum of cations because of intense leaching under higher rainfall. The dominant clay type is kaolinitic. This soil is classified in to Clayey-skeletal, kaolinitic, isohyperthermic, Rhodic Kanhaplustults. The climatic data indicated that the land receives highest rainfall, experiencing a dry season of nearly 4 months in a year and as a cumulative having the highest moisture index (138 %) and comes under the per-humid climatic condition.

Chethalli soils

Soils of Chethalli area in Coorg district, Karnataka are dark reddish brown to dark red (5YR 3/4 /2.5YR 3/6), very deep, non-gravelly sandy clay, slightly acidic and well drained. The soils have very high organic carbon content in the surface with decreasing trend with depth. The illuvial clay content in the sub-surface layers is very high which might be due to illuviation process. The water pH is little higher than KCl pH. It was moderately acidic to slightly acidic. The soil has total potential acidity ranged between 8.0 and 11.5 cmol (p+)kg^{-1}, low cation exchange capacity and the least base saturation by sum of cations. The CEC clay ratio is more than 0.2, which indicate comparatively less dominance of 1:1 layer silicate clays. This soil is classified in to Fine loamy, mixed, isohyperthermic, Pachic Argiustoll. The climatic data indicated that the soil receives high rainfall, experiencing 4 month dry season in a year and comes under moist sub-humid climatic region.

Tyamagondalu series

Tyamagondalu series of Bangalore region are very deep and cutans present which having colour of dark reddish brown to dark red (2.5 YR 3/4 to 3/6) might be due to rubrifaction process. The change in clay content of the surface and subsurface layer is very drastic i.e., the surface layer has too low clay content. Soils are non-gravelly clayey textured and slightly acidic. The organic carbon content is low to medium range, might be due low organic input and high rate of decomposition. The climatic data analysis classifies this area into semi-arid soils. The total potential acidity ($BaCl_2$-TEA) is very low

Table 2. *Important properties of major red and lateritic soils formed under varied climates*

Sl. No.	Depth (cm)	Horizon	Moist Colour	Per cent Clay	Coarse Fragments (Vol. %)	Texture	Organic Carbon %
1	**Per-humid: Koppa soil: Clayey-skeletal, Kaolinitic, isohyperthermic, Rhodic Kanhaplustults**						
	0–26	Ap	5YR 3/3	38.5	20	gcl	1.63
	26–45	AB	2.5YR 3/4	38.6	40	vgcl	0.90
	45–86	Bt1	2.5YR 3/4	46.9	65	egc	0.80
	86–120	Bt2	2.5YR 3/6	54.7	70	egc	0.61
	120–160+	BC	2.5YR 4/4	31.6	25	gcl	0.33
2	**Moist sub-humid: Chethalli soil: Fine-loamy, mixed, isohyperthermic Pachic Argiustoll**						
	0–31	Ap	7.5YR 3/2	26.7	-	scl	3.46
	31–47	Bt1	10YR 3/2	36.4	-	scl	1.31
	47–71	Bt2	5YR 3/3	39.6	-	sc	1.10
	71–105	Bt3	5YR 3/4	44.6	-	sc	0.55
	105–151+	Bt4	2.5YR 3/6	51.2	-	vgc	0.54
3	**Semi-arid: Tyamagondalu series: Fine, mixed, isohyperthermic, Kandic Paleustalfs**						
	0–13	Ap	2.5YR 3/5	12.8	-	sl	0.50
	13–34	Bt1	2.5YR 3/4	40.1	-	sc	0.46
	34–80	Bt2	2.5YR 3/4	43.3	-	sc	0.50
	80–110	Bt3	2.5YR 3/6	48.0	-	c	0.49
	110–160+	Bt4	2.5YR 3/6	49.7	-	c	0.36
4	**Hot humid: Peruva series: Clayey-skeletal, kaolinitic, isohyperthermic, Typic Ustorthents**						
	0–19	Ap	5YR 3.5/4	36.5	45	vgsc	2.18
5	**Hot humid: Enathu Series: Clayey-skeletal, kaolinitic, isohyperthermic, Lithic Dystrustepts**						
	0–18	Ap	7.5YR 3/2	43.5	60	vgc	1.32
	18–40	Bw	5YR 3/4	44.5	40	vgc	0.89
6	**Hot humid: Kallurkkad series: Clayey-skeletal, kaolinitic, isohyperthermic, Oxic Dystrustepts**						
	0–20	Ap	2.5YR 4/6	46.5	40	vgc	2.05
	20–52	Bw1	2.5YR 4/6	48.2	45	vgc	0.41
	52–73	Bw2	2.5YR 5/8	50.5	60	vgc	0.22
7	**Hot Humid: Pullangod series: Clayey, kaolinitic, isohyperthermic, Ustic Kandihumults**						
	0–17	Ap	5YR 3/4	27.0	10	sc	2.16
	17–49	Bt1	2.5YR3/4	30.6	10	sc	1.90
	49–87	Bt2	2.5YR 3/6	35.6	10	sc	1.23
	87–127	Bt3	2.5YR4/4	35.3	40	vgsc	0.77
	127–150	Bt4	7.5YR5/6	31.1	40	vgc	0.65
8	**Hot Humid: Kanjirappally series: Clayey-skeletal, kaolinitic, isohyperthermic, Ustic Kandihumults**						
	0–13	Ap	5YR 3/3	33.0	30	gscl	2.24
	13–32	Bt1	5YR 3/4	39.5	35	gsc	1.63
	32–56	Bt2	2.5YR 3/6	38.0	40	gsc	1.17
	56–83	Bt3	2.5YR 3/6	40.5	40	gsc	0.95
	83–112	Bt4	2.5YR 4/6	36.0	35	gsc	0.83
	112-151	Bt5	2.5YR 4/6	34.5	40	gscl	0.06
9	**Hot Humid: Anayadi series: Clayey, kaolinitic, isohyperthermic, Typic Kandiustults**						
	0–17	Ap	5YR 4/4	27.8	10	scl	0.89
	17–37	Bt1	5YR 4/6	34.6	10	scl	0.77
	37–63	Bt2	5YR 4/6	46.2	10	sc	0.39
	63–93	Bt3	5YR 4/6	44.1	10	sc	0.48
	93-125	Bt4	5YR 4/6	48.5	10	c	0.28
	125–150+	Bt5	2.5YR 4/6	47.0	10	c	0.28

