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Effect of Rhizosphere on Release of Fixed Ammonia

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Abstract– *Greenhouse experiments with two crops, namely Maize (var-Gangasafed-2) and wheat [C-306), grown in three soils (Inceptisol, Vertisol and Alfisol)] was undertaken to determine the rates of release and fixation of NH4+ in the rhizosphere of both the crops in comparison to non-rhizosphere soil. Crops were grown for a period of 43 days. A set of pots without crops was kept to compare between rhizosphere and non rhizosphere effect. Destructive sampling was done periodically at 0th, 15th, 22nd, 29th, 36th, 43rd day after emergence and samples were analysed for Fixed NH4+. From 22nd day onwards, release of fixed NH4+ was found to be significantly higher in rhizosphere than in the non rhizosphere. Root induced release of fixed NH4+ was maximum in Inceptisol. On the other hand rate of release of fixed NH4 in rhizosphere was lowest in Alfisol. Moreover in Alfisol under wheat there was no significant difference between rhizosphere and non rhizosphere in the rate of release of fixed NH4+.*

Ammonium can be fixed by clay minerals of agricultural soils in considerable amount (Li *et al.,* 1990). Alluvial soils contain up to 3300 kg non-exchangeable NH_4-N per ha between 0-90 cm soil depth (Scherer and Werner, 1991). The concentration of non-exchangeable NH_4-N is influenced by the clay content, the type of clay minerals and the K saturation of interlayers and varies from soil to soil (Mengel *et al.,* 1990). Fixation of the NH_4+ ions by clay minerals is an alternate way of building the N pool in soils to optimize N crop recovery and minimize losses (Mamo *et al.,* 1993).

It is well established that this N pool plays an important role in the N dynamics of many aerable soils (Weimar and Scherer, 1993) and contributes considerably to the N-nutrition of upland crops (Yang *et al.,* 1992).

According to Scherer (1993), non-exchangeable NH_4^+ should be considered as a potential available N source. Release of ammonium from the interlayers depends not only on clay mineral characteristics but also on plant species (Scherer and Ahrens, 1996).

The results of Stucki *et al.* (1984) obtained in reduced clay suspensions suggest that NH_4^+ fixation might be promoted by decreasing redox potential in flooded soils, because of the reduction of structural Fe^{+3} causing an increase in the negative charge of certain clay minerals. Investigating the availability of non-exchangeable ammonium in wetland rice fields, Keerthisinghe *et al.* (1984) calculated that up to 100 kg of fixed NH_4-N ha^{-1} may be released during the growing period of rice in a soil with vermiculite as the main clay mineral, since rice plants are able to secrete O_2 into the rhizosphere which oxidises Fe^{2+} and Fe_3^+, there is report of release of fixed NH_4^+ by increasing redox potential in the immediate vicinity of the roots. Schneiders and Scherer (1998) observed that ammonium formed by mineralization after flooding was converted, to a substantial degree, into non-exchangeable form, when sufficient amounts of expandable 2.1% minerals were present. The newly fixed NH_4^+ was protected from N losses via nitrification and denitrification process but was completely available to the following rice crop. The release of fixed NH_4^+ was highest in the rhizosphere of rice plants where the Eh was greatly increased by the O_2 secretion of the roots and decreased with growing distance from the roots.

Since there is lack of systematic studies on the effect of rhizosphere of C_3 and C_4 plants on release of fixed ammonia in soils of different mineralogical compositions the present studies have been undertaken.

Materials and Methods

Bullk surface soil samples (0-0.15 m) classified as Inceptisol, Alfisol and Vertisol were collected from IARI research farm (New Delhi), Bhubaneshwar (Orrisa) and Raipur (Chhatisgarh), respectively.

Preparation of Soil Samples

The soil samples were thorougly air dried in shade, ground in a wooden mortar and pestte and passed through 2 mm sieve. The sieved soil was stored in the plastic containers and used for various experiments. Some important characteristics of experimental soils are given in Table 1.

Greenhouse experiment

Greenhouse experiments were carried out with maize (var. Ganga Safed-2) in *kharif* season followed by wheat (var. C-306) in *rabi* season in the Division of Soil Science and Agricultural Chemistry, I.A.R.I., New Delhi. Polypropylene pots of one kg capacity and 500 g capacity were used to grow maize and wheat, respectively. In order to compare between rhizosphere and non-rhizosphere soil, two sets of pots were used, one set was with the crop and another set was without the crop.

One month before sowing, FYM was applied at a rate of 5 g kg^{-1} and allowed to decompose nitrogen, phosphorus and potassium were applied as N, P_2O_5 and K_2O at the rate of 60, 30 and 30 mg kg^{-1} at the time of sowing.

Collection and Processing of Soil Samples

Starting from the day of emergence, five periodic samplings were done at an interval of one weak. Destructive sampling was done and on each sampling event, sampled pots were discarded. Entire soil of cropped pot was taken as rhizosphere soil and that of non-cropped pot was taken as non rhizosphere soil. The soils were separated from the root manually by carefully shaking the plants over a paper sheet. Immediately after sampling, moisture content was determined by using oven dry method.

Samples were air-dried and processed for the determination of different parameters.

Laboratory Analysis

The soil samples generated from the greenhouse experiment were analysed for the following parameters.

Non-exchangeable NH_4^+-N

Non exchangeable NH_4^+-N concentration was determined by the method of Silva and Bremner (1966). One gram of finely ground (< 100 mesh) soil was treated with 20 mL of KOBr solution for 2 hour. Sixty mL of water was added to the mixture. The mixture was heated on a hot plate and boiling was allowed for five minutes. Mixture was cooled, supernatant liquid was discarded and residue was transferrd to centrifige tube. After washing the residue twice with 0.5 N KCl, 20 mL of 5 N HF - 1 N HCl solution was added, tube was stoppered and shaken for 24 hr. The entire content was steam

Results and Discussions

The three soils collected were analysed for various properties. Alfisol was acidic in reaction with a pH of 5.3. Vertisol and Inceptisol were alkaline with pH 7.9 and 8.1, respectively. Electrical conductivity was highest (0.63 dS m-1) for Vertisol, followed by Inceptisol (0.51 dS m^{-1}) and Alfisol (0.07 dS M-1). Vertisol had higher CEC [51.2 cmol (p$^+$) kg^{-1}] than Inceptisol [21.3 cmol (p$^+$) kg^{-1}] and Alfisol [5.3 cmol (p$^+$) kg^{-1}]. Organic carbon content was highest in Vertisol (0.71%), followed by Inceptisol (0.56%) and Alfisol (0.34%) respectively.

Available phosphorus content of Inceptisol was the highest (27.6 mg kg^{-1}), followed by Vertisol (18.62 mg kg^{-1}) and Alfisol (9.2 mg kg^{-1}).

Vertisol had maximum clay content (56.5%) and the texture was silty clay, whereas the textures of Alfisol and Inceptisol were sandy loam and silty loam, respectively.

Status of fixed ammonium

The status of fixed NH_4^+ was monitored over the period of 43 days and trend of change in the status has been depicted in figures. 1 to 3 and described below.

Inceptisol

Maize

On the zero day of emergence, the concentration of fixed NH_4^+ was 116.5 mg kg^{-1} in both rhizosphere and in non-rhizosphere. With time, there was depletion in the concentration, indicating release of fixed NH_4^+. On the last day of sampling, *i.e.* on 43rd day the concentrations were 95 and 111.5 mg kg^{-1} in rhizosphere and in non-rhizosphere, respectively (Fig. 7).

Wheat

In rhizosphere the concentration of fixed NH_4^+ was 114 mg kg^{-1} on the zero day of emergence (Fig. 10). The value was same for

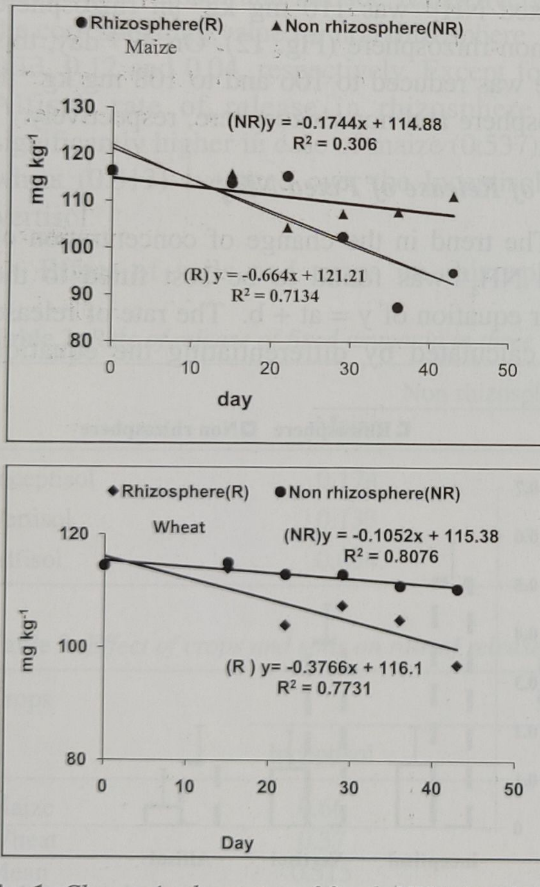

Fig. 1. *Change in the status of fixed- NH_4^+ (mg kg^{-1}) in Inceptisol under maize and wheat*

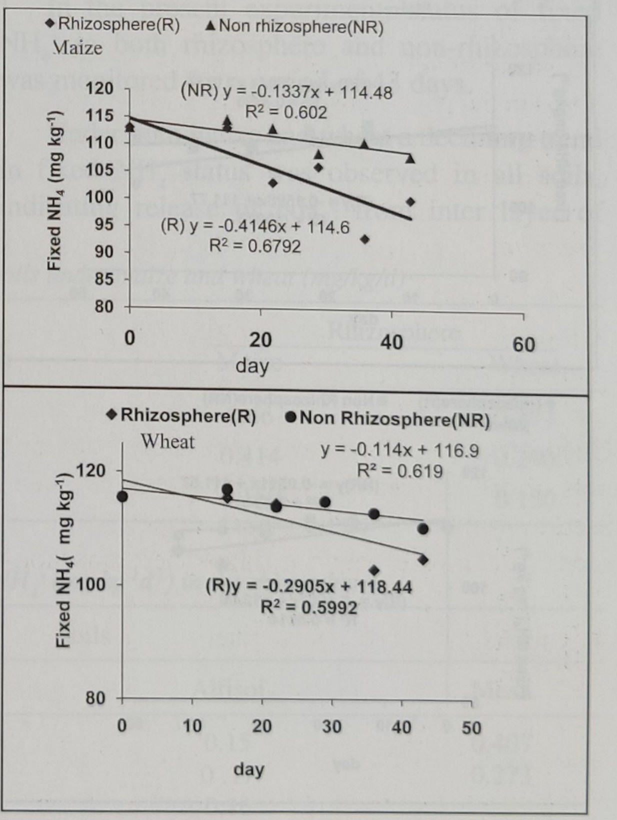

Fig. 2. *Change in the status of fixed- NH_4^+ (mg kg^{-1}) in Vertisol under maize and wheat*

non-rhizosphere. Over the time, there was change in the concentration in both the cases. On 43rd day, the concentration reduced to 97 mg kg^{-1} in rhizosphere and to 110 mg kg^{-1} in non-rhizosphere.

Vertisol

Maize

In case of Vertisol, the concentration of fixed NH_4^+ on the zero day of emergence was 113. mg kg^{-1} in both rhizosphere and non-rhizosphere. With time there was reduction in the concentration (Fig. 8). On 43rd day, the concentrations were 100 mg kg^{-1} in rhizosphere and 108 mg kg^{-1} in non-rhizosphere.

Wheat

In case of Vertisol, the concentration of fixed NH_4^+ was 115 mg kg^{-1} in both rhizosphere and non-rhizosphere on zero day of emergence (Fig. 1). With time there was depletion in the concentration. On 43rd day the concentration reduced to 105 mg kg^{-1} in rhizosphere and to 110 mg kg^{-1} in non-rhizosphere.

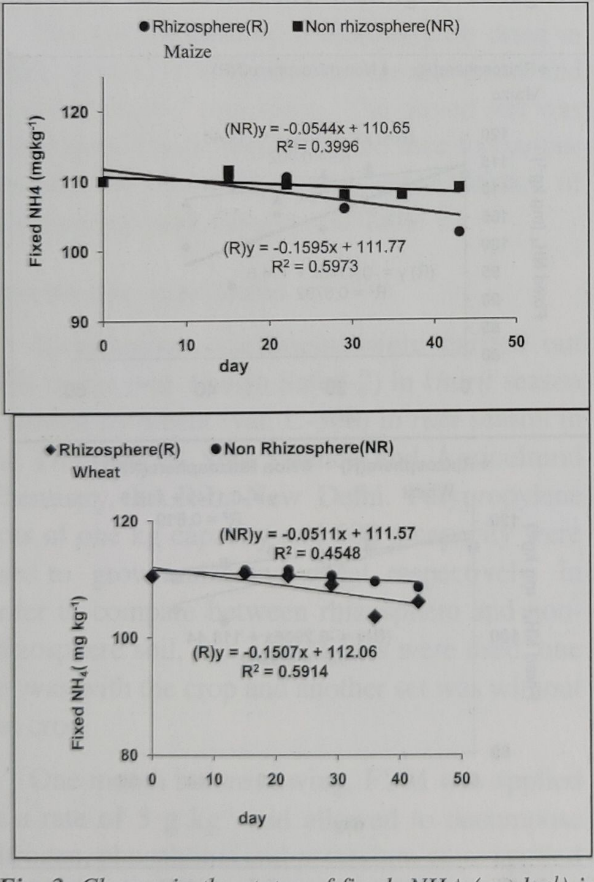

Fig. 3. Change in the status of fixed- NH_4^+ (mg kg^{-1}) in Alfisol under maize and wheat rhizosphere

Alfisol

Maize

In Alfisol, on zero day of emergence the concentration of fixed NH_4^+ was 110 mg kg^{-1} in both rhizosphere and non-rhizosphere (Fig. 9). On 43rd day the status reduced to 102 mg kg^{-1} in rhizosphere and to 109 mg kg^{-1} in non-rhizosphere.

Wheat

On the zero day of emergence concentration of fixed NH_4^+ was 110 mg kg^{-1} in rhizosphere and non-rhizosphere (Fig. 12). On 43rd day, this value was reduced to 106 and to 108 mg kg^{-1} in rhizosphere and non-rhizosphere, respectively.

Rate of Release of Fixed NH_4^+

The trend in the change of concentration of fixed NH_4^+ was found to be best fitted to the linear equation of y = at + b. The rate of release was calculated by differentiating the equation

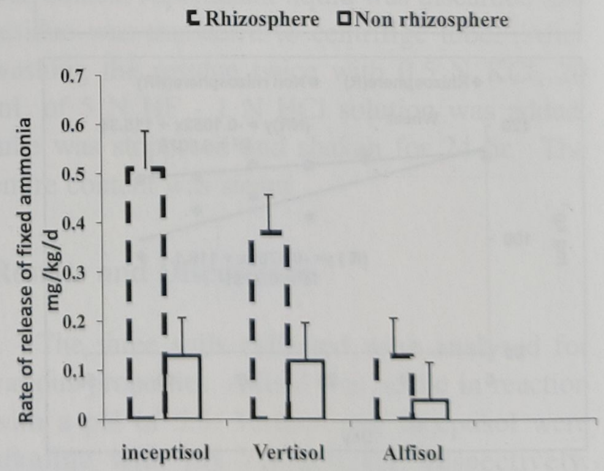

Fig. 4. *Effect of rhizosphere on rate of release of fixed ammonia in different soils*

with respect to the time.

$$d(at + b)$$

Rate of release = $\frac{d(at + b)}{dt}$ a = slope of the equation

The rate of release of fixed NH_4^+ in different soils under maize and wheat has been shown in Table 2.

The comparative effect of rhizosphere and non rhizosphere on rate of release of fixed ammonia are shown in Fig. 4.

Rate of release was significantly higher in rhizosphere than in non-rhizosphere in all three soils. Effect of rhizosphere was found to be highest in case of Inceptisol, whereas it was lowest in Alfisol. The rates of release of fixed NH_4+ in rhizosphere average over both the crops were 0., 0.51,0.38 and 0.13 mg kg^{-1} d-1 for Inceptisol, Vertisol and Alfisol, respectively and the corresponding value for non rhizosphere were 0.13, 0.12 and 0.04, respectively. Except for the Alfisol, rate of release in rhizosphere was significantly higher in case of maize (0.537) than wheat (0.313) averaged over the Inceptisol and Vertisol.

