Chapter 8
Linking Minerals to Selected Soil Bulk Properties

Abstract Minerals in soils are the result of both inheritance and authigenic formation of both primary and secondary minerals. Comprehensive reviews on the soil clay minerals and other minerals in the past indicate that there are not many attempts to show the influence of minerals in soil genesis and management. A search for links between mineralogy and soil properties of agricultural importance is likely to be difficult because many a time the description of minerals actually present in a soil is inadequate or incomplete. Further, as soil minerals often differ from "type" minerals, it is very much necessary to investigate the properties of these minerals relevant to the properties of the soil in bulk. Despite our general understanding on the role of minerals in soils, it is necessary to investigate the properties of the minerals, especially clay minerals, their mixtures and surface modifications in the form that they occur in the soil. From the few examples under different agro-climatic situations cited it is evident that unless the mineralogical description is accurate enough for the purpose intended, it would not be prudent to look for their significance in soils. With the use of high resolution mineralogy, identification and explanation of many enigmatic situations in soils can be conveniently solved. Therefore, the advanced information developed provides adequate mineralogical database that would explain discretely many unresolved issues of the nutrient management in terms of specific soil minerals in general, and clay minerals in particular and their significance in soil as a sustainable medium for plant growth. It is hoped that this synthesis would help to assess the health and quality of soils while developing suitable management practices to enhance and sustain their productivity in the 21st century.

Keywords Soil minerals · Characterisation of clay minerals · High end instruments · Nutrient management · Suitable management practices

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8.1 Introduction

Minerals in soils are the result of both inheritance and authigenic formation of both primary and secondary minerals. Comprehensive reviews on the soil clay minerals and other minerals in the past indicate that there are not many attempts to show the influence of minerals in soil genesis and management (Pal et al. 2012a). A review in the past on this subject and related issues (Newman 1984; Ghosh 1997; Wilson 1999) pointed out that the increase in agricultural productivity during the middle of the twentieth century was due to human influence, which vastly improved the soil fertility on all types of soil. However, actual productivity does vary widely and this fact shows that there are other factors of productivity beyond our control. One intrinsic factor in yield variation is soil type, which is related to the soil composition and its position in the landscape. Clay is an important soil constituent controlling its properties. Despite the fact that there is ample evidence to show that the amount of clay in a soil has a very important bearing on the genesis, characteristics, and physical and chemical properties of soils, it would be more appropriate to see what significance clay mineral *type* and other soil minerals have in soils. A search for links between mineralogy and soil properties of agricultural importance is likely to be difficult because many a time the description of minerals actually present in a soil is inadequate or incomplete. Further, as soil minerals often differ from “type” minerals, it is very much necessary to investigate the properties of these minerals relevant to the properties of the soil in bulk. In this endeavour, Pal et al. (2000a, 2012a) demonstrated a good number of examples that indicated despite soil clay minerals being a mixture of several components, adequate description is possible. Synthesis of the present dataset on the nature and characteristics of primary and secondary minerals of Indian soils has established a link between minerals and selected bulk soil properties. It is hoped that this synthesis would help to assess the health and quality of soils while developing suitable management practices to enhance and sustain their productivity in the 21st century.

8.2 Clay and Other Minerals in Adsorption and Desorption of Major Nutrients

8.2.1 Organic and Inorganic Carbon

8.2.1.1 Vertisols

Vertisols occupy only 8.1% of the total geographical area of the country but have 29% share in total soil organic carbon (SOC) stock (0–150 cm soil depth) of 29.32 Pg, indicating the role of surface area (due to the dominating amount of smectite clay minerals) in accumulating OC. Vertisols and soils with vertic characters under agricultural land uses under both short and long-long term experiments also displayed their potential to sequester OC under both arable and submerged conditions and they are also capable enough to sequester OC even in humid climates (Pal et al. 2015). Results on Vertisols indicated that legume-based improved management (IM) advocated by ICRISAT (detailed in Chap. 6) could sequester OC at the rate of 5 mg year^{-1} in the first 100 cm soil depth even without FYM and gypsum addition. When FYM added (10 Mg FYM ha^{-1}) along with 100% of recommended doses of NPK, Vertisols showed potential to sequester an additional amount of 330 kg OC ha^{-1} year^{-1} (Pal et al. 2015).

Zeolites improve hydraulic properties of soils by enriching soil exchange complex with Ca^{2+} ions in arid to HT climate (Pal et al. 2013). In order to follow the decomposition resistance of soil organic matter under high-temperature, experiments with Ca-zeolite and organic manure showed a slight increase in C/N ratio in soils of the Philippines, Paraguay and Japan. In addition, carbon accumulation in humic fractions as well as the degree of humification and aromaticity of humic acids increased (Truc and Yoshida 2011). In semi-arid dry region of India, zeolitic (heulandite) Vertisols (Teligi soils, Bellary, Karnataka; Jhalipura soils, Kota, Rajasthan; Jajapur, Mehboobnagar, Andhra Pradesh) (Pal et al. 2003), under wetland rice–rice/rice–wheat system showed wider C/N ratio (Table 8.1), indicating enough potential to sequester atmospheric carbon (Sahrawat et al. 2005). This suggests that the presence of zeolites could be beneficial for soil organic matter conservation under global warming (Pal et al. 2013).

8.2.1.2 Red Ferruginous (RF) Soils

Total stock of soil organic carbon (SOC) is 9.55 Pg in the first 30 cm depth, and out of this stock, Indian soils of the arid (cold arid and hot arid) and semiarid climate have a share of about 40%, the soils of sub-humid, humid and per-humid 47%, and the Ultisols of about 1% (Bhattacharyya et al. 2000a). Therefore, RF soils of HT climate are not impoverished in OC. RF soils under dry climate contain <1% OC but SAT Alfisols under permanent fallow with grass cover could sequester OC up

Table 8.1 Selected properties in surface (0–30 cm) soil samples of zeolitic Vertisols under rice cultivation

Benchmark soil series	District/state	Soil taxonomy	pH (1:2)	Clay CEC	SOC (%)	Total N (%)	SOC: N
Jhalipura	Kota/Rajasthan	Typic Haplusterts	8.1	77	0.53	0.0443	12:1
Jajapur 1	Mehboobnagar/Andhra Pradesh	Sodic Haplusterts	8.5	62	0.88	0.082	11:1
Teligi	Bellary/Karnataka	Sodic Haplusterts	8.0	90	1.03	0.062	17:1
Teligi1	Bellary/Karnataka	Sodic Haplusterts	7.8	99	0.88	0.0551	14:1

Adapted from Sahrawat et al. (2005) and Pal et al. (2003)

to $\sim$1.5, $\sim$1% under horticulture and 1.78% under forest in the first 30 cm of the profile (Bhattacharyya et al. 2014; Pal et al. 2015). A short term experiment on SAT Alfisols under sorghum-castor bean rotation (Sharma et al. 2005) indicated that conventional tillage with the application of Glyricidia loppings along with 90 kg ha^{-1} N provided the best soil quality index (SQI), increased vegetative growth and root biomass, which in turn enhanced soil organic matter. Srinivasarao et al. (2013) pointed out that the importance of identification and management factors that cause enhanced C sequestration in SAT soils. They also indicated that recommended management practices for SAT soils that include locally available organic resources, are capable of improving the SOC sequestration.

