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Clay and Clay Minerals for Soil Health and Human Welfare*

D.K. DAS
Former Head and Emeritus Scientist, Div. of Agril. Physics, IARI, New Delhi;
AD-115-C, Shalimar Bagh, New Delhi - 110088

The clay fractions consisting mostly of secondary aluminosilicate minerals and the silt and sand fractions comprising of various primary as well as secondary minerals together constitute the inorganic components of soils. Clay is the most reactive constituent and controls most of the soil physical, chemical and physico-chemical properties. In soils, the clay, however, exists as a complex of clay minerals associated with amorphous, inorganic and organic constituents. These constituents have different degree of interaction producing complexes with varying stability and properties. The nature of the complex reactions depend on the unique properties of the clay mineral structures, the water content of the system, the nature of exchangeable cations and the nature of organic molecules. These complexes of great importance have been utilized in industries and technology leading to products of human welfare. In the field of agriculture knowledge of these interactions is important in understanding the soils' behaviour and adopting suitable management practices for their sustained productivity. The present paper briefly deals with the different aspects of the important role of clay and clay minerals in maintenance of soil health and productivity, the various applications of clays in industries for manufacturing products of day to day utility by the society and also different technological uses of clays for human needs and welfare. The presentation forms the dominant component of the *first lecture* organised by and delivered at the Bidhan Chandra Krishi Viswa Vidhyalaya, West Bengal in memory of Dr. S.C. Das, an eminent clay mineralogist of our country.

I express my sincere gratitude to the Bidhan Chandra Krishi Viswa Vidyalaya for inviting me to deliver the first lecture in the memory of my highly esteemed *Guru*, Dr. S.C. Das. I feel deeply honoured and highly priviledged to get this opportunity to pay my humble tribute to him, an outstanding teacher and researcher and above all a great humanist.

Dr. S.C. Das belonged to the 'Calcutta School of Soil Science' created by the great visionary, the doyen of colloid science and father of clay research in India, Dr. J.N. Mukherjee. With double Doctorate Degree from University of Calcutta and University of Leeds, London, Dr. Das worked in Brindlay's Laboratory in London on muscovite structure and initiated systematic work on clay minerology at IARI for the first time with inspiration from Dr. S.P. Raychaudhury. Starting with investigations on 'Clay Pan' formation, nature and extent of salinity, extent of sodimization of clays, other exchangeable cations, micronutrient contents of soils etc., Dr. Das made significant contributions on mineralogy of clays from major soils groups of India including that of West Bengal, the genesis and transformation of clay minerals in relation to those of coarse fractions (silt and sand), ion exchange reaction in clays and clay minerals with special reference to zinc, nutrient ion potential, Q/I (of soil potassium), as well as phosphate sorption / desorption by clays and oxides of aluminium and iron in soil. As a teacher Dr. Das was super excellent. He provided continuously excellent guidance and positive encouragement to all students, irrespective of whether he was chairman of Advisory Committee or not and to all his colleagues in original thinking, problem identification and efficient implementation of programmes. He was a straight-forward person and provided self-less service. I express my sincere gratitude to the Department of Soil Science and Agricultural Chemistry of BCKV for giving me this honour of paying homage to one of the most eminent clay

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mineralogists of India. I compliment particularly Dr. Murari Haldar, Head, Department of Soil Science, BCKV and his colleagues for their relentless efforts and persuasive attitude for institution of this much overdue Memorial Lecture. Considering the primary interest of Dr. S.C. Das in clay mineralogy, the role of clays and clay minerals in enhancing soil productivity on a sustained basis and the fact that clays find myriad applications in industries and in all walks of life, I have chosen the topic of my lecture "Clays and Clay Minerals for Soil Health and Human Welfare".

1. Clay Research in India

Clay research in India owes greatly to Prof. J.N. Mukherjee. Outstanding contribution by him and his co-workers on the concept of diffuse double layer, neutralisation of the charge of colloids, nature of soil acidity (Mukherjee, 1922a,b; 1966, 1975, Mukherjee and Mitra, 1942) have great significance and present day relevance. Comprehensive reviews on clay mineral research in India by a number of researchers (Mukherjee *et al.*, 1971; Raman and Ghosh, 1974; Sarma and Sidhu, 1982; Ghosh and Bhattacharya, 1983; Ghosh 1977; Sanyal, 2001; Das 2003 and Pal, 2003) provide valuable information on clay mineral distribution and transformation, ion exchange and colloid chemical properties and mineralogy in relation to pedology, paleopedology and polygenesis. The 15th Prof. J.N. Mukherjee-ISSS Foundation Lecture by Ghosh (1977) dealt with fundamental and basic research on electrometric investigations, nature of clay acid, ion exchange reactions, clay constituents, clay-organic interactions and research on industrial uses of clays. In review 'Four Decades of Research in Agricultural Physics, specially on Soil Mineralogy, Das (2003) discussed the techniques in identification and quantification of clay constituents, distribution of clay minerals in soils, genesis and transformation of clay minerals in soils, amorphous constituents of soil clays and phosphate reaction and products in Indian soils. A comprehensive reviewed by Pal (2003) dealt with identification of major soil clay minerals, role of clays, clay and other minerals in pedology, paleopedology and polygenesis of soils and minerals and edaphology. These reviews clearly indicate that a proper understanding on the interrelationships of minerology and soil properties of agricultural importance and knowledge on the recent development on various technological uses of clays and clay minerals are basic requisities for judicious management of soil and water resources for sustainable agriculture as well as human welfare. The developments in industrial application of clays and clay minerals are briefly presented first in this paper.

