POTASSIUM FIXATION IN COARSE TEXTURED SOILS

BY

MOHAMED ABDUL LATHIFF

A Thesis
Submitted to the Faculty of Graduate Studies
in Partial Fulfilment of the Requirements
for the Degree of

Doctor of Philosophy

Department of Soil Science
University of Manitoba
Winnipeg, Manitoba
Canada

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POTASSIUM FIXATION IN COARSE TEXTURED SOILS

BY

MOHAMED ABDUL LATHIFF

A Thesis submitted to the Faculty of Graduate Studies of the University of Manitoba in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

ABSTRACT

POTASSIUM FIXATION IN COARSE TEXTURED SOILS

Mohamed Abdul Lathiff

The objective of this study was to determine: (i) the potassium (K) fixing ability of selected coarse textured soils of Manitoba, (ii) the probable causes of fixation and (iii) the availability of fixed K to wheat.

Potassium fixation was measured on 22 coarse textured soils of Manitoba after addition of a range of applied K (0 to 1000 mg kg^{-1}). The fixed K was defined as the difference between the amount of applied K and the changes in extractable K due to K additions after equilibration, using ammonium acetate as an extractant. At application rates of 50 and 1000 mg K kg^{-1}, fixed K varied from 12 to 84 % and 4 to 53 %, respectively. In all soils, fixed K increased with increasing K application rates and exhibited a decreasing % fixation. The amount of K fixation measured at various depths in soil profiles was comparable to that of surface soils. The sand, silt and clay fractions of the soils were all responsible for K fixation in coarse textured soils. In general, calcareous soils fixed more K than non-calcareous soils. Positive linear relationships were observed between K fixation and CEC, organic matter, exchangeable Ca, exchangeable Mg, pH and a negative linear relationship was observed with % K-saturation of the soils. However, the relationship between K fixation and the amount of clay was not very significant. The clay mineralogy of the high fixing soils was dominated by vermiculites whereas the medium and low fixing soils consisted of all four clay minerals; namely, montmorillonites, vermiculites, illites and kaolinites. Although the K fixation values observed were different among the soils from the same (Almasippi) association, no appreciable differences in clay mineralogy were found among these soils.

Potassium fixation in soils seems to be a concentration dependent, equilibrium surface phenomena. At a given level of applied K, a maximum amount of K fixation is attained within a short period of time. The amount of K fixed from the subsequent K application decreased as the amount of previously added K increased. The observed K fixation behavior of these coarse textured soils could be described by the Langmuir adsorption isotherm. Potassium fixation maximum (capacity) of the soils estimated by using the Langmuir model was highly variable among the soils indicating unique capacities for K fixation in different soils.

Availability of fixed K to wheat as measured by crop uptake in the growth chamber experiment showed that the fixed K was not immediately available to the growing crop. The nonexchangeable K release as determined by HCl extraction has indicated a variability in K supplying power of different soils from the nonexchangeable source. Although, adding K to K fixing soils was shown to increase the step-K, the amount of this portion of K which increased due to K fixation was always less than the amount of K fixed in those soils, indicating that part of the fixed K may have been involved in mineralogical transformation.

ACKNOWLEDGEMENTS

I express my deep and sincere gratitude to Dr. R.J. Soper, my advisor, for his invaluable guidance, constant encouragement and support given to me throughout my graduate program. I also wish to express my deep appreciation to Dr. C.M. Cho for his invaluable guidance, encouragement and suggestions throughout the program. I also acknowledge Dr. M.A. Zwarich for his valuable advice and helpful suggestions during the period of study. I also wish to express my sincere thanks to Dr. M. Pritchard and Dr. T.E. Bates, the external examiner for their suggestions and for correcting the manuscript.

I sincerely thank Val Huzel, for giving me technical support throughout the program. I also appreciate the support given by the Canada-Manitoba Soil Survey staff, John Madden, Peter Haluschak, Dr. W. Michalyna and all the other academic and non-academic staff members, and the graduate students of the department of Soil Science.

I acknowledge the Canadian International Development Agency, for the financial assistance in the form of a scholarship, the Department of Agriculture, Sri Lanka, for granting me leave to carry out this study. I am specially thankful to Dr. S.L. Amarasiri, the Deputy Director of Agriculture (Research), Department of Agriculture, Sri Lanka, for his invaluable support and constant encouragement to make this program a success.

Finally, a special thanks to my parents, late Mr. M.M. Mohamed and Mrs. U. Mohamed, my wife Nooriya, son Nabil, and daughter Nihad for their support, patience and understanding.

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CHAPTER 1

INTRODUCTION

The importance of potassium fixation in soils and its implication on crop production has been identified by many workers throughout the world (Attoe, 1948; MacLean, 1968; Arifin and Tan, 1973; Barber, 1979; Ross et al., 1989). Potassium fixation in soils has been defined as the conversion of either soil solution or exchangeable K into a non-exchangeable form. Depending on the conditions and the types of clay mineral in the soil, the amount of added K that becomes unavailable to a crop is variable. A number of factors have been identified as main causes determining the amount of K fixation in a given soil.

The mechanism of K fixation in soils has been studied by many workers. It is generally accepted that the major portion of K becomes fixed against a normal rapid exchange by other metal cations due to the good fit of K^+ in the holes created between and adjacent to oxygen layers of 2:1 type clay minerals (Barshad, 1954 b). In this position the K^+ becomes electro-statically bound and establishes a chemically stable configuration (Gaultier, 1981). Many workers (Mortland and Gieseking, 1951; Barshad 1951; Arifin and Tan, 1973) have confirmed that this type of fixation is accompanied by the formation of mica-like minerals.

It is generally accepted that fixation of added K leads to a drastic reduction of available K to plants (Page et al., 1963; Kaila, 1967). Often high rates of K fertilizers are required to correct K deficiencies in soils containing high K fixing minerals in order to assure an adequate supply of this nutrient for maximum production. Other workers (MacLean, 1962; MacLean and

Brydon, 1971) have suggested that the fixation of added K has some beneficial aspects, since it reduces K losses by leaching and by luxury consumption yet it maintains a potentially available K pool.

Fixation of added K and its release is assumed to be happening according to an equilibrium existing between various forms of potassium in the soil (Kaila, 1967). Therefore, under certain conditions K fixation may occur and under other conditions K release may occur in the same soil. Nevertheless, researchers have observed that there were differences in the ability of crops to utilize nonexchangeable K from different soil conditions (Lawton and Cook, 1954). Thus the availability of fixed K to crops cannot be easily predicted by a simple technique, since there may be many different possible equilibria existing between the fixed forms and exchangeable and solution forms of K.

Studies on K fixation and availability of fixed K to crops have mainly concentrated on soils with high clay contents (MacLean, 1962; MacLean and Brydon, 1971; Ross et al., 1989). No detailed work has been done on K fixation in sandy (coarse textured) soils. However, recent work (a series of field experiments and a growth chamber experiment) on coarse textured soils of Manitoba (Murage, 1984) has indicated that there was a loss of a major portion of applied K within a single season of cultivation. In a growth-chamber experiment about 70% of the applied K in all the treatments was unaccounted for by the crop removal and the exchangeable K measured by 1 N NH_4OAc extraction. These coarse textured soils (sands to sandy loams) of Manitoba, derived from lacustrine deposits cover about 1.1 million hectares of land area (Anonymous, 1991). They have low exchangeable K and response to K fertilizer is often expected. Therefore it was felt that knowledge of K fixation in these coarse textured soils is crucial in making potassium fertilizer recommendations. In some parts of the United States the

K fixation tendencies of individual soils are considered in making normal fertilizer recommendation practices (McLean, 1976; McLean et al., 1982; Pichtel et al., 1986).

The main objectives of this study were to determine (a) the K fixing ability of selected coarse textured soils, (b) the relationship between K fixation and soil characteristics, (c) the mineralogical composition of the selected coarse textured soils, (d) the factors affecting K fixation, (e) the K fixation maximum of coarse textured soils, (f) the availability of fixed K to wheat and (g) the non-exchangeable K release patterns of selected coarse textured soils.

CHAPTER 2

LITERATURE REVIEW

2.1 POTASSIUM FIXATION

Fixation is defined as the amount of adsorbed K which is not replaceable by NH_4^+ (Barshad 1951, 1954 b). The K fixation phenomenon was first recognized by Dyer in 1894 (Reitemeier, 1951). In his study in the Hoos field at Rothamsted, Dyer (1894) calculated that of 3797 kg K ha^{-1} applied over 38 years, about one half was accounted for by the crop removal and that extractable by 1 % citric acid. Comparison with the adjacent control plot indicated that the other half had become nonexchangeable. Another study conducted by Frear and Erb in 1918 (Reitemeier, 1951) showed that in a plot of Hagerstown silt loam, which had received 1673 kg K ha^{-1} during a period of 36 years, approximately one-fourth of that was accounted for by crop removal; half of the remainder was extractable by 0.3 N NH_4Cl, and the rest had been converted to nonexchangeable forms. Since then it has been confirmed that a majority of soils have the property of fixing applied K in nonexchangeable forms (Reitemeier, 1951).

Potassium fixation has been extensively studied in soils (Mortland et al., 1957; McLean & Simon, 1958; Dennis & Ellis, 1962; MacLean 1962; MacLean & Brydon 1963; Rich & Lutz 1965; Lutz 1966; Page et al. 1967; MacLean and Brydon 1971; Arifin and Tan 1973; Barber 1979; Shaviv et al. 1985; Ross et al. 1989).

2.1.1 Potassium Fixation Mechanism

The mechanisms of K fixation in soils and clays have been studied by a number of workers. By alternate wetting and high-temperature drying of bentonite, Truog and Jones (1938) noted that the strong attraction between K ions and the clay surfaces resulted in K fixation. According to Page and Baver (1940), when montmorillonite is dried in the presence of K ions ($r=0.133$ nm), K ions lose their shell of water molecules, enter the hexagonal spaces ($r=0.14$ nm) found between two adjacent silica tetrahedral layers and become fixed. That fixation processes are limited to interlayer ions such as K has been explained in terms of the good fit of K (the crystalline radius and coordination number are ideal) into the hexagonal spaces between two adjacent silica tetrahedral layers (Barshad, 1951, 1954 b). In the hexagonal position the K becomes electrostatically bound and establishes a chemically stable configuration (Gaultier, 1981; Gouling, 1983). This type of fixation results in the formation of mica-like minerals (Mortland and Gieseking, 1951; Barshad, 1950, 1952, 1954 b; Arifin and Tan, 1973). The formation of the mica-like minerals is illustrated by X-ray diffraction (XRD) as the d (001) spacing decreases from 1.5 to 1.0 nm (Everett and Ellis, 1962).

Vermiculite is generally considered responsible for K fixation in soils (DeMumbrum and Hoover, 1958). Kittrick (1966) studied the mechanisms of K fixation by vermiculite and concluded that the ion fixation process by vermiculite involves irreversible interlayer contraction. Kittrick (1966) identified two important interlayer forces involved in ion fixation by vermiculite. The forces include (i) the electrostatic attraction between the negatively charged layers and the positive interlayer ions and (ii) the expansion due to ion hydration. He found that K fixation occurs in vermiculite when electrostatic forces of attraction exceed those of hydration. According to others (Wear and White, 1951; Sawhney, 1972; Douglas, 1977) the low hydration energy of K is a major factor affecting K fixation. Because of the high energies of hydration, cations like

Na, Ca, and Mg are not normally fixed by 2:1 type clay minerals (Ebrel 1980). Cations smaller than K are not fixed because they do not fit closely enough in the hexagonal spaces. On the other hand, cations larger than K are too big to enter the hexagonal spaces (Malavolta, 1985). Many workers (Page et al. 1967; Deist and Talibudeen 1967 a,b; Shaviv et al. 1985) have observed that the entry of K into the interlayer positions not only leads to a contraction of the clay mineral but also leads to a decrease in CEC.

Another type of fixation mechanism is considered to happen via formation of insoluble K compounds, especially aluminosilicates. According to Volk (1938) and Agarwal (1960) high pH values will accelerate the formation of such compounds. Under those situations the detected K fixation will exceed the decrease of initial CEC. Such behavior was observed by York et al. (1953), Pratt and Goulben (1957), and Page et al. (1967).

Reeuwijk and De Villers (1968) studied K fixation in some synthetic amorphous aluminosilicates and postulated a 'sieve' mechanism for K fixation in these materials. Barber (1979) also observed that K ions are held against NH_4^+ extraction in amorphous alumino-silicates.

2.1.2 Clay Mineralogical Changes Associated with Potassium Fixation

Volk (1934) was possibly the first person to suggest that K added in the form of fertilizer caused an increase in the hydrous mica content of soil. Since then, studies on mineralogical changes associated with K fixation in soil clays have been conducted by many workers (Barshad, 1948; Barshad and Kishk, 1970; Ross et al., 1985, 1989).

Barshad (1948) was able to reversibly transform vermiculite to biotite by treatment with a potassium solution at 70 C and then transform biotite to vermiculite by heating with a Mg solution. The only change observed during this process was a cation exchange between K and Mg and the accompanying change in extent of hydration. The hydration of mica particles during the weathering process is considered as mainly the result of replacement of K by Ca, Mg and H ions (Barshad, 1950). Barshad (1948) observed that as a result of K or NH_4 fixation in vermiculite, there was a decrease in basal spacing from 1.4 to near 1.0 nm. He concluded that the entrapment of K in the hexagonal cavities of the interlayer oxygen causes the collapse of the unit sheet to 1.0 nm d(001) spacing of mica. Later similar observations were made by Barshad and Kishk (1970). Most recently Ross et al. (1985) observed clay mineralogical changes in vermiculite following the addition of K and NH_4^+ in some Canadian soils. They observed that the fixation of K and NH_4^+ by soil minerals, especially vermiculite, collapses the 1.4 nm spacing of this mineral to the 1.0 nm spacing of micaceous minerals. They also observed a sharp increase in the 1.0 nm peak intensity in the XRD patterns of the soil clays following the application of K for 6 years. Arifin and Tan (1973) also noted a gradual appearance of d(001) spacing at 1.0 nm with increasing K fixation while reconstituting the existing mica in clays. In contrast, Marel in 1959 (Rich and Lutz, 1965) presented XRD data showing that, on K saturation of certain soil clays containing 'open illite' (vermiculite), the original 1.47 to 1.42 spacing shifted to spacings between 1.02 and 1.20 nm and when NH_4 saturated, shifted to spacings between 1.06 and 1.28 nm. Rich and Lutz (1965) observed that K and NH_4 fixation by soil clays resulted in both the decrease in intensity of the 1.4 nm XRD peak and its shifting toward 1.0 nm.

In vermiculite, K sorption causes collapse in alternate layers producing regularly interstratified 1.0 and 1.5 nm layer sequence (Sawhney, 1967). Further K sorption resulted in the collapse of the 1.5 nm layers within the interstratified mixture until the entire sample was converted to mica-like structure 1.0 nm layers. Similar layer collapse was observed when Mg^{2+} saturated vermiculite (Rhoades and Coleman, 1967) and when K depleted micas (Weed and Leonard, 1968) were reacted with KCl.

In the case of montmorillonite, where the layer charge was smaller than in vermiculite, K saturation resulted only in a partial interlayer collapse, producing a 1.2 nm structure; however when the K saturated montmorillonite was heated, the interlayer spacing changed to 1.0 nm and K was fixed (Sawhney 1972).

2.1.3 Factors Affecting Potassium Fixation in Soils

The degree to which K fixation occurs in soils and clays depends on a number of factors. Among them the type of clay mineral, the charge density of the mineral, the extent of interlayering, the moisture content, the pH of the surrounding solution, the concentration of K ions and the nature as well as the concentration of competing cations in the surrounding medium are considered the most common factors that affect K fixation (Rich, 1968; Thomas & Hipp, 1968). Volk (1934) summarized the main factors that affected K fixation such as: (a) fixation was increased by drying; (b) the fixation depended on the quantity of the clay fraction, but the type of clay was even more important; (c) the treatment of soil with HCl decreased fixation; whereas the treatment with Na_2CO_3 increased it; (d) continuous K manuring decreased further fixation, and increased the formation of a muscovite-type mineral; and (e) the amount of K fixed was increased with the amount of K added, whereas the % of added K fixed was decreased.

Some other factors that contribute to cation fixation in general are compiled by Goulding (1983).

2.1.3.1 Type of Clay Mineral

The type of clay is considered to be the most important factor that affects fixation. In general, weathered micas and vermiculites are considered to have the highest fixation capacities, while montmorillonites and kaolinites have low capacities (Raney and Hoover, 1946; Barshad, 1948, 1950; Kunze & Jeffries, 1953; Agarwal, 1960; Dennis & Ellis, 1962; Page et al., 1967;

Rich, 1968; Arifin and Tan, 1973). Van der Marel (1954) concluded that the high K fixing capacity of Dutch soils was a consequence of an open-layer structured illite from which the K was removed by weathering. Weathered micas and vermiculites fix K under moist as well as dry conditions, whereas montmorillonites usually fix K only when the soil is air-dried (Rich, 1968). The results observed by Stanford (1947) indicated that illite was capable of fixing K under moist conditions and additional fixation occurred when the clay was dried.

MacLean and Brydon (1963) studied K fixation by different fractions of Canadian soils and observed that the degree of K fixation usually decreased with increasing particle size. They observed that, though more K was fixed in the clay fractions than in the silt fractions of most of the soils, there was considerable fixation by the fine and medium silts. They also observed that fixation was relatively slight in the coarse silt and sand fractions as opposed to finer fractions (Table 2.1). Rich and Lutz (1965) studied K fixation in 25 soils having varying amounts of vermiculite, micas and kaolinite in their composition, and noted that fixation on a unit weight basis increased with decrease in particle size, but, because of its abundance as well as high fixing ability, the 2 to 0.2 μm fraction was generally the most important. MacLean and Brydon (1971) studied K fixation by clays of 11 selected horizon samples obtained from eight profiles and found that soils containing mixtures of vermiculite and montmorillonite had a high capacity to fix added K. Another corresponding sample, from a C horizon and consisting of well-ordered muscovite, gave the lowest degree of K fixation (Table 2.2). According to the same workers, predominantly montmorillonitic clay with some mica layers fixed an intermediate amount of added K.

2.1.3.2 Charge Density of Clay Minerals

The amount of K fixation is also strongly influenced by the charge density on the layer silicate. In vermiculites, Walker (1957) observed that minerals with high-charge density fixed

Table 2.1. Fixation of added potassium into non-exchangeable form by total soil and by different particle size fractions.

Soil	K FIXED				
	by total soil*	by size fractions** (μm)			
		<2	2-5	5-20	20-2000
	%				
1. Charlottetown (FSL)	27	44	49	39	9
2. Castor (FSL)	32	52	44	-	8
3. Fort William (LS)	16	44	-	24	17

* K added at 585 mg kg^{-1} soil (MacLean, 1962)
** K added at 1800 mg kg^{-1} soil (MacLean and Brydon, 1963)

Table 2.2. Fixation of added K by soil clays obtained from horizon samples (MacLean and Brydon, 1971).

Soil series	Horizon	Major clay minerals	K Fixed*
			%
1. Bayswater	Ae	mica, kaolinite, vermiculite, montmorillonite	91
2. Poitras	Ae	mica, kaolinite, vermiculite, montmorillonite	100
3. Poitras	C	mica, kaolinite	29
4. Breton	C	mica, kaolinite, montmorillonite	69

* K added at 3950 mg kg^{-1} clay

more K than those with low-charge density. Mortland and Gieseking (1951), and Wear and White (1951) related K fixation to tetrahedral negative charge as in hydrous mica or vermiculite and found a trend for greater fixation with increasing tetrahedral charge. In montmorillonites where one finds mostly octahedral negative charge, less fixation is detected (Sawhney, 1969). Weir (1965) also observed that K fixation by montmorillonites is very low unless the charge density of the clays is very high. Laffer et al. (1966) observed that low-charge density montmorillonite (Wyoming) stayed at 1.5 nm when K saturated. However, some soil montmorillonites have a greater capacity to fix K than do many specimen type montmorillonites because, these soil montmorillonites have a higher charge density and probably have wedge positions near mica-like zones where selectivity for K is high (Rich, 1968). Sawhney (1969) studied the ease of collapse of interlayer positions in minerals with different layer charge densities and found that the large charge density in vermiculite resulted in the collapse of the interlayer position instantly on K sorption. He also noted that the collapse in one layer prevented the entry of K in the adjacent layer, and produced a regularly interstratified mica-vermiculite layer sequence. In contrast, the lack of collapse in montmorillonites is attributed to their small charge density (Sawhney, 1969). Chen et al.(1987) who studied the relationship between K fixation and oxidation state of octahedral iron using smectites and soil clays, found that the increase in the net negative charge of the clay accompanying the conversion of Fe^{3+} to Fe^{2+} caused some of the layers to completely or partially collapse. Since K fixation is the entrapment of K between collapsed layers, they concluded that the reduction of octahedral Fe^{3+} will enhance K fixation. Conversely, Barshad and Kishk (1970) found that the reduction of crystal structure iron from Fe^{3+} to Fe^{2+} caused a decrease in fixation even though the CEC increased as a result of this change in vermiculites.

2.1.3.3 Moisture Content

The importance of wetting and drying and freezing and thawing on K fixation has been observed by numerous researchers (Attoe, 1946; Luebs et al., 1956; Hanway & Scott, 1957; Scott et al., 1957; McLean & Simon, 1958; Hanway & Scott, 1959; Cook & Hutcheson, 1960; Scott & Hanway, 1960). From these reports, it was clear that increasing the number of wetting and drying or freezing and thawing cycles increased K fixation. Stanford (1947) found that montmorillonite did not fix K until it was dried. He also observed that H, Fe, and Al ions in the exchangeable positions would prevent fixation of K by illite in acid soils under moist conditions. However, Raney and Hoover (1946) observed that a montmorillonitic soil fixed large amounts of K during moist storage for one month and more K was fixed when the soil was air-dried at the end of storage. Kardos (1955) indicated that illite and montmorillonite are not responsible for K fixation in the moist state whereas, vermiculite appears to be of major importance. However, Stanford (1947) demonstrated that illite is capable of fixing K under moist conditions. He also showed that illite fixed additional K when the sample was oven-dried. Barshad (1954 b) stated that illite became vermiculite upon the release of K and that vermiculite was responsible for further fixation. DeMumbrum and Hoover (1958) found no evidence of fixation (just release) of K by illite under the sequence of moist, dry, and remoistened conditions. But they found marked fixation of added K by vermiculite in moist conditions with small additional fixation under dry conditions. Those workers considered illite as a release mineral and vermiculite as a fixation mineral.

It has been observed that some soils required larger applications of K than did others before any fixation would occur (Scott et al., 1957). They also observed that high initial levels of exchangeable K must be present before consistent fixation takes place, whereas low initial levels of exchangeable K were favorable to release of the element. When intermediate amounts of KCl were added, both fixation and release were noted, depending upon the moisture level of the soil. Therefore, according to Scott et al. (1957) fixation and release could not be predicted according to any one equilibrium without defining the degree of drying. This indicated that a soil may have different equilibria under different moisture conditions.

The amount of fixed K in a given soil has been shown to be related to the K status of the soil. By heating certain Illinois soils, Bray and DeTurk (1938) concluded that unfertilized soils, originally medium to low in exchangeable K, would tend to fix part of the original or added K whereas those soils originally high in exchangeable K would tend to liberate it. Fine et al. (1940) reported that freezing and thawing (essentially a drying and wetting process) increased exchangeable K when the soil was low or had received small additions of K, but soils with high levels of exchangeable K showed a decrease in exchangeable K. Matthews and Sherrell (1960) observed that some Ontario soils had a relatively constant K equilibrium level of 1.11 ± 0.12 % K saturation, regardless of soil type. But drying the soils fixed K if the percent K saturation was > 1.11, and released K if the percent K saturation was < 1.11. Dowdy and Hutcheson (1963) observed that when exchangeable K values were above 0.45 ± 0.10 $cmol_c$ kg^{-1} level for field-moist samples, K is fixed on drying, whereas it is released when the initial K level is lower.

2.1.3.4 pH

Volk (1934) reported that a marked increase in K fixation occurred in soils when the pH was raised to about 9 or 10 with Na_2CO_3. Martin et al. (1945) observed no fixation up to the pH values of 2.5; but between pH 2.5 and 5.5, the amount of K fixation increased very rapidly. Stanford (1947) observed that K fixation in illite increased uniformly as the pH increased from 3.8 to about 7 by adding NaOH; maximum fixation was reached when pH was about 9. He concluded that H ions in certain positions within the mineral crystals were neutralized by the addition of NaOH, and that process in some manner facilitated the entrance of K ions into lattice positions where fixation took place. In more recent publications, Kim et al. (1983 a,b) reported K fixation via formation of K-Al and K-Fe-taranakites at pH values as low as 3.0 to 3.5.

According to Rich & Black (1964), lack of K fixation at low pH is probably due to large numbers of H_3O^+ and their ability to replace K well.