Ultisols, Alfisols and Mollisols of HT climate have OC concentration ranges from 1.0 to 5% (please refer to Table 3.2), which is relatively high as compared to SAT Alfisols. These soils are developed under thermic, hyperthermic (Nilgiri Hills in Kerala and Tamil Nadu, Manipur, Meghalaya, Nagaland, Arunachal Pradesh, Assam, Tripura and Mizoram), isohyperthermic (Andaman and Nicobar, Kerala, Tamil Nadu, Madhya Pradesh and Maharashtra) soil temperature regime, and udic (Andaman and Nicobar, Arunachal Pradesh, Manipur, Meghalaya, Assam, Tripura, Nagaland, Mizoram, Nilgiri Hills in Kerala and Tamil Nadu) and ustic (Kerala, Karnataka, Tamil Nadu, Madhya Pradesh and Maharashtra) soil moisture regime (Bhattacharyya et al. 2009). Soils in a wet climate under forest have high OC content, sufficient to qualify as Mollisols. The OC addition to Ultisols and Alfisols has been possible as a result of, favourable soil temperature and moisture regime. It is known that 2:1 expanding clay minerals provide higher surface area for OC accumulation. But a high positive OC balance in kaolin dominated RF soils clearly indicates a positive role of this mineral and other hydroxy-interlayered clay minerals because kaolin (like the other hydroxy-interlayered minerals) often shows a relatively high value of CEC $\sim$30 cmol (p+) kg^{-1} (Ray et al. 2001) than that of well crystalline kaolinite. Therefore, besides the dominating effect of humid climate in cooler winter months with profuse vegetation, the soil substrate quality in terms of larger surface area is of fundamental importance in OC sequestration in soils (Bhattacharyya et al. 2014; Pal et al. 2015).

The formation and persistence of acidic and fairly weathered Mollisols and OC rich (>1%) Alfisols on zeolitic Deccan basalt of HT climate (Bhattacharyya et al. 2005, 2006) in contrast to commonly found alkaline Mollisols in temperate humid climate and Ultisols of HT climate, suggests that Ca-zeolite is an another important substrate for OC sequestration. The Ca-zeolites (as soil modifier) are sources of bases to prevent complete transformation of smectite to kaolinite by maintaining relatively high base saturation level in acidic Mollisols and Alfisols.

8.2.1.3 IGP Soils

The sustainability ratings of some soil series of the IGP for the rice-wheat cropping system indicate many soil constraints, including low soil organic carbon (SOC) (Bhattacharyya et al. 2004). The SOC and inorganic carbon (SIC) stocks of the IGP (0–150 cm depth) are 2.0 and 4.58 Pg, respectively. The SOC stock of the IGP constitutes 6.45% of the total SOC stock of India, 0.30% of the tropical regions and 0.09% of the world in the first 30 cm depth of the soil. The corresponding values of SIC are 3.20% for India, 0.17% for the tropical regions and 0.06% for the world, respectively. Thus the soils of the IGP are impoverished in OC compared to tropical regions and the world in general and to India in particular (Bhattacharyya et al. 2004). For soils of the IGP, Bhattacharyya and co-workers (2004) indicated that five AESRs (warm to hot moist, hot moist humid to per-humid, warm to hot per-humid, warm to hot per-humid and warm to hot per-humid) covering 6% area of the IGP are in the sufficient zone of OC and the remaining nine AESRs covering 94% area are under deficient zone. However, some areas under humid climate do not have sufficient SOC because of intensive agricultural practices (Abrol and Gupta 1998).

It is generally observed that among the agricultural systems such as rice–wheat, rice–rice, cotton-wheat and groundnut, the cereal-based systems contribute to higher accumulation and stabilization of organic matter, especially in rice–wheat systems (Bhattacharyya et al. 2007a, b), because decomposition of organic matter in the absence of oxygen is slow, incomplete and inefficient. It is also due to the formation of recalcitrant complexes with organic matter in these soils that render organic matter less prone to microbial attack (Sahrawat 2004a, b). Thus the SOC built up under submerged conditions is the reason for high status of organic matter and productivity in rice–rice and rice–wheat systems in the IGP. The Indian Council of Agricultural Research-National Bureau of Soil Survey and Land Use Planning (ICAR-NBSS & LUP) reassessed the SOC stock of the IGP in 2005, and observed that there has been 30% increase in SOC in 0–20 cm depth over the value assessed in 1980. Soils of the sub-humid part of the IGP (Vertic Endoaqualfs at Mohanpur, West Bengal, Pal et al. 2010) with double or triple rice-based agricultural land uses under long-term experiments showed their potentiality to sequester OC under submerged conditions and still show potential to sequester OC (Majumder et al. 2007; Mandal et al. 2007, 2008), suggesting the benefit of higher soil surface area (caused by 2:1 expanding clay mineral) in better OC sequestration even in sub-humid to humid climates.

The SIC stocks in soils of the arid and semi-arid ecosystems of the IGP seem to be useful during the establishment of vegetation by appropriate ameliorative methods in these soils, as the plant roots can dissolve the immobile $CaCO_3$ and can ultimately trigger the process of Ca^{2+} release in the soil and thus act as a natural ameliorant for sodic soils (Bhattacharyya et al. 2004). The benefit of such chemical reaction is realized recently when the naturally occurring grassland systems was continued on IGP sodic soils for almost four decades (Jangra et al. 2015). These authors report that by increasing plant biomass a marked improvement in soil organic carbon was observed (from 0.20 to 0.44%). The extensive root system of *Desmostachya bipinnata*, the dominant grass, through biological production of carbonic acid by the roots, seems to play an important role in solubilisation of native $CaCO_3$ present in the sodic soils. The dissolved Ca^{2+} ions caused a substantial decrease in soil pH, electrical conductivity and an increase in exchangeable

Ca and Mg. The huge SIC stock thus remains as a hidden treasure that would improve the drainage and help in the establishment of vegetation and also sequestering OC in the soils (Bhattacharyya et al. 2004). The overall increase in SOC stock in the benchmark spots under agriculture, practised for the last 25 years, suggests that agricultural management practices of the National Agricultural Research System (NARS) did not cause any decline in SOC (Bhattacharyya et al. 2007a, b).

8.2.2 Nitrogen

8.2.2.1 Vertisols

Increasing demand for nitrogen (N) fertilizers to produce food grains has always stimulated research to gain knowledge on the various forms of N in soils. One of the forms of mineral N is fixed NH_4-N, and several reports indicate that many tropical Vertisols are endowed with large amounts of fixed ammonium (Sahrawat1995). Vermiculites, illites and smectites are often considered able to fix NH_4-N (Nommik and Vahtras 1982). Smectites have no selectivity for non-hydrated monovalent cations such as K^+ because of their low layer charge (Brindley 1966). NH_4^+ ion, also a non-hydrated monovalent cation with almost the same ionic radius as K, is not expected to be fixed in the interlayers of smectites. It is equally difficult to understand the NH_4 ion fixing capacity of illites, because they do not expand on being saturated with divalent cations (Sarma 1976). Earlier reports indicate that Vertisols developed in the basaltic alluvium of the Deccan basalt of Peninsular India, do not contain vermiculite (Dhillon and Dhillon 1991). However, a recent report indicates that vermiculite content in such soils ranges from 2.0 to 3.5% in the silt, 3.5 to 10% in the coarse clay and 5.0 to 9.5% in the fine clay fractions (Pal and Durge 1987). The identification of vermiculite by XRD analysis in different soil size fractions is fraught with some difficulty in the ubiquitous presence of chlorite. Its presence is resolved by following the progressive reinforcement of the 1.0 nm peak of mica while heating the K-saturated samples at 25, 110, 300 and 550 °C, and its quantity is estimated semi-quantitatively (Pal et al. 2012b). Thus, it would be prudent to attribute the observed NH_4-N fixation in Vertisols (Sahrawat 1995) to the presence of vermiculite only.