Effect of soils and crops on rhizospheric effect on release rate of fixe ammonia has been shown in table 3. Among crops maize was superior than wheat and among soils Inceptisol was highest in releasing fixed ammonia

Fixed NH_4^+ or non exchangeable NH4 is that fraction of inorganic nitrogen which is strongly trapped in the interlayer spaces of some 2:1 layer silicate clay minerals such as vermiculite, fine-grained micas and smectites. This form of NH_4 is not extractable by 2 M KCl. Fixed NH_4 is involved in the nitrogen dynamics of soil (Mengel and Scherer, 1981) and plays an important role on the availability of nitrogen in soils with high clay content (Feigenbaum *et al.,* 1974). This can be considered as potential available nitrogen source and a slow release reservoir of nitrogen. The release of fixed NH_4 depends upon concentration of NH_4^+ in soil solution, nature and amount of clay content and also on plant species.

In the present experiment, status of fixed NH_4^+ in both rhizosphere and non-rhizosphere was monitored for a period of 43 days.

Under both maize and wheat a declining trend in fixed NH_4 status was observed in all soils, indicating release of NH_4^+ from inter layer of

Table 2. *Rate of release of fixed ammonia in three different soils under maize and wheat (mg/kg/d)*

	Non rhizosphere		Rhizosphere	
	Maize	Wheat	Maize	Wheat
Inceptisol	0.174	0.105	0.66	0.377
Vertisol	0.133	0.114	0.414	0.290
Alfisol	0.054	0.051	0.159	0.150

Table 3. *Effect of crops and soils on rate of release of fixed NH_4^+ (mg kg^{-1}d^{-1}) in the rhizosphere*

Crops	Soils			
	Inceptisol	Vertisol	Alfisol	Mean
Maize	0.66	0.41	0.15	0.407
Wheat	0.37	0.28	0 .17	0.273
Mean	0.515	0.345	0.16	

C.D.(<0.05)Soil: 0.054 ; Crop: 0.044 ; Soil*Crop: 0.078

clay with the time. Rate of release was significantly higher in rhizosphere than in non-rhizosphere in all soils. Significant relationship between release of fixed NH_4 and types of plant species has been reported by Scherer and Ahrens (1996).

Faster rate of depletion soil solution NH_4^+ concentration due to plant uptake and accelerated rate of nitrification in rhizosphere, might be the reason behind this.

Besides this, weathering of minerals by root system through production of acids and complexing compounds has been studied by several authors (Mortland *et al.,* 1956; Boyle and Voizt, 1973). Yong Sang *et al.* (2005) observed mobilization of fixed NH_4^+ in the rhizosphere of rice due to secretion of organic acids (oxalic acid, citric acid) and protons. Protons could enter the wedge zone of clay minerals and displace non-exchangeable NH_4^+ thus enhanced the release of NH_4^+ from interlayer.

Rhizosphere induced release of fixed NH_4^+ was found to be maximum in Inceptisol in comparison to other two soils. Preponderance of NH_4^+ fixing clay minerals (Vermiculite and Mica) in Inceptisol is reason behind this.

On the other hand rate of release of fixed NH_4^+ in rhizosphere was lowest in Alfisol. Moreover in Alfisol under wheat there was no significant difference between rhizosphere and non rhizosphere in the rate of release of fixed NH_4+. Coating of clay minerals by Fe_2^+ oxides and resultant prevention of release of fixed NH_4^+ has been reported by Yong Sang *et al.* (2005).

Conclusions

Fixed ammonia may be a significant component in the nitrogen cycle in case of Inceptisols where micaceous clay minerals dominate over other type of clay minerals.

References

Boyel, J.R. and Voigt, G.K. 1973. Biological weathring of silicate minerals. Implications for tree nutrition and soil genesis. *Plant and Soil,* **38** : 191-201.

Feigenbaum, S. and Hadas, A. 1974. Method of same preparation for 15N determination in soil extracts by emission spectrometry. *Soil Science,* **117** : 168-170.

Keerthisinghe, G. and Mengel, K. 1984. The release of non-exchangeable ammonium (15N labelled) in wet land rice soils. *Soil Science Society of America Journal,* **48** : 291-294.

Li, C., Fan, X. and Mengel, K. 1990. Turnover of interlayer ammonium in loess -derived soil grown with winter wheat in the Shaanxi province of China. *Biology and Fertility of Soils,* **9** : 211-214.

Mamo, M., Taylor, RW. and Shuford, J.W. 1993. Ammonium fixation by soil and pure clay minerals. *Communications in Soil Science and Plant Analysis*, **24** : 1115-1126.

Mengel, K.I., Horn, D. and Tributh, H. 1990. Availability of interlayer ammonium as related to root vicinity and mineral type. *Soil Science,* **163** : 805-813.

Mengal, K. and Scherer, H.W. 1981. Release of nonexchangeable (fixed) ammonium under field conditions during the growing season. *Soil Science,* **131** : 226-232.

Mortland, M.M., Lawton, K. and Uehara, G. 1956. Alteration of biotite to vermiculite by plant growth. *Soil Science*, **82** : 477-481.

Scherer, H.W. and Werner, W. 1991. The significance of the non-exchangeable NH_4-N in the nitrogen dynamics of the soil and for the nitrogen nutrition of the plants. *Rostlinna Vyroba*, **37** : 435-440.

Scherer, H.W. 1993. Dynamics and availability of the non-exchangeable NH_4-N. *European*

Journal of Agronomy, **2** : 149-160.

Scherer, H.W. and Ahrens, G. 1996. Depletion of nonexchangeable NH_4_N in the soil root interface in relation to clay mineral composition and plant species. *European Journal of Agronomy,* **5** : 1-7.

Schneiders, M. and Schrener, H.W. 1998. Fixation and release of ammonium in flooded rice soils as affected by redox potential. *European Journal of Agronomy*, **8** : 181-189.

Silva, J.A. and Bremner, J.M. 1966. Determination and isotope-ratio analysis of different forms of nitrogen in soils, 5. fixed ammonium. *Soil Science Society of America Proceedings,* **30** : 587-594.

Stucki, J.W., Golden, D.C. and Roth, C.B. 1984. Effects of reduction and reoxidation of strctural iron on the surface charge and dissolution of dioctahedral smectite clays. *Clay Mineral*, **32** : 350-356.

Weimar, S. and Scherer, H.W. 1993. Release of non exchangeable NH_4-N after planning of rye grass in relation to water content and as affected by nitrate supply. *Z. Pflanzenernaher. Bodenk*., **156** : 143-148.

Yang, X., Scherer, H.W. and Werner, W. 1992. Fixation and release of ammonium by two typical paddy soils after incroporation of farmyard manure. *European Journal of Agronomy,* **1** : 29-35.

YongSong, Z. Shao-Xing, Hua, Lin-Xian. Yong and Scherer, H.W. 2005. Effect of organic acids and protons on release of non-exchangeable NH_4^+ in flooded paddy soils. *Pedosphere*, **15** : 273-280.

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Characterization and Comparison of Clay from Iraq and Iran for Bricks Production

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Abstract– *The clay composition from Kurdistan (Iraq) have not been investigated by researchers until today. The main aim of this research work was to investigate the clay samples obtained from various areas of Kurdistan and compare with clay imported from Iran. X-ray fluorescence (XRF) technique was used to analyse the chemical composition of the clays form both regions. The results reveals that the chemical composition of some selected elements (O, Si, Ca, Al, Fe(II), and Mg) of Koya clay sample (KoS)is very similar to that of clay imported from Iran. Other clay samples from Kurdistan can also be used for making bricks after the enrichment of their chemical composition.This novel research concludes that the clay samples obtained from Kurdistan, Iraq possess strong potential for making high strength bricks.*

Key words: Clays, Bricks, XRF, Kurdistan, Chemical Composition

Brick is a rectangular block of clay which is heated in furnace, or kiln until it becomes hard. The hard bricks are capable to be used for the construction of walls, houses, and other permanent structures (Bailey and Lister, 1989; Phonphuak *et al.*, 2016). Bricks are used in the construction of buildings and safety walls since long times ago. The Great Wall of China is the most famous example of clay bricks from the ruins of ancient civilization. Mineralogical, chemical, physical changes can affect the properties of bricks (Karaman *et al.*, 2006; Murray, 2006; Oti *et al.*, 2009). The major components of soil are inorganic solids which primarily consists of crystalline minerals and non-crystalline substances such as organic matter, air, and water (Dong and Stucki, 2011; Muri *et al.*, 2004; Reeves *et al.*, 2006). There is a high correlation between soil reflectance and several soil properties such as mineralogy, organic matter (Fathivand *et al.*, 2006), moisture content, particle size distribution, iron oxide content, colour and soluble salt content (Albrecht *et al.*, 2006; Meunier, 1994; Poon and Chan, 2006). XRF analysis can be used in the comprehensive study of the composition and physical characteristics of soil. Argiclays areusually composed of argillaceous crystalline hydrous aluminium silicates containing Ca, Na, and K in which Mg and can be substituted for aluminium. The usual commercially available clays are montmorillonite, kaolinite, and illite (Kelleher and O'dwyer, 2002). Mudstone or clay stone belongs to natural clays which contains several clay minerals having one or more impurities. Major impurities in the mudstone are amorphous silica, amorphous alumina, free iron oxide minerals, quartz grain, gypsum, limestone, and other soluble salts. The inappropriate amount of these impurities significantly affect the clay characteristics which

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ultimately results in poor quality bricks. The clay deposits on the top of the earth crust are white in color and unsuitable for making high quality bricks. The clay color changes from brown to reddish-brown while moving from top and middle (Hajipour *et al.*, 2012; Jodin-Caumon *et al.*, 2012; Limthongkul *et al.*, 2001). Kaolinite clay consists of one tetrahedral silica sheet and one octahedral alumina sheet which is found asthin micrometre platelets stacked together by strong hydrogen bonds along with pseudo hexagonal basal faces which make up individual crystals (Ryan and Radford, 1987; Sin *et al.*, 2014). The mineralogical composition has a major influence on the uses of clays in different industrial applications (Chandrasekhar and Ramaswamy, 2002; Meena and Omar, 2015; Omar and Omar, 2016; Trigo *et al.*, 2004).

Clays available at Kurdistan (Iraq) are not explored for their suitability in bricks making industry. The purpose of this research is to explore and characterize clays collected fromvarious areas of Kurdistan and comparing their chemical composition with the clays imported from Iran.

Materials and Methods

The clay samples were collected from various areasof Kurdistan namely, KoS: Koya sample, DoS: Dokan sample, SuS: Sulaimani sample, DuS: Duhok sample, ErS: Erbil sample; and two clay samples were imported from Iran namely BS1: Basic sample 1, and BS2: Basic sample 2. The elemental concentration and their emitted energies were determined using energy dispersive X-ray fluorescence (EDXRF). All measurements were carried out under vacuum, using a Rigaku NEX CG with RX9, Mo, Cu, and Al targets. Chemical elements of Mg, Br, Si, Pb, K, Ca, Ti, Cr, Mn, Fe, Ni, Rb, Sr, Y, Zr, Nb, and Mo were calculated for all clay samples. The EDXRF Kα, Lα, and Mα lines intensities were measured for all elements, in which the applied voltage increased in general with the required lines energies. The X-ray measuring time was 100s for all targets except Al target was 200s.

Results and Discussion

The XRF analyses were carried out for seven clay samples which were collected from various areas in the Kurdistan Region of Iraq and those from Iran. The intensity and mass percentage of elementspresent were indicated by XRF technique. The clay samples are irradiated with X-rays and their intensity as a function of energy was calculated over the energy range 1-20 keV at the same computing conditions. The XRF intensity peaks (Figure 1) of elements such as Mg-Kα, Br-Kα, Si-Kα, Pb-Mα, K-Kα, Ca-Kα, Ca-Kβ, and Ti-Kα of the clay samples revealed that the intensity of Ca-Kα in the SuS was higher than other clay samples, which indicate the existence of a high ratio of calcium element in the SuS sample. Also, the higher intensity peak of Si-Kα has been observed in the ErS clay sample with respect to other clay samples.

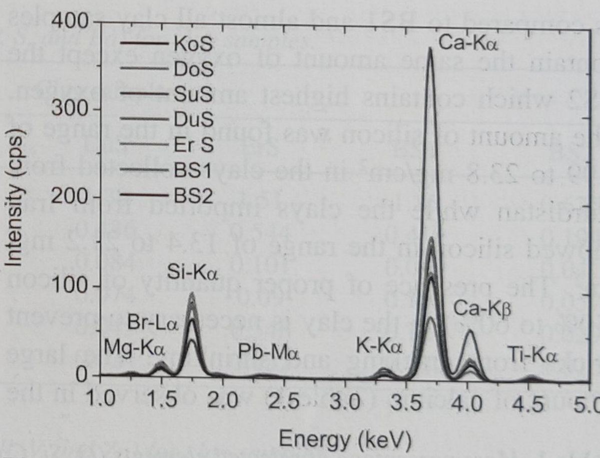

Fig. 1. *The XRF intensity of various clay samples showing the intensity peaks of elements (Mg, Br, Si, Pb, K, Ca, and Ti)*

The intensity peaks of various elements such as Cr-Kα, Mn-Kα, Fe-Kα, Fe-Kβ and Ni-Kα in the clay samples revealed (Figure 2) that the prominent peak of Fe-Kα were observed in all clay samples, but DoS showed highest peak of Fe-Kα.

The Strontium element showed highest intensity peak (Figure 3) in the SuS along with the high intensity of Niobium and Molybdenum elements. All other clay samples showed very prominent peak intensities for Niobium and Molybdenum elements.

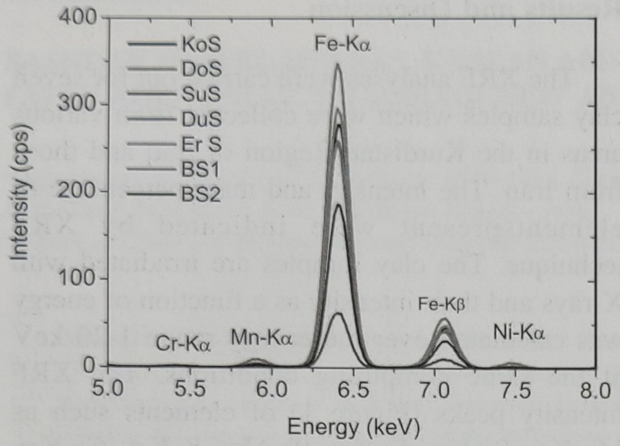

Fig. 2. *The XRF intensity of various clay samples showing the intensity peaks of elements (Cr, Mn, Fe and Ni)*

The DoS contains a large amount of oxygen as compared to BS1 and almost all clay samples contain the same amount of oxygen except the BS2 which contains highest amount of oxygen. The amount of silicon was found in the range of 8.99 to 23.8 mg/cm^2 in the clays collected from Kurdistan while the clays imported from Iran showed silicon in the range of 13.4 to 21.2 mg/cm^2. The presence of proper quantity of silicon (50% to 60%) in the clay is necessary to prevent bricks from cracking and shrinking. The large amount of calcium (Table 1) was observed in the SuS40.1 mg/cm^2 in comparison to other clays, which ultimately results in slake and an eruption on the surface of bricks. The amount of aluminum amount was observed in the range of 3.7 to 7.73 mg/cm^2. Large amount of aluminum exhibit negative effect on the quality of bricks which make them prone to staining from brickwork face and hard water from sprinkler systems. The quantity of iron in the clay below 5% helps bricks to fuse stand, but above this amount adversely effect the colour of bricks. The small amount of magnesium was observed in the clays which is vital for good quality and brilliant colored bricks but it's excess amount can cause the faster decay of bricks.

