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2nd Prof. S.K.Mukherjee CMSI Foundation Lecture

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Soil Modifiers: Their Advantages and Challenges

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I am immensely honoured by the invitation of the Clay Minerals Society of India (CMSI) to deliver the 2nd Prof. S.K.Mukherjee CMSI Foundation Lecture during its 18th Annual Convention. I get an opportunity to pay my humble tribute to late Prof. S.K.Mukherjee whom I admired most as a brilliant teacher, researcher, educationist and a great human being. Prof. S. K. Mukherjee as Acharya P. C. Ray Professor of Agricultural Chemistry, drew many among us in late 1960s who just completed graduation in science with chemistry, to the fascinating world of soils, saying ' **young person, soil research can offer you more than a lifetime of fascinating problems to unravel**.'

After unraveling some enigmatic problem in soils and soil minerals for the last three and a half decade a realization came to my mind that we have not talked and written enough about other minerals in soils that change the pedo-chemical environment of soils, which is essential for better soil use and management. Therefore I have chosen a topic mainly on non-clay minerals that are termed as 'Soil Modifiers'. Making such exercise is warranted especially when we are very concerned about linking pedology and edaphology for making judgments for the best and pragmatic land use planning.

Since the beginning of the 1990 the presence of soil modifiers such as gypsum, calcium carbonate, palygorskite and zeolites, is being adequately reported in soils by the researchers of the NBSS&LUP, Nagpur (ICAR). This presentation is a review of the published literature that may help understand the unique role of soil modifiers in fine-tuning the exiting soil classification scheme and also the management practices to enhance and sustain the productivity of Indian soils. The presentation has been organized in the following themes.

- Gypsum: Definition of saline-sodic soils
- Gypsum: Preventer of sodicity in Vertisols of SAT environment
- Calcium Carbonates: Resilience of sodic soils
- Calcium Carbonate: Soil sustainability
- Palygorskite: Drainage of Vertisols
- Ca-Zeolites: Tropical soil formation

- Mitigation of adverse Holocene climate change in zeolitic Vertisols
- Zeolites in redefining sodic soils
- Zeolites sustain rice productivity on Vertisols
- Zeolites on adsorption and desorption of major soil nutrients
- Concluding remarks

Gypsum: Definition of Saline-Sodic soils

By definition saline-alkali soils are those whose pH seldom crosses 8.5, but have ECe (electrical conductivity of the saturation extract) > 4 m mhos/cm and ESP (exchangeable sodium percentage) > 15 (Richards, 1954). Soluble salts of these soils under leaching with water with low Ca^{2+} ions turn out to be alkali (Richards, 1954). However, limited experimental evidence indicate that when leached such soils in the N-W parts of the IGP (Indo-Gangetic Alluvial Plains) do not turn out to be more sodic; rather their ESP is reduced (Leffelaar and Sharma, 1977; Abrol and Bhumbla, 1978). Obviously during leaching such soils exhibit better drainage. Based on limited experimental details Abrol and Bhumbla (1978) argued that the usually recognized two categories of salt-affected soils 'saline' and 'saline-sodic' are no different from each other and that both should be categorized as 'saline' because in such soils plant growth is not adversely affected by the excess ESP or the soil physical properties or lack of Ca^{2+} ions. However, few questions are still remained unanswered. (a) How in saline-sodic environment soils get recharged with Ca^{2+} ions during leaching? (b) and what is the source of Ca^{2+} ions especially when the formation of $CaCO_3$ under semi-arid climate is a natural degradation process which exhibits regressive pedogenesis to immobilize both Ca^{2+} ions and inorganic carbon (Pal *et al.*, 2013a)?

Reduction of ESP can be caused only through the increased solubilities of naturally present $CaCO_3$ and gypsum (Dieleman, 1963). Saline-sodic soils are calcareous and have pH values > 8.0 and in this alkaline soil reaction displacement of exchangeable Na by Ca^{2+} from $CaCO_3$ is of doubtful significance (Yaalon, 1958). Only option left is the presence of gypsum in such soils, otherwise reduction in ESP during leaching cannot be explained scientifically. However, neither the field examination nor laboratory data show the presence of gypsum (Goyal *et al.*, 1974) despite the fact Ca^{2+} and Mg^{2+} ions constitute as subdominant cations in soil saturation extract in alkaline environment (pH- 8.0) and as dominant proportions in soluble cations in irrigation water alongside dominant amount of CO_3 and HCO_3 ions (Leffelaar and Sharma, 1977). This chemical environment strongly suggests the probable presence of gypsum in soil parent materials. It is evidenced in the occurrence of 'real' saline-sodic soils (having reduced water transmission rate) in the N-W parts (Sharma and Mondal, 1981) as well as lower parts of the Gangetic alluvium (Pal *et al.*, 2010) when they are irrigated with highly sodic waters and rain water, respectively.

Generally in the IGP soils, Na and Mg dominate on the soil exchange complex and Na is the dominant cation and Cl the dominant anion in the saturation extract. In contrast in Gypsic Vertisols (Pal *et al*., 2003), Ca^{2+} and Mg^{2+} are the dominant cations on exchange complex whereas in saturation extract Ca^{2+} ion is more than Mg and Na and SO_4 is more than Cl and CO_3. Base saturation (BS) exceeds 100. These are better drained soils as indicated by the saturated hydraulic conductivity (sHC), which is >> 20 mm/ hr. Therefore, the few chemical analyses are of mandatory requirements to define saline-sodic soils. They are (i) SO_4 content of the saturation extract of soils; it may be more than Cl ions in gypsic soils (Pal *et al*., 2003), (ii) BS of soils to check if it exceeds more than 100; gypsic soils have BS > 100 (Pal *et al*., 2003), (iii) sHC of soils to check if it is high; gypsic soils show very high sHC(>> 20mm/hr, Pal *et al*., 2003) and (iv) finally the gypsum content of soils.

With the above data base 'saline-sodic soils' with gypsum can be finally designated by 'saline soils'. This offers a challenge to pedologists especially to the soil mappers for an appropriate mapping unit required for pragmatic soil management.

Gypsum: Preventer of Sodicity in Vertisols of SAT Environment

Under rain-fed situation, continuous efforts to grow cotton, pigeon pea and sorghum in Gypsic Vertisols of semi-arid parts of southern India indicate no development of sodicity (ESP < 5) in the profile despite the rapid formation of $CaCO_3$, due to favourable solubility of gypsum (Pal *et al*., 2009). At present gypsum helps to mitigate the adverse effect of climate change from humid to semi-arid during the Holocene. The present sustainability of crop productivity in such soils would however be further improved by using good quality irrigation water so long gypsum remains available with time. In absence of gypsum these soils would lose sustainability as they would turn out to be sodic with poor sHC. Therefore, proper classification of these soils at the subgroup level like 'Gypsic' would be necessary for their better management (Pal *et al*., 2003).

Calcium Carbonates: Resilience of Sodic Soils

The adverse arid and semi-arid climatic conditions induce precipitation of $CaCO_3$ with a concomitant development of sodicity in the subsoils (Pal *et al*., 2000). The subsoil sodicity impairs the sHC of soils. However, such soils show enough resilience under the improved management.

Calcium carbonates make IGP sodic soils resilient: After reclamation with gypsum some sodic soils of the N-W parts of the IGP (Sakit and Zarifa Viran) classified earlier as Natrustalfs, now are better drained and OC (organic carbon) enriched Haplustalfs. Generally gypsum as amendment is added in much less amount than estimated by 'Gypsum Requirement'. Thus the success of this reclamation protocol is not all due to gypsum added because it does not enrich soil solution by excess Ca^{2+} ions after replacing Na ions on the soil exchange sites. This change has been mainly facilitated by a rapid dissolution of the native pedogenic $CaCO_3$ (PC). The rate of dissolution of PC during 30 months' cultural practice with gypsum in Zarifa Viran soils (Natrustalfs) has been estimated to be 254 mg/100g soil in the top 1m of the profile. This indicates a much higher rate (~ 100 mg/100g soil/year) (Pal *et al*., 2009) than its rate of formation (0.86 mg/100g soil/year) in the top 1m profile (Pal *et al*., 2000).

Calcium carbonates make sodic Vertisols resilient: Non-zeolitic and non-gypsic Vertisols (Sodic Haplusterts) under SAT environment show poor sHC even at ESP $\geq 5 < 15$, and have poor crop productivity, and are impoverished in OC but rich in $CaCO_3$. Such soils show enough resilience under improved management (IM) system of the ICRISAT (International Crops Research Institute for Semi-Arid Tropics) (Wani *et al*., 2003) that does not include any amendment like gypsum and FYM. The average grain yield of the IM system over thirty years was five times more than that in the traditional management (TM) system. Adaptation of the IM system improved physical, chemical and biological properties of soils to the extent that Sodic Haplusterts now qualify for Typic Haplusterts. Constant release of higher amount of Ca^{2+} ions during the dissolution of $CaCO_3$ (8.4 mg/100g soil/year in 1m profile) under the IM system, compared to slower rate of formation of $CaCO_3$ (0.10 mg/100g soil/year in 1m profile), provided soluble Ca^{2+} ions enough to replace unfavourable Na^+ ions on the soil exchange sites. Higher exchangeable Ca/Mg ratio in soils under IM system improved the sHC for better storage and release of soil water during dry spell between rains. Adequate supply of soil water helped in better crop productivity and higher organic OC sequestration. The improvement in Vertisols' sustainability suggests that the IM system is capable of mitigating the adverse effect of climate change (Pal *et al*., 2012a).

Calcium Carbonate: Soil sustainability

Both IGP soils and Vertisols have substantial stock of $CaCO_3$ (SIC) in the first 1.5 m depth, which remains as a hidden treasure that can help improve the drainage, establishment of vegetation, and also sequestration of OC in soils (Bhattacharyya *et a*l., 2004). The continuance of agronomic practices of the NARS (National Agricultural Research Systems) and ICRISAT can provide the most important Ca^{2+} ions both in solution and exchange sites of soil. These resilient soils still contain nearly 2-7 % $CaCO_3$. In view of the rate of its dissolution (~ 100 mg/100g soil/year for IGP soils, and 21 mg/100g soil/year for Vertisols, Pal *et al*., 2011, 2012a), it is envisaged that under SAT environment, total dissolution of $CaCO_3$ would take a time of couple of centuries. Such chemical environment would not allow both Haplustalfs and Haplusterts to transform to any other soil order so long $CaCO_3$ would continue to act as a soil modifier (Pal *et al.*, 2011, 2012b).

Palygorskite: Drainage of Vertisols

The dispersibility of clay colloids impairing the sHC of Vertisols is generally an effect of ESP and EMP (exchangeable magnesium percentage) in the presence or absence of soil modifiers. But few zeolitic Vertisols of Maharashtra in SAT western India show sHC < 10 mm /hr., although the soils are non-sodic (Typic Haplusterts, Pal *et al*., 2012a,b). Such Vertisols have neutral to mildly alkaline pH, ESP < 5, but EMP increases with depth. In some soils EMP is greater than ECP (exchangeable calcium percentage) at depth below 50 cm. Silt and coarse-clay fractions contain palygorskite. This mineral is the most Mg-rich of the common clay minerals and its fibre does not associate into aggregate in soils and suspensions even when the soils are saturated with Ca^{2+} ions. Thus palygorskite particles move downward in the profile preferentially over smectite and eventually clog the soil pores (Newman and Singer, 2004). Therefore, Vertisols with this mineral have high EMP values, causing dispersion of clay colloids. This interaction causes drainage problems when such soils are irrigated, presenting a predicament for crop production. In view of their poor drainage conditions and loss of productivity, non-sodic Vertisols (Typic Haplusterts) with palygorskite must be considered naturally degraded soils. Thus a new initiative is warranted to classify them.

Ca-Zeolites: Tropical Soil Formation

Mollisols, Alfisols, and Vertisols are the members of Mollisols-Alfisols-Vertisols association on the zeolitic Deccan basalt areas in HT (humid tropical) climate and are persisting since the early Tertiary. The transformation of smectite (the first weathering product of the Deccan basalt), to kaolin (KI-HIS, kaolinite-hydroxy-interlayered smectite) during HT weathering began at the end of the Cretaceous and continued during the Tertiary. With a combination of high temperature and adequate moisture, the HT climate of the Western Ghats and Satpura Range provided a weathering environment that should have nullified the effect of parent rock composition in millions of years, resulting in kaolinitic and/or oxidic mineral assemblages consistent with either residua and haplosoil models of tropical soil formation (Chesworth, 1973, 1980) like in Ultisols and Oxisols (Bhattacharyya *et al.*, 1993, 1999, 2006). Instead the soils of the zeolitic Deccan basalt have KI-HIS and represent Mollisols, Alfisols and Vertisols. Therefore, the formation and persistence of Mollisols, Alfisols and Vertisols provide an example that in an open system such as soil, the existence of a steady state is a useful concept, and Jenny's state factor equation is also essentially valid. The knowledge gained on the role of zeolites in the persistence of soils not only provides a deductive check on the inductive reasoning on the formation of soil in the HT climate, but also throws light on the role of these minerals in preventing loss of soil productivity even in an intense leaching environment.

Mitigation of Adverse Holocene Climate Change in Zeolitic Vertisols

Many productive Vertisols (Typic Haplusterts) under rain-fed conditions have been rendered unproductive for agriculture under irrigated conditions in the longer-term. However, some zeolitic Vertisols (Typic Haplusterts) of the semi-arid moist parts of western India is under irrigated sugarcane production for the last twenty years. These soils lack salt-efflorescence on the surface; and are not waterlogged at present, suggesting that these soils are not degraded due to their better drainage. However, these soils are now Sodic Haplusterts in view of their pH, ECe and ESP values, but their sHC > 10 mm hr^{-1} .Continuous supply of Ca^{2+} ions from Ca-zeolites in these soils helps maintain a better drainage system. In view of the present good agricultural practices these soils show potentiality to mitigate the adverse effect of climate. However, the sustainability of crop productivity in the dry climate depends on the solubility and supply of Ca^{2+} ions from zeolites seems sufficient to overcome the ill effects of the pedogenic threshold of dry climates. Such situations are unique in nature; but predicting a time scale when these soils will run out of zeolites is difficult unless a new research initiative in this direction is taken up.

Zeolites in Redefining Sodic Soils

Naturally-occurring zeolites in some soils of sub-humid, semi-arid and arid climates showing high ESP (>15) avoided a rise in pH, but favoured an increase in exchangeable Ca/Mg, and hydraulic properties. Therefore, fixing a lower limit either of ESP 5 – 15 (Pal *et al*. 2003) or at ESP >15 for sodic shrink–swell soils may have no practical relevance to their use and management. Because, sodic Vertisols with zeolites as modifiers indicate that despite having high ESP, these soils support rain-fed crops. Therefore, fixing a lower limit for sodic subgroup of Vertisols either at ESP 5–15 or at ESP >15 may not reflect the impairment of drainage of soils. In view of the pedogenetic processes that ultimately impair the drainage of soils, evaluation of Vertisols for deep-rooted crops on the basis of sHC alone showed that an optimum yield of cotton on Vertisols of semi-arid part of Central India can be obtained when the soils are non-sodic (ESP < 5) and have sHC≥ 20 mm h^{-1}. It is reported that 50% reduction in yield in the sodic (ESP > 5) soils with sHC <10mm h^{-1}. This shows that sHC as a single parameter can indicate dispersibility, the most influencing factor of soil sodicity

(Kadu *et al.*, 2003). Therefore, characterization of soil sodicity on the basis of sHC alone appears to be an incontrovertible parameter as compared to ESP or SAR (sodium absorption ratio); and thus Pal *et al.* (2006) advocated a value of sHC < 10 mm h^{-1} in distilled water (weighted mean in 0–100 cm depth of soil) for defining a sodic soil.

Zeolites Sustain Rice Productivity on Vertisols

In semi-arid western India (< 1000 mm mean annual rainfall, MAR), sugarcane and rice are grown under irrigated conditions whereas rice is grown under rain-fed conditions in areas of sub-humid moist climatic conditions of central India (with MAR >1400 mm). The sHC decreases rapidly with depth in Vertisols, but the decrease is sharper in non-zeolitic Sodic Haplusterts; and the weighted mean of sHC in 0-100 cm depth is < 10 mm h^{-1}. In non-zeolitic Typic Haplusterts, the sHC is > 10 mm h^{-1}, and in zeolitic Typic Haplusterts it is > 20 mm h^{-1}, and these soils (Kheri soils at Jabalpur, and Sakka soils at Dindori, of Madhya Pradesh), are cultivated to rice as rain-fed crop in areas with $\geq$ 1400 mm MAR. Interestingly, zeolitic Sodic Haplusterts (Teligi soils at Bellary of Karnataka, in areas with < 700 mm MAR also have sHC > 20 mm h^{-1}); and these soils are cultivated to rice under canal irrigation. The enhanced sHC (>20 mm h^{-1}) in zeolitic Vertisols due to the presence of zeolite appears to be just adequate for the period of submergence required for the rice crop, and post-rainy season crops are successfully grown with good yields. Morphological examination of such soils showed no sign of gleyed horizons and soil moisture regime does not reach aquic conditions (Pal *et a*l., 2013b). Such situations are unique in nature and pose a great challenge to the soil mappers to classify them as per the US Soil Taxonomy as they have good productive potential despite being sodic in nature. Sustainability of rice cropping system in such soils will, however, depend on rate of dissolution of Ca-zeolite on a time scale, and a new research initiative on this topic is warranted.

Zeolites on Adsorption and Desorption of Major Soil Nutrients

Organic carbon: In semi-arid dry region of India zeolitic Vertisols (Teligi soils at Bellary of Karnataka; Jhalipura soils at Kota of Rajasthan and Jajapur at Mehboobnagar, of Andhra Pradesh), under wetland rice-rice/rice-wheat system have a tendency to show wider C/N ratio, indicating enough potential to sequester atmospheric carbon. This suggests that the presence of zeolites could be beneficial for soil organic matter conservation under global warming (Pal *et al.*, 2013b).

Nitrogen: Zeolites have the ability to protect NH_4^+ on zeolite exchange sites from microbial conversion of NH_4^+ to NO_3^- because nitrifying bacteria are too large to fit into the channels and cages within zeolite structure where NH_4^+ resides on exchange sites (Pal *et al.*, 2013b). This way the protection of NH_4^+ suggests that emission of N_2O from FYM and inorganic N fertilizers would amount to a small fraction of the total world greenhouse gas emission from zeolitic soils because out of 500,000 km² Deccan basalt areas in the Indian sub-continent, zeolitic soils is expected to cover a considerable area. However, a map showing areas under zeolitic soils is awaited. Such basic understanding is essential to include fixed NH_4-N for assessing the potentiality of N available in zeolitic soils especially as N_2O emission from Indian agricultural soils is a small fraction (about 1%) of the global warming caused by CO_2 emissions (Bhatia *et al.*,2004, 2012).

Potassium desorption: Mollisols, Alfisols and Vertisols developed on the zeolitic Deccan basalt or in its alluvium, are stated to be adequately supplied with K, and therefore, responses to applied K are not generally obtained. These soils have high to very high available K status even in the sub-surface; although they are not micaceous like the soils of the IGP. The apparent incompatibility between medium to high available K status in surface horizons (≥250 kg K ha^{-1}) and low in biotite mica in soils of the Deccan basalt areas needs further insight in view of pronounced selectivity of zeolites for K^+ and NH_4^+ ions. Extractable K (available K) is generally determined by extracting with 1 N ammonium acetate (NH_4OAc) solution (pH 7). Zeolites can contribute K in addition to K on the soil exchange sites as they have pronounced selectivity also for NH_4^+ ion (Pal *et al.*, 2013b).

Potassium adsorption: K adsorption/fixation in Vertisols does not appear to be sufficiently severe to conclude that K becomes unavailable to plants. The observed moderate amount of K adsorption in the Vertisol has been attributed to the presence of vermiculite because fine clay smectites (low-charge dioctahedral type) do not have any K selectivity. However, in the presence of zeolites K adsorption should not be totally attributed to vermiculite as zeolites also have strong selectivity for K^+ ion. In view of the role of zeolites in adsorption and desorption of K^+ and NH_4^+ ions alongside vermiculite, a fresh research initiative is warranted to pinpoint the selective contribution of zeolite, biotite and vermiculite on a time scale when they co-exist in soil environments (Pal *et al.*, 2013b).

Concluding Remarks

- This review on data from limited locations highlights the unique role of modifiers in soil environments.
- To record such roles fresh initiative of the pedologists is earnestly solicited.
- To keep the required balance between exchangeable and water soluble Ca^{2+} ions in soil systems becomes a challenge for land resource managers to maintain soil health.

- This way probably sustained crop productivity even under different soil environmental and climatic conditions seems to be attainable.

References

Abrol, I.P. and Bhumbla, D.R. 1978. Some comments on terminology relating to salt-affected soils. In: Proc. Dryland-Saline-Seep Control, 11th Int. Congr. Soil Sci., Edmonton, Canada, June 1978, pp. 6-19 and 6-27.

Bhatia, A., Pathak, H. and Aggarwal, P.2004. Inventory of methane and nitrous oxide emissions from agricultural soils of India and their global warming potential. *Curr. Sci.,* 87: 317–324.

Bhatia, A., Aggarwal, P. K., Jain, N. and Pathak, H. 2012. Greenhouse gas emission from rice–wheat growing areas in India: spatial analysis and upscaling. *Greenhouse Gases: Sci. Technol.,* **2**: 115–125.

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., Pal, D.K., Chandran, P., Mandal, C., Ray, S.K., Gupta, R.K. and Gajbhiye, S.K. 2004. Managing soil carbon stocks in the Indo-Gangetic Plains, India, Rice-Wheat Consortium for the Indo-Gangetic Plains, New Delhi, p.44.

Bhattacharyya, T., Pal, D.K., Lal, S., Chandran, P. and Ray, S.K. 2006. Formation and persistence of Mollisols on zeolitic Deccan basalt of humid tropical India. *Geoderma,* **146:** 609-620.

Chesworth, W.1973. The parent rock effect in the genesis of soil. *Geoderma,* **10:** 215–225.

Chesworth, W. 1980. The haplosoil system. *Am. J. Sci*., **280**: 969– 985.

Dieleman, P.J. 1963. Reclamation of salt-affected soils in Iraq. Inst. Land Reclamation and Improvement. ILRI Pub. 11, Wageningen.

Goyal, V.P., Ahuja, R.L., Bhandrai, R.C., Siyag, R.S. and Sharma, A.P. 1974. Deatiled Soil Survey of Government Agricultural Farm Hansi and Its Adjoining Areas. Haryana Agricultural University, Hissar, India, 83pp.

Kadu, P. R., Vaidya, P. H., Balpande, S. S., Satyavathi, P. L. A. and Pal, D. K. 2003. Use of hydraulic conductivity to evaluate the suitability of Vertisols for deep rooted crops in semi-arid parts of Central India. *Soil Use & Managnt.*, **19**: 208-216.

Leffelaar, P. A. and Sharma, R. 1977. Leaching of a highly saline-sodic soil. *J.Hydrol,* **32**: 203-218.

Neaman, A., Singer, A. and Stahr, K. 1999. Clay mineralogy as affecting disaggregation in some palygorskite-containing soils of the Jordan and Bet-She'an Valleys. *Austr. J. of Soil Res.*, **37:** 913–928.

Pal, D. K., Dasog, G. S., Vadivelu, S., Ahuja, R. L. and Bhattacharyya, T. 2000. Secondary calcium carbonate in soils of arid and semi-arid regions of India. In: (R. Lal, J.M. Kimble, H. Eswaran, and B.A. Stewart, Eds), *Global Climate Change and Pedogenic Carbonates*, Lewis Publishers, Boca Raton, Fl, pp.149-185.

Pal, D. K., Bhattacharyya, T., Ray, S. K. and Bhuse, S. R. 2003. Developing a model on the formation and resilience of naturally degraded black soils of the Peninsular India as a decision support system for better land use planning. NRDMS, DST Project Report, NBSSLUP (ICAR), Nagpur, 144p.

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., Bhattacharyya, T., Chandran, P. and Ray, S. K. 2009. Tectonics-climate-linked natural soil degradation and its impact in rainfed agriculture: Indian experience. In: (S.P. Wani, J. Rockstrom, and T. Oweis, Eds), Rainfed Agriculture: Unlocking the Potential, CABI International, Oxfordshire, U.K., pp.54-72.