Table 3. *Types of acidity and related factors and its distribution in soil profile*

Depth (cm)	Horizon	pH (Water)	pH (KCl)	ΔpH	BaCl$_2$-TEA Acidity (cmol (p+) kg^{-1})	KCl Acidity (Al) (cmol (p+) kg^{-1})	CEC (cmol (p+) kg^{-1})	ECEC (cmol (p+) kg^{-1})	BS (%)	CEC /Clay Ratio	ECEC / Clay Ratio
Perhumid: Koppa soil: Clayey-skeletal, Kaolinitic, isohyperthermic, Rhodic Kanhaplustults											
0–26	Ap	6.6	-5.1	-1.5	9.0	-	8.5	7.0	96	0.22	0.18
26–45	AB	6.8	5.9	-0.9	10.7	-	6.9	4.6	92	0.18	0.12
45–86	Bt1	6.4	5.7	-0.7	9.6	-	6.6	4.1	84	0.14	0.09
86–120	Bt2	5.9	5.4	-0.5	9.0	-	6.3	3.7	71	0.11	0.07
120–160+	BC	5.1	5.4	0.3	7.4	-	5.1	2.7	96	0.16	0.09
Moist subhumid: Chethalli soil: Fine-loamy, mixed, isohyperthermic Pachic Argiustoll											
0–31	Ap	6.4	5.7	-0.7	7.9	-	16.5	15.9	57	0.62	0.59
31–47	Bt1	6.1	5.4	-0.7	9.4	-	10.0	9.2	90	0.28	0.25
47–71	Bt2	6.9	5.8	-1.1	9.4	-	10.2	8.5	96	0.26	0.22
71–105	Bt3	5.7	4.9	-0.8	8.9	-	9.9	7.0	99	0.22	0.16
105–151+	Bt4	5.5	4.7	-0.8	11.5	-	8.6	8.2	86	0.17	0.16
Semi-arid: Tyamagondalu series: Fine, mixed, isohyperthermic, Kandic Paleustalfs											
0–13	Ap	6.8	5.5	-1.3	0.02	-	2.9	2.7	93	0.23	0.21
13–34	Bt1	5.9	4.7	-1.2	0.05	-	8.0	6.0	75	0.20	0.15
34–80	Bt2	6.1	5.0	-1.1	0.03	-	8.7	6.9	80	0.20	0.16
80–110	Bt3	6.5	5.2	-1.3	0.03	-	9.1	7.6	83	0.19	0.16
110–160+	Bt4	6.5	5.4	-1.1	0.03	-	9.4	8.1	86	0.19	0.16
Hot humid: Peruva series: Clayey-skeletal, kaolinitic, isohyperthermic, Typic Ustorthents											
0-19	Ap	4.8	4.1	-0.7	13.5	1.1	6.8	2.3	17	0.19	0.06
Hot humid: Enathu Series: Clayey-skeletal, kaolinitic, isohyperthermic, Lithic Dystrustepts											
0-18	Ap	4.9	4.1	-0.8	16.6	2.1	7.6	3.2	14	0.17	0.07
18-40	Bw	5.1	4.1	-1	10.4	1.4	8.1	2.6	15	0.18	0.06
Hot Humid: Kallurkkad series: Clayey-skeletal, kaolinitic, isohyperthermic, Oxic Dystrustepts											
0-20	Ap	5.1	4.2	-0.9	10.1	0.6	6.5	1.6	15	0.14	0.03
20-52	Bw1	4.7	4.6	-0.1	10.3	0.0	7.1	0.6	09	0.15	0.01
52-73	Bw2	5.0	4.8	-0.2	8.6	0.0	6.6	0.9	14	0.13	0.02
Hot Humid: Pullangod series: Clayey, kaolinitic, isohyperthermic, Ustic Kandihumults											
0-17	Ap	4.9	4.9	0	14.5	0.6	5.2	4.1	67	0.15	0.12
17-49	Bt1	5.1	3.9	-1.2	10.4	0.0	5.6	3.2	58	0.15	0.09
49-87	Bt2	5.3	4.0	-1.3	9.3	0.0	5.8	3.6	63	0.15	0.09