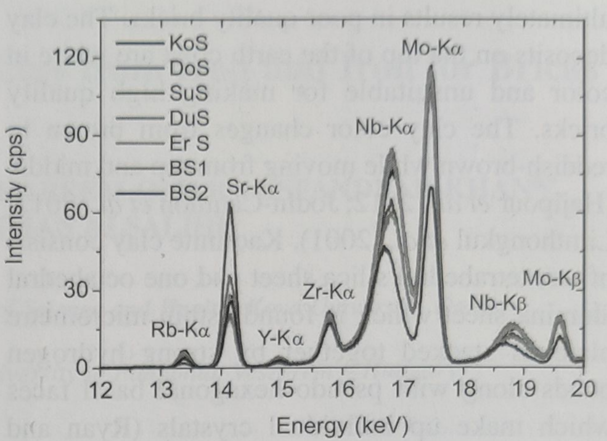

Fig. 3. *The XRF intensity of various clay samples showing the intensity peaks of elements (Rb, Sr, Y, Zr, Nb and Mo)*

The sufficient amount of potassium was observed in the range of 0.67 to 1.15 mg/cm^2

Table 1. *Mass percentage of selected elements (O, Si, Ca, Al, Fe(II), and Mg) for clay samples.*

	Clay samples						
Elements (mass%)	KoS	DoS	SuS	DuS	ErS	BS1	BS2
O	43.5	52.8	43.7	45	42.5	40.6	66.9
Si	21.3	23.1	8.99	19.8	23.8	21.2	13.4
Ca	18.5	8.95	40.1	18.5	17.3	21.4	11.3
Al	7.73	4.83	3.7	6.57	7.45	6.46	4.34
Fe(II)	3.95	4.16	1.25	3.74	4.29	2.29	1.84
Mg	2.07	4.68	0.81	4.01	2.44	3.11	2.25

(Table 2) in both BS1 and BS2 while KoS contains 1.63 mg/cm^2 which is the maximum amount in comparison to all clays and is very effective to improve the quality of clay for using making bricks. The Ti, Mn, P and Ba elements was observed in very small percentage in the clays which may have negligible effect on the quality of bricks. The sulfur element has the great effect on the bricks which reacts with potassium and calcium causes significant problems such as cracking, crumbling, expansion, and instability of bricks in the wall. The clays obtained from Kurdistan contains small amount of sulfur which makes them suitable candidates for making good quality bricks.

The amount of heavy metals in clays were observed in very small quantity. The presence of strontium, chromium, cobalt, nickel, and zinc were observed in the range of 0.019 to 0.084 mg/cm^2, 0.013 to 0.038 mg/cm^2, 0.006 to 0.016 mg/cm^2, 0 to 0.019 mg/cm^2, and 0.01 to 0.008 mg/cm^2, respectively (Table 3). The presence of such minute quantity of heavy metals in the clays exhibit no defect in the quality of bricks. The vanadium was present in all types of claysin very small amount ranged from 0.005 to 0.015 mg/cm^2. Tin, rubidium, chlorine, copper, yttrium, and lead elements (Table 4) were observed in very small amount which may have no effect on the texture and the quality of bricks.

Conclusion

Clay quality and chemical composition is the key factor in getting high quality bricks. This research work concludes on the basis of X-Ray fluorescence results that clays collected from Kurdistan possess strong capability in bricks industry. KoS sample among them was observed to be the best in comparison to BS1 and BS2. DoS, SuS, DuS, and ErS clay samples needs a little modification in their chemical composition; which will make them capable for making bricks with same quality as that made from the clays of Iran. KoS sample exhibit strong capability for

Table 2. *Mass percentage of selected elements (K, Ti, Mn, P, S, and Ba) for clay samples.*

	Clay samples						
Elements (mass%)	KoS	DoS	SuS	DuS	ErS	BS1	BS2
K	1.63	1.46	1.57	1.39	1.51	1.15	0.675
Ti	0.474	0.309	0.197	0.436	0.544	0.419	0.194
Mn	0.009	0.154	0.019	0.084	0.101	0.099	0.041
P	0.064	0.054	0.051	0.074	0.09	0.109	0.057
S	0.047	0.015	0.08	0.045	0.548	0.727	0.029
Ba	0.038	0.016	0.006	0.024	0.032	0.032	0.016

Table 3. *Mass percentage of selected elements (Sr, Cr, Co, Ni, V, and Zn) for clay samples*

	Clay samples						
Elements (mass%)	KoS	DoS	SuS	DuS	ErS	BS1	BS2
Sr	0.032	0.019	0.084	0.021	0.031	0.044	0.019
Cr	0.023	0.038	0.014	0.034	0.038	0.034	0.013
Co	0.015	0.018	0.008	0.016	0.016	0.014	0.006
Ni	0.013	0.04	0	0.019	0.017	0.02	0.007
V	0.012	0.013	0.009	0.012	0.015	0.008	0.005
Zn	0.01	0.008	0.007	0.008	0.01	0.01	0.005

Table 4. *Mass percentage of selected elements (Sn, Rb, Cl, Cu, Y, and Pb) for clay samples.*

	Clay samples						
Elements (mass%)	KoS	DoS	SuS	DuS	ErS	BS1	BS2
Sn	0.009	0.008	0.01	0.01	0.009	0.006	0.002
Rb	0.008	0.006	0.002	0.006	0.007	0.007	0.003
Cl	0.008	0.009	0.033	0.008	0.008	0.048	0
Cu	0.006	0.007	0.002	0.004	0.005	0.005	0.003
Y	0.002	0.002	0.001	0.002	0.002	0.003	0.001
Pb	0.002	0.001	0.001	0.001	0.002	0.001	0.0009

bricks making and thus can be used instead of importing clays from Iran. By doing so, the country will be safe from buying clays and huge transportation costs which can benefit the country economy.

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References

Albrecht, M. A., Evans, C. W. and Raston, C. L. 2006. Green chemistry and the health implications of nanoparticles. *Green Chemistry,* **8**: 417-432.

Bailey, S. and Lister, J. S. 1989. Structures, compositions, and X-ray diffraction identification of dioctahedral chlorites. *Clays and Clay Minerals,* **37**: 193-202.

Chandrasekhar, S. and Ramaswamy, S. 2002. Influence of mineral impurities on the properties of kaolin and its thermally treated products. *Applied Clay Science,* **21**: 133-142.

Dong, H. and Stucki, J.W. 2011. Advances in clay science in China. *Clays and Clay Minerals,* **59**: 435-437.

Fathivand, A., Amidi, J. and Najafi, A. 2006. The natural radioactivity in the bricks used for the construction of the dwelling in Tehran areas of Iran. *Radiation Protection Dosimetry,* **123**: 391-393.

Hajipour, M. J., Fromm, K. M., Ashkarran, A. A., de Aberasturi, D. J., de Larramendi, I. R., Rojo, T., Serpooshan, V., Parak, W.J. and Mahmoudi, M. 2012. Antibacterial properties of nanoparticles. *Trends Biotechnology,* **30**: 499-511.

Jodin-Caumon, M. C., Mosser-Ruck, R., Randi, A., Pierron, O., Cathelineau, M. and Michau, N. 2012. Mineralogical evolution of a claystone after reaction with iron under thermal gradient. *Clays and Clay Minerals,* **60**: 443-455.

Karaman, S., Ersahin, S. and Gunal, H. 2006. Firing temperature and firing time influence on mechanical and physical properties of clay bricks. *Journal of scientific & Industrial Research,* **65**: 153-159.

Kelleher, B. and O'dwyer, T. 2002. Intercalation of benzamide into expanded kaolinite under ambient environmental conditions. *Clays and Clay Minerals,* **50**: 331-335.

Limthongkul, P., Wang, H. and Chiang, Y. M. 2001. Nanocomposite Li-ion battery anodes produced by the partial reduction of mixed oxides. *Chemistry of Materials,* **13**: 2397-2402.

Meena, B. I. and Omar, K. A. 2015. Chemical analysis of rainwater and study effect of vehicle emissions on human health in kurdistan region. *Oriental Journal of Chemistry,* **31**: 689-695.

Meunier, J. 1994. The composition and origin of vanadium-rich clay minerals in Colorado Plateau Jurassic sandstones. *Clays and Clay Minerals,* **42**: 391-401.

Muri, G., Wakeham, S. G., Pease, T.K. and Faganeli, J. 2004. Evaluation of lipid biomarkers as indicators of changes in organic matter delivery to sediments from Lake Planina, a remote mountain lake in NW Slovenia. *Organic Geochemistry,* **35**: 1083-1093.

Murray, H.H. 2006. Structure and composition of the clay minerals and their physical and chemical properties. *Developments in clay science,* **2**: 7-31.

Omar, K. A. and Omar, N. S. 2016. Lead Removal from Agricultural Soil of Kurdistan Region by Fe3O4 Nanoparticles. *ARO,* **2**: 24-31.

Oti, J., Kinuthia, J. and Bai, J. 2009. Engineering properties of unfired clay masonry bricks. *Engineering Geology,* **107**: 130-139.

Phonphuak, N., Kanyakam, S. and Chindaprasirt, P. 2016. Utilization of waste glass to enhance physical–mechanical properties of fired clay brick. *Journal of Cleaner Production,* **112**: 3057-3062.

Poon, C. S. and Chan, D. 2006. Paving blocks made with recycled concrete aggregate and crushed clay brick. *Construction and Building Materials,* **20**: 569-577.

Reeves, G. M., Sims, I. and Cripps, J. (Eds.). 2006. *Clay materials used in construction*: Geological Society of London.

Ryan, W. and Radford, C. 1987. *Whitewares production, testing, and quality control: including materials, body formulations, and manufacturing processes*: Pergamon.

Sin, N. M., Mamat, M., Malek, M. and Rusop, M. 2014. Fabrication of nanocubic ZnO/SnO film-based humidity sensor with high sensitivity by ultrasonic-assisted solution growth method at different Zn: Sn precursor ratios. *Applied Nanoscience,* **4**: 829-838.

Trigo, R. M., PozoVázquez, D., Osborn, T. J., CastroDíez, Y., Gámiz Fortis, S. and Esteban Parra, M.J. 2004. North Atlantic Oscillation influence on precipitation, river flow and water resources in the Iberian Peninsula. *International Journal of Climatology,* **24**: 925-944.

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Assessment of Pedogenic Evolution of Zeolites and Associated Minerals at a Representative Site of Baramati, Pune

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Abstract–*The role of zeolites and associated minerals were assessed for pedogenic evolution of soils through geological and mineralogical analysis of a representative site at Baramati, Pune. Zeolites minerals were identified and characterised in the field as well as in the laboratory using petrographic microscope and X-ray diffraction (XRD), whereas, shape, size, structure as well as elemental composition were investigated using scanning electron microscope (SEM),Transmission Electron Microscope (TEM) and energy dispersive x-ray spectrometer (EDX), and nature of particles were identified based on high energy electron diffraction (HEED), whereas,* ^{14}C *Dating were used for determining the age of soil formation and development for their nutrient status. The presence of vesicular and non-vesicular basalt with distinct physical characteristics was observed. Vesicular basalts were dominantly coarse grained, hydrothermally altered and rich in zeolites, whereas, non-vesicular basalt were fine grained, very hard and compact. Both the rocks were dominated by plagioclase feldspar, pyroxenes, olivine, glass and iron oxide minerals and were in phase of transformation and neomineralization to secondary clay minerals thereby releasing their cations to the soil system. Study indicated zeolites were predominantly sodic (mordenite, mesolite) and calcic (okenite, prehnite, gyrolite, scolecite, heulandite, stilbite) as well as fluorine rich (apophyllite). Heulandite and stilbite were the dominant zeolite minerals in soil and are invariably fractured and weathered, resulting the release of Ca to the soil system as observed in EDX analysis of fresh and weathered minerals. The presence of crystalline zeolite along and within the lava lobes, their subsequent weathering and Ca leaching leading to a calcic horizon below the soil surface indicated the level of degradation.Study indicated particle size varies from 50-500nm and forms from ovular, rounded, prismatic, irregular and rod shaped due to differences in chemical composition. It has also been observed that with the decrease of particle size, there is higher release of calcium and sodium to the soil system in comparison to larger particle size probably due to increase in the reactive surface area and also due to monocrystalline as well as polycrystalline nature of zeolite minerals. Soils were very shallow, gravelly sandy loam and very poor in organic carbon, highly degraded and are of recent age of formation (650 to 910yr).*

Key words: Pedogenic evolution, Zeolites and associated minerals, Calcic horizon, Soil degradation

Role of geological formation indicated an important stress parameter and define the quantum of degradation due to change in short-variation as well as long term gradual change mostly covering temperature and precipitation and also plays an important role in the development of multiplier effects of abiotic stresses as most of the nutrient reserves in the soil is controlled by nature and composition of parent rock (Maurya and Vittal, 2010). Various soils are formed as a resultant of permutations and combinations of various parent materials and climates because of ecto and endodynamomorphic processes. Mineralogical alteration and transformation is also an important stress indicator in soils and rocks to delineate

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the type, nature and extent of abiotic stresses as well the water holding capacity of different rocks distributed in any site. Basic geology/minaralogy is of significance in assessing the sites for example, like the presence of zeolites in the farm area of National Institute of Abiotic Stress Management indicated the presence of an edaphic stressor that releases Ca^{+2} ions in to the soil solution in the upper horizons (Maurya and Vittal, 2010). Zeolite (Mordenite, Mesolite, Scolecite, Heulandite, Stilbite) and associated minerals (Okenite, Prehnite, Gyrolite and Apophyllite) were formed with the alterations of feldspars and pyroxenes minerals and these occur as secondary minerals in cavities, joint spaces, cracks and fissures in basalts and scoriaceous lavas (Sabale and Vishwakarma, 1996).Formation of zeolites are governed by various edaphic factors as indicated by the different shapes and forms ranging from acicular (mesolite), needle (mordenite), fibrous (okenite), mammilary and rosette (stilbite) (Ming and Mumpton, 1989). Studies indicated that these zeolites can provide sufficient bases to prevent transformation of smectite to kaolinite (Bhattacharyya et al., 1993), act as soil modifiers (Pal et al., 2006, 2013a) as well as transitory ecosystem engineers (Zade et al., 2017). Vaidya and Pal, 2002, indicated the role of microtopography in zeolite degradation whereas, Bhattacharyya et al., 1999 & 2015, demonstrated that ferruginous Alfisols is due to base rich zeolites and also studied the distribution of zeolitic soils in India. Most of the above studies pertain to high rainfall zones (>1000 mm) and there is general lack of information on pedogenic evolution of zeolites in the rain shadow area with rainfall less than 500mm.

Materials and Methods

Zeolites and host rock samples were collected from different Stone Quarry, Geological Profiles, Drill Cores and Soil Profiles down to 5m depth. Thin sections of rocks were prepared to study the optical properties of minerals using the polarizing microscope (Nikon, Model No ECLIPSE E200POL) and minerals were identified following Kerr (2010). Different forms and size of zeolite and associated mineral were powdered after washing the samples with distilled water. These samples were subjected to X-ray diffraction (XRD) analysis (XRD Model: Bruker AXS, D8 Advanced diffractometer) at a scanning speed of $1^{\circ}2\theta$ per minute and the scanning were carried out from 2-65 degrees and the minerals were identified based on their d values using ASTM Cards (1963). Scanning Electron Microscope (SEM) (Model JEOL) was used to identify the nature, size and chemical composition of zeolites and associated minerals following the standard procedures. A few samples were also subjected to Transmission Electron Microscope (TEM) to study the shape, size, nature of crystallinity, atomic arrangement of elements present. In this method a drop of aqueous solution containing the zeolite particles was placed on the carbon-coated copper grid, dried and kept under vacuum in desiccators before loading them onto a specimen holder and samples were analyzed using TEM Model: JEM 2100, JEOL. Elemental compositions of zeolites were determined using Energy dispersive X-ray (EDX) (INCAx-Sight, Oxford Instruments) fitted with both SEM &TEM.