2.1.3.5 Competing ions

Researchers have observed that ion fixation by 2:1 clay minerals may be influenced by the kind of adsorbed cations in the system. In studies with the silicate ion, Mortland and Gieseking (1951) found that montmorillonite clays dried with K_2SiO_3 were altered in their swelling properties and fixed K in large amounts. Soils and clays saturated with Mg, Ca, and Na show higher fixation capacity, while saturation with H, NH_4, and K ions results in a lower fixation (Wiklander, 1950; Agarwal, 1960; Grim, 1968). Everett and Ellis (1962) observed that for a given level of exchangeable K, more fixation of K occurred when Ca was the complementary ion.

2.1.3.6 Other Factors

Degree of interlayering with hydroxy-Al and hydroxy-Fe^{3+} have been related to K fixation (Rich and Obenshain, 1955). They concluded that hydroxy-Al and hydroxy-Fe^{3+} interlayer groups acted as props to decrease K fixation.

The amount of fixed K in a given soil has been shown to be related to the amount of K added. Many workers have observed that the amount of K fixation increased with increased K additions (Volk, 1934; Attoe, 1948; McLean and Simon, 1958; Arifin and Tan, 1973; Barber, 1979; Richards et al., 1988). Arifin and Tan (1973) also observed that K fixation tendencies of clays conformed to the Langmuir adsorption isotherm.

Soil management practices have been shown to influence the amount of K fixation. Volk (1934) observed that soils which had received potassium fertilizer in the field for several years fixed only about one half as much K as the unfertilized soils.

2.2 AVAILABILITY OF POTASSIUM

Exchangeable K in soils originates by the weathering processes, from the K-bearing minerals, mainly micas and feldspars. Soil exchangeable K levels are influenced by a number of factors such as soil mineralogy, soil environment, CEC of the soil, species of cations on the exchange complex and cropping history (Milford and Jackson, 1966). The exchangeable K that is available to plants is dependent on the dynamics existing between the various K-bearing forms and, possibly more important, the rate of transfer between these forms (Sparks 1980). Depending on the conditions, the element is converted from one phase to the other. Many of these reactions in soils are quite complex, and therefore, the prediction of plant available K is often difficult (Sparks et al., 1980).

2.2.1 Relationships Between Various Forms of Soil Potassium

The potassium that is immediately available to plants is present in the soil solution. When the concentration of soil solution K is diminished to a certain point, it is replenished from other forms of K in the soil. The rate at which a soil replenishes soil solution K is dependent on the transformations taking place between various K forms and the status of their respective equilibria with the soil solution (Fig. 1). The model (Fig. 1), as suggested by Jackson (1964) shows the reversibility of the non-exchangeable to exchangeable or solution phase transformation.

2.2.1.2 Availability of Potassium from Various Forms

Soil K potentially available to plants includes exchangeable, nonexchangeable, and mineral K forms (Fig.1). Out of these three forms, the exchangeable K is the most readily

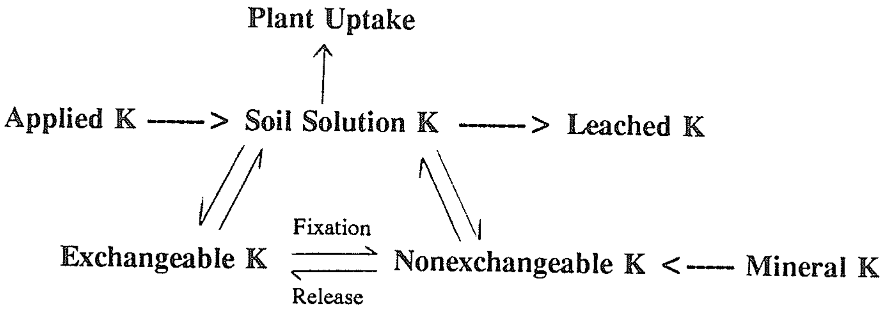


Fig.1. The dynamics between the various K phases in soil (Modified from Jackson,1964).

available, because it is in direct equilibrium with the soil solution. Researchers (Pratt, 1951; MacLean, 1961) have confirmed that exchangeable K before cropping was closely correlated with K uptake of a crop. On the other hand, Doll and Lucas (1973) observed that many soils of temperate regions are low in exchangeable K and they depend on transformations from the nonexchangeable forms to replenish the exchangeable or solution K. Many workers (Schmitz and Pratt, 1953; Binnie and Barber, 1964) found that in soils having a high K supplying power, the nonexchangeable K released during the cropping period made a significant contribution to the total K uptake by plants. According to Sparks (1980) the chemical equilibria existing between the nonexchangeable and exchangeable K are very complex and are dependent on the overall K status of various forms. For example, continuous removal of that nutrient from soil solution and exchangeable form will, with time lead to release of K from either nonexchangeable or fixed forms (Ayres et al., 1947; Jackson, 1964; Sparks, 1980). On the other hand, high-equilibrium K concentrations, whether in solution or in the exchange form, will restrict K release from nonexchangeable forms (Mortland, 1961).

There are a number of reports which indicate the utilization of fixed or nonexchangeable K by plants grown on temperate region soils (Bray and Deturk, 1938; Reitemeier et al., 1951; Smith and Matthews, 1957; Richards and McLean, 1961; Barber and Matthews, 1962; Conyers and McLean, 1969; Tabatabi and Hanway, 1969; Richards et al., 1988). For example, Gholston and Hoover (1948) studied the K released by using a continuous cropping technique and found that, in every case, more than 50% of K removed by eight successive crops was released by the soil from the nonexchangeable forms. A very recent study by Richards et al. (1988) in some southern Ontario soils indicated that there was a close relationship between total K uptake and the uptake of nonexchangeable K removed by eight successive crops of alfalfa grown in the greenhouse. They observed that among soils, nonexchangeable K uptake accounted for 0 - 86% of the total K removed by eight harvests of alfalfa. In three long-term field trials, the same workers (Richards et al., 1988) have observed that continuously cropped corn, which received no applied K, removed 24 to 35 kg nonexchangeable K ha^{-1} yr^{-1}. Many workers have observed that the K removed by plants exceeded the initial exchangeable K levels by considerable amounts (Ayres et al., 1947; Reitemeier et al., 1951; Hemingway, 1963).

Doll and Lucas (1973) reported that the labile K pool that replenishes the solution or exchange phase is the K associated with soil micaceous minerals, namely, illite or fixed K in vermiculites. However, the mineral K released by weathering during a growing season is relatively small (Jackson, 1964; Black, 1968). From the above discussion, it is clear that, though various forms of K are present in the soil, the chemistry of their relationship is complex. However, the exact nature of the relationship is based on the K status of each form, cropping patterns and degree of weathering.

In general, the K supplying power of soil has been related mainly to the clay fraction of the soil (McEwen and Matthews, 1958; Kaila, 1967; Tabatabi and Hanway, 1969); however, many other studies have demonstrated significant K release from the silt fraction (Merwin and Peech, 1951; Doll et al., 1965; Munn et al., 1976; Richards and Bates, 1988). For example, Merwin and Peech (1951) found that four New York soils released 40 to 83% of the total K from the clay, 15 to 51% from silt, and 2 to 18% from the sand fraction to an NH_4OAc extraction subsequent to nine wetting and drying cycles. MacLean and Brydon (1963) found that some Canadian soils released 21 to 83% of the total K from the clay, 13 to 49% from silt, and 4 to 58% from the sand fraction to a H-resin. Within a size fraction, Richards and Bates (1988) also found large differences in the amount of K extracted by boiling 1 M HNO_3 from some southern Ontario soils. Boiling 1 M HNO_3 extracted 2.6 - 8.6 % of the total K present in the silt fraction, 8.6 - 20.6 % of the total K in the coarse clay fraction, and 8.3 - 19.6 % of the total K in the fine clay fraction. MacLean and Brydon (1963) concluded that since the most reactive K occurs at or near the surface of the minerals, K-release will not necessarily be related to X-ray data descriptive of the crystalline material only. Therefore one cannot simply relate the amount of clay present in the soil with the availability of K to plants as the clay was not the only fraction which supplies K to plants.

Various methods have been employed to extract nonexchangeable K from soils and clays. Some common methods employed by many workers include: exhaustive cropping of soil in the greenhouse (Hoagland and Martin, 1933; Ayres at al., 1947; Gholston and Hoover, 1948; Smith and Matthews, 1957, MacLean, 1961; Richards and McLean, 1961; Sinclair, 1979), boiling HNO_3 (Haylock, 1956; MacLean, 1961; Conyers and McLean, 1969; Martini and Surez, 1977), hot HCl (Singh and Goulding, 1983), leaching with dilute HCl (MacLean, 1961), electrodialysis (Reitemeier et al., 1951; Ayres et al., 1947), electro-ultrafiltration (EUF) (Wanisuria et al., 1981), Na-tetraphenylboron ($NaBPh_4$) with EDTA (Scott et al., 1960; Scott and Reed, 1962), H-Saturated resins (Pratt, 1951; MacLean, 1961; Barber and Matthews, 1962; Martin and Sparks, 1983), and Ca-Saturated exchange resins (Talibudeen et al., 1978). These and many other methods have been reviewed by Martin and Sparks (1985).

The rate of reaction between the various forms of soil K determine the magnitude of leaching, release, and fixation in soils. Cook and Hutcheson (1960) investigated the rate of transformation and release of K from biotite and illite. Potassium release from these minerals was extremely slow as compared with reactions between soluble and exchangeable forms.

2.2.1.3 Availability and Potassium Fixation

It is generally accepted that the fixation of added K leads to a reduction of plant available K. Highly K depleted micaceous and vermiculitic minerals have been shown to fix large amounts of added K (Page et al., 1963). Often high rates of K fertilizers were required to correct the K deficiencies in soils containing those minerals. For example, Page et al. (1963) have shown the need for large K fertilizer applications (175 kg of K ha^{-1}) to California soils having a high K fixation to correct K deficiency problems in cotton (Gossypium hirsutum L.). Other studies (Hoagland and Martin, 1933; Richards and McLean, 1961) have also indicated that only a small fraction of fixed K is available to plants.

Many workers (McLean & Simon, 1958; MacLean, 1962; Kaila, 1967; MacLean and Brydon, 1971) have suggested that fixation of added K may be beneficial since it reduces K losses by leaching and by luxury consumption; it also maintains a potentially available K pool.

According to Kaila (1967) the equilibrium existing between K in soil solution, exchangeable K, and nonexchangeable K is reversible:

$$\textbf{Non-exchangeable K} \rightleftharpoons \textbf{Exchangeable K} \rightleftharpoons \textbf{Soil Solution K}$$

For example, with soils in which the minerals are highly K depleted, significant fixation of applied K may occur, with only a small amount being recoverable by plants in a given season. In contrast, as the soil solution is depleted by the excess removal of K by plants; the added K that is fixed on fertilizer addition may become available to plants. This is evidenced by the observation that the release of nonexchangeable K by intensive cropping results in depletion of K from 2:1 clay minerals (Hoagland and Martin, 1950; McLean and Simon, 1958). The more the mineral is depleted the higher becomes the fixation of subsequently applied K (MacLean, 1962; Munn and McLean, 1975; Mengel and Kirkby, 1980). In order to obtain satisfactory yields from such soils higher fertilizer rates are often required because of the fixation of K by the clay minerals. Thus, the applied K that is fixed is assumed to be satisfying the sites vacated by K release in response to crop demand. Many workers (Mortland, 1961; Bates and Scott, 1964; Kaila, 1967) have concluded that both the fixation and release of K can occur simultaneously under certain conditions.

There are differences in the ability of crops to utilize nonexchangeable K (Drake and Scarseth, 1940). Those differences partly depend on the level to which plant roots are able to deplete K from solution and exchange forms, without any serious interference in their development (Kaila, 1967). Therefore, in nature, probably many different equilibria exist between the fixed K forms and the solution and exchange forms of K. The exact nature of these equilibrium reactions would be location specific and also dependent on the type of crop grown.

Sequences of K^+ and NH_4^+ application and subsequent release have been studied by many workers. Beauchamp (1982) found that the addition of either K^+ or NH_4^+ on day 2 tended to inhibit the release of the other added on day 1 in Ontario soils. Nommik and Vahtras (1982) have reviewed many aspects of NH_4^+ fixation and the relationships with K^+.

2.2.1.4 Factors Affecting Soil Potassium Transformations

Release of K from interlayers is an exchange and diffusion process (von Reichenbach, 1972). According to Mengel (1985), diffusion depends mainly on the expansion of the mineral and therefore it depends on soil moisture; exchange depends on the cation species and their concentrations near the surface of the material. Net release of K will only occur if the K concentration in the adjacent solution is low. Martin and Sparks (1983) studied the release of nonexchangeable K from a sandy loam and a loamy sand to an ion exchanger and found a net release of K with a K concentration in the contact solution of about 1 to 2 μmol L^{-1}. This is a concentration level to which a plant root may deplete the soil solution level in the rhizosphere (Mengel, 1985). Net release depends also on the K concentration of the contact solution, the K release rate being always higher at lower contacting K concentrations (Mortland, 1958). The velocity of K release, however, varied considerably between the various minerals. According to Scott and Smith (1966), for the release of 90% of the total interlayer K, the following durations were required: vermiculite 30 minutes, phlogophite (Mg biotite) 1.5 days, biotite 3 days, and muscovite 315 days. This may explain that muscovite (K mica), although rich in K, is much inferior to biotite in supplying K to plants. Jackson and During (1979) investigating the K release of six different soils with vermiculite, illite, and smectite as the main clay minerals, found critical K concentrations (at which no net release occurs) in the contact solution to be in the order of 0.1 to 2 mmol L^{-1}.

Release of interlayer K depends also on the exchanging cation species. Calcium and Na^+, when replacing K in the interlayer, bring about an expansion of the mineral which in turn will favor K release (Scott and Smith, 1966). Ammonium and H^+, when exchanging for interlayer K, do not expand the mineral and may thus obstruct K diffusion and release (Scott and Smith, 1966). Ammonium adsorbed to edge positions of the mineral also brings about a contraction and thus obstructs the release of interlayer K. The favorable effect of Ca^{2+} and Na^+ on K release was reported by Jackson and During (1979) who pre-treated the soils with Ca^{2+} and Na^+ before measuring the release of K. High release rates were found especially when the treatment was carried out at a higher temperature (50 C).

White (1950) showed that K removal from illite produced a montmorillonite. Mortland et al. (1956) were able to demonstrate clearly that biotite may be altered to vermiculite by continuous K removal by plants. In 1957, the same authors also showed that K fixed by vermiculite and montmorillonite is available for plant growth. The same workers also noted that K from biotite is more available to plants than that from illite or muscovite. Malquori et al. (1975) found that wheat was able to exploit the K of biotite. A natural transformation of biotite to vermiculite within a soil profile has been observed by Walker (1949). As the stage of weathering advanced, the biotite profiles lost colour and showed an increase in the C-axis spacing. The 1.4 nm spacing, characteristic of vermiculite, appeared at later stages. The process is visualized at first as a replacement of the more accessible K^+ by Mg^{2+}, Ca^{2+}, and water molecules. With further replacement toward the center of the flakes, the binding of the layers decreases and basal plane spacing increases. A mixed layer structure arises in which increasing numbers of layers are converted to the vermiculite type (Reitemeier, 1951).

There is considerable evidence in the literature that plants may feed on interlayer K. Capability of exploiting interlayer K differs among plant species. Mengel (1985) cited several studies where monocotyledonous plants fed better from interlayer K than dicotyledons. Interlayer K is not a permanent everlasting K source for plants. Obviously with an increase in depletion of interlayer K, the release rate may decrease and eventually will not meet the crop requirement. According to Mengel (1985) higher losses of interlayer K result in an increase of K fixation potential. It has been recognized that (a) soil temperature (Sparks and Liebhardt, 1982); (b) wetting-drying and freezing-thawing cycles (Attoe, 1946; Hanway and Scott, 1957; Bates and Scott, 1964); and (c) freezing (Fine et al., 1940) also have an influence on the transformation of K between nonexchangeable, exchangeable, and solution forms.

CHAPTER 3

MATERIALS AND METHODS

3.1 SOIL SAMPLES

Twenty two coarse textured surface soil samples and 13 samples from 3 profiles were obtained for these studies from the Canada-Manitoba Soil Survey, University of Manitoba. The majority of the samples obtained were collected from non-cultivated fields. The samples for the growth chamber study were collected early in the fall of 1984 from 0-15 cm depth of cultivated fields. The soil samples were air-dried, ground to pass through a 2 mm sieve, and stored at room temperature. The locations and some physical and chemical properties of the soils are given in Tables 3.1 to 3.5.

3.2 METHODS OF CHEMICAL ANALYSIS

3.2.1 Soil pH

Soil pH was determined according to the procedures outlined by Schofield and Taylor (1955). A 1:2 ratio (w/v) of soil to 0.01 M $CaCl_2$ solution was prepared. Samples were shaken and allowed to equilibrate for 30 minutes. Soil pH measurements were made with a digital pH meter equipped with glass and calomel electrodes.

Table 3.1. Selected properties of some coarse textured surface Manitoba soils (Batch I).

Location (Nearest town)	Soil Series	Soil No.	Text. Class	MS	FS	VFS	Silt	Clay	Org.C	$CaCO_3$ equiv.	pH	Exch.K
							%					$cmol_c\ kg^{-1}$
Rathwell (NE8-8-8W)	Elm Creek	RWL7	LFS	3	68	9	10	10	0.42	0.0	7.4	0.50
St.Claude (NW35-8-7W)	Almasippi	SC357	VFSL	14	25	35	11	15	4.73	7.5	7.6	0.18
Portage LP (SE15-10-7W)	Long Plain	SC315	LS	49	30	5	7	6	3.47	0.0	7.2	0.10
St.Claude (SE26-7-7W)	St.Claude	SC297	FSL	4	26	24	26	20	4.86	20.7	7.9	0.20
Steinbach (SE16-6-7E)	Lenswood	STA90	FSL	5	50	22	12	10	3.21	2.8	7.4	0.10
Gladstone (NW17-13-11W)	Almasippi	WBN66	LFS	4	50	29	7	10	2.20	9.2	7.8	0.30
Gladstone (SE28-14-12W)	Willowcrest	WBN41	FS	3	67	21	4	5	1.46	0.0	6.8	0.40
Elm Creek (NW NE1/4 22-8-5W)	Long Plain	GY1	FS	2	58	31	4	5	0.80	0.0	6.8	0.20
Elm Creek (NW1/4 14-8-5W)	St.Claude	GY14	FS	0	22	45	14	19	2.50	18.0	8.2	0.35
Barnsley (SE1/4 26-7-5W)	Willowcrest	GY50	FS	1	43	48	3	5	1.60	0.0	7.1	0.36
Brandon (NW7-10-18W)	Stockton	BRA1	FSL	21	43	13	8	12	2.04	0.0	7.1	0.20

MS = Medium Sand FS = Fine Sand VFS = Very Fine Sand

Table 3.2. Selected properties of some coarse textured surface Manitoba soils (Batch II).

Location (Nearest town)	Soil Series	Soil No.	Text. Class	MS	FS	VFS	Silt	Clay	Org.C	CaCO3 equiv.	pH	Exch.K
				%								cmol$_c$ kg^{-1}
La Broquerie (SW12-6-8E)	Pine Ridge	STA24	FS	24	56	7	2	2	0.13	0.0	6.1	0.20
Steinbach (SW19-6-7E)	Poppleton	STA33	FSL	5	45	27	9	12	6.35	4.3	7.6	1.30
Kenville (NW18-36-27W)	Silver Creek	SWR7	FS	7	44	46	2	0	1.29	0.0	6.2	0.29
Kenville (NW22-36-27W)	Sevick	SWR53	LFS	6	34	46	8	5	4.87	0.0	5.9	0.58
Kenville (SW28-36-27W)	Gilbert	SWR57	LFS	10	29	42	8	7	2.58	0.0	6.2	0.40
Kenville (SE12-36-27W)	Craigford	SWR77	FS	6	54	27	7	5	3.39	1.3	7.7	0.39
Hallboro (SW35-13-15W)	Stockton	TW-HAL1	LFS	17	53	14	7	8	1.28	0.0	5.6	0.20
Rathwell (NW27-7-8W)	Dobbin	SC369	LFS	2	65	19	7	7	1.01	0.0	6.7	0.40
MacGregor (NW12-12-10W)	Long Plain	PGW189	LFS	1	66	19	7	7	3.00	0.0	7.5	0.30
MacGregor (SE1-12-10W)	Willowcrest	PGW195	LFS	2	66	20	5	7	1.40	0.0	7.3	0.49
Souris (SE9-8-21W)	Lauder	TW-SOU1	FS	2	57	32	3	6	1.01	0.0	6.9	0.10

MS = Medium Sand FS = Fine Sand VFS = Very Fine Sand

Table 3.3. Selected properties of a soil profile of the Lenswood series.

Soil No.	Horizon	Depth	Text. Class	MS	FS	VFS	Silt	Clay	Org.c	$CaCO_3$ equiv.	pH	Exch.K
		cm					%					$cmol_c\ kg^{-1}$
STA90	Ah	0-14	FSL	5	50	22	12	10	3.21	2.8	7.4	0.10
STA91	ACagj	14-26	LFS	5	57	23	6	8	0.43	7.6	7.5	0.16
STA92	AC	26-42	LFS	5	66	16	6	6	0.26	13.8	7.7	0.14
STA93	Ckgj	42-48	FS	4	61	27	4	2	-	7.3	7.7	0.13
STA94	CKgj	48-76	FS	4	43	46	5	2	-	6.7	7.7	0.14
STA95	CKgj	76-110	FS	12	41	40	3	3	-	2.5	7.6	0.13

Table 3.4. Selected properties of a soil profile of the Almasippi Series.

Soil No.	Horizon	Depth	Text. Class	MS	FS	VFS	Silt	Clay	Org.C	$CaCO_3$ equiv.	pH	Exch.K
		cm					%					$cmol_c\ kg^{-1}$
WBN66	Ap	0-15	LFS	4	50	29	7	10	2.20	9.2	7.8	0.30
WBN67	AC	15-20	FS	4	67	21	4	4	0.14	4.7	7.8	0.12
WBN68	Ckgj	20-67	FS	5	56	30	3	6	-	10.4	7.8	0.21
WBN69	Ckg	67-130	FS	6	56	34	2	2	-	10.9	7.8	0.29

Table 3.5. Selected properties of a soil profile of the Long Plain series.

Soil No.	Horizon	Depth	Text. Class	MS	FS	VFS	Silt	Clay	Org.c	$CaCO_3$ equiv.	pH	Exch.K
		cm					%					$cmol_c\ kg^{-1}$
GY1	Ap	0-30	FS	2	58	31	4	5	0.8	0.0	6.8	0.20
GY2	Aejg	30-60	S	1	72	22	2	3	0.2	0.0	6.9	0.21
GY3	AB	60-80	S	1	59	32	4	4	0.3	0.0	7.0	0.18
GY4	Bg	81-100	S	2	70	19	4	5	0.3	0.0	7.1	0.19
GY5	BC	100-120	LS	2	51	34	6	7	0.2	0.2	7.1	0.21
GY6	Cg	120+	LS	1	51	35	8	5	-	0.3	7.3	0.20

MS = Medium Sand, FS = Fine Sand, VFS = Very Fine Sand.

3.2.2 $CaCO_3$ Equivalent

The $CaCO_3$ equivalent of the soils was determined by using a pressure calcimeter as described by Skinner and Halstead (1958) and Skinner et al., (1959). In this method carbonates are treated with hydrochloric acid in a closed system under constant volume and temperature, and the increase in pressure as read on a manometer is related linearly to the content of CO_2 in the carbonates.

3.2.3 Organic Carbon

The procedure used for determining organic carbon is the Walkley-Black method, modified for automatic titration, based on the oxidation of readily oxidizable carbon of soils by $Cr_2O_7^{2-}$ with sulphuric-acid-heat-of-dilution. Excess of $Cr_2O_7^{2-}$ in the solution is back-titrated with Fe^{2+}, with the end point in the titration determined by a potentiometric measurement using platinum and calomel electrodes (Raveh and Avnimelech, 1973).

3.2.4 Exchangeable Cations

Exchangeable Na, K, Ca and Mg were determined as described by Thomas (1982). Five gram soil samples in 250 mL centrifuge bottles were shaken with 100 mL neutral 1 N ammonium acetate (NH_4OAc) on a horizontal shaker for 30 minutes and filtered through Whatman No. 42 filter papers. The clear filtrate was analyzed for Na, K, Ca and Mg using an atomic absorption spectrophotometer.

3.2.5 Cation Exchange Capacity

Cation exchange capacity (CEC) was determined by the ammonium saturation method described by Chapman (1965). A 10 g soil sample was shaken for 1 hour with 50 mL 1 N NH_4OAc (pH 7.0) and allowed to stand overnight. The extract obtained after filtering the solution was retained for the determination of exchangeable cations. The soil was then leached with 99% isopropyl alcohol to remove the excess NH_4OAc and subsequently with 10% acidified NaCl to displace the NH_4^+ from the exchange complex. The leachate was distilled and the ammonia displaced was measured by titration against 0.1 N H_2SO_4.

3.3 METHOD OF POTASSIUM FIXATION AND EXCHANGEABLE K EXTRACTION

In this study potassium fixation is defined as the amount of added potassium which is not extractable by 1 N NH_4OAc.