2. Industrial Applications of Clays and Clay Minerals

Clays find enormous potential in industry since these can be used as low cost raw materials for manufacturing high value performance chemicals used for human consumption. The relevant properteis of clay minerals which determine its suitability are clay-water interaction, clay-organic interaction, sub-micro size Si / Al ratio, development of active sites and catalysis. Clays, the natural material either as found or after processing to purified forms are used in different industries such as petroleum, pharmaceutical, pesticides formulation, textile and ceramic industries etc. and other technological uses (Bhat and Sidheswaran, 1996).

2.1 Spectacular advance in petroleum industries in use of clays

(i) Since the investigation on use of thixotropic system using bentonites as oil drilling mud advances have been made in C-axis expansion and incorporation of oligomers i.e. 'pillard clays'. (ii) Bentonites after leaching with acids produce active clays which are used as bleaching earth in oil refineries. (iii) Three-dimensional - seismic imaging, slant drilling, and other engineering advances are tripling the recovery of petroleum from geologic reservoirs; and (iv) Subtle argon-age dating of clay minerals across a potential basin is used to predict its yield of oil (Smith, 1999).

2.2 Pharmaceutical and house hold products

(i) Clays are used for manufacture of soaps, detergents, catalysis and in intercalation phenomena (eg. Bentones are used as viscosity modifiers (thickness) in cosmetic preparation). (ii) Kaolin and attapulgite are used in pharmaceutical preparation (calamine lotion).

2.3 Use of clay in pesticide formulations

(i) Clays are used as carriers or diluents in view of its vital bearing on the potency, uniform dispersion, retention of pesticide by the plant leaves etc. (ii) Clays used as dust carriers are talc, pyrophyllite, bentonites, kaolins, attapulgites and volcanic ash etc.; as wettable powder attapulgite is used with active ingredient and for granular formulations attapulgite, bentonite etc. are used (David, 1996). Granular formulations are *extensively used for combating some of the noxious* pests like borers, aphids, other sucking insects pests, soil borne insect pests, and have less toxicity hazards in handling as well as in application but have more residual toxicity.

2.4 Adsorption of textile dye by organo-clay complex

Decontamination and decolourization of waste water from textile industry are burning problems. The property of adsorption of textile dye by organo-clay complex is used for this purpose. Examples are organo-clay complex prepared by interaction of bentonite with quaternary ammonium compounds. The dye molecules have high affinity towards the organo-clays. Organo-clays prepared with Rajasthan bentonite have been found to have capacity to adsorb Remazol Blue from aqueous solution. The comparative effectiveness of various compounds are in the order : N-cetylpyridium bentonite > Hexadecyltrimethylamine Bentonite > Smectone -PBT-SW > Baragel (Bhatt and Pandya, 1998).

2.5 Use of clays in ceramic industry and other technological uses:

(i) The rheological properties of clays are made use of in its large scale utilization in ceramic industries. (ii) Clays find multiple uses such as in construction of roads, dams, irrigation canals, drainage canals, mud houses, in manufacture of bricks, tiles, stoneware pipes. (iii) Bentonite linings are used for reservoir and in landfills for waste disposal. Since bentonite has swelling and shrinkage properties, mixtures of illite and bentonite were found to be better than either illite or bentonite alone for use as clay liners (Sivapullaiah and Savitha, 1996).

3. Use of Artificial and Natural Zeolites in Industry and Agriculture

A broader successful story has been the invention for manufacture of artificial zeolites / molecular sieve absorbents / catalysts (from Kaolinite) which found myriad applications in industries. Now moving forward into major use are natural zeolites which are found in volcanogenic sedimentary rocks. They possess exciting surface and structural properties such as *high adsorption, cation exchange, dehydration-*rehydration and catalytic properties which have led to their bulk application in industries as well as in agriculture (Mumpton, 1999).

3.1 Application of natural zeolites in industry, medical and other uses:

(i) *Industry* : Natural zeolites are used as building stone, light weight aggregates and possolans in cement and concretes; as energy exchangers in solar refrigerators and as consumer deodorizers, in pet litters etc.

(ii) *Pollution control* : in the drying of acid gases.

(iii) *Waste management* : in the separation of oxygen from air and in removal of NH_3 from municipal and industrial waste water and drinking water.

(iv) *Nuclear waste handling* : Zeolites find their use in extraction of ^{137}Cs and ^{90}Sr from nuclear wastes and mitigation of radioactive fallout.

(v) *Medical and biotechnology* : Zeolites are used as NH_3 filters in kidney-dialysis units and as bactericides, insecticides and antacids for animals and people.