Zeolites are known to have pronounced selectivity for NH_4^+-N over $Ca^{2+,}$ Mg^{2+} and Na^+; and it is difficult to remove NH_4^+ from zeolite exchange sites by these less selective cations. Therefore, NH_4^+ is slowly released, however its rate of release from vermiculite and zeolite in a zeolitic Vertisols is not yet known. Thus, it would not be prudent to attribute the observed NH_4-N fixation in Vertisols (Sahrawat 1995) entirely to the presence of vermiculite only (Pal et al. 2012b). Such a basic understanding is essential to include fixed NH_4-N in assessing the potential of N available in tropical soils in general and the Vertisols in particular A new research initiative in this direction is thus awaited.

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^+ ion resides on exchange sites (Ming and Allen 2001). This way the protection of NH_4^+ suggests that emission of N_2O from organic (farmyard manure) and inorganic N fertilizers would amount to a small fraction of the total world greenhouse gas emissions from zeolitic soils, because out of 500,000 km^2 Deccan basalt area in the Indian subcontinent (Pal et al. 2000a), zeolitic soil is expected to cover a considerable part (Pal et al. 2013). Bhattacharyya et al. (2015) in their recent study have updated the knowledge on the occurrence of Ca-rich zeolites in cracking clay soils in the IGP area and black soil region (BSR), and reported an area ~2.8 m ha, of which BSR and IGP occupy ~92 and ~8%, respectively. In addition, this study provides an approximate map on the distribution of Ca-rich zeolites in Indian soils. Such map would be of much help to include fixed NH_4-N in assessing the N available in zeolitic soils, especially when 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).

8.2.2.2 RF Soils

RF soils need N fertilization for agricultural production. One of the forms of mineral N in soils is fixed NH_4-N and some selected tropical soils contain large amounts of fixed N (Dalal 1977). Information on fixed N in soils of HT climate, especially under paddy or lowland rice is scarce, despite the fact that Fe rich soils under submerged environments do sequester good amount of OC (Sahrawat 2004a). Iron (Fe) is present in large amounts in RF soils and reducible Fe influence the NH_4 production or N mineralization in submerged soils. In the absence of oxygen, ferric Fe serves as an electron acceptor and affects organic matter oxidation and NH_4 production (Sahrawat 2004b). Similar kind of pedochemical reactions in OC rich RF soils of HT climate under rice in Kerala, Goa, and NEH, is expected to benefit the soils in enriching their fixed NH_4 status and minimizing the effect of N fertilizers. Information on fixed NH_4-N is also scarce for RF soils of the semi-arid tropics (SAT) (Burford and Sahrawat 1989). Realizing its importance in the N economy of RF soils, Sahrawat (1995) determined the NH_4-N distribution in a benchmark Alfisol (Patancheru soils at ICRISAT, Patancheru farm, Telangana). The amount of fixed NH_4-N as per cent of total N varied from 14.0 to 30.8% and the values generally increased with soil depth. Vermiculites are the only clay minerals to fix NH_4-N. Patancheru soils do contain vermiculites in their silt, coarse and fine clay fractions, and the translocation of fine clay-vermiculite has enriched the subsoils with vermiculite (Pal et al. 2012b) that explains the observed increasing fixation of NH_4-N with soil depth (Sahrawat 1995). In soils of HT climate, NH_4-N is also expected to get fixed in discreet vermiculite and also in its hydroxy-interlayered counterpart. The NH_4^+ ion, also a non-hydrated monovalent cation with almost the same ionic radius as K, is expected to be fixed in the vermiculite interlayers, and this way NH_4^+ ion may be protected from microbial conversion of NH_4^+ to NO_3^-. The prevention of such conversion suggests that the emission of N_2O from organic (farm yard manure) and inorganic N fertilizers from RF soils under arable and submerged conditions would also amount to a small fraction of the total world greenhouse gas emission (Bhatia et al. 2004, 2012). Like in Vertisols such basic understanding is essential to include fixed NH_4-N for assessing potentiality of available N in RF soils.

8.2.2.3 IGP Soils

Like any other important soil types of India, the IGP soils also need N fertilizers to sustain crop productivity. The amount of fixed N in the IGP soils is very rarely reported. Therefore, it is difficult to highlight the role of specific clay minerals capable to fix NH_4^+ ions. However, it will not be too imprudent to anticipate the role of 2:1 clay minerals in fixing NH_4^+ ions in view of the observed K adsorption and fixation reactions (Pal et al. 2000a). In general, micaceous IGP soils do contain vermiculite and low charge vermiculite or high charge smectite in the finer soil fractions (Pal et al. 2000a). In view of their K adsorption capacity, it can be safely assumed that the IGP soils can also adsorb NH_4^+ ions and get fixed in the interlayer of vermiculite and smectite which are in considerable amount (Pal et al. 2000a). This way NH_4^+may be protected from microbial conversion of NH_4^+ to NO_3^-. The prevention of such conversion would minimize the emission of N_2O from organic and inorganic N fertilizers from the IGP soils under arable and submerged conditions. However, fresh research initiative in this area of soil research will highlight the extent of fixed N in the IGP soils of different bio-climates.