Pal, D.K., Lal, Sohan, Bhattacharyya, T., Chandran, P., Ray, S.K., Satyavathi, P.L.A., Raja, P., Maurya, U.K., Durge, S.L., Kamble, G.K., 2010. Pedogenic thresholds in benchmark soils under rice-wheat cropping system in a climosequence of the Indo-Gangetic alluvial plains. Final Project Report, Division of Soil Resource Studies, NBSS&LUP (ICAR), Nagpur. 193 pp.

Pal, D. K., Bhattacharyya, T. and Wani, S. P. 2011. Formation and management of cracking clay soils (Vertisols) to enhance crop productivity: Indian Experience. In: (Lal, R. and Stewart, B.A. Eds), *World Soil Resources*, Francis and Taylor, pp.317-343.

Pal, D. K., Wani, S. P. and Sahrawat, K. L. 2012a. Role of calcium carbonate minerals in improving sustainability of degraded cracking clay soils (Sodic Haplusterts) by improved management: an appraisal of results from the semi-arid zones of India. *Clay Res.*, **31**: 94-108.

Pal, D. K., Wani, S. P. and Sahrawat, K.L. 2012b. Vertisols of tropical Indian environments: Pedology and edaphology. *Geoderma*, **189-190**: 28-49.

Pal, D. K., Sarkar, D., Bhattacharyya, T., Datta, S.C., Chandran, P. and Ray, S.K. 2013a. Impact of climate change in soils of semi-arid tropics (SAT). In: (T. Bhattacharyya, D.K. Pal, D. Sarkar and S.P. Wani, Eds.), *Climate Change and Agriculture*. Studium Press , New Delhi, pp.113-121.

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

Richards, L.A. (Ed.), 1954. *Diagnosis and improvement of saline and alkali soils*, USDA

Agricultural Handbook, vol. 60. US Government Printing Office, Washington, DC.

Sharma, D.R. and Mondal, R.C. 1981. Case study on sodic hazard of irrigation warers. *J. Indian Soc. Soil Sci.*, **29**:270-273.

Wani, S. P., Pathak, P., Jangawad, L. S., Eswaran, H. and Singh, P. 2003. Improved management of Vertisols in the semi-arid tropics for increased productivity and soil carbon sequestration. *Soil Use & Managt.*, **19**:217-222.

Yaalon, D.H. 1958.Studies on the effect of saline irrigation water on calcareous soils.II. The behavior of calcium carbonate. Bull. Council Irs. **7G**: 115-122.

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Using Nanoclay Polymer Composite for Efficient Delivery of N and P to Pearl Millet Grown in a Smectite Dominant Soil in a Green House Experiment

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Abstract : *The hypothesis is that the exfoliated and dispersed nanoclay in the superabsorbent polymer matrix controls the rate of diffusion of ions /molecules out of absorbed water by the polymer matrix. The objective of the study was to assess the P and N release from fertilizer loaded nanoclay superabsorbent polymer composite (NCPC) and to test its potential as a carrier of slow release fertilizer in synchronization of plant's demand using pearl millet (Pennisetum glaucum) as a test crop. In general, availability of Olsen P, 0.01M $CaCl_2$-extractable P and total mineral N in soils significantly enhanced on application of fertilizer loaded NCPC over conventional fertilizer (CF), at the same fertilizer dose. Further, nutrients availability in soils receiving low dose of fertilizer (LDF) as NCPC (NCPC-L) was statistically at par with that of high dose of fertilizer (HDF) as CF (CF-H), particularly at critical crop growth stages. At HDF, NCPC addition (NCPC-H) registered 65% additional biomass yield and 52 and 42% additional N and P uptake by pearl millet over CF (CF-H), respectively. Similarly, at LDF, biomass yield, N and P uptake increased to 59, 41 and 40%, respectively, under NCPC (NCPC-L) treated soils than that in CF (CF-L) treated soil. Different non-labile pools of inorganic P fractions increased significantly under CF application as compared to NCPC application, irrespective of fertilizer doses.*

Key words: Nanoclay superabsorbent polymer composite (NCPC), slow release fertilizer, pearl millet, P and N uptake

The utilization efficiency of N is about 30-40% (Ladha *et al.*, 2005) owing to surface runoff, leaching, and volatilization losses. P use efficiency is about 15-25% (Malhi *et al.*, 2002) due to conversion of water-soluble P into water-insoluble P after reaction with soil minerals and subsequent decrease of P availability. These low use efficiencies causes large economic and resource losses and results in very serious

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***Corresponding author:** S. C. Datta (E - mail: samar1953@yahoo.com) environmental problems (Al-Zahrani, 2000). Amongst the various technological options available, slow- or controlled release fertilizers technologies such as nanoclay superabsorbent polymer composite have shown its potential in enhancing nutrient use efficiency by reducing nutrient losses. The hypothesis is that the exfoliated and dispersed nanoclay in the superabsorbent polymer matrix controls the rate of diffusion of ions / molecules out of absorbed water by the polymer matrix.

Superabsorbents are three-dimensionally crosslinked hydrophilic polymers that are water insoluble, hydrogel forming, and capable of absorbing large amounts of aqueous fluids. Effectiveness of superabsorbent polymers (SAP) in agriculture to improve soil moisture retention capacity and improving plant growth has been assessed in several investigations (Anupama *et al*., 2007; Singh *et al*., 2011). Recently, research efforts focused on incorporating fertilizers in to superabsorbent polymeric networks to supply water and nutrients simultaneously (Liang *et al*., 2007; Zhong *et al*., 2013). However, these superabsorbents are based on pure polymer, and so they were too expensive and not suitable for saline water and soils (Mohan *et al*., 2005). When nutrients are loaded into a hydrogel, they are released quickly with high permeability. So, research on the preparation of supersorbent materials with good physical strength and nutrient-holding capacities was initiated. Among the various methods used, the introduction of inorganic clay, such as kaolin (Liang and Liu, 2007), montmorillonite (Lee *et al*., 2004), Attapulgite (Li *et al*., 2004), mica (Lin *et al*., 2001) into a pure polymeric network is a good method for reducing production costs and improving the swelling properties and hydrogel strengths. Moreover, it was reported that kaolin nanopowder incorporation into a superabsorbent polymeric network can decrease the diffusion coefficient of urea release from urea-loaded composite hydrogels (Liang and Liu, 2007). Our previous study (Sarkar *et al*., 2014) also indicated that incorporation of nanosized clay into superabsorbent polymer network decrease the rate of nutrient release from fertilizer loaded nanoclay superabsorbent polymer composites (NCPC) in distilled water. The research work on effectiveness of nanoclay superabsorbent polymer composites as a slow release fertilizer is still in a developing stage and need to be studied thoroughly. Therefore, the objectives of the present article were to assess the P and N release behaviour from fertilizer loaded nanoclay superabsorbent polymer composite (NCPC) in comparison with conventional fertilizer (CF) using pearl millet as a test crop.

Materials and methods

Synthesis of fertilizer loaded NCPC

Smectite dominated nanoclay was separated from soil (Vertisols). Then the isolated nanoclay was used (10 wt%) to prepare a nanoclay superabsorbent polymer composite (NCPC) by copolymerization of partially neutralized acrylic acid, acrylamide using radical initiator (ammonium persulfate) and crosslinker (*N,N'*-methylene bisacrylamide). The details about synthesis of NCPC can be seen from our previous study (Sarkar *et al.*, 2014). The loading of the NCPC with urea and *di*-ammonium phosphate (DAP) were carried out by immersing pre-weighed dry gels into the aqueous solution of respective fertilizer for 20 h to reach swelling equilibrium. Thereafter, the swollen gels were dried at 60 ^{0}C for 6 days, milled and screened. The component analysis showed that DAP loaded NCPC contained 16.9% P_2O_5 and 6.6% N and urea loaded NCPC contained 17.4% N.

Experimental conditions and treatment details

A greenhouse experiment was carried out in kharif season at the Indian Agricultural Research Institute (IARI), New Delhi. In a CRD experiment, pearl millet (*Pennisetum glaucum*, variety: Pusa composite-383) was grown in a Vertisols with 10 kg capacity (7 kg soil) pots (2 plants/pot) under five treatments (three replicates) consisting of T_1: control (no NP), T_2: high dose of fertilizer (HDF) as NCPC (NCPC -H), T_3: low dose of fertilizer (LDF) as NCPC (NCPC-L), T_4: HDF as conventional fertilizer-CF (CF-H) and T_5: LDF as CF (CF-L). High dose of fertilizer (HDF) corresponds to N & P_2O_5 @ 60 and 40 mg kg^{-1} soil, respectively, whereas low dose of fertilizer (LDF) corresponds to N & P_2O_5 @ 30 and 20 mg kg^{-1} soil, respectively. In all the treatments (including control) K_2O were applied @ 20 mg kg^{-1} soil in the form of KCl. To simulate leaching loss of mineral nitrogen in natural field condition we leached each pot at 15th day after sowing the crop with 3.5 l of de-ionized water and the leachates were collected in a reagent bottle. The total mineral N leached from the soil was determined by multiplying the concentration of mineral N in the leachate and volume of leachate. The pots were kept weed-free and irrigated on need basis to ensure that water was not a limiting factor. Some of the important physicochemical properties of the experimental soil analyzed by standard methods were: texture (Jackson, 1973) clay loam with sand 27.6%, silt 17.2% and clay 55.2%; pH_w (Jackson, 1973) (1:2.5, soil:water) 8.2; electrical conductivity (Jackson, 1973) (EC_w 1:2, soil:water) 0.22 ds m^{-1}; organic carbon (Jackson, 1973) 0.34%; Olsen phosphorus (Olsen *et al.*, 1954) 11.5 mg/kg soil; total mineral N (Keeney and Nelson, 1982) 35.6 mg/kg soil; P-fixing capacity (Jackson, 1973) 37%; available potassium (Jackson, 1973) 156 mg/kg soil.

Sampling, measurements and data analysis

Sub-samples of soils were drawn by a tube auger from each pot at an interval of 10, 20, 30, 40, 50 and 60 days after sowing

(DAS) and subsequently processed for further analysis. Total mineral N in soil was estimated by following the procedure given by Keeney and Nelson (1982). Phosphorus from soil samples were extracted with Olsen extractant (0.5 *M* $NaHCO_3$) and 0.01 *M* $CaCl_2$ solution (soil:extractant ration of 1:10) and P-content in the extracts were determined by ascorbic acid method (Watanable and Olsen, 1965). Inorganic P in soil samples was fractionated after harvest of the crop using the procedure developed by Peterson and Corey (1966). Plants were harvested at 60 days after sowing and dry weight recorded after drying them in a hot-air oven till constant weight. Samples were digested in a 2:1 mixture of HNO_3 and $HClO_4$ and P concentra-tion was determined by molybdo-phosphoric acid method. Total nitrogen in plant samples were determined by micro-Kjeldahl method.

Experimental data were analyzed following standard statistical methods of Gomez and Gomez (1984). Data obtained were subjected to analysis of variance (ANOVA) using statistical software MSTATC. The Dunçan's Multiple Range Test was used to segregate significance of difference among the mean values.

Results and discussion

Inorganic P fractions at harvest of the crop

Figure 1a indicated that saloid-P contents recorded under treatments NCPC-H and CF-H were at par and significantly higher compared to other treatments (control, NCPC-L and CF-L). Further, the concentration of saloid-P in soils treated with NCPC-L and CF-L were at par. Addition of conventional fertilizer (CF-H and CF-L) induced a significant increase in Al-P content of soil as compared to other treatments (Fig. 1b). Further, CF-H registered significantly higher content of Al-P in soil over CF-L treatment. Similarly, Fe-P content in the soils was not affected on addition of NCPC (NCPC-H and NCPC-L) over control (Fig. 1c). Whereas, conventional fertilizer application (CF-H and CF-L) induced significantly higher Fe-P content in the soil as compared to other treatments. Treatment CF-H registered higher Fe-P content in soil than that

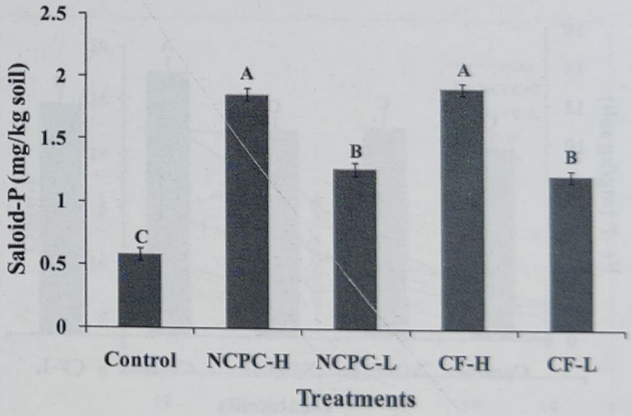

Fig. 1a. *Concentrations of Saloid-P as affected by different fertilizer treatments in soil.*
NCPC –H =, high dose of fertilizer(N & P_2O_5 @ 60 and 40 mg kg^{-1} soil, respectively) through NCPC
NCPC-L = low dose of fertilizer(N & P_2O_5 @ 30 and 20 mg kg^{-1} soil, respectively) through NCPC
CF-H =High dose of fertilizer in conventional mode.
CF-L = Low dose of fertilizer in conventional mode.

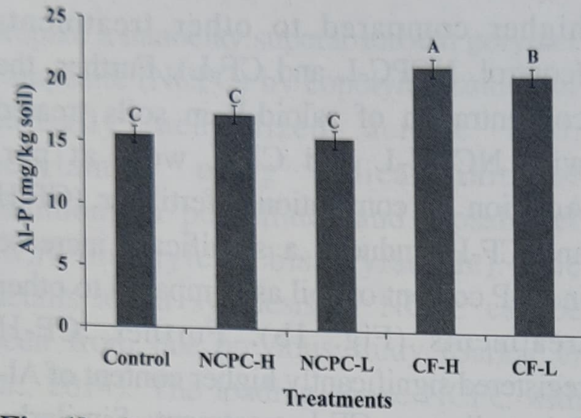

Fig. 1b. *Concentrations of Aluminium-P (Al-P) as affected by different fertilizer treatments in soil.*

NCPC –H =, high dose of fertilizer(N & P_2O_5 @ 60 and 40 mg kg^{-1} soil, respectively) through NCPC

NCPC-L = low dose of fertilizer(N & P_2O_5 @ 30 and 20 mg kg^{-1} soil, respectively) through NCPC

CF-H=High dose of fertilizer in conventional mode.

CF-L= Low dose of fertilizer in conventional mode.

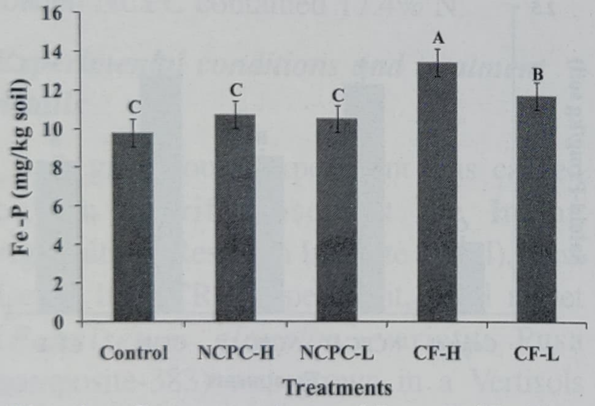

Fig. 1c. *Concentrations of Iron-P (Fe-P) as affected by different fertilizer treatments in soil.*

NCPC –H =, high dose of fertilizer(N & P_2O_5 @ 60 and 40 mg kg^{-1} soil, respectively) through NCPC

NCPC-L = low dose of fertilizer(N & P_2O_5 @ 30 and 20 mg kg^{-1} soil, respectively) through NCPC

CF-H=High dose of fertilizer in conventional mode.

CF-L=Low dose of fertilizer in conventional mode.

recorded under treatment CF-L. Unlike other fractions, Occluded-P fractions in the soils treated with CF-H, CF-L and NCPC-H were remained at par (Fig. 1d). Occluded-P content measured under CF-H was significantly higher than that of other treatments (NCPC-H, NCPC-L and control). A calcium-P (Ca-P) fraction was increased significantly on addition of CF as compared to NCPC treatments, irrespective of fertilizer dose (Figure 1e). In general, the reactions of P with soils are concentration dependent. This implies that one single application of highly soluble P is likely to result in a rapid reduction of available forms due to fixation in to soil medium. Application of highly soluble conventional DAP fertilizer resulted in very

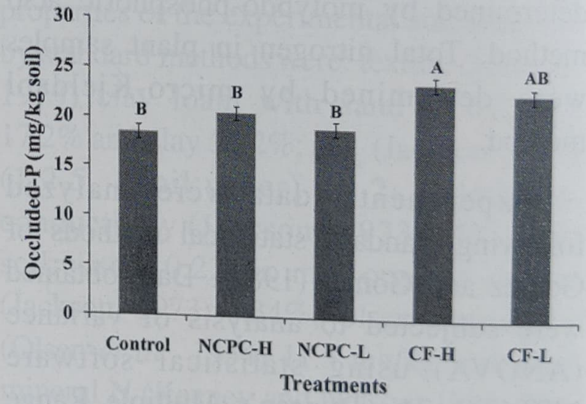

Fig. 1d. *Concentrations of Occluded-P (Ocl-P) as affected by different fertilizer treatments in soil.*

NCPC –H =, high dose of fertilizer(N & P_2O_5 @ 60 and 40 mg kg^{-1} soil, respectively) through NCPC

NCPC-L = low dose of fertilizer(N & P_2O_5 @ 30 and 20 mg kg^{-1} soil, respectively) through NCPC

CF-H =High dose of fertilizer in conventional mode.

CF-L = Low dose of fertilizer in conventional mode.

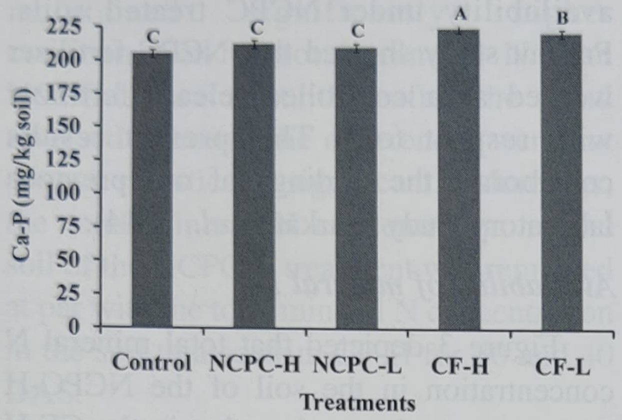

Fig. 1e. *Concentrations of Calcium-P (Ca-P) as affected by different fertilizer treatments in soil.*

NCPC –H =, high dose of fertilizer(N & P_2O_5 @ 60 and 40 mg kg^{-1} soil, respectively) through NCPC

NCPC-L = low dose of fertilizer(N & P_2O_5 @ 30 and 20 mg kg^{-1} soil, respectively) through NCPC

CF-H=High dose of fertilizer in conventional mode.

CF-L = Low dose of fertilizer in conventional mode.

high concentration of inorganic phosphate in to soil that might have contributed to its higher fixation and subsequent increase in non-available inorganic fractions (Shaviv and Schnek, 1989). On the contrary, application of DAP through NCPC resulted in controlled release of phosphate in synchronization with plant's uptake rate so as to minimize the time of contact with soil particles which might have contributed to reduced phosphate fixation.

Phosphorus availability

Lowest amount of Olsen-P and 0.01*M* $CaCl_2$-P were found in control where no P was added compared to treatments receiving P-fertilization, irrespective of sampling periods (Fig. 2a,b). There were a general increase in Olsen-P (Fig. 2a) and 0.01*M* $CaCl_2$-P (Fig. 2b) availability in soils up to 2nd sampling (20 DAS) with the treatment NCPC-H and NCPC-L, thereafter it decreased gradually. Availability of P (Olsen-P and 0.01*M* $CaCl_2$-P) decreased continuously for all other treatments with progress of sampling periods. In general, at same dose of fertilizer application, P availability (Olsen-P and $CaCl_2$-P) under NCPC treated soil was higher than its corresponding CF treatment for 20, 30 and 40 DAS. Application of HDF as conventional form (CF-H) registered significantly higher Olsen-P and $CaCl_2$-P availability in soil than the treatment with LDF as NCPC (NCPC-L) throughout the growth stages except at 30 and 40 DAS,

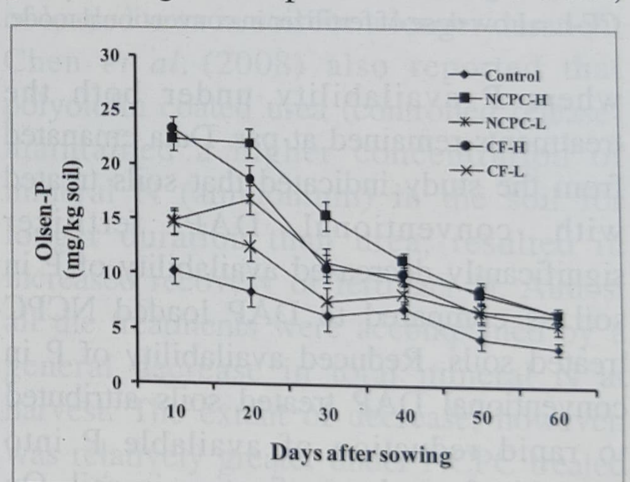

Fig. 2. *Changes in availability of Olsen-P as affected by different fertilizer treatments*

NCPC –H =, high dose of fertilizer(N & P_2O_5 @ 60 and 40 mg kg^{-1} soil, respectively) through NCPC

NCPC-L = low dose of fertilizer(N & P_2O_5 @ 30 and 20 mg kg^{-1} soil, respectively) through NCPC

CF-H =High dose of fertilizer in conventional mode.

CF-L = Low dose of fertilizer in conventional mode.

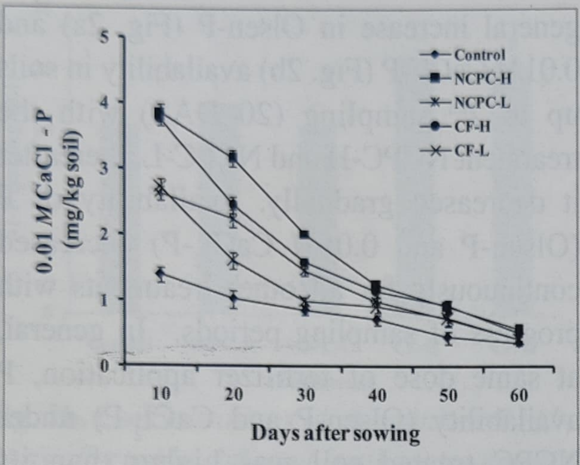

Fig. 2b. *Changes in availability of 0.01M $CaCl_2$-extractable-P as affected by different fertilizer treatments.*
NCPC –H =, high dose of fertilizer(N & P_2O_5 @ 60 and 40 mg kg^{-1} soil, respectively) through NCPC
NCPC-L = low dose of fertilizer(N & P_2O_5 @ 30 and 20 mg kg^{-1} soil, respectively) through NCPC
CF-H= High dose of fertilizer in conventional mode.
CF-L = Low dose of fertilizer in conventional mode.

where P availability under both the treatments remained at par. Data emanated from the study indicated that soils treated with conventional DAP fertilizer significantly decreased availability of P in soil as compared to DAP loaded NCPC treated soils. Reduced availability of P in conventional DAP treated soils attributed to rapid reduction of available P into insoluble form due to fixation in soil. On the other hand increased availability of P on addition of NCPC might be due to controlled release of nutrients into fixing medium as reported by previous study (Barrow *et al.*, 1985). Data recorded on different inorganic P fractions were in conformity with the data on better P availability under NCPC treated soils. Present study showed that NCPC fertilizer worked as a controlled release fertilizer with respect to P. This present results corroborate the findings of our previous laboratory study (Sarkar *et al.*, 2014).