Results and Discussions

Study area and field observations

Study areas are located in the semi-arid tract of the plains of Western Ghats with the elevation varied from 547 to 565m MSL and were developed on subdued basaltic terrain with weathered rocks. Traps were observed to weathered to a depth of 5 m (Fig. 1a), whereas, on plateau top it was only upto 15-20cm, as observed in the soil profile (Fig. 1b). Study of the geoflow indicated the formation and development of zeolites along the lobes (Fig. 1c), between the lobes (Fig. 1d), within the vesicular cavities (Fig. 1e) and within the big cavities developed due to movement of CO_2, F, Cl and CH_4 gases during the magmatic eruption and their accumulations and movement at different places within the system. Variations were observed in drill core samples showing moderately to highly weathered hydrothermally altered (HTA) vesicular basalt of different grades with zeolites crystal growth (Fig. 1f). Soils were shallow to very shallow (5-21 cm deep), brown to pale brown colour with texture of loamy sand, gravelly sandy loam to sandy clay loam and are associated with severe erosion, gravels and stones and rock out crops and are classified as Loamy-skeletal, mixed, isohyperthermic (calcareous), Lithic Ustarthents and belong to the subgroups of Entisols Order of Malegaon series (Prasad et. al., 2009). The soils developed were never harvested for cropping since its development due to its limited soil depth and murum characterized

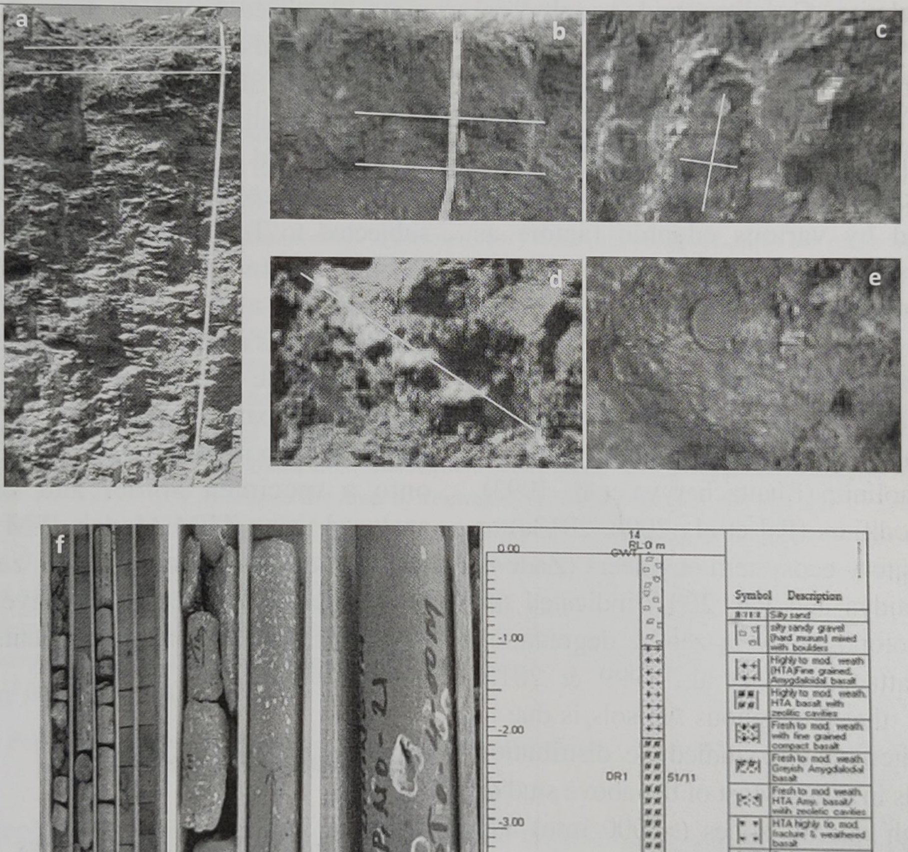

Fig.1. *(a) Geological cross section with different horizons having altered horizon (marked with yellow line), unaltered, weathered zeolites in different growth stages, (b) A horizon (0-15 cm) with gravelly sandy loam underlain by AC horizon of (15-23 cm) and followed by C horizon, (c) a close view of Fig 1a showing development of zeolite along the lava toes in the F2 flows of vesicular basalt, (d) development of zeolite within the lava toes (e) within the vesicular cavities, (f) drill core samples from Bore Log 14 showing moderately to highly weathered HTA vesicular basalt of different grades with zeolite crystal growth of 4m which is overlain by gravel and boulder horizon of 1m thick.*

by poor water holding capacity as well as their position in place. Lithic contact observed at very shallow depth (within 10-50 cm) were hard enough to prevent the root penetration that limit the crop establishment and encouraged the run-off which has manifested in the form of rill, gullies formation and rock outcrops.

Forms and development of zeolites

Different forms of zeolites and associated minerals developed in the area were needle as well as radiating fibrous crystals of mordenite (Fig.2a&b), acicular crystals with a slanted domal termination of mesolite (Fig. 2c), radiating crystals of scolecite (Fig. 2d), robust prismatic radiating crystals of heulandite (Fig. 2e), rosette shaped minerals of stilbite (Fig. 2f &g) over red bolls and altered basalt, cotton like clusters with very soft tiny fibrous radiating and fragile crystals of okenite (Fig. 2h), nodular crystals of prehnite (Fig. 2i) in the cavities of vesicular basalts, small rounded gyrolite (Fig. 2j) minerals in the geode, prismatic mineral of apophyllite (Fig.2k) on the surface of vesicular basalt. Zeolite minerals collected from different sources indicated that they were in different growth stages of their development as indicated in Figs 2a-k. The development of different forms with variations in their chemical composition was controlled by the magmatic segregation, mineral/chemical composition of associated host rocks as well as secondary process and microclimate of the area (Maurya et al. 2014).

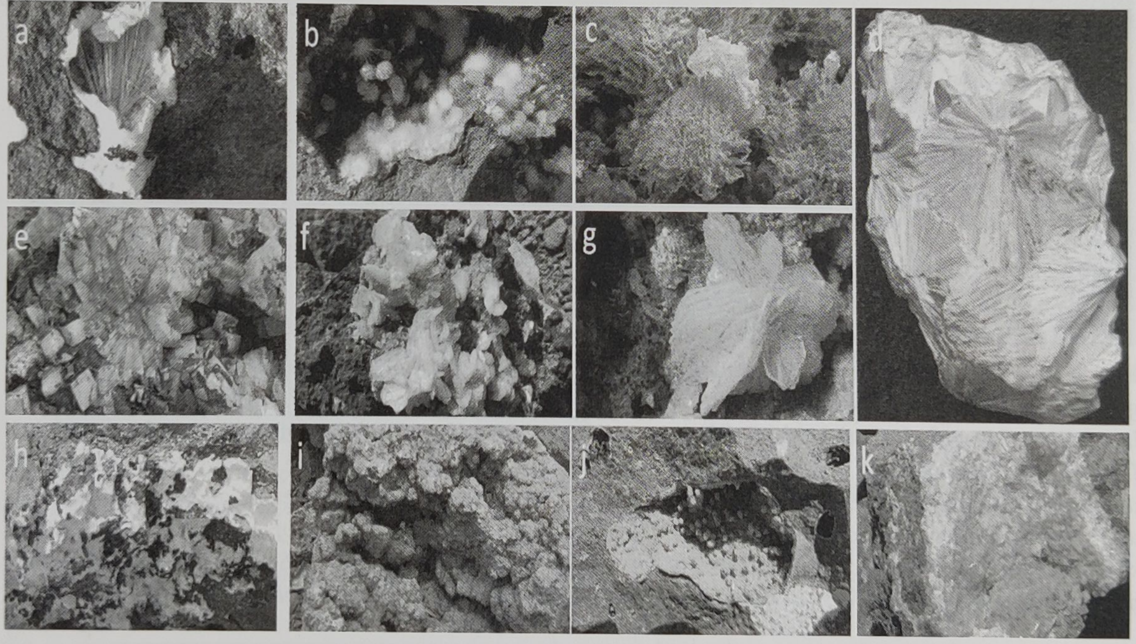

Fig. 2. *Forms of Zeolites and associated minerals. Needle & radiating fibrous crystals of mordenite (a & b); acicular crystals of mesolite (c); radiating crystals of scolecite (d); prismatic & radiating crystals of heulandite (e); rosette shaped stilbite (f &g); fibrous radiating crystals of okenite (h); nodular crystals of Prehnite (i); rod shaped gyrolite (j) ; prismatic mineral of apophyllite (k)*

Microscopic analysis

The rocks in the study area are exposed since their formation for weathering and alteration. Study on rock thin section indicated the different types of textural arrangement of minerals in different varieties of rocks. Both coarse and fine grained vesicular and non-vesicular basalts were found and were dominated by Na-Ca feldspar, pyroxene and olivine minerals with varying proportionate and were rich in Na, Ca, K, Fe, Mg, Si & Al and other trace elements. Due to the development of different stresses these minerals were in different stages of alteration and / neomineralization along the week planes resulting development of secondary saussurite and clay minerals (Fig. 3c). During these processes minerals also release the most soluble cations which accumulate in the profile section. Details of stages of primary mineral transformation into secondary minerals (phase transformation/ neoformation), dissolution, tectonic effects and Ca leaching were observed under microscope (Fig.3a-i) as well as in the field. Study indicated that the presence of intermediate stage of mineral transformation is responsible for high nutrient content of soil in the low lying area of the region.

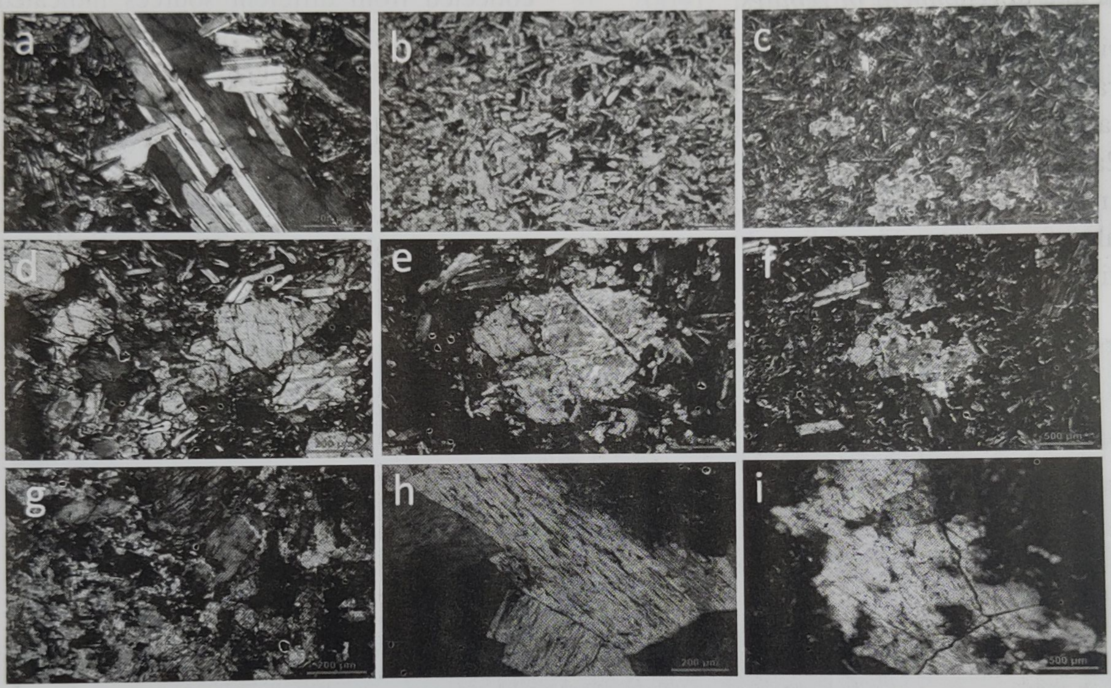

Fig. 3. *(a) Plagioclase feldspar showing Carlsbad and lamellar twining in basalt, (b) Feldspar with even grained texture showing neomineralization, (c) Very fine grained plagioclase feldspars are transforming into saussurite and clay mineral,(d) Olivine, pyroxene and feldspar in different stage of alteration, (e) Dissolution, leaching and tectonic effects in pyroxenes minerals, (f) Olivine minerals are dissoluted along the fracture planes, (g) Dissolution of ferromagnesian (olivine and pyroxenes) and zeolite minerals and neoformation of secondary clay minerals, leaching and accumulation of calcium, (h) Prismatic stilbite crystal showing etching and dissolution along the cleavage plane, (i) Stilbite minerals showing dissolution and etching effects along the boundary wall and within the mineral grains.*

X-ray diffraction analysis

Selected zeolites and associated minerals were subjected to x-ray diffraction study for its crystallinity, phase transformation and alteration. Based on their dominant d value with corresponding 2θ value minerals were identified following ASTM, 1963. Sharpness of peaks and their intensity were taken as an indicator for mineral crystallinity, and it was observed that the minerals with sharp peaks indicated highly crystalline. XRD of heulandite & stilbite shows strong peak at 9.047A° & 9.234A° respectively (Fig. 4a & b).

Scanning Electron Microscope and Energy Dispersive X-ray analysis

Most of the zeolite minerals were subjected to SEM and EDX analysis to confirm the crystal

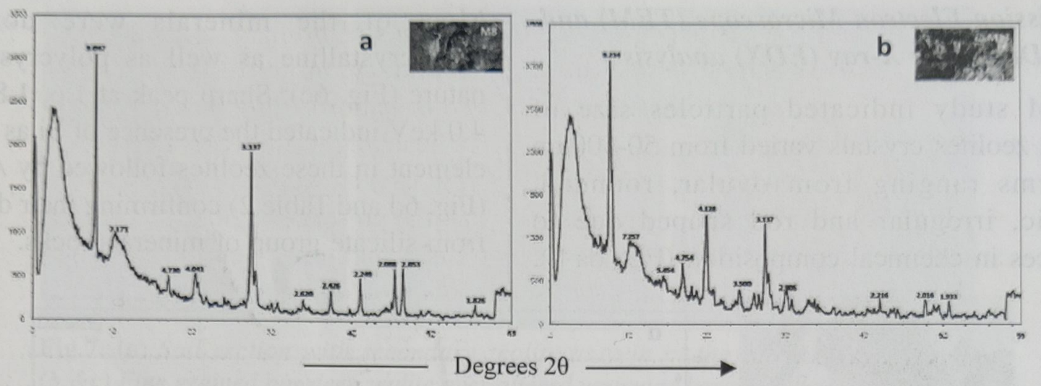

Fig. 4. *XRD diagram of powered heulandite (a) and stilbite (b) minerals*

shape and size with their chemical composition and based on these observation minerals were identified with standards. It was observed that the crystal sizes varied from 2-50µm with prismatic, rod and oval shape as dominant phases and Si & Al are the dominant element followed by variable presence of Ca, Na, Mg, F, K and Fe in most of the studied minerals. A representative analysis of heulandite mineral indicated that crystals were prismatic shape with 2-20µm size and there was dominance of Si followed by Al, Ca and Na (Fig.5a & b and Table 1).

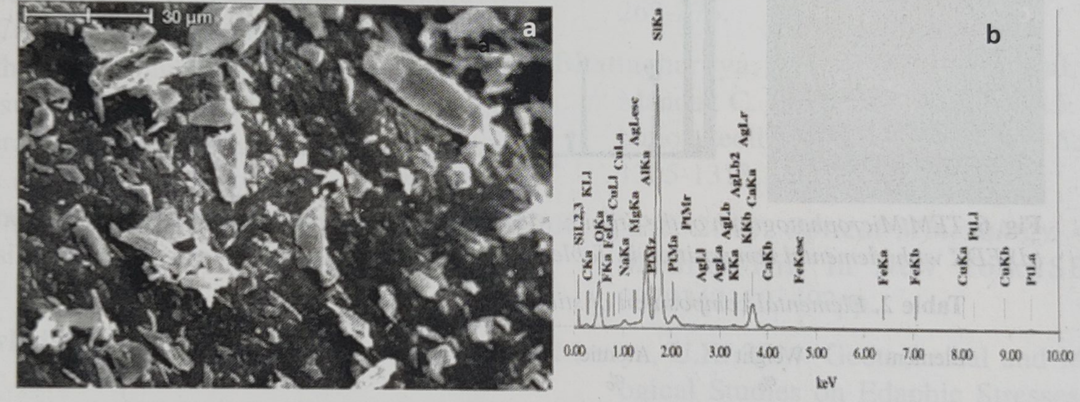

Fig. 5. *SEM Microphotograph of the Heulandite with their (a) shape and size, (b) EDX with elemental composition in Table 1.*

Table 1. *Elemental composition of heulandite*

Element	(KeV)	Mass%	Error %	At %	K
C K	0.277	7.57	0.36	13.71	1.0240
OK	0.525	35.47	0.26	48.23	33.5595
NaK	1.041	1.28	0.13	1.21	1.2492
MgK	1.253	0.14	0.08	0.12	0.1146
Al K	1.486	9.43	0.07	7.61	9.3833
SiK	1.739	31.84	0.08	24.66	32.9324
KK	3.312	0.25	0.10	0.14	0.3066
CaK	3.690	5.68	0.12	3.08	7.5700
FeK	6.398	0.07	0.23	0.03	0.0788
CuK	8.040	1.24	0.47	0.42	1.4448
Ag L	2.983	0.07	0.26	0.01	0.0720
Pt M	2.048	6.97	0.40	0.78	5.1955
Total		100.00		100	

Transmission Electron Microscope (TEM) and Energy Dispersive X-ray (EDX) analysis

TEM study indicated particles size of different zeolites crystals varied from 50-500nm and forms ranging from ovular, rounded, prismatic, irregular and rod shaped due to differences in chemical composition (Fig. 6a-b). Most of the minerals were dominantly monocrystalline as well as polycrystalline in nature (Fig. 6c). Sharp peak at 1.6, 1.8 and 3.6-4.0 keV indicated the presence of Si as the major element in these zeolites followed by Al and Ca (Fig. 6d and Table 2) confirming their derivatives from silicate group of minerals/rocks.

