

**IMPACT OF MINERALOGY ON POTASSIUM DYNAMICS AND
RETENTION BEHAVIOR IN BANGLADESH SOILS USED IN RICE
CROPPING SYSTEMS**

A Thesis

by

SUMITRA BOSE BISWAS

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

May 2008

Major Subject: Soil Science

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Approved by:

Co-Chairs of Committee,	Charles T. Hallmark
	Frank M. Hons
Committee Members,	Bruce Herbert
	Richard H. Loeppert
Head of Department,	David D. Baltensperger

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ABSTRACT

Impact of Mineralogy on Potassium Dynamics and Retention Behavior in Bangladesh

Soils Used in Rice Cropping Systems. (May 2008)

Sumitra Bose Biswas, B.S., National University, Bangladesh

Co-Chairs of Advisory Committee: Dr. Charles T. Hallmark
Dr. Frank M. Hons

The combination of rising population and increasing food demand has placed tremendous pressure on the soil resource in Bangladesh, especially floodplain soils where rice may be grown year round. Although these floodplain soils contain minerals high in potassium (K) such as micas, K deficiency in rice paddy soils is increasing throughout Bangladesh. Harvesting of straw from fields exacerbates the removal of nutrients including K, and intensive cropping with unbalanced fertilizer has resulted in depletion of “readily available” K in large areas.

Five representative floodplain soils in rice production were sampled by horizon to determine physical, chemical and mineralogical properties, assess soil K, investigate plant available K, and understand impacts of redox on K fixation and release.

Total and nonexchangeable K were determined using concentrated hydrogen fluoride (HF) digestion and 1.0 M HNO₃ digestion, respectively, along with NH₄OAc-extractable K. Cation exchange capacity under both oxidized and reduced conditions was determined. Assessment of adsorption and release of K as a function of redox was

done in conjunction with seven different concentrations of potassium chloride (KCl) solution and three different soils.

Significant amounts of K were present in all fractions of silts and clays. Potassium concentration was greatest in the coarse clay fraction. High HNO_3 -extractable K suggested that much of the K in soils was from mica interlayers. Acidic soils contained less K in all fractions than the less weathered, calcareous soils. The clay fractions exhibited mostly mica, vermiculite, smectite and kaolinite. The cation exchange capacity (CEC) of reduced soils was less under oxidized condition, due to collapse of the interlayer in response to increased layer charge upon structural Fe reduction.

The adsorption of K was greater for calcareous soils under both oxidized and reduced conditions than for the acidic soils. Less native K was extracted under oxidized conditions than under reduced conditions. Less adsorption under reduced conditions may be due to an increase in solution Fe^{2+} which can compete with K^+ for exchange sites on clays.

DEDICATION

To my husband (Bhajan), who gave unconditional support and love.

To my two precious children, Saptarshi (Beau) and Soumyajit.

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CHAPTER I

INTRODUCTION

Potassium (K) plays an important role in rice production in the Indo-Gangetic Plain (IGP) of South Asia. This macronutrient is extracted in large quantities by intensive cropping systems (Panaullah et al., 2006). Rice production often removes large quantities of K from soil, resulting in soils with a negative K balance even after the application of recommended fertilizers (Bijay-Singh et al., 2004). The average ratio of nitrogen (N)-phosphorus (P) - potassium (K) in fertilizer that is used in Bangladesh is 1:0.5:0.11 (BARC, 1998) and this ratio supplies less K than that required by modern rice cultivars which is 1:0.26:0.33 (100 kg N, 26 kg P, 33 kg K ha⁻¹). Inadequate and unbalanced fertilizer application may be one reason for declining K nutrition in rice fields that results in lower rice yield (Panaullah et al., 2006).

Soil K exists in soil solution, and in exchangeable and non-exchangeable (fixed and structural) forms. The amount of solution and exchangeable potassium is usually a small fraction of total K (1–2% and 1–10%, respectively). The bulk of soil K usually is associated with K-bearing micas and feldspars (Sekhon, 1995).

Most soils in the IGP, including those in Bangladesh, are usually regarded as high in K due to high rainfall, irrigation water and release from K-rich clay minerals (Dobermann et al., 1996a, 1996b, 1999). Potassium removal is large in intensive rice production due to the removal of straw along with grain from rice fields for easier tillage (Timsina and Connor, 2001). Also, harvested straw is used as fuel, animal feed and thatching (Panaullah et al., 2006).

Recent soil tests showed that the available K concentrations of soils from the IGP are below 0.1 cmol/kg soil, indicating they are becoming K-deficient even though regarded as high in K content (Dobermann et al., 1999, Regmi et al., 2002; Srivastava et al., 2002; Bijay-Singh et al., 2003). As limited research results are available on the uptake and balance of K for rice systems in Bangladesh, the objectives of this study were to: 1) determine physical, chemical and mineralogical properties of five floodplain soils of Bangladesh, 2) assess different types of K (total K, plant available K, nonexchangeable K) in these soils, and 3) determine the influence of redox on K adsorption and release.

CHAPTER II

LITERATURE REVIEW

Potassium is the seventh most common element in the Earth's crust and is essential for plant growth. Potassium, along with N and P, are the three major macronutrients contributing to many functions in plants. The essentiality of this macronutrient was known after Von Liebig's published work in 1840 (Sparks, 2000). The range of total K content in the upper 0.2 m of the soil profile usually ranges between 3000 and 100,000 kg ha⁻¹. Ninety-eight percent of the total K is normally bound in mineral form and only 2% is regarded to be in soil solution and exchangeable phases (Schroeder, 1979; Bertsch and Thomas, 1985).

Potassium is the largest cation in nonhydrated form (0.133 nm), and has a higher number of oxygen atoms (8-12) surrounding it in the mineral structure, suggesting that the K-O bond is relatively weak (Sparks and Huang, 1985). Potassium has higher polarizability (0.088 nm³) than Ca²⁺, Li⁺, Mg²⁺, and Na⁺ but lower than for Ba²⁺, Cs⁺, NH₄⁺, and Rb⁺ ions (Rich, 1968, 1972; Sparks and Huang, 1985). Ions having higher polarizability are preferred in ion exchange reactions (Sparks, 2001).

FORMS OF SOIL K

There are four forms of K in soil: solution K, exchangeable K, fixed or nonexchangeable K, and structural or mineral K. The bulk portion of total soil K is in the mineral fraction, and exchangeable and nonexchangeable levels of K are regarded as a small portion of the total (Sparks and Huang, 1985). The most important aspect of K

transformations in soils under rice cropping systems is the rate at which the non-exchangeable portion is released to exchangeable and soluble forms. Kinetic and equilibrium reactions between the four forms of soil K affect the level of K in soil solution and readily available forms for plant uptake at any particular time (Fig. 1). The four forms of K in the order of their availability to microbes and plants are solution > exchangeable > fixed > mineral K (Sparks and Huang, 1985; Sparks, 1987; Sparks, 2000).

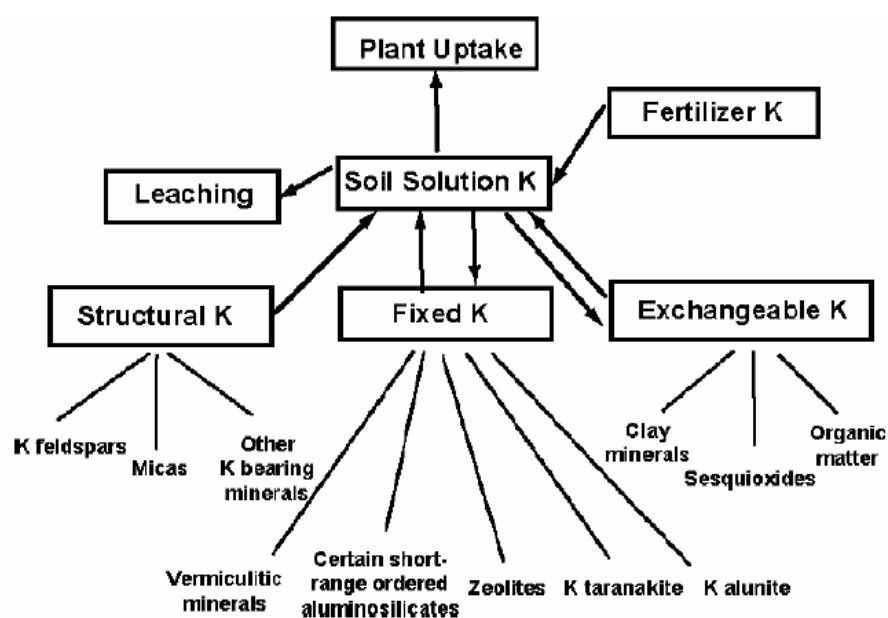


Fig. 1. Interrelationships of various forms of soil K (from Sparks and Huang, 1985).

Soil Solution K

Soil solution K is the form readily available for microbial and plant uptake. The levels of soil solution K generally are low unless a recent application of a K-fertilizer has been made. Thus, continuous renewal of K in the soil solution for adequate nutrition of

high yielding varieties of rice and wheat is obvious. The content of K in soil solution is in the range of 2 to 5 mg K L⁻¹ for agricultural soils of humid regions, and is an order of magnitude higher in arid region soils (Haby et al., 1990). Solution K levels are affected by equilibrium and kinetic reactions that occur between the forms of soil K, soil moisture content, concentration of bivalent cations in solution, and the exchanger phase (Sparks and Huang, 1985; Sparks, 2000). Potassium concentration in soil solution also depends on the degree of replenishment of K in solution from nonexchangeable sites. Factors that decrease the K concentration of soil solution influence the release of K from the nonexchangeable K reserve (Hay et al., 1976). Buffering capacity of clay minerals also affects the concentration of K in soil solution. Well-buffered clay minerals containing mica and vermiculite maintain higher levels of K in the soil solution than weakly-buffered allophanic soils (Parfitt, 1992).

Exchangeable K

The exchangeable form of K is readily available to plants, exchangeable with other cations, and electrostatically bound as an outer-sphere complex to the surface of clay minerals and humic substances. Exchangeable K is held by different bond strengths at different adsorption sites on clay minerals. These adsorption sites can be planer or edge positions of clay minerals or the negative charges created by carboxylic and phenolic groups of humus colloids compared to pH-dependent negative charges on clay (Kirkman et al., 1994). The number of exchange sites derived from isomorphic substitution is constant, but the negative charge on humic and amorphous clay colloids increases with increasing pH due to the dissociation of H⁺ from weak acid groups (Gast,

1977). Both kinetic and thermodynamic factors affect the amount of K^+ held by clay minerals at exchange sites (Parfitt, 1992). Other factors that affect the K^+ concentration on exchange sites are affinity of exchange sites for K^+ in relation to the nature of the soil surface and concentration of K^+ compared to the concentration of other cations especially bivalent cations, on exchange sites of clay minerals (Barber, 1984).

Nonexchangeable K

Potassium in nonexchangeable form is not fixed in the mineral crystal, but is held between adjacent tetrahedral layers of dioctahedral and trioctahedral micas, vermiculites, and intergrade clay minerals such as chloritized vermiculite (Rich, 1972; Sparks and Huang, 1985; Sparks, 1987). This K is not readily accessible for exchange with other exchangeable cations. According to Goulding (1987), there are several adsorption sites for K^+ on clay minerals (Fig. 2). Adsorption sites for K^+ on planar surfaces (p-site) have low K^+ selectivity, those on wedge (w-site) and edge positions (e-site) have medium K^+ selectivity, and sites at the interlayer (i-site) and crack positions (c-site) have high K^+ selectivity. Potassium in wedge, edge, cracks and step positions is regarded as fixed potassium. Such positions are between the crystal layers of mica, integrated mica-like illite, and vermiculite.

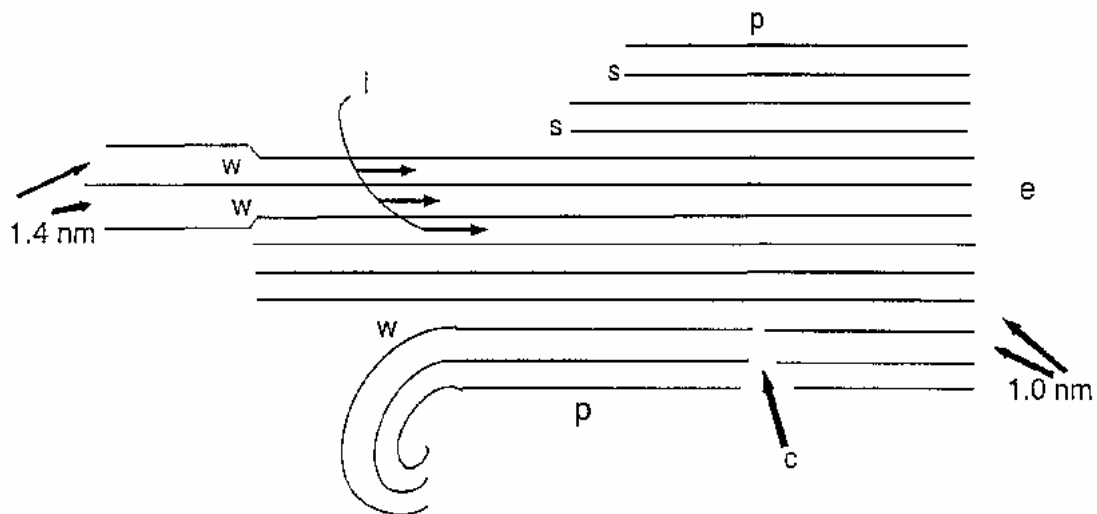


Fig. 2. Model of 2:1 layer silicate with planar (p), edge (e), interlayer (i), wedge (w), crack (c), and step (s) potassium exchange sites (Goulding 1987).

The amount of fixed K in soils depends on the quantity and type of clay, particle size distribution and addition and removal of K from minerals (Kirkman et al., 1994). Nonexchangeable K is sparingly available to plants (Mengel, 1985; Sparks and Huang, 1985; Sparks, 1987). Soils having K^+ -depleted interlayer sites adsorb added K more strongly (Metson, 1960). Potassium uptake by plants and microbes, or leaching of K^+ from soils results in release of fixed K^+ into soil solution. Mineral and fixed K are regarded as the major reservoirs of soil K, but both forms are nonexchangeable, and differ in K. Release of fixed K is reversible, whereas the release of mineral K is irreversible (Kirkman et al., 1994). The release of nonexchangeable K replenishes the exchangeable K pool when the latter pool is diminished due to leaching and crop removal (Sparks et al., 1980). According to Metson (1960), degree of weathering has a greater influence on the release of K from the nonexchangeable pool than the age of

soils. During illite formation, the maximum release of fixed K occurs (Metson, 1960). The intensity of weathering of primary and secondary clay minerals governs the amount of mineral and fixed K, whereas exchangeable K mostly depends on the type of clay mineral and its negative charge. As an example, exchangeable K is higher in mica- and vermiculite-rich soils than in allophanic soils (Parfitt, 1992). Weathering of mica results in decreased particle size, increased surface area and increased negative charge of soils. This is why soils having smectitic minerals contribute to greater exchangeable K than soils having interstratified micaceous minerals, even though the latter minerals are regarded as a large reservoir of nonexchangeable K (Kirkman et al., 1994).

Mineral K

Mineral, or structural K is also known as native, matrix, unweathered or inert K (Metson, 1980). The bulk of total soil K is in mineral forms as K-bearing primary minerals like muscovite, biotite and feldspar. The amount of K in minerals depends on the type of parent materials and the age of soil (Sparks and Huang, 1985). Structural K is regarded as covalently bonded within the crystal structure of various K-bearing minerals like feldspars, micas and volcanic glasses (Metson, 1968). These minerals are concentrated in the coarser fractions of soils (Metson, 1980), and the alteration of these minerals is limited in the coarser fraction of clay during soil development (Metson, 1980). Decreased particle size favors alteration of minerals. Secondary layer silicates derived from the weathering of minerals can retain some of the structural K (Kirkman et al., 1994). Weathering of primary minerals containing higher K content must take place before a significant amount of K becomes available for plant uptake. The degree of

weathering however depends on the environment and composition and structure of primary minerals (Fieldes and Swindale, 1954). The order of plant available K from common K-bearing minerals is biotite > muscovite > orthoclase and microcline (Huang et al., 1968; Sparks, 1987). Mineral K is regarded as slowly available to plants and depends on the degree of weathering (Sparks and Huang, 1985; Sparks 1987).

FACTORS AFFECTING POTASSIUM AVAILABILITY

Dynamics of Solution and Exchangeable K

The rate of reaction between soil solution and exchangeable K phases depends largely on the type of clay minerals present (Sparks, 2001), and the method used to measure the kinetics of K exchange (Sparks, 1989, 1995; Amacher, 1991; Sparks et al., 1996). Kaolinite, hydrous mica, montmorillonite (smectite), and vermiculite vary significantly in selectivity for ions, ion binding affinity, and the type of ion exchange reaction. Fundamental differences in these clay minerals mentioned above result in different kinetics of K exchange (Sparks, 2001).