3.2 Agricultural application of natural zeolites

Studies in Japan, Ukraine, Italy, Bulgaria, Cuba and Russia etc. have demonstrated great potentialities of use of zeolites in the field of agriculture, particularly as (a) soil amendments to improve cation exchange capacity and water retention capacities of sandy / clay poor soils, (b) as soil zeoponic substrate for green houses and space missions and (c) as dietary supplements to improve animal production. Examples of some research results are cited below:

(i) *Japan* : (a) Extensive use as amendments for sandy, clay-poor soils; (b) pronounced selectivity of clinoptilolite for NH_4^+ and K^+; (c) use of zeolite as slow release chemical fertilizers and (d) use of 4-8 tonnes/acre zeolite as soil conditioner increased yield of wheat (13-15%), egg plant (19-55%), apples (13-38%) and carrots (63%).

(ii) *Ukraine* : 15 tonnes/ha of zeolite increased yields of potatoes, barley, clover and wheat.

(iii) *Italy* : Natural zeolites have been used as dusting agents to kill aphids affecting fruit trees (acting as desiccant).

(iv) *Bulgaria* : (a) Clinoptilolite has been used as principal constituent of artificial soil; (b) Zeoponics - a nutrient treated zeoponic substrate has been used for growing crops in green houses.

(v) *Cuba* : (a) Tomatoes and cucumbers are grown using zeoponic substrate; (b) Vegetables are supplied to Moscow from green house.

(vi) *In Russian Space Station 'Mir'* cabbage and radishes have been grown using a treated Bulgarian clinoptilolite synthetic soils.

(vii) *India* : In India occurrence of zeolites have been reported in sodic soils of the IGNP (Kapoor *et al.*, 1981) and in ferruginous soils of Western Ghats (Bhattacharya *et al.*, 1999). Zeolite is acting as a saviour against soil degradation in humid acidic ferruginous soils - the heulandites provide constant supply of bases preventing soils from losing their productivity even in intense leaching environment (Bhattacharya *et al.*, 2001). Mining zeolites from shrink-swell soils of semi-arid part of Western ghats and addition in humid ferruginous soils to prevent chemical degradation and preserve biodiversity hold great promise.

4. Influence of Clays, Clay Minerals and Associated Compounds on Soil Physical Properties

Clay, oxides and organic materials have extensive surfaces which possess positive or negative charges and interact with water and ions. The complex interactions govern the physical properties of soils. The nature, size and quantity of clay fractions play dominant role in influencing soil physical properties. Soil structure, the pedotransfer functions i.e. the matric suction-water content and hydraulic conductivity and water diffusivity vs water content relationships are greatly affected by the extent and nature of clay in soil.

4.1 Soil structure

Three district groups of soil colloidal materials have cementation and aggregating effects - clay particles themselves, inorganic colloids of aluminium and iron oxides and organic colloids. Clay-to-clay particle interaction, particularly under reduced moisture supply, takes place due to electrostatic and vander Waal's forces. Aggregate formation is dependent upon the linkages established by polyvalent exchangeable cations on the clay particle. These cations also act as bridges to form clay-organic complexes leading to the formation of stable aggregates (Biswas and Jagan Nath, 1982; Das and Agrawal, 2002). The properties of colloidal clay surfaces change as a result of interaction with organic colloids.

In the ferruginous, black and alluvial soils of India widely differing in their mineralogy, the size range of stable aggregates depended on the dominant clay mineral, Kaolinite influencing < 50 μm aggregates (ferruginous soil) and smectite in the formation of 250-1000 μm aggregates (black soils) (Table 1). The influence of cohesive forces between clay particles was more than the clay-iron oxide interaction in the smectite soils. In basaltic black soils of Malwa Plateau, Madhya Pradesh, smectite, the dominant crystalline mineral in the clay fractions influenced the state of aggregation, the pedotransfer functions i.e. moisture retention characteristics and hydraulic conductivity, water holding capacity etc. (Table 2) (Krishnamurti and Singh, 1975, Krishnamurti and Rengasamy, 1976).

The amorphous constituents of soil clays play a significant role in affecitng physical and chemical properties of soils (Krishnamurti, 1982) since they have large surface area, high chemical reactivity and high cation exchange capacity. The amorphous

Table 1. Simple correlation coefficients between water stable aggregates and soil constituents

No.	Soil groups	Size range of stable aggregates (μm)	Correlation coefficeints with		
			Clay (<2 mm)	Free Fe_2O_3	Organic matter
1	Ferruginous soils	2-50	+0.620**	+0.830**	-0.337
2	Black soils	250-1000	+0.737**	+0.672**	-0.064
3	Alluvial soils	2-50	+0.764**	+0.383*	-0.091

**Significant at 0.1% level. *Significant at 5.0% level. (Krishnamurti *et al.*, 1977).

Table 2. Correlation coefficients between the physical parameters and the soil constituents of basaltic soils of Madhya Pradesh

Physical parameter	Clay (<2μ)	Smectite content (on soil basis)	Silt (2-50 μ)	Fine sand (50-(200 μ)	Coarse sand (200-2000 μ)	Organic matter	Free iron oxides
1. Water stable aggregates							
>0.1 mm	-0.809**	-0.883**	+0.633**	+0.658**	+0.292	+0.787**	-0.652**
>0.25 mm	+0.347	+0.939**	-0.626**	-0.518*	-0.072	--0.664**	+0.672**
>0.5 mm	+0.612**	+0.455	-0.303	-0.633**	-0.359	-0.478	+0.211
2. Available water content	+0.625**	+0.457	-0.348	-0.573*	-0.272	-0.468	+0.178
3. Hydraulic conductivity	-0.356	-0.783**	+0.297	+0.415	-0.294	+0.229	-0.344
4. Water holding capacity	+0.852**	+0.953**	-0.706**	-0.647***	-0.176	-0.749**	+0.698**

**Significant at 1% level; * Significant at 5% level (Krishnamurti and Singh, 1975).

materials bound the kaolinite particles less than 1μ in size into units 1-2 μ in size, with further aggregation by the free iron hydroxides (Krishnamurti and Rengasamy 1976).