8.2.3 Phosphorus

8.2.3.1 Vertisols

A critical analysis of the findings of several researchers on phosphorus (P) adsorption by soil minerals (Sanyal and DeDatta 1991) indicated a significant correlation of P sorption parameters with clay content, and these authors proposed that this is a mere reflection of the effect of specific surface area on P adsorption. In soils, hydrous oxides of iron and aluminium occur as fine coatings on the surfaces of clay minerals (Haynes 1983), and these coatings have large specific surface areas that can adsorb large amounts of added P. This characteristic suggests that crystalline aluminosilicate minerals merely play a secondary role in P adsorption (Ryden and Pratt 1980). Fine clay smectites of Vertisols of HT, SHM, SHD, SAM, SAD, and AD of Peninsular India are partially hydroxy-interlayered (Pal et al. 2009). The hydroxy interlayering in smectite interlayers is not a contemporary pedogenic process because in the prevailing mild to moderately alkaline pH conditions, the hydroxides of iron and aluminium cannot remain as positively charged cations to enter the negative environment of the interlayers of smectites (Pal et al. 2012c). The presence of hydroxy-interlayered smectite (HIS) in the fine clay fractions indicates that the hydroxy-interlayering in the smectite interlayers did occur when positively charged hydroxy interlayer materials entered into the interlayer spaces at a pH far below 8.3 (Pal et al. 2012c). Moderately acidic conditions are optimal for the hydroxy-Al interlayering of smectite, and the optimum pH for interlayering in smectite is 5.0–6.0 (Rich 1968a, b). The pH of the Vertisols is mildly to moderately alkaline, which would favour congruent dissolution of 2:1 layer silicates (Pal 1985). This scenario discounts the hydroxy-interlayering of smectites during the formation of Vertisols in the Holocene period (Pal et al. 2012c) and the creation of any positively charged hydroxides that can fix added P, as in highly weathered acidic soils. Therefore, the highest surface area of smectite and/or hydroxides of iron and aluminium with no positive sites play a small role in the adsorption of added negatively charged phosphate ions in Vertisols. This supports the ICRISAT's classical experimental observations on P adsorption and desorption on Vertisols (Kasireddipalli soils), which clearly indicate that P adsorption is not a major problem in the Vertisols and that all the adsorbed P is easily exchangeable by P^{32} and a small amount of P is adsorbed in the non-exchangeable form (Sahrawat and Warren 1989; Shailaja and Sahrawat 1994; Warren and Sahrawat 1993). ICRISAT (1988) envisaged that $CaCO_3$ could adsorb P because the effective sorption by $CaCO_3$ is not well understood, and P adsorption is not always related to $CaCO_3$ content but to the quality of the $CaCO_3$. The SAT Vertisols contain $CaCO_3$ of both nonpedogenic (NPC) and pedogenic (PC) origin, and both of them effervesce with HCl and cannot be distinguished without examining the soil thin sections under a microscope (Pal et al. 2000a). During the formation of Vertisols in the SAT environment, NPCs (pedorelict) dissolve, and the soluble Ca^{2+} ions released from NPCs become precipitated as PC at a pH of approximately 8.2 and may also react with phosphate ions to form Ca-P. Both PC and Ca-P may have the least solubility in the prevailing mild to moderately alkaline pH conditions of Vertisols. This makes it clear why Ca-P in the SAT Vertisols has a dominant share among the other soil P compounds, such as Fe–P and Al–P. Thus less soluble Ca-P causes a very low level of soluble extractable P (<5 mg kg^{-1} soil) by Olsen's method (ICRISAT 1988). It is interesting to note that grain sorghum grown on Vertisols responds little to applied P unless the level of Olsen's P was <2.5 mg kg^{-1} soil (ICRISAT 1988). Additionally, some leguminous crops such as chickpea and pigeon pea do not respond well to fertilizer P than sorghum and pearl millet (ICRISAT 1981) because the root systems of chickpea exude organic acids (malic or citric) (ICRISAT 1988) and those of pigeon pea produce piscidic acid (Ae et al. 1990). These acids dissolve Ca–P and Fe–P, making more P available to the plants. The root exudates containing such organic acids and the rootlets in the soil through which rainwater passes, or other sources of CO_2, can cause an increase in the solubility of PC and Ca–P. The improved management (including pigeon pea) in the long-term heritage watershed experiment at the ICRISAT Center, Patancheru, under rain-fed conditions (Pal et al. 2012a, b) indicates that during the last 24 years, the rate of dissolution of $CaCO_3$ was 21 mg year^{-1} in the first 100 cm of the Kasireddipalli soils, which caused a slight increase in exchangeable Ca/Mg and a decrease in pH (Pal et al. 2012a, b). The rate of dissolution of Ca–P under the present improved management system is sufficient, as it does not warrant the application of a high dose of added P fertilizer. However, predicting a time scale when soils will be devoid of Ca–P is difficult unless a new research initiative in this direction is taken up.

Many SAT Vertisols contain zeolites (Pal et al. 2006a) and thus attention is needed to follow the role of zeolites on P adsorption and desorption phenomenon. Studies indicate that the dissolution of apatite-rich phosphate rock is enhanced by the exchange of dissolved Ca^{2+} on to zeolite exchange sites. The addition of NH_4^+-, H^+-, or Na^+-exchanged, clinoptilolite-rich tuff significantly increased solution P concentration when compared with phosphate rock without zeolite additions (Ming and Allen 2001). Soils occurring in the Deccan basalt areas under semiarid and HT climate, contain heulandite [$(Na, K)Ca_4(Al_9Si_{27}O_{72})$ $24H_2O$], which is rich in Ca^{2+} ions, and thus the soils are highly base-saturated. Therefore, the scope of P fertilization by dissolution and ion exchange with zeolite in such soils is expected to be limited. In smectitic Vertisols of the Deccan basalt areas, P adsorption is not a major problem and all the adsorbed P is easily exchangeable by P^{32} and a small amount is adsorbed in the nonexchangeable form (Sahrawat and Warren 1989; Warren and Sahrawat 1993).

8.2.3.2 RF Soils

Large doses of P are required for moderate to highly acidic RF soils to get desired crop response even when crop requirement of P is relatively low (Datta 2013). Nature and amount of clay, organic matter, and hydrous oxides of iron and aluminium affect P adsorption in such soils (Sanyal and DeDatta 1991).

It is often reported that soils rich in clay kaolinite may contribute to P adsorption in highly weathered soils of HT climate. But the added P is adsorbed more in soils with low pH wherein activity of iron and aluminium is high. Thus, the Fe and Al-oxy-hydroxides ordinarily present in RF soils have phosphate fixing ability. These hydroxides occur as fine coatings on surfaces of silicate clay minerals (Haynes 1983) and have large specific surface area that causes adsorption of large amounts of added P. This physical adsorption implies that in P adsorption these oxy-hydroxides have a merely secondary role (Ryden and Pratt 1980). But, these minerals can adsorb negatively charged phosphate ions only when they remain as cations in highly acidic medium. In many Alfisols and Ultisols of India are highly acidic and their KCl pH values remain close to equal or greater than water pH (Bhattacharyya et al. 2000b; Chandran et al. 2004, 2005), indicating the presence of gibbsite and/or poorly crystalline materials (Smith 1986). A negative/zero/positive ΔpH indicates the presence of variable charge minerals such as gibbsite and/or sesquioxides (Bhattacharyya et al. 1994). Therefore, gibbsite and/or sesquioxides showing a positive ΔpH could be a better substrate to absorb negatively charged phosphate ions, and this is evident from the continuous increment in yield of rice up to 120 kg P_2O_5 ha^{-1} in gibbsitic soils of Meghalaya (Datta 2013). This suggests that the highest surface area of 2:1 expanding silicate clay minerals and/or Fe and Al-oxy-hydroxides with no positive sites, have little role in the adsorption of added negatively charged phosphate ions in mild to moderately acidic soils.

Adsorption of P is observed in mildly acidic SAT Alfisols (Patancheru soils), which contain hydroxy interlayered vermiculite (HIV) in the silt and coarse clay fractions, and hydroxy-interlayered dioctahedral smectite (HIS) in the coarse and fine clays (Pal and Deshpande 1987). HIV and HIS minerals may not be responsible for P adsorption because the hydroxy-interlayering of vermiculite and smectite is not a part of the contemporary pedogenic process in the prevailing mild acidic pH conditions. Under such mild acidic pH, the Fe and Al-oxy-hydroxides do not exist as positively charged cations and thus cannot enter the negative environment of the interlayers of vermiculites and smectites (Pal et al. 2012b). Therefore, the formation of HIV and HIS did occur when positively charged hydroxy interlayer materials enter into the interlayer space at a pH 5.0–6.0 (Rich 1968a). The observed P adsorption is thus related to the formation of Ca–P as Patancheru soils like any other SAT Alfisols, contain ~1% $CaCO_3$ (Pal et al. 2014). Calcification is one of the contemporary pedogenetic processes in soils of SAT environments (Pal et al. 2000b).

8.2.3.3 IGP Soils

Role of Fe and Al-oxy-hydroxides in fixing the added P is now well understood. The IGP soils with neutral to alkaline pH values may not have any substantial amount of such oxides. This evident from an early research on P fixation by Kanwar and Grewal (1960) who reported about 30% P fixation capacity of calcareous and alkali soils due to the presence of free sesquioxides. On the other hand Velayutham et al. (2002) reported the presence of substantial amount of P in alkali soils and thus such soils responded to added P after few years of initial cropping with rice and wheat. Although work on characterization and estimation of amorphous constituents in soils of India was intensified in 1970s, proper methods for their characterization and for obtaining data for verifying the effects on soil properties are still awaited (Krishna Murti 1982).