Table 3. *Continued...*

Depth (cm)	Horizon	pH (Water)	pH (KCl)	ΔpH	$BaCl_2$-TEA Acidity (cmol (p+) kg^{-1})	KCl Acidity (Al) (cmol (p+) kg^{-1})	CEC (cmol (p+) kg^{-1})	ECEC (cmol (p+) kg^{-1})	BS (%)	CEC /Clay Ratio	ECEC / Clay Ratio
87-127	Bt3	5.3	4.1	-1.2	7.3	0.0	6.3	3.4	54	0.14	0.08
127-150	Bt4	5.5	4.2	-1.3	7.3	0.0	6.7	3.8	56	0.14	0.08
Hot Humid: Kanjirappally series:Clayey-skeletal, kaolinitic, isohyperthermic, Ustic Kandihumults											
0-13	Ap	4.4	4.3	-0.1	13.0	1.0	5.4	1.9	17	0.16	0.06
13-32	Bt1	4.4	4.3	-0.1	11.9	0.8	5.6	1.2	08	0.14	0.03
32-56	Bt2	4.5	4.3	-0.2	10.8	0.5	5.5	0.9	07	0.14	0.02
56-83	Bt3	4.5	4.4	-0.1	09.7	0.0	5.7	0.3	06	0.14	0.01
83-112	Bt4	4.4	4.4	0	10.8	0.0	4.9	0.4	08	0.14	0.01
112-150+	Bt5	4.4	4.4	0	8.7	0.0	4.7	0.6	13	0.14	0.02
Hot Humid: Anayadi series: Clayey, kaolinitic, isohyperthermic, Typic Kandiustults											
0-17	Ap	4.8	4.1	-0.7	11.6	1.2	5.3	2.7	28	0.19	0.10
17-37	Bt1	5.2	4.1	-1.1	12.8	1.7	6.8	3.2	21	0.20	0.09
37-63	Bt2	5.1	4.0	-1.1	16.8	2.3	5.5	3.7	25	0.12	0.08
63-93	Bt3	5.3	4.1	-1.2	14.4	1.9	5.6	3.3	24	0.13	0.07
93-125	Bt4	5.3	4.0	-1.3	12.0	1.7	5.8	3.7	35	0.12	0.08
125-150+	Bt5	4.7	4.2	-0.5	18.2	1.6	5.6	3.5	35	0.12	0.07

(Table 3). The CEC is also very low, may be due to low organic carbon content. The CEC clay ratio and exchangeable bases are very low. Soil has dominance of highly weathered clay minerals and classified into Fine, mixed isohyperthermic, Kandic Paleustalfs.