Modern microscopic techniques have shown that organic matter is not uniformly distributed over mineral surfaces but much of it is particulate even in clay fractions. Organic matter may be coated with clay and vice versa. The organic materials differ from the inside to the outside of aggregates. The stable organo-mineral microstructures resistant to dispersion contain organic materials intensively altered by microbial activity. Microscopic analyses have shown that kaolinite and oxides infill pores which decrease hydraulic conductivity and create water logging and reducing conditions. The production of reducing conditions by bacteria in the presence of Fe-smectites results in the reduction of Fe to the ferrous state. This has implications for particle-particle interactions and swelling and illustrates the complex links between microorganisms, mineralogy and soil physical properties.

4.2 Pedotransfer functions

In a mineral soil moisture retention is mainly a function of amount and nature of soil clay (Ali *et al.*, 1966). The water-retention curves for Padegaon black soils (dominantly montmorillonitic), Sabour alluvial soils (dominantly illitic) and Suri lateritic soil (dominantly Kaolinitic) resembled those of pure bentonite, illite and Kaolinite. The moisture retention at any particular tension followed the order : black soil (smectite) > alluvial soil (illite) > laterite > kaolinite (Ali and Biswas, 1971). Black soils with smectitic clay mineral are characterized by high swell/shrinkage potential. The self mulching characteristics and high percentage of pseudo-aggregates of black soils are related to their high small / shrinkage property. This property is not so marked in soils having kaolinite as the dominant clay mineral (Biswas and Karale, 1974). Using soil data of 600 locations, pedotransfer functions were generated by using correlation and multiple regression technique (Rai *et al.*, 2003).

(Fc (%, vol) = 0.1462* sand (%) + 0.3742* silt (%) + 0.5801* clay (%) WP (%, vol) = 0.245* sand + 0.1099* silt (%) + 0.3816* clay (%)

The higher regression coefficient values for clay, followed by silt and sand, respectively, indicate increased field capacity and wilting point in teh soils having finer sized particles (silt and clay). The pedo-functions available water and saturated hydraulic conductivity as a function of Si+Cl gave a polynomial fit and power fit with 52% and 77.04% of variability, respectively (Fig. 1 and 2).

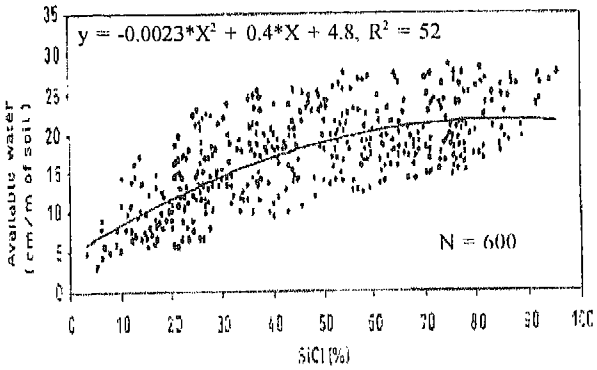

Fig. 1. Available water in the soil profile as related to silt plus clay content (Si+Cl)

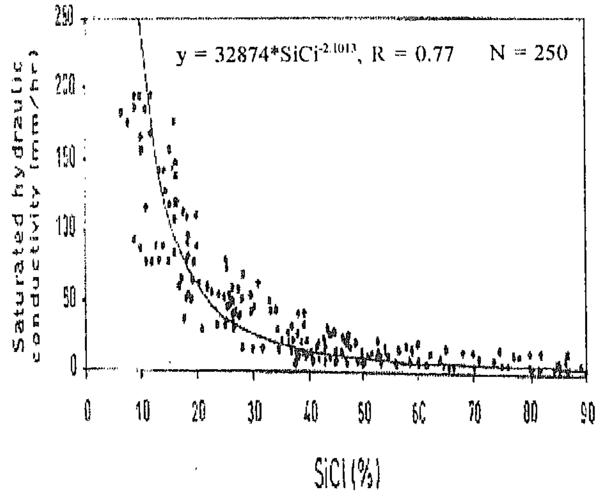

Fig. 2. Saturated hydraulic conductivity as related to silt plus clay content (Si+Cl)

4.3 Surface area

In mineral soil the clay fractions impart to the soil a very important property i.e. the surface area which is the seat for all the chemical, physical and biological activities of soil. Soil clays from black soil groups, being dominantly smectitic, have highest internal as well as total specific surface area (Das and Das, 1966; Biswas and Jaganath, 1982). Soil clays from red and lateritic soils have, however, higher specific surface area in comparison with the nature of clay minerals present, because of the presence of amorphous aluminium and iron oxides.