8.2.4 Potassium

8.2.4.1 Vertisols

Vertisols are stated to be adequately supplied with potassium (K), and therefore, responses to applied K are generally not obtained (Pal et al. 2012b). Extensive research on K behaviour in Indian Vertisols for the last two-and-a-half decades may be a good example for understanding the basic issues of K adsorption and desorption (Pal 2003). As the Deccan basalt does not contain micas (Pal and Deshpande 1987), the Vertisols derived from its alluvium contain small amounts of micas, which are concentrated mainly in their silt and coarse clay fractions (Pal et al. 2001). Micas are added to Vertisols during the erosional and depositional episodes experienced by the Deccan basalt areas during the post-Plio-Pleistocene transition period (Pal and Deshpande 1987). Petrographic and scanning electron microscope (SEM) examinations of the muscovites and biotites of the Vertisols of Peninsular India indicate little or no alteration (please refer to Fig. 2.2a, b) (Pal et al. 2001; Srivastava et al. 2002). Therefore, highly available K status of Vertisols is related to the retention of elementary layers of the micas, which favours the release of K^+ even though its content is low. The precise nature of silt and clay sized micas was determined on the basis of the X-ray intensity ratio of peak heights of 001 and 002 basal reflections of 1.0 nm minerals (micas) (Pal et al. 2001). The ratio is generally greater than unity in the silt but is close to unity in the clay fraction (please refer to Fig. 2.2c). The ratio >1 suggests the presence of muscovite and biotite minerals. If muscovite minerals were present alone, the ratio would have been close to unity. In the event of a mixture of these two micas, both will contribute to the intensity of the 1.0 nm reflections, whereas the contribution of biotite to the 0.5 nm reflection would be nil or negligible, thus giving a higher value to the intensity ratio of these reflections (Pal et al. 2001). Thus, the silt fractions of the soils contain both muscovite and biotite; whereas the clay fractions are more muscovitic in character (please refer to Fig. 2.2c). The enrichment of soils with muscovite is not favourable so far as the K release is concerned. This is evidenced by the reduced rate of K release in the Vertisols compared with the much higher rate of K release from the biotite-enriched soils of the Indo-Gangetic Plains (IGP) (Pal et al. 2001) when they were subjected to repeated batch type Ba–K exchange under identical experimental conditions (Pal and Durge 1989). Muscovite and biotite micas co-exist in soil environments. The weathering of muscovite in the presence of biotite is improbable. Therefore, the quantity of muscovite cannot be used as an index of K reserve in soils (Pal et al. 2001). For this reason, a selective quantification of biotite mica in the common situation in which soils contain mixtures of biotite and muscovite was envisaged (Pal et al. 2001). The contents of biotite in Vertisols and their size fractions were estimated through a rigorous and exhaustive Ba-K exchange reaction. The cumulative amount of K released at the end of final extraction by the soil's size fractions when the release of K nearly ceased was considered as mainly coming from biotite (Pal et al. 2006b) (Fig. 8.1). The amount of clay biotite, silt biotite and sand biotite in the representative Vertisols of central India ranged from 1.0 to 1.6, 0.2 to 0.3 and 0.2 to 0.4%, respectively, constituting 7–19, 2–3 and 2–5% of the total mica in the respective size fractions. In the <2 mm fine earth fraction, the biotite quantity does not exceed 1%, which constitutes approximately 6–8% of the total mica. For any size fraction, the cumulative amount of K released on a biotite weight basis follows the order: cumulative amount of K released on the entire mica weight basis > cumulative amount of K released on the

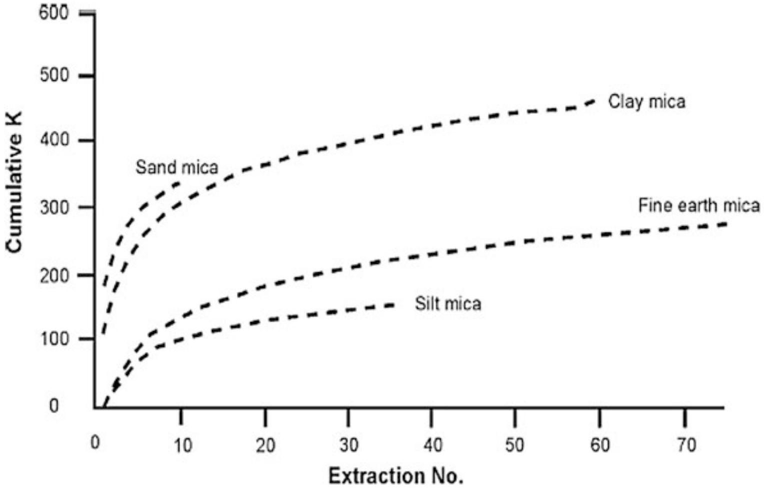

Fig. 8.1 Relationship between numbers of extractions and cumulative K release (mg/100 g^{-1} mica) of micas in various size fractions of a Vertisol (Adapted from Pal et al. 2006b)

weight basis of the size fraction (Table 8.2). The significant positive correlation between the cumulative K release of soils and their size fractions is mainly from biotite and is established from the statistical analysis of bivariate data sets of several parameters that directly or indirectly influence K release. The significant positive correlations between cumulative K release from sand, silt and clay and their corresponding total K contents, respectively (Table 8.3), indicate that the K release is a function of total K content in micas and feldspars. However, the positive correlations between total K contents in sand, silt, clay and soil and their mica contents

Table 8.2 Cumulative K release from a representative Vertisol and its size fractions

Horizon	Depth (cm)	Fine earth (<2 mm) cumulative K release in 75 extractions			Sand (2–0.05 mm) cumulative K release in 10 extractions			Silt (0.05–0.002 mm) cumulative K release in 35 extractions			Clay (<0.002 mm) cumulative K release in 60 extractions		
		SF[a]	MB	BB	SF	MB	BB	SF	MB	BB	SF	MB	BB
		mg K 100 g^{-1}											
Ap	0–15	69	429	6059	20	272	7000	16	191	7004	114	561	6990
Bw1	15–41	41	277	4230	12	162	7006	15	195	7009	92	509	6998
Bw2	41–70	39	267	4097	23	297	6997	13	184	7011	88	502	6999
Bss1	70–95	45	261	4638	15	191	6986	14	161	6990	91	433	7000
Bss2	95–135	49	286	4793	24	334	6991	15	162	6991	92	462	6999
Bss3	135–155	37	235	3849	13	147	6907	16	184	7008	94	471	6984

Adapted from Pal et al. (2006b)

[a] *SF* On the basis of size fraction; *MB* On the basis of mica content; *BB* On the basis of biotite content

(Table 8.3) indicate the predominant influence of mica to supply K to the plants grown in Vertisols. Furthermore, significant positive correlations between the cumulative K release of sand, silt, clay and soil and their respective mica contents (Table 8.3) indicate that the K release from either the soils or different size fractions are controlled mainly by mica. However, better correlations than those between the cumulative K release of sand, silt, clay and soil and their biotite contents (Table 8.3) provide incontrovertible evidence that the K release in soils is primarily controlled by biotite mica. This further supports the earlier observations on the inertness of muscovite mica in the release of K in the presence of biotite (Pal et al. 2001). The released amount of K from sand-, silt- and clay-sized biotite (Table 8.3) is in contrast to the relationships observed between cumulative K release and particles of specimen biotite by earlier researchers (Pal 1985; Pal et al. 2001). This indicates that large-sized biotite particles have a lower K selectivity than finer particles. Comparable cumulative amounts of K released from sand and silt biotite (Table 8.3) indicate that not only the sand-sized but also some portion of silt-sized biotite of the Vertisols have a greater number of elementary layers along with little weathered biotite. It is observed that during the formation of Vertisols since the Holocene (Pal et al. 2009), there has been no substantial weathering of biotite under the SAT environments. This validates the earlier hypothesis (Srivastava et al. 2002) that the formation of Vertisols reflects a positive entropy change due to a lack of any substantial weathering of primary minerals. The relevance of the almost-unaltered biotites (please refer to Fig. 2.2b) is that both sand and silt biotites have highly favourable K release potential, which is reflected in the medium to highly available K status of the Vertisols of India. Agronomic experiments on the Vertisols of central India have indicated crop response to K fertilizers after two