The kinetics of K exchange on kaolinite and montmorillonite are more rapid than with vermiculitic and micaceous minerals, where exchange is extremely slow. Adjacent tetrahedral layers in kaolinitic clays are held by H bonds and, therefore, the only available sites for ion exchange are on edge and planer surfaces. However, instead of having H bonds within the inner peripheral space, montmorillonite can swell with adequate hydration, allowing the exchange of ions into the interlayer space (Sparks, 2001). Vermiculitic and micaceous minerals are 2:1 phyllosilicates with peripheral spaces that hinder many ion exchange reactions (Sparks, 2001). Micaceous minerals

have more restrictive interlayer spaces than vermiculite because the interlayer spaces of micaceous minerals show selective affinity for certain cations such as K^+ and Cs^+ (Sparks, 2001). Bolt et al. (1963) recognized three types of binding sites for K exchange in hydrous mica and hypothesized that the rapid kinetics are associated with external planar sites, slower kinetics are due to edge sites, and the slowest kinetics are reactions at internal exchange sites.

Retention of K

Retention behavior and dynamics of K play significant roles in soil fertility. Many studies have inferred that a complex interaction of major and minor minerals in soil control the fixation and release of applied and native K, in turn influencing the availability of K to plants. Clay mineralogy of agriculturally important soils is usually very diverse with respect to types of mineral species, their relative properties and degrees of crystallinity, etc. Therefore, K fixation and release studies should give due emphasis to the complex clay mineralogy of soils. It has also been reported that the change in surface charge that occurs during Fe reduction increases the ability of minerals to fix interlayer cations, including Na^+ (Lear and Stucki, 1989), Ca^{++} , Cu^{++} , and Zn^{++} (Khaled and Stucki, 1991).

Many factors affect K^+ fixation in clay minerals and soils, such as the type and quantity of clay minerals, the charge density of clays and their capacity for interlayering, soil moisture content, concentration of K^+ along with the concentrations of other competing cations, and pH of the soil solution (Rich, 1968; Sparks and Huang, 1985).

Weathered mica, vermiculite, and montmorillonite are common minerals that fix K^+ . Dioctahedral vermiculite is the major mineral that fixes K^+ in acid soils. Weathered micas fix K^+ under both dry and moist conditions, while montmorillonite generally fixes K^+ only under dry condition (Rich, 1968). Layer silicates with high charge density fix more K^+ than those with lower charge density (Walker, 1957).

Introduction of hydroxy Al^{3+} and Fe^{3+} interlayer groups into layer silicates can decrease K fixation (Rich and Obenshain, 1955). Volk (1934) noted a marked increase in K fixation in soil with a pH increased to about 9 or 10 by adding Na_2CO_3 .

There was no fixation of K^+ at pH around 2.5, but fixation increased rapidly between pH 2.5 to 5.5. The rate of K^+ fixed was slower above pH 5.5 (Martin et al., 1946). Cations such as Al^{3+} precipitate as hydroxy polycations as pH increases above 5.5. The formation of hydroxyl polycations with increasing pH increases the number of OH groups and the formation of gibbsite-like structures (Thomas, 1960). The charge on clay cannot be neutralized by Al^{3+} at pH around 8.0, and K fixation cannot be prevented. Trivalent Al and $Al(OH)_x$ are dominant species at pH around 5.5, but at a pH below 3.5, H_3O dominates (Coleman and Harward, 1953; Thomas and Hipp, 1968).

Potassium Leaching from Soil

Leaching of soil solution K can govern the release of K from soil minerals but this type of mechanism largely depends on the soil pH, movement of K in soils, soil cation exchange capacity (CEC), liming and rate of K uptake by plants and microbes (Terry and McCants, 1968; Sparks, 1980 et al.; Sparks, 2000). Soils vary in CEC and thus in retaining applied K. Leaching is also affected by the amount of clay in soils and

soil organic matter. Soils having higher CEC retain K more strongly than soils with lower CEC (Sparks and Huang, 1985).

According to Sparks and Huang (1985), leaching of K from sandy soils is regarded as a common problem. Retention of K can often be enhanced in sandy, Atlantic Coastal Plain soils after application of lime, since in such variable charge soils, the CEC is increased as soil pH is increased. Nolan and Pritchett (1960) observed increased retention of K in a Lakeland fine sand (thermic, coated Typic Quartzipsamment) after liming the soil to pH 6 to 6.5. They also found that less leaching occurred at pH 6.0 to 6.5 due to enhanced substitution of K for Ca than Al, which was more abundant at low pH. Lutrick (1963) found that K leaching occurred on unlimed but not on limed areas when 112 to 224 kg K ha⁻¹ was applied on a Eustis loamy fine sand (sandy, siliceous, thermic Psammentic Paleudult).

Release of K from Soil Minerals

Clay minerals retain the bulk of plant available K as exchangeable K and release it when the concentration in soil solution decreases due to plant uptake or to an increase in soil moisture. High K-saturation of the clay minerals with high CEC results in a high soil solution K concentration, whereas low K-saturation is in equilibrium with low K concentration.

Several processes govern the release of K⁺ from clay minerals. Dissolution of micas followed by the formation of weathering products, and transformation of K-bearing mica to 2:1 layer silicates by replacing the K⁺ with other hydrated cations are assumed to be two processes. These processes are related to the soil environment and the

stability of micas, which influence the mechanisms of K release (Sparks and Huang, 1985; Sparks, 2000). Different physiological and mineralogical factors such as particle size, chemical composition, physical imperfection, degree of tetrahedral tilting, hydroxyl orientation, degree of K depletion, alteration of layer charge and associated reactions, hydronium ions, biological activity, wetting and drying, inorganic cations and other factors affect the release of K from clay minerals (Sparks and Huang, 1985). Biological activities favor the release of K from micas and can become a complex process when organic acids are formed (Mortland et al., 1956; Boyle et al., 1967; Weed et al., 1969; Sawhney and Voight, 1969).

All soils contain relatively small but measurable quantities of biochemical compounds like organic acids. Organic acids such as oxalic and citric acids can affect the release of K from micas and feldspars (Song and Huang, 1988). According to their observation, the order of ease of K^+ release from different minerals by oxalic and citric acids is biotite > microcline > orthoclase > muscovite.

The activity of K^+ in solution surrounding mica particles greatly affects the release of K^+ by cation exchange from those minerals. Replacement of K^+ from interlayers by other cations from solution occurs when the level of K^+ in solution is less than the critical level. Potassium can also re-enter the interlayer of mica expansible 2:1 minerals if the critical K^+ level in solution is sufficiently high. This critical level is higher for trioctahedral minerals such as biotite and lower for muscovite (Scott and Smith, 1967; Newman, 1969; von Reichenbach, 1973; Henderson et al., 1976).

Clay fractions influence the release of K^+ from soils upon drying (Scott and Hanway, 1960). Leaching and redox potential are two other factors that effect K^+ release. Leaching can influence K^+ release from minerals by carrying away reaction products and converting micas to 2:1 expandible layer silicates if the leaching water chemistry is favorable for this kind of reaction. Oxidation and reduction phenomena are of great importance to soil fertility because the availability of plant nutrients depends in large degree on the surface chemistry of soil minerals. Oxidation and reduction can also induce K^+ release from micas. In biotite K is held strongly upon oxidation of structural Fe, thus, the release of K is less from this mineral if the soil environment favors the oxidation of structural Fe, and it is the opposite if structural Fe is reduced. The in-place reduction of Fe^{3+} to Fe^{2+} in secondary minerals (vermiculite, montmorillonite, illite) also occurs, and creates an environment in which some of the beneficial effects of weathering may be reversed, such as the retention of K^+ (Sparks, 2001). Structural Fe reduction increases K^+ fixation in smectitic clay minerals (Stucki and Shen, 1993). This is due to numerous changes that occur in the physical-chemical properties of the soil mineral, including swelling capacity in water (Stucki et al., 1984), electrical charge (Stucki and Roth, 1977; Lear and Stucki, 1985), and surface area (Lear and Stucki, 1989). Redox potential, however, does not directly affect the chemical weathering of feldspars. Complexing organic acids and oxidation state, however, can influence the chemical alteration/weathering of feldspars (Sparks, 2001).

Increasing temperature can also increase K^+ release from biotite (Rausell-Colom et al., 1965) and K feldspars (Rasmussen, 1972). Scott et al. (1973) found that

tetraphenyl boron extraction of preheated mica (heated to 1273⁰ K) resulted in increased rate of K⁺ extraction from muscovite, but decreased the rate for biotite and had little effect on phlogopite except at a very high temperature. Less K⁺ extraction from biotite was due to the oxidation of Fe²⁺ at high temperature during heating before extraction. The factors that affect the release of K⁺ from muscovite, however, are still not well understood.

MINERALOGY OF THE BENGAL BASIN

The Bengal Basin in Bangladesh is regarded as one of the most densely populated recent flood plains of the world (Datta and Subramanian, 1997). Bengal Delta, one of the largest deltas in the world, is in the Bengal Basin. The Bengal Delta is situated in the flow of the Ganges-Brahmaputra-Meghna(GBM) river system (Coleman, 1981). According to Datta and Subramanian (1997), this alluvial basin is very important because of its size, huge deposition of sediments, frequent siltation, and an elevation lower than mean sea level.

The Bengal Basin, surrounded by the Indian shield on the west, and by the Nagalusi orogenic belt on the east, is open to the Bay of Bengal on the south, and is bordered by the Shillong shield on the north (Sengupta, 1966). Low feldspar and high quartz content indicates the low relief tropical weathering condition in this basin (Potter, 1978). The significant occurrence of carbonate minerals in the Bengal Basin is associated with the deposition of detrital carbonates on the upper reaches during sediment drainage (Datta and Subramanian, 1997). Irion (1991) reported that the average illite content of world river basin sediments is in the range of 40% to 60%, which is very

similar to that of the Bengal Basin. The abundance of illitic minerals in the Bengal Basin is due to the presence of muscovite in the parent rocks (Griffin et al., 1968; Segall and Kuehl, 1992). Kaolinite is the second most common clay mineral after illite. Sediments may be the source of kaolinite (Brinkman 1977; Islam and Lotse, 1986), and is an indication of rapid soil-forming process (kaolinization). Irion (1991) reported a low content of chlorite in the basin due to the low quantity of minerals in the river sediments draining exclusively lowland tropical areas. The presence of montmorillonite in this basin is very low, indicating an insufficient amount of eruptive igneous rocks in the drainage basin.

According to Naidu (1985) and others, 73% to 78% illite and 22% chlorite by weight were found in the bed sediments of the Ganges River. Subramanian (1980) observed 46% illite, 28.7% kaolinite, 22.8% chlorite and 2.5% montmorillonite in suspended sediments from the Ganges River at Calcutta. Illite is one of the most dominant clay minerals in the northeast Bay of Bengal, and this is also the location where the Ganges-Brahmaputra River system drains the sediment load carried from the Himalayas (Rao et al., 1988; Kolla and Rao, 1990; Segall and Kuehl, 1992; Wijayananda and Cronan, 1994).

MINERALOGY OF THE INDO-GANGETIC ALLUVIAL BASIN

Potassium in soils of the Indo-Gangetic alluvial plains in India is derived from K feldspars and micas (Sidhu, 1984). Microcline and orthoclase are representative of K feldspars in these soils. Mica minerals present are muscovite and biotite in the coarser fractions and illite in the finer fractions. Part of illite's charge originates in the octahedral

layer, unlike muscovite. Sand fractions are dominated in decreasing order by quartz, micas, and feldspars (Sidhu and Gilkes, 1977; Kapoor et al., 1982; Pundeer et al., 1978). Silt fractions resemble the sand fraction in mineralogical assemblage. Illite, vermiculite, and differing amounts of smectite, chlorite, and kaolinite are common clay minerals. The illites are predominantly dioctahedral (Kapoor et al., 1981; 1982; Sidhu and Gilkes, 1977). Salt affected alluvial soils in the Indo-Gangetic Plain contain smectite–mica and chlorite–vermiculite interstratified minerals. In the lower Gangetic Basin, illite and smectite are the dominant clay minerals. Mishra et al. (1996) found that whereas smectite–illite–chlorite is the most common clay mineral phase in the terraces, clays of flood plain soils in the middle and lower Gangetic plains are dominated by an illite–smectite–chlorite phase.

Dominant minerals in the silt fraction of soils in the entire Indo-Gangetic Plain include quartz–feldspar, quartz–mica or quartz alone. In Pakistan, representing the western part of the Indo-Gangetic Plains, soils under rice–wheat systems contain large amounts of mica (about 50%) in sand and silt fractions and illite (about 50%) in clay fractions (Akhtar and Jenkinson, 1999). Besides illite, the clay fraction also contains kaolinite, montmorillonite, chlorite, and vermiculite (Bajwa, 1989). These soils experience moderate levels of weathering of original K-minerals with a large amount of applied K reportedly fixed (Ranjha et al., 1992).

K-STATUS IN SOILS OF BANGLADESH AND OTHER ASIAN COUNTRIES

The combination of rising population and increasing food demand has placed tremendous pressure on the land resource of Bangladesh. The population of Bangladesh

is expected to reach 250 million by 2025. Expansion of cultivated land is hardly realistic in this densely populated country, so crop intensification is the main vehicle for increasing food output (Cassman et al., 2003). Rice is the staple food for millions of people in Bangladesh. During the last 30 years of the 20th century, rice cropping was intensified in Bangladesh along with other Asian countries. This intensification in combination with unbalanced fertilization has resulted in depletion of K in soils over large areas in China (Jiyun et al., 1999), India (Hasan, 2002) and other countries in Southeast Asia (Dobermann et al., 1996b, 1998).

Improved farming practices and use of high yielding crop varieties, along with fertilizer N application, increased crop production in China significantly in the 1960's (Jiyun et al., 1999). At the same time, soils were becoming more deficient in plant nutrients, except N. Phosphorus became the next most deficient nutrient and yield-limiting factor. Hence, P fertilizer application became important for further increases in crop yield. Increased crop production together with increased use of N and P fertilizers resulted in K-deficiency first in southern China in early 1970 and extended to northern China (Hoa, 2003). Unbalanced fertilizer application, which has more N than P and K, became very common during 1950 to 1980 in China. China attempted to use a more balanced fertilizer beginning in the late 1980's, but N was still applied at a rate proportionally higher than P and K. Fertilizer use in China today is still not properly balanced. Inadequate K application along with removal of straw from Chinese rice fields has caused increased K-deficiency and significant responses of crop yield to K-fertilizer application (Jiyun et al., 1999). In a similar fashion, Bangladeshi farmers use a large

amount of rice straw as animal feed and for domestic fuel thus removing a substantial amount of soil K every year. They also use unbalanced fertilizer formulations, so K deficiency may become widespread throughout the country.

Dobermann et al. (1998) reported that coarse-textured and highly weathered soils (Oxisols, Ultisols) typically show K deficiency in South and Southeast Asia. They also noted that most of the soils of the great alluvial floodplains were generally regarded as high in extractable K. It was also thought that K addition through indigenous sources such as irrigation and flood water would make K a rare limiting factor in irrigated rice systems (Kawaguchi and Kyuma, 1977; De Datta and Mikkelsen, 1985; Bajwa, 1994). Potassium inputs in irrigation water may be more than 30 kg ha⁻¹ year⁻¹ in rice-wheat areas where ground water is used (Pasricha, 1998). However, widespread K-deficiency has been observed on fine textured soils, which includes alluvial, illitic soils in India (Tiwari et al., 1985), vermiculitic clay soils of central Luzon, Philippines (Oberthuer et al., 1995), and lowland rice soils of Java (Scri Adiningsih et al., 1991).

Potassium nutrition has become a very important factor in increasing crop production in Asia. Substantial applications of properly balanced fertilizer replenish the soil K pool which is being removed by intensive cropping systems (Bijay-Singh et al., 2004). Most soils in the Indo-Gangetic Plains are historically deficient in N. Potassium deficiency is emerging in some Indo-Gangetic Plains soils due to the micaceous nature of these soils (Ladha et al., 2002).

Several chemical and biochemical changes occur in rice soils during the flooding season, which influences the transformation and availability of nutrients

(Ponnamperuma, 1972, 1985; Cao and Hu, 1995). Submerged soils are regarded as high in exchangeable K^+ and Na^+ compared to upland soils, especially in the cultivated layer (Bijay-Singh et al., 2004). Flooded soils are different in the control of acidity and alkalinity due to the partial pressure of CO_2 buffering carbonates in the flood water. Thus, the changes in pH and redox influence the chemical equilibria and availability of various nutrients to plants. Most chemical changes are reversed during draining (Bijay-Singh et al., 2004).