4.4 Soil amelioration through application of clay

Mixing of clay in coarse textured highly permeable sandy / loamy sand soils of Rajasthan reduced percolation rate, increased bulk density and water availability which resulted in higher yields of wheat, barley, pearlmillet, sorghum crops (Gupta *et al.*, 1984).

Clay-substrate application to sandy open-cast limestone mined wasteland in western Rajasthan improved its water retention capacity, enhanced rainwater harvesting, and improved growth of plantation and native species and thereby rehabilitated the waste land (Sharma *et al.*, 1998). Changes in surface characteristics of degraded soils (oxisols) through addition of beneficiated (Ca, Mg, K saturated in 8:4:1 ratio) bentonite have been reported in Australia. There was increase in CEC, surface charge density and in forage sorghum biomass production.

Application of bentonite alongwith $NaCl+Na_2CO_3$ mixture has reduced percolation loss from water storage tank, decreased infiltration rate and hydraulic conductivity of sandy loam soils and enhanced water harvesting through rum off inducement. Water requirement of a 100 day rice crop (*Oriza sativa* L.) was reduced from 346 to 255 cm by the application of bentonite + salts (Das and Dakshinamurti, 1975). Improvement in wettability of water repellent sandy soils in western Australia through addition of clay (Kaolinite) has significantly increased crop yields.

5. Mineralogy in Relation to Soil Chemical Properties, Nutrient Fixation and Release and Bioavailability of Heavy Metals

5.1 Soil acidity

The concept of nature of "soil acidity" developed by J.N. Mukherjee and later on referred by Jenny in the article "Soil Acidity-Merry Go Round" has great relevance. There are Al^{3+} ions rather than H^+ ions which cause toxicity in acid

Table 3. Effect of clay mixing in coarse textured soil on crop yield

Location	Soil texture	Crop & variety	Grain yield (q/ha) at additional clay					C.D. at 5%
			0%	1%	2%	5%	10%	
Durgapura	Sand	Wheat (Kalyan sona)	27.2	31.1	34.8	39.5	--	3.14
		Barley (Local)	24.3	27.0	36.8	34.5	--	6.50
		Pearl millet (Hybrid)	10.8	12.7	13.6	15.6	--	2.66
Hyderabad	Sandy loam	Sorghum (CSH-6)	22.6	24.6	27.6	31.8	34.5	4.44
		Sorghum (1st Ratoon)	18.8	19.5	20.0	23.0	24.0	3.85
		Wheat (HD-2129)	19.7	21.5	22.9	25.2	28.8	1.60
		Maize (Ganga-5)	21.5	23.0	23.5	25.5	26.5	3.98
Sabour	Sandy loam	Wheat (HD-1553)	32.6	33.9	37.1	42.7	--	4.93
		Maize	26.0	28.1	31.5	35.5	--	5.63
		Mung	7.6	9.6	9.3	11.7	--	1.20
Hissar	Sandy loam	Mung	17.8	21.4	--	--	--	--
		Black gram	23.8	26.2	--	--	--	--

(Gupta *et al.*, 1984)

soils. Recent studies reveal that the acid soils of Tripura, Kerala, Goa and Ranchi contain mica and vermiculites alongwith a dominant proportion of Kaolin. These vermiculites are hydroxy interlayered vermiculites (HIV) which decrease with soil depth (Bhattacharya *et al.*, 1998, Chandran and Ray, 2001; Chandran *et al.*, 2002 and Ray *et al.*, 2001). During humid tropical weathering huge quantity of Al^{+3} ions is liberated to cause higher acidity. Vermiculites adsorb the Al^{+3} ions as hydroxy-cations to form the HIV. The vermiculites thus act as a natural sink for continuous supply of Al^{+3} ions and may help the plants to surive without getting affected by Al-toxocity.

Saigusa and Matsuyama (2002) enumerated the role of chloritized 2:1 minerals in nonallophanic Andesols of Japan. The origin of these minerals has been mainly attributed to the loess dust from China. These 2:1 minerals have negative constant charge and thus contain Al^{3+} in their interlayer when base saturation is low. One of the main yield determining factors in nonallophanic Andesols is Al^{3+} toxicity rather than H^+ ion toxicity. Yields of Al-sensitive crops such as alfalfa, barley, wheat, burdock, sorghum etc. were governed by subsoil acidity (Al-toxicity) through the nitrogen and / or water uptake. Application of gypsum in plough layer were much effective on alleviation of subsoil acidity than that of lime. Al^{3+} in nonallophanic Andesols were proved to be effective on suppression of some soil borne diseases such as root rot of kidney bean, potato scab, dumping-off diseases of rice etc.

5.2 Nutrient release and fixation

Mixtures of minerals present in soil clays and in silt and sand fractions greatly influence the ion exchange and release and fixation of nutrients (eg K and P) and their supply to plants.