Potassium fixation was measured using additions of 5 mL of KCl solutions containing 0, 50, 100, 200, 400 and 1000 μg K mL^{-1} to duplicate 5 g air-dried 2 mm sieved samples of soil in 50 mL glass beakers. The initial moisture content of the samples exceeded field capacity. Control samples were wetted with distilled water. Excess moisture in the samples was allowed to evaporate at room temperature until the moisture content was about field capacity. Samples were then covered with parafilm and kept moist for 3 days and then air-dried at room temperature for another 3 days.

Exchangeable K of the treated soil samples was extracted in 100 mL of neutral 1 N NH_4OAc by shaking for 30 minutes on a horizontal shaker and filtering through a No. 42 Whatman filter paper. The clear filtrate was analyzed for K using an atomic absorption spectrophotometer.

The fixed potassium was calculated as follows:

$$K_{fixed} = K_{applied} - (Exch.K_{treated} - Exch.K_{control}) \qquad (3.1)$$

Where,

K_{fixed} = the amount of K fixed from added fertilizer (mg K kg^{-1} soil)

$K_{applied}$ = the amount of fertilizer K applied to each sample (mg K kg^{-1} soil)

$Exch.K_{treated}$ = the amount of exchangeable K in treated soil samples (mg K kg^{-1} soil)

$Exch.K_{control}$ = the amount of exchangeable K in control (0 added K) sample (mg K kg^{-1})

The percent K fixed of the added fertilizer K was calculated as follows:

$$\% \text{ K fixed} = \frac{\text{Amount of K fixed (mg K kg}^{-1}\text{)}}{\text{Amount of K added (mg K kg}^{-1}\text{)}} \times 100 \qquad (3.2)$$

3.4 POTASSIUM FIXATION IN SAND FRACTION

Sand fractions (0.05 - 2.00 mm) were separated from Almasippi, Elm Creek and Rignold soils by mechanical means without using any chemical treatment. The whole soil samples were first soaked in distilled water for one day, then the samples were transferred to a 'milkshake' container with 200 mL distilled water and mixed for 5 minutes in an electric stirrer. The suspensions were then wet-sieved using a 50 μm sieve with plenty of distilled water until the filtrate was essentially clear. The sand fraction remaining on the sieve was collected, air-dried, and visible plant residues were removed.

Five grams of air-dried sand fraction were used for fixation studies as outlined earlier.

3.5 MINERALOGICAL ANALYSIS

3.5.1 Particle Size Distribution

Soil carbonates were destroyed by 1 N HCl as described by McKeague (1978), and organic matter, Fe-oxides and amorphous materials were removed as outlined by Jackson (1956).

Sand was separated from silt and clay fractions by wet-sieving. The separated sand fractions were air-dried and the coarse, medium and fine sand fractions were separated by dry-sieving. Air-dried sand fractions were used for further experiments whenever needed.

Clay was separated from the silt fraction by centrifugation. In this method, the sample which contained the silt and clay fractions was placed in a 250 mL centrifuge bottle and was spun at 500 rpm for 7 minutes in an International Model UV centrifuge. At the end of the prescribed period, the supernatant which contained the clay was siphoned into a flocculation vessel. Deionized water was added to the centrifuge bottle and the particles were resuspended and centrifuged again. This process was repeated 6 to 8 times until the supernatant was almost clear. The silt fractions were further separated into coarse (50-20 μm) and fine silt (20-2 μm) fractions using different centrifugation time as described by Jackson (1956).

The clay fractions were further subdivided by centrifugation into two size fractions 2.0 to 0.2 μm (coarse clay) and less than 0.2 μm (fine clay).

3.5.2 X-ray Diffraction Analysis

A Phillips X-ray diffractometer equipped with a Cu target and Fe filter was employed to qualitatively examine the mineralogy of the various fractions.

Samples in preferred orientation were prepared by pipetting a 1 mL suspension on 35 x 25 mm slides as outlined by Jackson (1956). The fine sand samples were ground to a smaller particle size before deposition on glass slides. Two sets of slides for each sample were prepared for diffraction analysis; the first being magnesium-saturated and the second potassium-saturated. The magnesium slides were solvated with glycerol.

Four sets of diffractograms were obtained from each sample: the magnesium-saturated material; potassium-saturated air-dried material; potassium-saturated after it had been heated at 300 and 550 C for 2 hours. The samples were scanned from 3 to 32° 2Θ at a rate of 2° 2Θ per minute. The clay minerals were identified from XRD peak intensities according to the method described by Brown (1961).

3.6 EFFECT OF DRYING ON POTASSIUM FIXATION

The purpose of the study was to compare wet fixation with the standard wet and air-drying procedure.

Nine coarse textured soil samples were randomly selected from the soil collection and two levels of K (0 and 100 mg kg^{-1} soil) were added in 4 replicates. Samples were incubated at field capacity as mentioned in the standard procedure. At the end of the incubation, samples were divided into two groups and one group was analyzed for K directly without air-drying. The second group of samples were kept open for 3 days until the samples were fully air-dried. Air-dried samples were analyzed for exchangeable K as usual and K fixation was calculated using the equation 3.1 and 3.2

3.7 EFFECT OF INCUBATION PERIOD ON POTASSIUM FIXATION

The purpose of this experiment was to compare the effect of different incubation periods on K fixation. Three coarse textured soil samples were selected and treated with 5 levels (50, 100, 200, 400, and 1000 mg kg^{-1} soil) of K as KCl. All the treatments were made as described in the standard K fixation method. Control samples were wetted with deionized water. Excess moisture was evaporated from all the samples until moisture content was about field capacity. Treated samples were then divided into 5 groups and the first group was incubated for 3 days as was done in the standard method; the second, third, fourth and the fifth groups were incubated for 6, 9, 12 and 15 days, respectively, at room temperature (about 25 C). At the end of each prescribed incubation period, duplicate samples were air-dried and analyzed for exchangeable K.

3.8 EFFECT OF PREVIOUSLY FIXED POTASSIUM ON SUBSEQUENT FIXATION

Two coarse textured soil samples, one from the Almasippi (Haywood) and the other from the Lenswood (S4) soil series, were selected to study the effect of previously fixed K on subsequent K fixation.

Six soil samples (25 g each, air-dried, 2 mm sieved) from each soil were treated with six levels (0, 50, 100, 200, 400 and 1000 mg K kg^{-1} soil) using KCl. The samples were incubated at field capacity for 3 days at room temperature. The samples were then allowed to air-dry for one week. The excess KCl from the treated soils was leached out by deionized water. Disappearance of chloride in the leachate (as indicated by a negative chloride test) was used as an indication of the complete removal of soluble K. Then the soil samples were again allowed to air-dry for one week.

Four samples (5 g each) from each treated soil were weighed into 50 mL glass beakers and 5 mL of deionized water was added to two samples, and 5 mL of KCl solution containing 400 μg K mL^{-1} was added to the other two. The initial moisture content of the samples exceeded field capacity. Excess moisture in the sample was allowed to evaporate at room temperature until the water content was about field capacity. Then the samples were covered and incubated for 3 days then air-dried later.

Each sample was analyzed for exchangeable K; and the fixed K from the newly added KCl was calculated by using the equations 3.1 and 3.2.

3.9 EFFECT OF $CaCO_3$ ON POTASSIUM FIXATION

Previous results of potassium fixation studies indicated that the carbonated soils were capable of fixing more K than the non-carbonated soils. To study the effect of carbonate on K fixation, a coarse textured non-carbonated soil which was used in the growth chamber experiment was selected and artificially carbonated by adding and mixing five levels (0, 0.25, 0.50, 1.00, and 2.00 % by weight) of laboratory grade $CaCO_3$.

Fifty grams of carbonated soil from each level was weighed into a 200 mL beaker and a sufficient amount of deionized water was added to wet the soil. The excess moisture was evaporated until the moisture content was about field capacity, then the samples were covered and incubated at room temperature for one week and air-dried.

Six samples (5 g each) from each level of carbonated soil were weighed into 50 mL beakers and treated in duplicate with 3 levels (0, 100 and 400 mg K kg^{-1} soil) as was done in the standard K fixation method. Samples were incubated, air-dried and then K fixation was measured.

3.10 EFFECT OF DIFFERENT CATIONS ON THE EXCHANGE COMPLEX ON K FIXATION

3.10.1 Effect of Ca and Mg ions (Method 1)

Two soil samples, one calcareous and the other non-calcareous were selected to study the effect of Ca and Mg ion on K fixation. Two 25 g soil samples from each soil were loosely packed in two separate small plastic columns and then the first column was leached with 300 mL of 0.2 M $CaCl_2$ and the second column with 300 mL of 0.2 M $MgCl_2$ solutions. The leaching rate was maintained at about 0.2 mL min^{-1}. At the end of leaching, the excess Ca and Mg from the soil was leached with deionized water until the leachate was free of chloride and then the samples were air-dried. Potassium fixation was carried out by adding two levels (0 and 100 mg K kg^{-1} soil) in duplicate to the Ca and Mg enriched soils. Potassium fixation was also measured from an untreated soil as a check.

3.10.2 Effect of Ca and Na ions (Method 2)

Three soil samples were selected and treated with solutions containing four different ratios of Na:Ca ions as NaCl and $CaCl_2.2H_2O$ to obtain four levels of exchangeable Ca and Na on the exchange complex.

Sixteen air-dried soil samples (5 g each) from each soil were weighed into 90 mL centrifuge tubes to which were added 50 mL of 1 N NaOAc (pH 5) to destroy carbonate content as described by Jackson (1956). Samples were kept in the water bath at 80 C until all the carbonates were destroyed. The samples were then centrifuged and the supernatant portion discarded. The same process was repeated until all the carbonates were destroyed. At the end, all the samples were washed once with neutral 1 N NaOAc.

All the carbonate-free samples were transferred to 250 mL centrifuge bottles and divided into four groups (four samples each). The first group of samples were shaken with 100 mL 0.1 N NaCl solution for 30 minutes, centrifuged and the supernatant portion was discarded. This process was repeated three times. The excess NaCl in the sample was removed by two 95% isopropyl alcohol washing. The second and third groups were treated in a similar manner by using 100 mL 0.1 N solutions containing (Na:Ca) in the ratio of 3:1 and 1:3 respectively. The fourth group of samples were shaken with 100 mL 0.1 N $CaCl_2$ solutions. At the end, Na and Ca enriched samples were air-dried.

Potassium fixation was carried out on the air-dried treated samples by adding in duplicate two levels (0 and 400 mg K kg^{-1} soil) as KCl.

3.11 AVAILABILITY OF FIXED POTASSIUM TO WHEAT

Soil samples were gathered in the spring of 1985 from four sites in Manitoba to study the availability of fixed K to wheat grown in pots. The sites for soil sampling were selected based on the previous results of K fixation studies to represent low to high fixing soils. The location and some physico-chemical properties of the soils studied are given in Table 3.6.

Six kilograms of air-dried soil were weighed into each pot and four levels (0, 50, 100, and 200 ppm) of K (dry soil weight basis) was applied by dissolving the required amount of KCl in 700 mL water. The mixing of potassium was done by placing the 6 kg soil of each pot on a sheet of strong polythene and spraying the 700 mL KCl solution uniformly as possible by a small hand sprayer. A check treatment was also prepared in a similar manner but 700 mL deionized water was added. All the treated and nontreated soil samples were allowed to dry for 4 days.

Table 3.6. Some characteristics of soils used for the Growth Chamber Experiment.

Soil Properties	Soil Series			
	Long Plain (Elm Creek)*	Willowcrest (Barnsley)	Almasippi (St.Claude)	Lenswood (Steinbach)
Texture	Fine Sand	Fine Sand	Loamy F.S	F.S.Loam
% Sand	93	89	86	79
% Silt	3	4	6	10
% Clay	5	7	8	11
% $CaCO_3$ eq.	0	0	0	9
% Org.C	1.1	1.7	2.4	3.1
C.E.C ($cmol_c$ kg^{-1})	7.1	9.9	12.2	14.5
pH ($CaCl_2$)	6.9	7.2	7.1	7.6
Exch.K (mg kg^{-1})	94	94	144	52

* Approximate Location.

After air-drying, five gram of soil sample was taken from each pot to determine the exchangeable K content. The amount of K fixed from the added K was calculated as shown below:

$$K_{\text{fixed}} = K_{\text{applied}} + \text{Exch.K}_{\text{before trt.}} - \text{Exch.K}_{\text{after trt.}} \qquad (3.3)$$

The basal fertilizer application consisted of N as $Ca(NO_3)_2.4H_2O$ and P as H_3PO_4 at a concentration of 100 ppm each, 10 ppm Cu as $CuSO_4.5H_2O$, 20 ppm Zn as $ZnSO_4.7H_2O$, and 50 ppm S as $CuSO_4.5H_2O$, $ZnSO_4.7H_2O$ and $CaSO_4.2H_2O$. The nutrients were applied in a liquid form and mixed thoroughly with soil prior to planting.

Eight wheat (Triticum aestivum L.) seeds (c.v. Columbus) were placed 2 cm below the surface and sufficient water was added for germination. Each treatment was replicated three times, thus giving 48 pots placed at random in the growth chamber which were regularly rotated for a complete randomization. The temperature of the growth chamber was 22 C during the day and 17 C at night and the day length was 16 hours. Humidity of the chamber was 50% in the day and 70% at night. The plants were grown under light intensity of 500 to 550 microeinsteins m^{-2} sec^{-1} within and above the canopy.

After germination, wheat seedlings were thinned to four per pot. Throughout the experiment, moisture content of the pots was maintained at about field capacity. Twenty five days after seeding, each pot received an extra addition of N as $Ca(NO_3)_2.4H_2O$ at a concentration of 100 ppm. The experiment was carried out up to the heading stage (52 days) then the tops were harvested. At the end of the experiments, soil from each pot was carefully separated and divided into two halves. The first half was air-dried, roots were separated and discarded, soils were thoroughly mixed and sampled for exchangeable K analysis. The second half was carefully washed (wet-sieved) with water and roots were collected. The above ground and below ground portions of the plant were dried to a constant weight at 70 C and samples were weighed and ground for chemical analysis. Availability of fixed K to wheat was calculated by the method described below.

Plant parts were analyzed for total K by nitrate-perchlorate digestion. The soil samples were analyzed for exchangeable K by using 1 N NH_4OAc as described earlier.

3.11.1 Measurement of Fixed Potassium Available to Wheat

In the context of this study, exchangeable K is defined as the soil K that is extractable with 1 M NH_4OAc. Therefore, nonexchangeable K is defined as the soil K which is not subject to extraction with 1 N NH_4OAc. Nonexchangeable K taken up by wheat was calculated by

$$\text{NEK} = \text{KUP} - (\text{Exch.K}_{\text{after}} - \text{Exch.K}_{\text{end}}) \qquad (3.4)$$

Where:

NEK = the amount of nonexchangeable K removed by wheat during the experiment (mg K kg^{-1} soil)

KUP = total amount of K taken up by wheat (mg K kg^{-1} soil)

$\text{Exch.K}_{\text{after}}$ = the exch.K after the treatment with K (mg kg^{-1} soil)

$\text{Exch.K}_{\text{end}}$ = the exch.K at the end of experiment (mg kg^{-1} soil)

3.12. NON-EXCHANGEABLE POTASSIUM RELEASE

3.12.1 Hydrochloric Acid Reflux Method.

The same four soils used for the growth chamber experiment were selected to study the non-exchangeable K release pattern to an acid extractant. In addition, the soils were treated with two levels (400, and 1000 mg K kg^{-1} soil) to study the changes in non-exchangeable K release pattern to an acid extractant. The K treated soils were prepared the same way as that for the K fixation studies.

The chemical method used to determine the amount of non-exchangeable K which might be available to plants in a growing season was proposed by Singh et al. (1983). The HCl-reflux method is actually a modification of Haylock (1956) and MacLean's (1961) methods, in which HNO_3 was used as an extractant. In this (HCl reflux) method a K fraction was removed by soaking 5 g of air-dried soil in 100 mL 0.1 N HCl over night. The solution was filtered from the soil, and the soil transferred to an extraction thimble and the thimble placed in a modified Soxhlet extractor (modification B of Singleton and Lavkulich (1978)), a straight syphon, allowing flow directly from the barrel to the collecting flask with some glass wool for support. Condensed vapor (at 80 C) from 50 mL boiling 20.24% HCl (6.52 N) was allowed to percolate through the soil for 15 minutes per extraction (12 minutes boiling + 3 minutes to drain) for a total of 10 extractions. After each extraction the acid was removed from the boiling flask by pipette and a fresh aliquot added; this procedure, was done via a side-arm on the collecting flask. The used acid was transferred to a 100 mL volumetric flask and analyzed for K by an atomic absorption spectrophotometer.

The 6.52 N HCl is a constant boiling mixture, the vapor of which therefore has the same composition as the acid. This ensures a constant concentration of acid in contact with the soil (Singh et al., 1983).

The total amount of nonexchangeable K extracted by HCl (mg K kg^{-1} soil) is given by

$$\text{NEK (extracted)} = \text{Sum.K} + 0.1\ \text{N HCl.K} - 1.0\ \text{N } NH_4OAc.K \qquad (3.5)$$

Where,

NEK (extracted) = total nonexchangeable K extracted (mg K kg^{-1})

Sum.K = the sum of the K extracted by 6.52 N HCl in 10 sequential extraction (mg K kg^{-1})

0.1 N HCl.K = total 0.1 N HCl extractable K prior to the sequential extraction (mg K kg^{-1})

1.0 N NH_4OAc.K = the amount of K extracted by 1 N NH_4OAc (mg K kg^{-1})

Since the exchangeable K was removed with 0.1 N HCl prior to the sequential extractions, a subtraction was included to account for differences between the amount of K extracted with 0.1 N HCl and that extracted with 1 N NH_4OAc.

Haylock (1956) termed the constant amount of K released in the final few HNO_3 extractions as 'constant-rate K'. However, in this experiment, the amount of K released at the last HCl extraction was considered as the amount of constant-rate K that was extracted during a single extraction, as the values of that extract had reached a constant or near constant level of K. Therefore the total constant-rate K released was calculated as

$$\text{Total Const.-rate K} = \text{Const.-rate K} \times \text{number of 6.52 N acid extr.} \quad (3.6)$$
$$(\text{mg K kg}^{-1} \text{ soil})$$

Finally, the step-K is taken to be the difference between NEK (extracted) and the total constant-rate K released, and is expressed in mg K kg^{-1} soil.

CHAPTER 4

PRELIMINARY RESULTS

4.1 PROBLEM IDENTIFICATION

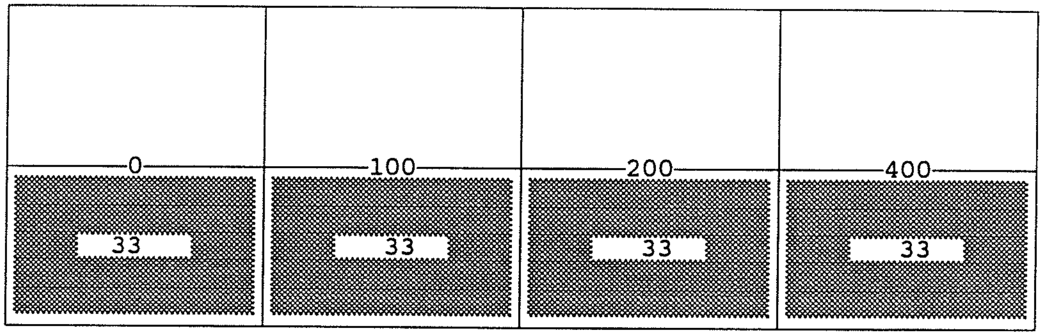
Plant responses to potassium application in coarse textured soils have been widely observed. The results from a three year field experiment initiated in 1982 in Manitoba, showed that large responses can be obtained to the addition of K to wheat in a coarse textured soil (Murage, 1984). To study the maximum production of wheat under rainfed conditions with K as the nutrient variable, experiments were set up by Murage (1984) in three locations in Manitoba namely Haywood, Elm Creek and Winkler. These three locations were chosen on the basis of the available soil K content. The Haywood site was chosen to represent a low K level while the Elm Creek and Winkler sites were chosen to represent medium and high K levels respectively. Some physical and chemical properties of the three soils used in the field experiments are given in Table 4.1.

These experiments consisted of four replicates and were laid down in a split-plot design. The main plots received four rates of K (0, 100, 200 and 400 kg ha^{-1}) as KCl. The K was broadcast and mixed completely with the top soil to 7.5 cm deep. At the time of seeding, each replicate was divided lengthwise into two equal halves to provide eight sub-plots per replicate (Fig. 4.1). One set of sub-plots from each replicate received an extra 33 kg K ha^{-1} banded with the seed at a depth of 2.5 cm. At all sites, wheat was grown to maturity. These experiments

Table 4.1. Selected properties of the soils used for field and laboratory experiments (Murage, 1984).

Location	Soil Series and Sub group	Texture	MS	FS	VFS	Silt	Clay	Org.C	$CaCO_3$ equiv.	pH	Exch.K
			%								$cmol_c\ kg^{-1}$
HAYWOOD	Almasippi* Gleyed-Carbonated Rego Black	LFS	1	57	26	6	9	1.61	2.0	8.1	0.11
ELM CREEK	Elm Creek* Orthic Black	SCL	2	37	25	14	22	2.90	1.0	8.2	0.63
WINKLER	Rignold* Gleyed Black	VFSL	2	32	35	12	19	2.55	0.3	8.0	1.09

* Soil Series.



☐ Basal fertilizer broadcast and mixed with top soil to 7.5 cm deep at the beginning of the experiment in 1982.

▨ 33 kg K ha^{-1} banded with the seed to 2.5 cm deep every year at the time of seeding in addition to broadcast K.

Fig. 4.1 Layout of the field experiment (Murage, 1984).

were continued for three years at all three locations. Each year 33 kg K ha^{-1} was banded with the seed as described earlier. No other additions of K were made in the second and third years. The grain yield data obtained from the Haywood site in the second year are reported in Table 4.2. The first year data for this site were similar to the second year data; but the third year data (not reported here) were somewhat different and showed that banding (33 kg K ha^{-1}) alone was not enough to attain maximum yield. Grain yields for the other two sites (Elm Creek and Winkler) are not reported here since the yields were not significantly affected by the addition of K.

The results (Table 4.2) indicate a large response to applied K at the Haywood site on a coarse textured soil. Grain yield increased from 601 kg ha^{-1} at 0 application rate to 2558 kg ha^{-1} at 400 kg K ha^{-1} application. When 33 kg K ha^{-1} was banded in plots which had not received any broadcast K, the grain yield was similar to that of 400 kg K ha^{-1} broadcast. The grain yields from plots which received banded plus broadcast K were not influenced by the increasing levels of broadcast K indicating that 33 kg K ha^{-1} banded with the seed was sufficient to overcome K deficiencies whereas 200 kg ha^{-1} broadcast K was not. The better grain yield with 33 kg K ha^{-1} banded alone could have been due to several reasons: (i) due to the easy availability of K arising from its close proximity to seeds; (ii) due to availability of more K to the crops as a result of reduced K fixation. In the case of banding the fertilizer as opposed to mixing with soil, the volume of the soil in contact with the fertilizer is less. The other reasons for higher grain yield with banding may be the combination of both easy availability and less fixation of K. But, none of the reasons mentioned here were confirmed during the time these experiments were conducted.

Later, a growth chamber experiment was conducted by Murage (1984) using the same Almasippi (Haywood) soil used in the field experiment to study the influence of K fertilization on wheat. This factorial experiment consisted of five levels of K (0, 25, 50, 100 and 200 ppm)

Table 4.2. Influence of K mixed with soil and K banded with the seed on grain yield (kg ha^{-1}) at the Haywood site (Murage, 1984).

K mixed	K banded with the seed kg ha^{-1} 0	 33
kg ha^{-1}	Grain Yield kg ha^{-1}	
0	601 a	2609 d
100	1414 b	2670 d
200	1953 c	2652 d
400	2558 d	2561 d
Main Effect of Banding	1632 A	2623 B

Means with the same small or capital letter are not significantly different at 5% level according to Tukey's Studentized Range Test.

as KCl and replicated three times. One crop of wheat was grown to maturity. The results (not presented here) indicated that about 70% of the applied K from all the treatments was unaccounted for by the crop uptake and the exchangeable K measured by 1 N NH_4OAc extraction. The results from the growth chamber experiment indicated that the applied K in the Almasippi soil may have been fixed in nonexchangeable forms as it was not immediately available to the growing crops.

Murage's (1984) field experiment also suggests that less K fixation may have been the probable cause for the better efficiency of banded K as opposed to the broadcasting of K fertilizer in the Haywood site. The wheat grown in the other two soils of the field experiment did not respond to the addition of K. The lack of response to K addition in those two soils may have been due to higher exchangeable K content than the Almasippi soils or due to the release of K from the nonexchangeable forms as reported by Richards (1985) and others. In order to understand the K fixing behavior of those soils as opposed to the Almasippi soil, a K fixation study was initiated using all three soils used in Murage's field experiment.

4.1.1 Potassium Fixation by three Manitoba Soils in which the Field Experiments were conducted in 1982

Soil samples used in this laboratory study were collected by Murage in 1982 from the three field experimental sites. The soil samples were treated with five levels of K (50, 100, 200, 400, and 1000 mg kg^{-1}) as KCl, maintained at field capacity for three days, and then air-dried for three days before the exchangeable K analysis. Amount of K fixed was measured as the difference between the amount of K applied and the increase in extractable K after equilibration using 1 N NH_4OAc as an extractant. The K fixation results are given in Table 4.3.