Availability of mineral N

Figure 3 depicted that total mineral N concentration in the soil of the NCPC-H treatment was lower than that in the CF-H treatment for the early sampling period (10 and 20 DAS). After that time the NCPC-H treatment tended to maintain a higher concentration of total mineral N in the soil, although the differences were not always statistically significant. Similarly, at early stage (10 and 20 DAS) treatment CF-L

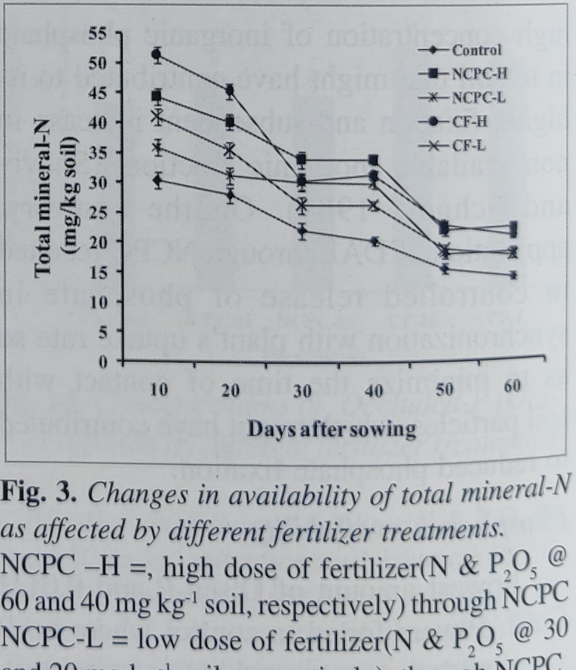

Fig. 3. *Changes in availability of total mineral-N as affected by different fertilizer treatments.*
NCPC –H =, high dose of fertilizer(N & P_2O_5 @ 60 and 40 mg kg^{-1} soil, respectively) through NCPC
NCPC-L = low dose of fertilizer(N & P_2O_5 @ 30 and 20 mg kg^{-1} soil, respectively) through NCPC
CF-H= High dose of fertilizer in conventional mode.
CF-L = Low dose of fertilizer in conventional mode.

maintained significantly higher concentration of total mineral N than NCPC-L treatment, thereafter the trend reversed although the differences were not always statistically significant. Moreover, the total mineral N concentration in the soil of the NCPC-L treatment was remained at par with the total mineral N concentration in the soil treated with CF-H for 30 and 40 DAS.

The leaching loss of mineral N at 15 days showed that significantly higher mineral N was lost from soils receiving conventional CF as compared to NCPC treated soils, irrespective of fertilizer dose (Figure 4). Further, loss of mineral N from CF-H treated soil was significantly higher than that recorded under CF-L treated soil. Similarly, NCPC-H registered significantly higher leaching loss of mineral N over NCPC-L. Rapid hydrolysis of urea under conventional fertilizer and subsequent nitrification resulted in higher mineral-N in soils treated with CF than that in NCPC treated soils, particularly at initial stages. The higher leaching loss of mineral N under conventional fertilizer resulted lower mineral N content in soil at middle stages (30 DAS) of crop growth as compared to NCPC treated soils. Mikkelson *et al.* (1994) also reported reduction in N leaching loss under controlled release fertilizer (CRF) application. At middle stages of crop growth (30 and 40 DAS), mineral-N content was higher in NCPC treated soils as compared to conventional fertilizers. This indicated that NCPC could maintain a gradual release of loaded urea in soil for a longer duration. Chen *et al.* (2008) also reported that polyolefin coated urea (controlled release) maintained a higher concentration of mineral N (ammonium) in the soil for longer duration than urea, resulted in increased recovery of fertilizer N. Almost all the treatments were accompanied by a general decrease in total mineral N at harvest. The extent of decrease, however, was relatively greater under NCPC treated soils as compared to CF which indicated higher uptake of nutrient in former cases.

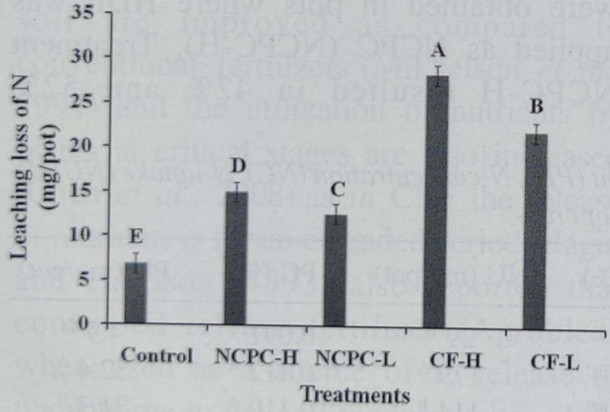

Fig. 4. *Leaching loss of mineral N as affected by different fertilizer treatments.*

NCPC –H =, high dose of fertilizer(N & P_2O_5 @ 60 and 40 mg kg^{-1} soil, respectively) through NCPC
NCPC-L = low dose of fertilizer(N & P_2O_5 @ 30 and 20 mg kg^{-1} soil, respectively) through NCPC
CF-H= High dose of fertilizer in conventional mode.
CF-L = Low dose of fertilizer in conventional mode.

Biomass yield, plant height and P and N uptake

Significant increases in biomass yields above the control (Table 1) were recorded with the application of different fertilizer treatments. Addition of NCPC-H registered significantly highest biomass yield (29.0 g/pot) while the lowest was observed for absolute control (5.4 g/pot). Application of NCPC-H boosted 65.0% additional biomass yield over CF-H. Whereas, biomass yield recorded under NCPC-L was 59.0% higher than that recorded under CF-L treatment (Table 1). Biomass yield of pearl millet at LDF application as NCPC (19.4 g/pot) was remained statistically at par with application of HDF as CF (17.6 g/pot). Data on plant height of pearl millet followed the same trend as observed for biomass yield (Table 1). Plant height of pearl millet plant ranged from 136 cm under NCPC-H to 63 cm for control treatment. Application of NCPC-H induced 30.0% higher plant height over CF-H. While, NCPC-L resulted in 40.0% higher plant height over plant height recorded under CF-L.

The influence of fertilizer application on P and N accumulation in pearl millet was noticeable (Table 1). Application of P fertilizer either as NCPC or CF induced significant increase in P-content in pearl millet straw, irrespective of fertilizer doses. The P-content recorded under all P-fertilization treatments were at par and varied from 0.091% (CF-L) to 0.130% (CF-H). Nitrogen content in pearl millet was unaffected under CF-L, but increased significantly for all other N-fertilization treatments (NCPC-H, NCPC-L and CF-H) compared to control where fertilizer N was not added (Table 1). Nitrogen content in the straw varied from 0.54% under control to 0.65% under CF-H. Application of NCPC-H, NCPC-L and CF-H were equally effective in maintaining N-content in pearl millet. The maximum uptake of P (32.4 mg/pot) and N (179 mg/pot) by pearl millet were obtained in pots where HDF was applied as NCPC (NCPC-H). Treatment NCPC-H resulted in 42% and 52%

Table 1. *Pearl millet plant dry matter (DM), Plant height (PH), N-concentration (NC), N-uptake (NU), P-Concentration (PC) and P-uptake (PU) at the harvest of crop.*

Treatments	DM (g/pot)	PH (cm)	NC (%)	NU (mg/pot)	PC (%)	PU (mg/pot)
Control	5.4^{D}	63^{D}	0.54^{D}	29^{D}	0.091^{B}	4.9^{D}
NCPC-H	29.0^{A}	136^{A}	0.62^{BC}	179^{A}	0.112^{A}	32.4^{A}
NCPC-L	19.4^{B}	113^{B}	0.59^{BC}	114^{B}	0.110^{A}	21.3^{B}
CF-H	17.6^{B}	105^{B}	0.65^{AB}	118^{B}	0.130^{A}	22.9^{B}
CF-L	12.2^{C}	81^{C}	0.57^{CD}	81^{C}	0.126^{A}	15.3^{C}

*mean separation within columns by the Duncan's test; $P < 0.05$

NCPC –H =, high dose of fertilizer(N & P_2O_5 @ 60 and 40 mg kg^{-1} soil, respectively) through NCPC

NCPC-L = low dose of fertilizer(N & P_2O_5 @ 30 and 20 mg kg^{-1} soil, respectively) through NCPC

CF-H =High dose of fertilizer in conventional mode.

CF-L = Low dose of fertilizer in conventional mode.

additional uptake of P and N, respectively, over the CF-H, while treatment NCPC-L resulted in 40% and 41% higher uptake of P and N, respectively, over the CF-L. Results indicated that application of P and N fertilizers as NCPC induced significantly higher uptake of P and N than CF, at same dose of fertilizer. Further, uptake of P and N measured under treatment NCPC-L and CF-H remained at par (Table 1).

The increased availability of P and N on addition of fertilizer as NCPC than CF application might have contributed to higher biomass yield and nutrient uptake by pearl millet under NCPC treated soils. Nutrient uptake is an important process, which decides all improvement in plant growth, yield and quality of crop produces. When controlled release fertilizers (CRF) are applied the chemical properties of the soil are improved as compared to conventional fertilizers (Mikkelson *et al.*, 1994) and the utilization of nutrients by plants at critical stages are also increased (Chen *et al.*, 2008) as in CRF the release of nutrients is for an extended period. Hagin and Harrison (1993) also reported that controlled release fertilizer (Agroblen) when used as a source of P, release of phosphorus to the soil medium takes place at rates and contents that allow the growing plant to maintain maximum expression of its genetic capability. Moreover the reduction of nutrient immobilization by the chemical and biological reactions might have enhanced the P availability to crops (Agroblen) at critical physiological stages, thereby increasing the uptake of phosphorus (Bolan *et al.*, 1993). The use of CRF might have allowed the nutrients to be used more efficiently by plants than soluble conventional N fertilizers by reducing N leaching and other losses and providing a constant supply of nutrients to the roots (Mikkelson *et al.*, 1994; Hauck, 1985). Moreover, superabsorbent polymer acts as a micro-reservoir to retain and supply nutrients to crops along with moisture, and thus could increase the utilization efficiency of nutrients and water at the same time (Liang, 2007). All the reasons specified above might have enhanced the uptake of P and N by pearl millet when fertilizer loaded NCPC was applied to the soils.

Conclusions

Results of greenhouse experiment indicated that biomass yield and nutrients uptake by pearl millet due to application of fertilizer loaded NCPC increased significantly over conventional fertilizers. Addition of fertilizer as NCPC at half dose of the conventional fertilizers gave same amount of biomass yield and nutrients uptake. Thus use of NCPC as a carriers of nutrients could be an alternative and effective option to save costly chemical fertilizers. An investigation on combined effect of water absorbency and slow nutrient release property of the NCPC and the economic analysis are also to be considered as a worthwhile topic for future studies.

Acknowledgements

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References

Al-Zahrani, S.M. 2000. Utilization of polyethylene and paraffin waxes as controlled delivery system for different fertilizers. *Ind. Eng. Chem. Res*. **39**: 367–371.

Anupama, Kumar, R., Jat, M.L. and Parmar, B.S. 2007. Performance of a new superabsorbent polymer on seedling and post planting growth and water use pattern of chrysanthemum grown under controlled environment. *Acta Hort*. **74**: 43-50.

Barrow, N.J. 1985. Comparing the effectiveness of fertilizers. *Fert. Res.* **8:** 85-91.

Bolan, N.S., Hedley, M.J. and Loganathan, P. 1993. Preparation, forms and properties of controlled release phosphate fertilizers. *Fert. Res***. 35**: 13-24.

Chen, D., Freney, J.R., Rochester, I., Constable, G.A., Mosier, A.R. and Chalk, P.M. 2008. Evaluation of polyolefin coated urea (Meister) as a fertilizer for irrigated cotton. *Nutr. Cycl. Agroecosyst*. **81**: 245-254.

Gomez, K.A. And Gomez, A.A. 1984. *Statistical Procedures for Ag-ricultural Research.* John Wiley and Sons, New York.

Hagin, J. and Harrison, R. 1993. Non-acidulated and partially acidulated phosphate rocks as controlled release P fertilizers. *Fert. Res.* **35**: 25-31.

Hauck, R.D. 1985. Slow release and bio-inhibitor-amended nitrogen fertilizers. In: O.P. Engelstad, Ed.), *Fertilizer Technology and Use.* Third Edition, Medison, WI. pp: 293-322.

Jackson, M.L.1973. *Soil Chemical Analysis*. Prentice Hall of India Pvt. Ltd., New Delhi.

Keeney, D.R. and Nelson, D.W. 1982. Nitrogen inorganic forms. In: (Page AL, Miller RH, Keeney DR, eds.) *Methods of Soil Analysis*. Agronomy monograph 9 **Part 2**, 2nd edn. American Society of Agronomy, Madison Wisconsin. pp 643–698.

Ladha, J.K., Pathak, H., Krupnik, T.J., Six, J. and Van Kessel, C. 2005. Efficiency of fertilizer nitrogen in cereal production: retrospect and prospects. *Adv. Agron*. **87**: 85-156.

Lee, W. F. and Yang, L. G. 2004. Superabsorbent polymeric materials. XII. Effect of montmorillonite on water absorbency for poly (sodium acrylate) and montmorillonite nanocomposite superabsorbents. *Polym. Adv. Technol*. **92**: 3422-3429.

Li, A., Wang, A. and Chen, J. 2004. Studies on poly(acrylic acid)/attapulgite superabsorbent composites. II. Swelling behaviour of super absorbent composites in saline solutions and hydrophilic solvent mixtures. *J. Appl. Polym. Sci.* **94**: 1869-1876.

Liang, R. and Liu, M. 2007. Preparation of poly(acrylic acid-co-acrylamide)/kaolin and release kinetics of urea from it. *J. Appl. Polym. Sci.* **106**: 3007-3017.

Liang, R., Liu, M. and Wu, L. 2007. Controlled release NPK compound fertilizer with the function of water retention. *React. Funct. Polym.* **67**: 769-779.

Lin, L., Wu, J.H., Yang, Z. and Pu, M.L. 2001. Synthesis and properties of poly(acrylic acid)/mica superabsorbent nanocomposite. *Macromol. Rapid Commun.* **22**: 422-424.

Malhi, S.S., Haderlein, L.K., Pauly, D.G. and Johnston, A.M. 2002. Improving fertilizer phosphorus use efficiency. *Better Crops.* **86**: 8-9.

Mikkelson, R.L., Williams, H.M. and Behel, A.D. 1994. Nitrogen leaching and plant uptake from controlled release fertilizers. *Fert. Res.* **37**: 43-50.

Mohan, Y.M., Murthy, P.S.K. and Raju, K.M. 2005. Synthesis, characterization and effect of reaction parameters on swelling properties of acrylamide-sodium methacrylate superabsorbent copolymers. *React. Funct. Polym.* **63**: 11-26.

Olsen, S.R., Cole, C.V., Watanable, F.S. and Dean, L.A. 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate, *USDA Circular*, 9398. 1-19.

Petersen, G.W. and Corey, R.B. 1966. A modified Chang and Jackson procedure for routine fractionation of inorganic soil phosphates. *Soil Sci. Soc. Am. Pro.* **30**: 563-565.

Sarkar, S., Datta, S.C. and Biswas, D.R. 2014. Synthesis and characterization of nanoclay–polymer composites from soil clay with respect to their water-holding capacities and nutrient-release behavior. *J. Appl. Polym. Sci.* **131**: doi: 10.1002/app.39951

Shaviv, A. and Schnek, M. 1989. Reactions of a granulated super-phosphate and ammonium sulphate mixtures in calcareous soils. *Geoderma.* **44**: 17-27.

Singh, A., Sarkar, D.J., Singh, A.K., Parsad, R., Kumar, A. and Parmar, B.S. 2011. Studies on novel nanosuperabsorbent composites: swelling behavior in different environments and effect on water absorption and retention properties of sandy loam soil and soil-less medium. *J. Appl. Polym. Sci.* **120**: 1448-1458.

Watanabe, F.S. and Olsen, S.R.1965. Test of an ascorbic acid method for determining phosphorus in water and $NaHCO_3$ extracts from soils. *Soil Sci. Soc. Am. Pro.* **29:** 677-678.

Zhong, K., Lin, Z., Zheng, X., Jiang, G., Fang, Y., Mao, X. and Liao, Z. 2013. Starch derivative-based superabsorbent with integration of water-retaining and controlled-release fertilizers. *Carbohydrate Polymers.* **92**: 1367-1376.

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Calcareousness and Subsoil Sodicity in Ferruginous Alfisols of Southern India : An Evidence of Climate Shift

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Abstract : *We report alkaline, sodic and smectitic ferruginous Alfisols from semi-arid part of southern India. Such Alfisols on micro-low (ML) position in a catena are spatially associated with non-sodic soil at micro-high (MH) positions. The soils of the MH are well drained, sandy clay loam to sandy clay in texture, acidic to slightly alkaline with less $CaCO_3$ and non-sodic. However, soils on ML is clayey, alkaline (9.1 – 9.4) and calcareous (10-13%) with high available water content and high sodicity (ESP 16-41%). The saturated hydraulic conductivity (sHC) of the ML soils is almost nil in the sub-surface horizons due to high ESP resulting in dispersion of clay and clogging of soil pores. Mineralogical studies indicate the presence of smectite-kaolinite (Sm-K) interstratified mineral, which was formed during the past humid tropical climate, where as the formation of the high charge smectite occurred during the prevailing semi-arid climate in both MH and ML soils. Sm-K is dominant in MH soils whereas smectite is dominant in ML soils. Micro- topography of the study area indicates that the ML positions are repeatedly flooded with surface water during brief and high-intensity showers, which provided steady supply of alkalis by hydrolysis of feldspars at MH sites leading to precipitation of calcium carbonate at high pH, development of subsoil sodicity and persistence of Sm-K and smectite in ML sites. Due to formation $CaCO_3$ and concomitant development of sub-soil sodicity, the sHC of the ML soils were impaired. Similar micro-topographical situation in the formation of sodic and non-sodic soils on ML and MH positions respectively was reported earlier in soils of the Indo-Gangetic Plains (IGP), but in swell-shrink soils of central India a reverse situation was observed. The present study, however, indicates the need of a detailed study to explain the development of sodicity in soils of red and black soil associations in tropical India. Earlier studies by NBSS&LUP (ICAR) demonstrated that the formation of sodic soils is the result of climate shift from humid to semi-arid climate during the Holocene period. The study reaffirms the need of precise understanding of pedogenic processes for pragmatic land resource inventory even at larger scales for proper management of soil resources.*

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It is widely believed that the ferruginous Alfisols are generally formed in high rainfall areas, and thus are acidic, non-calcareous, non sodic, and kaolinitic in nature. However, in tropical Indian environment, these soils occur in varied ecosystems ranging from arid to per humid region and are developed on different parent materials. They are acidic to neutral in reaction, have noncalcareous to calcareous, and their clay fractions contain smectites alongside dominant amount of kaolin clay minerals. Therefore, the relationship between their spatial distribution at different soil taxonomic categories (Soil survey staff, 2006) and the present soil forming factors is extremely difficult to establish (Murali *et al*., 1978; Rengasamy *et al*., 1978; Rengasamy, 1983). These semi-arid tropical (SAT) soils are considered as relict paleosols (Pal and Deshpande, 1987; Pal *et al*., 1989). Earlier reports on the ferruginous soils of Indian SAT indicated the evidence of initiation soil degradation due to aridity and reflected in the formation of pedogenic carbonates (PC) and concomitant development of subsoil sodicity (Pal *et al*., 2000; Srivastava *et al*., 2001). These authors, however, did not elaborate the possible role of micro topography in the formation of sodic ferruginous soils in SAT as demonstrated earlier in the formation of sodic soils in SAT environments of the Indo-Gangetic Plains (IGP) (Pal *et al*., 2003). In the present paper, we demonstrate the role of micro-topography in the formation of calcareous and sodic Alfisols with smectite as dominant mineral alongside small amount of Sm-K mineral in a catena under SAT climate of Andhra Pradesh where climate shift from humid to semi-arid did occur in the Holocene period.

Materials and Methods

Three Alfisols occurring in a transect (a soil catena) were selected from the research farm of CRIDA (ICAR), Hyderabad during the detailed soil survey of the farm on 1:5000 scale. The farm is located in an undulating topography under SAT climatic condition in the Rangareddy district of Andhra Pradesh. Soils were sampled from MH (P1 and P3) and ML (P2) positions (Fig. 1). These are developed in granite-gneiss parent material and classified (Typic Rhodustalfs: P1, Typic Natrustalfs: P2 and Typic Haplustalfs: P3) as per Soil Taxonomy (Soil Survey Staff, 2006). The morphological properties of each pedon and its individual horizons were described following the procedure of soil survey manual (Soil Survey Division Staff, 1995, Bhattacharyya *et al.,* 2009). The particle size distribution was determined by the international pipette method after removal of organic matter, $CaCO_3$ and Fe-oxides. Sand, silt, clay and fine clay fractions were separated according to the size segregation procedure of Jackson (1979). The sHC, $CaCO_3$ equivalent, cation exchange capacity (CEC), and extractable cations were determined by standard procedures (Richards, 1954; Piper, 1966;

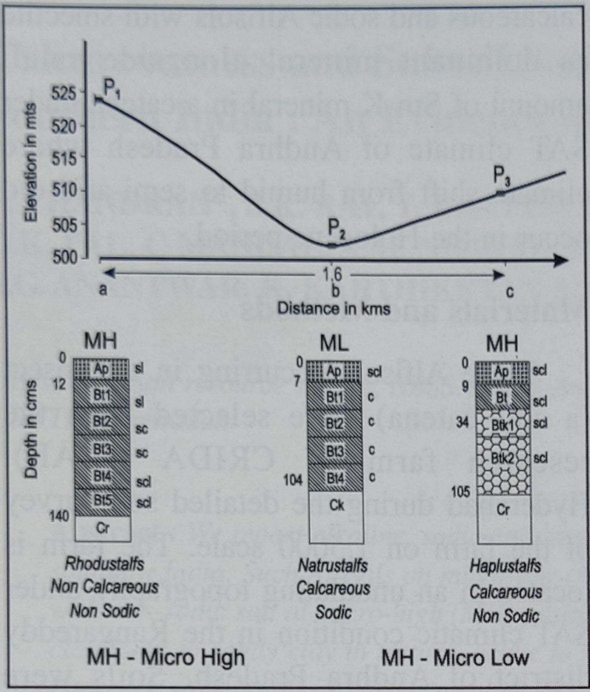


Fig. 1. *Schematic diagramme of the landscape representing the pedon sites in Rengareddy District, Andhra Pradesh*

Jackson, 1973). For mineralogical analysis, silt and clay fractions were subjected to X-ray diffraction (XRD) of the parallel oriented Ca/K saturated samples with a Philips diffractometer using Ni-filtered Cu-Kα radiation and at a scanning speed of $2^0 2\theta$/minute.

Results

Morphometric properties indicate that soils are reddish brown to dark reddish brown in colour with hue of 5YR to 2.5YR, deep, with well-developed structures and clay enriched B horizons (Table 1) and are grouped as ferruginous soils (Rengasamy *et al*., 1978). The Pedon 1 is non calcareous unlike the other two (Table 1). Soil structure varies from sub angular to angular blocky and consistency as sticky and plastic indicating good amount of clay. Texture varies from sandy clay loam to clay with fine and coarse gravels range from 10-60%.