5.2.1 K-fixation and release

Significant contributions on K-release and fixation have been made in recent times by Sanyal and Coworkers (Raychaudhuri and Sanyal, 1999, 2000; Dhar and Sanyal, 2000; Kaushik *et al.*, 2000) and Srinivasa Rao and coworkers (Srinivasa Rao *et al.*, 2000, 2002). It is revealed that (i) cumulative K release is highest in swell-shrink soils, followed by alluvial soils. (ii) K release is highly correlated with illite and non-exchangeable K content of red and lateritic soils and Vertisols, but not in alluvial soils. (iii) More degraded state of illite in swell-shrink and red/lateritic soils, as compared to illite dominated soils, helps the mineral to influence the overall release pattern. (iv) Vertisols show a sigificant negative correlation between K fixation and illite content. (v) Red and laterite soils retain a considerable portion of applied K and retention is significantly correlated with kaolinite content. (vi) A combination of smectite-illite in a mineral suite is most efficient in releasing native and fixed K. (vii) High exch. K in smectites basically reinforces the efficiency of the extracting

Table 4. Infiltration and hydraulic conductivity of soil treated with bentonite and salts

	Treatments	Infiltration rate (mm/hour)	Depth of wetting front (cm)	Hydraulic conductivity (cm/hour)
A	Control	18.0	19.5	4.92×10^{-1}
B	Soil + bentonite (1%)	15.0	16.3	3.93×10^{-1}
C	Soil + bentonite (2%)	10.8	13.2	2.21×10^{-1}
D	Soil + bentonite (1%) + NaCl (0.75%) + Na_2CO_3 (0.75%)	3.0	5.8	3.48×10^{-3}
E	Soil + bentonite (2%) + NaCl (0.75%) + Na_2CO_3 (0.75%)	1.5	3.5	1.02×10^{-3}

(Das and Dakshinamurti, 1975)

solution, while illite acts as a source of K.

Work of Sanyal and co-workers further demonstrate : (i) considering low native K content and high release of native and applied K, Indian Vertisols need careful management to prevent K mining and to sustain productivity, (ii) in alluvial soils - rich in native K but low release of K may be insufficient to sustain productivity in the long run, (iii) red and lateritic soils could fix applied K considerably. Such information is very useful for K fertilizer recommendation.

5.2.2 Phosphate sorption

Phosphate sorption in soil in governed to a large extent by clay content (a reflection of the effect of specific surface area) and presence of amorphous Fe and Al oxides (in acid, red and laterite soils) and Ca and Mg in Vertisols and calcareous soils (Table 5). Phosphate application leads to the formation of a number of phosphate reaction products in soils. Research to enhance availability of P from such products through suitable management practices needs special attention (Das and Datta, 1967, 1968, 1969).

Sanyal and De Datta (1991) reported that acid ammonium oxalate extractable Fe and Al proved to be important criterion for P adsorption. This extraction dissolves amorphous and poorly crystalline oxides of Fe and Al - and has little or no effect on crystalline Fe and Al minerals. Ryden and Pratt (1980) reported that amorphous iron oxide gels sorb 100 times more P than crystalline aluminosilicates. Das and Datta (1967, 1968, 1969) identified a number of phosphate reaction products in Indian soils. Highly acid phosphate solution also reacts with soil minerals

Table 5. Phosphate Reaction Products in Indian Soils

Soils with dominant clay minerals	Phosphate added	Reaction products
Acid soils	MAP	Ammonium tarnakites
Titabar (Assam) (Kaolinite)	MPP	Potassium tarnakites
East Birendranagar (Tripura) (Kaolinite)		Partial substitution of NH_4^+ and Al^{3+} by K^+ and Fe^{3+} occurred in taranakite structure
	MCP	Colloidal and amorphous Fe-Al phosphates, brushite, monetite
Calcareous soils ($CaCO_3$+$MgCO_3$)	MAP	Struvite, newberryite and brushite
Pusa (Bihar) Illite	MPP	Brushite and monetite
Musheri (Bihar) Illite	MCP	Brushite, monetite
Black soils	MAP	Similar to calcareous soils
Nagpur (Maharashtra) (Smectite)	MPP	Small amount of taranakites were also formed in Nagpur soils
Padegaon (Maharashtra) (Smectite)	MCP	
Red soil	MAP	As in acid soils
Bangalore (Karnataka)	MPP	As inacid soils
(Kaolinite) (amorphous Al & Fe oxides)	MCP	Brushite, monetite, Ca-Al phosphate
Laterite soil	MAP	Similar in acid soils
Karnataka (Kaolinite,	MPP	Similar in acid soils
amorphous Al & Fe oxides)	MCP	Fe-Al phosphate, brushite

MAP - Mono ammonium phosphate, MPP - Monopotassium phosphate, MCP - Monocalcium phosphate.

forming different phosphate compounds (Table 5).

The clay minerals have constant negative charge on siloxane surface and pH-dependent charge on edge face region. Specific adsorption of P occurs on edge-face region (Mulzadi *et al.*, 1966). The proportion of siloxane surface area to edge-face surface area and hence the permanent negative charge to pH dependent charge varies with the clay minerals.

At low P levels, Kaolinite dominant soils sorb highest amount of P followed by illite and 2:1 expanding layer mineral dominated soils. This is attributed to spilling over of negative charge from basal planes to edge face region in 2:1 expanding layer minerals and to a lesser extent in illite, which weaken the attractive forces between the positively charged edge face of 2:1 minerals and phosphate. The above sequence of P adsorption changes at high P rates. This is ascribed to electrostatic adsorption on low affinity sites, which are abundant in 2:1 expansible layer minerals (Tomar *et al.*, 1995).