The Almasippi soil showed higher fixing ability than the Elm Creek or Rignold soils at all levels of added K. In all three soils, the amount of K fixation increased with increasing application rates of K while the % K fixation decreased with increased application rates in Almasippi and Rignold soils. In general, the amount of K fixation observed at any level of application was not directly related to the clay or silt content (Table 4.1) of those soils. A wide variation in K fixation was observed between Elm Creek and Rignold soils which contained about the same amount of clay and silt. However, at the higher levels of K application, the amount of K fixed was negatively related to the amount of exchangeable K.

Table 4.3: Influence of amount of applied K on K fixation in three Manitoba Soils.

Applied K	Amount of K Fixed* Soil Series and (Location) Almasippi (Haywood)	Elm Creek (Elm Creek)	Rignold (Winkler)
	mg K kg^{-1}		
50	(100) 50 a	(12) 7 a	(24) 12 a
100	(73) 73 a	(14) 14 a	(17) 17 a
200	(74) 148 ab	(26) 52 ab	(15) 31 a
400	(67) 269 cb	(25) 99 b	(11) 43 a
1000	(42) 421 c	(25) 253 c	(17) 166 b

* % Fixation given in parentheses.

Values followed by the same letter in any column are not significantly different at the 1% level according to Tukey's Studentized Range Test.

The observed results in this experiment indicated that these soils have the ability to fix K against 1 N NH_4OAc extraction. In particular, the large amount of K fixation observed in the Almasippi soil was comparable to the amount of K unaccounted for in Murage's growth chamber experiment. Although there could be many reasons why the observed K fixation was not positively related with clay or silt fraction of soils, the magnitude of K fixation in the sand fraction needs to be known for a clear understanding of K fixation in coarse textured soils. Therefore, it was decided to look at K fixation in the sand fractions of these soils. An experiment was thus set up to compare the K fixation behavior of the sand fractions of the Almasippi, Elm Creek and Rignold soils.

4.1.2 Potassium Fixation in the Sand Fraction

To obtain the sand fraction, soil samples from each of the Almasippi, Elm Creek and Rignold soils were soaked in distilled water, dispersed with milkshake machine and passed through a 50 μm sieve. No chemicals were used in the separation process in order to avoid any reactions with the sand fractions. The separated sand fractions were air-dried before K fixation studies. Potassium fixation studies were carried out using 5 g of sand by adding only two levels of K (100 & 400 mg kg^{-1}) as KCl. Results of K fixation by the sand fractions are given in Table 4.4.

From Table 4.4 it is clear that the sand fraction of the Almasippi soil had a higher ability to fix K than the sand fractions of the other soils studied. The K fixation observed in the sand fraction is an indication of the presence of K fixing minerals in the sand size fractions and that fixing minerals are more abundant in the Almasippi soils. As observed in the whole soil, increasing the amount of K added increased the amount of K fixed in all three soils. In all three soils, the total amount of K fixed by the sand fractions at any application level is less than the amount fixed by the same amount of whole soils, with the exception of Elm Creek in which the

Table 4.4. Influence of amount of applied K on K fixation in sand fraction (between 0.05 to 2.00 mm particles) of Almasippi, Elm Creek and Rignold soils.

	Amount of K fixed*		
	Soil Series		
Applied K	Almasippi(85)#	Elm Creek(64)	Rignold(69)
	mg K kg^{-1}		
100	(59) 59 a	(24) 24 a	(7) 7 a
400	(29) 117 b	(18) 73 b	(8) 34 a

* % Fixation given in parentheses.
\# % Total Coarse fraction in whole soil given in parentheses.
Values followed by the same letter in any column are not significantly different at the 1% level.

amount of K fixed by the sand fraction at 100 mg K kg^{-1} application level was higher than the amount fixed by the whole soil (see Table 4.3). By considering the amount of K fixed in the whole soil at 400 mg K kg^{-1} application level and the amount of K fixed in the sand fraction alone at the same level of application and the proportion of sand, silt and clay fractions in the whole soil, it is evident that the K fixing ability of the silt plus clay (Table 4.5) of Almasippi soil was much higher than Elm Creek and Rignold soils.

The differences in K fixation observed in these soils lead to speculation that the types of mineral present in the Almasippi soil are different from those in the Elm Creek and Rignold soils. The observed results also illustrate that the clay and silt fractions were the major components responsible for K fixation in these coarse textured soils.

Table 4.5. The K fixing ability of whole soil, sand fractions and silt plus clay fractions of three Manitoba soils*.

	Almasippi	Elm Creek	Rignold
		K fixation by whole soil mg K kg^{-1}	
Whole soil (Table 4.3)	269	99	43
Sand fraction (Table 4.4)	99	47	23
Silt + Clay	170	52	20
		K fixation by silt plus clay mg K kg^{-1}	
Silt + Clay	1133	144	65

* Calculations were made using the amount of K fixed at the 400 mg kg^{-1} K application.

4.1.3 K Fixation in the Very Fine Sand and Fine Sand Fractions of the Almasippi (Haywood) Soil

The sand fraction of the Almasippi soil was divided into very fine sand (0.05 - 0.1 mm) and fine sand (0.1 - 2 mm) fractions by dry-sieving. Potassium fixation studies were carried out to measure the ability of each sand fraction to fix added K. The fixation values are presented in Table 4.6.

As seen on Table 4.6, both the very fine sand (VFS) and fine sand (FS) fractions of the Almasippi soil fixed added K. In general, the VFS fraction fixed a larger amount of K than the FS fraction. As observed in the whole soil, the amount of K fixation increased and percent K fixation decreased with increased K application rate. The total amount of K fixed by VFS plus FS is comparable to that of K fixed by the total sand fractions of the soil (see Table 4.4). These results again illustrate that sand fractions, specifically VFS fractions, have a high capacity to fix added K in the Almasippi soil. However, their contribution towards K fixation is much less than the silt plus clay fractions (see Table 4.5).

Table 4.6. Influence of amount of applied K on K fixation in the very fine sand and fine sand fractions of the Almasippi soil.

Applied K	Amount of K Fixed* Sand Fraction Very Fine Sand (26)#	Amount of K Fixed* Sand Fraction Fine Sand (58)
	mg K kg^{-1}	
100	(69) 69 a	(55) 55 a
400	(40) 159 b	(29) 115 b

* % Fixation given in parentheses.

\# % Coarse fraction in whole soil given in parentheses.

Values followed by the same letter in any column are not significantly different at the 1% level.

Table 4.7. Influence of the amount of applied K on K fixation in the Almasippi soil after two seasons of cropping.

Potassium applied in 1982	Exch.K at the end of 2nd season	Newly applied K	Amount of K fixed from newly applied K*
kg ha^{-1}		mg K kg^{-1}	
0	49	400	235 a
100	51	400	205 ab
200	58	400	198 ab
400	88	400	157 b

*Values followed by the same letter in any column are not significantly different at the 5% level according to Tukey's Studentized Range Test.

4.2 EFFECT OF PREVIOUS K APPLICATION ON SUBSEQUENT FIXATION IN THE ALMASIPPI SOIL

An experiment to study the effect of previous applications of K fertilizer on the residual capacity to fix K was carried out using the Almasippi soil. Soil samples were collected at the end of the second cropping season from all of the K broadcast (including the check) sub-plots of Murage's (1984) field experiment located at the Haywood site. Exchangeable K was measured and K fixation was determined by adding K at the rate of 400 mg K kg^{-1} as KCl. The effects of previous applications on subsequent fixation are given in Table 4.7 (Page 51).

The results shown in the second and in the last column of Table 4.7 are the means of four values. The values reported in the second column represent the residual exchangeable K values at the end of the second cropping season. The amount of subsequent fixation from the newly applied K decreased as the amount of residual K (or the amount of previously applied K) increased. The soil with 49 mg kg^{-1} residual K fixed 235 mg K kg^{-1} from the newly applied source while the soil with 88 mg exchangeable K kg^{-1} fixed only 157 mg K kg^{-1} from the subsequent application. In other words the soil which had received the K fertilizer (400 mg kg^{-1}) in the field fixed only about 40% of the added fertilizer while the unfertilized soil fixed about 60% indicating that the soil which had received a high dose of K previously in the field had lost some of its ability to fix K from the subsequent application. This would suggest that this soil had fixed a considerable portion of the K added in the field and thus a portion of its fixing sites had become filled.

From the preliminary studies it is evident that (a) although the coarse textured Almasippi soil fixed more K than the other soils studied, the clay plus silt fraction of that soil fixed more K on a weight basis than sand fractions; (b) the higher K fixation observed in the Almasippi soil as compared to the other two soils studied, may be due to differences in clay mineralogical compositions of these soils; (c) previous additions of K reduced the K fixing ability of the soil; (d) the amount of K fixation in a given soil may be related to the exchangeable K content of the soil and hence there may be an equilibrium between the fixed K and the exchangeable K.

The observations made from the preliminary experiments indicated the need for a detailed study on K fixing abilities and the cause(s) of fixation of various coarse textured soils of Manitoba. The following chapter will concentrate on the following:

(a) the K fixing abilities of selected coarse textured soils;

(b) the relationship between K fixation and the soil characteristics;

(c) the relationship between K fixation and the clay mineralogy of soils;

(d) the K fixing capacity of soils;

(e) the availability of fixed K to wheat; and

(d) the non-exchangeable K release patterns of selected coarse textured soils.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 POTASSIUM FIXATION IN COARSE TEXTURED SOILS

5.1.1 Potassium Fixation in Surface Soils (Batch I)

A preliminary experiment conducted in the laboratory on K fixation (see Chapter 4) with three Manitoban soils indicated that the coarse textured Almasippi soil had a high ability to fix added K in non-exchangeable forms. Some evidence for K fixation has been obtained from Murage's (1984) growth chamber experiment in which an Almasippi soil fixed a large amount of K in non-exchangeable forms and the fixed K was not available to the growing crops. Soils with a high capacity for fixation of K often require high rates of K fertilizer to assure an adequate supply of this nutrient for maximum production. This is particularly true when K is mixed with the soil, as may occur in the practice of broadcast application of fertilizer instead of its placement at the time of seeding. The high K fixing behavior observed in the Almasippi soil prompted the need for a detailed study on the extent to which Manitoban coarse textured soils will fix applied K. The main purpose of this study was to compare the extent of K fixation by 11 coarse textured soils.

Soil samples for this study were selected from the collection of samples previously taken by Canada-Manitoba Soil Survey, University of Manitoba. Selected samples were collected mainly from uncultivated fields of the Southern Manitoba region. Some of the characteristics of the soils used in these experiments are given in Table 3.1.

Potassium fixation values shown in Table 5.1 indicate that the fixation increased with increased K application in all the soils studied. In general, the percentage K fixation decreased with increased K additions. Similar trends have been reported by other workers (Attoe, 1948; McLean and Simon, 1958; Barber, 1979). Among the 11 soils studied, Lenswood soil (STA-90) fixed the largest amount of K at all the application levels while Long Plain soil (GY-1) fixed the lowest amount. At application rates of 50 and 1000 mg K kg^{-1} the fixed K varied from 12 to 84% and 12 to 53% respectively. In general, K fixation values among the different soils studied are highly variable.

Although K fixation has been widely studied in soils and clays (Mortland et al., 1957; McLean and Simon, 1958; MacLean, 1962; MacLean and Brydon, 1963; MacLean, 1968; MacLean and Brydon, 1971; Shaviv et al., 1985), the K fixation values obtained from other workers are often not comparable because of the different methods of measurement. However, some fixation values obtained from Canadian soils warrant attention. MacLean (1962) reported that 16 to 71% of the 585 ppm added K was fixed against 1 N NH_4OAc extraction by the surface samples of 11 Canadian soils upon five cycles of wetting and drying at 70 C. The clay and silt content of the soils used by MacLean (1962) varied from 6 to 36% and 17 to 55%, respectively. The soils used by MacLean (1962) were considerably higher in clay and silt content than the soils used in the present study. In another study under field condition, MacLean (1977) reported that a major portion of added K was fixed by the top layers of a loam and a sandy loam soil when an excessive rate of 2,232 kg K ha^{-1} was added to the fallow plots in a three period. His study also indicated no evidence of leaching of added K beyond 30 cm depth during the period of study.

Table 5.1. Influence of amount of applied K on K fixation in coarse textured surface soils (Batch I).

Soil No.	RWL7	SC357	SC315	SC297	STA90	WBN66	WBN41	GY1	GY14	GY50	BRA1
Applied K	Amount of K fixed*										
	mg K kg^{-1}										
50	(30) 15 a	(66) 33 a	(68) 34 a	(50) 25 a	(84) 42 a	(52) 26 a	(18) 9 a	(12) 6 a	(48) 24 a	(30) 15 a	(38) 19 a
100	(28) 28 ab	(56) 56 a	(46) 46 a	(54) 54 a	(84) 84 b	(51) 51 a	(31) 31 ab	(26) 26 ab	(43) 43 ab	(30) 30 ab	(37) 37 a
200	(23) 46 b	(48) 96 a	(44) 88 b	(52) 104 b	(74) 147 c	(50) 99 ab	(28) 55 bc	(14) 27 ab	(36) 72 b	(22) 44 ab	(37) 73 b
400	(23) 93 c	(48) 192 b	(35) 139 c	(46) 182 c	(69) 274 d	(41) 162 b	(24) 94 c	(13) 50 ab	(30) 121 c	(21) 84 b	(40) 158 c
1000	(19) 191 d	(33) 328 c	(20) 202 d	(33) 326 d	(53) 534 e	(29) 286 c	(14) 136 d	(12) 124 b	(24) 244 d	(18) 175 c	(29) 290 d

* % Fixation given in parentheses.

Values followed by the same letter in any column are not significantly different at the 5% level according to Tukey's Studentized Range Test.

5.1.2 Potassium Fixation in Profile Samples

Among the 11 surface soil samples studied, three soil profiles were selected, based on low (Long Plain - GY1), medium (Almasippi - WBN66) and high (Lenswood - STA90) amounts of K fixation observed at the surface depth to study the effect of depth on K fixation. Some physical and chemical properties of the selected soil profiles are given in Tables 3.2 to 3.5.

5.1.2.1 Potassium Fixation in the Lenswood Soil Profile

The amount of K fixation increased and percent K fixation decreased with increased application of K (Table 5.2) as observed in the surface soil samples (Table 5.1). Variations in the amount of K fixation were observed within the profile at each level of K application. Although the differences in the amount of K fixation within the profiles were not significant at the low levels of K applications, the amount of K fixation decreased significantly with increasing depth of the soil at the highest level of K application. Variation in K fixation observed with increasing depth could be attributed to the clay and silt content of the soil, since the clay and silt content decreased with increasing soil depth within the Lenswood soil profile (Table 3.3). The amounts of K fixed in the deepest horizons of this Lenswood soil profile were markedly higher than the amounts of K fixation observed in other soils (Table 3.1 and 5.1) that had higher clay and silt contents.

5.1.2.2 Potassium Fixation in Almasippi Soil Profile

As with the Lenswood soil profile, the amount of K fixation increased and the percentage fixation decreased with increased application rates throughout the profile (Table 5.3). However, the amount of K fixation in the Almasippi soil profile was generally lower than the amount fixed in the Lenswood soil profile at any level of K application. In general, as observed in the Lenswood soil profile, the amount of clay and silt content decreased with increased depth of soil

Table 5.2. Influence of amount of applied K on K Fixation in a soil profile of Lenswood series (STA-90).

Soil Depth (cm)	0-14	14-26	26-42	42-48	48-76	76-110
Applied K	Amount of K fixed*					
	mg kg^{-1}					
50	(84) 42 a	(100) 50 a	(78) 39 a	(96) 48 a	(92) 46 a	(74) 37 a
100	(84) 84 ab	(85) 85 ab	(73) 73 a	(92) 92 b	(81) 81 ab	(79) 79 a
200	(74) 147 abc	(80) 159 c	(72) 143 ab	(76) 151 bc	(69) 137 ab	(66) 132 a
400	(69) 274 d	(70) 281 c	(61) 244 c	(52) 206 b	(44) 176 a	(52) 207 b
1000	(53) 534 d	(55) 546 d	(43) 425 c	(28) 282 b	(17) 170 a	(21) 210 a

* % Fixation given in parentheses.

Values followed by the same letter in any row are not significantly different at the 5 % level, according to Tukey's Studentized Range Test.

Table 5.3. Influence of amount of applied K on K fixation in a soil profile of Almasippi series (WBN-66).

Soil Depth (cm)	0-15	15-20	20-67	67-130
Applied K	Amount of K fixed*			
mg kg^{-1}				
50	(52) 26 a	(64) 32 a	(78) 39 a	(76) 38 a
100	(51) 51 a	(57) 57 a	(67) 67 a	(65) 65 a
200	(50) 99 a	(53) 105 a	(61) 122 a	(53) 106 a
400	(41) 162 a	(39) 155 a	(41) 164 a	(40) 158 a
1000	(29) 286 a	(21) 207 a	(22) 217 a	(22) 221 a

* % Fixation given in parentheses.

Values followed by the same letter in any row are not significantly different at the 5 % level, according to Tukey's Studentized Range Test.

(Table 3.4). However, the amount of K fixation was not significantly affected by the depth of the soil at any level of K application.

5.1.2.3 Potassium Fixation in Long Plain Soil Profile

As with the other two profiles studied, the amount of K fixation increased with increased application rate in the Long Plain soil profile (Table 5.4). However, the percentage of K fixed was not decreased in all the horizons with increased K application rates. In general, the amount of K fixation at any level of K application was significantly higher in the deepest horizons than in the surface horizon. At the two highest levels of application, the amount of K fixation significantly increased with increased soil depth. The increased K fixation observed with increased depth may be in part due to the increased amount of silt or silt plus clay content of the soil (Table 3.5). The other possibilities for increased fixation with increased depth of the soil are; increased pH values and carbonate content of the soil as well as a change in minerals.

Potassium fixation studies in soil profiles indicated a unique behavior of each soil series with increasing depths of soils. At the lowest level of K application, the Lenswood and the Almasippi did not show any significant increase of K fixation with increased soil depths. However, at other levels of application variations were observed with increasing depths in the Lenswood soils. Among the three profiles studied the Lenswood soil showed decreasing K fixation with increased depth of soil while the Long Plain soil series showed the opposite trend. There were no differences in K fixation observed with increasing depth at any level of K application in the Almasippi soil. The variations observed among profiles and within a profile may be due to variation in the amount of clay and silt content and partly due to variations in pH and carbonate content of soils.

The results observed in the present study are not comparable with studies of others as the methods of K fixation and the soil types are not nearly the same. However, in MacLean's

Table 5.4. Influence of amount of applied K on K fixation in a soil profile of Long Plain series (GY-1).

Soil Depth (cm)	0-30	30-60	60-80	81-100	100-120	120+
Applied K	Amount of K fixed*					
	mg kg^{-1}					
50	(12) 6 a	(50) 25 bc	(32) 16 ab	(16) 8 a	(14) 7 a	(64) 32 c
100	(26) 26 ab	(39) 39 bc	(28) 28 ab	(17) 17 a	(24) 24 ab	(55) 55 c
200	(14) 27 a	(28) 55 b	(33) 66 b	(27) 53 b	(34) 68 b	(49) 98 c
400	(13) 50 a	(13) 53 a	(30) 121 bc	(24) 94 ab	(37) 146 cd	(45) 178 d
1000	(12) 124 a	(14) 140 a	(17) 173 a	(21) 208 ab	(31) 305 b	(32) 317 b

* % Fixation given in parentheses.

Values followed by the same letter in any row are not significantly different at the 5 % level, according to Tukey's Studentized Range Test.

(1968) study on three profiles, the surface (0 -15 cm) and subsurface (15 - 30 cm) soil samples from sandy clay loam and sandy loam in texture fixed more than 90% of the 250 ppm added K. In his study as observed in the present study with Long Plain series, subsurface samples fixed relatively more K than the surface soil samples.

5.1.2.4 Potassium Fixation in Sand Fractions

In a preliminary study, it was observed that the sand fraction of the Almasippi (Haywood) surface soil fixed K against 1 N NH_4OAc extraction. In order to study the effect of depth on K fixation in the sand fraction, four soil samples, two from the deepest horizons of the Long Plain profile, one from the middle of the Lenswood profile and one from surface soil of Almasippi (Haywood) were selected and fine sand fraction was separated from the VFS, silt and clay fractions by a wet-sieving procedure, after removing organic matter and carbonates. Potassium fixation was determined by using 5 g sand fractions as described earlier.

The sand fractions of Almasippi, Lenswood and Long Plain soils have the ability to fix added K (Table 5.5). As observed in the whole soil, the amount of K fixation increased and the percentage fixation decreased with increasing amount of K application. With the exception of sample GY 5, the amounts of K fixation in the sand fractions are somewhat less than the amount fixed by the corresponding whole soils. At any level of K application the amount of K fixation observed among the sample was not very different. The lack of differences in K fixation among the samples studied indicates that the sand fractions of these four soils have the same ability to fix added K regardless of the depth of soils. Potassium fixation observed in the sand fractions of Almasippi (Haywood) soil was comparable to the amount of K fixed by the same fraction in the previous study (see Table 4.5). However, a preliminary study indicated that VFS fractions of Almasippi (Haywood) soil had a higher capacity for K fixation than the FS fractions of the same soil. By taking into consideration the amounts of silt, clay and sand fractions of the whole

Table 5.5. Influence of amount of applied K on K fixation in the sand fraction (0.1 to 2.00 mm) after removing carbonates and organic matter.

	Sample No. and Depth (cm)			
	Haywood 0-15	STA94 48-76	GY5 100-120	GY6 120+
Applied K	Amount of K fixed by sand*			
mg kg^{-1}				
50	(68) 34 a	(68) 34 a	(54) 27 a	(58) 29 a
100	(53) 53 b	(50) 50 b	(55) 55 b	(57) 57 b
200	(41) 81 c	(44) 88 c	(40) 80 c	(47) 93 c
400	(27) 109 c	(26) 104 d	(23) 91 c	(31) 122 d

* % Fixation given in parentheses.

Values followed by the same letter in any row are not significantly different at the 5 % level, according to Tukey's Studentized Range Test.

soil, the total contribution of sand fractions towards the K fixation in each horizon was much less than the contribution of the silt plus clay fractions. Types of clay mineral present in the soil and other factors such as pH and presence of carbonate also should be taken into consideration as the factors that determine the amount of K fixation in these soils. A detailed discussion on the relationship between K fixation and the soil characteristics will be covered in a separate section.

MacLean and Brydon (1963) have studied the K fixation in different sized fractions of some Canadian soils. They observed that the amount of K fixation decreased with increased particle size of the fractions; however, there was considerable fixation in the fine and medium silt fractions. The K fixation by the sand varied from 7 to 18% while medium silt, fine silt and clay fixed 10 to 37; 35 to 60; and 39 to 79 % of the 1755 ppm added K, respectively. By taking into consideration the amount of added K in the present study, the amount of K fixed by the sand fraction was higher than the amount of K fixed by the soil used in the MacLean and Brydon's (1963) study. Although no assessments were made on the ability of the silt and clay fractions to fix K in these experiments, a preliminary study indicated that the silt plus clay can fix a very high amount of added K in coarse textured soil.

5.1.3 Potassium Fixation in Surface Soils (Batch II)

The coarse textured soil samples used in the previous study (Section 5.1.1) were obtained mainly from the selected soil series (Almasippi association) of southern Manitoba region. In order to study the K fixing ability of coarse textured soils from a wide range of soil series from other parts of Manitoba; another 11 samples were selected from a collection of samples previously collected by Canada - Manitoba Soil Survey, University of Manitoba. Some properties of the selected soils samples are given in Table 3.2.

In general, the K fixation values shown in Table 5.6 indicate that the fixation increased with increased K application with the exception that five soils did not show any increase beyond

Table 5.6. Influence of amount of applied K on K fixation in coarse textured surface soils (Batch II)

Soil No.	STA24	STA33	SWR7	SWR53	SWR57	SWR77	TWN-HAL1	SC369	PGW189	PGW195	TWN-SOU1
Applied K	Amount of K fixed*										
	mg K kg^{-1}										
50	(30) 15 a	(74) 37 a	(26) 13 a	(4) 2 a	(36) 18 a	(38) 19 a	(30) 15 a	(24) 12 a	(18) 9 a	(38) 19 a	(34) 17 a
100	(21) 21 a	(68) 68 b	(17) 17 a	(28) 28 ab	(32) 32 a	(60) 60 ab	(24) 24 a	(16) 16 a	(21) 21 a	(23) 23 a	(27) 27 a
200	(25) 49 b	(70) 140 c	(19) 37 b	(31) 62 bc	(30) 60 a	(56) 112 b	(23) 46 a	(18) 36 a	(18) 36 a	(22) 44 a	(31) 62 b
400	(22) 89 c	(65) 259 d	(19) 76 c	(24) 96 c	(25) 101 a	(53) 212 c	(14) 54 a	(12) 46 a	(18) 72 a	(23) 91 b	(24) 97 c
1000	(14) 141 d	(50) 495 e	(12) 120 d	(9) 92 c	(8) 84 a	(31) 312 d	(4) 40 a	(4) 36 a	(6) 59 a	(11) 114 b	(11) 105 c

* % Fixation given in parentheses.