MH soils

Physical and chemical characteristic (Tables 1 & 2) show that out of the two pedons in MH, P1 is acidic (pH 5.3 to 6.5) whereas P3 is alkaline (pH 8.0-8.4) with an increasing trend of pH with depth. The soils have high clay content just below the plough layer indicating that these soils are formed in the past humid climate which is common in ferruginous soils of SAT climate (Pal *et al*., 1989; Chandran *et al*., 2000). Available water content (AWC) of the soils are relatively low and varies from 5.3 to 9.3%. The soils have better sHC than the soils at the ML position (Table 1), but it is less than the threshold limit of 10 mm/hr except the surface soils of Pedon 1. The organic carbons in these soils are low, owing to the SAT climate and low organic inputs during the cultivation

In contrast to the general understanding that ferruginous soils are devoid of inorganic carbon ($CaCO_3$), laboratory studies indicate that these soils contain some amount of $CaCO_3$ even though the pH is <5.5 in Pedon 1 (Table 2). This indicates that the laboratory determination of carbonate should be made mandatory in the routine analysis, because it is an

Table 1. *Morphological and physical properties of soils*

Lab. no.	Horizon	Depth (cm)	Matrix Colour (M)	Texture[1]	Structure[2]	Efferve-scence[3]	B.D (Mg m^{-3})	Water retention (%)			sHC (cm hr^{-1})	COLE	LE
								33 kPa	1500 kPa	AWC			
					Pedon -1, Hayatnagar1(Typic Rhodustalfs)								
6418	Ap	0-12	5 YR 4/4 D& 3/4	gsl	f 2 sbk	nil	1.7	10.1	4.8	5.3	2.44	0.09	0.08
6419	Bt1	12-29	2.5 YR 3/4	sl	f 2 sbk	nil	1.6	16.1	10.4	5.7	0.66	0.08	
6420	Bt2	29-55	2.5 YR 3/4	sc	f 2 sbk	nil	1.6	15.6	10.1	5.6	0.26	0.07	
6421	Bt3	55-86	2.5 YR 3/4	sc	m 2 sbk	nil	1.9	18.2	11.2	7.0	0.85	0.09	
6422	Bt4	86-102	2.5 YR 3/4	scl	m 2 sbk	nil	1.6	19.2	11.2	7.9	0.15	0.09	
6423	Bt5	102-140	2.5YR 3/4	scl	m 2 sbk	nil	1.6	15.2	8.8	6.4	0.82	0.09	
	Cr	140^{+}				Weathered granite-gneiss.							
					Pedon -2, Hayatnagar 9. (Typic Natrustalfs)								
6457	Ap	0-7	7.5 YR 4/3 D & 3/3	gscl	m 1sbk	ev	1.6	17.8	9.2	8.6	0.39	0.10	0.22
6458	Bt1	7-20	5 YR 3/4 D & 3/3	c	c 2 abk	ev	1.6	28.2	14.0	14.2	0.07	0.15	
6459	Bt2	20-60	5 YR 3/4 R	c	c 3 sbk	ev	1.9	38.7	16.5	22.1	Nil	0.22	
6460	Bt3	60-83	5 YR 4/4	c	c 3 abk	ev	1.6	48.8	18.7	30.0	Nil	0.27	
6461	Bt4	83-104	5YR 4/4	c	c 3 abk	ev	1.5	48.5	22.6	25.9	Nil	0.27	
	Ck	104^{+}				Weathered granite gneiss with calcium carbonate							
					Pedon 3, Hayatnagar14 (Typic Haplustalfs)								
6492	Ap	0-9	2.5 YR 3/4 D& 3/3	scl	m 1 sbk	es	1.6	10.4	4.8	5.6	0.31	0.05	0.06
6493	Bt	9-34	5 YR 3/4 M	scl	m 2 sbk	es	1.7	15.2	6.7	8.5	0.35	0.06	
6494	Btk$_1$	34-68	5 YR 3/4 M	scl	m 2 sbk	ev	1.5	18	8.6	9.3	0.57	0.07	
6495	Btk$_2$	68-105	5 YR 3/4 M	scl	m 2 sbk	ev	1.7	15	6.7	8.3	0.16	0.05	
	Cr	105^{+}				Weathered granite-gneiss.							

[1]: gsl: gravelly sandy loam, sl: sandy loam, scl : sandy clay loam, sc: sandy clay, c: clay

[2] f : fine ,m: medium, c: coarse. 1 : weak, 2 moderate,3 :strong, sbk: subangular blocky, abk: angular blocky;

[3] es : strongly effervescent, ev: violent effervescent;

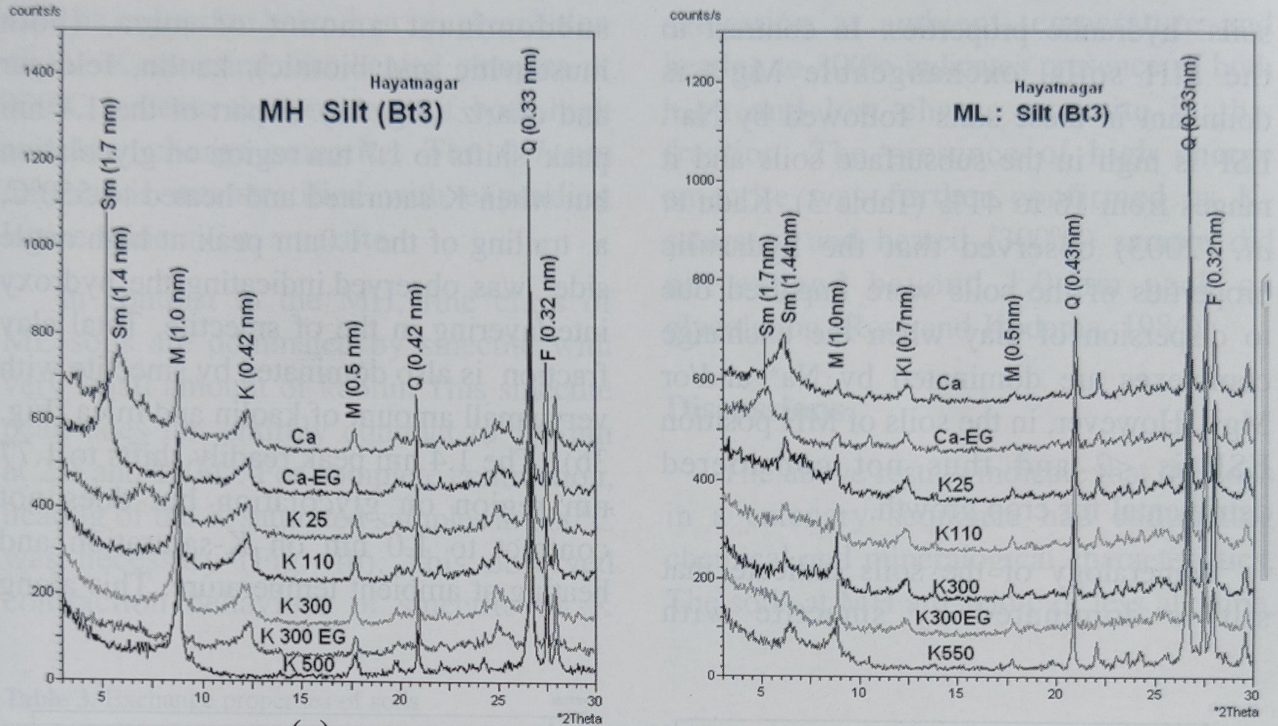
BD- bulk density; sHC –saturated hydraulic conductivity; COLE – coefficient of linear extensibility, LE-linear extensibility.

indication of initiation of carbonate precipitation and concomitant development of subsoil sodicity in ferruginous Alfisols of SAT climate. Both MH and ML soils are calcareous but the content of Ca CO_3 is low in light texture soils than heavy textured soils suggesting the definite role of texture in its accumulation in the soil profile under SAT climate. Ca^{2+} ion is dominant in the exchange sites followed by Mg^{2+} in soils of MH positions.

X-ray diffractogram of the silt indicate these soils (Fig. 2a) have dominant peaks at 1.4, 1.0 and 0.7 nm. The 1.4 nm mineral expands to 1.7 nm on glycolation and collapses readily to 1.0 nm peak on K saturation and heat treatment indicating the presence of high charge smectite (low charge vermiculite) in the sample, a weathering product of biotite mica. Kaolin and smectite are the dominant minerals in the total clay fraction with subordinate amount of mica and quartz (Fig. 3a). The 1.4 nm peak of smectite shifts entirely to 1.7 nm during glycolation and but does not collapse to 1.0 nm region during K saturation at ambient temperature, but does so only at 110°C indicating presence of both high and low charge smectite. On glycolation the 0.7 nm peak of kaolin, shifts

Table 2. Particle size distribution and chemical properties of soils

Horizon	Size class and particle diameter (mm) (%)				pH (1:2)			EC (1:2) dS m^{-1}	Organic carbon (%)	Carbonate as Ca CO_3 Equivalent (%)
	Sand (2-0.05)	Silt (0.05-0.002)	Clay (<0.002)	Fine Clay (<0.0002)	H_2O	1 *N* KCl	Δ pH (-ve)			
Pedon-1.Hayatnagar 1. (Typic Rhodustalfs)										
Ap	73.0	18.3	8.7	5.4	6.5	4.1	2.4	0.09	0.7	0.8
Bt1	58.0	27.2	14.8	9.5	5.3	4.1	1.2	0.07	0.5	0.9
Bt 2	54.2	10.7	35.1	24.5	5.3	4.3	1.0	0.09	0.6	0.9
Bt3	54.8	8.7	36.5	16.7	5.7	4.5	1.1	0.09	0.4	0.7
Bt4	59.7	11.9	28.4	11.5	6.4	4.2	2.2	0.06	0.2	1.0
Bt5	71.2	6.4	22.4	15.1	6.5	4.3	2.2	0.05	0.1	1.2
Pedon -2. Hayatnagar 9. :(Typic Natrustalfs)										
Ap	56.0	10.8	33.2	9.9	8.2	7.3	0.9	0.14	0.8	7.4
Bt1	46.1	10.7	43.2	12.9	9.1	7.6	1.5	0.29	0.3	10.6
Bt2	44.2	12.3	43.5	12.8	9.2	7.9	1.3	0.41	0.2	9.9
Bt3	40.5	17.7	41.8	13.0	9.4	7.9	1.5	0.63	0.2	10.0
Bt4	45.3	12.1	42.6	15.5	9.2	7.9	1.3	0.11	0.2	12.6
Pedon 3. Hayatnagar 14I.Typic Haplustalfs)										
Ap	66.8	12.6	20.6	14.9	8.0	5.9	2.2	0.12	0.5	2.1
Bt	65.7	13	21.3	9.5	8.2	7.2	1	0.13	0.7	11.1
Btk_1	51.6	14.5	33.9	8	8.2	7.5	0.8	0.12	0.6	31.6
Btk_2	63.7	9.0	27.3	20.9	8.4	7.3	1.1	0.14	0.3	22.8



(a) (b)

Fig. 2. *Representative XRD of Silt fraction (50-2μm) of MH and ML soils Ca- ca saturated, Ca_EG: Ca saturated and glycolated, K25, K110, K300, K 550, K300 EG: K-saturated and heated to 25,110,300, 550^{0}C and glycolated respectively. Sm=smectite , KI= kaolin, M=mica, Q=quartz and F=feldspar*

towards low angle side indicating that it is not a true kaolinite but interstratified with smectite. This was further confirmed from the broad base and branches in the tips of 0.7 nm peak. This is common in ferruginous soils of southern India (Pal *et al.*, 1989; Chandran *et al.*, 2000, 2005). The fine clay fractions of MH soils are dominated by 0.7 nm mineral with smectite and mica in subordinate amounts (Fig. 4a). The broad 0.7 nm peak on glycolation indicates that it is not a discrete kaolinite but appears to be interstratified with smectite, indicating this to be a smectite-kaolinite mineral (Sm-K).

ML soils

These soils are alkaline in reaction (pH 8.0 to 9.4) with pH increasing with depth. In contrast to the MH, these soils have high AWC (8.6 – 30.0%) (Table 1). High AWC is due to high exchangeable sodium and clay smectite in these soils. In Typic Natrustalfs (P2) the sHC in subsurface layers is zero even after 5 days of saturation (Table 1), indicating the impairment of soils' hydraulic properties. In contrast to the MH soils, exchangeable Mg^{2+} is dominant in these soils followed by Na^{+}. ESP is high in the subsurface soils and it ranges from 16 to 41% (Table 3). Kadu *et al.* (2003) observed that the hydraulic properties of the soils were impaired due to dispersion of clay when the exchange complexes are dominated by Na^{+} and/or Mg^{2+}. However, in the soils of MH position ESP is <2 and thus not considered detrimental for crop growth.

Mineralogy of the soils indicate that silt is dominated by smectite with subdominant amount of mica, (both muscovitic and biotitic), kaolin, feldspar and quartz (Fig. 2b). A part of the 1.4 nm peak shifts to 1.7 nm region on glycolation but when K saturated and heated to 550^{0}C, a trailing of the 1.0nm peak at high angle side was observed,indicating the hydroxy interlayering in the of smectite. Total clay fraction is also dominated by smectite with very small amount of kaolin and mica (Fig. 3b). The 1.4 nm peak readily shifts to 1.77 nm region on glycolation but does not contract to 1.0 nm on K-saturation and heating at ambient temperature. This along

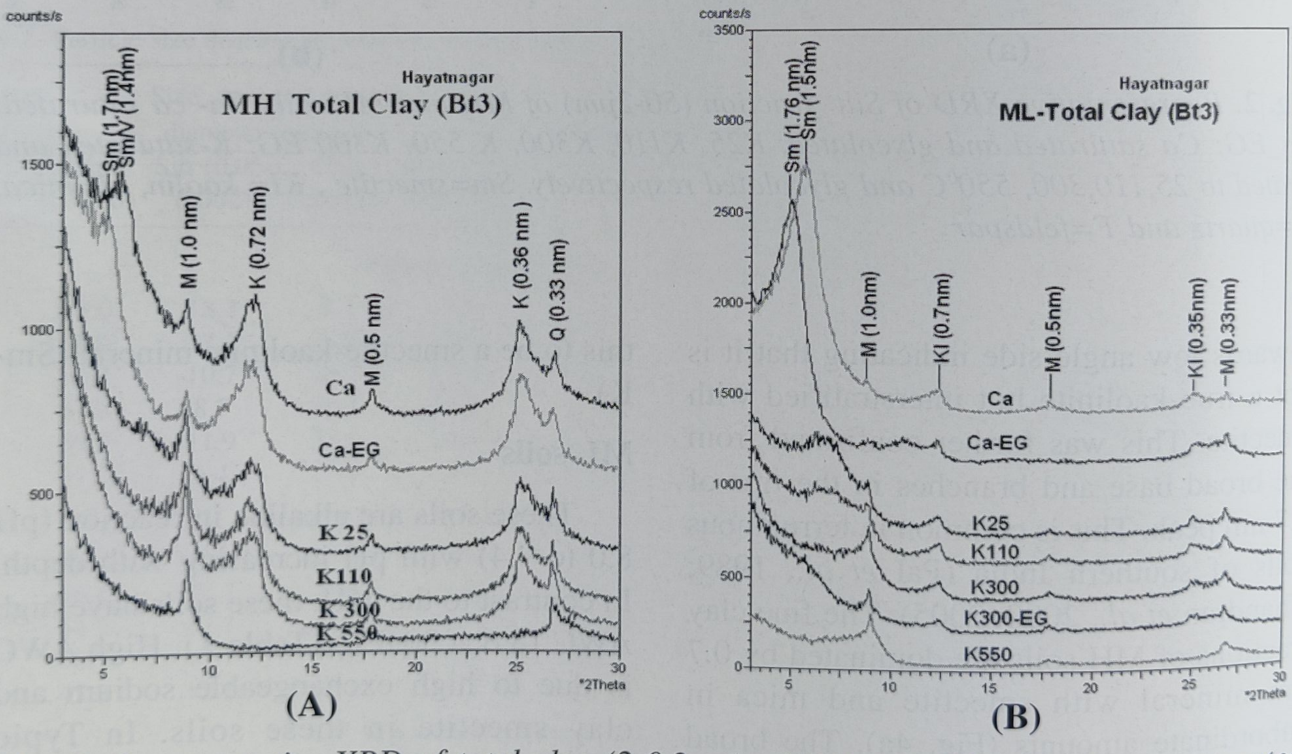


Fig. 3. *Representative XRD of total clay (2-0.2μm) of MH and ML soils Ca- ca saturated, Ca_EG: Ca saturated and glycolated, K25, K110, K300, K 550, K300EG: K-saturated and heated to 25,110,300, 550^{0}C and glycolated respectively. Sm=smectite, KI= kaolin, M=mica, Q=quartz*

with its expansion behaviour on glycolation of the K-saturated and heated samples at 300⁰C indicate the presence of both high and low charge smectite. The 0.7 nm mineral is interstratified with expanding lattice mineral i.e. smectite.

In contrast to the MH, fine clays of ML soils are dominated by smectite with very small amount of kaolin. This smectite peak does not entirely contract to 1.0 nm at 25⁰ and 110⁰C. For complete contraction, heating of the K saturated samples at 300⁰C was necessary (Fig. 4b). This observed contraction behaviour of smectite on K saturation at ambient temperature and heating to 300⁰c indicates presence of both high and low charge smectite in this fraction. The presence of high charge smectite was further confirmed as K-saturated and heated (300⁰C) sample did not expand beyond 1.0 nm peak on glycolation (Ross and Kodama, 1984).

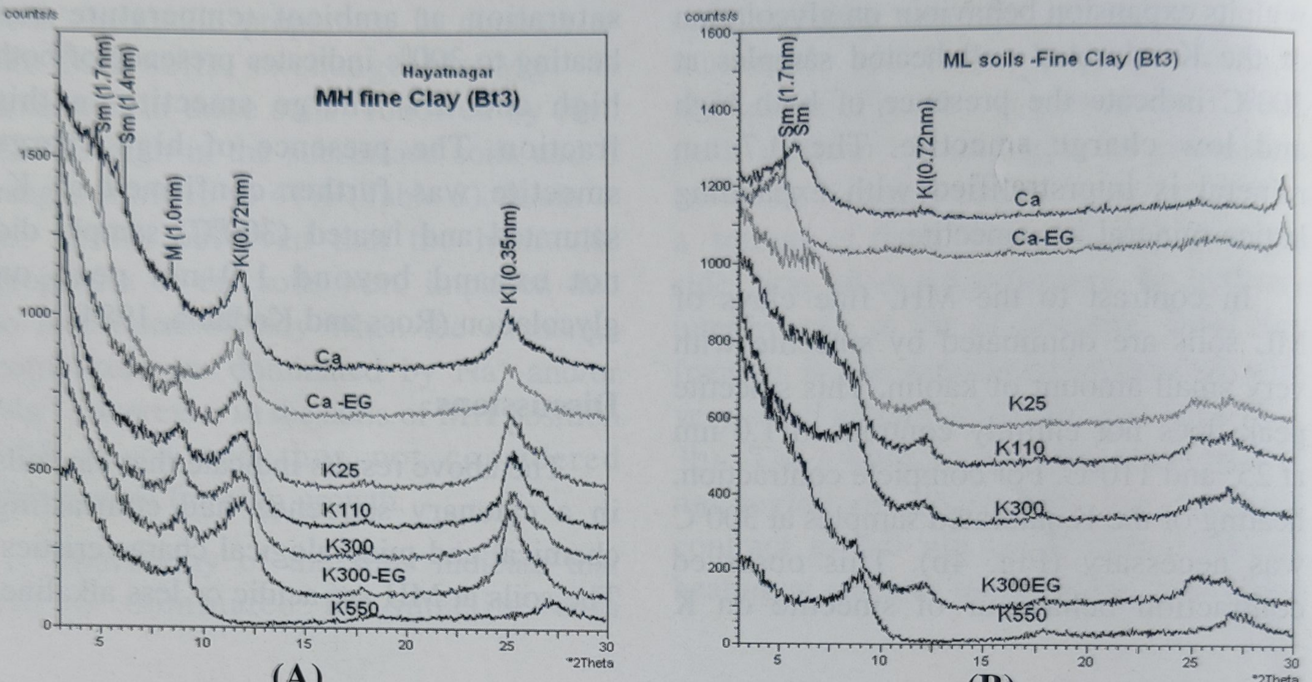
Discussions

The above results indicate that the soils in a catenary sequence had contrasting chemical and mineralogical characteristics. The soils at MH are acidic or less alkaline,

Table 3. Exchange properties of soils

Horizon	Extractable bases					CEC soil	B.S. (%)	CEC clay (cmol (p+) kg-1 Clay)	ESP	EMP	Ca/Mg ratio
	Ca^{2+}	Mg^{2+}	Na^+	K^+	Sum						
	(cmol (p+) kg^{-1} Soil)										
Pedon-1, Hayatnagar 1,(Typic Rhodustalfs)											
Ap	4.0	2.1	0.0	0.3	6.4	8.1	79	99	0.5	26	2
Bt1	4.4	4.5	0.2	0.2	9.3	14.2	65	96	1.4	32	1
Bt 2	6.6	3.6	0.2	0.2	10.6	15.2	70	43	1.6	24	2
Bt3	7.4	4.9	0.3	0.3	12.9	15.0	86	41	2.1	33	1
Bt4	8.8	6.5	0.3	0.2	15.8	18.6	85	66	1.7	35	1
Bt5	11.0	6.9	0.3	0.2	18.4	22.0	83	99	1.4	31	2
Pedon -2, Hayatnagar 9,(Typic Natrustalfs)											
Ap	13.3	3.3	0.3	0.3	17.2	18.6	92	56	1.5	18	4
Bt1	8.4	7.7	3.8	0.2	20.1	24.0	84	56	15.9	32	1
Bt2	2.9	10.3	8.9	0.2	22.4	24.0	93	55	37.2	43	0.3
Bt3	2.2	12.2	10.7	0.3	25.4	26.1	98	62	41.2	47	0.2
Bt4	2.6	11.2	11.0	0.3	25.1	27.0	93	63	40.7	41	0.2
Pedon 3, Hayatnagar14, 9Typic Haplustalfs)											
Ap	11.4	2.2	0.2	0.2	14	14.6	96	71	1.6	15	5
Bt	11.3	1.5	0.3	0.2	13.2	16.2	82	76	1.6	9	8
Btk_1	15.2	1.6	0.3	0.2	17.3	17.6	98	52	1.5	9	10
Btk_2	11.2	1.6	0.3	0.2	13.3	18.6	71	68	1.5	9	7

CEC: cation exchange capacity, BS –base saturation, ESP- exchangeable sodium percent, EMP— exchangeable magnesium percent



(A) (B)

Fig. 4. *Representative XRD of fine clay (<0.2µm) of MH & ML soils Ca- ca saturated, Ca-EG: Ca saturated and glycolated, K25, K110, K300, K 550, K300EG: K-saturated and heated to 25,110,300, 550°C and glycolated respectively. Sm=smectite , KI= kaolin, M=mica.*

and those at ML are highly alkaline due to accumulation of bases from the higher topographic position. The microlows are repeatedly flooded with surface water during brief high-intensity showers, and so the soils are subject to cycles of wetting and drying. This provides a steady supply of alkalis by hydrolysis of feldspars, leading to precipitation of calcium carbonate at high pH and development of subsoil sodicity. This impairs the hydraulic properties of soils and eventually leads to the development of Alfisols with a relatively high ESP in the subsoils. The semi-arid climate and topography interact to facilitate greater penetration of bicarbonate-rich water in ML than MH positions. The sHC of the soils at ML position is almost zero in the subsurface layers due to higher amount of clay smectite and ESP. The SAT climate of the area induced precipitation of carbonates which in turn has increased Na^+ ion in the exchange complex (Pal *et al.*, 2000). This is common in black soil regions of India wherein SAT climate induces the precipitation of calcium carbonates with a concomitant development of subsoil sodicity (Vaidya and Pal, 2002). The formation of $CaCO_3$ and illuviation of clay can be considered as the two pedogenic processes occurring simultaneously as contemporary events in the drier climates in ML position. Similar micro-topographical situations in the formation of sodic and non-sodic soils on ML and MH positions, respectively was reported earlier in soils of IGP (Pal *et al*., 2003). In contrast to this, in swell-shrink soils of central India, a reverse situation was observed; sodic soils occur in MH and non sodic soils as ML position.

The clay mineralogical make up indicates that MH soils are dominated by kaolin, and ML soils with smectite probably due to differences in drainage conditions. The presence of kaolin in all the fractions of these soils of semi-arid climate and its occurrence as Sm-K interstratified mineral indicate the prevalence of humid climate in the past (Pal and Deshpande, 1987; Chandran *et al*., 2000). Smectite clay minerals are ephemeral in the humid tropical climate and they transform into kaolinite (Pal *et al*., 1989, Bhattacharyya *et al*., 1993). Therefore, the associated ferruginous soils with huge amount of smectite were formed in the humid climate of the past geological period. But the high charge smectite in the silt and clay fraction are the weathering product of biotite during the present SAT environment. Therefore, the climate change from humid to semiarid in the Holocene period is also reflected through the transformation of smectite to Sm-K and formation. Huge amount of smectite in the soils of ML position is preserved due to replenishment of bases in the micro depression. Earlier studies demonstrated the initiation of development of sodicity in ferruginous soils of south India as a result of climate shift from humid to semi-arid climate during the Holocene period (Chandran *et al*., 2000; Srivastava *et al*., 2001). Natarajan *et al*. (2006) also reported high $CaCO_3$ and ESP in ML soils of Sivagangai block of Tamil Nadu, in association with ferruginous soils in lateritic landscape but no explanation for such contrasting chemical environment was offered. Thus the development of $CaCO_3$ and sodicity in the soils of ML position may be widespread due to the replenishment of bases from surrounding MH areas, in similar SAT areas of southern India. Although the rate of formation of carbonates in such SAT soils is not alarming at present, but due care is needed while irrigating these soils.