Soil analysis is an important tool when evaluating soil nutrient status, and results are often used as the basis for fertilizer recommendations. This practice is justified in cases where a correlation between soil test results and crop response to fertilizer applications has been established. Generally, crop responses to a fertilizer nutrient should be lower the higher the content of the nutrient in a soil. A small proportion of the K required by plants comes from direct contact through root interception, whereas the largest fraction of the K needed by plants has to be transported from soil to roots via diffusion. Transport happens mainly in soil solution, the liquid phase of the soil, by mass flow (with the water moving to the plant roots) and diffusion along a concentration gradient that is created by the absorbing roots. In the immediate proximity of roots, soil solution is rapidly exhausted of nutrients due to uptake by plants. A continuous supply of K to growing plants is only insured when the rate of K release to soil solution and transport to roots keeps pace with the K uptake.

The rate and quantity of the release of non-exchangeable to exchangeable and soluble K^+ primarily depend on the level of K^+ in the soil solution, the type and amount

of clay minerals present (Martin and Sparks, 1985; McLean, 1978), the degree of exposure of edges of clay minerals to the soil solution, and the position of non-exchangeable K^+ with respect to outer edges. Soils therefore vary in releasing non-exchangeable K^+ rapidly enough to meet the needs of crop production and may be slow enough to restrict the yield (Bijay-Singh et al., 2004).

Plant available K depends on the size of the available K pool in soil and transport mechanisms of K from soil solution to the root zone and from the root zone into plant roots (Barber, 1984). Many plant factors (e.g. variety, root system, antagonistic and synergistic mechanisms in ion uptake) and soil factors (pH, organic materials) also affect plant availability of K (Hoa, 2003). Dry lowland soils containing vermiculite, illite, or other 2:1 layer clay minerals may result in increased K^+ fixation and reduced solution concentration during flooding, so that rice depends on non-exchangeable reserves for K^+ uptake. Regmi (1994) observed in a long-term experiment with a rice–wheat rotation in the Tarai plain of southern Nepal that the proportion of added K^+ that was fixed ranged from 46 to 56% in a wet/dry equilibration, and fixation was linear with addition rates of up to 25 mM K kg⁻¹ soil.

Scientists have a rather poor understanding of the behavior of K in soils subjected to cycles of flooding. Iron is an important and abundant constituent and may be present as Fe(II) (reduced form) or Fe(III) (oxidized form). Iron oxidation state within crystal structures of soil minerals is an important factor in understanding K behavior (Stuki and Shen, 1993). Soils containing appreciable quantities of mica (especially biotite), illite, vermiculite and Fe-containing smectite, structural Fe may undergo

reduction during flooding and oxidation during periods of drainage. It has been reported that Fe reduction from Fe^{+3} to Fe^{+2} plays a significant role in fixing K in smectite clay minerals (Stucki and Shen, 1993). Weathering of primary minerals is regarded as an oxidative process. In this process, Fe^{2+} converts to Fe^{3+} and soil minerals become expansive types which release various nutrients including K (Stucki and Shen, 1993). But according to Lear and Stucki (1989), surface charge density increases upon Fe reduction and increases the ability of the minerals to fix K^+ and other interlayer cations (Chen et al., 1987; Khaled and Stucki, 1991). Stucki and Huo (1996) observed a strong direct correlation between Fe(II) (reduced Fe) and K^+ fixation in smectite minerals. But this correlation was weaker and inverse in the case of illite minerals, probably due to the change in electrostatic force between K and structural OH groups.

Stucki and Shen (1993) proposed a hypothesis on the behavior of illite in releasing K during Fe reduction. The hypothesis was that Fe (II) is added to the octahedral sheet of illite during reduction; the dipole moment of structural OH groups becomes more canted to the c-axis and therefore creates a weaker attractive bond or stronger repulsive force between clay layer and the interlayer K ions, resulting in release of K to soil solution.

The behavior of clay minerals greatly depends on the type of clay mineral that is present (Stucki and Shen 1993). According to their observation, if illite dominates, reduction may enhance availability of K, whereas smectite domination may result in K fixation during reducing conditions. If these minerals are precisely balanced, no net

change in K availability would occur, because the amount that one releases would be fixed by the other.

CHAPTER III

MATERIALS AND METHODS

SOILS AND ROUTINE ANALYSES

Five soils from four different thanas of Bangladesh (Fig. 3) were described and sampled by horizon from freshly exposed pits and auger borings in March 2005. Soil samples for this study were selected from these soils. Soil samples were air-dried and crushed to pass a 2-mm sieve.

Particle size distribution of these soils was assessed by the pipette method described by Kilmer and Alexander (1949) and Steele and Bradfield (1934). Sands were wet-sieved, dried at 105⁰C overnight, and dry sieved in a nest of sieves.

Soil pH was determined in distilled water in a 1:1 ratio (weight: volume) and after an equilibration period of 1 hour. The pH was measured by a glass electrode following method 8C1a (Soil Survey Laboratory Staff, 1996).

The CEC of the soils was determined at pH 8.2 as described by the Soil Survey Laboratory Staff (1996) and using an automatic extractor (Holmgren et al., 1977). Soils were saturated with 1N NaOAc at pH 8.2, washed with ethanol and the exchangeable Na was replaced with 1N NH₄OAc. Concentrations of Na were analyzed by flame emission on the atomic absorption spectrometer.

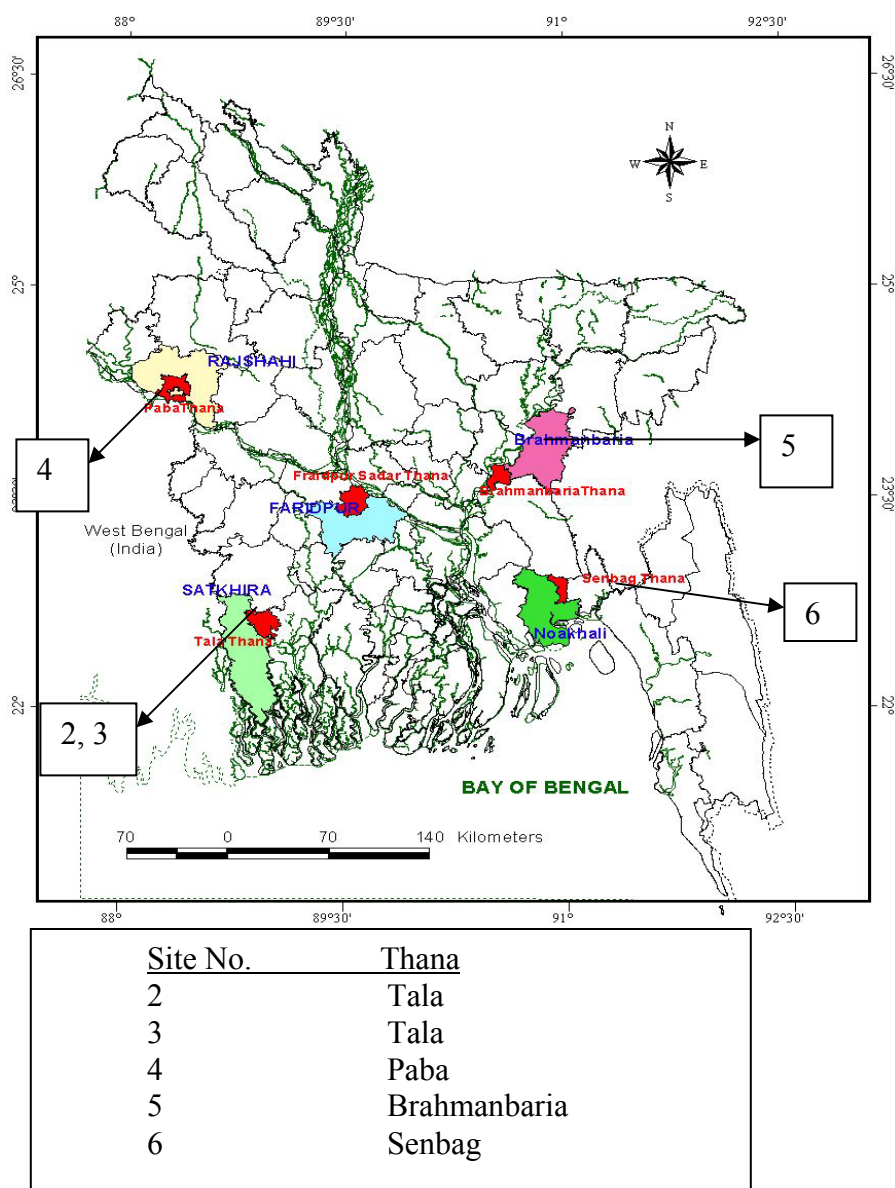


Fig. 3. Soil sampling sites in four selected thanas.

Bases extracted in 1M NH_4OAc pH 7.0 were determined following extraction of about 5 g samples with 50 ml of solution using an automatic extractor (Holmgren et al., 1977). Extractable Ca and Mg were quantified by atomic adsorption using a N_2O -acetylene flame, while Na and K were analyzed by flame emission with an air-acetylene flame.

Total C of the study soils was quantified using a medium-temperature resistance furnace and scrubbing train as described by Nelson and Sommers (1982). The quantity of inorganic C from CaCO_3 equivalent was subtracted from the total C to give the percentage of organic C.

The quantity of CaCO_3 was determined using the Chittick procedure as described by Dreimanis (1962). This method which measure the volume of CO_2 released upon reaction with carbonate with HCl allows the quantification of calcite and dolomite based on reaction time. Results were used to calculate the CaCO_3 equivalent.

All sixteen soil samples from the five profiles (surface and subsurface soils) were used in the routine determination of the physical, chemical and mineralogical properties described above. As described in a later section selected horizons were used for nonexchangeable K, total K and cation exchange capacity (CEC) in both oxidized and reduced condition. Three surface soils from three different profiles (Tala-2, Paba-4 and Senbag-6) with different pH and clay content were selected to determine the impact of redox on CEC in different periods of time. Three other surface soils with different pH and clay content from three different profiles (Tala-3, Paba-4 and Senbag-6) were used to observe the release and retention of K from those soils as a function of redox.

CLAY MINERALOGY

For the separation of sand, silt and clay, about 50 g of sample were shaken overnight with 50 ml of 5% Na_2CO_3 and 150 ml of deionized water to facilitate dispersion. Sands were removed with a 300-mesh screen by wet sieving. Sands were dried in a 105°C oven and weighed. Clays were separated from silts using an automatic fractionator. Separated silts were dried at 105°C , while clays were concentrated by flocculating with MgCl_2 , decantation and centrifugation. Clay fractions were further separated into fine clay and coarse clay by centrifugation. Mineralogy of the clay fractions was determined by X-ray diffraction on oriented samples. Clays were initially saturated using 0.5 M MgCl_2 and centrifugation. After removal of excess MgCl_2 by washing with water and water-ethanol mixtures, oriented clays were vacuum deposited onto unglazed ceramic tiles. One oriented clay sample received about 3 ml of 10% ethylene glycol treatment, while the other two oriented samples were X-rayed at room temperature and after heating to 350°C and 550°C . Clay samples were scanned from 2° to $32^\circ 2\theta$ using $\text{CuK}\alpha$ radiation.

Kaolinite was identified by a 0.7nm peak in all treatment but was destroyed when heated to 550°C . Smectite was identified by the 1.8 nm peak upon expansion with ethylene glycol but that was at 1.4 nm in the air-dry samples, and collapsed to 1.0 nm upon heating. Vermiculite was identified by a 1.4 nm peak with ethylene glycol treatment but that collapsed to 1.0 nm upon heating. Chlorite was identified as a 1.4 nm peak that remained upon heating to 350°C and 550°C . A peak at 1.0 nm in the ethylene glycol scan was identified as mica.

TOTAL POTASSIUM

Total K concentration was determined on selected whole soils and silt, coarse clay, and fine clay samples following the procedure described by Bernas (1968). Where needed, samples were ground to pass a 200-mesh sieve, and 50 mg (whole soil, silt, fine clay and coarse clay samples) were placed into acid digestion vessels along with 0.5 ml of aqua regia and 3 ml of HF. The closed vessels were placed into an oven at 110⁰C for an hour. After cooling, decomposed samples were transferred to plastic beakers with the aid of 4 to 6 ml of water. Then 2.8 g of H₃BO₃ acid were added immediately to the decomposed samples and stirred with a Teflon magnetic stirrer for 15 minutes to promote the formation of soluble fluoroborates from insoluble complex fluorides. About 40 ml of water and 5 ml of 2% NaCl were added to the clear homogenous sample solution. The solution was transferred to a 100-ml volumetric flask and brought to volume with deionized water. The sample solutions were analyzed for K by flame emission using an air-acetylene flame.

NITRIC ACID EXTRACTABLE K

The procedure developed by Pratt and Morse (1954) for HNO₃- extractable K was modified by using a digestion block instead of a hot oil bath. Selected samples were ground in a disc mill grinder for about 12 seconds, and 2.5 g of finely ground soil samples were placed into digestion tubes. Twenty five ml of 1.0 N HNO₃ were added, and then tubes were placed into a preheated digestion block at 113⁰C for 25 minutes. After removing tubes, the contents were filtered using number 42 Whatman filter paper and filtrates were collected in 100-ml volumetric flasks. Residues were washed four

times with 15 ml of 0.1 N HNO₃. After cooling, the solutions were brought to volume. Concentrations of K were determined using flame emission.

SOIL CATION EXCHANGE CAPACITY IN AN OXIDIZED CONDITION

Five g of air-dried soil were placed into a 50-ml centrifuge tube. Samples were ground to pass a 200-mesh sieve. Each sample was saturated with 40 ml of 0.1M MgCl₂. After 20 minutes of shaking, the suspension was centrifuged at 2000 rpm for 5 minutes and the supernatant was decanted. The saturation step was repeated two more times. After each centrifugation, a vortex stirrer was used to resuspend the soil.

After saturation with Mg²⁺, samples were washed with 40 ml of deionized water. Suspensions were centrifuged for 25 minutes at 2000 rpm, and supernatants were decanted. These steps were repeated for two more times.

Magnesium was displaced from the exchange sites using Ca²⁺. Thirty ml of 0.1 M Ca(NO₃)₂ was added to each sample and were shaken for 20 minutes after the washing. Sample suspensions were centrifuged at 2000 rpm for 5 minutes and supernatants were poured into 100-ml volumetric flasks. The process was repeated twice more, after which the solutions were brought to volume with distilled water. Displaced Mg²⁺ was determined by atomic absorption using an acetylene-nitrous oxide flame.

SOIL CATION EXCHANGE CAPACITY IN A REDUCED CONDITION

Five g of air dried soil from each sample were placed into centrifuge tubes. Twenty ml of deionized water were added to each along with 0.05 g of dried and finely ground clover to serve as a C source for microbes. The tubes were shaken by vortex stirrer and placed into a glove box in a reduced environment (chamber) where the

maximum concentration of O_2 was less than 2 ppm. Samples were shaken very slowly on a reciprocal shaker inside the glove box until reduction was achieved. The redox potential was checked daily to make sure the samples were reduced. When the redox of the soils ceased to decrease further, then the mean redox of the samples was measured. The mean corrected redox of these samples was -38 mV. The samples were removed from the glove box, centrifuged, and the water decanted. The samples were placed back into the glove box for saturation with Mg^{2+} . Reagents were placed into the glove box 2 to 3 days prior to saturation to remove O_2 from reagent solutions used during the washing and displacement procedure. Deionized water used to make the reagent was boiled to reduce the concentration of O_2 in the water.

The procedure previously described (saturation with 0.1M $MgCl_2$, washing with deionized water, displacement by 0.1 M $Ca(NO_3)_2$) was followed inside the glove box. Samples in the capped centrifuge tubes were taken from the glove box during each centrifugation period and were placed back after centrifugation. Supernatants were decanted inside the glove box. Displaced Mg^{2+} was determined by atomic absorption as described previously.

ADSORPTION ISOTHERM OF THREE SELECTED SOILS (OXIDIZED)

Five g of soil samples from Tala-3, Paba-4, Senbag-6 were placed into weighed 50 ml centrifuge tubes. Eight rates of K were used. Rates were based upon a percentage of the soil CEC (0, 2, 5, 10, 20, 50, 100, and 150% of CEC) and corresponded to 0, 2.92, 7.30, 14.6, 29.2, 73.0, 146, and 219 mmol K kg^{-1} soil. Solutions were prepared that would deliver the required level of K^+ in 1 ml when diluted to 20 ml. Thus 1 ml for each

rate was added along with 19 ml of distilled water. Samples were equilibrated for 48 hours. Samples were also shaken on a reciprocal shaker during the equilibrium period, then centrifuged at 2000 rpm for 10 minutes. The extracts were diluted and analyzed for K^+ in the equilibrium solution using flame emission. The soil samples were then equilibrated again in 20 ml of 1M NH_4OAc solution during four hours of shaking. Then the samples were centrifuged at 2000 rpm for 10 minutes and the supernatants were collected. This 1M NH_4OAc step was done twice. The supernatants were diluted to measure the K displaced from the colloid by atomic absorption spectrometer.