5.3 Mineral surfaces and bioavailability of heavy metals, contaminant transport and environmental remediation

There is a continuous flux of heavy metal and contaminants and pollutants into the biosphere from both natural and anthropogenic sources. A complex variety of abiotic and biotic processes affects their speciation and distribution, including adsorption onto and desorption from mineral surfaces, incorporation in precipitates or co-precipitates, release through the dissolution of mienrals, and interactions with plants and microbes. Some of these processes can effectively isolate heavy metals from the biosphere, whereas others cause their release or transformation to different species that may be more (or less) bioavailale and / or toxic to organisms (Brown *et al.*, 1999).

5.3.1 Molecular-level speciation

Molecular-level speciation of metalloid arsenic (As) and heavy metal contaminant lead (Pb) in the mine tailings using extremely intense X-rays from synchrotron and X-ray absorption fine structure (XAFS) spectroscopy by Brown *et al.* (1999) show that up to 50% of these contaminants in the samples may be present as adsorbed species on mineral surfaces, which make them potentially more bioavailable than when present in sparingly soluble form. Study of selenium (Se VI) sorption on Fe^{2+}-containing sulphates show that this element undergoes redox reactions that transform it into less bioavailable and less toxic species. This type of information on molecular-level speciation of heavy metal and metalloid contaminants in various environmental setting is needed to prioritize remediation effects and to assess their potential hazards to human and other organisms.

5.3.2 Remediating contaminated soil

Application of soluble or solid phase phosphates (i.e. apatites) to contaminated soils and sediments induces the dissolution of the 'native' Pb minerals, the desorption of Pb adsorbed by hydrous metal oxides, and the subsequent formation of pyromorphites *in situ* (Traina *et al.*, 1999). This process results in decrease in the chemical lability and bioavailability of the Pb without its removal from the contaminated media. This and analogous approaches may be useful strategies for remediating contaminated soil and sediments.

5.3.3 Characterization of complex mineral assemblages

This has implication for contaminant transport and environmental remediation. Studies on contaminant-mineral interaction on model mineral systems have provided foundation for understanding reactive surface functional groups on individual mineral phases. The information, however, cannot be readily extrapolated to complex mineral assemblages in natural systems. The less abundant mineral and organic substrates may act as important surface chemical modifiers. There is complex coupling of reactivity between permanent charge phyllosilicates and variable charge Fe-oxohydroxide phases. Surface chemical modifiers control colloid generation and transport processes in surface and sub-surface environments as well as transport of solutes and ionic tracers (Bertsch and Seaman, 1999). A complete understanding of the surface chemistry of complex mienral assemblages is prerequisite to accurately assess environmental and human health risk of contaminants or in designing environmentally sound, cost effective chemical and biological remediation strategies.

6. Soil Minerals - Organic - Microbial Interactions

Minerals, organic matter and microorganisms of the pedosphere are the key factors influencing soil formation (pedogensis) and other soil processes. The interaction of soil minerals with organic material and microorganisms affects the metabolic transformation of natural and xenobiotic organic compounds and the fate of metals and other inorganic components. On the other hand, natural organic components and microorganisms influence mineral weatheirng, aggregate formation, and surface properties, as well as the reactivity of soil mienrals with nutrients and environmental pollutants.

6.1 Clay-organic interaction

6.1.1 Clay-humus complex : Clays interact with humic substances to form complexes of varying stability and properties. These interactions are of great importance in nature and industry. The nature of complexation reaction depends on nature of organic molecules, the water content of the system, nature of exchangeable cations on the clay surface and the unique properties of the clay mineral structures (Mortland, 1970; Ghosh, 1997).

Study of the complexes formed bythe interaction of humid acid (HA) isolated from farm yard manure with Cu, Co, Zn, Ca and Mg montmorillonites show the amount of HA retained follows the order : Cu > Co > Zn > Ca > Mg. The X-ray study of the complexes indicate entry of some humic acid into the interlayers of minerals. The electron micrographs of zinc and copper montmorillonite-HA complex show the formation of microaggregates of irregular and elongated shape by the association of HA on clay surface (Manjaiah and Ghosh, 1995). The study of the properties of natural clay-organic complexes isolated from Alfisols and Ultisols of Karnataka show that in both the soil groups, <2 μm size complex possessed higher organic carbon compared to coarser size fractions. The organic component of the complex imparted high CEC, higher surface area, and lower P and K fixation capacity. The sesquioxides and allophanes also had their share in overall CEC, surface area and P and K fixation capacity of the complexes (Table 6). The XRD and DTA observations revealed the clay-organic complexes to be of surface adsorbed type. Transmission electron microscopy revealed that microaggregates of various shape i.e. spherical, irregular and elongate, attached themselves through their edges and faces to form larger aggregates. The surface adsorption of extraneous materials at the free edges of the mineral was conspicuous which might have assisted in face to face or edge to edge sharing of the particles. In the process of formation of larger size aggregates, the development of channels and pores of different size and shape could be seen in electron micrographs which could play a significant role in determining the moisture retention and other physical properties of soil (Manjaiah and Ghosh, 1996).