Peruva series

Peruva soil series of Kerala are very shallow, which reveals that highest surface soil erosion by mean of sheet erosion. Soil is dark reddish brown in colour (5YR 3.5/4), gravelly sandy clay and well drained, very strongly acidic nature with high organic carbon content. Soil has both exchangeable and non-exchangeable acidity with low CEC and per cent base saturation indicating dominance of kaolinite type of clays and also classified into Clayey-skeletal, kaolinitic, isohyperthermic, family of Typic Ustorthents. The land is experiencing hot humid climate with a dry spell extending to 4 months and high moisture index of 60 per cent.

Enathu series

Land area covering Enathu series are shallow with two subsequent developed horizons. They are gravelly clay in texture, well drained, high in OC content and dark brown in colour (7.5YR 3/2 / 5YR3/4). The per cent clay in surface and sub-surface layers are high and also are very strongly acidic in nature. The soil has potential acidity of ($BaCl_2$-TEA) 13.5 cmol (p+) kg^{-1} with low CEC and per cent base saturation. The CEC to clay ratio is very low

Table 4. *Exchangeable bases, base saturation and its distribution*

Depth (cm)	Horizon	Exchangeable bases					$BaCl_2$-TEA Acidity	CEC Sum of cations	BS Sum of cations %
		Ca	Mg	Na	K	Total			
					cmol (p+) kg^{-1}				
Per-humid: Koppa soil: Clayey-skeletal, Kaolinitic, isohyperthermic, Rhodic Kanhaplustults									
0–26	Ap	5.1	0.85	0.17	0.94	7.03	9.0	16.0	44
26–45	AB	3.1	0.56	0.16	0.80	4.63	10.7	15.3	30
45–86	Bt1	2.5	0..57	0.19	0.87	4.09	9.6	13.7	30
86–120	Bt2	2.1	0.70	0.18	0.75	3.69	9.0	12.7	29
120–160+	BC	1.6	0.67	0.17	0.30	2.73	7.4	10.1	27
Moist sub-humid: Chethalli soil: Fine-loamy, mixed, isohyperthermic Pachic Argiustoll									
0–31	Ap	12.4	2.25	0.20	0.99	15.9	7.9	23.7	67
31–47	Bt1	7.2	1.39	0.17	0.49	9.2	9.4	18.6	50
47–71	Bt2	6.6	1.30	0.17	0.43	8.5	9.4	17.9	48
71–105	Bt3	5.2	1.27	0.16	0.38	7.0	8.9	15.9	44
105–151+	Bt4	6.8	1.10	0.17	0.14	8.2	11.5	19.8	42
Semi-arid: Tyamagondalu series: Fine, mixed, isohyperthermic, Kandic Paleustalfs									
0–13	Ap	2.0	0.30	0.10	0.30	2.7	0.02	2.7	100
13–34	Bt1	5.0	0.60	0.20	0.20	6.0	0.05	6.1	98
34–80	Bt2	6.4	0.30	0.10	0.10	6.9	0.03	6.9	100
80–110	Bt3	6.9	0.40	0.20	0.10	7.6	0.03	7.6	100
110–160+	Bt4	7.3	0.20	0.50	0.10	8.1	0.03	8.1	100
Hot humid: Peruva series: Clayey-skeletal, kaolinitic, isohyperthermic, Typic Ustorthents									
0-19	Ap	0.9	0.10	0.12	0.05	1.17	13.5	14.7	08
Hot humid: Enathu Series: Clayey-skeletal, kaolinitic, isohyperthermic, Lithic Dystrustepts									
0-18	Ap	0.5	0.30	0.15	0.19	1.09	16.6	17.7	06
18-40	Bw	0.61	0.27	0.21	0.13	1.22	10.4	11.6	11
Hot humid: Kallurkkad series: Clayey-skeletal, kaolinitic, isohyperthermic, Oxic Dystrustepts									
0–20	Ap	0.61	0.22	0.05	0.30	0.97	10.1	11.1	09
20–52	Bw1	0.38	0.12	0.02	0.20	0.63	10.3	10.9	06
52–73	Bw2	0.58	0.20	0.10	0.10	0.91	08.6	9.6	09
Hot Humid: Pullangod series: Clayey, kaolinitic, isohyperthermic, Ustic Kandihumults									
0-17	Ap	2.50	0.58	0.21	0.17	3.46	14.5	18	19
17-49	Bt1	2.54	0.44	0.18	0.08	3.24	10.4	13.6	24
49-87	Bt2	2.88	0.47	0.19	0.10	3.64	9.3	13.0	28
87-127	Bt3	2.18	0.85	0.27	0.08	3.38	7.7	10.6	32
127-150+	Bt4	2.23	1.10	0.30	0.15	3.8	7.3	11.0	34
Hot Humid: Kanjirappally series:Clayey-skeletal, kaolinitic, isohyperthermic, Ustic Kandihumults									
0-13	Ap	0.54	0.12	0.17	0.07	0.90	13.0	13.9	06
13-32	Bt1	0.26	0.06	0.07	0.05	0.44	11.9	12.3	04
32-56	Bt2	0.21	0.05	0.06	0.05	0.37	10.8	11.2	03
56-83	Bt3	0.16	0.06	0.05	0.05	0.32	9.7	10.1	03
83-112	Bt4	0.21	0.06	0.06	0.07	0.40	10.8	11.2	04
112-150+	Bt5	0.39	0.09	0.08	0.07	0.63	8.7	9.3	07
Hot Humid: Anayadi series: Fine, kaolinitic, isohyperthermic, Typic Kandiustults									
0-17	Ap	0.51	0.42	0.17	0.38	1.48	11.6	13.1	11
17-37	Bt1	0.77	0.33	0.02	0.33	1.45	12.8	14.3	10
37-63	Bt2	0.77	0.25	0.03	0.33	1.38	16.8	18.2	08
63-93	Bt3	0.78	0.25	0.03	0.31	1.37	14.4	15.8	09
93-125	Bt4	1.31	0.28	0.04	0.38	2.01	12.0	14.0	14
125-150+	Bt5	1.54	0.25	0.05	0.10	1.94	18.2	20.1	10