Values followed by the same letter in any column are not significantly different at the 5% level according to Tukey's Studentized Range Test.

the 400 mg K kg^{-1} application rate. At application rates of 50 and 1000 mg K kg^{-1}, the fixed K varied from 4 to 74% and 4 to 59%, respectively. Among the 11 soils studied the Poppleton (STA-33) and Craigford series (SWR-77) fixed the highest and the second highest amounts of K, respectively, at any level of K application. The two soil samples (STA-33 and SWR-77) which showed the high fixing ability are calcareous while the remaining nine samples are non-calcareous. The K fixation values observed in these Batch-II soil samples are in general, less than the values observed in the Batch I of surface soil samples. However, as observed in the Batch I, the K fixation values observed in this Batch do not seem to be related to the clay content of the soils.

So far the K fixation pattern observed in the 22 surface coarse textured soils and 13 samples from three profiles indicated that the amount of K fixation in a given soil is dependent on the amount of K applied. In general, the amount of K fixation has been shown to increase with increased application rate. The variations in K fixation observed among the soil samples do not seem to be related to the clay contents of the soils. The variations in K fixation observed among the soils studied may be related to the mineralogical compositions of the clay minerals and other characteristics of the soils. Therefore, the next two sections will concentrate on the relationship between K fixation and (i) some selected soil characteristics; and (ii) the mineralogical composition of the soils respectively.

5.1.4 Relationship Between K Fixation and Soil Characteristics

5.1.4.1 Simple Linear Regression Analyses

As seen in the previous sections, simple linear regression analyses have shown that the amount of K fixed in the surface soils of Batch-I and the profile samples was not directly related to the clay content of the soil. Since K fixation was also observed in the sand fractions of the soils and evidence found in the literature (Martin et al., 1945; Ataga, 1973) shows that CEC of the soils could be related to K fixation, it was decided to relate K fixation to other characteristics of the soils. As a start only the first batch of surface samples was used in this statistical analyses. Although relationships were found between the amount of K fixed at any level of K application and soil characteristics, the 400 mg K kg^{-1} application rate was selected for reporting as the rate was medium among the various rates used in this study. The general pattern of the relationship observed with various soil characteristics and 400 mg K kg^{-1} application rate was comparable to all the other levels of application.

Simple linear regression analyses of the first batch of surface soil samples (Table 5.7) show that there is a statistically significant positive relationship between the amount of K fixed and exchangeable Ca ($r^2 = 0.72$), CEC ($r^2 = 0.71$) and organic C. ($r^2 = 0.49$) of the soil and a negative relationship with the percent K saturation ($r^2 = 0.68$) and exchangeable K ($r^2 = 0.36$). However, no significant relationship was found between clay content and the amount of K fixation in the first batch of coarse textured soils.

Simple linear relationships between soil characteristics of 22 surface soil samples (Batch I and Batch II) and the % K fixed at 400 mg K kg^{-1} application rate were computed and found almost similar relationships with minor exceptions as observed in the first batch of eleven soil samples. The relationships given in Table 5.8 indicate that soil CEC was closely related ($r^2 = 0.61$) to the % K fixation. The second most important parameter was the % soil organic C

Table 5.7: Simple linear regression relating % K fixation at 400 mg K kg^{-1} application rate to some soil properties (Batch I).

Soil Properties	Equation	r^2
Exch. Ca ($cmol_c$ kg^{-1})	$Y = 10.13 + 2.23x$	0.72 **
CEC ($cmol_c$ kg^{-1})	$Y = 9.47 + 1.35x$	0.71 **
K Saturation (%)	$Y = 52.25 - 8.47x$	0.68 **
Organic C (%)	$Y = 16.72 + 7.55x$	0.49 **
Exch. K ($cmol_c$ kg^{-1})	$Y = 54.79 - 73.62x$	0.36 *
Silt (%)		0.25 ns
Exch Mg ($cmol_c$ kg^{-1})		0.23 ns
Clay (%)		0.18 ns
pH		0.17 ns
Fine Sand (%)		0.13 ns
$CaCO_3$ equiv. (%)		0.09 ns
Very Fine Sand (%)		0.02 ns

Table 5.8: Simple linear regression analysis relating K fixation at 400 mg K kg^{-1} application rate and some soil characteristics of 22 coarse textured soils.

Soil Properties	Equation	r^2
CEC ($cmol_c\ kg^{-1}$)	$Y = 7.80 + 1.31x$	0.61 **
Exch. Ca + Mg ($cmol_c\ kg^{-1}$)	$Y = 10.59 + 1.25x$	0.61 **
Organic C (%)	$Y = 14.60 + 6.87x$	0.48 **
Exch. Ca ($cmol_c\ kg^{-1}$)	$Y = 12.79 + 1.61x$	0.41 **
Exch. Mg ($cmol_c\ kg^{-1}$)	$Y = 22.94 + 1.68x$	0.39 **
pH	$Y = -61.92 + 13.23x$	0.32 **
K-Saturation (%)	$Y = 43.39 - 5.02x$	0.27 **
Sand (%)	$Y = 100.09 - 0.82x$	0.24 *
Silt + Clay (%)	$Y = 18.12 + 0.82x$	0.24 *
Clay (%)	$Y = 18.34 + 1.56x$	0.22 *
Silt (%)	$Y = 19.69 + 1.50x$	0.22 *
CaCO3 equiv. (%)		0.15 ns
Fine Sand (%)		0.12 ns
Exch. K ($cmol_c\ kg^{-1}$)		< 0.01 ns
Very Fine Sand (%)		< 0.01 ns

($r^2 = 0.48$). Other factors related to K fixation in the 22 coarse textured soil include exchangeable Ca, Mg, pH, K-saturation, sand, silt and clay content of the soil.

At this point no definite explanation could be given why these properties should be related to K fixation in these coarse textured soils. However, a possible explanation for the relationship observed between CEC and K fixation may be due to the fact that all the potential fixing sites are part of the exchange sites found in the soil complex, an increase in CEC would result in increased K fixation. The relationship between CEC of the soil and K fixation observed in this study is in accordance with the results observed by other workers (Martin et al., 1945; Ataga, 1973).

Since soil CEC is related to K fixation and a major portion of the exchange sites were occupied by Ca in most of the soils and Ca and Mg in other soils, (see Appendix A) these elements would be expected to relate to K fixation. This may be part of the reason why individually Ca and Mg were related to K fixation. When both the Ca and Mg in the soil which is almost equivalent to the soil CEC, were considered, the observed relationship was very similar ($r^2=0.61$) to that of soil CEC. No work has been reported by others on the relationship between the amount of exchangeable cations such as Ca and Mg on the soil complex and K fixation, yet Wiklander (1950) observed that clays saturated with Ca ions fixed more K than clays saturated with H, K or NH_4 ions. MacLean (1962) also found increased K fixation in (artificially) Ca-saturated soils. However, Joffe and Levine (1946) reported that K fixation was reduced when K had to compete with Ca for the exchange positions.

The role of organic matter in K fixation is obscure. Potassium fixation measured in the three profile samples (see section 5.1.2) showed that fixation increased with increasing depth in one profile while it decreased in the other profile with no change in K fixation in the third profile, but the organic matter content in the deepest horizons of all three soils was insignificant. From the above observation it was evident that organic matter had no effect on variations in K fixation observed in those profile samples. However, the K fixation observed in the surface samples of soil was positively related to organic matter content. The reason for this relationship may be due to the direct relationship between the amount of organic matter and the soil CEC ($r^2 = 0.86$) as observed in Table 5.9 and may not be due to K fixation by organic matter. A study conducted by Martin et al. (1945) examined the role of organic colloids on K fixation. When 5% of dialyzed alfalfa meal was added to two soil samples followed by a few weeks moist incubation, there was no appreciable effect on K fixation. Since organic matter is a property which contributes to soil CEC, and in the present study the CEC was found to be related to K fixation, naturally one would expect the organic matter to relate with K fixation. Therefore, the mineral CEC which really includes all the potential K fixing sites would be found only when the contribution to CEC by organic matter is deducted from the total soil CEC.

A significant linear relationship was found between K fixation and pH of the soils. Likewise, the effect of soil pH on K fixation has been widely observed in soils by various workers (Volk, 1934; Martin et al., 1945; Thomas and Hipp, 1968). Martin et al. (1945) showed, in a soil adjusted to a series of descending pH values by successively larger acid treatments, that at pH values between 2.5 and 5.5, the amount of K fixation increased very rapidly, and above pH 5.5 the fixation increased more slowly. The same workers have observed a marked increase in K fixation when a soil with very low fixing power was leached with Na_2CO_3. The results from the present study have confirmed that the amount of K fixation of a given soil is dependent on the pH of the soil, and any increase in pH would increase K fixation in these soils.

The relationship observed between K fixation and % K saturation in the present study is in accordance with the results observed by MacLean (1962) who observed that soils with a low degree of K fixation were associated with relatively high values of percent K saturation. The

Table 5.9. The linear relationship between independent variables of 22 coarse textured soils.

Variables*	Relationship	r^2
CEC Vs (Ca + Mg)	+	0.99 **
Org.C Vs CEC	+	0.86 **
Org.C Vs (Ca+Mg)	+	0.85 **
Silt Vs Exch. Mg	+	0.76 **
Clay Vs Silt	+	0.74 **
Clay Vs Exch. Mg	+	0.65 **
CEC Vs Exch. Ca	+	0.65 **
CEC Vs Exch. Mg	+	0.63 **
Org.C Vs Exch. Ca	+	0.59 **
CEC Vs Silt	+	0.54 **
Org.C Vs Exch. Mg	+	0.51 **
CEC Vs (Clay + Silt)	+	0.50 **
CEC Vs K-sat.	-	0.49 **
Clay Vs pH	+	0.44 **
CEC Vs Clay	+	0.39 **
Org.C Vs K-sat.	-	0.38 **
Exch. Ca Vs K-sat.	+	0.37 **
Exch. Mg Vs pH	+	0.36 **
Org.C Vs Silt	+	0.31 **
Org.C Vs (Clay + Silt)	+	0.29 **
Clay Vs K-sat.	-	0.29 **
Silt Vs K-sat.	-	0.28 *
Silt Vs pH	+	0.26 *
CEC Vs pH	+	0.24 *
Org.C Vs Clay	+	0.23 *
Exch. Mg Vs K-sat.	-	0.22 *
pH Vs K-sat.	-	0.17 ns
Org.C Vs pH	+	0.14 ns
Silt Vs Exch. Ca	+	0.10 ns
Org.C Vs Exch. K	+	0.09 ns
Exch. Ca Vs Exch. Mg	+	0.09 ns
Exch. K Vs K-sat.	+	0.07 ns
Exch. Ca Vs pH	+	0.06 ns
Exch. Ca Vs Exch. K	+	0.06 ns
CEC Vs Exch. K	+	0.05 ns
Clay Vs Exch. Ca	+	0.04 ns
Exch. Mg Vs Exch. K	+	0.01 ns
Silt Vs Exch. K	-	$<$0.00 ns
Exch. K Vs pH	+	$<$0.00 ns
Clay Vs Exch. K	-	$<$0.00 ns

* Units as in Table 5.8

relationship observed in the present study on coarse textured soils clearly suggests that the K-saturation of a given soil is an indication of the potential for K fixation. Results observed in the present study indicated that soils with high K-saturation fixed low amounts of K while soils with low K-saturation fixed high amounts. These results however, disagree with those of Barber (1979) who found no relationship between the amounts of fixed K and the exchangeable K or K saturation.

Although statistically significant relationships were observed with sand, silt+clay, clay and silt content of the soils and K fixation, they individually account for only 22 to 24 % of the variations in K fixation observed in these coarse textured soils (Table 5.8). However, MacLean (1962) observed a highly significant linear correlation with clay content showing that K fixation increased regularly with increased clay content in some Canadian soils. The absence of a highly significant relationship between the clay content of the soils and the amount of K fixation in the present study may be in part due to differences in clay mineralogical composition of the soils. Since the K fixation capacities of different clay minerals are different, relationships between K fixation and clay contents of soils would be possible only when the soils are grouped on the basis of their dominant clay mineralogy.

From the above relationships (Table 5.8) it is evident that factors such as CEC, exchangeable Ca, Mg, pH and the amount of K in soils (K-saturation) can also influence the amount of K fixation of a given soil. Therefore, K fixation cannot be fully related to a single soil property.

5.1.4.2 Calcareous Soils and K Fixation

Although no direct relationship was observed between carbonate content and K fixation in the 22 coarse textured soils (Table 5.8), it was evident from Table 5.6 that the calcareous soils fixed more K than the non-calcareous soils.

The results given in Table 5.10 are the mean K fixation values of calcareous, non-calcareous and acidic soils. Among the soils studied, calcareous soils fixed more K at all K application levels than the non-calcareous soils. Calcareous soils fixed almost double the amount of K as non-calcareous soils at each level of K application. The difference in fixation between the non-calcareous alkaline and the acidic soils is not very great. These observations lead to the conclusion that calcareous coarse textured soils have a higher K fixing ability than non-calcareous soils. It is also evident from Table 5.10 that the average amount of silt plus clay content and CEC of the calcareous soils was higher than non-calcareous or acidic soils. Likewise the % K-saturation of the calcareous soils was lower than non-calcareous and acidic soils. These differences in silt plus clay content, CEC and % K-saturation may be major reasons why calcareous soils have more fixation than other coarse textured soils. Since the carbonate presence in the soil is an easily measurable soil characteristic, it could possibly be used to identify high K fixing soils.

Although reports are scarce on any direct relationship between the carbonate content of the soil and K fixation, increase in K fixation due to liming an acid soil has been widely observed. Volk (1934) observed that lime addition does cause increased K fixation in soils. MacLean (1962) has also observed that liming of four acid soil samples to raise the pH to about the neutral point increased K fixation slightly. The exact reason for this increase has not been ascertained as yet, but the effect of Ca ion and pH of the soil on K fixation has been widely connected with the liming effect. Increased pH due to liming the soil may be partly responsible for the K fixation.

Table 5.10. The effect of carbonate on percent K fixation in 22 coarse textured soils[#].

Soil	No.[@]	CEC	K-sat[*]	Silt+Clay	50	200	1000
					K added mg kg^{-1}		
		cmol$_c$ kg^{-1}	%		Amount of K Fixed %		
Calcareous	7	27	1.32	25.3	59	55	36
Non-calcareous (pH > 7.0)	6	17	2.24	13.6	29	26	17
pH (< 7.0)	9	12	3.36	10.0	24	24	10

[#] Data extracted from Tables 3.1, 3.2, 5.1 & 5.6

[@] Total number of soil samples

[*] K-sat = K-saturation

5.1.5 Summary

The purpose of this investigation was to study the K fixation behavior of coarse textured soils of Manitoba. The results indicated that coarse textured soils are capable of retaining K against 1 N NH_4OAc extractions. In general, K fixation values among the different soils studied are highly variable. Generally the amount of K fixed increased and percentage fixation decreased with increased K application.

Potassium fixation studied in the three complete profile samples indicated that soils are capable of fixing K throughout the profile. Variations in the amount of K fixed were observed among the horizons of two out of the three profiles studied. Changes in the amount of clay and silt content with increased depth may partly be responsible for the variations observed within these two profiles. Although the clay, silt and organic matter contents were generally reduced with increased depth in a third profile, the amount of K fixed at the surface level was comparable to that of the deep horizons. The absence of change in K fixation with depth in the third profile may have been caused by the K fixing minerals present in the sand and silt size fractions. Potassium fixation measured in the sand fractions of different soils obtained from the different depths has confirmed that sand fractions were partly responsible for K fixation in these coarse textured soils.

Among the soil characteristics tested the soil CEC was found to be highly correlated with K fixation. Though the role of exchangeable Ca and Mg and organic matter content on K fixation is not very clear, positive relationships observed with these properties may be partly due to their connection with the soil CEC. Grouping the soils based on the presence and absence of calcium carbonate indicated that calcareous soils fixed more K than non-calcareous soils. Higher fixation observed in the calcareous soils than non-calcareous soils may be partly due to the higher amount of silt plus clay found in those calcareous soils.

5.2 RELATIONSHIP BETWEEN K FIXATION AND CLAY MINERALOGICAL COMPOSITION

Although the linear regression analyses did not show any close relationship between K fixation and clay content of the soils, the preliminary studies indicated that the total amount of K fixed by the sand fraction was much less than the amount fixed by the corresponding whole soil. From the same studies, it was evident that the clay plus silt fractions of some coarse textured soils had a very high capacity to fix added K. Because of the relatively high K fixing capacities of the clay and silt fractions of the soils, special attention was paid to the identification of the mineral components of these separates.

5.2.1 Clay Mineralogy of Three Soils

Three soil samples, two of them (one low fixing - Rignold and one high fixing - Almasippi) from the samples used in the preliminary experiment and one (high fixing - Lenswood) from the first batch of soil samples, were selected to study the mineralogy of the clay and silt fractions. Samples were fractionated by a centrifuging procedure to obtain two sizes each of silt and clay fraction as outlined earlier.

5.2.1.1 Qualitative Mineralogical Analyses of Three Soils

The results of X-ray diffraction analyses of the three soils have shown (Table 5.11 & Appendix B-1 Figs. A - C) that the mineralogy of the coarse silt fraction of the Almasippi and Rignold soils consisted of very small amounts of vermiculite whereas the Lenswood soil showed a small amount of vermiculite in addition to illite and kaolinite. The fine silt fraction of the Almasippi soil was dominated mainly by vermiculite but contained a small amount of kaolinite and illite. The fine silt fraction of the Lenswood soil was very similar to the Almasippi soil. In the case of the Rignold soil, the fine silt fraction consisted of illite and kaolinite as dominant clay

Table 5.11. Mineralogy of the clay and silt fractions of three coarse textured soil series*.

Size Fractions	Quartz	Kaolinite	Illite	Vermiculite	Montmorillonite
		Almasippi			
Fine Clay <0.2 μm	-	-	-	-	xxxx
Coarse Clay 0.2 - 2 μm	xxx	xxx	xx	xxxx	xx
Fine Silt 2 - 20 μm	xxx	xx	xx	xxxx	x
Coarse Silt 20 - 50 μm	xxxx	x	-	x	-
		Lenswood			
Fine Clay <0.2 μm	-	-	-	-	xxxx
Coarse Clay 0.2 - 2 μm	xxx	xxx	x	xxxx	xxx
Fine Silt 2 - 20 μm	xxx	xx	x	xxxx	x
Coarse Silt 20 - 50 μm	xxxx	x	x	xx	-
		Rignold			
Fine Clay <0.2 μm	-	x	xx	-	xxx
Coarse Clay 0.2 - 2 μm	xx	xxx	xxx	xx	xx
Fine Silt 2 - 20 μm	xxxx	xx	xx	x	-
Coarse Silt 20 - 50 μm	xxxx	x	x	x	-

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* -: Not Identifiable; x: Identifiable; xx: Weak X-ray pattern; xxx: Medium X-ray pattern; and xxxx: Strong X-ray pattern.

minerals, and vermiculite as a minor mineral. The coarse clay fraction of the Almasippi soil showed vermiculite as the dominant clay mineral. A small amount of kaolinite and illite were also present in the same coarse clay fraction of Almasippi soil. The coarse clay fraction of the Lenswood soil showed almost similar mineralogical pattern as the Almasippi soil. The coarse clay fraction of the Rignold soil was different from the other two soils showing almost equal amounts of illite and kaolinite in addition to a smaller amount of vermiculite and montmorillonite. The fine clay fraction of Almasippi and Lenswood soils was mainly montmorillonite while the Rignold soil consisted of montmorillonite with a small amount of illite and a very small amount of kaolinite. Except for the coarse silt fraction, the clay mineralogy of other fractions of the Almasippi and the Lenswood soils were comparable.

5.2.1.2 Relationship Between Clay Mineralogy and Potassium Fixation.

As observed in the preliminary and other experiments, the Almasippi (Haywood) and Lenswood (STA 90) soils fixed larger amounts of K than the Rignold (Winkler) soil. For example, at the 100 mg K kg^{-1} application rate the Almasippi, Lenswood and Rignold soils fixed 73, 84 and 17 mg K kg^{-1}, respectively. The Almasippi and Lenswood soils consisted of 9 and 10 % clay, respectively, while Rignold consisted of 19 % clay. From the clay mineralogical analysis it was evident that Almasippi and Lenswood soils had very large amounts of vermiculite in the coarse clay and fine silt fractions, while the Rignold soil had only small amounts of vermiculite in corresponding size fractions. Vermiculite, which is found in the coarse clay and silt fractions of the soil, is one of the high K fixing clay minerals. This may explain why a higher K fixation was observed in the Almasippi and the Lenswood than in the Rignold soil. Since vermiculite was found in the coarse silt fractions of all three soils studied, one could expect this mineral to be present even in the very fine and fine sand fractions of the soils. The observed K fixation in the sand fraction of soils (see Table 4.4 & 5.5) may be due to sand size vermiculite minerals present in that fraction. However, the X-ray diffraction analysis of sand fractions of the Almasippi (Haywood) and the Lenswood (STA 90) soil samples did not show any detectable x-ray pattern for vermiculite.

The fine clay fractions of the Rignold soil consisted of montmorillonite, illite and kaolinite while the other fractions consisted mainly of kaolinite and illite with a small amount of vermiculite. With regard to the different clay minerals, the vermiculites have the greatest capacity for K fixation (DeMumbrum and Hoover, 1958). Illite may or may not fix potassium, depending on the degree of weathering and K^+ saturation of the lattice. Montmorillonites have been shown to fix K^+ only in a dry state (Rich, 1968) whereas kaolinites are generally considered as nonfixing minerals (Joffe and Levine, 1946). Therefore, the small amount of K fixation observed in the Rignold soil may have been caused by the small amount of vermiculite and possibly illites found in the soil.

Although the three soils tested in this study originated from the three different parent materials, the clay mineralogical results indicated that two soils (Almasippi and Lenswood) have similar clay mineralogical components in each fraction analyzed as opposed to the third (Rignold) soil sample. These results demonstrate the relationship between the amount of K fixation and the clay mineralogical component of the soils. The Almasippi and Lenswood soils, which had a high vermiculite content fixed a higher amount of K than the soil with very low vermiculite content.

5.2.2 Clay Mineralogy of nine Coarse Textured Soils

As seen on Tables 5.1 and 5.6, the amount of K fixation was highly variable among the 22 coarse textured surface soils studied. Specifically, the soils originating from the same parent material (e.g. soils from Almasippi Association: Willwcrest (GY-50) Vs Long Plain (SC-315)) also showed variations in K fixation. In order to understand the variations in amount of K fixation in relation to the clay mineralogical compositions of the soils, a set of nine soil samples out of

22 surface soils that originated from similar parent material (belonging to the Almasippi association) were selected and prepared for X-ray diffraction analysis as described earlier.

5.2.2.1 Qualitative Analyses of nine Soils

Mineralogical analysis and the X-ray diffraction patterns of samples obtained from various soil series of the Almasippi association are given in Tables 5.12 and Appendix B-2 respectively. X-ray diffractograms of the nine soils studied indicate that the clay mineralogical composition of the individual fractions are generally very similar. The fine clay fraction of most of the soils studied consisted of mainly montmorillonite as the major and illite as the minor clay mineral. However, St.Claude soil consisted of only montmorillonite in the fine clay fraction.

The coarse clay fractions of all the soils studied consisted of four clay minerals; kaolinite, illite, vermiculite and montmorillonite; however, the amounts of each clay mineral found in the different soils were variable. The Almasippi (SC 357), Willowcrest (GY 50) and the Long Plain (SC 315) soils consisted of montmorillonite as a major clay mineral whereas illite was a major clay mineral in Willowcrest (PGW 195) soil. The other soil samples showed varying amounts of all four clay minerals in the coarse clay fractions.

The fine silt fractions of most of the soils studied consisted of three major clay minerals, namely kaolinite, illite and vermiculite; however, only the Almasippi (SC 357) soil showed montmorillonite in addition to the other three clay minerals. Among the soils tested Almasippi (WBN 66) showed medium X-ray pattern while St.Claude (SC 297) and Willowcrest (PGW 195) showed weak X-ray pattern for all three clay minerals in the fine silt fraction. The rest of the soils studied showed varying amounts of these three clay minerals in the fine silt fractions.

The coarse silt fractions of all the soils studied consisted of mainly kaolinite, illite and vermiculite; however, the amount of each mineral present in this fraction was smaller than the amount present in the other fractions of the soils.

Table 5.12. Mineralogy of the clay and silt fractions of nine coarse textured soils[*].

Size Fractions	Kaolinite	Illite	Vermiculite	Montmorillonite
SC 357 - Almasippi				
Fine Clay[1]	-	xx	-	xxxx
Coarse Clay	xxx	xxx	xx	xxxx
Fine Silt	xx	xx	xx	xx
Coarse Silt	x	x	x	-
WBN 66 - Almasippi				
Fine Clay	-	x	x	xxxx
Coarse Clay	xxx	xx	xxx	xxx
Fine Silt	xxx	xxx	xxx	-
Coarse Silt	xx	xx	xx	-
GY 14 - St Claude				
Fine Clay	-	-	-	xxxx
Coarse Clay	xxx	xxx	xxx	xxx
Fine Silt	xx	xxx	x	-
Coarse Silt	x	x	x	-

* - Not identifiable; x: Identifiable; xx: Weak X-ray pattern; xxx: Medium X-ray pattern; and xxxx: Strong X-ray pattern.