ADSORPTION ISOTHERMS OF THREE SELECTED SOILS (REDUCED)

The selected soils from Tala-3, Paba-4, Senbag-6 were incubated as described for CEC in reduced condition. Twenty ml of deionized water were added along with 0.05 g of dried and finely ground clover to serve as a C source for microbes. The tubes were shaken well by vortex stirrer and placed into a glove box in a reduced environment (chamber) where the maximum concentration of O_2 was less than 2 ppm. Samples were shaken on a reciprocal shaker inside the glove box until the samples were reduced. The redox potential was checked daily to make sure the samples were reduced. When the redox of the soils ceased to decrease further, then the mean redox of the samples was measured. Once a sustained mean redox potential of -60 mV was obtained, the samples were centrifuged and solutions analyzed as described in the oxidized absorption isotherm procedure except the procedure was performed in a glove box under very low O_2 partial pressure.

CHAPTER IV

RESULTS AND DISCUSSIONS

SELECTED PROPERTIES OF THE STUDY SOILS

The properties of soil horizons which were selected for detailed study are given in Table 1. Complete data on all horizons are in Appendix A, and descriptions of the soils are in Appendix B.

The soils developing from Ganges alluvium have distinctly different properties from those developing from Meghna alluvium (Table 1). Calcium carbonate is absent in the Meghna-alluvium derived soils (Brahmanbaria-5 and Senbag-6) and soil pH values for these soils range from 5.0 to 7.6, while most horizons derived in Ganges alluvium are calcareous (up to $84 \text{ g CaCO}_3 \text{ kg}^{-1}$) and all are moderately alkaline (pH range of 7.7 to 8.3). The Meghna alluvium-derived soils have lower clay content (49 to 186 g kg^{-1}) as compared to the Ganges alluvium-derived soils (127 to 500 g kg^{-1}). All soils have a high silt content, and organic C tends to decrease with depth.

Table 1. Selected properties of the study soils.

Site Name	Soil Horizon	Depth cm	Texture*	Soil pH	Total Clay	Organic C	CaCO ₃ g/kg	Total Silt	Fine Clay
----- Ganges Alluvium -----									
Tala-2	Ap1	0-7	SiL	7.9	189	16.8	84	755	51
	Ap2	7-10	SiL	8.1	193	8.5	69	769	73
	Bw3	38-68	SiL	8.3	218	6.8	52	708	75
Tala-3	Ap1	0-6	SiL	7.9	239	9.6	ND**	605	92
	Ap2	6-14	SiL	8.1	240	7.5	10	606	85
	Bw2	30-40	SiL	8.1	127	3.2	62	716	48
Paba-4	Ap1	0-10	SiCL	8.0	332	12.6	51	616	117
	Ap2	10-19	SiCL	8.0	355	9.4	40	601	134
	2Bw1b	55-76	SiC	7.7	500	6.2	ND	471	220
----- Meghna Alluvium -----									
B.Barria-5	Ap1	0-8	SiL	5.5	142	18.3	ND	779	26
	Ap2	8-14	SiL	7.0	158	9.1	ND	804	38
	Bw4	44-78	Si	7.6	117	3.1	ND	848	39
	Bw5	78-100	SiL	7.4	186	4.3	ND	804	58
Senbag-6	Ap1	0-10	Si	5.0	49	10.7	ND	913	13
	Ap2	10-25	Si	6.6	69	5.4	ND	886	21
	Bw3	42-52	Si	6.7	112	2.8	ND	811	31

*Si = silt, SiL =silt loam, SiCL = silty clay loam, SiC = Silty clay

**ND- Not determined, as no reaction with HCl was noted.

CLAY MINERALOGY OF THE STUDY SOILS

The clay fractions of the surface horizons of each study soil were further separated into coarse and fine clays by centrifugation and subjected to X-ray diffraction to identify and semi-quantify the clay mineralogy. Selected diffractograms are presented in Appendix C, and the interpretations of the diffractograms are given in Table 2.

The coarse clay fraction of each horizon had a higher concentration of mica than the fine clay in all of the surface horizons (Table 2), and substantial amounts of mica were noted in all surface horizons. The presence of kaolinite was also significant in both clay fractions of all soils. As these are relatively young soils, the kaolinite is believed to be inherited from the parent alluvium rather than resulting from pedogenesis. The Senbag and Brahmanbaria soils had more vermiculite than the three soils developing from the Ganges alluvium, and only a trace amount of vermiculite was present in the coarse clay fraction of Tala-3 soil. This suggests that the more acidic nature of the Meghna alluvium soils (Brahmanbaria and Senbag) resulted in the weathering of some mica to vermiculite, while the alkaline conditions for the three soils of Ganges alluvium showed less weathering of mica to vermiculite. The fine clay fractions of the soils had higher concentrations of smectite than the coarse fractions and only trace amounts or no smectite was present in the coarse clay fractions. Chlorite was found in the coarse clay fraction of all soils, and was almost absent in the fine clay fractions.

Table 2. Mineral composition of the coarse and fine clay fractions of selected surface horizons of the study soils.

Site	Horizon	Clay Fraction	Mica	Smectite	Vermiculite	Chlorite	Kaolinite	
Tala-2	Ap1	Fine	** (23)	***	---	T	**	
		Coarse	*** (36)	T	**	**	**	
Tala-3	Ap1	Fine	** (20)	****	---	---	**	
		Coarse	*** (44)	T	T	**	***	
Paba-4	Ap1	Fine	** (22)	***	---	---	**	
		Coarse	*** (42)	T	*	**	**	
	Ap2	Fine	** (22)	****	---	T	**	
		Coarse	*** (44)	---	*	**	***	
B.Barria-5	Ap1	Fine	** (16)	**	**	---	**	
		Coarse	** (26)	T	***	*	**	
Senbag-6	Ap1	Fine	(insufficient quantity for analysis)					
		Coarse	** (19)	---	**	**	***	

*Less than 10%; **10-30%; ***30-50%; ****greater than 50% and --- none is present. Mica values in parentheses are percentages calculated from total K values based on 8% K content in mica.

TOTAL K BY HF DIGESTION

The soil horizons selected for detailed study were fractionated into sand, silt, and clay then clays were separated into fine ($<0.2 \mu$) and coarse ($2-0.2 \mu$) fractions. Total K was determined on each fraction (excluding sands) and the bulk soils using HF digestion. Results are given in Table 3.

Significant concentrations of K were present in all fractions of the clays and silts. Potassium concentration was greatest in the coarse clays of all the soils studied (Table 2) which is attributed to the high content of mica in this fraction, but significant concentrations of K were also found in the fine clay and silt fractions. Soils from Ganges alluvium (Tala-2, Tala-3, and Paba-4) had slightly higher total K in all fractions throughout the profile than the soils from Meghna alluvium (Brahmanbaria-5 and Senbag-6). This trend was most apparent in the clay fractions and was attributed to a greater content of mica in Tala-2, Tala-3, and Paba-4 soils than the soils from Brahmanbaria-5 and Senbag-6 (Table 2). The concentration of total K was greatest in the Paba-4 soil (average of 23.3 g kg^{-1} total K throughout the profile) and was least in the soil from Senbag-6. These difference are due to the different characteristics of these soils such as the different parent materials, degree of leaching as inferred from soil pH or draining condition (hydrological status), and the abundance of mica , and interstratified 1.0 nm/1.4 nm minerals.

The amount of K in each size fraction was calculated from K concentration in the fraction (Table 3) and the particle size distribution (Table 1), and results are given in Table 3. Clearly, silt contributed the most of total K to the whole soil, followed by the clay fractions. Coarse clay contributed more total K to the bulk soil than fine clay. The amount of K in the sand fraction was calculated as the difference between bulk soil total K and silt plus clay contributions. As a result, all analytical errors accumulated in this function and values ranged from -1.5 to 6.3 g kg⁻¹ soil. Clearly, the sand contribution of K to soil total K was substantially less than the contributions from the silt and clay fractions.

The total K values in the coarse and fine clay fractions were used to calculate the mica content in each horizon, and results are presented in Table 2. Assumptions in these calculations were that all the K was from mica and that the mica had a K-concentration of 8%. The calculated mica contents generally agreed with the estimates from the X-ray diffractogram interpretations.

Table 3. Total potassium (K) as determined by HF digestion in the bulk soils, silt, fine and coarse clay fractions.

Site Name	Horizon	Total K in Fraction				Total K Contribution to Soil				
		Bulk Soil	Silt	Fine Clay	Coarse Clay	Silt	Fine Clay	Coarse Clay	Total Clay	Sand*
----- g kg ⁻¹ -----										
Tala-2	Ap1	21.9	19.2	19.4	30.3	14.5	1.0	4.2	5.2	2.2
	Ap2	21.9	20.5	19.3	37.0	15.8	1.4	4.4	5.8	0.3
	Bw3	23.2	19.6	5.6	29.9	15.1	0.4	4.3	4.7	3.0
Tala-3	Ap1	19.5	19.6	16.8	36.5	11.9	1.5	5.4	6.9	0.7
	Ap2	20.1	18.7	18.0	34.0	11.3	1.5	5.3	6.8	2.0
	Bw2	19.9	15.3	4.3	30.5	11.0	0.2	2.4	2.6	6.3
Paba-4	Ap1	22.6	21.5	18.1	34.7	13.2	2.1	7.5	9.6	-0.2
	Ap2	22.4	22.2	18.3	36.8	13.3	2.5	8.1	10.6	-1.5
	2Bw1 b	24.9	27.4	4.6	32.0	12.9	1.0	9.0	10.0	2.0
BBaria-5	Ap1	17.7	18.3	13.6	22.0	14.3	0.4	2.6	3.0	0.4
	Ap2	17.7	17.7	13.4	23.6	14.2	0.5	2.8	3.3	0.2
	Bw4	21.4	18.7	3.5	23.6	15.9	0.1	1.8	1.9	3.6
	Bw5	22.1	21.0	8.3	23.5	16.9	0.5	3.0	3.5	1.7
Senbag-6	Ap1	15.8	16.3	10.3	15.4	14.9	0.1	0.6	0.7	0.2
	Ap2	15.9	17.2	12.9	16.5	15.2	0.3	0.8	1.1	-0.4
	Bw3	20.2	19.2	5.4	24.5	15.6	0.2	2.0	2.2	2.4

*Calculated as difference in bulk soil K and sum of silt and clay K.

NITRIC ACID EXTRACTABLE K

The non-exchangeable K pool is in dynamic equilibrium with the plant-available K pool and acts as an important source of slow release K (De Datta, 1985), and HNO₃-extractable K represents a more active portion of the non-exchangeable K pool.

Soils having a higher rate of release of non-exchangeable K have a predominance of K-bearing minerals such as mica and illite in the clay fraction compared to soils which are low in non-exchangeable K (Table 4) (Metson, 1968). The rate decreases in proportion to a lower abundance of micaceous clays and increasing abundance of 1:1 layer and oxide clays (Metson and Lee, 1977; Metson, 1980). The K removed by 1M boiling nitric acid increases with clay concentration and with a decrease in the degree of weathering (McLean and Watson, 1985).

Higher concentrations of HNO₃-extractable K were present in the soils from Tala-2, Tala-3, and Paba-4 (Ganges alluvium) than in the Brahmanbaria-5 and Senbag-6 soils (Table 4). This result suggested that soils developed in the more acidic and lower clay content Meghna alluvium have a lower content of micaceous minerals, or that the K in micas has been completely or partially weathered from the mica interlayer by weathering. Since the quantity of exchangeable K would also be a constituent of the HNO₃-extractable K, the difference in this was reported in table-4 as non-exchangeable K. This fraction would be most related to the amount of K that was associated with mica interlayers. Since the exchangeable K values are quite small compared to the HNO₃ extractable K, the distribution of non-exchangeable K is almost identical to that of HNO₃-extractable K.

Feldspar was not identified in the clay fraction using X-ray diffraction, so all HNO_3 -extractable K is likely from mica, except for the minor contribution from exchangeable K. These results reflected the mineralogy of the study soils and indicated that the rate of release of less soluble forms of non-exchangeable K would be expected higher in soils developed in Meghna alluvium. The non-exchangeable pool is also higher in calcareous soils than the acidic soils.

The ratio of HNO_3 -extractable K to total K presented in Table 4 suggests that the soils of the Meghna alluvium (Brahmanbaria-5, Senbag-6) have lower amounts of K in micas and a greater proportion in forms that are released more slowly (i.e., feldspars) compared to the soils of the Ganges alluvium. The X-ray analysis (Table 2) also suggested the loss of K from micas resulting in formation of more vermiculite in the acidic Meghna alluvium.

Table 4. Status of total K and nitric acid extractable K for selected soil horizons.

Site Name	Horizon	g kg ⁻¹				
		Total K	HNO ₃ Extractable K	Exchangeable K	Non-exchangeable K	HNO ₃ - Extractable K to Total K Ratio
Tala-2	Ap1	21.9	18.7	0.12	18.6	0.86
	Ap2	21.9	21.0	0.16	20.8	0.96
	Bw3	23.2	20.7	0.16	20.5	0.89
Tala-3	Ap1	19.5	12.1	0.08	12.0	0.62
	Ap2	20.1	11.9	0.08	11.8	0.59
	Bw2	19.9	13.3	0.04	13.3	0.67
Paba-4	Ap1	22.6	16.6	0.16	16.5	0.74
	Ap2	22.4	21.5	0.16	21.4	0.96
	2Bw1b	24.9	23.5	0.23	23.2	0.94
B.Barria-5	Ap1	17.7	5.6	0.04	5.6	0.32
	Ap2	17.7	5.7	0.04	5.7	0.32
	Bw4	21.4	7.7	0.04	7.7	0.36
	Bw5	22.1	7.3	0.04	7.3	0.33
Senbag- 6	Ap1	15.8	2.0	0.04	1.9	0.13
	Ap2	15.9	2.2	0.00	2.2	0.14
	Bw3	20.2	10.7	0.04	10.7	0.53

CATION EXCHANGE CAPACITY OF THE STUDY SOILS IN REDUCED AND OXIDIZED CONDITIONS

Cation exchange capacity and exchangeable K are important tools to assess plant-available K. Soils under study are from rice fields and undergo flooding for several months each year, so it is useful to observe the charge characteristics of the soils under contrasting oxidized and reduced conditions.

Readily plant-available K comes from two sources, exchangeable K and soluble K. The exchangeable form of soil K is exchangeable with other cations and is in dynamic equilibrium with solution phase K. Commonly, the quantity of exchangeable K is much greater than the solution phase of K. The quantity of exchangeable K is given in Table 5 for the horizons that were studied for CEC in oxidized and reduced conditions. Additional exchangeable K data are included in Appendix A. Results indicate that exchangeable K is greater in soils developed from Ganges alluvium than in Meghna alluvium.

The CEC of the oxidized soils ranged from 4.1 to 26.8 $\text{cmol}(+) \text{kg}^{-1}$ for the surface and subsurface soils, while the CEC of the same horizons when reduced ranged from 2.4 to 26.1 $\text{cmol}(+) \text{kg}^{-1}$ (Table 5). The average CEC of these soils in oxidized condition was 14.6 $\text{cmol}(+) \text{kg}^{-1}$ and that in reduced condition was 12.2 $\text{cmol}(+) \text{kg}^{-1}$. Although both sets of CEC data tended to be lower for the soils with lower pH and was higher for the soils with higher pH, the relationship between the soil clay content and CEC was more apparent. Since CEC increases with an increase in layer charge, a greater clay content results in more layer charge per unit of soil. Regression analysis for total

clay with CEC_{ox} (Fig. 4) and total clay vs. CEC_{red} (Fig. 5) indicated significant relationships exist (r^2 for clay vs. CEC_{ox} , 0.719 and r^2 for clay vs. CEC_{red} , 0.828). The r^2 values were significant at the 95% confidence level.