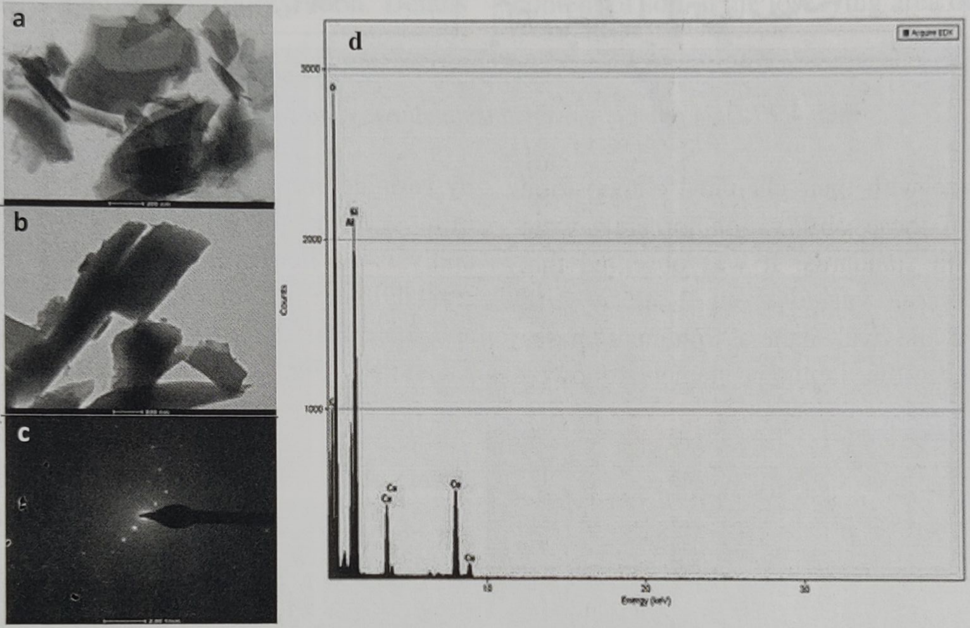

Fig. 6. *TEM Microphotograph of the Stilbite. (a& b) size of zeolite particles, (c) HEED and (d) EDX with elemental composition in Table 2.*

Table 2. *Elemental composition of stilbite*

Element	Weight %	Atomic %	Uncert. %	Detector Correction	k-Factor
C(K)	24.58	37.27	0.28	0.26	.940
O(K)	37.26	42.41	0.23	0.49	.974
Al(K)	6.78	4.57	0.07	0.92	.027
Si(K)	16.69	10.82	0.11	0.92	.000
Ca(K)	4.14	1.88	0.06	0.98	.083
Cu(K)	10.53	3.01	0.11	0.99	.667

Secondary Zeolite Association in Profile Section

Thin section studies as shown in Fig. 3a-i indicated the weathering of basalt minerals (feldspar, pyroxene, olivine and zeolites), which releases the soluble cations (Ca, Na & K), accumulate as secondary zeolite horizons at different levels (both in the soil and subsoil horizon) in the profile (Fig.7 a,b,c). These weathered zeolites will be the potential source of micronutrient (Ca) to the soil as well as it will act as soil modifiers.

Conclusions

Different forms of zeolites have developed which were mostly polycrystalline and are predominantly calcic and sodic as well as fluorine

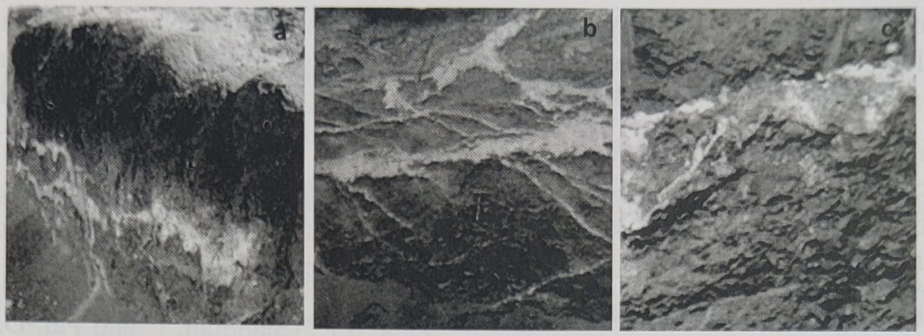

Fig.7. (a) *Soil section with secondary zeolite as vein in the subsurface horizon; (b &c) Fine grained powdery zeolite over altered vesicular basalt in the sub-surface.*

rich. Heulandite and stilbite were the dominant zeolite minerals in soil and are invariably fractured and weathered. Breaking of pyroxenes as well as zeolite minerals into two parts perpendicular to the cleavage plane indicated the effects of tectonic stresses. Dissolution of mineral grains along the cleavage and fracture planes leading to release of major cations (Si followed by Al, Ca, Na, K and F) and due to leaching action, the most soluble cations accumulate in the subsurface horizon. Transformation and neomineralization of primary to secondary clay minerals as well as primary zeolite to secondary zeolite indicated the pedogenic evolution of soils by releasing their cations to the soil system.

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References

A.S.T.M. 1963. Index (Inorganic) to the Powder Diffraction File, American Society for Testing and Materials, Philadelphia PA, USA

Bhattacharyya, T., Pal, D.K. and Deshpande, S.B. 1993. Genesis and transformation of minerals in the formation of red (Alfisols) and black (Inceptisols and Vertisols) soils on Deccan Basalt in the Western Ghats, India. *J. Soil Sci.* **44**: 159-171.

Bhattacharyya, T, Pal, D.K. and Srivastava, P. 1999. Role of Zeolites in persistence of high altitude ferruginous Alfisols of the humid tropical Western Ghats, India. *Geoderma* **90**: 263-276.

Bhattacharyya, T., Chandran, P., Pal, D.K., Mandal, C. and Mandal, D.K. 2015. Distribution zeolitic soils in India. *Curr. Sci.* **109:** 1305-1313.

Kerr, P.F. 2010. *Optical Mineralogy.* 4th ed., McGraw-Hill in New York,ISBN 10 0070342180, 492pp.

Maurya, U.K. 2014. Geotechnical and Mineralogical Studies on Edaphic Stresses of the Deccan Trap Formations at NIASM Site, Malegaon, Baramati, Maharashtra. *Clay Research.* **33** (2): 97-109.

Maurya, U.K. and Vittal, K.P.R. 2010. *Geology of the NIAM Site, Malegaon*. NIAM Technical Bulletin -1, National Institute of Abiotic Stress Management (ICAR), Baramati. 13p.

Ming, D.W. and Mumpton, F.A. 1989. Zeolites in Soils. In Minerals in Soil and Environments (2nd Edition)-SSSA Book Series, 1 : 873-911.

Pal, D.K., Bhattacharyya, T., Ray, S.K., Chandran, P., Srivastava, P., Durge, S.L. and Bhuse, S.R. 2006. Significance of soil modifiers (Ca-Zeolites and gypsum) in naturally degraded Vertisols of the Peninsular India in redefining the sodic soils. *Geoderma.* **136**: 210-228.

Pal, D.K., Wani, S.P. and Sahrawat, K.L. 2013a. Zeolitic soils of the Deccan basalt areas in India: their pedology and and edaphology. *Current Sci.* **105** : 309-318.

Prasad, J., Bhaskar, B.P. and Sarkar, D. 2009. Detailed Soil Survey of Malegaon Khurd, Baramati. NBSSLUP Annual Report, pp 41-42.

Sabale, A.B. and Vishwakarma, L.L. 1996. Zeolites and associated secondary minerals in Deccan Volcanics: study of their distribution, genesis and economic importance. National Symposium on Deccan Flood Basalts, India. *Gondwana Geol. Mag.* **2,** 511-518, Spl.

Vaidya, P.H. and Pal, D.K. 2002. Microtopography as a factor in the degradation of Vertisols in central India. *Land Deg Devt.* **13** : 429-445.

Zade S.P., Chandran, P. and Pal, D.K. 2017. Ca-zeolites as Transitory Eco-System Engineers: Hydro-pedological Evidance in Cracking Clay Soils (Vertisols) of Semi-Arid Marathwada Region, Maharashtra. *Clay Res.* **36** (2) : 90-105.

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Role of Soil Clays for Watershed Management in Mewat Region of Haryana

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Abstract–*Watershed management is an important technique for sustainable development of an area. A study was undertaken to assess the importance of clay fraction of soils in the management of Buraka micro-watershed in Mewat region of Haryana. The watershed is located in the foot hills of Aravallis comprising Buraka, Panchgaon and parts of Chila and Gwarka villages covering an area of 542.4 ha in Agro-ecological Subregion (AESR) No. 4.1. The elevation ranges from 259 to 340 m above MSL and slope varies from nearly level to steep, directed from south-east to north-west. The geology is sandstone and quartzite in hills and alluvium in plains. The area has been surveyed on 1:12,500 scale by using the Survey of India toposheets on 1:25,000 scale, cadastral maps on 1:4,000 scale and geo-coded IRS P6 LISS IV MSS imageries on 1:12,500 scale. Soil samples have been collected from different horizons of representative pedons as well as random (auger bores) observations in each interpreted physiographic units as per the heterogeneity of the terrains. Soil samples have been analysed for different physical and chemical properties using standard procedures. On the basis of image data interpretations and field checks seven landform units viz., hill tops, side slopes, inter hill basin, upper piedmont plain, middle (Buraka A to Buraka J) piedmont plain, lower piedmont plain and stream terraces have been identified in the study area. Ten soils have been identified and mapped into 21 soil mapping units as phases of soil series under Entisols and Inceptisols. The soil texture comprises sand, loamy sand, gravelly sandy loam and sandy loam covering 55.40 ha (10.22%), 133.90 ha (24.69%), 116.50 ha (21.48%) and 206.70 ha (38.10%), respectively. The soils of Aravalli hills are having gravelly sandy loam texture whereas in the plains it is sandy loam, loamy sand and sand. The particle size distribution i.e. sand, silt and clay ranges from 54.80 to 93.85%, 2.90 to 31.70% and 2.25 to 17.50%, respectively. The data also reveals that Buraka F soils (soil units 13 and 14) are having comparatively higher clay content (12.50 to 17.50% with a mean value of 16.38%), located in Buraka, Panchgaon and Chilla villages of the watershed area. Besides, these areas occur on nearly level to very gently sloping lands on relatively lower elevations. Hence, these areas of the watershed are potential for conserving water flown from uplands to down streams and can be used as water reservoirs for cultivation and livestock needs as well as for domestic use. On the basis of the present study, three sites have been identified for delineation of water harvesting zones for storing excess runoff water. This will help the farming community to meet their water requirements during the dry spells. By this way the chances of crops failure during droughts can be minimized and the agricultural productivity can be enhanced and sustained.*

Key words: Mewat region, Buraka micro-watershed, landforms, soils, water harvesting zones

Introduction

Water is the life blood of agriculture. Watershed is an area of land and water bounded by a drainage divide within which the surface runoff accumulates and flows out of the watershed through a single outlet into a large river or reservoir. It is a management of manmade

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practices in an area by understanding the inter-relationships among land use, soil and water as well as the linkage between uplands and down streams (Biswas, 1987; Mishra and Ghosh, 1995; Pai *et al.*, 2007; Mahapatra *et al.,* 2018). Watershed management is primarily a land based programme, which is increasingly being focused on water, with its main objective being to enhance agricultural productivity through increased moisture conservation and protective irrigation for socio-economic development of rural people (Nagdev *et al.,* 2017a). Water management programme are mainly confined at community level, relying upon diverse, imaginative and effective methods for harvesting rain water in tanks and small underground storage structures. This necessitates need for conserving of water received through rains and water available from any other sources towards development of surface water storability through ponding and development of ground water through artificial recharge depending on location specific feasibility. In the Aravalli ranges of Haryana state, crop productivity is under stress due to undulating landscapes, declining ground water level, poor soil fertility and lack of suitable management practices coupled with hot semi-aridic climate with low rainfall (Nagdev *et al.*, 2017b). The development of Buraka micro watershed in Mewat region of Haryana is more about the management of water resources for the livelihood of the minor community. The farming sector very seriously depends on water availability. Socio-economic effect of the scarcity of irrigation water was felt during field survey of the watershed. It has been found that peoples are struggling to arrange water for irrigation, livestocks and other domestic needs. Farmers are facing hardship due to repeated crop failures because of non-availability of proper irrigation water especially during the *rabi* season. To overcome this problem, it is therefore essential to evolve suitable strategies for harvesting water from excess rainfall and all possible sources in the localised conditions. The textural composition of soils, mainly the finer fraction *i.e.* clay content makes a vital contribution as it controls storage of water and its movement, as well as absorption and release of nutrients, thus having overall impact on crop productivity. In this context, the present study was undertaken to determine the role of soil clays in the management of Buraka micro-watershed in Mewat region of Haryana for integrated development of the area.

Materials and Methods

Study area

The study area is located in the fringes of Aravallis comprising Buraka, Panchgaon and parts of Chila and Gwarka villages covering an area of 542.4 ha in Agro-ecological Subregion (AESR) No. 4.1 (Fig 1). It lies between 28° 10' to 28° 12' N latitudes and 76° 57' to 77° 00' E longitudes. The elevation ranges from 259 to 340 above MSL and slope varies from nearly level to

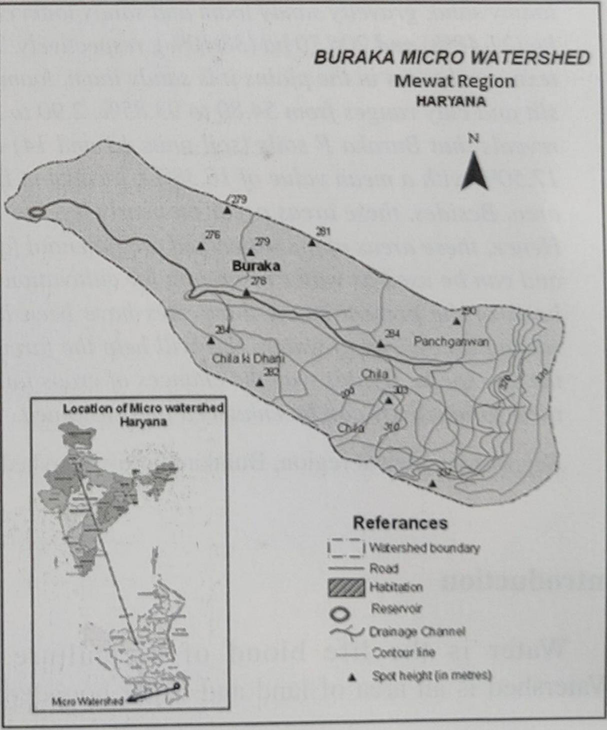


Fig. 1. *Study area: Buraka Micro-watershed, Mewat region, Haryana*

steep, directed from south-east to north-west. The geology is sandstone/quartzite in the hills and colluvium/alluviumin the plains. The rockout crops on the ridge consist of sandstone with inclusions of quartzite. The watershed soils are largely developed from local alluvium and colluvium parent materials and hilly soils in eastern part of the watershed from weathered sandstone / quartzite. Climate of the watershed is semiarid, continental and monsoonic with extreme summer and winter seasons. June is the hottest while January is the coldest month. The mean summer temperature is 33.0ºC and mean winter temperature is 15.8ºC. The mean annual temperature is 25.6ºC. The mean annual rainfall is 461 mm. Nearly 84 per cent of the rainfall is received during June to September months. Major crops grown are bajra, wheat, jowar, mustard, pigeon pea and barley.

Delineation of landforms

The geocoded IRS P6 LISS IV MSS data on 1:12,500 scale was interpreted to delineate landforms (physiography) and slope of the watershed area. Geomorphic features were interpreted on the basis of key image elements (Sahu *et al.,* 2016; Nagdev *et al.,* 2017c). Ground truth verification was made by traversing the watershed area for confirmation of different landform units and slopes at random points in the field and base map was prepared to study the soil and establish soil-physiography relationship.

Soil survey, sampling and analysis

Detailed soil survey was carried out on 1:12,500 scale and soils of different landform units and parent material were studied in the field in respect of their morphological properties by digging minipits and master profiles (Sehgal *et al.*, 1987; Bhattacharya *et al.*, 2009). Profile and random (auger bores) observations were taken in each interpreted physiographic units as per the heterogeneity of the terrains and the soil boundaries were delineated while traversing the area. The pedons of different types of soils were studied and soil samples were collected, processed (<2 mm) and analysed for important physico-chemical properties using standard procedures (Black 1965; Jackson 1966; Sharma *et al.*, 1987). The maps of soil texture and clay content of different soils were generated using GIS techniques.

Delineation of water harvesting zones

Based on the slope, landform, clay content of soils and its distribution, probable water harvesting zones were identified for storage of excess runoff water and map was generated using GIS techniques.