[1] Fine clay <0.2 μm; Coarse clay 0.2 - 2 μm; Fine silt 2 - 20 μm; and Coarse silt 20 - 50 μm.

Cont....

Cont....Table 5.12.

Size Fractions	Kaolinite	Illite	Vermiculite	Montmorillonite
		SC 297 - St Claude		
Fine Clay[1]	-	-	-	xx
Coarse Clay	xx	xx	x	xx
Fine Silt	xx	xx	xx	-
Coarse Silt	x	x	x	-
		PGW 195 - Willowcrest		
Fine Clay	-	xx	-	xxxx
Coarse Clay	xx	xxx	xx	xx
Fine Silt	xx	xx	xx	-
Coarse Silt	x	x	x	-
		GY 50 - Willowcrest		
Fine Clay	-	xx	-	xxx
Coarse Clay	xxx	xxx	xxx	xxxx
Fine Silt	xxx	xxx	xx	-
Coarse Silt	x	x	x	-

* - Not identifiable; x: Identifiable; xx: Weak X-ray pattern; xxx: Medium X-ray pattern; and xxxx: Strong X-ray pattern.

[1] Fine clay <0.2 μm; Coarse clay 0.2 - 2 μm; Fine silt 2 - 20 μm; and Coarse silt 20 - 50 μm.

Cont....

Cont....Table 5.12.

Size Fractions	Kaolinite	Illite	Vermiculite	Montmorillonite
WBN 41 - Willowcrest				
Fine Clay[1]	-	x	-	xx
Coarse Clay	xxx	xxx	xx	xxx
Fine Silt	xxx	xxx	xx	-
Coarse Silt	x	xx	x	-
GY 1 - Long Plain				
Fine Clay	-	xx	-	xxx
Coarse Clay	xx	xxx	x	xxx
Fine Silt	xx	xxx	xx	-
Coarse Silt	x	x	x	-
SC 315 - Long Plain				
Fine Clay	-	x	-	xxxx
Coarse Clay	xx	x	xx	xxxx
Fine Silt	xxx	xx	x	-
Coarse Silt	xx	x	x	-

* - Not identifiable; x: Identifiable; xx: Weak X-ray pattern; xxx: Medium X-ray pattern; and xxxx: Strong X-ray pattern.

[1] Fine clay <0.2 μm; Coarse clay 0.2 - 2 μm; Fine silt 2 - 20 μm; and Coarse silt 20 - 50 μm.

Although the soils studied showed similar clay mineralogical composition in each fraction of the soil, no clear distinction can be made in terms of the amount of each mineral present in the soils without a detailed quantitative analyses.

5.2.2.2 Relationship Between Clay Minerals and Potassium Fixation

The K fixation values observed at 400 mg K kg^{-1} application rate for the nine soil samples are given in Table 5.13. All these soil samples are believed to have originated from the same parent material and these are expected to consist of similar components of clay minerals. This seems to be true since the observed clay mineralogy of the soils was very similar in the nine soils tested. However, the amount of K fixation observed among these nine soils is seen to be different. The differences in K fixation observed in this study may not be attributed to a single clay mineral type as was done in the previous experiment. This can be seen by observing soil samples with similar clay and silt content. For example, when two soil samples from the same soil series (St. Claude GY 14 and SC 297) were compared, SC-297 fixed a larger amount of K than the sample GY-14. These two soil samples contained almost the same clay content but somewhat different amounts of coarse silt. Although actual quantities of each type of clay mineral present in the soil are important for reaching a definite conclusion; by considering the apparent concentration of vermiculite in terms of the intensity of vermiculite peaks, one would possibly expect more K fixation in sample GY-14 than sample SC-297, as it showed a strong vermiculite peak in the coarse clay fraction. A similar comparison can be made between various soils studied in this experiment. From this example it is clear that the source of K fixation in these soils may not be attributed to a single type clay mineral. Rather, a mixture of clay minerals in combination with other existing soil characteristics may be responsible for the measured fixation. For example, as seen in Table 5.13, though the St.Claude soils (SC-297 and GY-14) were calcareous, their CEC and exchangeable K contents were very different. The sample

Table 5.13. Potassium fixation and some selected characteristics of soil samples from the Almasippi association used in the X-ray analyses.

Soil No.	Soil Series	K Fixed*	Fine Clay	Coarse Clay	Fine Silt	Coarse Silt	$CaCO_3$ equiv.	K-Sat	CEC	Exch.K
		%	%						cmol$_c$ kg^{-1}	
SC 357	Almasippi	48	3.2	2.7	1.2	7.1	7.5	0.64	28	0.18
SC 297	St.Claude	46	4.7	4.7	2.2	5.9	20.7	0.55	36	0.20
WBN 66	Almasippi	41	2.8	1.8	1.0	4.8	9.2	2.14	14	0.30
SC 315	Long Plain	35	1.8	1.5	0.9	4.2	0.0	0.47	21	0.10
GY 14	St.Claude	30	5.8	2.4	1.5	12.7	18.0	1.66	21	0.35
GY 50	Willowcrest	30	1.8	1.6	0.7	3.1	0.0	2.76	13	0.36
WBN 41	Willowcrest	24	2.3	1.4	0.6	3.2	0.0	4.00	10	0.40
PGW 195	Willowcrest	18	3.1	1.7	0.8	3.9	0.0	3.84	13	0.50
GY 1	Long Plain	13	1.4	1.0	0.8	2.6	0.0	4.00	5	0.20

* K added at 400 mg kg^{-1}

SC-297 had a high CEC and low exchangeable K whereas the sample GY-14 had a low CEC and high exchangeable K. These differences in CEC and exchangeable K may in part explain the differences in K fixation observed in these soils. It appears here that for soils with similar clay mineralogical composition, the initial level of exchangeable K and the CEC may have a marked influence upon fixation of K, since there is obviously a limit to which fixation might take place in any system. A close negative relationship between the amount of K fixed and the K saturation of the soils observed in this study (Table 5.14) reinforces this conclusion.

Although no statistical relationship was found between K fixation and the amount of clay or silt in the soil, the coarse clay content showed a significant relationship ($r^2=0.48^*$) with K fixation. Though the coarse clay fractions of most of the soils studied showed strong vermiculite peaks, they also showed peaks for four other clay minerals. Therefore, it is not possible to single out one kind of clay mineral and relate it to K fixation, since not only vermiculite but also the role of illite and montmorillonite in K fixation have been well documented (Barshad, 1948; Kunze and Jeffries, 1953; Agarwal, 1960; Dennis and Ellis, 1962; Page et al., 1967; Rich, 1968 a; Ahamed and Davis, 1971; Sawhney, 1972; Arifin and Tan, 1973). The soil clays are usually a complex of various clay minerals with each differing in K fixing capacity. In addition, within a single clay mineral type, variations have been observed in their ability to fix added K. Specifically, soil vermiculites and montmorillonites have been known to consist of a number of species with differing CECs and their K fixing abilities have been shown to be different (Barshad and Kishk, 1970; Sawhney, 1972). Weir (1965) observed that within the montmorillonite mineral group, the greater the layer charge, the greater is the K fixation.

Researchers (Alexiades and Jackson, 1965; Coffman and Fanning, 1974) have employed K fixation as a means to quantify the amount of vermiculite in a soil. In their methods, it was assumed that the source of K fixation was only the vermiculites in the soil. However, from the

Table 5.14. Simple linear relationship between % K fixation@ and some properties of nine soils from the Almasippi association used in the X-ray analyses.

Soil Properties	Equation	r^2
Org. Carbon (%)	Y = 13.15 + 7.24 x	0.78 **
K Saturation (%)	Y = 47.29 - 6.99 x	0.75 **
CEC ($cmol_c\ kg^{-1}$)	Y = 13.08 + 1.03 x	0.68 **
Coarse Clay (%)	Y = 15.85 + 7.57 x	0.48 *
Fine Silt (%)		0.36 ns
Clay (%) (Fine + C.Clay)		0.31 ns
Exch.K ($cmol_c\ kg^{-1}$)		0.23 ns
Silt (%) (Fine + C.Silt)		0.17 ns
Fine Clay (%)		0.14 ns
Coarse Silt (%)		0.12 ns

@ K fixation at 400 mg K kg^{-1} application rate.

previous discussion, it is clear that for soils with a complex of clay minerals, where other minerals such as montmorillonite and illite could fix added K, this method would lead to an erroneous conclusion of the actual amount of vermiculite present in the soils. Therefore where the mineralogy of the clay and silt is complex, a more specific identification of the mineral characteristics than presented here is an obvious prerequisite to a clearer explanation of K fixation in these soils.

5.2.3 Summary

Clay analyses of three soil samples from three different soil series indicated the presence of a larger amount of vermiculite in the Almasippi (Haywood) and Lenswood (STA-90) soils than in the Rignold (Winkler) soil. The two soils with higher vermiculite fixed more K than the soil with a low vermiculite.

Clay analyses of nine soil samples from the Almasippi association, formed on similar parent material, but belonging to different series have shown similar clay mineralogical composition. The fine clay fraction of a majority of the soils studied consisted of only montmorillonite, while the coarse clay fraction of all soils consisted of four clay minerals namely kaolinite, illite, vermiculite and montmorillonite. Most of the soils showed a strong vermiculite peak in the coarse clay fraction as opposed to the other fractions.

Both fine silt and coarse silt fractions of the soils mainly consisted of kaolinite, illite and vermiculite. However, the amount of each mineral found in the coarse silt fraction was much smaller than the amount found in the fine silt fractions.

Although all the soils studied showed similar clay mineralogical composition in each fraction, the amount of each mineral type present in a particular fraction was variable. Since there are no very obvious differences in vermiculite content among the soils studied, it was not possible to relate the vermiculite content to the amount of K fixation in the soils. This may be due to the role of other clay minerals such as montmorillonite and illite in K fixation. However, though the clay mineralogy of these soils was very similar, the variations observed in K-saturation, CEC and coarse clay content of the soils were closely related to the variations in K fixation observed.

5.3 FACTORS AFFECTING POTASSIUM FIXATION IN COARSE TEXTURED SOILS

5.3.1 Effect of Moisture

The purpose of this investigation was to assess the effect of moisture on K fixation in coarse textured soils.

Potassium fixation increased in most soils on air-drying (Table 5.15). Exceptions were found in the case of the Almasippi (Haywood), Lenswood, and Elm Creek soils which did not fix more K on air-drying. The Lenswood and the Almasippi (Haywood) soils fixed the highest and the second highest amounts of K respectively in both wet and dry states. These two soils showed strong vermiculite peaks in their X-ray diffractograms (see Table 5.11 & Appendix B) indicating that vermiculite was the dominant clay mineral in the silt and coarse clay fractions. This may be the reason for the strong K fixation in the wet and dried state. Vermiculites have been shown to fix similar amounts of K in the wet and dry states (DeMumbrum and Hoover, 1958). On the other hand Kardos (1955) showed that illites and montmorillonites fixed K only if air-dried. Therefore it appears that the additional K fixation on air-drying that was measured on most soils may be due to the montmorillonite and illite clay minerals. The air-drying method of K fixation was used as a standard method throughout the study as this method approximates more nearly the condition encountered in the field where air-drying of soil after K application is a very frequent incidence. Many K fixation studies in soils have been conducted by oven-drying the soil at either 70 or 105 C as a standard procedure (e.g. MacLean, 1962; Rich and Lutz, 1965; Lutz, 1966; MacLean and Brydon, 1971; Richards, 1985). Definitely the K fixation values measured by this oven-drying procedure will be higher than when the air-drying procedure is used.

This study again reinforces the finding that the amount of K fixation depends on the type of clay minerals present. The larger amounts of K were fixed on air-drying only in those soil

Table 5.15. The effect of wet and air-drying treatment on K fixation in nine coarse textured soils.

Soil Series	Soil No.	Potassium Fixation*	
		Wet at field capacity	Air-dried at room temperature
		%	%
Almasippi	Haywood	71 a	74 a
Almasippi	WBN-66	36 a	51 b
Elm Creek	RWL-7	29 a	27 a
Lenswood	STA-90	78 a	80 a
Long Plain	LP1	11 a	34 b
Almasippi	S3	2 a	19 b
St.Claude	SC1	21 a	34 b
St.Claude	SC2	7 a	19 b
Willowcrest	S2	13 a	23 b

[*] Applied K 100 mg kg^{-1}

Potassium fixation values followed by the same letter in any row are not significantly different at 1% level.

samples which contain appreciable amounts of montmorillonite and illite. Nevertheless, in view of the highly significant amounts fixed in the moist state, it cannot be concluded that drying is indispensable for K fixation.

5.3.2 Effect of Duration of Incubation (Time Factor)

The purpose of this experiment was to study the effect of duration of incubation on the amount of K fixation. Three coarse textured samples were selected and from each of these, five sets of samples were prepared and treated with KCl as described earlier. Potassium treated samples were brought to field capacity and incubated at room temperature. The first set was incubated for 3 days as was done in the standard procedure, the second, third, fourth and fifth sets were incubated for 6, 9, 12 and 15 days, respectively. At the end of the stated incubation period, the samples were air-dried for 3 days and analyzed for exchangeable K. The K fixation values obtained at different levels of applied K at various incubation periods are given in Table 5.16.

In general, the length of incubation period had no significant effect on the amount of K fixed at any K application rate in any of the three soils studied. Although significant differences in the amount of K fixed were observed within the same level of K added with Lenswood and Almasippi soils, the increases were not consistent with increasing incubation period. The lack of any consistent increase in K fixation with increasing incubation periods indicates that an equilibrium is established within a very short period of time between exchangeable and fixed K in these soils. Thus, it appears that under the conditions of the experiment a soil will fix a maximum amount of K in a very short time and the amount of K fixation will depend on the amount of K applied. These results suggest that three days of incubation was sufficient for K fixation studies and in fact the incubation period may be shortened. Researchers have observed K fixation as a rapid process (Volk, 1934; Martin

Table 5.16. The effect of duration of incubation on K fixation in three coarse textured soils.

Soil Series		Duration of Incubation (days)				
		3	6	9	12	15
	K Applied mg kg^{-1}	Amount of K fixed* mg kg^{-1}				
Willowcrest (S2)	50	(28) 14 a	(34) 17 a	(22) 11 a	(26) 13 a	(36) 18 a
	100	(35) 35 a	(25) 25 a	(19) 19 a	(37) 37 a	(35) 35 a
	200	(28) 56 a	(22) 44 a	(22) 43 a	(31) 62 a	(26) 51 a
	400	(25) 98 a	(18) 73 a	(21) 82 a	(20) 78 a	(19) 75 a
	1000	(19) 194 a	(15) 151 a	(17) 173 a	(17) 167 a	(13) 129 a
Lenswood (S4)	50	(52) 26 a	(56) 28 a	(46) 23 a	(56) 28 a	(66) 33 a
	100	(59) 59 a	(52) 52 a	(49) 49 a	(64) 64 a	(63) 63 a
	200	(57) 113 a	(53) 106 a	(49) 97 a	(63) 125 a	(60) 120 a
	400	(53) 213 ab	(51) 202 a	(51) 201 a	(60) 241 b	(58) 230 ab
	1000	(43) 426 a	(37) 370 a	(39) 389 a	(42) 417 a	(39) 391 a
Almasippi (Haywood)	50	(70) 35 a	(66) 33 a	(64) 32 a	(56) 28 a	(68) 34 a
	100	(64) 64 a	(68) 68 a	(59) 59 a	(73) 73 a	(73) 73 a
	200	(62) 124 a	(66) 132 ab	(61) 122 a	(73) 146 b	(74) 147 b
	400	(65) 260 ab	(64) 254 a	(63) 249 a	(71) 283 b	(69) 277 b
	1000	(52) 524 a	(50) 504 a	(52) 517 a	(54) 539 a	(52) 521 a

* Percent fixation given in parenthesis.

K fixation values followed by the same letter in any row are not significantly different at the 5% level according to Tukey's Studentized Range Test.

et al., 1945). Martin et al. (1945) observed that equilibrium between exchangeable K and fixed K was established in 48 hrs. However, some other workers have reported that fixation of K in nonexchangeable form is a slow or gradual diffusion controlled process. For example, Martin and Suarez (1977) observed that fixation of K generally increased with increased K fertilization and time of incubation, when four soil samples were analyzed from Latosols and Andosols which had been treated with KCl and maintained at two different (continuously wet and wet-dry) conditions and extracted with ammonium acetate in the usual way at intervals over a 4 month period.

5.3.3 Effect of $CaCO_3$ on K Fixation

As observed in section 5.1.4.2, calcareous soils fixed more K than non-calcareous soils. In order to study the effect of $CaCO_3$ per se on K fixation, a non-calcareous soil sample (Long Plain - S1) was selected. The sample contained 5% clay and 3% silt and had a pH of 6.9. The selected sample was mixed with reagent grade $CaCO_3$ in different proportions to get five levels of $CaCO_3$. The artificially carbonated soils were incubated at field capacity for one week at room temperature and then air-dried. The air-dried samples were treated with three levels of K as KCl and K fixation was determined. The K fixation values and exchangeable K values for each $CaCO_3$ level are given in Table 5.17.

In general K fixation increased with increasing $CaCO_3$ content of the soil at both levels of K application (Table 5.17). The sample with no added $CaCO_3$ fixed only 33 and 23 % of applied K while the other sample with the highest level (2%) of added $CaCO_3$ fixed approximately 50 and 33 % of the applied K when K was added at the rate of 100 and 400 mg kg^{-1}, respectively. The main effect of $CaCO_3$ addition shown in the Table (5.17) as the average of K fixation values, clearly indicates a significant increase in the amount of K fixation with soil samples containing 1 % or more of $CaCO_3$.

Table 5.17. The effect of $CaCO_3$ on K fixation in a coarse textured soil (Long Plain - S1).

$CaCO_3$* in Soil	K added mg kg^{-1}			
	0	100	400	
%	Exch. K	Amount of K Fixed (mg kg^{-1})		Average@
0	95 a	33	93	63 a
0.25	91 a	41	115	78 ab
0.50	88 a	40	114	77 ab
1.00	89 a	43	125	84 b
2.00	86 a	48	131	90 b

* Newly added

@ Average of both 100 & 400 mg K kg^{-1} application rates.

Values followed by the same letter in any column are not significantly different at the 5% level according to Tukey's Studentized Range Test.

The effect of liming the soil on K fixation was studied and reported by Volk (1934). MacLean (1962) reported that liming four acid soils to about the neutral point increased fixation of added K in a range of 2 to 4 % when 585 ppm K was applied. He also noted that water soluble K of both control and K-treated samples were usually lower following liming. Reduction of exchangeable K content following liming has been widely observed (Attoe, 1946; York et al. 1953). Attoe (1946) has shown that the liming of a K fertilized Spencer silt loam (from pH 4.47 to 6.65) caused an increase in fixation of K under a moist soil condition. On air-drying of these soils a further fixation of applied K took place. York et al. (1953) observed that when 200 kg ha^{-1} K was added to an acid silt loam soil treated with $CaCO_3$ (at the rate of 20 me Ca/100g) and then oven-dried at 70 C, about 55% of the K was fixed. The same soil fixed only 30% of the added K when there was no $CaCO_3$ added. Although the results given in Table 5.17 showed quite conclusively that lime additions can cause increased K fixation in a coarse textured soil, further experiments are needed with a large number of soils to come to a firm conclusion.

5.3.4 Effect of Cations in the Exchange Complex

5.3.4.1 Effect of Ca and Mg ions (Method 1).

As indicated in sections 5.1.4.1 linear relationships were found independently between CEC, exch.Ca and Mg of the soil, and K fixation (see Table 5.7). The purpose of this study was to see if Ca and Mg per se have an effect on the subsequently added K. Two soil samples (calcareous and non-calcareous) were selected and leached with $CaCl_2$ and $MgCl_2$ solution separately. The samples treated with Ca and Mg ions were air-dried and K fixation was determined as described earlier.

The fixation values for each Ca and Mg treated soils are given in Table 5.18. Leaching with solutions containing Ca and Mg ions reduced the amount of exchangeable K in both soils.

Table 5.18. The effect of Ca and Mg ion on K fixation in two coarse textured soils.

Soil	Before Leaching		After Leaching With			
			Ca		Mg	
	Exch.K	Fixed K*	Exch.K	fixed K	Exch.K	Fixed K
	mg K kg^{-1}					
SC1 (St. Claude) (Calcareous)	90	28 a	43	33 a	60	35 a
S2 (Willowcrest) (Non-calcareous)	116	22 a	71	33 b	76	25 a

*Amount of K Fixed when 100 mg K kg^{-1} Applied
K fixation values followed by the same letter in any row are not significantly different at 5% level.

Before any leaching, the St.Claude soil fixed 28 mg K kg^{-1} while Willowcrest fixed 22 mg K kg^{-1}. Leaching the soil with a solution containing Mg had no significant effect on K fixation in both St.Claude and Willowcrest soils. However, in the Willowcrest (non-calcareous) soil, the amount of K fixation increased significantly due to leaching the soil with solution containing $CaCl_2$. In this experiment the % Ca-saturation of the soils either before or after leaching was not measured. Most probably the % Ca-saturation would have been quite different at the initial stage.

Increased K fixation due to increased Ca^{2+} on the exchange complex has been widely observed (Wiklander, 1950; MacLean, 1962). Dennis and Ellis (1962) observed that for a given level of exchangeable K, the amount of fixed K was much greater when Ca^{2+} was the complementary ion compared to Na. Large hydrated cations such as Ca^{2+} and Mg^{2+} are believed to keep the edges of layer silicate minerals apart and prevent the formation of a stable structure. Consequently, K^+ and other ions with low hydration energy would be selectively adsorbed and trapped between the layers. Sawhney (1966) studied Cs sorption and observed an increased Cs sorption by a Ca-vermiculite, compared to a K-vermiculite. The increased Cs sorption by the Ca-vermiculite was attributed to the different sorption rates by the different exchange sites: an initial fast sorption on external surfaces and edges followed by slow diffusion into the interlayers. On the other hand, the decreased Cs sorption by K-vermiculite was associated with the collapse of the partially hydrated vermiculite in suspension to 1.0 nm. Sumner and Bolt (1962) have observed that prolonged treatment of clay minerals with moderately strong salt solutions opened up the mineral lattice. However, Jackson and During (1979) observed that even a weak leaching solution (0.05 M Calcium acetate, pH 5) in contact with soil for brief periods of 2 to 3 hrs caused significant weathering at the clay mineral edges and released considerable amounts of K. The results observed (Table 5.18) in the present study indicate that the exchangeable K was drastically reduced by leaching and there is no doubt that this would have caused the soil to release K from the edges and interlayers of clay minerals as the concentration of the leaching solution and the duration of leaching were 4 and 8 times higher than the concentration and the leaching duration employed by Jackson and During (1979). As the weathering process initiated by penetration of hydrated cations into interlayer spaces of clay minerals takes place, interlayers are brought to an expanded state facilitating K ions to escape (Raney and Hoover, 1946; Wiklander, 1950). When the interlayer K ions are removed, these positions are occupied by the complementary ions (Rich and Black, 1964). Thus, as the Ca saturated and K depleted soils are supplied with K, more of the added K is expected to be fixed between the layers. Stanford (1947) observed that in calcareous soils, Ca, Mg, and Na were replaced quite readily by K, thus accounting for rapid fixation of K. The results observed in this experiment may in part explain the close relationship observed between K fixation and exchangeable Ca and % K saturation of the soils (Section 5.1.4).

5.3.4.2 Effect of Ca and Na ions on K fixation (Method 2)

The purpose of this study was to verify the effect of Ca and Na ion per se on K fixation in three soils. Two of the three soils selected contained large amounts of vermiculite in the clay and the third soil (Rignold) was high in illite and montmorillonite. All three soil samples were treated with NaOAc ($pH = 5$) to remove carbonates and were enriched with varying levels of Ca^{2+} by shaking and centrifuging the soils three times with solutions containing varying proportions (0:1, 1:3, 3:1, and 1:0) of Ca and Na ions. The enriched samples were air-dried and K fixation was determined after adding K as KCl at the rate of 400 mg kg^{-1}.

Results shown in Table 5.19 illustrate that either Na or Ca increased in the exchange complex depending on the proportions of the ions in the shaking solution. Exchangeable Mg and K content decreased as the proportion of Ca in the shaking solution increased. The decrease in the amount of exchangeable K due to shaking with Ca and Na ions was higher in the soil with higher exchangeable K content in the natural stage than the two soils with low exchangeable K contents. The amount of K fixed in treated soils increased with increased Ca or Na content. In general, soils with high Na fixed the highest amount of K as opposed to the soil treated with Ca alone. An exception was found in the Almasippi soil in which more K was fixed (Almasippi No.3) with higher amounts of Ca on the exchange complex. The increase in amount of K fixation compared to the natural soil was higher in the (Rignold) soil which contained illite and montmorillonite as a major clay mineral than in the other soils which were high in vermiculite.