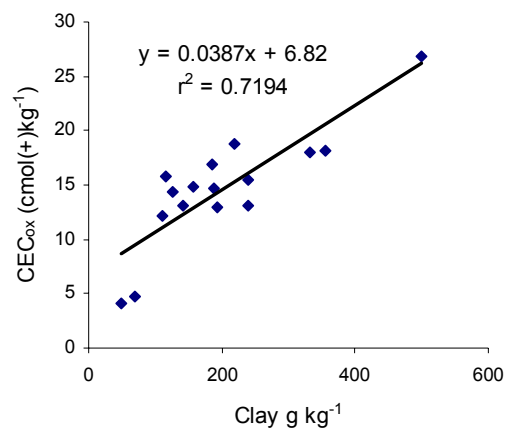


Fig. 4. The relationship of CEC of the oxidized soils to clay content.

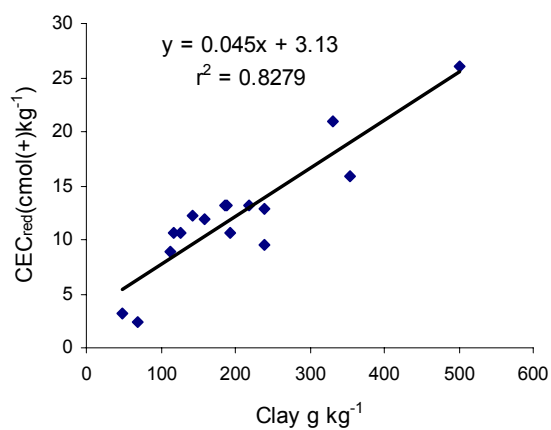


Fig. 5. The relationship of CEC of the reduced soils to clay content.

A comparison of the CEC values in oxidized and reduced conditions (Table 5) suggests that the soils generally exhibit lower CEC when reduced. To statistically confirm this, the data were subjected to a paired comparison analysis of CEC in oxidized condition vs. CEC in reduced condition. The statistical analysis showed that the mean decrease in CEC upon reduction was $2.43 \text{ cmol}(+) \text{ kg}^{-1}$, had a standard error of 0.5739, and that the decrease was statistically significant at the 99% confidence level ($p = 0.003$, $n = 16$).

Results of this CEC study were somewhat unexpected. The literature that was reviewed indicated that, upon reduction, the Fe^{3+} in clay octahedral layers is reduced to Fe^{2+} , increasing the layer charge of the clay. Surface charge of a soil in a reduced condition is usually greater than in an oxidized condition (Stucki and Roth, 1977; Stucki et al., 1984b; Komadel et al., 1995), but the data in Table 5 showed the study soils had lower CEC in the reduced condition. Further review of the literature recovered an article by Stucki and Huo (1996) where they observed the same results as obtained in this study. Apparently, increasing the layer charge upon reduction of octahedral Fe^{3+} results in clay layer collapse, trapping cations in the interlayer, and thus in less exchangeable cations including K^+ .

Table 5. Exchangeable K and cation exchange capacity (CEC) of selected soil horizons in reduced and oxidized conditions.

Site	Depth	Total clay	Exchangeable K in oxidized condition	CEC in oxidized condition	CEC in reduced condition
	cm	g/kg	-----	cmole(+) kg ⁻¹ soil	-----
Tala-2	0-7	189	0.3	14.7	13.1
	7-10	193	0.4	12.9	10.7
	38-68	218	0.4	18.8	13.1
Tala-3	0-6	239	0.2	15.5	9.5
	6-14	240	0.2	13.1	12.9
	30-40	127	0.1	14.4	10.6
Paba-4	0-10	332	0.4	18.0	21.0
	10-19	355	0.4	18.1	15.8
	55-76	500	0.6	26.8	26.1
B.Barria-5	0-8	142	0.1	13.1	12.3
	8-14	158	0.1	14.8	11.9
	44-78	117	0.1	15.8	10.6
	78-100	186	0.1	16.9	13.1
Senbag-6	0-10	49	0.1	4.1	3.2
	10-25	69	0.0	4.8	2.4
	42-52	112	0.1	12.2	8.9

ADSORPTION OF K IN OXIDIZED AND REDUCED SOILS

Potassium fixation and release play an important role in agriculture and K release and fixation mechanisms are generally affected by the nature of soil colloids, wetting and drying, lime content and Fe content of the soil (Sparks, 2001). However, mechanisms governing the fixation and release of K^+ in flooded soils are still not well understood. Therefore, the adsorption of K from solution by selected surface soils under both oxidized and reduced conditions was studied.

Three surface soils were selected from different sites, one with an acidic pH (Senbag-6) and two (Tala-3 and Paba-4) with a moderately alkaline reaction. In the first effort, when high concentration rates of K were added, the soils exhibited very little difference to added K (Figs. 6, 7, and 8). The difference in the adsorption or release was not clear. Additional adsorption isotherms were developed for the soils at much lower rates of K addition, because soils quickly became saturated when the higher rates of K were added. The rates of K addition used to develop Fig. 6 through 8 corresponded to the percent CEC of these soils, i.e., enough K to equal 0%, 2%, 5%, 10%, 20%, 50%, 100%, or 150% of the soils' CEC.

When lower rates (0, 2.92, 7.30, and 14.6 mmol K kg⁻¹) of K were added to soils, differences in release and adsorption at equilibrium of K were noted (Figs. 9, 10, and 11). All soils adsorbed more K from solution in oxidized than in reduced conditions. Also, the concentration of equilibrium K in solution was higher for the acidic soil in both oxidized and reduced conditions than for the soils of alkaline pH ($p < 0.05$ by ANOVA), while the behavior of the alkaline soils (Fig. 9 and 10) were similar.

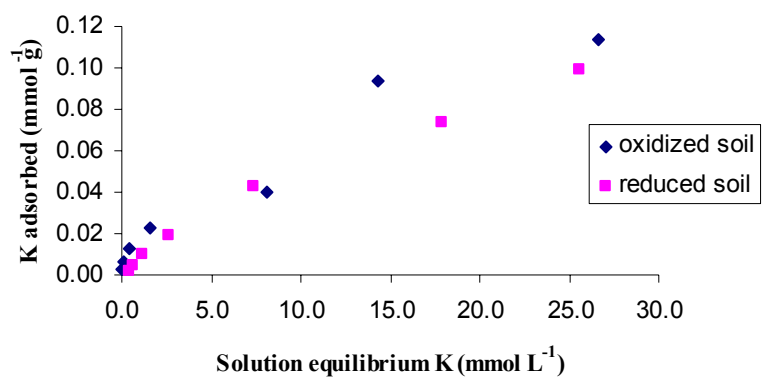


Fig. 6. Adsorption isotherm for K for the Ap1 horizon of Tala-3.

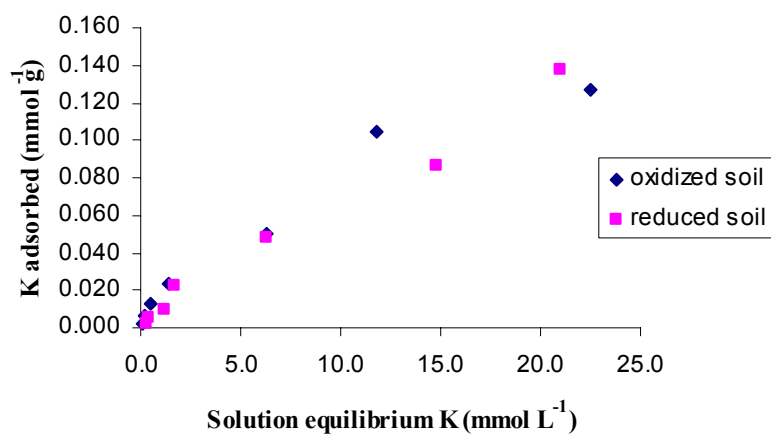


Fig. 7. Adsorption isotherm for K for the Ap1 horizon of Paba-4.

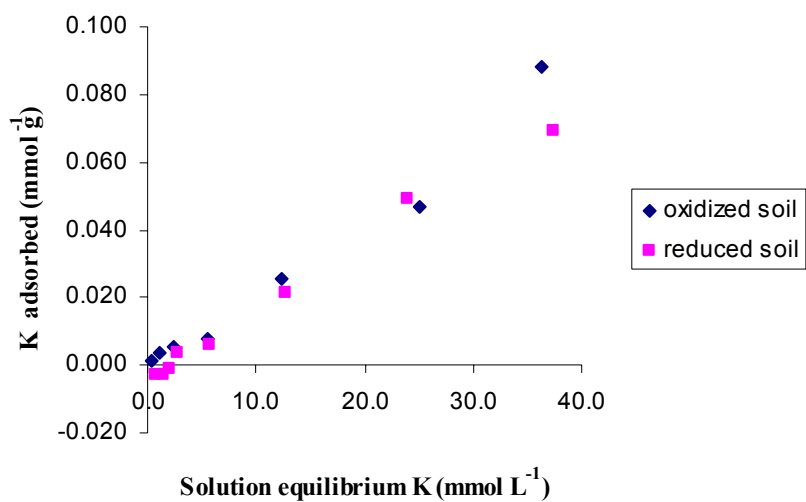


Fig. 8. Adsorption isotherm for K for the Ap1 horizon of Senbag-6.

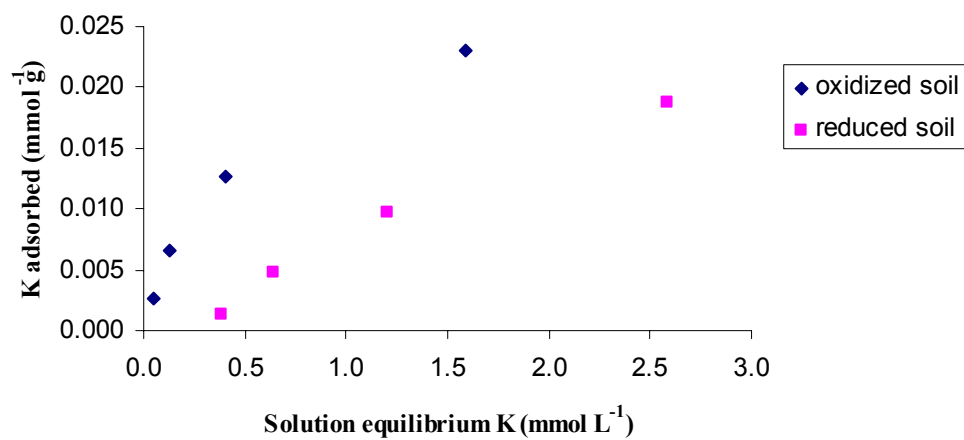


Fig. 9. Adsorption isotherm for K for the Ap1 horizon of Tala-3.

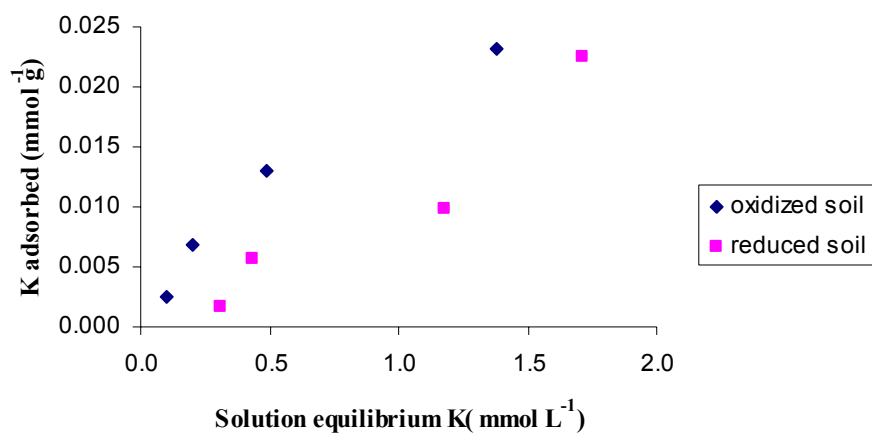


Fig. 10. Adsorption isotherm for K for the Ap1 horizon of Paba-4.

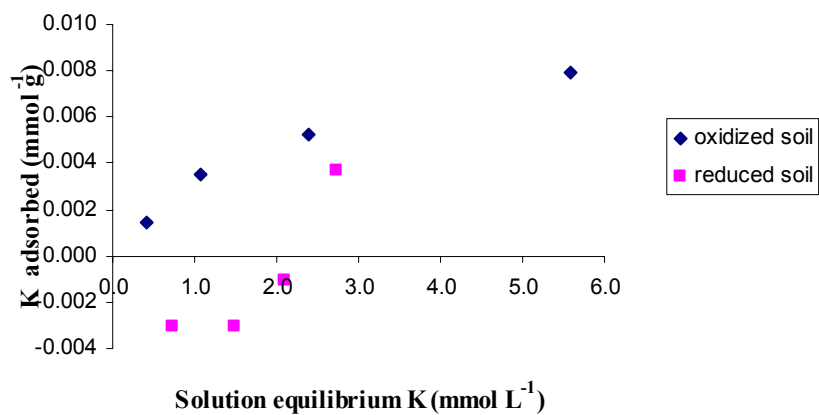


Fig. 11. Adsorption isotherm for K for the Ap1 horizon of Senbag-6.

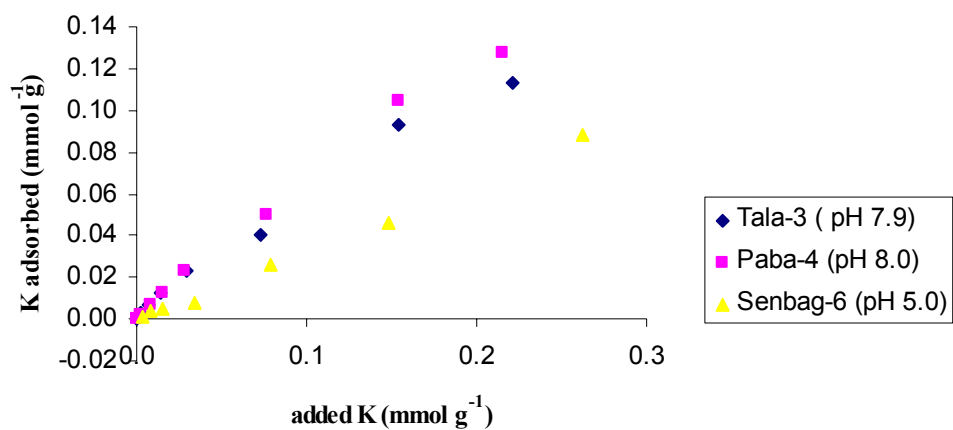


Fig. 12. Comparison of the amount of K adsorbed in oxidized condition by three study soils expressed as a function of added K per quantity of clay.

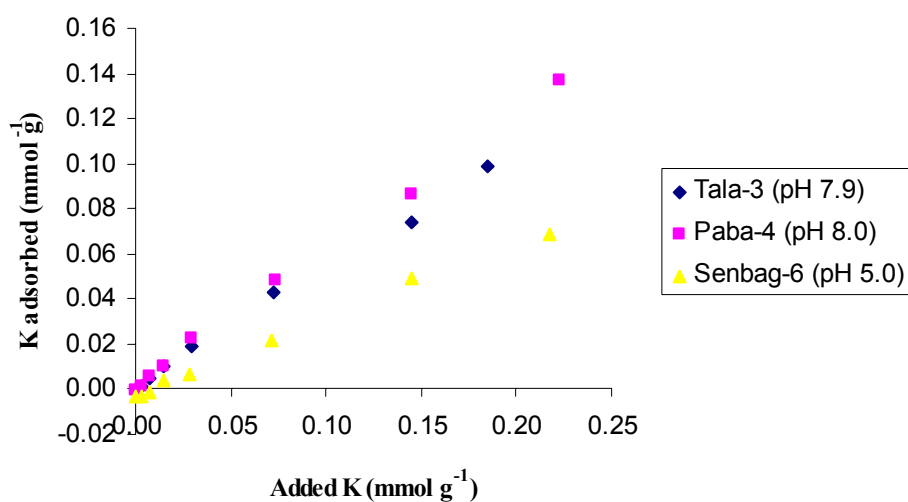


Fig. 13. Comparison of the amount of K adsorbed in reduced condition by three study soils expressed as a function of added K per quantity of clay.

Considering the low concentration points of added K, it was observed that the alkaline soils (Tala-3 and Paba-4) adsorbed slightly more K ($0.124 \text{ mmol g}^{-1}$ for the soil with pH 8.0 and $0.113 \text{ mmol g}^{-1}$ for the soil with pH 7.9) than the acidic soil (Senbag-6) ($0.088 \text{ mmol g}^{-1}$) in the oxidized condition (Fig 12). Potassium adsorption in reduced condition was also a little higher ($0.127 \text{ mmol g}^{-1}$ for the soil with pH 8.0 and $0.113 \text{ mmol g}^{-1}$ for the soil with pH 7.9) for both alkaline soils than the acid soil ($0.069 \text{ mmol g}^{-1}$) (Fig. 13). The ANOVA test was also significant in reduced condition ($\alpha= 0.05$). The relationship is significant at 95% confidence level. The overall average adsorption was slightly higher in calcareous soils ($0.328 \text{ mmol g}^{-1}$) than the acidic soil ($0.304 \text{ mmol g}^{-1}$) (Figs. 12 and 13).