and has highly weathered kaolinitic clay as dominant clay mineral. This soil is classified into Clayey-skeletal, kaolinitic, isohyperthermic, Lithic Dystrustepts. The land area is experiencing hot humid climate with three month of dry spell in a year and have high moisture index (42 %). CEC and per cent base saturation are very low.

Kallurkad series

Land area covering this series is moderately shallow and having colour of red (2.5 YR 4/6). The change in clay content of the surface and subsurface layer is not significant. Soils are gravelly and clayey textured with very strong acidity. The organic carbon (OC) content is high in the surface layer and the subsequent layers show low carbon. The prevailing climate of the area is hot humid soils with moisture index of 68 per cent. The total potential acidity ($BaCl_2$-TEA) is around 10 and have both exchangeable and pH dependent acidity. The cation exchange capacity also is very low, may be because of the low OC. The per cent BS and CEC clay ratio are low. Highly weathered kaolinitic clay minerals are dominating in this soil. The exchangeable bases are very low in content and classified into Clayey-skeletal, kaolinitic, isohyperthermic, Oxic Dystrustepts.

Pullangod series

Land area covering Pullangod series are deep, well drained, reddish brown to dark red (7.5YR 5/6 / 2.5YR 3/4), gravelly sandy clay and strongly acidic. The organic carbon content is high at all layers. There is not much difference in the percent clay between the surface and sub surface layers. The ΔpH is nearly zero. The exchangeable acidity is not available in this soil but non exchangeable acidity ($BaCl_2$-TEA acidity-1M KCl acidity) is high. The soil CEC and BS are low and classified into Clayey, kaolinitic, isohyperthermic family of Ustic Kandihumults. This area is experiencing hot humid tropical climate and a dry spell of 4-5 months.

Kanjirapally series

Land area covering Kanjirapally soils developed are red to dark red (5YR 3/3 /2.5YR 3/6), very deep, gravelly sandy clay, very strongly acidic and well drained. The organic carbon content of the soil is high organic carbon in the surface and gradually decreased in the sub-surfaces layers. The ΔpH is nearly zero. Both the cation exchange capacity and per cent base saturation are low, indicating dominance of low activity clays. This soil is classified in to Clayey-skeletal, kaolinitc, isohyperthermic, family of Ustic Kandihumults. The climatic data revealed that the soil receives highest rainfall, experiencing 3 month dry season in a year and as a cumulative effect having the high moisture index (83 %) and comes under the hot humid climatic condition.