The effect of shaking the soils with Ca and Na may be, as observed by Wiklander (1950) and Scott and Smith (1966), due to removal of exchangeable K from the exchange complex and hence the low % K-saturation. It has been shown very clearly in section 5.1.4.1 that soils with high K-saturation fixed less K than soils with low K-saturation.

Table 5.19. Fixation of K in Almasippi, Lenswood and Rignold soils enriched with varying levels of Ca and Na ions.

Soil	Ca:Na	Exchangeable Cations				K Fixed #	K Fixed
		Ca^{2+}	Mg^{2+}	Na^+	K^+		
		cmol$_c$ kg^{-1}				mg K kg^{-1}	%
Almasippi (Haywood)	0*	14.66	5.10	0.11	0.11	269 a	67
	0:1	2.50	0.21	18.37	0.07	287 b	72
	1:3	18.25	0.07	2.07	0.06	298 c	75
	3:1	20.80	0.12	0.30	0.08	308 d	77
	1:0	21.35	0.15	0.10	0.08	301 c	75
Lenswood (S4)	0	23.10	5.20	0.12	0.13	206 a	51
	0:1	5.90	2.67	17.34	0.09	300 c	75
	1:3	21.65	0.32	2.12	0.07	256 b	64
	3:1	25.65	0.18	0.31	0.07	257 b	64
	1:0	26.25	0.16	0.08	0.07	252 b	63
Rignold (Winkler)	0	16.81	7.28	0.41	1.09	43 a	11
	0:1	2.15	0.10	23.10	0.43	198 c	50
	1:3	21.40	0.07	3.60	0.29	143 b	36
	3:1	24.20	0.06	0.67	0.29	158 bc	40
	1:0	26.40	0.07	0.27	0.26	137 b	34

* 0 - represent the values for natural soil and others represent the treated soils.
# Added K 400 mg kg^{-1},
Values followed by the same letter in any soil are not significantly different at the 5% level according to Tukey's Studentized Range Test.

The other effect of shaking the soil with Ca and Na may be due to removal of interlayer K from the layer silicate minerals. This would be due to the large hydrated radius of these ions which keep the edges of layer silicate minerals apart leading to the expansion of the mineral lattice. Layer silicate minerals are highly susceptible to the release of interlayer K when their positions are occupied by large hydrated cations. It was shown by Scott and Smith (1966) with muscovite, biotite and vermiculite mineral samples that when the same extraction procedure (30 min shaking, filtering and leaching with another 40 ml of the extractant) was used, 1 N NaCl (pH 6.2) extracted more exchangeable K than 1 N NH_4OAc (pH 7) solution. They concluded that the interlayer K in those minerals was generally inaccessible to exchange with NH_4^+, but accessible to replacement by Na^+. Therefore, when exchange positions are occupied by large hydrated cations, this makes the soil highly depleted in K^+ thus giving greater possibility for a selective adsorption of K ion. If K is added to such a K-depleted soil, a greater quantity of these adsorbed (Ca and Na) ions will be replaced by the K ions and refixation of K could take place.

The observed results in this experiment are in accordance with the results observed by Wiklander (1950). Wiklander (1950) observed that clays saturated independently with Ca and Na ions resulted in increased fixation. However, Dennis and Ellis (1962) found that for a given level of exchangeable K, more fixation of K occurred when Ca was the complementary ion compared to Na. Susceptibility of interlayer K in clays to exchange with Na and Ca have been studied by many workers (Wiklander, 1950; Scott and Reed, 1962; Scott and Smith, 1966).

It was observed in section 5.1.4.2 that calcareous soils fixed more K than non-calcareous soils. In view of the present results this fact can be explained partly by the replacement of adsorbed Ca by K. Calcareous soils which may be similar to a soil leached with solution containing Ca^{2+} may have a greater possibility of having opened layer silicate minerals in which it is likely that to some extent Ca^{2+} would have occupied places where K can be fixed. This will be reflected in a tendency toward greater fixation of applied K in those soils than in non-calcareous soils. This experiment can be said to have demonstrated the intimate relationship between the nature of the adsorbed ions and the degree of fixation of subsequently added K; it has also demonstrated that there is an equilibrium between fixed K and exchangeable K in soils.

5.3.5 Effect of Previously Fixed Potassium

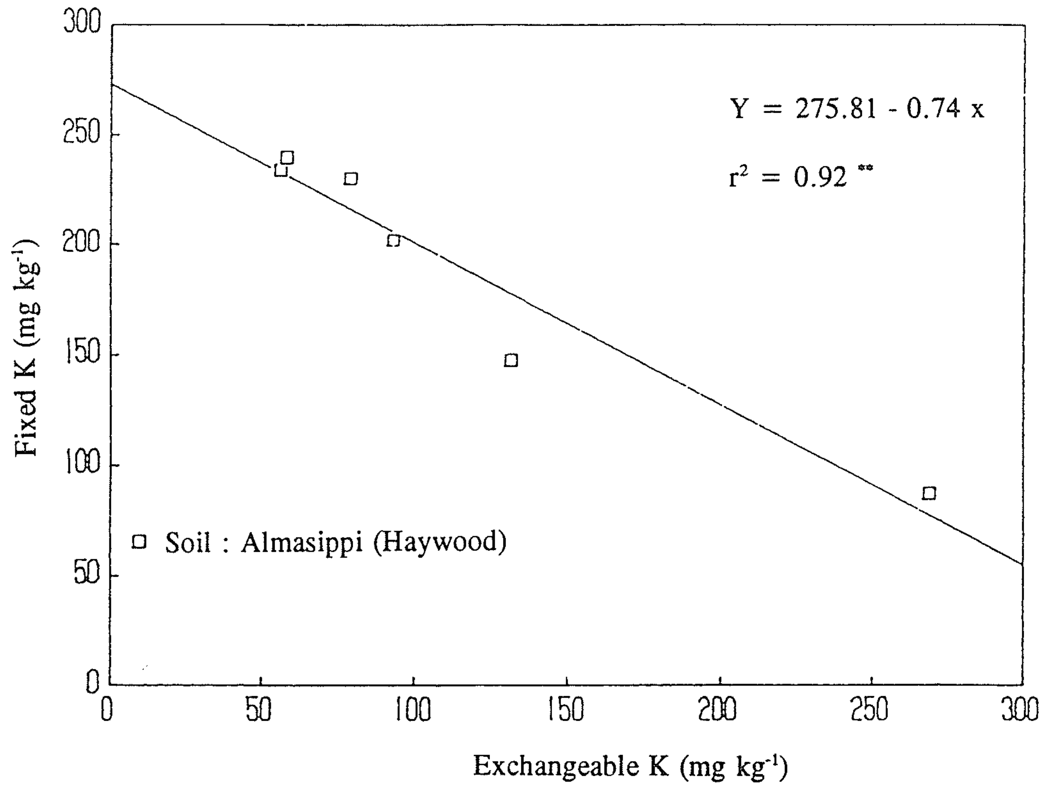
From a preliminary experiment it was observed that a soil which had received a large dose of K fertilizer in the field fixed only about half as much K as the unfertilized soil (see Table 4.7). In order to study the effect of previously fixed K on subsequent fixation, a laboratory experiment with two soil samples was carried out. The selected soils were treated with six levels of KCl in solution form and air-dried. The excess water soluble K was leached with distilled water until the leachate showed a negative test for chloride. The samples were then air-dried and exchangeable K was measured. A new dose of KCl (@ 400 mg K kg^{-1}) was applied to all the treated soils and K fixation measured.

Exchangeable K content increased in proportion to the amount of added K (Table 5.20). It has been observed from the previous studies that the amount of K fixation increased with the amount of K added. Therefore it is reasonable to believe that the amount of K fixed from the previously applied K would have increased with the amount of K applied. As can be seen from the Table 5.20 the amount of K fixed from the subsequent K application decreased as the amount of previously added K increased. This decrease was linearly related to the exchangeable K (see Fig. 5.1) for both Almasippi and Lenswood soils. This relationship is in agreement with the results observed in the simple regression analysis and other leaching studies in which exchangeable K and K saturation were negatively related to the amount of K fixation. Figure 5.2 indicates the influence of the amount of previously applied K on the amount of subsequent fixation. As seen from the Fig.5.2 the soil that received a large dose of K previously, fixed only

Table 5.20: Relationship between fixed K and exchangeable K of two coarse textured soils.

Soil	Previously Applied K	Exch.K After K Applied	Amount K Fixed when 400 mg kg^{-1} K applied	
	mg K kg^{-1}			%
ALMASIPPI (Haywood)	0	58 a	240 d	60
	50	65 a	234 d	59
	100	79 b	230 d	58
	200	93 c	202 c	51
	400	131 d	148 b	37
	1000	269 e	87 a	22
LENSWOOD (S4)	0	64 a	190 d	48
	50	74 ab	172 cd	43
	100	85 b	160 c	40
	200	113 c	155 c	39
	400	165 d	106 b	27
	1000	308 e	54 a	14

Values followed by the same letter in any column of any soil are not significantly different at the 5% level according to Tukey's Studentized Range Test.



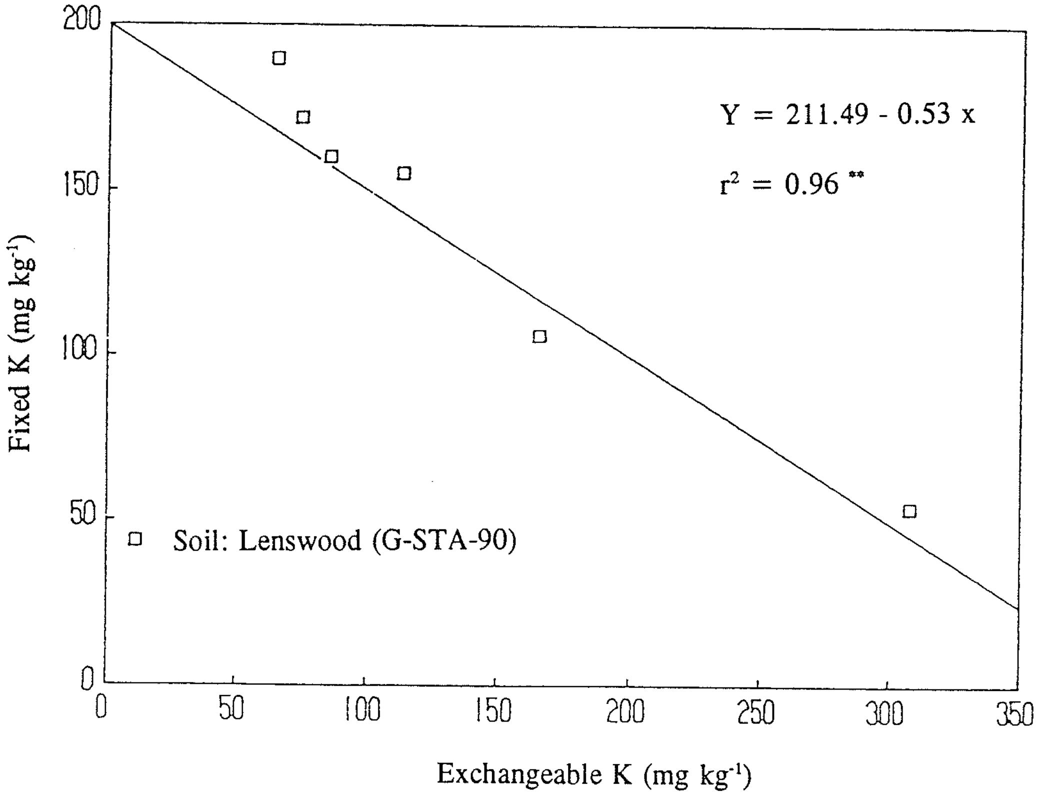


Fig. 5.1. The relationship between fixed K and exchangeable K of two coarse textured soils.

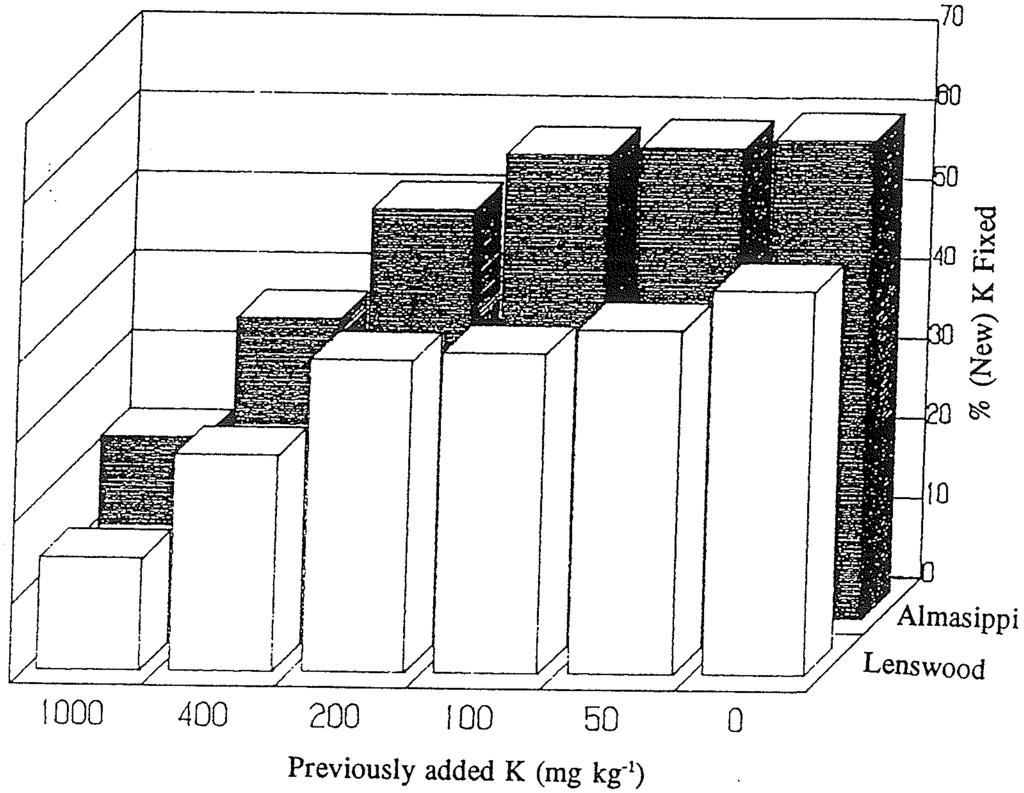


Fig. 5.2. The effect of previously applied K on subsequent fixation (Applied K 400 mg kg^{-1})

a small amount of K from the subsequent application. Since the fixation of K approaches a limiting value with increasing K applications, it is plausible that the fixation is dependent on the existence of a limited number of fixing sites in the soil minerals. All these findings clearly illustrate that each soil has its unique capacity to fix added K.

These studies suggest that K fixation is an equilibrium process in which the amount of K fixed is related to the amount of exchangeable K in the soil. As such, exchangeable K content of a given soil is an indication of the potential of the soil to fix added K from a subsequent application. As seen from Fig. 5.1 when the exchangeable K content of the Almasippi soil reaches about 373[1] mg K kg^{-1}, lower amounts of K fixation can be expected from the subsequent application. Likewise the Lenswood soil reaches this saturation point at about 398 mg kg^{-1} exchangeable K level.

Large K fertilizer applications to attain high exchangeable K content generally lead to mineralogical transformations in soils. These transformations mainly lead to the formation of minerals with basal spacing of 1.0 nm (Barshad, 1948; Jackson et al., 1952; Barshad and Kisk, 1970; Ross et al., 1985). Consequences of these transformation are the reductions of K fixing minerals or K fixing sites, reduction of CEC etc. (Wear and White, 1951). Soils with a high content of illite are examples of such an effect. The Rignold (Winkler) soil used in the previous experiment (see Table 5.11) consisted mainly of illite in the silt and clay fractions and had about 426 mg kg^{-1} exchangeable K and fixed only 43 mg K kg^{-1} from a subsequent application of 400 mg K kg^{-1}.

An equilibrium between fixed K, exchangeable K and soil solution K is known to occur in soils (Kaila, 1967). When large doses of K fertilizer are made, depending on the amount of K previously fixed, part of the applied K becomes fixed and an other part becomes exchangeable

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[1] Estimated from the graph by extrapolation

plus soil solution K. If the exchangeable K is depleted, the reverse reaction is expected to take place. As such, some of the fixed K becomes exchangeable with time. However, this reverse (release) reaction as opposed to the fixation reaction is rather slow and the chemical equilibria existing between the nonexchangeable and exchangeable K forms are very complex.

5.3.6 Summary

Increased K fixation with air-drying of soils indicated that air-drying following additions of K is one of the important factors in K fixation. However, the amount of K fixation was not affected by air-drying when the soil was high in vermiculite in the silt and clay fractions.

An experiment on the length of incubation period on K fixation indicated that K fixation is a rather quick process and three days of incubation were more than enough to attain a maximum amount of K fixation at a given level of K application. A non-calcareous soil treated with varying levels of $CaCO_3$ showed a decrease in exchangeable K content and an increase in K fixation with increased $CaCO_3$ content of the soil.

Leaching the soils independently with Ca and Mg ions indicated that Ca has a positive effect on K fixation in non-calcareous soils. Another experiment conducted to study the effect of varying levels of Ca and Na on the exchange complex has also shown these ions to increase K fixation in soils. Removal of K from the exchange complex by Ca and Na through cation exchange may be a major reason for increased K fixation in these soils. As K is removed from the soil complex the % K-saturation will decrease and thus a new equilibrium between fixed K and the exchangeable K will be attained. Depletion of interlayer K also may have taken place due to opening of the edges of layer silicate minerals by these large hydrated cations (Ca and Na). Amount of K fixation in a given soil is related to the amount of exchangeable K in the soil. A soil with a low exchangeable K content seems to fix more K than the same soil with a high exchangeable K content. This relationship seems to operate through an equilibrium process in which exchangeable K content of the soil is an indication of the potential of the soil to fix K from subsequent additions. A soil previously supplied with large amount of K fixed only a small amount from the subsequent application. It may be an indication that each soil has its own limited number of K fixing sites.

5.4 POTASSIUM FIXING CAPACITY OF COARSE TEXTURED SOILS

As observed in the previous section, each soil has its own capacity to fix added K. It is evident that soils which have fixed K from previous applications tended to fix less K from subsequent applications. The amount of K fixation increased with increased K addition but the % of added K fixed decreased. This type of pattern resembles the Langmuir type of adsorption isotherm, in which as sites are filled, it becomes increasingly difficult for adsorbate to find vacant sites for adsorption. By employing the Langmuir adsorption isotherm technique in K fixation studies one could possibly obtain the maximum point of fixation or the maximum amount of K a soil would fix from a infinite amount of K applied. In this chapter the maximum point of fixation will be referred to as the capacity for K fixation in a given soil. In fact, the capacity refers to the total amount of K fixation in a unit weight of soil when there has been no previous fixation. In this manner the maximum or the capacity for K fixation is considered as a constant value for a given soil.

The main purposes of this chapter are (i) to demonstrate that the K fixation in soils follows the Langmuir adsorption isotherm and (ii) to estimate the K fixation maximum of soils by employing the Langmuir model approach.

5.4.1 Potassium Fixation Isotherm

In general, K fixation can be considered as a concentration dependent equilibrium process. As previously seen in K fixation studies of batch-I and batch-II of surface soils and others (see Sections 5.1), the amount of K fixed increased with increasing K application rates. The fixed K was measured as the difference between the amount of applied K and the changes in the extractable K after equilibration, using a single 'equilibrium' extraction procedure with 1 N NH_4OAc as an extractant. The equilibrium system can be represented by the following equations:

$$(K) + (Soil) \rightleftharpoons (K+Soil) \quad (1)$$

Where K = Conc. of K in NH_4OAc solution,
K+Soil = Fixed K in soil.

$$K_{eq} = \frac{(K+Soil)}{(K)\ (Soil)} \quad (2)$$

When K fixation occurs, the concentration of the original solution reduces and reaches an equilibrium. This relationship between the amount of K fixed in the soil component and the equilibrium concentration of soil solution is called a 'fixation isotherm'. Adding K to a K fixing soil will reduce its ability for K fixation by the total amount of K fixed (K_f) in the soil components. Equation (2) can be written as

$$K_{eq} = \frac{K_f}{C\ (Max - K_f)} \quad (3)$$

By rearranging equation (3) and substituting K for K_{eq}, Y for K_f and S for Max the following equation is obtained:

$$Y = \frac{K\ C\ S}{1 + K\ C} \quad (4)$$

Where Y = Total Amount of K fixed ($\mu g\ g^{-1}$ soil),
C = Equilibrium Concentration of K ($\mu g\ mL^{-1}$), (Conc. of K in NH_4OAc solution),
K = Equilibrium Constant,
S = Fixation Capacity ($\mu g\ g^{-1}$ soil).

Most soils contain some fixed K initially which may be considered to be non-integral part of solid constituents and this component should be distinguished from the freshly fixed K that is observed when more K is added to the same soil during a fixation treatment. For the purpose of this chapter the term "initially fixed K" is referred to as "previously fixed K" and the freshly fixed K is referred to as "newly fixed K". Therefore all the K fixation measured throughout the present study are considered as "newly fixed" for this exercise.

Since Jackson et al. (1952) considered K fixation as the reverse weathering reaction of mica --> illite --> vermiculite --> montmorillonite and Barshad (1948) was able to reversibly transform vermiculite to biotite (mica) like minerals by treatment with a K solution, the amount of previously fixed K can be a factor affecting the new fixation. For a given soil the amount of newly fixed K will depend on the amount of previously fixed K. For example, a soil containing a large amount of illite is not expected to fix very large amount of K from a subsequent application since it has already fixed K between planes (Wear and White, 1951). Therefore in the above equation (4) the total amount of K fixed includes both the new K fixation that occurred during the treatment and the K previously fixed before the treatment. Since many workers (Barshad, 1948 and 1951; Mortland and Gieseking, 1951; Jackson et al., 1952; Arifin and Tan, 1973) have viewed K fixation as the formation of mica-like minerals but not as a (mica) primary mineral, the term ‘Y’ can be written as

$$Y = X_o + y_1 \tag{5}$$

Where X_o = Initially or previously fixed K ($\mu g\ g^{-1}$),
y_1 = Newly fixed K during the experiment ($\mu g\ g^{-1}$).

equation (4) can be transformed into a linear form

$$\frac{C}{(X_o + y_1)} = \frac{1}{S}\, C + \frac{1}{K\,S} \tag{6}$$

Thus, if K fixation in soils is a concentration dependent equilibrium surface phenomena following the Langmuir adsorption isotherm, the experimental plot of ($C/(X_o + y_1)$) vs the concentration (C) will give a straight line, the slope of which is the reciprocal of the fixation capacity (maximum) and the intercept may be used to calculate the equilibrium constant.

5.4.1.1 Procedure

The amounts of fixed K are normally obtained by adding solutions of progressively higher K^+ concentrations to a standard amount of material, and measuring loss of K^+ from the equilibrium solution. In this study, the whole soil is considered as an adsorbent or fixing material since the soil consists of a mixture of various K fixing clay minerals. The results obtained from the K fixation studies of batch-I and batch-II surface soil samples and other soils were utilized for this purpose. In each of the K fixation studies, six levels of K were used to measure K fixation. The concentration of K in the NH_4OAc extract was considered as an equilibrium concentration of K (this represents 'C' in Eq. 6) and the measured K fixation at each level of K application was considered as new fixation (this represents 'y_1' in Eq. 6). In order to complete the Langmuir plot (C/Y Vs C), the parameter 'previously fixed K' (X_o in Eq. 6) has to be estimated and added to the 'new fixation' to obtain the 'total K fixed'. The previously fixed K was estimated by using a statistical approach. In this approach (search method), the Langmuir model i.e. the relationship between C/Y versus C was assumed to be a linear form. The previously fixed K (X_o) in equation 6 was incremented by the value one from the initial value of zero until a linear relationship was obtained. This was attained by continually checking the values of the coefficient of determination (r^2) of the relationship C/Y versus C for each value of X_o. When the r^2 value reached 0.99, the corresponding X_o was taken as a value for previously fixed K. This search method was accomplished by a simple computer programme. The steps involved in that programme are given in Appendix C.1.

An alternate method for the above mentioned procedure was found. In the second (multiple regression) method, the Langmuir equation (6) was rearranged (see details in Appendix C.2) to obtain the equation shown below:

$$C = A_o x_1 + A_1 x_2 + A_2 \tag{7}$$

Where:
$x_1 = C y_1$,
$x_2 = y_1$,
C = Equilibrium concentration of K (μg mL^{-1}),
y_1 = New fixation during the experiment (μg g^{-1} soil),
Coefficients to be determined A_o, A_1 and A_2.

The relation between A_o, A_1 and A_2 with the parameters of eq.(6) are;

$$A_o = \frac{1}{S - X_o} \; ; \quad A_1 = \frac{1}{K(S - X_o)} \; ; \quad A_2 = \frac{X_o}{K(S - X_o)}$$

Where:
S = Fixation maximum (μg g^{-1} soil),
K = Equilibrium Constant,
X_o = Previously fixed K (μg g^{-1} soil).

A multiple regression of C on x_1 and x_2 was carried out for each soil and coefficients A_o, A_1 and A_2 were estimated. From the estimated coefficients, previously fixed K (X_o), fixation maximum (S) and equilibrium constants were computed. In this multiple regression method, the fixation maximum (capacity) was directly calculated from the three coefficients.