Negative adsorption (release) of K was observed when adsorption isotherms were constructed with just the first few quantities of added K (Figs. 14, 15, 16) which was hardly visible when considering all eight concentration points. Desorption was more pronounced in the acidic soil (Fig. 16) than the two alkaline soils (Figs. 14, 15), and the Paba-4 soil was the only alkaline soil that showed K release, although the release was at the lowest of concentrations and very small. Release of native K was significant under the reduced condition in the acidic Senbag-6 soil.

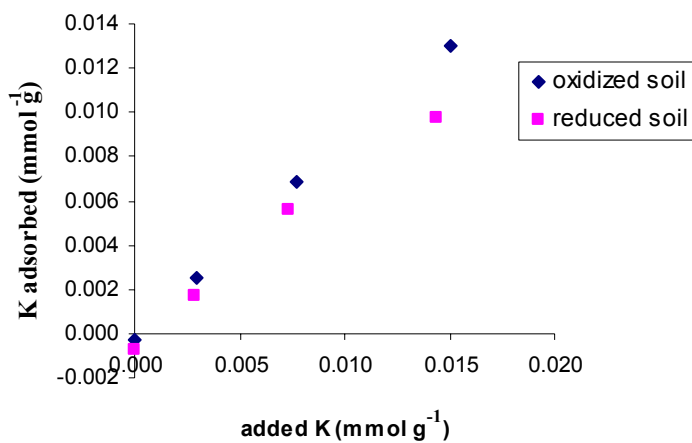


Fig. 14. Potassium isotherm for the Paba-4 soil in oxidized and reduced conditions and expressed as a function of added K per quantity of clay.

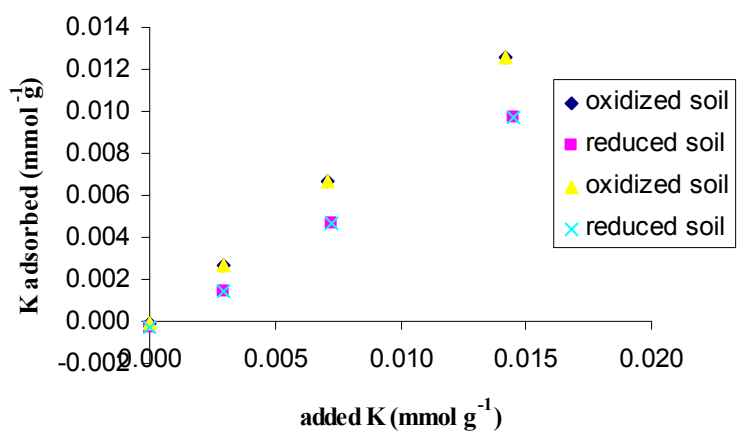


Fig. 15. Potassium isotherm for the Tala-4 soil in oxidized and reduced conditions and expressed as function of added K per quantity of clay.

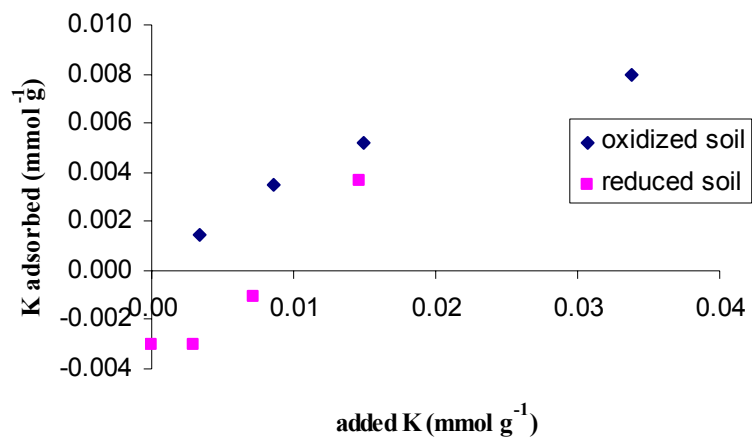


Fig. 16. Potassium isotherm for the Senbag-6 soil in oxidized and reduced conditions and expressed as function of added K per quantity of clay.

The diagonal straight lines mmol g^{-1} in Figs. 17 to 20 are hypothetical lines which were plotted assuming that the amount of K in equilibrium solution was equal to the amount of K added to the soil. This line allows a comparison of whether there is a net release of native K, if the analytically determined concentration is above the line, or adsorption of added K if the analytical concentration is below the straight line. Release of native K was higher in the reduced condition than in the oxidized condition in acidic soil (Figs. 17 and 18). A similar trend was observed with alkaline soil (Figs. 19 and 20). The status of equilibrium K was lower in H_2O than the $\text{NH}_4\text{OAC} + \text{H}_2\text{O}$ solution. This is because H_2O is extracting only the water soluble K in the solution while NH_4OAC is extracting the exchangeable and water soluble form of K.

The calcareous (Tala-3) soil exhibited slightly more adsorption than the acidic soil (Senbag-6). This calcareous soil is higher in mica, and have higher CEC ($18 \text{ cmol (+) kg}^{-1}$) and clay content (335 g kg^{-1}) compare to the acidic soil (CEC of $4.1 \text{ cmol (+) kg}^{-1}$; clay content of 49 g kg^{-1}) which might have resulted in more adsorption. In the acidic soils, hydroxy-Al compounds might block exchange sites of the clay layer, resulting in less adsorption. Less adsorption in the reduced condition could also be due to the increase in Fe^{2+} which would compete with K^+ for the exchange sites on the clay layer (Personal comment from Dr. Richard H. Loeppert). Also an increased layer charge in the reduced condition could influence the strength of cation retention on exchange sites and might have restricted further cation exchange. The relatively small adsorption or release of K in both calcareous or acidic soils in oxidized and reduced conditions may

be due to the presence of illitic material for which the retention and release of K is not strongly impacted by added K^+ . These soils are relatively rich in K bearing minerals.

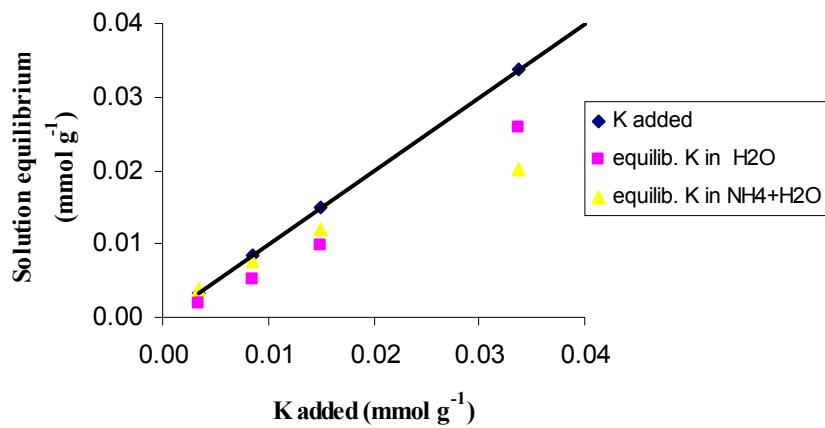


Fig. 17. Equilibrium K status in different extraction solutions of Senbag-6 soil in the oxidized condition.

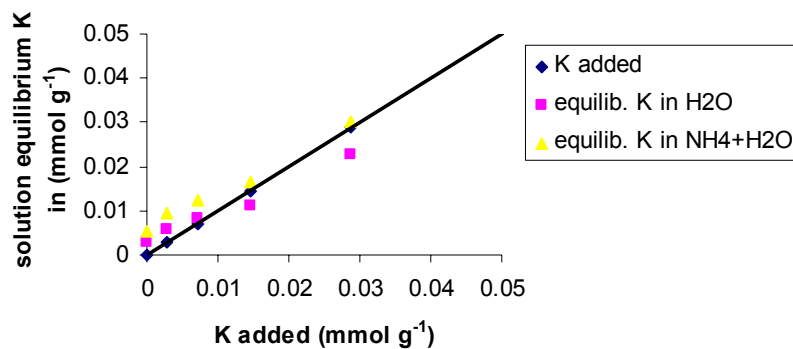


Fig. 18. Equilibrium K status in different extraction solutions of Senbag-6 soil in the reduced condition.

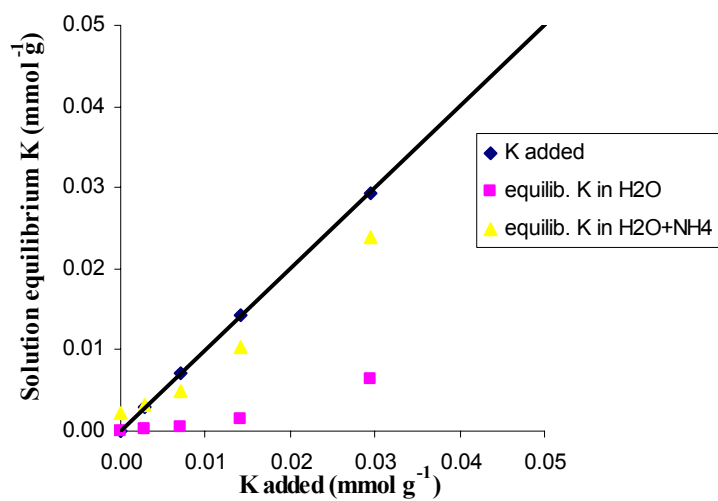


Fig. 19. Equilibrium K status in different extraction solutions of Tala-3 soil in the oxidized condition.

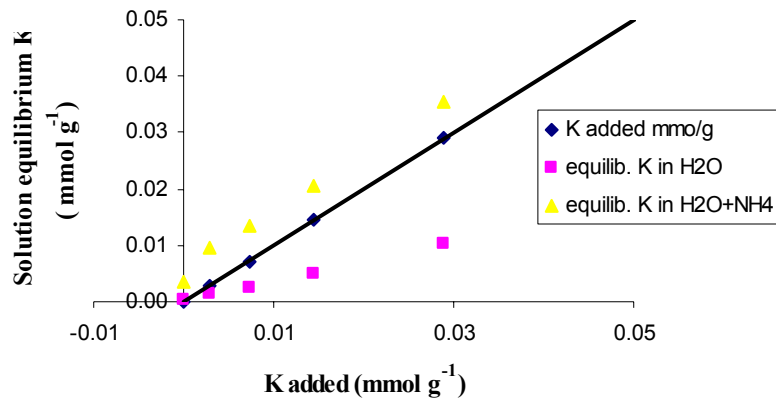


Fig. 20. Equilibrium K status in different extraction solutions of Tala-3 soil in the reduced condition.

CHAPTER V

CONCLUSIONS

The soils used in this study are from two different agro ecological zones, i.e., Ganges and Meghna alluviums. Both alluviums are dominated by micas and their weathering products, including vermiculite and are high in K. All soil horizons examined has measurable quantities of kaolinite which was believed to be inherited in the parent alluvium rather than the result of pedogenesis. The quantity of vermiculite in the soils was greatest in the acid soils developed in Meghna alluvium and likely is the result of acidic weathering. Soils derived from Ganges alluvium are alkaline (pH is higher) whereas the soils from Meghna are acidic in nature.

Clay content has an important role in regulating the total K of soils. More total K was present in soils from the Ganges alluvium compare to the soils from Meghna alluvium. This is attributed to the higher amount of mica present in the Ganges alluvium than the Meghna alluvium. It was also evident that the soils from Ganges alluvium which have higher total K values also have a higher clay content. Nitric acid extractable-K was higher in the alkaline soils developed in Ganges alluvium than the acidic soils developed in Meghna alluvium. The ratio of nitric acid extractable K to total K is lower in Meghna alluvium than the Ganges alluvium due to probable loss of K from mica (transformation of mica to 2:1 expansible layer silicates), which suggests that Meghna alluvium soils are more weathered soils than those from Ganges alluvium.

Lower CEC in reduced condition compared to the CEC in oxidized condition for both alluviums indicated less available K or other exchangeable cations during flooded or reduced conditions. This is an important factor for rice cultivation in Bangladesh, because rice plants grow in submerged or flooded condition. These soils did not show a significant response to added K under both oxidized and reduced conditions suggesting that exchangeable K^+ pool, non-exchangeable K pool or other K pools were replenishing the depleted solution K pools.

FUTURE RESEARCH

Effects of variation in soil moisture regimes on K availability and rice production have received little attention (Dobermann et al., 1998). Further study to investigate the response of rice to added K fertilizer by adding a specific K isotope could provide insight into fate of K added to soils. A more detailed understanding and development of simple models to describe the recycling of K from crop residues would help in recommendations of fertilizer application rates. Such research could provide basic information about how different straw management and tillage practice influence the amount of nutrient recycled and dynamics of the nutrient release (Dobermann et al., 1998).

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APPENDIX A**PHYSICAL AND CHEMICAL CHARACTERISTICS DATA FOR
THE FIVE STUDY SOILS**

APPENDIX B

FIELD DESCRIPTION FOR THE FIVE STUDY SOILS

SOIL SERIES: GRAY CALCAREOUS FLOODPLAIN SOIL PEDON: S05BA-002-000 COUNTY:
 PEDON CLASSIFICATION: FLUVAQUENTIC ENDOAQUEPT; FINE-SILTY, PARAMICACEOUS, CALCAREOUS, ISOHYPERThERMIC
 LOCATION: TALA AT THE RESEARCH SITE OF SAJID RAHMAN.
 LANDFORM: MEDIUM HIGHLAND ELEVATION (M): SLOPE: 0% SLOPE ASPECT:
 PARENT MATERIALS: ALLUVIUM FORMATION: GANGES ALLUVIUM (HOLOCENE)
 TOPOGRAPHY: NEARLY LEVEL DRAINAGE: POORLY DRAINED LANDUSE: RICE PADDY
 COLLECTORS: HALLMARK, SHOAIB, RAHMAN, TARIKUL DATE: 03/06/05

HORIZON	DEPTH (CM)	SOIL DESCRIPTION (COLORS FOR MOIST SOIL UNLESS STATED)
AP1	0-7	DARK GRAYISH BROWN (2.5Y 4/2) SILT LOAM; COMMON FINE FAINT LIGHT OLIVE BROWN (2.5Y 5/4) MOTTLES; STRUCTURELESS MASSIVE; FRIABLE; COMMON PORES; VERY MAN FINE AND MEDIUM ROOTS; UPPER PORTION PUDDLED; ROOTS ARE MOSTLY FOUND IN THIS LAYER; NO REACTION WITH AA-DIPYRIDYL; SLIGHTLY EFFERVESCENT; ABRUPT WAVY BOUNDARY.
AP2	7-10	VERY DARK GRAY (5GY 3/0) SILT LOAM; COMMON FINE DISTINCT DARK YELLOWISH BROWN (10YR 4/4) MOTTLES; STRUCTURELESS MASSIVE; FIRM; NO PORES; COMMON MEDIUM ROOTS; REDOX FEATURES ARE AROUND MEDIUM SIZED ROOTS; COMPACTED LAYER DUE TO PLOWING; POSITIVE REACTION TO AA-DIPYRIDYL; STRONGLY EFFERVESCENT; ABRUPT WAVY BOUNDARY.
AP3	10-15	DARK GRAYISH BROWN (2.5Y 4/2) SILT LOAM; COMMON MEDIUM DISTINCT GRAY (2.5Y 5/1) MOTTLES; STRUCTURELESS MASSIVE; FIRM; NO PORES; FEW FINE AND VERY FINE ROOTS; COMMON FINE AND MEDIUM BROWN (7.5YR 4/4) FE-MN STAINS ALONG ROOT CHANNELS; DISTURBANCE IS WEIGHT PACKING TO DESTROY STRUCTURE; NO REACTION WITH AA-DIPYRIDYL; STRONGLY EFFERVESCENT; CLEAR WAVY BOUNDARY.
BW1	15-21	DARK GRAYISH BROWN (2.5Y 4/2) SILT LOAM; FEW MEDIUM FAINT GRAYISH BROWN (2.5Y 5/2) MOTTLES; WEAK MEDIUM SUBANGULAR BLOCKY STRUCTURE; FRIABLE; COMMON FINE AND MEDIUM PORES; FEW VERY FINE ROOTS; COMMON FINE AND MEDIUM BROWN (7.5YR 4/4) FE-MN STAINS ALONG ROOT CHANNELS; FEW SHELL FRAGMENTS; NO REACTION TO AA-DIPYRIDYL; STRONGLY EFFERVESCENT; GRADUAL SMOOTH BOUNDARY.
BW2	21-38	DARK GRAYISH BROWN (2.5Y 4/2) SILT LOAM; COMMON MEDIUM PROMINENT BROWN (7.5YR 4/4) MOTTLES; WEAK COARSE PRISMATIC PARTING TO WEAK MEDIUM SUBANGULAR BLOCKY STRUCTURE; FRIABLE; COMMON MEDIUM PORES; FEW FINE ROOTS; GRAY (2.5Y 5/1) GLEYANS ON VERTICAL PED FACES; FEW SHELL FRAGMENTS; NO REACTION TO AA-DIPYRIDYL; STRONGLY EFFERVESCENT; GRADUAL SMOOTH BOUNDARY.
BW3	38-68	DARK GRAYISH BROWN (2.5Y 4/2) SILT LOAM; COMMON MEDIUM PROMINENT STRONG BROWN (7.5YR 4/6) MOTTLES; MODERATE COARSE PRISMATIC PARTING TO MODERATE COARSE SUBANGULAR BLOCKY STRUCTURE; FRIABLE; COMMON MEDIUM PORES; FEW FINE ROOTS; FEW GRAY (2.5Y 5/1) GLEYANS ON VERTICAL PED FACES; COMMON SHELL FRAGMENTS; COMMON FINE AND MEDIUM BROWN (7.5YR 4/4) FE-MN STAINS ALONG ROOT CHANNELS; NO REACTION TO AA-DIPYRIDYL; SOME PEDOTUBULES OF 2-3MM DIAMETER LINED WITH 7.5YR 4/4 IRON CONCENTRATIONS; STRONGLY EFFERVESCENT; CLEAR SMOOTH BOUNDARY.
AB	68-88	DARK GRAY (2.5Y 4/1) SILTY CLAY LOAM; COMMON MEDIUM PROMINENT DARK YELLOWISH BROWN (10YR 4/4) MOTTLES; STRUCTURELESS STRUCTURE; FIRM; NO PORES; NO ROOTS; FEW SHELL FRAGMENTS; NO REACTION TO AA-DIPYRIDYL; FEW PEDOTUBULES OF 2-3 MM DIAMETER LINED WITH 7.5YR 4/4 IRON CONCENTRATIONS; SLIGHTLY EFFERVESCENT.