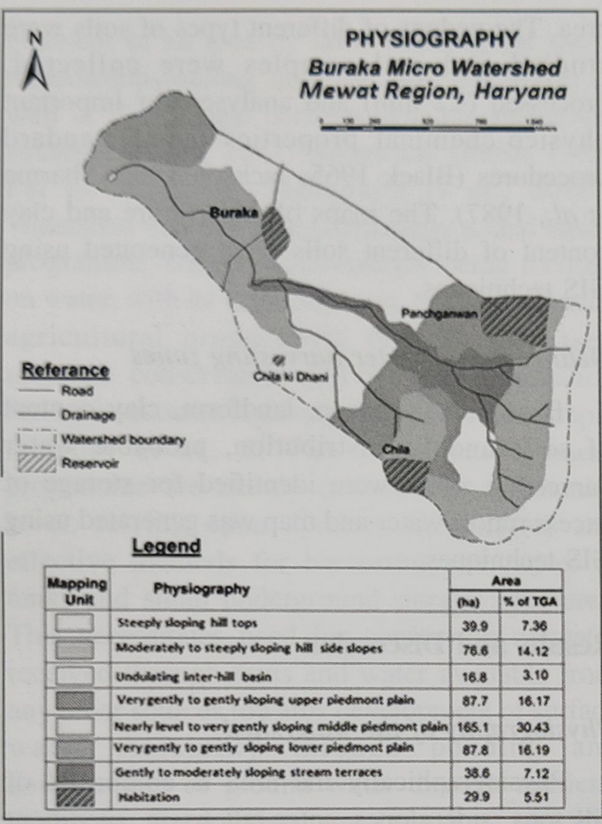
Results and Discussion

Physiography of the watershed

Physiographically the area is composed of hill tops, side slopes, inter-hill basin, piedmont plains and stream terraces and occurs on nearly level to steeply sloping landscape. The watershed is divided into seven physiographic units *viz*., (i) steeply sloping hill tops, (ii) moderately to steeply sloping hill side slopes, (iii) undulating inter-hill basin, (iv) very gently to gently sloping upper piedmont plain (v) nearly level to very gently sloping middle piedmont plain (vi) very gently to gently sloping lower piedmont plain and (vii) gently to moderately sloping stream terraces (Fig. 2). The elevation of the area ranges from 259 to 340 m above MSL and slope direction is from south-east to north-west. From the physiography map, it is revealed that two physiographic units viz., nearly level to very gently sloping middle piedmont plain and very gently to gently sloping lower piedmont plain are suitable for storage of runoff water as they occur on plains of lower elevations.

Soils of the watershed

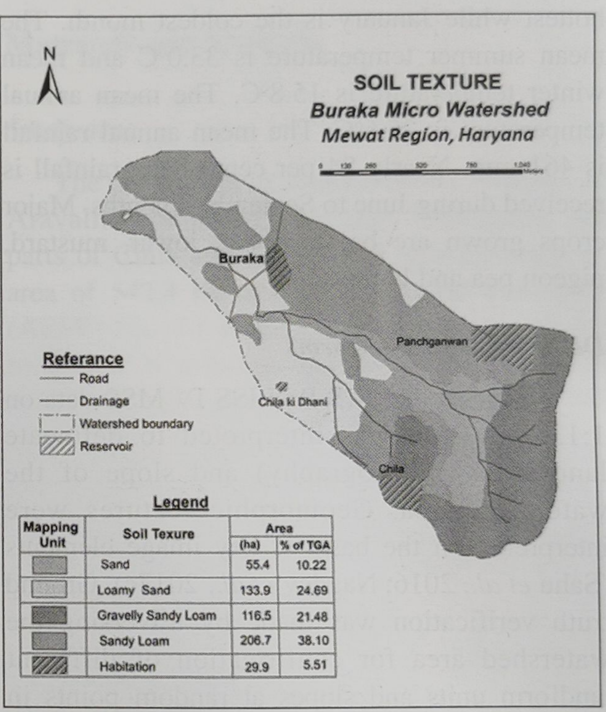
On the basis of study of soils in the field and



Mapping Unit	Physiography	Area	
		(ha)	% of TGA
☐	Steeply sloping hill tops	39.9	7.36
▒	Moderately to steeply sloping hill side slopes	76.6	14.12
☐	Undulating inter-hill basin	16.8	3.10
▓	Very gently to gently sloping upper piedmont plain	87.7	16.17
☐	Nearly level to very gently sloping middle piedmont plain	165.1	30.43
▒	Very gently to gently sloping lower piedmont plain	87.8	16.19
▓	Gently to moderately sloping stream terraces	38.6	7.12
▨	Habitation	29.9	5.51

Fig. 2. *Physiography of the study area*

their laboratory characterization, ten soils have been identified in the watershed area *viz*., Buraka A, B, C, D, E, F, G, H, I and J. Out of these ten soils, Buraka A, B,C, D and J soils occur on Aravalli hills, hill slopes and sloppy landscapes whereas, Buraka E, F, G, H and I soils occur on nearly level to gently sloping piedmont plains. Soils of Buraka A and B are developed on weathered sandstone/quartzite, Buraka C, D, E and F on colluvium/alluvium and Buraka G, H and I on alluvium/colluvium, respectively. Major area of the watershed is having sandy loam texture covering 206.70 ha (38.10%), followed by loamy sand, gravelly sandy loam and sand covering 133.90 ha (24.69%), 116.50 ha (21.48%) and 55.40 ha (10.22%), respectively (Fig. 3). The data from table 1 reveals that Buraka A and B soils are gravelly sandy loam in texture whereas Buraka C and J soils are sand, Buraka D, F, G and I soils are sandy loam and Buraka E and H soils are loamy sand in texture, respectively. The coarser texture of the soils is due to the fact that the soils are developed on sandstone/quartzite parent materials. Soils are, in general, neutral to slightly alkaline in nature. Buraka A and B soils are neutral (pH 6.7-7.1) whereas other soils are slightly alkaline (pH 7.5-8.4) in reaction. This is due to the reason that bases are leached from higher elevations (Buraka A and B soils) and their depositions in the lower elevations of the watershed (Buraka C to J soils).



Mapping Unit	Soil Texure	Area	
		(ha)	% of TGA
▒	Sand	55.4	10.22
░	Loamy Sand	133.9	24.69
▓	Gravelly Sandy Loam	116.5	21.48
▒	Sandy Loam	206.7	38.10
▨	Habitation	29.9	5.51

Fig. 3. *Soil texture of the study area*

Clay content and its distribution in soils

The particle size of the soils are presented in Table 1 and Fig. 3. It reveals that the particle distribution *i.e.* sand, silt and clay ranges from 54.80 to 93.85 %, 2.90 to 31.70 % and 2.25 to 17.50 %, respectively. It has been observed that the clay content varies from soil to soil and also in different horizons (Fig.4 and Table 1). It is 17.00 and 13.50 % in Buraka A and B soils and ranges from 2.25 to 3.50 % in Buraka C, 8.15 to 14.50 % in Buraka D, 3.50 to 8.00 % in Buraka

Table 1. *Physico-chemical properties of soils*

Soils	Depth (cm)	Sand (2-0.05 mm)	Silt (0.05-0.002mm)	Clay (<0.002 mm)	Texture	pH	CEC [cmol(p+) kg-1]	CEC/Clay
Buraka A	0-18	57.95	25.05	17.00	Gravelly sandy loam	6.7	6.49	0.38
Buraka B	0-16	54.80	31.70	13.50	Gravelly sandy loam	7.1	4.68	0.35
Buraka C	0-18	88.00	8.50	3.50	Sand	7.5	1.26	0.36
	18-42	93.85	3.65	2.50	Sand	7.5	0.92	0.37
	42-66	89.95	7.55	2.50	Sand	8.2	0.94	0.38
	66-96	88.30	9.20	2.50	Sand	8.3	0.94	0.38
	96-150	91.30	6.45	2.25	Sand	8.4	0.86	0.38
Buraka D	0-18	80.35	11.50	8.15	Loamy sand	7.6	2.90	0.35
	18-42	71.15	15.85	13.00	Sandy loam	7.8	4.68	0.36
	42-69	70.30	15.20	14.50	Sandy loam	7.7	4.90	0.34
	69-95	72.60	14.90	12.50	Sandy loam	7.8	4.39	0.35
	95-123	69.85	17.65	12.50	Sandy loam	7.8	4.41	0.35
	123-150	71.00	17.00	12.00	Sandy loam	7.8	4.30	0.36
Buraka E	0-18	81.70	10.80	7.50	Loamy sand	7.5	2.40	0.32
	18-40	82.00	10.00	8.00	Loamy sand	7.7	2.64	0.33
	40-67	85.10	7.40	7.50	Loamy sand	7.8	2.26	0.30
	67-96	87.00	5.75	7.25	Loamy sand	7.7	2.34	0.32
	96-127	89.00	7.50	3.50	Sand	7.7	1.08	0.31
	127-156	89.05	6.95	4.00	Sand	7.9	1.20	0.30
Buraka F	0-16	75.10	12.40	12.50	Sandy loam	7.5	4.87	0.39
	16-40	71.10	13.90	15.00	Sandy loam	7.7	5.70	0.38
	40-70	67.25	15.75	17.00	Sandy loam	7.8	6.46	0.38
	70-102	65.90	16.60	17.50	Sandy loam	7.8	6.48	0.37
	102-128	64.55	18.45	17.00	Sandy loam	7.8	6.63	0.39
	128-150	66.05	16.45	17.50	Sandy loam	7.9	6.48	0.37
Buraka G	0-17	73.10	15.90	11.00	Sandy loam	7.5	3.52	0.32
	17-45	70.35	17.15	12.50	Sandy loam	7.5	3.87	0.31
	45-72	70.40	16.10	13.50	Sandy loam	7.6	4.05	0.30
	72-100	66.20	17.30	16.50	Sandy loam	7.8	5.11	0.31
	100-127	67.25	17.75	15.00	Sandy loam	7.9	4.50	0.30
	127-150	66.30	18.70	15.00	Sandy loam	8.0	4.65	0.31
Buraka H	0-24	85.00	11.50	3.50	Sand	7.6	1.05	0.30
	24-53	77.50	14.30	8.20	Loamy sand	7.8	2.38	0.29
	53-80	77.00	14.50	8.50	Loamy sand	8.0	2.38	0.28
	80-106	79.50	13.00	7.50	Loamy sand	8.0	2.25	0.30
	106-135	81.80	11.45	6.75	Loamy sand	8.1	1.89	0.28
	135-154	82.00	12.00	6.00	Loamy sand	8.3	1.62	0.27
Buraka I	0-20	76.25	13.75	10.00	Sandy loam	7.5	2.90	0.29
	20-44	68.20	19.30	12.50	Sandy loam	7.6	3.63	0.29
	44-68	72.00	15.50	12.50	Sandy loam	7.7	3.50	0.28
	68-94	72.15	15.85	12.00	Sandy loam	7.7	3.48	0.29
	94-131	76.10	13.90	10.00	Sandy loam	7.7	2.70	0.27
	131-156	77.45	11.05	11.50	Sandy loam	7.8	3.22	0.28
Buraka J	0-18	85.15	8.85	6.00	Loamy sand	7.9	1.98	0.33
	18-45	92.10	2.90	5.00	Sand	8.1	1.60	0.32
	45-72	92.50	5.00	2.50	Sand	8.1	0.83	0.33
	72-111	93.25	4.25	2.50	Sand	8.2	0.83	0.33
	111-125	91.40	5.00	3.60	Sand	8.2	1.20	0.33
	125-160	92.75	4.20	3.05	Sand	8.3	0.98	0.32

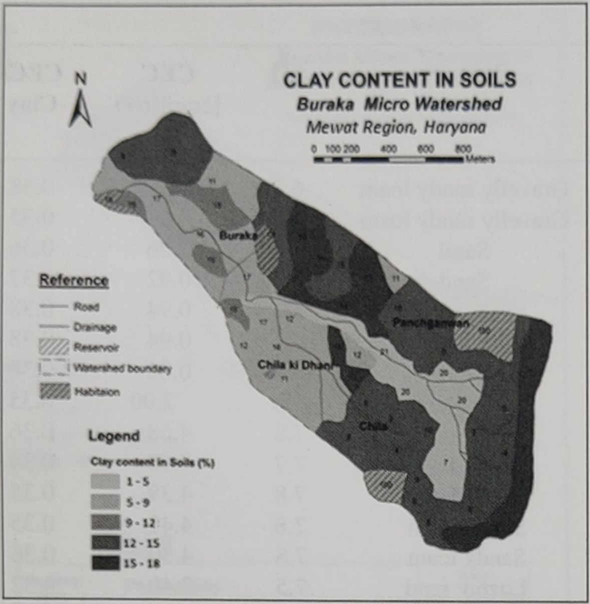
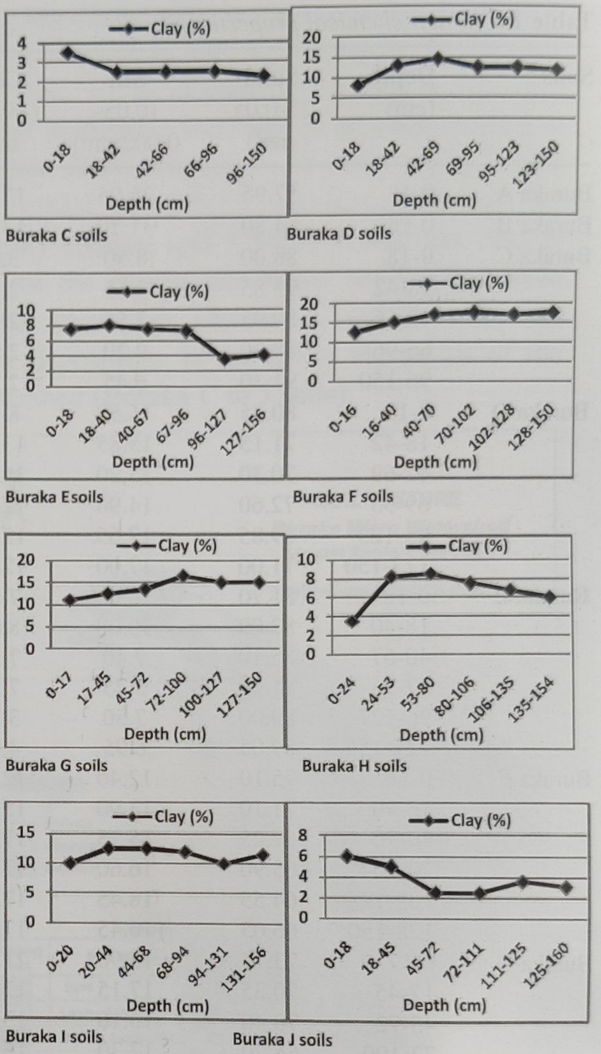


Fig. 4. *Clay content in soils*

E, 12.50 to 17.50% in Buraka F, 11.00 to 16.50 % in Buraka G, 3.50 to 8.50 % in Buraka H, 10.00 to 12.50 % in Buraka I and 2.50 to 6.00 % in Buraka J soils, respectively (Fig.5). The pattern of graphs in different soils is indicative of leaching (eluviation) and deposition (illuviation) of clay particles in surface and subsurface horizons of the soils.



Buraka C soils
Buraka D soils
Buraka E soils
Buraka F soils
Buraka G soils
Buraka H soils
Buraka I soils
Buraka J soils

Fig. 5. *Distribution of clay in different soils*

Cation exchange capacity:clay ratio

The cation exchange capacity (CEC) of the soils is generally very low to low varying from 0.77 to 6.63 cmol(p$^+$) kg^{-1} (Table 1). It is 6.49 and 4.68 cmol(p$^+$)kg^{-1} for Buraka A and B soils, whereas, it ranges from 0.86 to 1.26 cmol(p$^+$)kg^{-1} in Buraka C, 2.90 to 4.90 cmol(p$^+$)kg^{-1} in Buraka D, 1.08 to 2.64 cmol(p$^+$)kg^{-1} in Buraka E, 4.87 to 6.63 cmol(p$^+$)kg^{-1} in Buraka F, 3.52 to 5.11 cmol(p$^+$)kg^{-1} in Buraka G, 1.05 to 2.38 cmol(p$^+$)kg^{-1} in Buraka H, 2.70 to 3.63 cmol(p$^+$)kg^{-1} in Buraka I and 0.83 to 1.98 cmol(p$^+$)kg^{-1} in Buraka J soils, respectively. The CEC value is governed by the texture and mineralogy of the soils. The lower CEC value is due to comparatively coarser texture (loamy sand and sandy loam) of these soils. The CEC: Clay ratio was determined for qualitative assessment of clay mineralogy of the soils. The data (Table 1) reveals that the ratio is 0.38 and 0.35 in Buraka A and B soils, whereas, it varies from 0.36 to 0.38 in Buraka C, 0.35 to 0.36 in Buraka D, 0.28 to 0.33 in Buraka E, 0.37 to 0.39 in Buraka F, 0.30 to 0.32 in Buraka G, 0.27 to 0.30 in Buraka H, 0.27 to 0.29 in Buraka I and 0.32 to 0.33 in Buraka J soils, respectively. It indicates that the mineralogy in all three soils is of mixed type (Smith 1986, Nagdev *et al.*, 2017d).