Anayadi series

Land area covering Anayadi series in coastal Kerala occurs in a hot humid climate with high rainfall and 4 months of dry season in a year. The soils are deep, yellowish red in colour (5YR 4/6), non-gravelly clay and very strongly acidic to strongly acidic in nature. Soil has high OC in surface layer and low in the sub-surface layers which might be due to the addition of organic litters on the surface from the vegetation. Due to high rainfall, leaching of cations, the cation exchange capacity and base saturation are low. Based on the properties of soil, it has been classified into Clayey, kaolinitic, isohyperthermic family of Typic Kandiustults.

From the study, it was found that in all the pedons clay content increased with depth which might be due to downward translocation of finer particles from the surface layers (Murthy, 1988). Decreasing OC with increasing depth was noticed (Ashok Kumar and Prasad, 2010) which may be attributed to the addition of plant residues and farmyard manure to surface horizons (Thangasamy *et al.*, 2005). Cation exchange capacity of the soils was generally low in all the pedons and it varied from 2.1 to 15.2 cmol (p+) kg^{-1} of soil. Low CEC, low bases and high clay content indicate that the soils belong to hot humid tropical origin, presence of hydrous oxides of iron and aluminium and have dominance of low activity clays in tropics reported by many workers (Krishnan *et al.,* 2000, Chandran *et al.,* 2005, Sarkar *et al.,* 2002, Nayak *et al.,*1994, Sen *et al.,* 1997, Nair *et al.,* 2011). Base saturation was low in all the pedons, mainly because of the leaching due to high rainfall. The KCI-pH values of the soils were lower than aqueous pH values indicating the existence of net negative charge on colloidal particles. Irrespective of landforms, the organic carbon decreased with depth in all the pedons. This could be attributed to the addition of plant residues and farmyard manure to surface horizons. Although the extractable acidity by 1M KCl was low, the same obtained through $BaCl_2$-TEA was very high (Table 2). Low KCl-extractable aluminium and high total extractable acidity were also reported for highly weathered Oxisols of Puerto Rico (Beinroth, 1982).The CEC of the soils ranged from 12.0 to 29.8 cmol (p+) kg^{-1} soil. Low to moderate CEC in these soils was due to the mixed type of clay with dominance of kaolin, mica and other hydroxyl-inter layered clays. The cation exchange capacity increased with an increase in depth of all the profiles which is attributed to increase in clay content at lower depths.

Constraints and soil management

The characteristics of red and lateritic soils are influenced by their climatic conditions. The soils have major constraints of erosion, moisture stress and crusting apart from high soil acidity and associated toxicity of aluminium, iron and manganese toxicity, deficiency of N, high P fixation and low K reserves, apart from deficiencies of other nutrients such as Ca, Mg, S and trace elements like Zn and B. They have low to high productivity potential and are well suited to forests, and a variety of plantation and horticultural crops like coconut, cashew, rubber, tea, coffee, cocoa, cardamom, areca-nut, pepper, cinnamon, nutmeg, clove, banana, tapioca, pine apple, paddy, vegetables and floriculture etc. especially those crops which can have little tolerance to iron and aluminium toxicity. Measures involving proper soil-water and nutrient management and selection of crops, suiting different agro-ecological environments are important to alleviate moisture stress and nutrient deficiencies. To optimize land use on a sustainable basis, it is necessary to assess and monitor soil health through soil, water and climatic evaluation.

To enhance productivity, it is essential to improve rainfall infiltration, reduce water losses due to run off and evaporation, control soil loss and provide early season conditions for seed germination and emergence, to ensure strong crop establishment to compete better with weed species and to counter pest and disease incidences. Establishing provisions to capture run off and efficient replenishment of ground water are found useful for judicious use in supplemental irrigation whenever needed. Soil surface management including natural mulches with or without contour or graded bunds or border strips, planting open ridge furrow systems, ridging, installation of graded border strips contour bunds etc. have also been found beneficial on sloping lands. Freshly decomposed organic matter should be used as a fertilizer because it contributes more to CEC of the soil.

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