REMARKS: C HORIZON SEEMS TO BE THE CAPILLARY FRINGE FROM WATERTABLE THAT IS AT 88 CM DEPTH.

SOIL SERIES: GRAY CALCAREOUS FLOODPLAIN SOIL PEDON: S058A-003-000 COUNTY:
 PEDON CLASSIFICATION: AERIC ENDOAQUEPT; COARSE-SILTY, PARAMICAEOUS, CALCAREOUS, ISOHYPERTHERMIC
 LOCATION: NEAR JESSORE IN A FALLOW FIELD IDENTIFIED BY KUMAR BHANDERE.
 LANDFORM: MEDIUM HIGHLAND ELEVATION (M): SLOPE: 0% SLOPE ASPECT:
 PARENT MATERIALS: ALLUVIUM FORMATION: GANGES ALLUVIUM (HOLOCENE)
 TOPOGRAPHY: NEARLY LEVEL DRAINAGE: SOMEWHAT POORLY DRAINED LANDUSE: FALLOW
 COLLECTORS: HALLMARK, SHOAIB, PANAULLA, KUMAR AND TARIKUL DATE: 03/07/05

HORIZON	DEPTH (CM)	SOIL DESCRIPTION (COLORS FOR MOIST SOIL UNLESS STATED)
AP1	0-6	DARK GRAYISH BROWN (2.5Y 4/2) SILT LOAM; WEAK FINE AND MEDIUM SUBANGULAR BLOCKY STRUCTURE; FRIABLE; COMMON FINE AND MEDIUM PORES; COMMON FINE ROOTS; VERY SLIGHTLY EFFERVESCENT; ABRUPT WAVY BOUNDARY.
AP2	6-14	DARK GRAYISH BROWN (2.5Y 4/2) SILT LOAM; STRUCTURELESS MASSIVE; FIRM; VERY FEW FINE PORES; FEW FINE ROOTS; FEW FEW DARK YELLOWISH BROWN (10YR 4/4) FE-MN STAINS IN PORES; VERY SLIGHTLY EFFERVESCENT; ABRUPT WAVY BOUNDARY.
BW1	14-30	LIGHT OLIVE BROWN (2.5Y 5/3) SILT LOAM; FEW FINE FAINT GRAY (5Y 5/1) MOTTLES; WEAK MEDIUM SUBANGULAR BLOCKY STRUCTURE; FRIABLE; FEW FINE ROOTS; FEW MANY BLACK CONCRETIONS; VIOLENTLY EFFERVESCENT; GRADUAL SMOOTH BOUNDARY.
BW2	30-40	GRAYISH BROWN (2.5Y 5/2) SILT LOAM; FEW FINE DISTINCT DARK YELLOWISH BROWN (10YR 4/4) MOTTLES; WEAK MEDIUM AND COARSE SUBANGULAR BLOCKY STRUCTURE; VERY FRIABLE; FEW FINE ROOTS; FEW MANY BLACK CONCRETIONS; VIOLENTLY EFFERVESCENT.
C	100-110	GRAYISH BROWN (2.5Y 5/2) SILT LOAM; STRUCTURELESS MASSIVE; VERY FRIABLE; FEW FINE ROOTS.

REMARKS: WATER TABLE WAS AT 40 CM; VERY FEW SNAIL SHELL FRAGMENTS THROUGHOUT BW HORIZONS; SOIL SHOULD BE COARSE-SILTY; MICA VERY EVIDENT IN THE SAND FRACTION; IN ADJACENT RICE PADDY, POSITIVE TEST FOR AA-DIPYRIDYL IN LOOSE, PLOWED ZONE BUT GLEYED MATERIAL JUST BELOW THE COMPACTED ZONE DID NOT GIVE POSITIVE TEST; EARTHWORMS FOUND IN UPPER THREE HORIZONS; THE A HORIZON HAS BEEN MINED FROM THE SITE; AT LEAST THREE LEVELS IN RICE FIELDS BESIDE FALLOW FIELD WERE EVIDENT. ONE RICE FIELD WAS AT THE SAME LEVEL AS FALLOW FIELD. WE WENT ACROSS THE ROAD TO A SITE THAT WAS FALLOW AND ABOUT 30 CM HIGHER ANTICIPATING THAT IT WOULD HAVE MORE ORGANIC MATTER. FROM A PIT IT WAS EVIDENT THAT THE AP HAD LOW ORGANIC MATTER AND BRICK FRAGMENTS AND DISRUPTED BEDDING PLANES AT BASE ABOVE A BURIED A. APPARENTLY, THE FIELD HAD BEEN RAISED ABOUT 30 CM; THEREFORE, WE DID NOT DESCRIBE OR SAMPLE IN DETAIL.

SOIL SERIES: GRAY CALCAREOUS FLOODPLAIN SOIL PEDON: S05BA-004-000 COUNTY:
 PEDON CLASSIFICATION: VERTIC ENDOAQUEPT; FINE, SMECTITIC, NONACID, ISOHYPERThERMIC
 LOCATION: NORTH 24 DEG 23.718' BY EAST 88 DEG 31.778'. SITE P84 IN ARSENIC STUDY
 IN 2002 IN PABA.
 LANDFORM: MEDIUM HIGHLAND ELEVATION (M): 25 SLOPE: 0% SLOPE ASPECT:
 PARENT MATERIALS: ALLUVIUM FORMATION: GANGES ALLUVIUM (HLOCENE)
 TOPOGRAPHY: NEARLY LEVEL DRAINAGE: SOMEWHAT POORLY DRAINED LANDUSE: FALLOW
 COLLECTORS: HALLMARK, PANAUULLAH, JIBER, TARIKUL DATE: 03/08/05

HORIZON	DEPTH (CM)	SOIL DESCRIPTION (COLORS FOR MOIST SOIL UNLESS STATED)
AP1	0-10	DARK GRAYISH BROWN (2.5Y 4/2) SILTY CLAY LOAM, LIGHT OLIVE BROWN (2.5Y 5/3) DRY; FEW FINE DISTINCT YELLOWISH BROWN (10YR 5/6) MOTTLES; STRUCTURELESS MASSIVE; VERY HARD; FEW FINE AND MEDIUM PORES; FEW FINE AND MEDIUM ROOTS; FEW FEW YELLOWISH BROWN (10YR 5/6) FE-MN STAINS ALONG ROOT CHANNELS; FEW YELLOWISH BROWN (10YR 5/6) FE-MN STAINS IN PORES; COMMON SHELL FRAGMENTS; STRONGLY EFFERVESCENT; ABRUPT SMOOTH BOUNDARY.
AP2	10-19	VERY DARK GRAYISH BROWN (2.5Y 3/2) SILTY CLAY LOAM; FEW FINE DISTINCT YELLOWISH BROWN (10YR 5/6) MOTTLES; STRUCTURELESS MASSIVE; VERY HARD; VERY FEW FINE PORES; FEW FINE ROOTS; FEW FEW YELLOWISH BROWN (10YR 5/6) FE-MN STAINS ALONG ROOT CHANNELS; FEW YELLOWISH BROWN (10YR 5/6) FE-MN STAINS IN PORES; COMMON SHELL FRAGMENTS; STRONGLY EFFERVESCENT; ABRUPT SMOOTH BOUNDARY.
AP3	19-29	GRAYISH BROWN (2.5Y 5/2) SILTY CLAY LOAM; FEW FINE FAINT YELLOWISH BROWN (10YR 5/4) MOTTLES; STRUCTURELESS MASSIVE; FIRM; VERY FEW FINE PORES; FEW FINE ROOTS; COMMON DARK GRAYISH BROWN (2.5Y 4/2) COATINGS ON VERTICAL PED FACES; STRONGLY EFFERVESCENT; ABRUPT SMOOTH BOUNDARY.
2AB	29-55	DARK GRAY (2.5Y 4/1) SILTY CLAY; MANY FINE DISTINCT LIGHT OLIVE BROWN (2.5Y 5/4) MOTTLES; MODERATE MEDIUM ANGULAR BLOCKY PARTING TO MODERATE FINE ANGULAR BLOCKY STRUCTURE; FIRM; FEW FINE PORES; FEW FINE ROOTS; COMMON DARK GRAY (2.5Y 4/1) PRESSURE FACES; SOME MATERIAL OF ABOVE HORIZON ALONG MAJOR VERTICAL STRUCTURE UNITS (CRACK IN-FILLINGS); NONCALCAREOUS; GRADUAL SMOOTH BOUNDARY.
2BW1B	55-76	DARK GRAYISH BROWN (2.5Y 4/2) SILTY CLAY; COMMON FINE DISTINCT STRONG BROWN (7.5YR 5/6) MOTTLES; MODERATE MEDIUM ANGULAR BLOCKY PARTING TO MODERATE FINE ANGULAR BLOCKY STRUCTURE; FIRM; VERY FEW FINE PORES; VERY FEW FINE ROOTS; MANY DARK GRAY (2.5Y 4/1) PRESSURE FACES; SEEMS TO HAVE PRESSURE GENERATED CLAY CUTANS ON SOME VERTICAL SURFACES; NONCALCAREOUS; CLEAR SMOOTH BOUNDARY.
2BW2B	76-92	GRAYISH BROWN (2.5Y 5/2) SILTY CLAY LOAM; COMMON FINE FAINT LIGHT OLIVE BROWN (2.5Y 5/4) MOTTLES; MODERATE MEDIUM ANGULAR BLOCKY STRUCTURE; FRIABLE; COMMON FINE AND MEDIUM PORES; VERY FEW FINE ROOTS; COMMON SHELL FRAGMENTS; COMMON GRAY (2.5Y 5/1) GLEYANS ON VERTICAL PED FACES; SLIGHTLY EFFERVESCENT.
3A'B	92-102	DARK GRAY (2.5Y 4/1) SILTY CLAY; COMMON FINE FAINT LIGHT OLIVE BROWN (2.5Y 5/6) MOTTLES; MODERATE MEDIUM ANGULAR BLOCKY STRUCTURE; VERY FIRM; FEW FINE AND MEDIUM PORES; NONCALCAREOUS.

REMARKS: WATER TABLE PERCHED JUST ABOVE THE HORIZON AT 92 CM. UPPER THREE HORIZONS (AP1, AP2, AP3) WERE COMPACT AND MASSIVE; THE UPPER TWO HORIZONS WERE DRY, AND THE SOIL WAS CRACKED IN A HEXAGONAL PATTERN ABOUT 30 CM ACROSS AND TO THE BURIED SOIL BELOW. AT THE SURFACE CRACKS WERE 2-3 CM WIDE AND EXTENDED TO A DEPTH OF ABOUT 25 CM. AT TIMES, CRACKS EXTEND INTO THE BURIED SOIL AS AP HORIZON INFILLING OF CRACKS WAS NOTED IN THE BURIED SOIL.

SOIL SERIES: GRAY NONCALCAREOUS FLOODPLAIN SOILS PEDON: S05BA-005-000 COUNTY:
 PEDON CLASSIFICATION: AERIC FLUVAQUENTS; FINE-SILTY, PARAMICACEROUS, NONACID, ISOHYPERThERMIC
 LOCATION: NEAR BHARAMANBARIA
 LANDFORM: MEDIUM LOWLAND ELEVATION (M): SLOPE: 0% SLOPE ASPECT:
 PARENT MATERIALS: ALLUVIUM FORMATION: MANGAHNAN RIVER ALLUVIUM
 TOPOGRAPHY: NEARLY LEVEL DRAINAGE: POORLY DRAINED LANDUSE: RICE PADDY
 COLLECTORS: HALLMARK, PANAULLA, AND TARIKUL DATE: 03/10/05

HORIZON	DEPTH (CM)	SOIL DESCRIPTION (COLORS FOR MOIST SOIL UNLESS STATED)
AP1	0-8	DARK GRAYISH BROWN (2.5Y 4/2) SILT LOAM, LIGHT YELLOWISH BROWN (2.5Y 6/3) DRY; MANY FINE DISTINCT LIGHT OLIVE BROWN (2.5Y 5/4) MOTTLES; WEAK COARSE SUBANGULAR BLOCKY PARTING TO WEAK FINE SUBANGULAR BLOCKY STRUCTURE; FRIABLE; COMMON FINE AND MEDIUM ROOTS; NONCALCAREOUS; ABRUPT SMOOTH BOUNDARY.
AP2	8-14	VERY DARK GRAYISH BROWN (2.5Y 3/2) SILT LOAM; MANY FINE DISTINCT LIGHT OLIVE BROWN (2.5Y 5/4) MOTTLES; WEAK COARSE SUBANGULAR BLOCKY STRUCTURE; FIRM; COMMON FINE AND MEDIUM PORES; FEW FINE ROOTS; FEW DARK YELLOWISH BROWN (10YR 4/4) FE-MN STAINS ALONG ROOT CHANNELS; HORIZON IS NOT A VERY EFFECTIVELY FORMED PAN; STRUCTURE STILL PRESENT; NONCALCAREOUS; ABRUPT SMOOTH BOUNDARY.
BW	14-23	DARK GRAYISH BROWN (2.5Y 4/2) SILT LOAM; MANY MEDIUM DISTINCT OLIVE BROWN (2.5Y 4/4) MOTTLES; WEAK COARSE SUBANGULAR BLOCKY STRUCTURE; FIRM; FEW FINE PORES; NO ROOTS; FEW FINE LIGHT GRAY (2.5Y 7/1) SILT COATING IN PORES; NONCALCAREOUS; ABRUPT SMOOTH BOUNDARY.
AB	23-28	VERY DARK GRAY (10YR 3/1) SILT LOAM; MANY MEDIUM DISTINCT OLIVE BROWN (2.5Y 4/4) MOTTLES; WEAK COARSE SUBANGULAR BLOCKY STRUCTURE; FIRM; FEW FINE PORES; NO ROOTS; FEW FINE LIGHT GRAY (2.5Y 7/1) SILT COATING IN PORES; NONCALCAREOUS; ABRUPT SMOOTH BOUNDARY.
BW1B	28-44	DARK GRAYISH BROWN (2.5Y 4/2) SILT LOAM; MANY MEDIUM DISTINCT OLIVE BROWN (2.5Y 4/6) MOTTLES; WEAK COARSE SUBANGULAR BLOCKY STRUCTURE; FIRM; FEW FINE PORES; NO ROOTS; COMMON THIN VERY DARK GRAY (2.5Y 3/1) ORGANIC STAINS ON VERTICAL PED FACES; FEW THICK LIGHT GRAY (2.5Y 7/1) SILT COATING IN PORES; NONCALCAREOUS; CLEAR SMOOTH BOUNDARY.
BW2B	44-78	LIGHT OLIVE BROWN (2.5Y 5/3) SILT LOAM; MANY FINE DISTINCT YELLOWISH BROWN (10YR 5/6) AND COMMON MEDIUM DISTINCT GRAY (2.5Y 5/1) MOTTLES; WEAK COARSE PRISMATIC PARTING TO WEAK COARSE SUBANGULAR BLOCKY STRUCTURE; FIRM; FEW FINE PORES; NO ROOTS; FEW THIN VERY DARK GRAY (2.5Y 3/1) ORGANIC STAINS ON VERTICAL PED FACES; NONCALCAREOUS; GRADUAL SMOOTH BOUNDARY.
BW3B?	78-100	GRAY (2.5Y 5/1) SILT LOAM; COMMON MEDIUM DISTINCT LIGHT OLIVE BROWN (2.5Y 5/6) MOTTLES; WEAK COARSE PRISMATIC PARTING TO WEAK COARSE SUBANGULAR BLOCKY STRUCTURE; FIRM; FEW FINE PORES; NO ROOTS; FEW THICK VERY DARK GRAY (2.5Y 3/1) ORGANIC MATTER COATINGS ON VERTICAL PED FACES; COMMON 1-4 CM DIAMETER KROTOVINA INFILLED WITH 2.5Y 3/1 MATERIAL; NONCALCAREOUS.