Conclusions

The development of calcareousness and subsoil sodicity alongside the formation of high charge smectite in ferruginous soils of southern India is due to climate shift from humid to semi-arid during the Holocene period. The initiation of the natural degradation in terms of impairment of hydraulic properties of soil may become wide spread if the climatic aridity is continued. Therefore, management intervention to minimize the effect of this natural degradation is to be initiated to arrest such a menace. The study further reaffirms the need of precise understanding of pedogenic processes for pragmatic land resource inventory even at larger scale for proper management of soil resources.

References

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. *J. Soil Sci,* **44:**159-171.

Bhattacharyya, T., Sarkar D. and Pal, D.K.(Eds) 2009. *Soil Survey Manual*. NBSS & LUP publ. No.146, India. 400p.

Chandran, P., Ray, S.K., Bhattacharyya, T. Krishnan, P. and Pal, D.K. 2000. Clay minerals in two ferruginous soils of Southern India. *Clay Res.,* **19:**77-85.

Chandran, P. Ray, S.K. Bhattacharyya T., Srivastava, P., Krishnan, P. and Pal, D.K. (2005) Lateritic Soils of Kerala, India: their mineralogy, genesis and taxonomy. *Austr. J. Soil Res.,* **43**:839-852.

Jackson M.L. 1979. *Soil Chemical Analysis – Advanced Course*. Published by the author, University of Wisconsin, Madison, WI, USA.

Jackson M.L. 1973. *Soil Chemical Analysis*. Prentice Hall India Pvt. Ltd., New Delhi.

Kadu, P.R., Vaidya, P.H., Balpande, S.S., Satyavathi, P.L.A., Pal, D.K. 2003. Use of hydraulic conductivity to evaluate the suitability of Vertisols for deep-rooted crops in semi-arid parts of central India. *Soil Use Mgt,* **19:**208-216.

Murali , V., Krishna Murthi, G.S.R and Sarma, V.A.K. 1978. Clay mineral distribution in two toposequences of tropical soils of India. *Geoderma,* **20**:25-269.

Natarajan, A., Janakiraman, M., Manoharan, S., Balasubramaniyan , V., Murugappan, K., Udayakumar, J., Ramesh, M., Chandramohan, D., Niranjane, K. V., Krishnaswami, M., Sennimalai, P., Thankikodi, M., Kamaludeen, M., Krishnan, P., Rajamannar, G., Natarajan, S., Jagadeesan, P., and Vadivelu, S. 2006. Land resource inventory of Sivagangai block, Sivagangai District, Tamil Nadu, NBSS publ No.1028 NBSS & LUP, Nagpur. 261 p.

Pal, D. K. and Deshpande, S. B. 1987. Genesis of clay minerals in a red and black soil complex of southern India .*Clay Res*., **6**:6-13.

Pal, D.K., Dasog, G.S., Vadivelu, S., Ahuja, R. L., and Bhattacharyya, T. 2000. Secondary calcium carbonates in soils of arid and semiarid regions of India. In (Rattan Lal, J. M. Kimble, H. Eswaran, B.A. Stewart Eds) *Global Climate Change and Pedogenic Carbonates,* Lewis Publishers, Boca Raton, Florida, USA, pp. 150-185.

Pal, D. K., Srivastava, P., Durge, S. L. and Bhattacharyya, T. 2003.Role of microtopography in the formation of sodic soils in the semi-arid part of the Indo-Gangetic Plains, India. *Catena*, **51:**3–31.

Pal, D.K., Bhattacharyya, T., Chandran, P., and Ray, S.K. 2012. Linking minerals to selected soil bulk properties and climate change: A review . *Clay Research,* **31:**38-61.

Pal, D. K. and Deshpande, S. B., Venugopal, K.R., kalbande, A.R. 1989. Formation od di- and triocthedral smectite as an evidence for paleoclimatic changes in southern and central Peninsular India. *Geoderma* **45**: 175-184.

Pal, D. K., Bhattacharyya, T., Chandran, P., Ray, S.K., Satyavathi, P.L.A., Durge, S.L., Raja, P. and Maurya, U.K. 2009. Vertisols (cracking clay soils) in a climosequence of Peninsular India: Evidence of Holocene climate changes. *Quaternary International* **209**: 6-21.

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

Piper, C. S. 1966. *Soil and Plant analysis.* Hans Publishers, Bombay, India.

Rengasamy, P., Sarma, V. A. K., Murthy, R. S. and Krishna Murti, G. S. R. 1978. Mineralogy, genesis and classification of ferruginous soils of eastern Mysore plateau, India. *J. Soil Sci*., **29**:431-445.

Richards, L.A. (Ed.), (1954) *Diagnosis and Improvement of Saline and Alkali Soils*. USDA Agricultural Handbook, Vol. 60 US Government Printing Office, Washington, DC.

Rengasamy, P. 1983. Review on the genesis of red and black soils occurring in associations in the tropics with special reference to India, ICRISAT, Hyderabad (unpublished).

Ross, G.J. and Kodama, H. 1984. Problems in differentiating soil vermiculites and soil smectites: Agron. Abstr. Annual meeting of ASA, CSSA, Las Vegas, Nevada, 275pp.

Soil Survey Division Staff, 1995. *'Soil Survey Manual'* USDA Agriculture Handbook No. 18.New revised edition, Scientific Publishers, Jhodpur, India. p 437.

Srivastava, P., Chandran, P., Ray S.K. and Bhattacharyya, T. 2001. Evidence of Chemical degradation in Tropical Ferruginous Soils of Southern India. *Clay Res.,* **20**:31-41.

Srivastava, P., Bhattacharyya, T . and Pal, D. K. 2002 Significance of the formation of calcium carbonate minerals in the pedogenesis and management of cracking clay soils (Vertisols) of India. *Clays and Clay Miner*. **50**:111-126.

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

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Use of Clay from Primitive to the 21st Century

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Abstract: *The history of clays and their use may be traced back to ancient civilization. The focus on clay research was mainly on geological and the mineralogical aspect of clayey materials. People used clays primarily because of their easy availability. The rapid development of clay science and investigation on the extraordinary properties of clay minerals during the past few decades have created renewed interest among the researchers throughout the world. Over time, the empirical technology has been converted into scientific procedure. In this review paper attempt has been made to describe the use of clay minerals in diversified fields highlighting some novel applications. No other group of inorganic materials enjoy such a wide and diverse applications as clay minerals do.* **Key words :** *Historicul use, clays, clay minerals*

Clay has a very ancient root which goes back to the time in prehistory when someone found that clay could be made into a plastic mass when mixed with water, the mass could be given a shape which retained even after drying and the form could be made hard and impervious when fired. Since that time, pottery making has developed as an art rather than as a science. In primitive time clay was the only raw material for pottery making. In the present day an innumerable number of materials, both natural as well as synthetic, have been added to the list for making a variety of ceramic wares, but still clay is considered one of the important constituent. Even in the present day the rural artisans do wonders with the clay in making art objects and table wares. Ceramic manufacture is a curious blend of ancient art and modern science.

Clays and their classifications

Clays originate from the hydrothermal alteration of alkaline volcanic ash and rocks of the Cretaceous period (85-125 million years ago). Several geological processes may have led to the formation of clays during millions of years. Clays are composed of extremely fine crystals, usually plate-shaped with submicron particles in predominance. They are mostly phyllosilicates, i.e. hydrous silicates of Al, Mg, Fe, and other elements. They have large specific surface areas which make clays physically sorptive and chemically

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surface active. Plasticity is the unique property of clay which is very easy to determine but very difficult to define. This unique property makes clay an essential constituent for ceramic products for various domestic and industrial appliances viz. crockery, tiles, sanitary wares, table wares, refractory, building materials and electrical insulators.

Clay minerals are often characterized by certain properties, e.g.

- Plasticity
- Hardening on drying or firing (most clay minerals possess these properties but not all)
- Layer stacking disorder
- Base exchange capacity (some clay minerals possess very high values whereas some have extremely low value)
- The anisotropy of the layers
- A layer structure with one dimension in the nanometre range, the thickness of the 1:1(Tetra-Octa) layer is about 0.7nm and that of the 2:1 (Tetra-Octa-Tetra) layer is about 1nm
- The existence of several types of surfaces: external basal (planar) and edge surfaces as well as interlayer surfaces (Bergaya*et al.*, 1981)
- Modification of the external and also interlayer surfaces by adsorption, ion exchange or grafting

Clays are classified (Grim, 1968) on the basis of their crystal structure and the amount and location of charge per basic cell. The crystalline clays range from kaolins (1:1 layer lattice), which are relatively uniform in chemical composition (extensively used in ceramic manufacturing), to smectites, which widely vary in their compositions, high cation exchange capacities, and the ability to expand. The ease of separation of the individual layers is related to the interlamellar charges, x. The latter parameter changes from 0 for talc to x = 0.2 to 0.6 for smectites, to 0.6 to 0.9 for vermiculites, and to x = 1 to 2 for micas. Aqueous suspensions of clays are thixotropic and sensitive to ion concentrations.

Application of clays

Clays and clay minerals are extensively used in a wide variety of industrial applications. Their usages fall into two contrasting broad classes

- Clays are used because of their inertness and thermal stability (Table 1)
- Clays are used because of their reactivity and catalytic activity

1. Common clays: Large tonnages of common clays (Table 2) are used in ceramic production including bricks, tiles, terracotta, earthenware, stoneware, sewer pipes, paving bricks besides road construction, fill, and dam construction and in waste containment. The mineralogy and particle

Table 1. *Use of different clay minerals as inert components*

Clay minerals	Industry	Use
Kaolin	Paper, plastic, rubber, pesticide, pharmaceutical	Filler, carrier, diluent
	Refractory	Refractories
Vermiculite	Building, packaging, foundries	Heat insulation, sound dissipation, shock proof material thermal protection (roof of furnace)
Mica	Electrical industry, paints Cosmetics Coating	Insulation, UV-heat stable and under water paints Nacreous pigments Corrosion proof, polymer coating, under seal
Talcum, pyrophyllite	Plastic, rubber, paper, pesticide, insecticide	Filler
	Cosmetics, pharmaceutics	Powders, paste, ointment, lotions
	Refractory	Refractories

Adapted from Bergaya *et al.* (2006).

Table 2. *Properties of some Indian common clays* [a]

Clay	Panchmura	Dakshini Kalini	Paniria	Nayagaon	Dhaulia Balisai	Chunar pond clay
Source	Bankura, W. Bengal	Bankura, W. Bengal	Bankura, W. Bengal	Bhubaneswar, Orissa	Bhubaneswar, Orissa	Chunar, U.P.
Oxide composition						
SiO_2	66.70	66.37	61.77	76.29	60.43	63.18
Al_2O_3	14.73	12.34	16.03	10.95	17.98	17.03
$Fe_2O_3+TiO_2$	5.97	6.59	6.12	4.53	6.51	6.83
CaO+MgO	3.03	7.25	6.35	1.94	3.08	4.01
Na_2O+K_2O	2.23	3.94	2.59	2.03	5.16	4.00
L.O.I.	7.43	3.76	5.94	4.26	6.84	4.92
Water of plasticity%	29.85	23.50	28.08	28.82	28.21	26.63
Application temperature (Max.)°C	1150	1050	1100	1020	1020	1050
Minerals identified (XRD/DTA	Quartz, Illite, Muscovite	Quartz, Illite	Quartz, Illite	Quartz, Illite	Quartz, Illite	Quartz, Illite
Rheological Properties	Fair	Poor	Poor	Poor	Poor	Poor

[a] Courtesy by T. K. Mukhopadhyay, S. S. Chakrabarty, C. S. Prasad and K. C. Singhwho submitted reports to different Govt. Agencies.

size distribution determine their engineering properties. Although these clays are typically impure (may contain high amounts of mixed layer minerals notably muscovite, chlorites, illite and smectite), they contain sufficient clay minerals which help in the development of plasticity and to produce adequate strength, porosity and other properties to justify their use. In most cases they are mixture of several minerals (muscovite, illite and free quartz are very prominent in Indian clays) and compositions as well as thermo-mechanical properties vary widely from one place to another even within a short distance. Application temperature is rather short and narrow and poor rheological properties restrict the selection of fabrication methods. Even then common clays play a very important role in the livelihood of around 3 million rural potters in India. The potters use variety of non-plastic fillers with the locally available clays (the proportion varies according to size and shape of the wares as well as locality) and the same is mainly guided by their age old experience. The dolls of Krishnanagar (W. Bengal), horses of Bankura (W. Bengal), black pottery of Nizamabad (U. P.), clay figurines and idols of Pet (Maharashtra) and Travancore (Kerala), blue art pottery of Khurja (U.P.), table wares of Nagercoil (Tamilnadu) have crossed the geographical barrier and well appreciated in the overseas market. The artistic skill and elegance of the object are the assets although the products are very fragile as the products are fired in primitive furnaces which can only be controlled by experienced potters.All these clays are widely used by the rural potters as well by different manufacturers of building bricks, roofing tiles, and sewer pipes in spite of widely varying chemical and physical properties. There is enough scope for modernization and product diversification, however, very little interest has been shown by the technologists in this direction.

2. *Kaolins:* A major use of high purity kaolins is for ceramic products such as porcelain, bone china, and vitreous sanitary wares, which have been mentioned earlier. Low quality kaolins find applications in brick, pipes, and tiles. A typical porcelain composition comprises of 45-50 % clay, 25- 30% feldspar and 25-30% quartz which on heat treatment produces 15-20% mullite, 20-30% quartz and remaining phase being amorphous/glass(Fig.1). K_2O-Al_2O_3-SiO_2 phase diagram provides the necessary

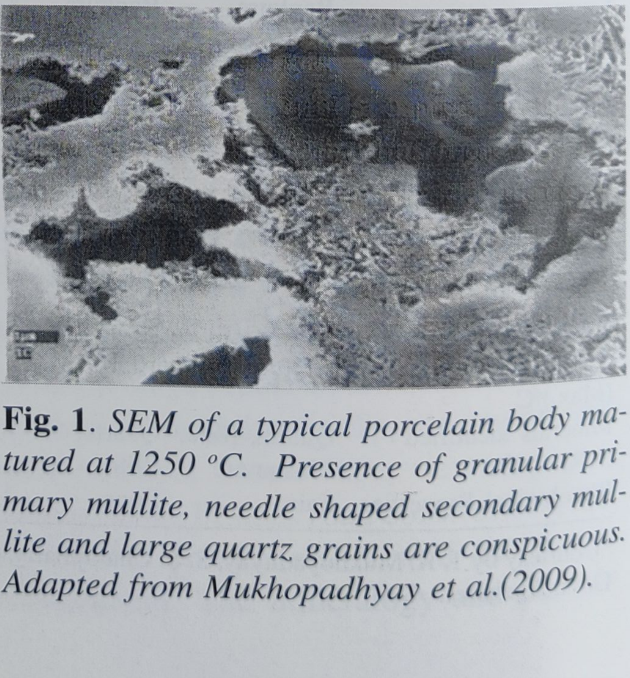

Fig. 1. *SEM of a typical porcelain body matured at 1250 °C. Presence of granular primary mullite, needle shaped secondary mullite and large quartz grains are conspicuous. Adapted from Mukhopadhyay et al.(2009).*

information regarding the composition of various types of traditional industrial porcelain. A very interesting aspect of porcelain lies with its properties that are relatively immune to small changes in body composition and processing condition like firing temperature, making it very suitable for industrial manufacture. This unique property stems out from the fact that densification of porcelain take place in the presence of a siliceous liquid phase generated from gradual melting of feldspar and subsequent eutectic formation. The composition of the liquid phase is altered by quartz dissolution which makes the glass more viscous. Higher temperature and time of firing increase quartz dissolution but at the same time rate of vitrification is slowed down due to lower fluidity of silica-rich glass. Minor variation in raw materials also do not affect the properties to a large extent since the major constituents of fired porcelain viz. glass, mullite and quartz content is not drastically altered.

Amongst the mullite containing bodies, triaxial porcelain containing clay, quartz and feldspar is significantly important because of its widespread applications. Mullite is formed by solid state decomposition of clay component and also by nucleation and crystallization of feldspathic glass in the body. Porcelain products have received wide application in a variety of fields ranging from electrical insulators to dinnerware including sanitary ware, crockery, floor and wall tiles and others within the white ware group.

The final microstructure of porcelain consists of acicular mullite crystals dispersed in feldspathic glass and partly dissolved quartz grains in silica rich glass. Zoellner (1908) proposed that strength of a porcelain body is dependent on the felt like interlocking of fine mullite needles. Choudhuri, (1975) reported that high aspect ratio of mullite impart strength and toughness to porcelain. Hence, firing temperature and generating the correct amount of properly sized mullite needles are vital in achieving the desired strength (Mukhopadhyay *et al.*, 2006).

Ceramic masses can be shaped because of the unique ability of the clay minerals to form card-house network. On the other hand, the ease with which clay particles form stable colloidal dispersion also allows the production of ceramic wares by slip casting. Chinese ceramists produced very thin walled “egg shell” porcelain with high mechanical strength utilizing delaminated kaolin (Harvey and Murray, 1997). The presence of smectites is undesirable in commercially available kaolins for most applications because of the deleterious effect of the former during firing.The largest amounts of processed kaolins are used in the paper industries as fillers within the network of cellulose fibres and as coating particles. Delamination of large particle size kaolin stacks can convert filler clay into high surface area platelets with superior opacity in light weight coatings. Gloss, brightness, opacity and smoothness improve with increasing coat mass and decreasing particle size (Li *et al*, 2001). The ≤ 2 μm fraction is particularly important in coating kaolins and high gloss paint kaolins. Coating of paper requires an exact tuning of the rheological properties of the highly concentrated slurries. Morphology of particle including shape and particle packing influence the rheological properties of kaolins. With same solid content, large particles result in higher viscosity than blocky particles. Polyphosphates and polyacrylates are usual electrolytes to produce slurry with high solid density. This increases the negative charge density at particle edges, providing steric stabilization to the dispersion (Van Olphen, 1977). Kaolins are widely used as fillers for plastic and rubber. To make the hydrophilic surface of the clay compatible with the organic material, the surface is modified by reacting with organic compounds. To improve the mechanical properties of the polymers, clay particles should be highly dispersed in the polymer matrix. Modern developments in this field not only aim to increase the bond strength between the filler particles and the polymer matrix but also to produce clay mineral-polymer nanocomposites (CPNC) where the fully delaminated mineral is dispersed in the matrix improving the thermal stability as well.

3. Bentonite: The use of bentonite in numerous applications is increasing with research on various fields. Major usages (Table 3) are iron ore pelletizing (13.3%), foundry moulding (23.5%), oil well drilling fluids (13.2%), adsorbents (29.4%), refining (3.1%), agronomy (7.3%), building industry (3.4%) and others (6.9%). In ceramics its use is very limited and very small quantity is said to be used in bone china ware manufacturing for increasing green strength. As a dispersive agent only small quantity of bentonite is used in paints, enamel, cosmetic, pharmaceutical industries beside waste water treatment plants. Swelling characteristic of smectites (particularly bentonites) find various applications and different swelling properties of clays with identical interlayer cations are mainly due to differences in layer charge densities (Weiss *et al.*, 1955).

In oil well drilling (Odom, 1984) the fluid acts as a lubricant to reduce the friction between the drilling string and the side of the wall while building up an impermeable filter cake of montmorillonite particles preventing the loss of fluid into the permeable rock as well as inflow of oil or gas from rock. Drilling fluids are mainly based on dispersed sodium bentonites. Bentonite dispersions are used to grout cracks and fissures in rocks, for soil injections, or to impede water and waste water movement through soils, sand or gravel. Bentonite also finds application in waterproof concrete walls, and mortar (Kroyer *et al.*, 2003) and bitumen emulsion. In shield tunnelling the thixotropic bentonite supports the soil in front of the shield until it is removed by the tools of the rotating shield. In paints and enamel paints it acts as thickening agent as well as impedes sagging of the paints. In non-polar systems the clay particles have to be modified to develop hydrophobic characteristics. The adsorption capacity of bentonites is gainfully utilized to absorb proteins and other high molecular compounds to stabilize beer, wines and improving the taste and quality of juices. Acid activated bentonites are extensively used for decolourizing vegetable and mineral oils and improving stability as well as taste. Carbonless copying papers are composed of paper sheets with different coatings on the back of the upper sheet (CB) and on the front of the lower sheet (CF). CB is coated with microcapsules containing the leuco dye (crystal violet lactone) and CF is covered with a coating colour consisting of an acid activated bentonite. The pressure of the pencil or the stroke of the typewriter breaks the microcapsule at the point of contact. As the solution is released, the dye is absorbed

Table 3. Uses of bentonite

Area of applications	Uses
Agriculture, horticulture	Soil improvement, composting, adsorption of mycotoxins
Building industry	Supporting dispersions for cut off diaphragm wall construction, shield tunnelling, subsoil sealing, antifriction agents for pipe -jacking and shaft sinking additions to concrete and mortar
Ceramics	Plasticising of organic masses, improvement in strength, fluxing agents
Foundries	Binding agents for moulding and core sand binding agents for anhydrous casting sands, thickening of blackwashes
Mineral oil industry	Drilling fluids, thickening of greases, decolouration, purification and stabilization of mineral oils, fats, waxes, paraffins
Paints, varnishes	Thickening, thixotroping, stabilising, anti-settling agent, coating materials, sealing cement, additives for waxes and adhesives
Pharmaceutical, cosmetics	Bases of creams, ointments and cosmetics, powders, tablets, drug carrier, odour control, liquid absorption
Tar exploitation	Emulsification and thixotroping of tar-water emulsions, tar and asphalt coatings, additives for bitumen.
Environmental technology	Forest and water conservation, fire extinguishing powders, binding agent for oil on water, manure treatment, waste water purification, sewage sludge pelletizing
Food industry	Refining, decolouration and stabilization of vegetables, animal oil, fats, fining of wine, juice, beer stabilization, purification of saccharine juice and syrup
Paper industry	Pigment and colour developer for carbonless copying paper

Adapted from Bergaya, *et al.*(2006).

on the coating colour of the CF front page and the colour develops at this point (Fahn and Fenderl, 1983).

Clay minerals as catalysts

In petrochemical processing, such as cracking, solid catalysts were used and the catalysts were based on acid treated clays. Treatment of clays with strong inorganic acids (HCl or H_2SO_4) is termed as acid activation of clays. Decomposition of clay minerals after treatment with sulphuric acid decreases in the order halloysite> montmorillonite> pyrophyllite = talc> illite> kaolinite. From industrial point of view, Ca- bentonite is usually treated with inorganic acids to exchange divalent calcium ions with hydrogen ions as well as to leach out Fe^{+3}, Fe^{+2}, Al^{+3} and Mg^{+2} ions thereby altering the layers of smectite and increasing porosity and surface area (Komadel, 2003). In order to exploit the exciting, greener technology in organic chemical manufacturing, we need to produce highly effective catalysts in flexible physical forms to suit a multitude of chemical process technologies. Clay minerals have an interesting set of properties and can be very effective catalysts for a wide variety of organic reactions. The activity of clay as effective catalysts originates from high surface area, local concentration effect (adsorption on the solid surface) and low dimension of the clay minerals, all these factors lead to enhanced reactivity. Most of the reactions catalysed by smectites make use of the acidic nature of acid treated clay minerals. Both Lewis and Bronsted activity are common. The total acidity and the ratio of Bronsted to Lewis sites change with the hydration state of the clay mineral. The Bronsted activity results from the dissociation of interlayer water molecules coordinated to polarising interlayer cations.

$$[M(OH_2)n]^{m+} + B \rightarrow [M(OH_2)_{n-1} OH]^{(m-1)+} + BH^+$$

Where B is an organic species in the interlayer space. M is usually Fe^{+3}, Al^{+3} or Cr^{+3}. The acid strength increases with decreasing size and increasing charge of the cations. Heating induces the small cations to migrate from their interlayer positions in smectites into the layer structure where they become practically non-exchangeable and the reduction in negative layer charge is the well-known Hofmann-Klemen effect (Hofman and Klemen, 1950). In case of Li-montmorillonite, heating results in Li^+ ions to migrate from the interlayer space into the vacant octahedral sites or into the hexagonal holes of the tetrahedral sheets (Theng *et al.*, 1997). This reduces the layer charge density which ultimately controls the distribution of cations in the interlayer space. For acid activated clays the activity derives from Fe^{+3}or Al^{+3}ions which have been liberated from the octahedral sheet and relocated to the crystal edges or into the interlayer region. Increase in Lewis acidity is effected by depositing $ZnCl_2$ or $AlCl_3$ onto clay mineral surfaces. The smectite clay minerals can accommodate larger molecules between their layers than do relatively rigid framework silicates (zeolites). However, activity of clays is relatively poor above 150°C as a result of dehydroxylation and collapse of layers. To overcome this problem pillared clays are produced by incorporating inorganic cations to prop the layers apart. Metal oxide pillared clay possesses several interesting properties for attractive material in catalytic reactions, such as large surface areas, high pour volume, tunable pore size (from micropore to mesopore), high thermal stability, strong surface acidity, and catalytic active substrates/metal oxide pillars. The activity and porosity of pillared clays are highly dependent on the method of preparation. Alumina and double pillared montmorillonite find application in *iso*-propanol conversion, *n*-butene isomerization, Friedel-Crafts alkylation and acylation of aromatics, catalytic cracking and dehydration and isomerization of alcohols while pillared saponite is more selective for covertingn-butene to *iso*-butene.