6.1.2 Interaction of proteins with mineral surfaces

Study of the influence of montmorillonite on catalytic activity of a chymotrypsin (protease enzyme) revealed that a chymotrypsin is denatured by the clay surface at pH below its isoelectric point. Simultaneous adsorption of both a chymotrypsin and casein results in a very large decrease in the reaction rate. If casein is added before a chymotrypsin, it acts as an organic coating protecting the enzyme structure in the adsorbed state.

6.1.3 Adsorption of Bt-Protein

Manjaiah (personal communication) studied adsorption of B_t - Protein on synthetic amorphous aluminosilicates. By increasing the Si/AL ratio, the adsorption of B_t-protein decreased. The equilibrium adsorption isotherms were of the L-type, while showing a plateau with higher concentration of B_t-protein added (Table 7).

6.1.4 Herbicide leaching

Organo-clays can play important role in catalytic activity of soil enzymes and reduce leaching of herbicides. Highest sorption of Fenuron

Table 6. Effect of complex forming components on change in CEC [cmol (p^+) kg^{-1}] and specific surface area (SSA) (m^2g^{-1}) of clay organic complexes

Sample	CEC			SSA		
	X	Y	Z	X	Y	Z
Vertisols						
Dharwad	68.2	74.1	84.1	620	640	680
Bijapur	70.9	78.9	74.1	800	835	895
Indore	77.2	124.2	146.3	790	814	913
Alfisols						
Bangalore	18.5	37.6	50.3	80	140	162
Dandeli	27.1	40.5	65.7	127	162	342
Palampur	23.3	41.0	40.0	218	317	500
Ultisols						
Khanapur	21.7	34.5	53	50	80	95
Sirsi	18.6	24.7	44.5	70	115	145
Kohima	20.5	20.5	26.1	460	428	486
Entisols						
Bentlu	23.9	52.2	75.7	139	270	470
Mohitnagar	28.9	94.8	140.8	121	200	537
Jorhat	27.1	45.8	45.7	494	460	690

X = Crystalline clay, Y = Clay-sesquioxide association, Z = Natural complex

Table 7. B_t-Protein adsorbed (p.c.) at different levels of added B_t-Protein on synthetic amorphous aluminosilicates with different Si/Al ratios (Manjaiah, personal communication)

Synthetic amorphous aluminosilicates	Concentrations (μg ml^{-1})				
	50	100	150	200	250
Si/AL = 0.5	20.16	17.94	13.95	10.68	8.57
Si/Al = 1.0	19.88	17.01	13.46	10.52	8.53
Si/AL = 2.0	18.02	16.86	13.29	10.47	8.41

and Clopyralid has been observed when high charge smectites have been saturated with quarternary alkylammonium cation and primary alkalammonium cations, respectively, thereby reducing their leaching losses.

6.1.5 Carbon sequestration

Information on the influence of clay minerals in enhancing the soil organic carbon (SOC) status is meagre. Study in associated Mollisols - Alfisols-Vertisols sequence in the Satpura ranges in central India (humid subtropical climate) and the western Ghats of Western India (humid tropical climate) reveals that the smectites have a considerable influence in organic carbon requestration to reach a quasi-equilibrium value under the set of climates.

The SOC quasi-equilibrium value of Mollisols and Alfisols formed in humid tropical climate is lesser than those formed in humid subtropical climate. However, irrespective of climatic variations SOC quasi-equilibrium value for Vertisols remain almost the same because of comparable smectite content.

6.2 Clay-microbial interaction:

Soil organisms (microorganisms and funna), well-defined biomolecules present in the secretions of organisms and humic substances interact with soil minerals. The interactions result in dissolution of minerals and formation of complexes. Knowledge on the nature and properties of mineral-organic complexes is meagre. Further, there is insufficient information on how and where most microbial activity occurs in situ and which microbes are the most important participants.

Soil mineral colloids play important role in abiotic transformation of organic compounds through catalysis. Some types of clay minerals significantly affect microbial life by modifying the physicochemical characteristics of microbial habitats, but little is known about direct surface interactions between clays and microbes, and about the mechanisms controlling the stability and activity of enzymes associated with the humic fraction (formation of enzyme-phenolic copolymers) and adsorbed to mineral colloids (Bollag *et al.*, 2002).

The rhizosphere is a zone of intense activity Minerals, organic matter, and microorganisms are intimately associated in soil rhizosphere where low-molecular-weight biochemicals are abundant and microbial activity is intense, and closely interact to govern environmental processes. The roles of these interacting processes in affecting dynamics of nutrients and toxic substances and their impact on the quality of ecosystems merit increasing attention.

6.3 Conclusion

Clay and clay minerals, mediated through physical, chemical and biological properties of soils and nutrient availability, can play vital role in restoration / prevention of degradation of soils and in maintaining soil health and soil resilience. Clays from natural deposits play vital role in industries meeting societal needs and human welfare. While study of the role of soil mienrals in relation to pedology and paleopedology would continue, future research need to be directed to investigations on soil mineralogy in relation to overall soil fertility. Study of clay-organic intractions is likely to help in understanding and synergistically exploiting the complexities of processes for evolving a durable IPNM. Research on clays as sink for soil pollutants contamination and remediation, carbon sequestration and its influence on changes of climate and land management, and the soil mineral - organic components - microorganisms interactions and their impact on the ecosystem and human welfare hold great promise.

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