Table 8.3 Co-efficient of correlation among various soil characteristics

Parameter		r
Cumulative K of sand	Total K in sand	0.635**
Cumulative K of silt	Total K in silt	0.771**
Cumulative K of clay	Total K in clay	0.822**
Total K in sand	Sand mica	0.933**
Total K in silt	Silt mica	0.766**
Total K in clay	Clay mica	0.981**
Total K in soil	Soil mica	0.979**
Cumulative K of sand	Sand mica	0.524*
Cumulative K of silt	Silt mica	0.694**
Cumulative K of clay	Clay mica	0.851**
Cumulative K of soil	Soil mica	0.429*
Cumulative K of sand mica	Sand biotite	0.894**
Cumulative K of silt mica	Silt biotite	0.917**
Cumulative K of clay mica	Clay biotite	0.978**
Cumulative K of soil mica	Soil biotite	0.435*

Adapted from Pal et al. (2006b)
*Significant at 0.05 level; **Significant at 0.01 level

years of cropping with hybrid cotton (Pal and Durge 1987). Therefore, the present available K status may not be sustainable over a longer term because the contents of sand and silt biotites are low. This information helps dispel the myth that the Vertisols are rich in available K and that they may not warrant the application of K fertilizers.

Potassium adsorption/fixation in Vertisols does not appear to be sufficiently severe to conclude that K becomes completely unavailable to plants. The study by Pal and Durge (1987) on K adsorption by the Vertisols of Peninsular India indicates that fine clay smectites adsorbed 50–60% of added K, amounting 25–30 mg K/100 g clay. This apparently suggests that the fine clay smectites of Indian Vertisols are close to beidellite (Bajwa 1980). Through a series of diagnostic methods to characterize the fine clay smectites, Pal and Deshpande (1987) confirmed that they are nearer to the montmorillonite of the montmorillonite–nontronite series. Because smectites can have no K selectivity (Brindley 1966), further characterization of fine clay smectites (Pal and Durge 1987) indicated the presence of vermiculites, which are generally not detected on the glycolation of Ca-saturated samples but can be detected by a progressive reinforcement of the 1.0 nm peak of mica while heating the K saturated samples from 25 to 550 °C (please refer to Fig. 2.7). The content of vermiculite was quantified following the method of Alexiades and Jackson (1965) by Pal and Durge (1987), and the vermiculite content ranged from 5 to 9% in the fine clay of Vertisols. Pal and Durge (1987) concluded that the observed K adsorption by the silt and clay fractions is due to the presence of vermiculite and not to smectite. The smectites of Vertisol clays belong to the low-charge dioctahedral type, and thus, they expand beyond 1.0–1.4 nm with the glycolation of K-saturation and heating the samples at 300 °C (please refer to Fig. 2.7). These smectites, when treated according to the alkylammonium method (Lagaly 1994), showed the presence of both monolayer to bilayer and bilayer to pseudotrilayer transitions. The layer charge of the half-unit cell of smectite ranges from 0.28 to 0.78 mol(−)/$(SiAl)_4O_{10}(OH)_2$, and the low-charge smectite constitutes >70% in them (Ray et al. 2003). The position of the higher charge with 0.78 units or lower appears to be due to the presence of small amounts of vermiculite as determined quantitatively by Pal and Durge (1987). The limited leaching in Vertisols and small amount of vermiculite would lessen the rate of added K-fertilizers when required. If K fertilizers are added as a basal dose, the K^+ ions would be fixed in the interlayer of vermiculite, which would make the NH_4 ions from N fertilizers more labile for ready assimilation by growing plants if not added as a basal dose.

Vertisols developed on the zeolitic Deccan basalt or in its alluvium, are also adequately supplied with K as evident from their high to very high available K status even in the subsurface (Table 8.4). Potassium release in soils is primarily controlled by biotite mica, which constitutes only about 1% in the <2 mm fine earth fraction in Vertisols. The apparent incompatibility between medium to high

Table 8.4 Selected soil properties of zeolitic Chromic/Sodic Haplusterts cultivated to rice crops

Depth (cm)	pH (1:2)	ECe (dS m^{-1})	$CaCO_3$ (<2 mm) (%)	Organic carbon (%)	ESP	sHC[a] (mm h^{-1})	Base saturation (%)	Available K (kg ha^{-1})
Sakka soils—Chromic Haplusterts								
0–15	5.2	0.26	1.6	0.73	0.9	18	93	429
15–34	5.3	0.16	1.7	0.54	0.9	36	109	343
34–59	5.3	0.26	1.9	0.40	0.9	35	106	343
59–93	5.4	0.10	2.0	0.38	1.1	10	93	343
93–141	7.3	0.12	4.1	0.39	1.2	15	115	429
141–155	7.9	0.21	10.0	0.22	0.8	16	107	343
Teligi soils—Sodic Haplusterts								
0–10	7.9	0.4	10.5	1.55	1.5	62	103	515
10–25	8.0	0.3	10.7	0.81	1.7	27	113	343
25–44	8.0	0.4	12.2	0.76	1.8	29	109	343
44–69	7.8	0.4	10.3	0.73	4.0	21	117	257
69–97	7.6	0.3	5.9	0.69	3.4	11	108	515
97–123	8.6	0.4	15.1	0.50	16.8	3	110	257

Adapted from Pal et al. (2003); [a]23 mm h^{-1} is the weighted mean sHC in 0–100 cm depth of Sakka soils and 24 mm h^{-1} is the weighted mean sHC in 0–100 cm depth of Teligi soils

ECe Electrical conductivity of the saturation extract; *ESP* exchangeable sodium percentage; *sHC* saturated hydraulic conductivity

available K status in surface horizons (250 kg K ha^{-1}; Table 8.4) and low biotite mica in soils of the Deccan basalt areas, need further insight in view of pronounced selectivity of zeolites for K^+ and NH_4^+ ions. Contribution of zeolites to available K of soils is not uncommon (Brown et al. 1969; Talibudeen and Weir 1972).

Potassium adsorption/fixation in Vertisols has been attributed to the presence of vermiculite only (Pal et al. 2012b). 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.

8.2.4.2 RF Soils

Potassium (K) is also one of the limiting nutrient elements in RF soils of India, especially in the HT climate areas (Pal et al. 2001). In micaceous soils of HT climate in NEH areas, crops respond to added K up to 80 kg K ha^{-1} (Datta 2013) because the soils are rich in sand size muscovite mica (Fig. 8.2a). K release from muscovite is inhibited in the presence of biotite (Pal et al. 2001). The X-ray intensity ratio of peak heights of 001 and 002 basal reflections of mica in the silt