Thermally activated acid treated kaolinite and smectites are used as catalysts in organic synthesis for a long time particularly from waste materials (Breen *et al*., 2002). Dehydroxylation of kaolinite to metakaolinite results in distorted SiO_4 sheets, while the octahedral sheets are predominantly altered and coordination number of Al atoms is reduced from 6 to 4. Metakaolinite with highest Al^V is the most acid reactive form. Total surface area and micro porosity of kaolinite increases with increasing temperature reaching a maximum at 875°C. (Duarte *et al*, 1995). A judicious choice of porosity and acidity can produce selective catalysts. Macedo *et al*. (1994) observed that partially dealuminated metakaolin acts as super acid and catalyse cracking of Cumene. Acid activated metakaolin has a higher CEC than the parent mineral and can be effectively used to remove hazardous Cd^+, Cu^{+2}, Cr^{+6} ions (Suraj *et al*., 1998). Pozzolanic activity of metakaolin is well known to develop cementitious material with lime. Use of metakaolinite blended cement in mortar or concrete increases their strength and durability as well as resistance to aggressive solutions of sulphates and chlorides. Zeolites are formed when metakaolin is treated hydrothermally with NaOH and KOH solutions. This is the basis of membrane based gas separation technique.

The expandable layers of clay minerals facilitate incorporation of catalytically active metal complexes by cation exchange and ligand exchange methods (Tao and Zou, 2002). Intercalation of metal complexes into the interlayer space of smectite is extensively used for synthesis of organic molecules and their conversion. Montmorillonite hydrolyses the carbamates and phosphorous containing pesticides (Wei *et al*, 2001; Smolen and Stone, 1998). Na-montmorillonite effectively catalyses the condensation of glycolaldehyde to monosaccharides. Salicylic aldehyde and derivatives have been synthesised by reaction of phenols with formaldehyde by montmorillonite KSF triethylamine (Bigi *et al*, 2000). Excellent yield of triarylmethanes from aromatic aldehydes with N,N – dimethylaniline catalysed by montmorillonite at 100°C (Zhang *et al*., 1997). Certain transition metals are noted for their ability to coordinate alkanes and generate carbenes from diazoalkanes (Wulfman *et al*., 1976). The most important commercial Diels-Alder reaction catalysed by smectite based catalysts is the cyclo-dimerization of oleic acids (Newton, 1984). Use of pillared clays, TM exchanged clays, acid treated clays, Ce or Sn-exchanged Al pillared clays, have been reported for catalytic cracking and isomerisation (n-alkanes to iso-alkanes, 1-hexanol to 2-and 3-hexanes), methanol to C_2-C_4 alkanes, Friedle Crafts alkylation and acylation of aromatics (phenol alkylation, cycloalkenes to polyalkenes, aniline alkylated by alkenes), acylation of aromatic hydrocarbons with carboxylic acids, nitration of aromatics, methylation of alkylnaphthalenes, citronella to menthone and isomenthon (Al/Fe pillared clay at 80°C) by hosts of researchers.

Redox reactions are associated with transition metals either substituted in the octahedral or tetrahedral sheets of the clay minerals as well as introduction of exchangeable cations between the clay layers. Fujita *et al*. (1987) patented two processes for production of alkylene glycol monoalkyl ether and oxidation of allylic alcohols to ketones using Ni^{+2}– F mica and (Hashimoto *et al.*, 1988) described the process of production of cyclohexanol and cyclohexanone from cyclohexene with Co^{+3} clay. Choudary *et al*. (1990, 1992) utilized Cr^{+3} pillared clay and vanadium pillared clay respectively for production of monocarbonyl compounds from arylmethylenes and selective epoxidation of allylic alcohols. Not enough attention has been paid to engineering of clays into catalyst particles, pellets, and membrane, that can survive industrial processing conditions.

Clay-Polymer nanocomposites

In the large field of nanotechnology, polymer matrix based nano composites have become a prominent area of current research and development. Exfoliated clay based nano composites have dominated the polymer literature. While the reinforcement aspects of nano composites are the primary area of interest, a number of other properties and potential applications are important including barrier properties, flammability resistance, electrical/electronic properties, membrane properties, polymer based compatibilization. Exfoliated clays could yield significant mechanical property advantages as a modification of polymeric systems. The sodium ions of montmorillonite clay can be exchanged with organic cations, such as those from an ammonium salt, to form an organo clay.

The ammonium cation may have hydrocarbon tails and other groups attached and are referred to as a "surfactant" owing to its amphiphilic nature. The extent of the negative charge of the clay is characterized by the cation exchange capacity. When sodium is replaced by much larger organic surfactants, the gallery expands and the XRD spacing may increase by as much as 2 to 3 folds. Nanocomposites can be formed from clays and organo clays in a number of ways including various in situ polymerization, solution and latex methods. Melt processing is considered more economical, more flexible for formulation and involves compounding and fabrication facilities commonly used in commercial practice. For most purposes, complete exfoliation of the clay platelets, i.e. separation of platelets from one another and dispersed individually in the polymer matrix, is the desired goal of the formation process. Three types of morphology may result, immiscible (conventional or micro composites), intercalated, and miscible or exfoliated. Complete exfoliation or so cannot be achieved unless there is a good thermodynamic affinity between the organo clay and the polymer matrix. This affinity can be affected to a very significant extent by optimizing the structure of the surfactant used to form the organo clay and the CEC of the clay, as this affects the density of the surfactant molecules over the silicate surface. Nylon 6 appears to have good affinity for the silicate surface, perhaps by hydrogen bonding, and as a result very high levels of exfoliation can be achieved in the matrix. Surfactants with single long alkyl tail give the best exfoliation. On the contrary, non-polar polyolefin segments have no attraction to the polar silicate surface and increasing the number of alkyls on the surfactants improves dispersion of the organo clay in the polyolefin matrix since a large number of alkyls decrease the possible frequency of the unfavourable polyolefin-silicate interaction and increase the frequency of more favourable polyolefin-alkyl contacts. Properly dispersed and aligned clay particles have proven to be very effective in increasing stiffness. The clay-polymer nano composite (CPNC) has a weight advantage over the glass-polymer composite. Furthermore, if the clay platelets are aligned in the plane of the sample, the same reinforcement should be seen in all directions within the plane, whereas fibres reinforce only along a single axis in the direction of their alignment. Nanosize of the clay platelets ensures better surface finish. Montmorillonite platelets are particularly effective for reducing coefficient of thermal expansion of plastics and are particularly useful for automotive applications. In situ polymerized PET (Poly ethylene terephthalate) exfoliated clay composites exhibit a 10 to 15 fold reduction in O_2 permeability with 1-5% clay which are potential material for barrier applications.

Surface modifications of clay minerals are studied because they allow the creation of novel materials and, hence, materials with novel applications. During the past decade, organically modified layer silicates have received much attention from the scientific and technological communities because of their use as fillers in clay polymer nanocomposites (CPN). The automotive, aerospace, and packaging industries view CPNs as promising materials for the 21st century due to their improved mechanical- and thermal-barrier and flame-retardant properties (Alexandre and Dubois, 2000; Zhu *et al.*, 2001; Sinha Ray and Okamoto, 2003; Ruiz-Hitzky *et al.*, 2004; Bergaya*et al.*, 2006; Carrado and Sandi, 2007; Hrachova *et al.*, 2009). The surface energy, structural features, and chemical characteristics of the clay minerals and the viscosity of the polymer matrix are key factors in ensuring the desired properties of the nanocomposite. Modification of clay minerals with organic materials is necessary to establish compatibility between the clay particles and the polymer matrix. Apart from the CPN applications, these intercalated montmorillonites are also used as rheological modifiers, as adsorbents of pollutants in waste-water treatments, as thickening and gelling agents in paints and lubricants (Patel *et al.,* 2006), and as drug-delivery vehicles for pharmaceutical purposes(Maguy and Lambert, 2010). Montmorillonite is the best of the smectite group of clay minerals for intercalation with organics because of its CEC, swelling behaviour, adsorption ability, and large surface area. The intercalation of organic cations into the interlayer space of montmorillonite is of paramount importance in the formation of a CPN because it changes two particular characteristics of the montmorillonite which help make it compatible with the hydrophobic polymer. Firstly, the intercalation changes the hydrophilic nature of the clay mineral to organophilic through ion exchange with the organic cations and, secondly, it increases the basal spacing which enhances the potential for delamination of clay platelets within the polymer matrix. The organic loading and basal spacing of the intercalated montmorillonite are, therefore, important properties because the degree of dispersion of the clay mineral in the polymer matrix depends on them. The dependence of the basal spacing and organic loading of intercalated montmorillonite with different organic intercalates is, therefore, worth studying. Lagaly (1994) observed that the lower chain alkylamines usually form a monolayer in the clay interlayer with d-values in the order of 1.36nm while the same increased to above 1.76 nm when the chain length of alkyl amine is further increased resulting in a bilayer formation. A considerable amount of work has been done using different intercalates with varying chain lengths and varying relative proportions (Xie *et al.*, 2001, 2002; Fajnorand Hlavaty, 2002; Liu *et al.*, 2007; Xi *et al.*, 2007; Onal and Sarikaya, 2008; Avalos *et al.*, 2009; Guegan *et al.*, 2009; Li and Jhang, 2009). Novel oriented transparent films of layered silica surfactant nanocomposites were synthesized by Ogawa in studies in which the chain length of the surfactants was varied (Ogawa, 1994). Espina *et al.* (1998) discussed the effect of simultaneous intercalation in another layered system they reported simultaneous intercalation of two n-alkyl amines into a-titanium phosphate systems and obtained new individual intercalation phases. Earlier studies which showed that basal spacing of intercalated montmorillonite depends on the orientation, organization, and population of the intercalate moieties dealt with a single intercalate only. In a more recent study, using a mixture of cationic and anionic intercalates, synergistic changes in basal spacings, organic loadings, adsorption, and adsorption capacity of the modified clay minerals (Chen *et al*., 2008) were reported. The influence of the structures of each intercalate within the mixture on the properties of the montmorillonites have yet to be explored. The limited thermal stability (<250°C) of conventional organo-ammonium intercalated montmorillonite reduces the expected improvements in the CPN properties. The current challenge is to prepare a nanofiller that can withstand higher melt processing temperatures (>300ºC), long residence times under high shear, and is stable in thermoset resins with high curing temperatures. Phosphonium-intercalated montmorillonites are promising candidates as high-temperature stable nanofillers for application in CPNs (Xie *et al*., 2002).

In a recent study (Ganguly *et al.,* 2010, 2011), a synergistic composition was formulated by varying the cationic head group structure of two phosphonium-based intercalate mixtures to increase both the basal spacing and the organic loading of the montmorillonite. Two alkyl phosphonium intercalates with different chain lengths and cationic head-group structures (groups attached to the phosphorous of the phosphonium salt) were chosen. They were mixed with each other in different molar ratios and the resulting solution mixtures were intercalated simultaneously within the interlayer space of montmorillonite to observe its effect on basal spacing and organic loading.

- During simultaneous intercalation of montmorillonite layers with mixtures of two intercalates, organic loading of the montmorillonite increased linearly with increase in the mole fraction percent of the longer-chain component of the intercalate mixture.
- Simultaneous intercalation with mixtures of two intercalates in montmorillonite manifested the effect of each individual component in the mixture.

The high surface to volume ratio of nano particles leads to a high reinforcement efficiency. Thus, clay polymer nano composites (CPNCs) with well dispersed platelets at a low clay loading of 2 to 5 wt% show high increased modulus, yield strength as well as reduced flame propagation and permeability. Owing to the nature of nano scale reinforcement, the CPNC may be treated as an improved grade of homo polymer, hence it may be used as a replacement for its matrix polymer in diverse multicomponent polymeric systems, viz. blends, composites or foams. These materials are finding applications as automotive parts, packaging appliances, building and construction, electrical and electronics, lawn and garden, and power tool applications. One of the uses for exfoliated clay in barrier applications involved a 20μm coating on the interior of a tennis ball to prevent depressurization. The product was developed by In Mat LLC, USA and marketed in 2001. In such applications, performance overrides the economic disadvantages of the inclusion of expensive materials.

Nonceramic applications of clays

Clay minerals are promising drugs in the treatment of irritable bowel syndrome. Clay minerals particularly smectites protect and are efficient against several "aggressors" that causes major disorders of the gut. The beneficial effects of clay minerals on the gastrointestinal mucosa are associated with two mechanisms of action (1) adsorption of the "aggressors" or their toxic secretions and (2) modification of the thickness and rheological properties of the adherent mucus reinforcing the natural defences of the gastrointestinal mucosa. Clay minerals provide protection against diarrhoeas induced by antibiotics treatments, chemotherapy and radiation, and HIV infection. Clay based herbicides have been designed to solve environmental problems. It is well known that a part of the herbicide undergoes surface migration and cause water contamination and impairs neighbouring crops. The problem becomes serious with hydrophobic herbicide (*acetochlor*) and anionic herbicide (*sulfometuron*). In the formulation clay enhances the slow release of the active ingredient. The adsorption of organic cations on clay modifies the nature of the clay mineral surface transforming it from hydrophilic to hydrophobic, act as an energy acceptor of the photo-excited molecule of the pesticide, thus becoming photo stabilized. Rytwo (2000) and Tropp and Rytwo (2001) observed that montmorillonite clay sprayed on plants reduced the herbicidal activity of bipyridal herbicides (*Paraquat and Diquat*) and exploiting clay-organic interactions the efficacy of molecules are enhanced.

A recent development is the use of space between layers of clay minerals as a nano reactor, nano particles/nano wire growth is limited by the interlayer space of clay minerals. Formation of nano silver/copper wire inserted in the interlayer space of selected smectite minerals for development of electrical and magnetic conductivity for various application is under research project. Nano sized palladium and silver particles have been prepared between kaolinite particles by intercalation of hydrazine, DMSO and potassium acetate. Palladium acetate adsorbed in the interlayer space of organophillic montmorillonite and subsequently reduced to Pd^Oparticles by ethanol is well known. Several transition metal sulphides and oxides e.g. CdS, ZnS, TiO_2,and Fe_3O_4 have been prepared by hydrolysis in between the layers of pillared montmorillonite and layered double hydroxides providing new types of catalysts and cosmetics.

Conclusions

Clay and clay minerals, either as such or after modification, will be recognized as the materials of the 21st century because they are abundant, inexpensive and environmental friendly. Clay has become indispensable to modern living. It is the material that supports the livelihood of rural artisans. It is the material for our daily use such as porcelain, brick, tiles, and sanitary wares. In non-ceramic applications clay finds utilization in paper, polymer composites, paints, cosmetics, adsorbent for pollutants, medical formulations, and catalysts support. These clay based products have been developed utilizing sub-micron dimension of clay platelets, its cation exchange capacity and high surface adsorption capacity. Clay is non-polluting and can be used as depolluting agent. Of great importance for the near future is the potential of some clays to be dispersed as nano size in polymer phase forming nano composites with superior properties. The unique edge-face chemistry, colloidal aggregation behaviour and morphological features of clay minerals remain relatively unexploited.

It is not out of context to opine that industrial mineral users, particularly in India, are rather conservative and do not readily accept new products. It is necessary to own the confidence of the users on the quality, consistency, cost competitiveness, technical support, and value of final product in comparison to the existing process or product. In one end archaeologists consider the clayey objects as a tool of identifying early human civilization and its progress and on the other side of the spectrum, high purity clay minerals find applications in space capsules, pharmaceuticals, catalysis, waste abatement, environmental protection, and packaging.

References

Alexandre, M. and Dubois, P. 2000. Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials. *Materials Science and Engineering Report*, **28**: 1-63.

Avalos, F., Ortiz, J.C., Zitzumbo, R., Manchado, M.A.L., Verdejo, R. and Arroyo, M. 2009. Phosphonium salt intercalated montmorillonites. *Applied Clay Science*, **43**: 27-32.

Bergaya, F., Cruz, M.I., Gatineau, L. and Fripiat, J.J. 1981. Adsorption of alcohols by smectites IV, Models.*Clay Minerals*, **16**: 115-122

Bergaya, F., Lagaly, G. and Vayer, M. 2006. Cation and anion exchange. In (F. Bergaya, B.K.G. Theng, and G. Lagaly, Eds)*Handbook of Clay Science*. Developments in Clay Science, Vol. 1, Elsevier Ltd., Amsterdam,pp. 979-1001.

Bigi, F., Conforti, M.L., Maggi, R. and Sartori, G. 2000. Trialkylamine controlled phenol-formaldehyde reaction over clay catalyst: Selective and environmentally benign synthesis of salicylic aldehydes. *Tetrahedron*, **56**: 2709-2712

Breen, C., Taylor, S., Burguin, E. and Centeno, M. 2002. Preparation and characterization of dealuminated metakaolin and its use in the transformation of waste plastics to aromatic hydrocarbons. *Journal of Colloids and Interface Science*, **247**: 246-250

Carrado, K.A. and Sandi, G. 2007. Metal nanoclusters on polymer-clay nanocomposite films. In (K. A. Carrado and F. Bergaya, Eds)*Polymer-Clay Nanocomposite Research.* CMS workshop lectures, Vol. 15, The Clay Minerals Society, Aurora, Colorado,pp. 298.

Chen, D., Zhu, J.X., Yuan, P., Yang, S.J., Chen, T.H., and He, H.P. 2008. Preparation and characterization of anion-cation surfactants modified montmorillonite. *Journal of Thermal Analysis and Calorimetry*, **94**: 841-848.

Choudhuri, S.P.1975.Ceramic Properties of hard porcelain in relation to mineralogical composition and microstructure: VI-thermal shock resistance and thermal expansion. *Trans. Ind.. Ceram. Soc.*, **34**: 30-34.

Choudary, B.M., Villi, V.L.K. and Prasad, A.D. 1990. A new vanadium pillared Montmorillonite catalyst for the regioselectiveepoxidation of allylic alcohols, Journal of Chemical Society, Chemical Communications, pp. 721-722.

Choudary, B.M., Prasad, A.D., Bhuma, V and Swapna, V. 1992. Chromium pillared clay as a catalyst for benzylic oxidation and oxidative deprotection of benzyl ethers and benzyl amines- a simple and convenient procedure. *Journal of Organic Chemistry*, **57**: 5841-5844

Durate, M.A.I., Macedo, J.C.D. and Alves, D.B. 1995. Generation of pores in metakaolin by acid dealumination. In (G.J. Churchman, R. W. Fitzpatric and R.A. Eggleton, Eds).*Clays: Controlling the Environment.* Proceedings of the 10th. International Clay Conference, Adelaide, Australia, 1993. CSIRO, pp.112-115.

Espina, A., Jaimez, E., Khainakov, S.A., Trobajo, C., Garcia, J.R. and Rodriguage, J. 1998. Synthesis of n-alkylamines intercalation compounds with a-titanium phosphate. Process selectivity and structural and morphological characterization. *Chemistry of Materials*, **10**: 2490-2496.

Fahn, R. and Fenderl, K. 1983. Reaction products of organic dye molecules with acid treated montmorillonite. *Clay Minerals*, **18**: 447-458

Fajnor, V.S. and Hlavaty, V. 2002. Thermal stability of clay/organic intercalation complexes. *Journal of Thermal Analysis and Calorimetry*, **67**: 113-118.

Fujita, T., Mizuno, K. and Saeli, K. 1987. Oxidation of alcohols, Japanese Patent, 62142134 A2

Ganguly, S., Dana, K. and Ghatak, S. 2010. Thermogravimetric study of n-alkyl ammonium-intercalated montmorillonites of different cation exchange capacity. *Journal of Thermal Analysis and Calorimetry,***100**: 71-78.

Ganguly, S., Dana, K., Mukhopadhyay, T. K. and Ghatak, S. 2011. Thermal degradation of alkyl triphenylphosphonium intercalated montmorillonites. *Journal of Thermal Analysis and Calorimetry.* **105** : 199-209

Grim, R.E. 1968. *Clay Mineralogy*, 2nd. Edition. McGraw-Hill, New York

Guegan, R., Gautier, M., Beny, J.M. and Muller, F. 2009. Adsorption of a C10E3 non-ionic surfactant on a Casmectite. *Clays and Clay Minerals*, **57**: 502-509.

Harvey, C.C. and Murray, H.H. 1997. Industrial clays in the 21st. Century: a perspective of exploration, technology and utilization. *Applied Clay Science,***11**: 285-310

Hashimoto, K., Asahi, Y. and Maki, T. 1988. Production of cyclohexanoland cyclohexanone, Japanese Patent, 63303936.

Hofmann, U. and Klemen, R. 1950. Verlust der Austauschfähigkeit von Lithiumionen an Bentonitdurch Erhitzung. *Zeitschriftfüranorganische und allgemeineChemie.* **262:** 95-99

Hrachova, J., Komadel, P., and Chodak, I. 2009. Natural rubber nanocomposites with organo-modified bentonites. *Clays and Clay Minerals*, **57:** 444 - 451.

Komadel, P. 2003. Chemically modified smectites. *Clay Minerals*. **38**: 127-138

Kroyer, H., Lindgreen, H., Jakobsen, H.J. and Skibsted, J. 2003. Hydration of Portland cement in the presence of clay minerals studied by ^{29}Si and ^{27}Al MAS NMR spectroscopy. *Advances in Cement Research.***15**:103-112.

Lagaly, G. 1994. Layer charge determination by alkylammonium ions. In: *Layer Charge Characteristics of 2:1 Silicate Clay Minerals,* CMS Workshop lectures, Vol. 6, *The Clay Minerals Society*, Boulder, USA,pp.1-46.

Li, J., Tanguy, P.A., Carreau, P.J. and Moan, M. 2001. Effect of thickner structure on paper coating color properties. *Colloid and Polymer Science*. **279**: 865-871.

Li, Z. and Jhang, W.T. 2009. Interlayer conformations of intercalated dodecyl trimethylammonium in rectorite as determined by FTIR, XRD, and TG analysis. *Clays and Clay Minerals*, **57**: 194-204.

Liu, X., Lu, X., Wang, R., Zhou, H., and Xu, S. 2007. Interlayer structure and dynamics of alkyl-ammoniumintercalated smectites with and without water: a molecular dynamics study. *Clays and Clay Minerals*, **55** : 554 - 564.

Macedo, J.C.D., Mota, C.J.A., de Menezes, S.M.C. and Camorim, V. 1994. NMR and acidity studies of dealuminated metakaolin and their correlation with cumene cracking. *Applied Clay Science*, **8**: 321-330

Maguy, J. and Lambert, J.F. 2010. A new nanocomposite: LDOPA/Laponite. *Journal of Physical Chemistry Letters*, **1:** 85-88.

Mukhopadhyay, T. K., Ghosh, S., Ghatak, S. and Maiti, H. S. 2006. Effect of pyrophyllite on vitrification and on physical properties of triaxial porcelain, *Ceramics International*, **32**: 871-876.