Delineation of water harvesting zones

From the study of the physiography and slope of different soils, it is revealed that Buraka A and B soils occur on steeply sloping hill tops and side slopes, Buraka C, D and J soils occur on sloppy landscapes. Hence these soils cannot be considered for storage of runoff water and thus not suitable for delineation of water harvesting zones. Among the remaining soils, Buraka E and H soils are very light textured having loamy sand texture (Table 1 and Fig. 3) with very low water holding capacity having clay content ranging from 3.50 to 8.50 % only. These soils are not suitable for storing runoff water and hence cannot be considered for delineation of water harvesting zones. Buraka F, G and I soils are comparatively high in clay content ranging from 12.50 to 17.50, 11.00 to 16.50 and 10.00 to 12.50 %, respectively. These three soils can be considered for storing excess runoff water during heavy rains. They are distributed in Buraka, Panchgaon and Chilla villages covering 119.0 ha (21.93%) area of the watershed, as depicted in Fig. 4. It is also observed from fig 6 that Buraka F soils have maximum weighted mean value of clay content *i.e.* 16.38 % followed by Buraka G (14.09%), Buraka D (12.33%), Buraka I (11.34%), Buraka H (6.86%), Buraka E (5.79%), Buraka J (3.53%) and Buraka C (2.53%), respectively. Hence Buraka F soils are capable of storing maximum runoff water in comparison to other soils.

Besides, Buraka F soils occur on nearly level land in lower elevations of the watershed. Therefore, areas covered under Buraka F soils are found to be most suitable for delineation of water harvesting zones. Taking into consideration of the above database and landscape position, three sites were demarcated for delineation of probable water harvesting zones in Buraka F soil areas and a map has been generated, as depicted in Fig. 7. These three water harvesting zones can be used as water reservoirs by the inhabitants of the watershed for their farming practices and other domestic needs mainly during dry seasons.

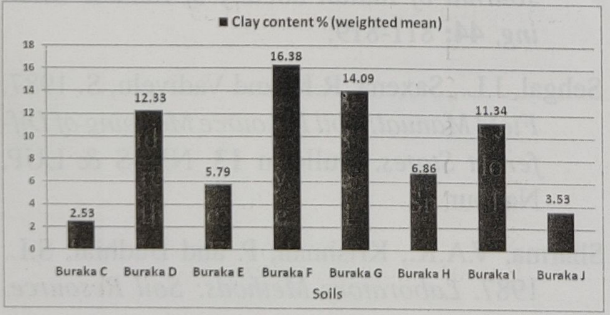


Fig. 6. *Weighted mean value of soil clays (%)*

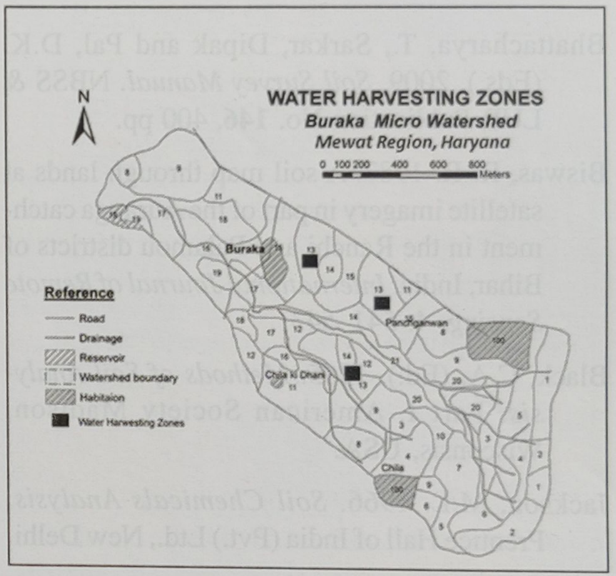


Fig. 7. *Probable water harvesting zones*

Conclusion

The study reveals the importance of clay fraction of soils for delineation of water harvesting zones and overall management of Buraka micro watershed in Mewat region of Haryana. Buraka F soils have comparatively higher clay content and are located in Buraka, Panchgaon and Chilla villages of the watershed area. These areas occur on nearly level land in relatively lower elevations. Hence these areas of the watershed are potential for conserving water flown from uplands (hilly areas) to down streams during monsoon and high intensive rainfalls (mainly the excess runoff water). The water reservoirs can be used for cultivation and livestock needs as well as for domestic use. In addition, it will be helpful for the farming community to meet their water requirements during the dry spells. By this way, the chances of crop failure during droughts can be minimized and the agricultural productivity can be improved and sustained. It will also help the planners and administrators for overall development of the minority people of the watershed.

References

Bhattacharya, T., Sarkar, Dipak and Pal, D.K. (Eds.). 2009. *Soil Survey Manual*. NBSS & LUP, Publication No. **146**, 400 pp.

Biswas, R. R. 1987. A soil map through lands at satellite imagery in part of the Auranga catchment in the Ranchi and Palamou districts of Bihar, India. *International Journal of Remote Sensing,* **4**: 541–543.

Black, C.A. (Ed.). 1965. *Methods of Soil Analysis*. Part I. American Society Madison, Wisconsis, USA.

Jackson, M.L. 1966. *Soil Chemicals Analysis*. Prentice Hall of India (Pvt.) Ltd., New Delhi.

Mahapatra, S. K., Nagdev, Ritu, Yadav, R. P. and Singh, S. K. 2018. Identification and characterization of the soils of Paschimi Nayyar River Watershed in Lesser-Himalayan Region of India. *International Journal of Current Microbiology and Applied Sciences (IJCMAS).***7(02**): 2185-2197.

Mishra, B.B. and Ghosh, S.K. 1995. Characteriztion of soils derived from mica rich parent materials in two topo sequences. *Journal of the Indian Society of Soil Science*, **43 (1**): 92-98.

Nagdev, Ritu, Mahapatra, S.K., Yadav, R.P. and Singh, S.K. 2017a. Delineation and characterization of Purvi Nayyar River Watershed in Mid- Himalayan Region of India using remote sensing and GIS techniques. *International Journal of Current Microbiology and Applied Sciences* (*IJCMAS).***6 (9):** 2047-2062.

Nagdev, Ritu, Mahapatra, S.K., Yadav, R.P. and Singh, S.K. 2017b. Land capability classification and management needs in Aravalli fringes in Southern Haryana for sustainable land use planning. *Journal of Soil and Water Conservation*, **16**(2): 117-125.

Nagdev, Ritu, Mahapatra, S.K., Meena, R.K., Surya, Jaya N., Yadav, R.P. and Singh, S.K. 2017c. Study of agri-climatic characteristics in north western Himalayas for enhancing productivity – a case study of Nagrota Bagwan block of Kangra district in Himachal Pradesh, India. *Asian Journal of Microbiology, Biotechnology and Environmental Sciences,* **19 (4)**: 997-1004.

Nagdev, Ritu, Mahapatra, S.K., Yadav, R.P. and Singh, S.K. 2017d. Assessment of soil resource potential of warm humid Kumaon Himalayas for sustainable productivity. *Journal of the Indian Society of Soil Science,***65 (2):** 138-147.

Pai, C.W., Wang, M.K. and Chiu, C.Y. 2007. Clay mineralogical characterization of a toposequence of perhumid subalpine forest soils in north eastern Taiwan. *Geoderma,* **138:** 177-184.

Sahu, Nisha, Singh, S.K., Obi Reddy, G.P., Nirmal Kumar, Nagaraju, M.S.S. and Srivastava, Rajeev. 2016. Large scale soil resource mapping using IRS P6 LISS IV and Cartosat-1 DEM in basaltic terrain of Central India. *Journal of Indian Society of Remote Sensing,* **44:** 811-819.

Sehgal, J.L., Saxena, R.K. and Vadivelu, S. 1987. *Field Manual: Soil Resource Mapping of Different States.* Bulletin **13**, NBSS & LUP, Nagpur.

Sharma, V.A.K., Krishnan, P. and Budhial, S.L. 1987. *Laboratory Methods: Soil Resource,* *Mapping of Different States in India*. Bulletin **14**, NBSS & LUP, Nagpur.

Smith, G.D. 1986. *The Guy D Smith Interview: Rationales for concept in Soil Taxonomy. SMSS Technical Monograph* **11**, SMSS, SCS, USDA.

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Effect of Manures and Amorphous Aluminosilicates on Amount and Stability of Adsorbed Humus on Coarse and Fine Clay of Different Soils from Long-term Fertilizer Experiment

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Abstract–*The present investigation was carried out to study the amount and stability of adsorbed humus against thermal and microbial decomposition in relation to nature and source of humus as well as amorphous aluminosilicate (AAS) content in coarse and fine clay. Three different organic manures namely farmyard manure (FYM), biogas slurry (BGS) and a decomposed green manure* Daincha *(Susana aculeata) compost (GMC) were taken for extraction of fulvic and humic acid from them. Clay samples separated from four soils of long term fertilizer experiment belonging to the orders of Inceptisol, Mollisol, Vertisol and Alfisol were fractionated into coarse clay (0.2-2mm)(CC) and fine clay (< 0.2 mm) (FC) each of which was again subdivided into two fractions one with amorphous aluminosilicates (AAS) and another without AAS. Humic acid (HA) and fulvic acid (FA) from different sources were mixed with different clay samples and shaken for 24 hours. The prepared clay-humus complexes were incubated for stability studies against microbial decomposition using mixed fungus culture of Trichoderma receeii and Aspergillous awamori. Thermal stability of clay-humus complexes were studied by incubating at 55 ° C and determining organic carbon content at 10 days interval. Statistical analysis with respect of the amount of humus adsorbed followed the sequences: a) Vertisol- clay> Inceptisol- clay> Mollisol- clay = Alfisol- clay. b) FC >CC >CC minus AAS > FC minus AAS ; c) BGS-humus > FYM-humus > GMC-humus and d) HA > FA. With respect to stability against both microbial and thermal decomposition the common sequences of stability observed were a) FC >CC >CC minus AAS > FC minus AAS, b) BGS-humus > FYM –humus > GMC-humus and c) HA > FA.*

Key words: Stability, humus, clay, amorphous aluminosilicate biogas slurry, farmyard manure, green manure compost

Introduction

Carbon sequestration and stability of clay organic complexes in soil are very important now with respect to global warming and maintenance of soil health with proper soil structure and permeability. In an earlier paper (Vennila and Datta 2004) adsorption of humic acid (HA) and fulvic acid (FA) extracted from three different organic manures namely biogas slurry (BGS), farmyard manure (FYM) and decomposed green manure (*Sesbania aculeata*)(GM) by two clay fractions (0.2-2 μ) and < 0.2 μ) from four different soils was studied before and after removing amorphous aluminosilicates by studying the respective adsorption isotherm fitted in Freundlich equation .

In the present investigation an attempt has been made to examine the effect of amorphous aluminosilicates, clay size fractions, type of soil and the type of manures as the source of humus

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on the extent of adsorption and decomposition rate of prepared humic and fulvic acid complex of clay by fitting humus decomposition data in first order equation.

Materials and Methods

Details of soil samples, humus extractions and preparation of clay –humus complex have been shown in another publication (Vennila and Datta 2004) The clay samples were fractionated into 0.2 - 2µ (coarse clay) and < 0.2 µ (fine clay) fractions by centrifugation at 12,000 rpm (= 17,000 g) for 10 minutes. Removal of amorphous aluminosilicates and its determination was done by the method of Fey and le Roux (1977). Clay minerals were identified and semi quantified by X-ray diffraction analysis (Datta and Satry 1993)

Incubation Study

The prepared clay-humus complex was incubated for thermal decomposition at 55 °C, which is sufficiently high to stop any microbial decomposition. Sampling was done at 10 days interval and organic carbon content was analyzed by using Tyurin's method (Kononova 1966). The experimental data of organic carbon was fitted to the first order exponential equation

$$C_t = C_o e^{-kt}$$

Where, C_t is the organic carbon of the sample at time t, C_o is the organic carbon content at the beginning of the incubation, k is the rate constant of decomposition. The rate constant was read off from the fitted equation.

For microbial decomposition study, the prepared clay-humus complex was incubated at 25 °C using fungal cultures Trichoderma receeii and Aspergillus awamori obtained from Indian Type Culture Collection (ITCC), Division of Mycology and Plant Pathology, IARI, New Delhi were. Rate constant of microbial decomposition was calculated similarly as in case of thermal decomposition.

Statistical Analysis

Analysis of variance were carried out on initial amount of adsorbed humus (Co) and rate constant of decomposition (k) as affected by the following four factors, viz. 1) Soil type 2) Clay size with or without Amorphous aluminosilicates 3) Source of humus and 4) Nature of humus. The levels were as follows:

(1) Soils with four levels from which clays have been separated for adsorption studies
  (i) Inceptisol (I)
  (ii) Mollisol (M)
  (iii) Vertisol (V)
  (iv) Alfisol (A)

(2) Clay size with or without amorphous aluminosilicates with four levels
  (i) Coarse clay with aluminosilicates (CCAA1)
  (ii) Coarse clay without aluminosilicates (CCAA0)
  (iii) Fine clay with aluminosilicates (FCAA1)
  (iv) Fine clay without aluminosilicates (FCAA0)

(3) Source of humus with three levels
  (i) Biogas slurry (BGS)
  (ii) Farmyard manure (FYM)
  (iii) Green manure compost (GMC)

(4i) Nature of humus
  (i) Humic acid (HA)
  (ii) Fulvic acid (FA)

Results and Discussions

Type of clay minerals and Amorphous Aluminosilicates (AAS) Present in the Clay Fractions

Clay minerals composition

Inceptisol was dominated by smectite both in coarse clay (41 %) as well as in fine clay (54

%)(Table 1) followed by mica and kaolinite. Vertisol was dominant in smectite in both the fraction and its smectite content was more than that of Inceptisol. Alfisol was dominant in kaolinite in both the fraction followed by mica. Mollisol however was dominant in mica in coarse clay fraction followed by kaolinite and chlorite whereas it was dominant in vermiculite (63 %)in fine clay fraction followed by small amount of

Decomposition of adsorbed humus from clay

Fig. 1 and Fig. 2 shows, respectively the thermal and microbial decomposition of adsorbed BGS-fulvic acid (in terms of % C) from a) coarse clay and b) fine clay both before and after removal of amorphous aluminosilicate. Fitted exponential equations with corresponding R^2 values have been shown in the figures. From R^2 values, it is clearly evident that carbon decomposition closely follows first-order reaction. For other soils and factors (figures are not shown) the same trend of decomposition curves has been obtained. From fitted equations, both initially adsorbed (Co) humus carbon (%) as well as the rate constant of decomposition, k has been recorded. Those values of C_0 given as H_{ad} averaged over a particular factor and the associated critical difference (CD values) at 1 % level have been shown in Tables 2. The main effect on rate constant, rc and associated CD values have been shown in Table 3. Table 4 shows the interaction effect on rate constant values. From the figures, visually it is very clear that amorphous aluminosilicate is mainly responsible for humus adsorption, removal of which greatly reduces the adsorption of humus on clay particle particularly on the fine clay fraction. The rate constant values also decrease with removal of amorphous materials. From tables 3 and 4, it is