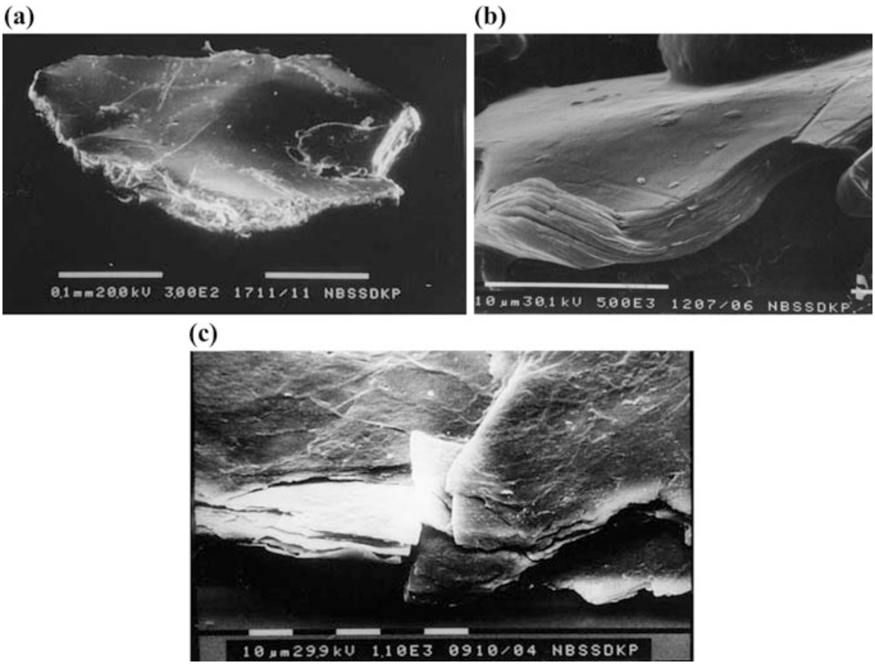

Fig. 8.2 Representative SEM photographs of unaltered muscovites in acidic Inceptisols (**a**), Dahotia soils, Assam of HT climate, and almost unaltered biotites with minor layer separation and bending of edges in SAT Alfisols (**b**), Patancheru, Andhra Pradesh and (**c**), Dyavapatna, Karnataka (Adapted from Pal et al. 2000a, 2001)

fraction of acidic Alfisols (Chandran et al. 2004), Ultisols (Chandran et al. 2005) and acidic Inceptisols (Pal et al. 1987) is greater than unity; and that of the clay fraction is close to unity (Table 8.5), indicating that silt fractions contain both muscovite and biotite, and the clay fraction is more muscovitic in character (Pal et al. 2001). The inertness of muscovite in releasing K makes K a limiting nutrient in RF soils of HT climate.

In a repeated batch type experiment with Ba–K exchange, K release from these soils (Dahotia soils of Assam in NEH, Pal and Durge 1989) was reduced to almost nil after a few extractions, indicating rather slow release of K from muscovite. Such highly weathered soils fix relatively high amount of added K (Fox 1982; Pal and Durge 1989) because of the presence of vermiculite in their silt (20–6 μm, and 6–2 μm) and coarse clay (2–0.6 μm) fractions, and low charge vermiculite in their medium (0.6–0.2 μm) and fine clay (<0.2 μm) fractions (Pal and Durge 1989). The fine clay of Dahotia soils fixes the most amount of the added K (Fig. 8.3.).

The predominance of kaolinite followed by illite is generally believed to be reason for the low nutrient holding capacity of RF soils (Alfisols) of the southern Peninsular India under SAT environment; and therefore application of balanced fertilizer including K is generally recommended. It is interesting to note that in

Table 8.5 X-ray intensity ratio of the peak heights of 001/002 basal reflection in the silt and clay fractions

Benchmark soil/soil series	Parent material	Size fractions	
		50–2 μm	<2 μm
Dahotia (Assam-HT climate) (Typic Haplaquept)	Alluvium	1.47	1.10
Akahugaon (Assam-HT climate) (Typic Haplaquept)	Alluvium	1.70	1.04
Patancheru (RF soil-SAT) (Udic Rhodustalf)	Granite-Gneiss	1.77	1.80
Nalgonda (RF soil-SAT) (Udic Rhodustalf)	Granite-Gneiss	2.00	1.87
Dyavapatna (RF soil-SAT) (Udic Rhodustalf)	Granite-Gneiss	2.25	2.16

Adapted from Pal et al. (2012a)

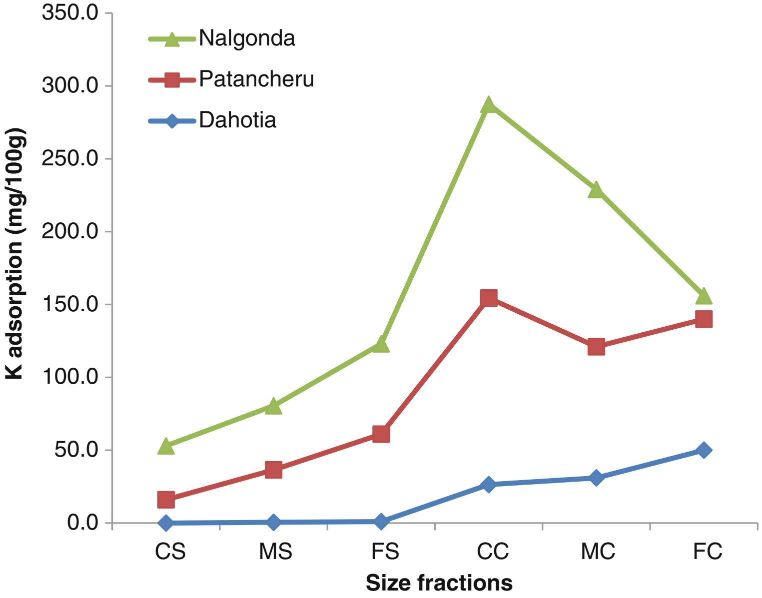

Fig. 8.3 Potassium adsorption by various size fractions of RF Alfisols of the SAT regions (Patancheru and Nalgonda, Andhra Pradesh, India) and acidic Inceptisols (Dahotia of the HT region in Assam, India). *CS* coarse silt (50–20 μm), *MS* medium silt (20–6 μm), *FS* fine silt (6–2 μm), *CC* coarse clay (2–0.6 μm), *MC* medium clay (0.6–0.2 μm), *FC* fine clay (<0.2 μm) (Adapted from Pal et al. 1993 and Pal and Durge 1989)

many of these soils crops do not respond to K fertilizer application (Pal et al. 2014). The X-ray intensity ratio of peak heights of 001 and 002 basal reflections of mica in the silt and clay fractions of many SAT Alfisols is near 2 (Patancheru, Nalgonda and Dyavapatna soils, Table 8.5), suggesting that these soils contain sufficient biotite.

The RF Alfisols of the SAT are relict paleosols but polygenetic in nature. Due to climate change from tropical humid to semi-arid during the Plio-Pleistocene transition period, the upper layers of the soils of the preceding tropical humid climate were truncated by multiple arid erosional cycles, which exposed the relatively less weathered lower layers wherein considerable amount of unaltered biotite particles remained in the sand and silt fractions (Fig. 8.2b, c) (Pal et al. 1989, 1993). Many of the proposed relationships between K release and mica particle size hitherto obtained either with soil or specimen minerals are, therefore, not valid in these polygenetic soils (Pal et al. 1993).

The cumulative K release from different size fractions of two benchmark RF soils (Alfisols) of SAT namely Patancheru and Nalgonda of southern India, showed a fairly high rate of K release (Pal et al. 1993) but the observed data indicated a contrasting particle size-K release relationship between silts and clays. K release increased with the fineness of clay size mica while it decreased with the fineness of silt size mica (Fig. 8.4). The zones in clay micas are at different stages of expansion unlike those of the silt mica, and under such circumstances K release would occur mainly by edge weathering as is evident from increased K release with the decrease in clay mica particle (Pal and Durge 1989).