Mukhopadhyay,T. K., Ghatak, S. and Maiti, H.S. 2009. Effect of pyrophyllite incorporation in porcelain composition on mechanical properties and microstructure, *Ceramics International*, **35**: 2555-2562.

Newton, L.S. 1984. Dimer acids and their derivatives- potential applications, *Speciality Chemicals,* 17.

Odom, E. 1984. Smectite clay minerals: Properties and uses. *Philosophical Transaction of the Royal Society of London* A. **311**: 391-409

Ogawa, M. 1994. Formation of novel oriented transparent films of layered silica-surfactant nanocomposites. *Journal of the American Chemical Society,* **116**: 7941-7942.

Onal, M. and Sarikaya, Y. 2008. Thermal analysis of some organo clays. *Journal of Thermal Analysis and Calorimetry*, **91**: 261-265.

Patel, H.A., Somani, R.S., Bajaj, H.C., and Jasra, R.V. 2006. Nanoclaysforpolymernano composites, paints, inks, greases and cosmetics formulations, drug delivery vehicle and waste watertreatment. *Bulletin of Materials Science*, **29**:133-145.

Ruiz-Hitzky, E., Aranda, P., and Serratosa, J.M. 2004. Clay_organic interactions: organoclay complexes and polymer-clay nanocomposites. In (S. Auerbach, K.A. Carrado, and P. Dutta, Eds). *Handbook of Layered Materials*Marcel Dekker, New York,pp. 91-154.

Rytwo, G., 2000. The use of clay organic interactions to improve efficacy of contact herbicides: addition of monovalent organocations to divalent herbicides. In *Proceedings of the 1st. Latin-American Clay Conference "Clays in Volcanic Environments"*Funchal, Madeira, 1, pp. 332-344.

Sinha Ray, S. and Okamoto, M. 2003. Polymer/layered nanocomposites: a review from preparation to processing. *Progress in Polymer Science*, **28:** 1539-1641.

Smolen, J.M. and Stone, A.T. 1998. Metal hydroxide surface catalysed hydrolysis of chlorpyrifos-methyl, chlorpyrifos-methyloxon and paraoxon. *Soil Science Society of America Journal,* **62**: 636-643

Suraj, G., Iyer, C.S.P. and Lalithambika, M. 1998. Adsorption of cadmium and copper by modified kaolinite. *Applied Clay Science.*, **13**:293-306

Tao, L.X. and Zou, D.X. 2002. Clay-intercalated metal complex catalysts and their molecular recognition catalysis. *Progress in Chemistry*, **14**: 200-206

Theng, B.K.G., Hayashy, S., Soma, M. and Seyama, H. 1997. NMR and X ray photoelectron spectroscopic investigation of lithium migration in montmorillonite. *Clays and Clay Minerals*, **45**: 718-723

Tropp, D. and Rytwo, G. 2001. The use of clay organic interactions to improve efficacy of contact herbicides: addition of monovalent organocations to diquat. *Applied Clay Science*, **18**: 327-333

Wei, J., Furrer, G., Kaufmann, S. and Schulin, R. 2001. Influence of clay minerals on the hydrolysis of carbamate pesticides. *Environment Science and Technology*, **35**: 2226-2232

Weiss, A., Koch, G. and Hofmann, U.K. 1955. Zurkenntnis von Saponit. *Ber. tsch. Keram. Ges.* **32**: 12-17.

Wulfman, D.S. McDaniel, R.S. Jr. and Peace, B.W. 1976. Metal salt catalysed carbenoids XIII. On the mechanisms of cyclopropanation and allylic C-H insertion by diazo esters in the presence of olefins and homogeneous copper catalysts. *Tetrahedron*, **32**: 1241-1251

Van Olphen, H. 1977. *An Introduction to Clay Colloid Chemistry,* 2nd edition, Wiley, New York.

Xi, Y., Zhou, Q., Fr ost, R., and He, H., 2007. Thermal stability of octadecyltrimethylammonium bromide-modified montmorillonite organo clay. *Journal of Colloid and Interface Science*, **311**: 347-353.

Xie, W., Gao, Z., Pan, W.P., Hunter , D., Singh, A. and Vaia, R. 2001. Thermal degradation chemistry of alkyl quaternary ammonium montmorillonite. *Chemistry of Materials*, **13**: 2979 - 2990.

Xie, W., Xie, R., Pan, W.P., Hunter , D., Koene, B., Tan, L.S., and Vaia, R. 2002 Thermal stability of quaternary phosphonium modified montmorillonites. *Chemistry of Materials,* **14**: 4837 - 4845.

Zhang, Z.H., Li, T.S. and Fu, C.G. 1997. Montmorillonite clay catalysis 4. An efficient and convenient procedure for preparation of 1,1 diacetates from aldehydes. *Journal of Chemical Research,* **5**: 174-175

Zhu, J., Morgan, A.B., Lamelas, F.J. and Wilkie, C.A. 2001. Fire properties of polystyrene_clay nanocomposites. *Chemistry of Materials*, **13:** 3774-80.

Zoellner, A. 1908. ZurFrage der Chemischem und PhysikalischenNatur der Porzellans," (Some Chemical and Physical Properties of Porcelains). *Sprechsaal*, **41**: 471-473.

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The Clay Mineral Maps of Tripura and their Application in Land Use Planning

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Abstract : *Earlier exercise on the preparation of maps on clay minerals for some Indian states did not have the well-defined boundaries because of inadequate spatial data. Appreciating this as an important exercise for efficient management of natural resources, required research initiative has been made by the National Bureau of Soil Survey and Land Use Planning (ICAR), Nagpur to complete the task of generating clay mineral maps of different states. In this endeavour we generated various theme maps of clay minerals of Tripura. The clay samples (<2 μm) of the selected soil series were analyzed by X-ray diffraction (XRD) method and the clay mineral content was estimated using the X-ray diffractograms. The soil parameters such as cation exchange capacity, clay and organic matter contents were used to correlate the mineral make-up in the clay fractions. The data on clay minerals for 48 soil series were utilized to generate a clay mineral map for the state. It is interesting to note that most of the 2:1 clay minerals are interstratified ones which appear to have a close relation with the land use patterns in terms of forest, plantation and agriculture in the state.*

Key words : Clay minerals, maps, land use

Mapping natural resources with special reference to soil, based on factors of soil formation was initiated during fifties. The refinement of soil maps at various scales is still in progress. However, maps showing soil mineral compositions are generally rare (Ghosh and Bhattacharyya, 1982). This is notwithstanding with the fact that the knowledge of clay mineral composition of soils is of paramount importance in fertilizer use, crop management and for various land uses since the soil properties such as water retention and release, nutrient adorption and desorption, and shrink-swell behaviour are significantly influenced by the nature and content of soil clay minerals.

Investigation on soil mineralogy took a definite step forward after the use of X-ray diffraction (XRD) techniques. In India, Prof. J.N. Mukherjee, was the first to initiate XRD analysis of soil clays, at the Colloid Research Laboratory of Calcutta University. Work on soil mineralogy in India has been reviewed periodically by many (Mukherjee, *et al.*, 1971; Ghosh and Raychaudhuri, 1974; Ghosh and Kapoor, 1982; Ghosh, 1998; Pal *et al.*, 2000). However, no systematic effort has yet been made to develop soil clay mineral maps that could be linked to various land uses.

The present endeavour is a beginning of generating clay mineralogy maps of the Indian states with Tripura as a case study. We used geographic information systems (GIS) with the available information on clay mineral compositions (Ghosh and Bhattacharyya, 1982; Bhattacharyya, et al., 1996a,b; 2003a, b).

Study Area

Tripura

Tripura covers an area of 10.5 m ha with four districts showing mean annual temperature of 24°C and mean annual rainfall of 2065-2678 mm (Fig. 1) (Bhattacharyya et al., 1996). The state was surveyed at 1:50,000 scale. A total of 48 soil series were identified (Bhattacharyya, 1997a,b,c) with four soil orders and 43 mapping units (Fig. 2). Dataset generated through world bank aided rubber project (Bhattacharyya, 1996), DST funded project (Bhattacharyya, 2003a,b) on soil erosion (Bhattacharyya, 2004), and Soil Erosion Studies of the state (Bhattacharyya *et al.*, 2007) are used for the present study.

Methods

Field and laboratory data along with chemical and mineralogical data were used to develop various GIS based thematic maps using ArcInfo (Ver 10.3). The methodology of generating the mineralogy map of the state is described in the following (Fig 3).

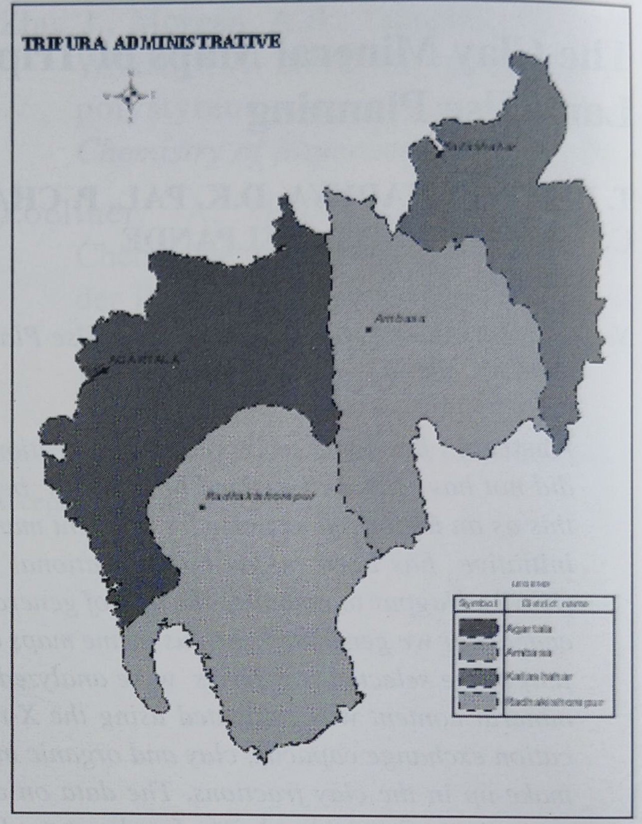

Fig. 1. *Tripura administrative map showing four different districts and their headquarters.*

Results

Clay mineralogy of Tripura

The soil acidity varies from 4.1 to 4.4 (water) and 3.7 to 3.8 (*N*KCl). The ammonium acetate, soil CEC ranging from 5.6 to 7.0 cmol(+) kg^{-1} indicates that these soils are dominated by kaolinite. Conversion of soil CEC into clay show clay

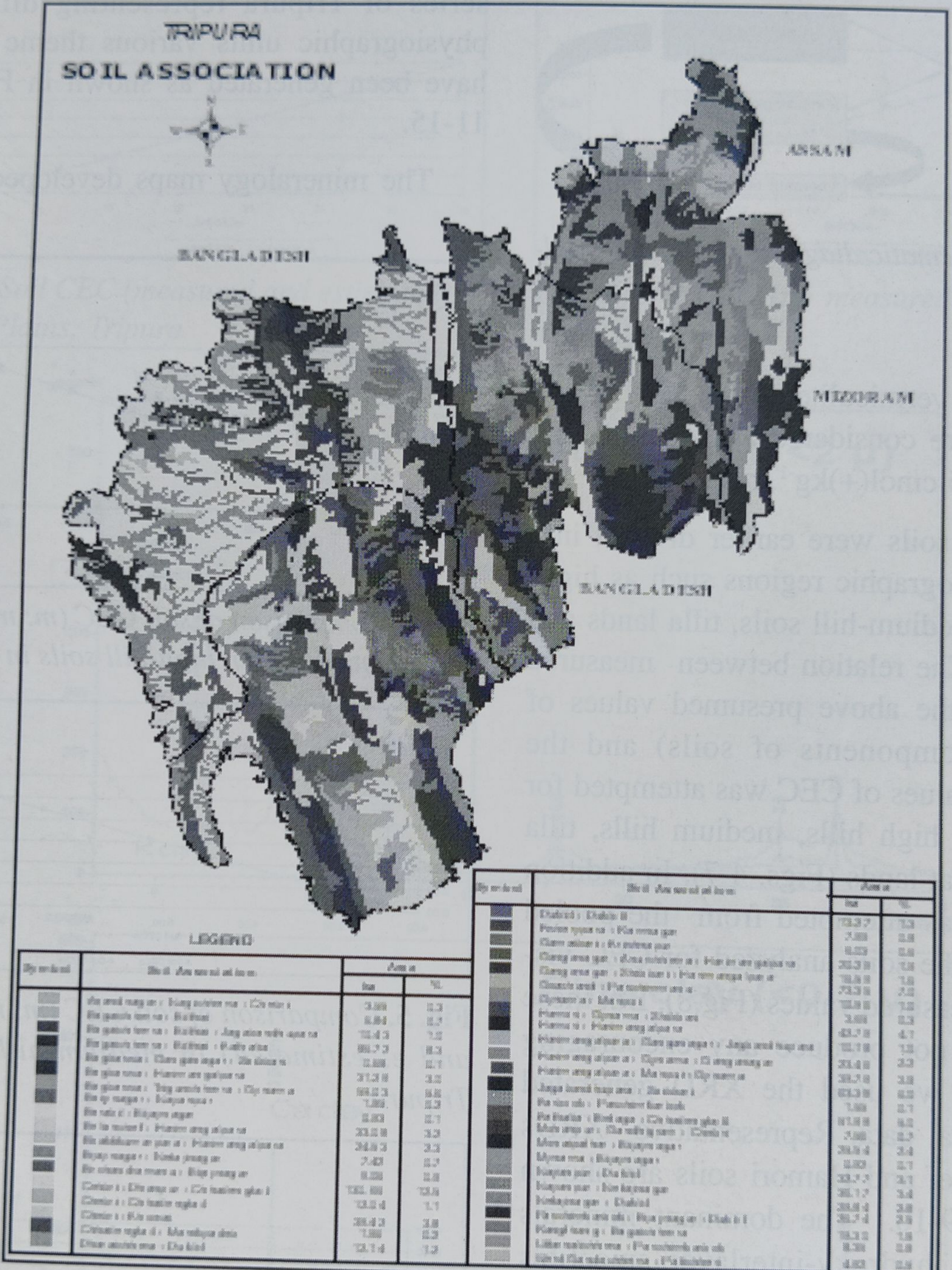

Fig. 2. *Soil series association map in Tripura*

CEC ranges from 11.0 to 16.0 cmol(+)kg^{-1} and suggests that these are low activity clay (LAC) soils. While estimating the minerals in various clay fraction using soil CEC we presume that CEC is largely contributed by clay and organic matter, and the CEC of humic acid, mica/hydroxy-interlayered smectite (M/HIS), HIS, hydroxy-

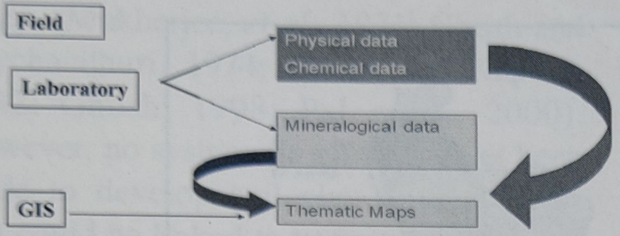

Fig. 3. *A schematic diagram of the methodology*

interlayered vermiculite (HIV), M/HIV and K/HIV were considered as 300, 40, 25, 30, 15 and 5 cmol(+)kg^{-1}, respectively.

Tripura soils were earlier divided into a few physiographic regions such as high-hill soils, medium-hill soils, tilla lands and flat lands. The relation between measured (following the above presumed values of different components of soils) and the estimated values of CEC was attempted for soils of the high hills, medium hills, tilla lands and flat lands (Figs. 4-7). In addition the same was attempted from the pooled data of all the soils analyzed for CEC vis-à-vis the measured values (Fig.8). But these efforts did not produce any encouraging datasets so we used the XRD generated mineralogical data. Representative XRDs of Belianchef and Hamori soils are shown in figures 9-10. The dominant minerals present are hydroxy-interlayer smectites (HISs), hydroxy-interlayer vermiculites (HIVs), mica- hydroxy-interlayer vermiculites (M/HIVs) and kaolinite-hydroxy-interlayer vermiculites (K/HIVs). On the basis of the semi-quantified values of these four minerals in the dominant soil series of Tripura representing different physiographic units various theme maps have been generated as shown in Figures 11-15.

The mineralogy maps developed were

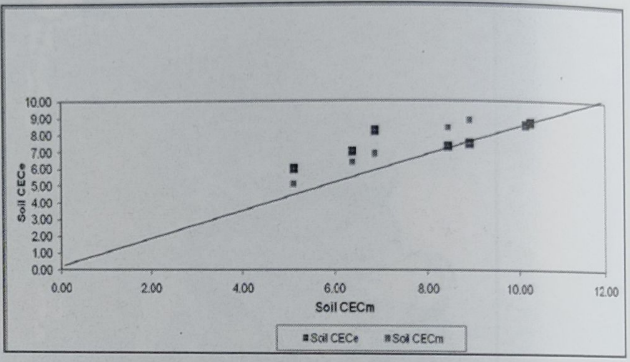

Fig. 4. *Comparison of soil CEC (m: measured and e: estimated) in high-hill soils in Tripura.*

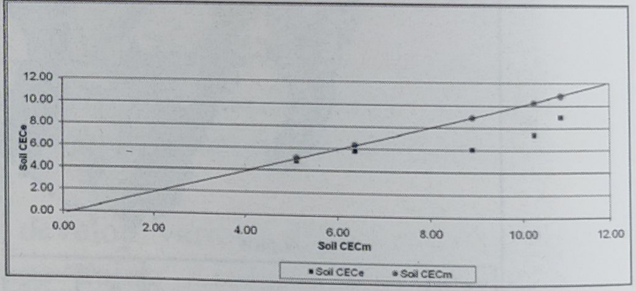

Fig. 5. *Comparison of soil CEC (m: measured and e: estimated) in medium-hill soils in Tripura*

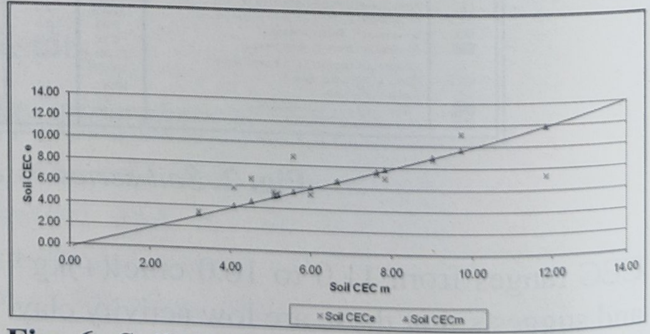

Fig. 6. *Soil CEC (m: measured and e: estimated) in Tilla lands, Tripura*

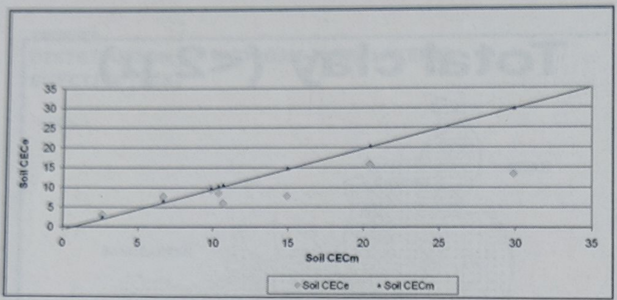

Fig. 7. *Soil CEC (measured and estimated) in Flood Plains, Tripura*

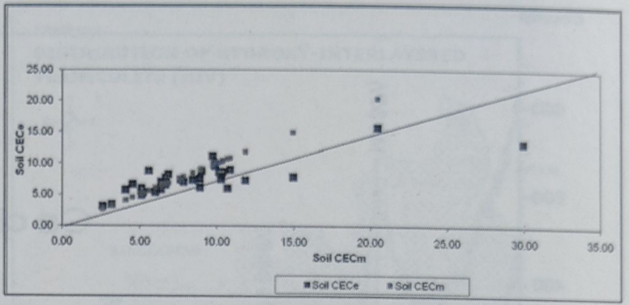

Fig. 8. *Soil CEC (m: measured and e: estimated) in Tripura*

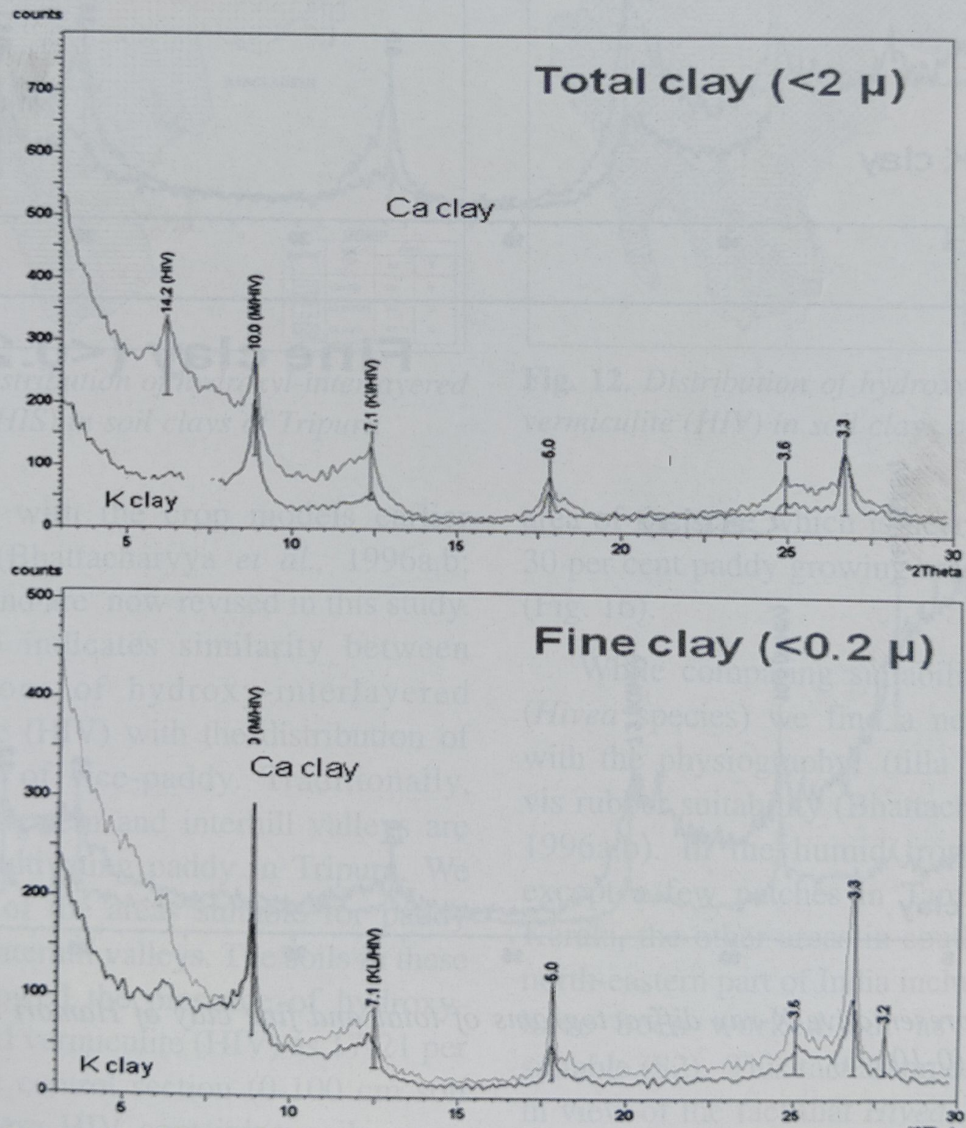

Fig. 9. *Representative X-ray diffractograms of total and final clay of Belianchef soils (Oxic Dystrudepts) (0-10 cm)*