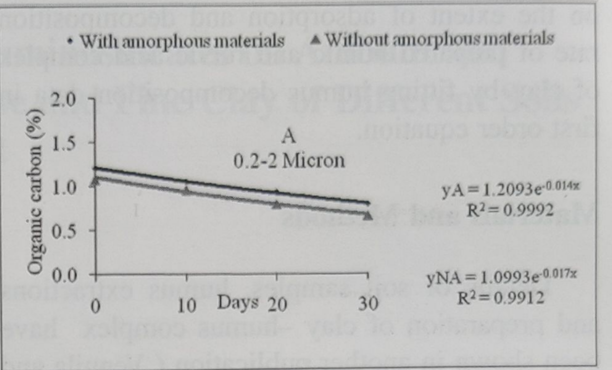

Fig. 1a

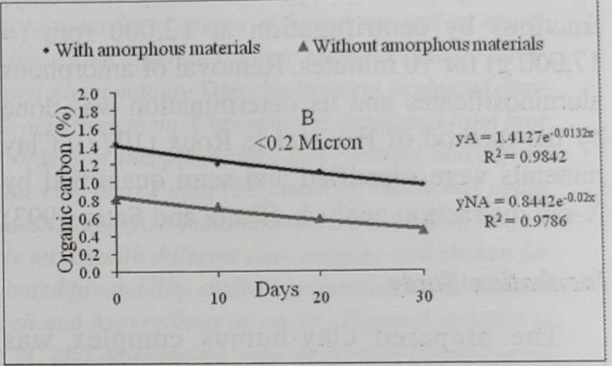

Fig. 1b

Fig 1. Thermal decomposition of adsorbed biogas slurry-fulvic acid on Inceptisol-clay with and without amorphous aluminosilicate, measured as changes in organic carbon (%) at 55°C. a. coarse clay, b) fine clay. Fitted equations of the curves are shown inside, YA=with amorphous material, YNA=without amorphous material

Table 1. Amorphous and crystalline components of clay fractions(%)

Soil type	0.2-2 μ clay					< 0.2 μ clay					
	AAS	Sm	Chl	Mica	Kao	AAS	Sm	Ver	Chl	Mica	Kao
Inceptisol	12	41	3	36	8	20	54	-	-	15	11
Mollisol	14	-	20	35	31	19	-	63	7	5	6
Vertisol	12	49	5	14	20	32	61		-	1	6
Alfisol	15	-	-	25	60	21			-	17	62

AAS=Amorphous aluminosilicate; Sm=Smectite;Chl=Chlorite; Kao=Kaolinite; Ver=Vermiculite

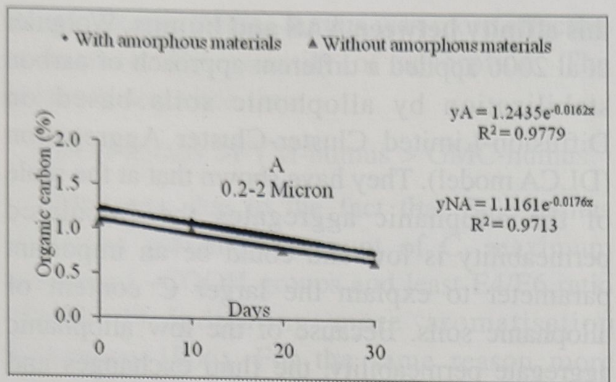

Fig. 1a

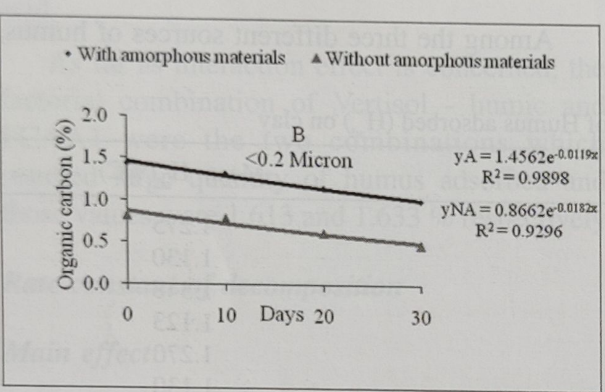

Fig. 1b

Fig 2. Microbial decomposition of adsorbed biogas slurry-fulvic acid on Inceptisol-clay with and without amorphous aluminosilicate, measured as changes in organic carbon (%) at 25°C. A. coarse clay , B)fine clay . Fitted equations of the curves are shown inside, YA=with amorphous material, YNA=without amorphous material

evident that the values of rate constant range from 0.012 d^{-1} to 0.023 d^{-1}. According to van veen and Paul (1981), native soil organic matter could be divided into three major fractions: the biomass, the decomposable organic matter comprising microbial products and the lignin fraction of litter and roots, and a recalcitrant fraction. The latter two fractions are affected by the physical and chemical protection. Protection leads to a decrease in the decomposition rate constant of the decomposable soil organic C fractions. For a model developed by them they have taken 0.08 d^{-1} as the rate constant of decomposable non-protected organic matter and 0.0008 as the rate constant of decomposable protected organic matter. Thus, the values of the rate constants we obtained in the present experiment lie in between these end values. Adsorbed humus is thus under partial protection from thermal and microbial decomposition. In this context it can be mentioned here that our experimental values are nearer to the decomposition rate constants of biomass, which is about 0.03 d^{-1} (van Veen and Paul 1981)

Factors affecting amount of humus adsorbed and their decomposition rate

Humus stabilization depend on both the amount of humus adsorbed as well as the resistance it shows against both thermal and microbial decomposition

Amount of humus adsorbed

Table 2 shows only the significant factorial effects including main and two factors interaction effect on the humus adsorbed (H_{ad}) and the critical differences at 1 % level. Among the four soils Vertisol-clay adsorbed maximum quantity (1.348 % C). The observed sequence on the basis of CD value was

Vertisol >Inceptisol >Mollisol=Alfisol

This was due to large quantity of smectite clay present in the Vertisol. As far as clay size and amorphous material is concerned, fine clay with amorphous aluminosilicate

(FCAA1) adsorbed maximum quantity of humus C (1.446 %). Removal of AAS from fine clay (FCAA0) drastically reduced its humus adsorption capacity. Similar is the case for coarse clay. The observed sequence was

FCAA1 > CCAA1 >CCAA0> FCAA0

This was because the content of AAS was more in fine clay than that of coarse clay (Table 3). Since fine clay has more surface area than coarse clay, it is expected that even after removal of AAS, fine clay with its higher surface area can hold more humus than that of coarse clay after removal of AAS. But it was found that FCAA0 adsorbed less humus than CCAA0. This shows that AAS was mainly responsible for humus adsorption. It is well known that in volcaninc ash derived soil, Andisol, a large amount of C is stabilized by allophane, which is amorphous aluminosilicate in nature (López-Ulloa *et al,* 2005). In the present experiment, it has also been found that AAS is largely responsible for soil carbon stabilization in non-volcanic soil. Similar results have also been obtained by Vennila and Datta (2004). To explain this a**ffinity between AAS and humus,** Woignier et al 2006 applied a different approach of carbon stabilization by allophonic soils based on Diffusion-Limited Cluster-Cluster Aggregation (DLCA model). They have shown that at the scale of the allophanic aggregates the calculated permeability is low and could be an important parameter to explain the larger C content of allophanic soils. Because of the low allophanic aggregate permeability, the fluid exchanges and chemical reactions are slow.

Among the three different sources of humus,

Table 2. Factorial effects and Critical difference for amount of Humus adsorbed (H_{ad}) on clay

Factorial Effect	Treatments	Mean H_{ad}(%C)
Soil Type	Inceptisol	1.275
CD(p<0.01)=0.041	Mollisol	1.130
	Vertisol	1.348
	Alfisol	1.123
Clay Type	CCAA1	1.270
CD(P<0.01)=0.041	CCAA0	1.130
	FCAA1	1.348
	FCAA0	1.123
Source of Humus	Bio-gas slurry	1.275
CD(p <0.01)=0.035	Farmyard Manure	1.221
	Green Manure Compost	1.162
Type of HumusCD(p<0.01)=0.029	Humic Acid	1.413
	Fulvic Acid	1.026
Inter action effect	Inceptisol-HA	1.482
Soil type × Humus type	Inceptisol-FA	1.068
CD(p<0.01)=0.058	Mollisol-HA	1.325
	Mollisol-FA	0.936
	Vertisol-HA	1.613
	Vertisol-FA	1.083
	Alfisol-HA	1.231
	Alfisol-FA	1.016
Inter action effect	CCAA1-HA	1.458
Clay type × Humus type	CCAA1-FA	1.082
CD(p<0.01)=0.058	CCAA0-HA	1.256
	CCAA0-FA	0.986
	FCAA1-HA	1.633
	FCAA1-FA	1.258
	FCAA0-HA	1.304
	FCAA0-FA	0.777

HA= Humic acid, FA=Fulvic acid ; CCAA1=Coarse clay with amorphousaluminosilicate,
CCAA0= Coarse clay without amorphousaluminosilicate,FCAA1= Coarse clay with amorphous aluminosilicate,
FCAA0= Fine clay without amorphous aluminosilicate,

Biogas slurry (BGS) –humus was more effective to increase the quantity of adsorption. The observed sequence was

BGS-humus >FYM-humus > GMC-humus

This was due to the fact that BGS-humus contained maximum amount of C, maximum number of –COOH groups and least E4/E6 ratio (Table 2) indicating more aromatisation Kononova 1966). For the same reason more amount of Humic acid was adsorbed than fulvic acid.

As far as interaction effect is concerned, the factorial combination of Vertisol - humic and FCAA1 were the two combinations which resulted large quantity of humus adsorbed and those values were 1.613 and 1.633 % respectively

Rate constant of decomposition

Main effect

Table 3 shows the main effects on the rate constants (rc) of microbial and thermal decomposition of adsorbed humus on clay. All the four factors affect significantly at 1 % level the rate of decomposition. For the three factors, viz., a) Clay type, b) source of humus and c) type of humus, both microbial decomposition at 25 °C and thermal decomposition at 55 °C followed almost the same sequence of rate constant. More the value of rate constant less is the stability. Thus with respect to stability the observed sequence was

a) Clay type

FCAA1>CCAA1 >CCAA0 > FCAA0

This shows that amorphous aluminosilicate imparts maximum stability against both microbial and thermal decomposition. This is in conformity with our finding in the last section that AAS is mainly responsible adsorption of large amount of humus.

b) Source of humus

The observed sequence was

BGS-humus >FYM-humus>GMC –humus

This was due to more number of –COOH groups and more aromatization of BGS-derived humus as stated earlier

Table 3. Main effect on rate constants (rc) of microbial and thermal decomposition of adsorbed humus on clay

Factors	Levels	Mean rc(d^{-1}) Microbial decomposition (25°C)	Mean rc (d^{-1}) Thermal decomposition (55°C)
Soil Type	Inceptisol	0.02	0.017
CD(p<0.01)=0.0014	Mollisol	0.018	0.018
	Vertisol	0.014	0.018
	Alfisol	0.017	0.015
Clay Type	Coarse ClayAA1*	0.016	0.015
CD(P<0.01)=0.0014	Coarse ClayAA0	0.018	0.018
	Fine ClayAA1	0.014	0.014
	Fine ClayAA0	0.022	0.022
Source of Humus	Bio-gas slurry	0.016	0.016
CD(p <0.01)=0.0014	Farmyard Manure	0.017	0.017
	Green Manure Compost	0.018	0.018
Type of Humus	Humic Acid	0.016	0.016
CD(p<0.01)=0.001	Fulvic Acid	0.018	0.018

*AA1= with amorphous aluminosilicate, AA0= without amorphous aluminosilicate

Table 4. Interaction effect on rate constant(rc) of decomposition of adsorbed humus

Microbial decomposition		**Thermal decomposition**	
Soil type × Humus type	Mean rc(d^{-1})	**Soil type × Humus type**	**Mean rc(d^{-1})**
CD(p<0.01)	**0.0016**	**CD(p<0.01)**	**0.002**
Inceptisol-HA*	0.022	Inceptisol-HA	0.016
Inceptisol-FA	0.018	Inceptisol-FA	0.019
Mollisol-HA	0.016	Mollisol-HA	0.020
Mollisol-FA	0.02	Mollisol-FA	0.017
Vertisol-HA	0.012	Vertisol-HA	0.018
Vertisol-FA	0.017	Vertisol-FA	0.018
Alfisol-HA	0.015	Alfisol-HA	0.012
Alfisol-FA	0.018	Alfisol-FA	0.017
Soil type × Humus source		**Soil type × Clay type**	
CD(p<0.01)	**0.002**	**CD(p<0.01)**	**0.003**
Inceptisol-BGS#	0.018	Inceptisol-CCAA1$	0.016
Inceptisol-FYM	0.02	Inceptisol-CCAA0	0.020
Inceptisol-GMC	0.022	Inceptisol-FCAA1	0.014
Mollisol-BGS	0.018	Inceptisol-FCAA0	0.020
Mollisol-FYM	0.018	Mollisol-CCAA1	0.017
Mollisol-GMC	0.019	Mollisol-CCAA0	0.019
Vertisol-BGS	0.014	Mollisol-FCAA1	0.015
Vertisol-FYM	0.014	Mollisol-FCAA0	0.024
Vertisol-GMC	0.014	Vertisol-CCAA1	0.017
Alfisol-BGS	0.015	Vertisol-CCAA0	0.018
Alfisol-FYM	0.016	Vertisol-FCAA1	0.015
Alfisol-GMC	0.019	Vertisol-FCAA0	0.022
		Alfisol-CCAA1	0.012
		Alfisol-CCAA0	0.015
		Alfisol-FCAA1	0.010
		Alfisol-FCAA0	0.022
		Clay type× Humus type	**0.002**
		CD(p<0.01)	
		CCAA1-HA	0.015
		CCAA1-FA	0.016
		CCAA0-HA	0.017
		CCAA0-FA	0.019
		FCAA1-HA	0.014
		FCAA1-FA	0.013
		FCAA0-HA	0.020
		FCA0-FA	0.023

*HA= Humic acid, FA=Fulvic acid ; #BGS=Biogas slurry,FYM=Farmyard manure GMC=Green manure compost;$CCAA1=Coarse clay with amorphousaluminosilicate, CCAA0= Coarse clay without amorphousaluminosilicate,FCAA1= Coarse clay with amorphous aluminosilicate, FCAA0= Fine clay without amorphous aluminosilicate,

c) Type of humus: Between two types of humus viz. a) Humic acid and b) Fulvic acid, the former made more stable complex with clay against both microbial and thermal decomposition with significantly smaller values of rate constant.

However, as far as the factor soil type was concerned, different sequences were observed with respect to thermal and microbial decomposition.

For stability against microbial decomposition, the observed sequence was

Vertisol-clay > Alfisol-clay = Mollisol-clay > Inceptisol-clay

Whereas for thermal decomposition, the stability sequence was

Alfisol-clay> Inceptisol-clay= Vertisol – clay=Mollisol-clay

Interaction effects

Table 4 shows significant two factor interaction effects on rate constant of both microbial as well as thermal decomposition. For microbial decomposition only two interaction effects were significant i.e., a) Soil type × Humus type and b) Soil type × Humus source. For thermal decomposition, three interaction effects were significant, i.e., a) Soil type × Humus type b) Soil type ´Clay type and c) Clay type × Humus type. Among these interaction effects, the Vertisol-HA combination resulted maximum stability (0.012 d^{-1}) against microbial decomposition and Alfisol-HA resulted maximum stability (rate constant 0.01 d^{-1}) against thermal dcomposition

Conclusion

On the basis of the above studies it can be concluded that amorphous aluminosilicate and biogas slurry derived humus are two important components to result maximum stability of adsorbed humus against both thermal and microbial decomposition.

References

Datta, S.C. and Sastry, T.G. 1993. Potassium release in relation to mineralogy of silt and clays. *J. Indian Soc. Soil Sci.* 41 : 452.

Fey, M.V. and le Roux, J. 1977. Properties and quantitative estimation of poorly crystalline components in sesquioxide soil clays *Clays Clay Min.* **25:** 285-294.

Kononova, M.M. 1966. *Soil organic matter, its nature, its role in soil formation and in soil fertility* (2nd ed.). Pergamon Press Ltd., London. p. 544

López-Ulloa, M, Veldkamp, E and de Koning, G. H. J. 2005. Soil Carbon Stabilization in Converted Tropical Pastures and Forests Depends on *Soil Type Soil Sci Soc Am J.* 69 : 1110-1117.

van Veen, J.A. and Paul, E.A. 1981. Organic carbon dynamics in grassland soils. I. Background information and computer simulation *Canadian J Soil Sci.* **61**: 185-201

Vennila, A. and Datta, S.C. 2004. Adsorption of Humic and fulvic acid from different sources on soil clay as affected by amorphous aluminosilicate content, size of clay fraction and soil types. *Caly Research.* 23(1&2), 9-20.

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Grim, R.E., Bray, R.H. and Bradley, W.R. 1937. The mica in argillaceous sediments. *Am. Miner.* **22**:813-829.

Brindley, G.W. 1961. Chlorite minerals. In *(G. Brown,* Ed.) *The X-ray Identification and Crystal Structures of Clay Minerals,* Mineralogical Society, London, pp.242-296.

Theng, B.K.G. 1974. *The Chemistry of Clay Organic Reactions,* Adam. Hilger, London, 343 pp.

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