K release increased with the increase in particle size of silt sized mica, which are almost unweathered sand and silt biotites (Fig. 8.2b, c). This particular K release trend is normally obtained with specimen micas (Pal 1985). Thus, quite favourable K release rate from both silt and clay micas explains as to why crop response to fertilizer K is seldom obtained in many of RF Alfisols under SAT environments.

It is often reported that micas, hydrous micas and vermiculites have high adsorption/fixation properties. But mica indeed does not expand on being saturated with divalent cations and unlikely adsorbs added K (Sarma 1976). In such reactions interlayer charge density of the mineral is of fundamental importance. Kaolinites are of no significance in such a reaction, while vermiculites are converted to mica by layer contraction by K. Smectites would not possess this property as their layer charge is too low and they do not adsorb K selectively (Rich 1968b) unless the charge density is high like in high charge smectite or low charge vermiculite (Pal and Durge 1989).

Due to impoverishment of vermiculite, the observed K adsorption by silt and clay fractions of benchmark RF Alfisols of Patancheru and Nalgonda series (Fig. 8.3) may be attributed to smectite content because it increases with the decrease in soil size fractions (Pal et al. 1993). However, perusal of the K adsorption data (Fig. 8.3) indicates an incompatibility between the amount of clay smectite and the extent of K adsorption by clay fractions. Despite sufficient amount of smectite, the finer fractions of clay particularly the fine clay fractions (<0.2 μm) does not adsorb K proportionately. Soil clays contain both low and high charge smectites and their co-existence is, however, related to their respective genesis in paleoclimatic environments (Pal et al. 1989). Pal et al. (1989) demonstrated that considerable amount of well crystallized clay size low charge dioctahedral smectite

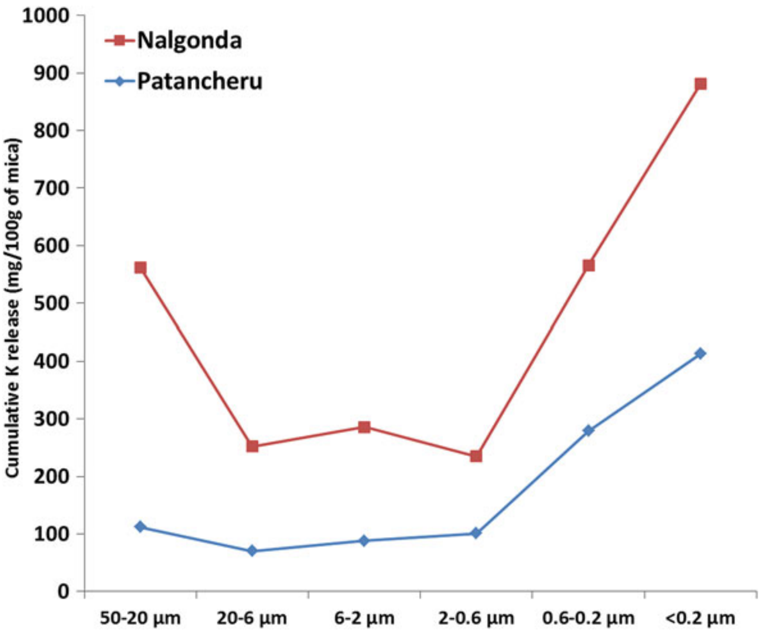

Fig. 8.4 Potassium release from various size fractions of RF Alfisols (Patancheru and Nalgonda) of southern India *CS* coarse silt (50–20 µm), *MS* medium silt (20–6 µm), *FS* fine silt (6–2 µm), *CC* coarse clay (2–0.6 µm), *MC* medium clay (0.6–0.2 µm), *FC* fine clay (<0.2 µm) (Adapted from Pal et al. 1993)

was the first weathering product of granite-gneiss that survived transformation to kaolinite in a Pre-Pliocene tropical humid climate and is preserved to the present along with kaolinite, which does not participate in K adsorption.

The biotite which somehow survived HT climate weathering, altered to trioctahedral smectite in the silt and coarse clay fractions under the semi-arid climate of the Plio-Pleistocene transition period. The results on the selective K adsorption by trioctahedral smectite and not by dioctahedral smectite are in accord with those reported earlier with high and low charge smectites respectively (Pal and Durge 1987, 1989). SAT Alfisols are generally rich in clay, especially fine clays and therefore, it is envisaged that these soils may have less K adsorption/fixation problem (Pal et al. 2000a).

8.2.4.3 IGP Soils

Alluvial soils, one of the major soil groups in India, are important with respect to agricultural potential. These soils contain a good amount of sand and silt size micas, especially biotites (please refer to Fig. 4.7). These micaceous soils are rich in available K, and the K applied to many benchmark soils undergoes fixation, indicating the presence of 2:1 minerals capable of fixation of added K. Crops in benchmark soils of semi-arid climate seldom respond to K-fertilizer even under continuous cropping over long periods of time (Pal and Mondal 1980). But, in soils of per humid climate crops respond to K-fertilizers (Roy et al. 1978) even though soils contain a considerable amount of muscovite with subordinate amount of biotite (Pal et al. 1987).

Much of the investigative work on potassium and mineralogy is related to specimen minerals and therefore, many of the proposed relationships are speculative (Rich 1972; Sarrna 1984). In order to gather precise information on the K release and adsorption reactions of the IGP benchmark soils in relation to the specific nature of soil minerals Pal and Durge (1989) made an extensive study.

Following the repeated batch type for Ba-K exchange, Pal and Durge (1989) reported the K release from soil mica increased with a decrease in soils' particle size, and the rate of K release was dependent upon the nature of soil mica, biotite mica in particular (Pal et al. 2001). The much reduced rate of K release with higher number of extractions was due to more of muscovite character of soil mica, suggesting that muscovite was a rather useless source of K reserve. The observed negative correlation between K release and particle size, a trend opposite to that of specimen minerals (Reichenbach 1972; Pal 1985), is explained on the basis of edge weathering of soil mica. Zones in soil micas are expected to contain layer minerals in different stages of expansion and this fact is evidenced by the observed interstratification of mica and expanded layers found upon X-ray examination of silt and clay fractions of soils (Pal and Durge 1989). Under such circumstances K release occurs mainly by edge weathering of soil mica as evident from the higher K release with the decrease in particle size (Fannings and Keramidas 1977). The slower release by coarser, as opposed to finer mica particles, by edge weathering could be best explained as suggested by Reed and Scot (1962). These authors explained this phenomenon in terms of (i) the smaller peripheral surface with larger particles, per unit weight of material, across which K ions may diffuse, and (ii) the greater distance that K ions must diffuse, with larger particles, for a given fraction of K removed.

Vermiculite as defined by Alexiades and Jackson (1965) is responsible for the adsorption of K. The observed selective adsorption of K by smectite (Pal and Durge 1989), is a fact in contrast to the behaviour of specimen mineral (Rich 1968a, b) and soil clay smectite of dioctahedral nature (Pal and Durge 1987). The higher correlation coefficient at 1% level of significance ($r = 0.899$) between the K adsorption value (mg/100 g) and the vermiculite plus smectite content (g/100 g) of the silt and the clay fractions, as compared to only the vermiculite content ($r = 0.725$) does suggest that clay smectites also adsorbed K selectively. The smectite, as defined according to Alexiades and Jackson (1965), expanded to 17 Å peak on glycolation but contracted readily to 1.0 nm on K-saturation at 110 °C indicating its high layer charge density and thus demonstrates the critical role of layer charge density in the adsorption of K by clay smectites of the many IGP soils developed in the micaceous alluvium of Himalayan origin. Research results obtained on the nature of mica and smectite and their fundamental relation to K release and fixation have important implications in K management of the vertic and non-vertic IGP soils (Pal et al. 2010).

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