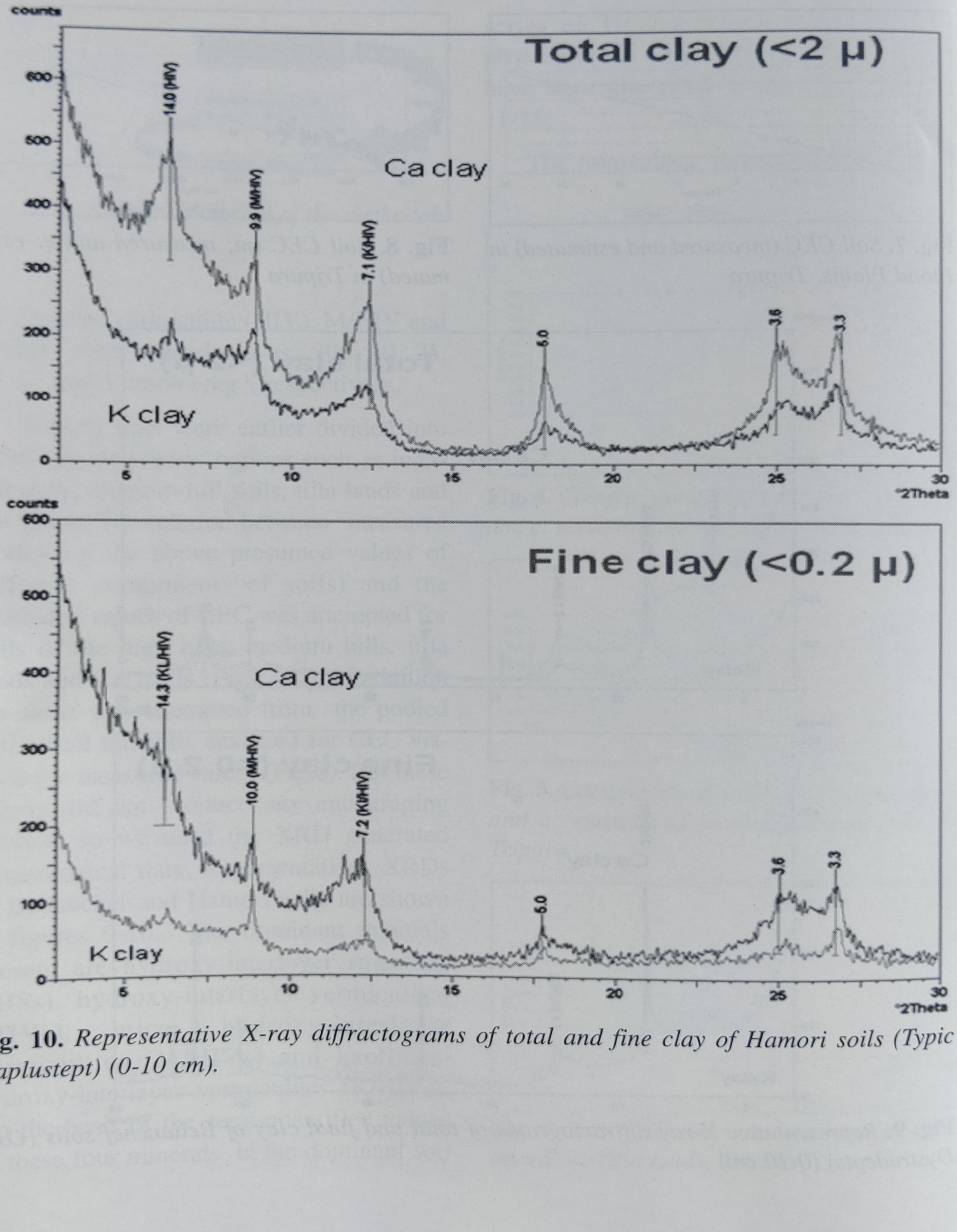

Fig. 10. *Representative X-ray diffractograms of total and fine clay of Hamori soils (Typic Haplustept) (0-10 cm).*

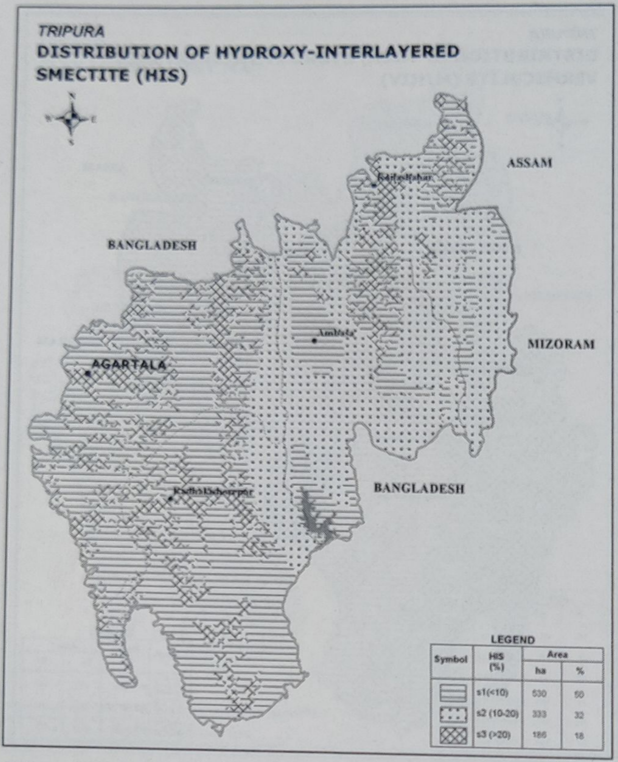

Fig. 11. *Distribution of hydroxyl-interlayered smectitie (HIS) in soil clays of Tripura*

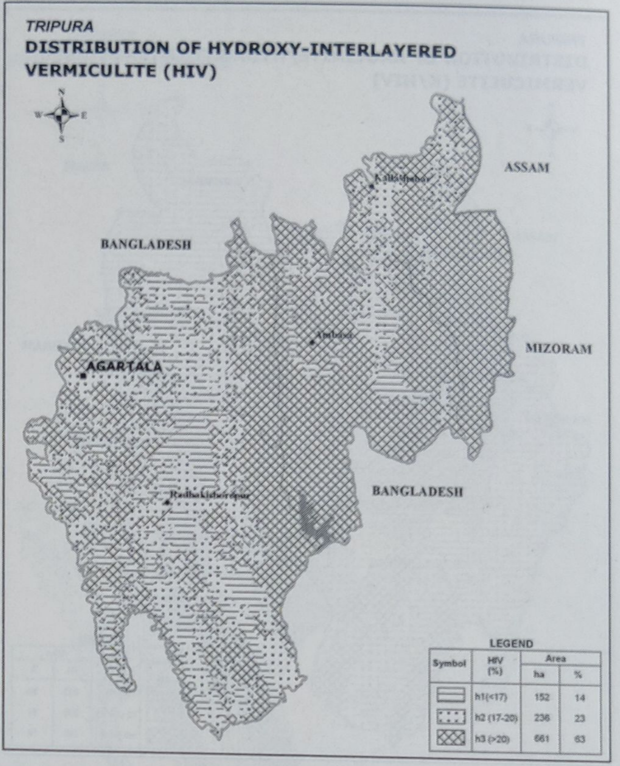

Fig. 12. *Distribution of hydroxy-interlayered vermiculite (HIV) in soil clays of Tripura*

compared with the crop models earlier prepared (Bhattacharyya *et al.,* 1996a,b; 2003a,b) and are now revised in this study. Figure 16 indicates similarity between distributions of hydroxy-interlayered vermiculite (HIV) with the distribution of suitability of rice-paddy. Traditionally, southern, western and interhill valleys are used for cultivating paddy in Tripura. We find most of the areas suitable for paddy are in the interhill valleys. The soils in these valleys showed the presence of hydroxy-interlayered vermiculite (HIV) as 17-21 per cent in the control section (0-100 cm soil depth). These HIV containing soils cover nearly 23 percent of the total geographical area of the state which is nearly similar to 30 per cent paddy growing areas of Tripura (Fig. 16).

While comparing suitability of rubber (*Hivea* species) we find a near similarity with the physiography (tilla lands) vis-à-vis rubber suitability (Bhattacharyya *et al.,* 1996a,b). In the humid tropical climate except a few patches in Tamil Nadu and Kerala, the other areas in southern and the north-eastern part of India including Tripura have been worked out as moderately suitable (S2). This fact assumes importance in view of the fact that *Hivea*, traditionally a tropical tree, experiences problem in the north-east (Tripura) due to cool winter days

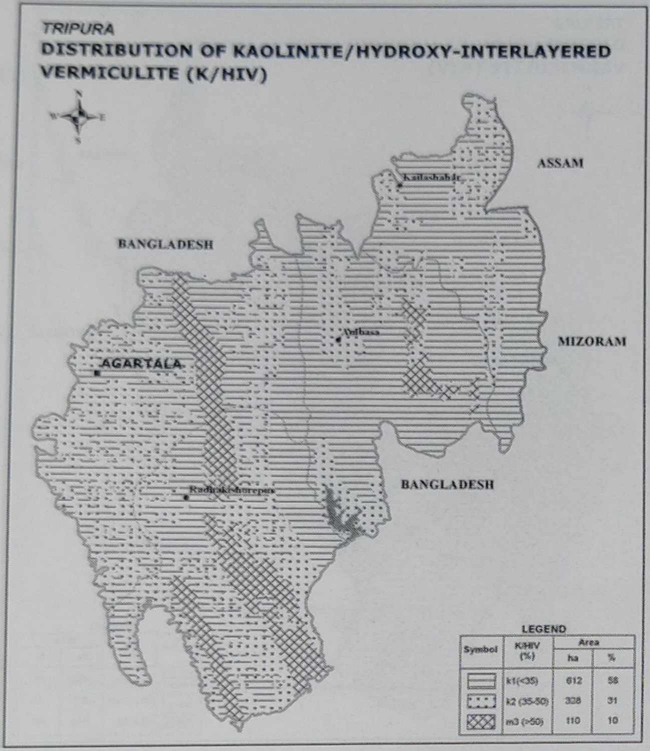

Fig. 13. *Distribution of kaolinite/hydroxy-interlayered vermiculite (K/HIV) in soil clays of Tripura*

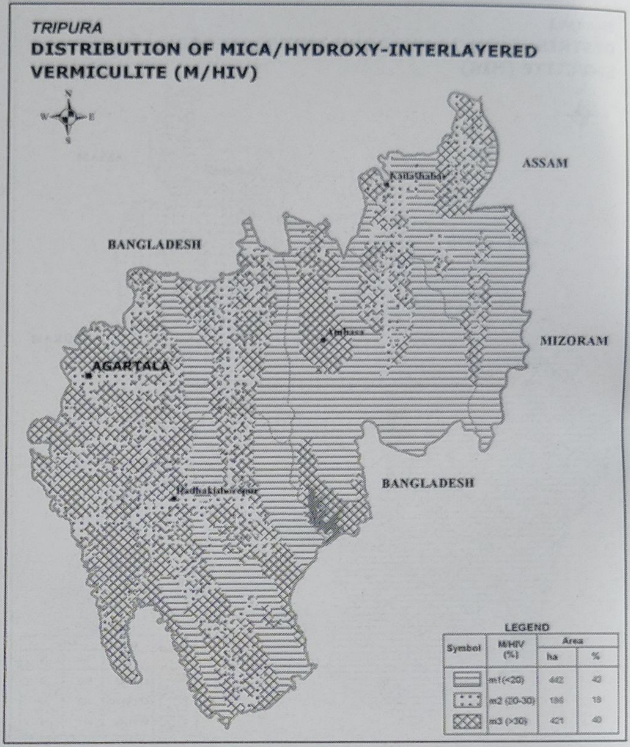

Fig. 14. *Distribution of mica/hydroxy-interlayered vermiculite (M/HIV) in soil clays of Tripura*

(Bhattacharyya 1997a,b,c) affecting latex formation. Mineralogical analysis indicates (Fig. 17) the Tilla lands suitable for rubber are represented by kaolinitic soils which also contain HIV minerals with<35 per cent kaolinite. In humid tropical weathering environment, presence of vermiculite/low charge smectites is common. This suggests that minerals in clay fractions have not yet reached the stage of kaolinites during humid tropical weathering where huge quantity of Al^{3+} ions are liberated to cause higher acidity. For Tripura soils total acidity (H^+) in 0-30 cm soil depth was worked out as 149 kg ha^{-1}. Estimation of amount of Al sequestered in surface soil (0-30 cm) for Tripura was estimated to be 65 kg ha^{-1} (Bhattacharyya, 2010). It is interesting to note that vermiculites and/or smectites adsorb these Al^{3+} ions to form hydroxy-interlayered vermiculites and hydroxy-interlayered smectites. These minerals in turn form interstratified minerals with kaolin as identified by the presence of Kl/HIV, Kl/HIS (Bhattacharyya, 2003a,b). These vermiculites thus act as a natural sink to sequester Al ions and thus keep the deleterious effect of Al-toxicity at bay. This is important since this finding explains a possible reason of better performance of

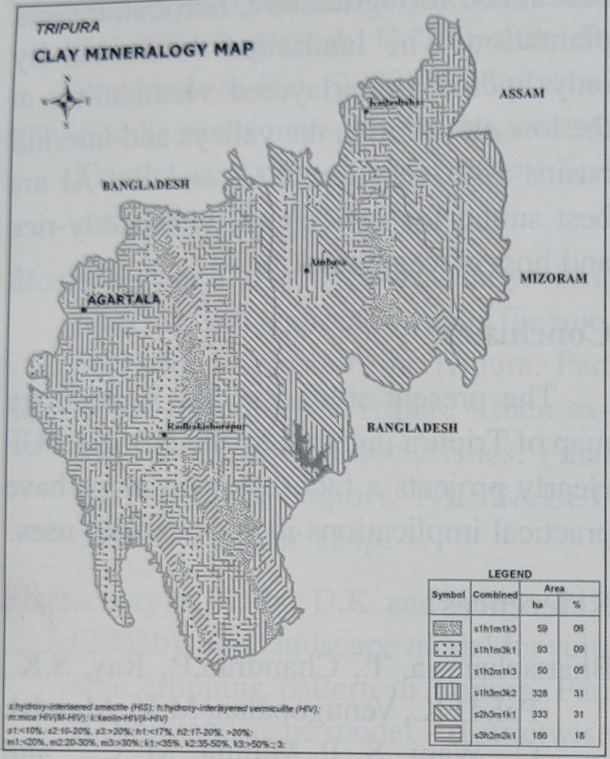

Fig. 15. *Clay mineralogy map of Tripura*

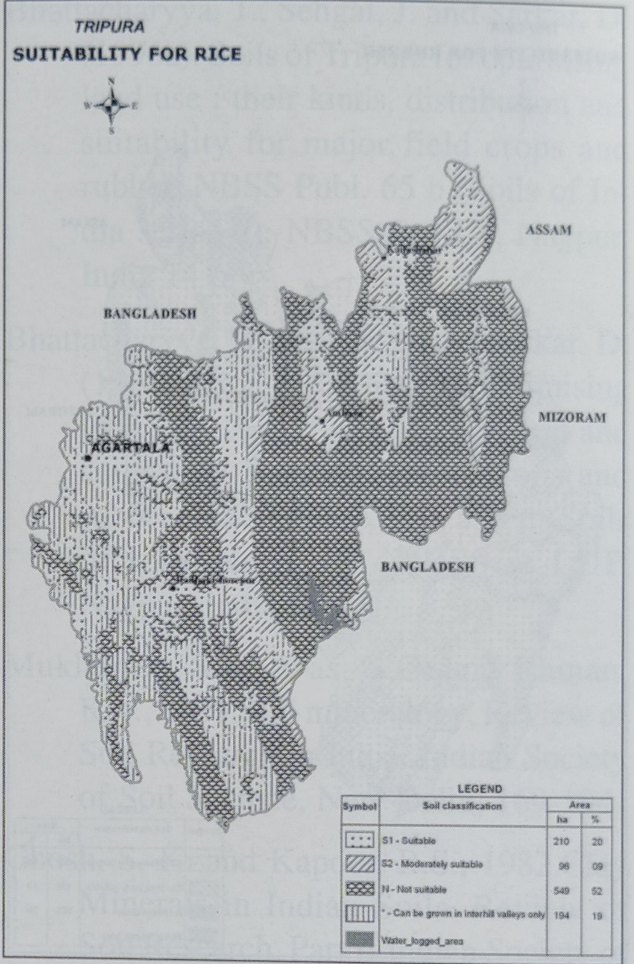

Fig. 16. *Suitability for rice in Tripura*

most of the plantation trees (coffee, tea, rubber, pineapple, cashew and a host of other horticultural crops) which are generally known as acid loving crops/trees. Besides, this finding has an implication in the measurement of lime requirement (LR) which is normally estimated on the basis of plough layer. Since roots of most of the perennial crops including commercial plantations penetrate deep into the soils, the soil depth for LR demands rethinking.

With the availability of mineralogical information of Tripura soils the earlier relation established (Bhattacharyya *et al.*, 2010) to link physiography on the landscape (elevation), chemical properties of soils (KCl Extr-Al indicating degree of acidity vis-à-vis degree of Al-sequestration by minerals to reduce Al-toxicity) and different types of minerals stands for revision (Fig. 18). It is noticed that soils of higher elevation showing high to moderate Al contain mica, hydroxy-interlayered vermiculites as a dominant mineral where naturally occurring forests thrive. The tilla lands with moderate elevation showing very high Al are dominated by kaolinite, hydroxy-interlayered vermiculite, interstratified minerals and these lands are

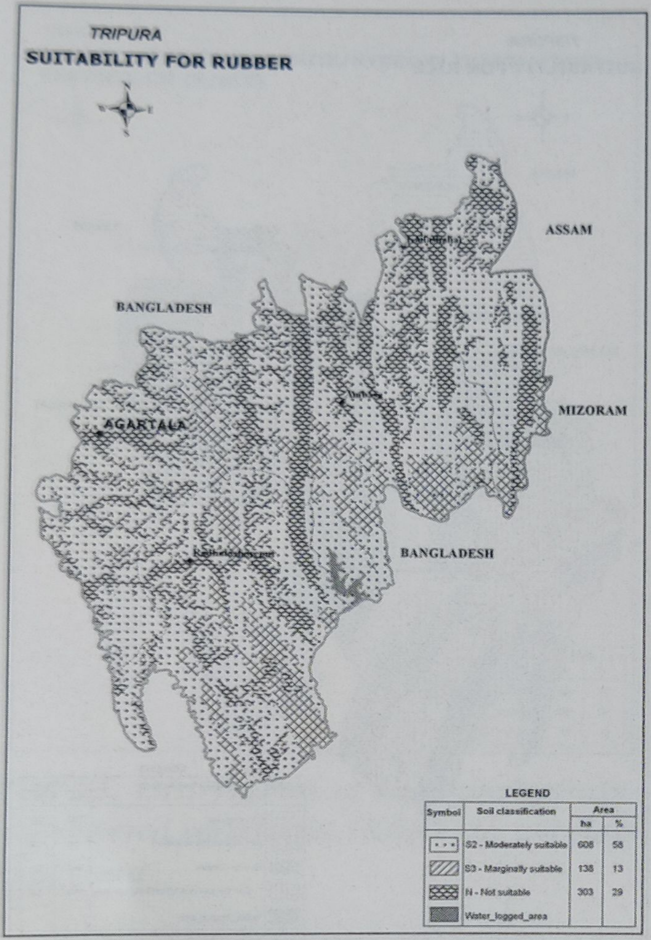

Fig. 17. *Suitability for rubber in Tripura*

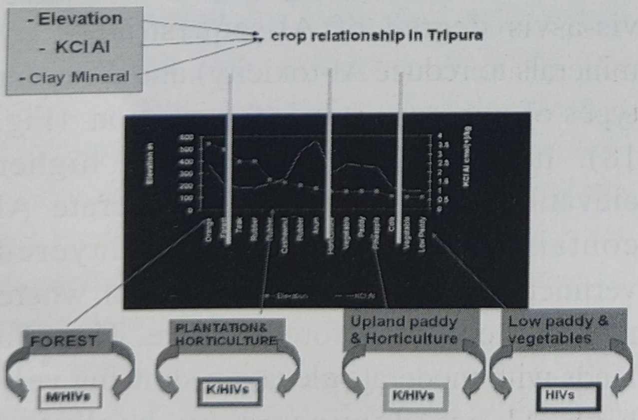

Fig. 18. *Relation between soil, site, mineralogy and land use in Tripura*

best suited for agriculture, horticulture and plantation. The landscape dominated by only hydroxyl-interlayered vermiculites at the low elevation in the valleys and interhill basins with very low KCl and Ext-Al are best suited for agriculture with paddy-rice and host of vegetables.

Conclusion

The present study on clay mineralogy map of Tripura initiated by the NBSS&LUP clearly projects a fact that such maps have practical implications in various land uses.

References

Bhattacharyya, T., Chandran,P., Ray, S.K., Pal, D.K., Venugopalan, M.V., Mandal, C., Wani, S. P. Manna, M. C., and Ramesh, V. (2007a) Carbon sequestration in red and black soils I. Influence of morphological properties *Agropedology,* **17:** 1-15.

Bhattacharyya, T., Chandran,P., Ray, S.K., Pal, D.K., Venugopalan, M.V., Mandal, C., Wani, S. P. Manna, M. C. and Ramesh, V. (2007b). Carbon sequestration in red and black soils II. Influence of physical and chemical properties *Agropedology,* **17:** 16 -25.

Bhattacharyya, T., Chandran,P., Ray, S.K., Pal, D.K., Venugopalan, M.V., Mandal, C., Wani, S. P. Manna, M. C. and Ramesh, V. (2007c). Carbon sequestration in red and black soils III. Identifying systems through carbon stock and bulk density of soils. *Agropedology,* **17:** 26- 34.

Bhattacharyya , T., Sarkar, Dipak, Pal, D.K., Mandal, C., Baruah, U., Telpande, B. and Vaidaya, P.H. (2009) Soil Information System for resource management-Tripura as a case study, *Current Science* **99:** 1208-1217.

Bhattacharyya, T., Pal, D.K. and Vaidya, P.H. (2003b) Soil landscape model for suitable cropping pattern in Tripura. Part I. Soil Resources in Tripura – their extent, nature and characteristics. Final DST Project Report. NBSS&LUP (ICAR), Nagpur 114p.

Bhattacharyya, T., Pal, D.K. and Vaidya, P.H. (2003b) Soil landscape model for suitable cropping pattern in Tripura. Part II. Soil landscape model – districtwise soil-landscape model, soil-series-crop model, soil-landscape-crop simulation model. Final DST Project Report. NBSS&LUP (ICAR), Nagpur 139p.

Bhattacharyya , T., Sarkar, Dipak, Pal, D.K., Mandal, C., Baruah, U., Telpande, B. and Vaidya, P.H. (2010) Soil Information System for resource management-Tripura as a case study, *Current Science* **99:** 1208-1217.

Bhattacharyya, T., Ram Babu, Sarkar, D., Mandal, C. and Nagar, A.P. (2002) Soil Erosion of Tripura, a model for soil conservation and crop performance, NBSS Publication No. 97, NBSS&LUP, Nagpur, 80p.+ 1 sheet of map (1:250,000 scale).

Bhattacharyya, T., Sehgal, J. and Sarkar, D. (1996a). Soils of Tripura for optimising land use : their kinds, distribution and suitability for major field crops and rubber. NBSS Publ. 65 b (Soils of India series 6). NBSS & LUP, Nagpur, India 14 p.

Bhattacharyya, T., Sehgal, J. and Sarkar, D. (1996b). Soils of Tripura for optimising land use: their kinds, distribution and suitability for major field crops and rubber. NBSS Publ. 65 a and c (Soils of India series 6). NBSS & LUP, Nagpur, India 154 p.

Mukherjee, S.K., Das, S.C. and Raman, K.V., 1971.Soil mineralogy, Review of Soil Research in India. Indian Society of Soil Science, New Delhi, 169-194.

Ghosh, S. K. and Kapoor, B.S., 1982.Clay Minerals in Indian Soils. Review of Soil Research, Part II.Indian Society of Soil Science, New Delhi, 703-710.

Ghosh, S.K. and Raychaudhuri,S.P.,1974. Distribution of clay minerals in Indian Soils.Mineralogy of soil clays and clay minerals. Bull. No. 9, Indian Society of Soil Science, 143-163.

Ghosh, S.K. and Bhattacharyya, T., 1982. Mineralogy of Soils of Bihar, Uttar Pradesh, Gujarat and Rajasthan, in Mineralogy of Soil Potassium, pp. 15-29. Published by Potash Research Institute of India, Gurgaon, Haryana, India.

Pal, D.K., Bhattacharyya, T., Deshpande, S.B. Sarma, V.A.K. and Velayutham, V. (2000) Significance of minerals in soil environment of India. NBSS Review series 1, NBSS&LUP, Nagpur, 68p.

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Examples are

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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