REMARKS: THE SILT COATINGS IN THE SUBSOIL MAY BE AREAS OF CLAY STRIPPING OR FERROLYSIS;

SOIL SERIES: GRAY NONCALCAREOUS FLOODPLAIN SOIL PEDON: S05BA-006-000 COUNTY:
 PEDON CLASSIFICATION: AERIC ENDOAQUEPTS; COARSE-SILTY, PARAMICACEOUS, NONACID, ISOHYPERThERMIC
 LOCATION: SENBAG SITE S-2. ABOUT 100 M SOUTH OF PUMP.
 LANDFORM: MEDIUM HIGHLAND ELEVATION (M): SLOPE: 0% SLOPE ASPECT:
 PARENT MATERIALS: ALLUVIUM FORMATION: LOWER MANGAHNA ESTUARY ALLUV.
 TOPOGRAPHY: NEARLY LEVEL DRAINAGE: SOMEWHAT POORLY DRAINED LANDUSE: FALLOW
 COLLECTORS: HALLMARK, PANAUULLAH, AND TARIKUL DATE: 03/11/05

HORIZON	DEPTH (CM)	SOIL DESCRIPTION (COLORS FOR MOIST SOIL UNLESS STATED)
AP1	0-10	DARK GRAYISH BROWN (2.5Y 4/2) SILT; COMMON FINE DISTINCT DARK YELLOWISH BROWN (10YR 4/6) MOTTLES; WEAK MEDIUM SUBANGULAR BLOCKY STRUCTURE; FRIABLE; COMMON FINE AND MEDIUM ROOTS; VERY FEW 1-2 CM DIAMETER BRICK FRAGMENTS; NONCALCAREOUS; ABRUPT SMOOTH BOUNDARY.
AP2	10-25	GRAY (2.5Y 5/1) SILT; STRUCTURELESS MASSIVE; FIRM; FEW FINE PORES; VERY FEW FINE ROOTS; COMMON STRONG BROWN (7.5YR 4/6) FE-MN STAINS ON ROCK FRAGMENTS; NONCALCAREOUS; ABRUPT SMOOTH BOUNDARY.
BW1	25-27	YELLOWISH BROWN (10YR 5/6) SILT LOAM; COMMON MEDIUM PROMINENT DARK GRAYISH BROWN (2.5Y 4/2) MOTTLES; WEAK COARSE SUBANGULAR BLOCKY STRUCTURE; FIRM; FEW FINE PORES; VERY FEW FINE ROOTS; FEW BLACK CONCRETIONS; NONCALCAREOUS; ABRUPT SMOOTH BOUNDARY.
BW2	27-42	OLIVE BROWN (2.5Y 4/3) SILT LOAM; FEW MEDIUM DISTINCT DARK GRAY (2.5Y 4/1) AND FEW FINE DISTINCT DARK YELLOWISH BROWN (10YR 4/6) MOTTLES; WEAK COARSE PRISMATIC PARTING TO WEAK MEDIUM SUBANGULAR BLOCKY STRUCTURE; FRIABLE; FEW FINE PORES; VERY FEW FINE ROOTS; COMMON MEDIUM BLACK CONCRETIONS; FEW GRAY (2.5Y 5/1) SILT COATING ON PED FACES; VERTICAL CRACKS SEPARATED ABOUT 10-15 CM AND INFILLED WITH MATERIALS FROM ABOVE; NONCALCAREOUS; CLEAR SMOOTH BOUNDARY.
BW3	42-52	OLIVE BROWN (2.5Y 4/3) SILT; COMMON FINE DISTINCT YELLOWISH BROWN (10YR 5/6) MOTTLES; WEAK COARSE PRISMATIC PARTING TO WEAK MEDIUM AND COARSE SUBANGULAR BLOCKY STRUCTURE; FRIABLE; FEW FINE PORES; FEW FINE ROOTS; FEW BLACK CONCRETIONS; COMMON GRAY (2.5Y 5/1) SILT COATING ON PED FACES; THICK CONTINUOUS 2.5Y 4/1 COATINGS ON PRISM FACES; NONCALCAREOUS; GRADUAL SMOOTH BOUNDARY.
CB	52-80	LIGHT OLIVE BROWN (2.5Y 5/3) SILT; COMMON FINE DISTINCT OLIVE BROWN (2.5Y 4/6) MOTTLES; WEAK COARSE PRISMATIC STRUCTURE; FRIABLE; VERY FEW FINE ROOTS; FEW FEW FE-MN STAINS; THIN BEDDING PLANES PRESERVED AND CUT BY PRISM SIDES; NONCALCAREOUS.

APPENDIX C

X-RAY DIFFRACTOGRAMS OF SELECTED SOIL HORIZONS

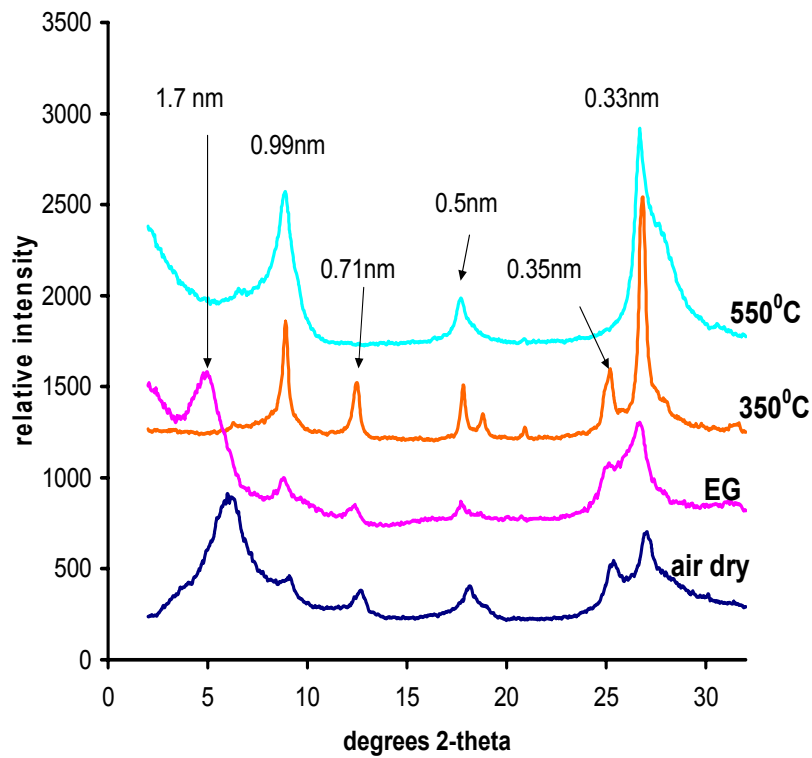


Fig. C-1. X-ray diffractograms for the fine clay (<math><0.2\mu</math>) of the Ap1 horizon of Tala-2.

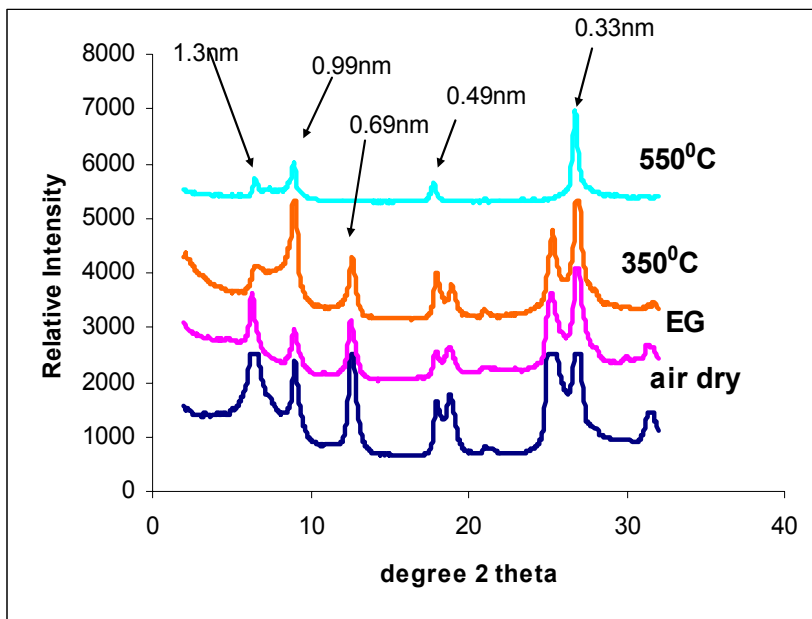


Fig. C-2. X-ray diffractograms for the coarse clay (<math><0.2 \mu</math>) of the Ap1 horizon of Tala-3.

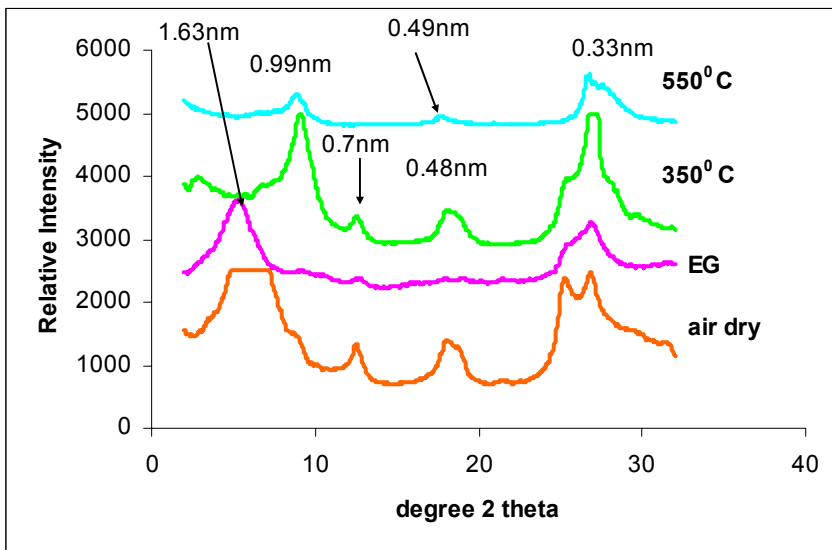


Fig. C-3. X-ray diffractograms for the fine clay (<math><0.2 \mu</math>) of the Ap1 horizon of Tala-3.

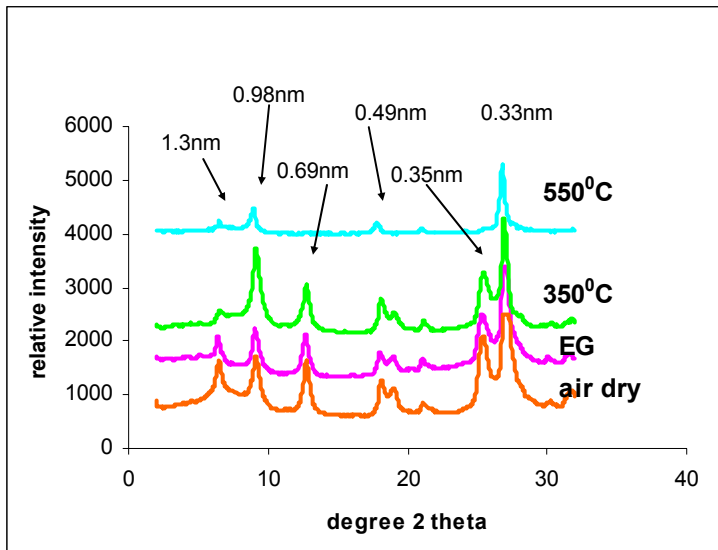


Fig. C-4. X-ray diffractograms for the coarse clay (<math><0.2 \mu</math>) of the Ap1 horizon of Paba-4.

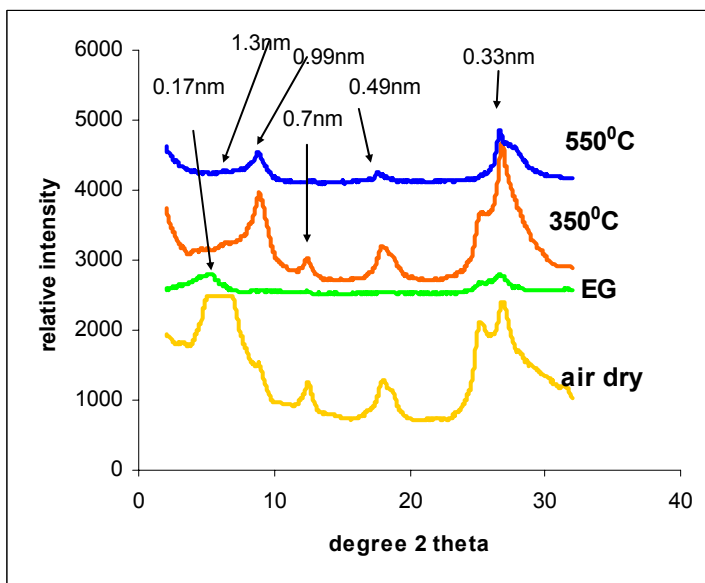


Fig. C-5. X-ray diffractograms for the fine clay (<math><0.2 \mu</math>) of the Ap1 horizon of Paba-4.

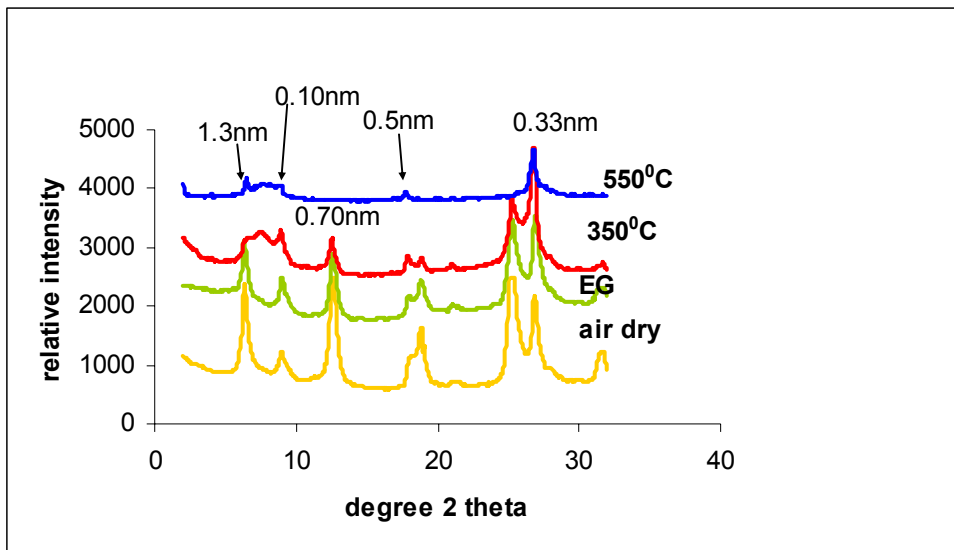


Fig. C-6. X-ray diffractograms for the coarse clay (<math><0.2 \mu</math>) of the Ap1 horizon of Senbag-6.

VITA

Sumitra Bose Biswas received her B.S. in Chemistry from the National University in Bangladesh. She received her M.S. in Soil Science from Texas A&M University, College Station, Texas, in May 2008. During her experience at Texas A&M University she taught undergraduate laboratories in AGRO 301 (Soil Science) in summer 2005 and summer 2006 and presented her thesis research poster in ASA-CSSA-SSSA annual meeting in Indianapolis, IN, in 2006.

She may be contacted at: Department of Soil and Crop Sciences, 370 Olsen Blvd. College Station, Texas 77843-2474, USA; or (mitrabbd@yahoo.com).