The relationship between the amount of K fixed and the corresponding equilibrium concentrations of soil solutions of two representative soil samples and their Langmuir plots (using the first method) are shown in Figs. 5.3 and 5.4. Sample calculations of a fixation maximum for soil RWL-7 is given in Appendix C.3 and C.4. The fixation maxima estimated by using the two methods for several soils are given in Table 5.21.

5.4.2 Previously Fixed K and Fixing Capacity

The results shown in Table 5.21 indicate that the values for previously fixed K estimated by using the two methods are different for a given soil. In general, the search method (1) estimated higher values for previously fixed K than the multiple regression method (2) for the surface soil samples. As an example, the estimated previously fixed K for Long Plain (GY 1) soil was 266 and 16 mg kg^{-1} soil by search and multiple regression methods respectively. In contrast, the multiple regression method estimated higher values of previously fixed K for most of the profile soil samples studied. Variations in the amount of previously fixed K were also observed among the different soil series as well as within the same series of soils studied. As far as the profile samples were concerned, the amount of previously fixed K did not show any increasing or decreasing pattern with increasing depth of soils.

Although two different methods were used in this investigation to estimate the previously fixed K, it should be born in mind that any of these methods does not clearly separate the previously fixed K from the K that is an integral part of the crystal structure but does give a value for previously fixed K which is in terms of K fixed from a recent addition.

Although the values of previously fixed K estimated by the two different methods for a given soil sample are different, the values estimated for the fixation maximum (capacity) are comparable. The close agreement found between the two methods for estimating the fixation maximum of 25 soil samples is presented in Fig. 5.5. For a practical reason, out of 30 soil samples estimated (see the last column of Table 5.21) for fixation maximum, five samples were omitted in the above comparison. From the Fig. 5.5 it is clear that regardless of the differences

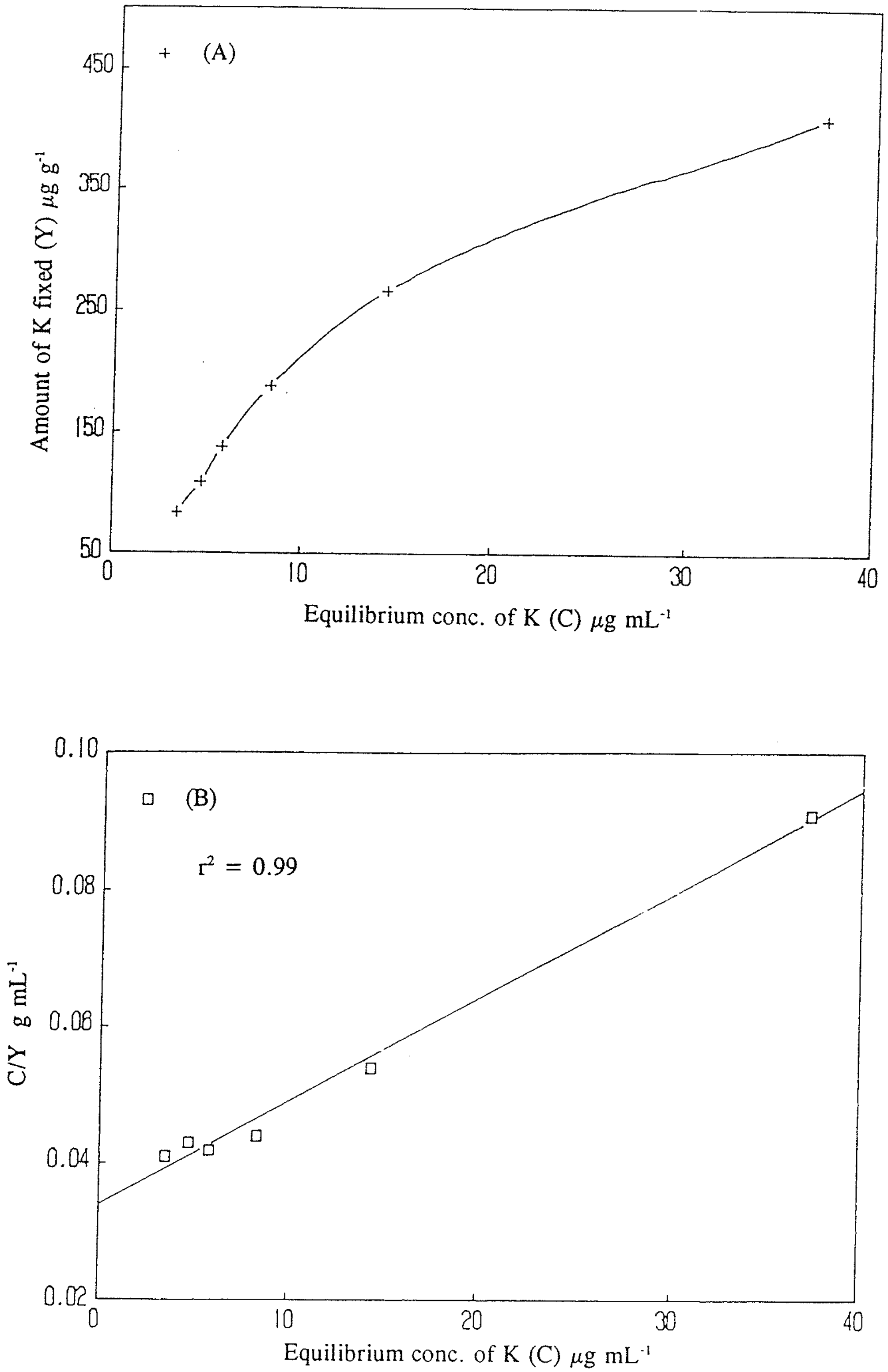
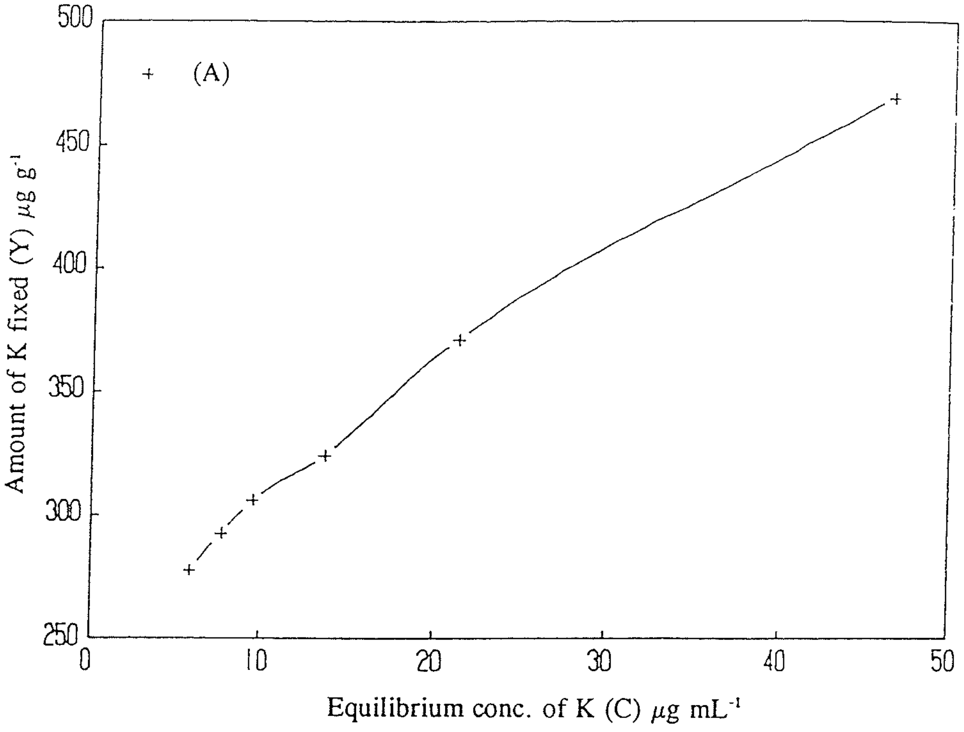


Fig. 5.3. (A) The relationship between K fixation vs equilibrium concentration of K and (B) the Langmuir plot of the St.Claude soil (SC-297) data.



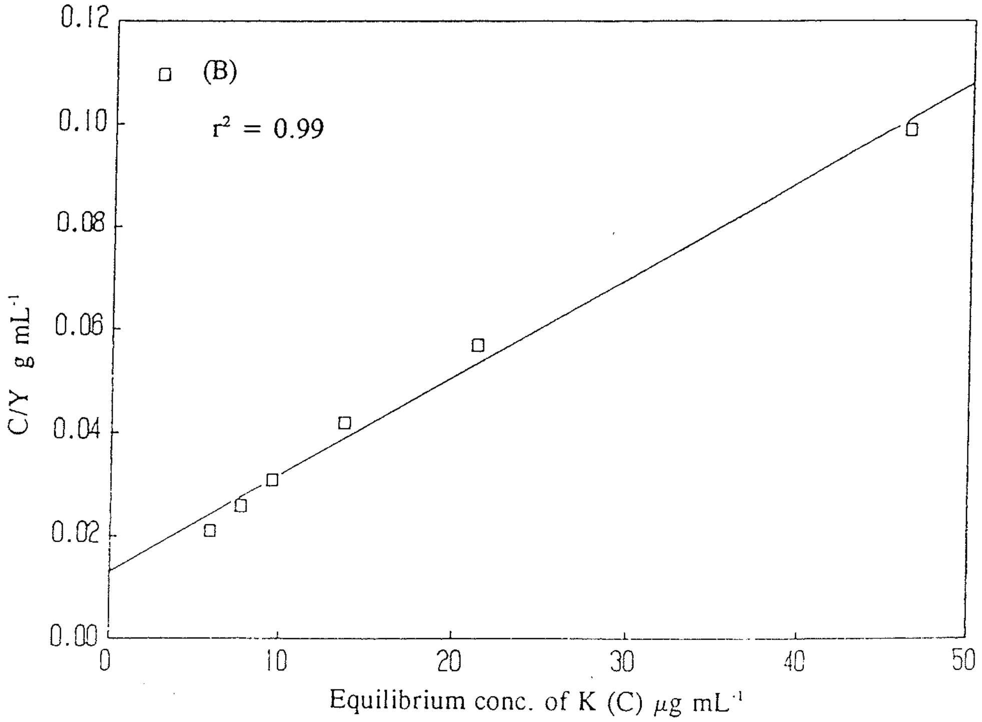


Fig. 5.4. (A) The relationship between K fixation vs equilibrium concentration of K and (B) the Langmuir plot of the Elm Creek soil (RWL-7) data.

Table 5.21. Previously fixed K, and fixation maximum of some coarse textured soils estimated by using search (Method 1) and multiple regression (Method 2) techniques based on the Langmuir model.

Soil No.	Soil Series	Previously Fixed K	Fixation Maximum	Previously Fixed K*	Fixation Maximum
		METHOD 1		METHOD 2	
		mg kg^{-1}			
RWL 7	Elm Creek	278	529	43	620
SC 357	Almasippi	128	690	182	683
SC 315	Long Plain	66	347	104	364
SC 297	St.Claude	84	665	112	628
STA 90	Lenswood	129	943	122	947
WBN 66	Almasippi	56	531	66	511
WBN 41	Willowcrest	50	250	79	261
GY 1	Long plain	266	412	16	602
GY 14	St.Claude	273	587	50	610
GY 50	Willowcrest	267	483	28	564
BRA 1	Stockton	302	670	79	619
STA 24	Pine Ridge	128	286	16	233
STA 33	Poppleton	120	984	167	929
SWR 7	Silver Creek	113	255	26	218
SWR 53	Dickson	107	219	-	-
SWR 57	Gilbert	95	194	-	-
SWR 77	Craigford	128	554	276	660
TWN-HAL 1	Stockton	96	143	-	-
SC 369	Dobbin	73	116	-	-
PGW 189	Long Plain	59	127	-	-
PGW 195	Willowcrest	57	204	104	243
TWN SOU 1	Lauder	60	192	-	-
		Soil from Growth-chamber experiment:			
S1	Long Plain	52	99	13	73
S2	Willowcrest	204	323	17	256
S3	Almasippi	57	132	-	-
S4	Lenswood	87	625	154	616
		Soil from Profiles:			
GY 2	Long Plain	306	461	32	271
GY 3	: :	69	322	121	350
GY 4	: :	355	608	36	720
GY 5	: :	466	865	90	870
GY 6	: :	90	646	108	623
STA 91	Lenswood	240	1074	270	1078
STA 92	: :	128	760	191	766
STA 93	: :	113	443	297	609
STA 94	: :	95	284	-	-
STA 95	: :	105	347	-	-
WBN 67	Almasippi	56	321	132	373
WBN 68	: :	118	392	796	1040
WBN 69	: :	139	440	536	800

* Values unable to be estimated are represented by '-' symbol.

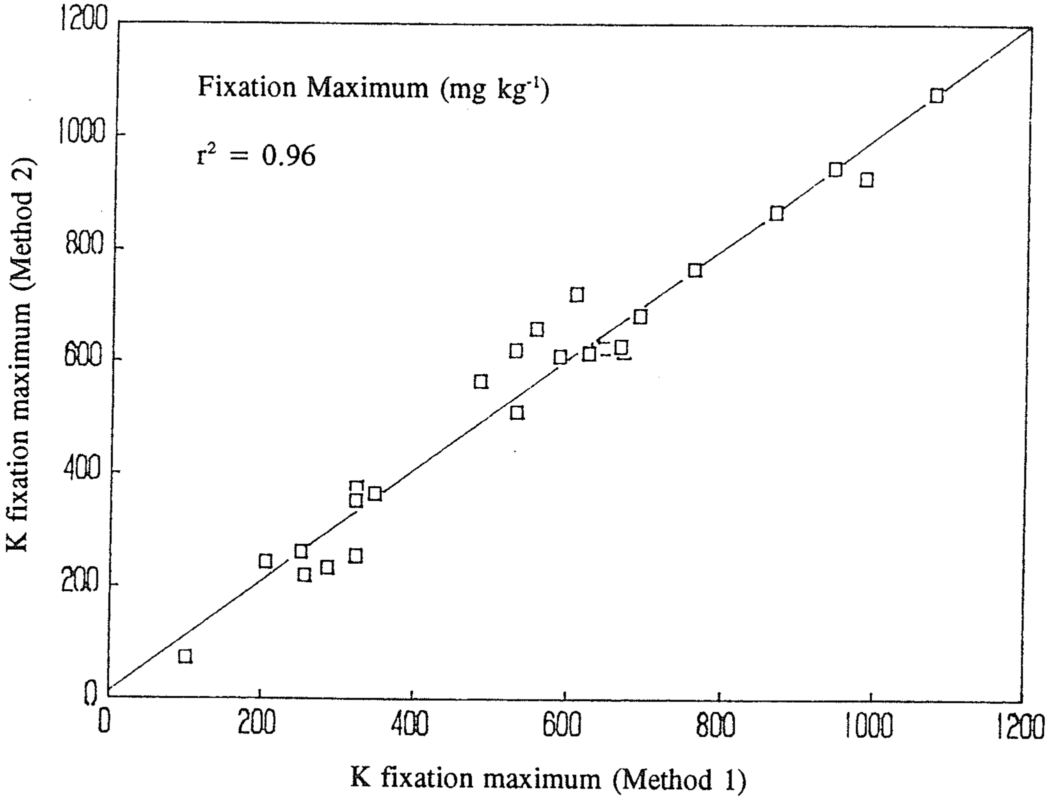


Fig. 5.5. Comparison of two methods of K fixation maximum determination.

in previously fixed K, the values of fixation maximum obtained from these two methods are similar in magnitude.

There were varying K fixation capacities among the soil series as well as within the soil series tested. As far as the profile samples are concerned, as observed for previously fixed K, K fixation capacity did not show any decreasing or increasing pattern with increasing depth of soil. The high K fixation maxima observed in certain soils may be in part related to their clay mineralogical composition. For example, the soil sample STA 90 (Lenswood) was shown to consist of vermiculite as the major clay mineralogical component in the coarse clay fractions of the soil (see Table 5.11). Therefore, it is evident that K fixation capacity of a given soil sample is an independent character and it may be controlled by the amount of K fixing material present in that soil. The magnitude of the K fixation maximum is an indication of K fixing capacity of a given soil sample and refers to the total amount of K fixation in a unit weight of soil when there was no previous fixation. Soil weathering and other changes in soil clay mineral composition may influence the K fixation maximum of a given soil and the amount of K fixation.

It was observed earlier that the fixation maxima estimated by using the two different methods for one soil are comparable. However, variations in K fixation maxima were observed among the soils studied. These variations in fixation maxima are similar to the variation pattern observed in the amount of K fixation at the highest level (1000 mg K kg^{-1} soil) of K applied to all the surface and profile soil samples. The relationship between fixation maximum estimated by the 'search' method (1) and the amount of K fixation observed at 1000 mg K kg^{-1} application level is illustrated in Fig. 5.6. The relationship between K fixation at 1000 mg K kg^{-1} application level and K fixation maxima estimated using the second method was also highly significant ($r^2=0.75$) as tested against 25 soil samples. In general, the soil samples which have fixed the

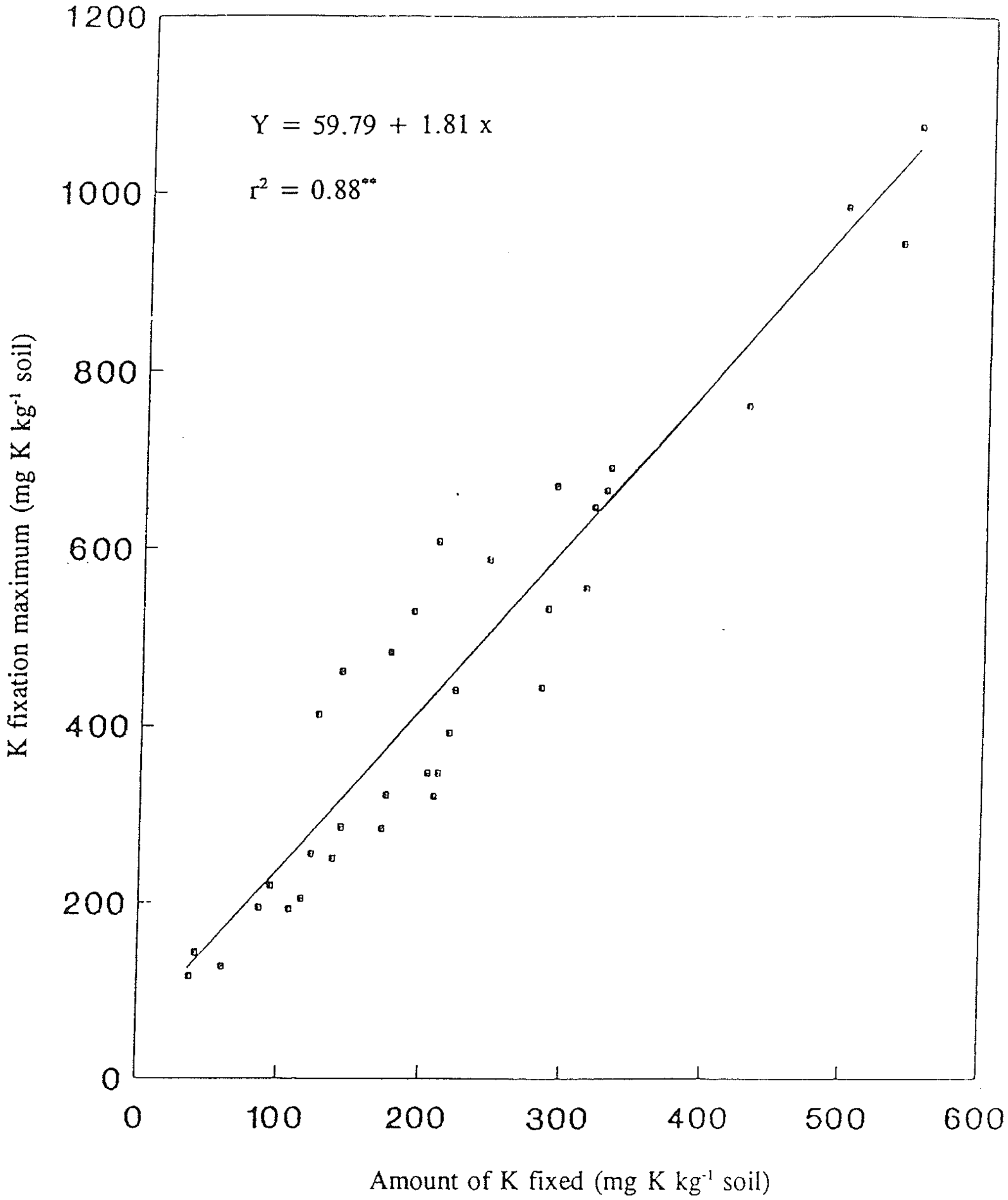


Fig. 5.6. The relationship between K fixation maximum and the amount of K fixed when 1000 mg K was initially added to a kilogram of soil.

largest amount of K at the highest application level (see Table 5.1 and 5.6) showed the largest fixation maximum. Likewise the soil samples which have fixed the lowest amounts of K at the same level of K application showed the lowest K fixation maximum. Therefore, the K fixation pattern observed in these coarse textured soils (e.g. see Tables 5.1 and 5.6) indicates that the amount of K fixation is dependent upon K application rates as well as the K fixing capacities of the soils. Since K fixation is a concentration dependent equilibrium process and the total amount of K fixation of a given soil is controlled by the K fixing capacity of the soil, the amount of K fixation is expected to increase with increased application rates.

The relationship between K fixation maximum estimated by using the 'search' method and the amount of K fixed at 1000 mg K kg^{-1} application level for the 22 surface soil samples also showed a similar relationship ($Y = 1.81\ x + 59.79$, $r^2=0.88$) as the 35 soil samples. Thus, the relationship observed in Fig. 5.6 demonstrates that the amount of K fixation at 1000 mg K kg^{-1} application level can be used to estimate the fixation maximum (capacity) of other coarse textured soils in the region.

From this study it is evident that the K fixation behavior in soil can be expressed by a Langmuir's adsorption isotherm and is an indication that the fixation behavior is closely associated with surface phenomena. Although Arifin and Tan (1973) have observed that K fixation tendencies of soil clays conformed to the Langmuir's adsorption isotherm, their approach was not clearly elaborated. One of the steps involved in estimating the fixation capacity of a soil is finding the amount of previously fixed K.

Although two methods have been suggested for finding the previously fixed K of a soil, individually these two methods have their deficiencies. In the second (multiple regression) method, the previously fixed K and the fixation maximum are estimated from the coefficients, however, the first (search) method is still preferable since it is less complex. Whichever the method may be, the amount of previously fixed K cannot be neglected from equation (6) since the total amount of K fixed at any level of K application includes both the previously fixed K and the new fixation. This is specially true for high fixing soils which have received high doses of K in the past. However, the relationship observed between K fixation maximum and the amount of K fixed at 1000 mg K kg^{-1} K application level could be a useful quick way of estimating the K fixation maximum of these soils.

5.4.3 Summary

Potassium fixation behavior of coarse textured soils is a concentration dependent equilibrium process and it can be expressed by the Langmuir's adsorption isotherm. Finding the previously fixed K, before any new fixation occurs is an important part of the process of computing the parameters of fixation isotherm. Even though variations were found in the estimated values for previously fixed K between two methods employed, the estimated K fixation maximum values are comparable. Potassium fixation maximum estimated for the surface soil samples indicated that the values are highly variable among the different soils. The relationship observed between the K fixation maximum and the amount of K fixed at 1000 mg K kg^{-1} K application level seems to be an important short cut to predict K fixation maximum for these coarse textured soils.

5.5 AVAILABILITY OF FIXED POTASSIUM TO WHEAT: A GROWTH CHAMBER EXPERIMENT

A growth chamber experiment using four coarse textured soils was conducted to study the availability of fixed K to wheat. Some of the physical and chemical characteristics of the soil samples used in this experiment are given in Table 3.6 while the K fixation observed by adding three levels of K in the laboratory are given in Table 5.22.

Table 5.22. Influence of amount of applied K on K fixation in four coarse textured soils.

Soil Series	Amount of K applied mg kg^{-1}			
	0	50	100	200
	Exch.K mg kg^{-1}	Amount of K fixed* mg kg^{-1}		
Long Plain	99	(28) 14	(19) 19	(22) 43
Willowcrest	98	(32) 16	(25) 25	(27) 54
Almasippi	143	(56) 28	(34) 34	(27) 53
Lenswood	49	(76) 38	(67) 67	(59) 117

* % Fixation given in parentheses.

The four soils were prepared for the growth chamber experiment by adding four levels of K (0, 50, 100 and 200 mg kg^{-1} soil) as KCl as described earlier (see section 3.11). The treated samples were air-dried and exchangeable K and K fixation were measured from the sub-samples. The pots were filled with soils and four wheat seedlings were grown to the heading stage. Plants were harvested (shoots and roots separately) and analyzed for K. The exchangeable K in the soil was determined initially, after addition of fertilizer (at seeding) and after harvest of the crop to estimate the amount of K fixation and K taken up by plants.

5.5.1 Dry Matter Yield

The plant response to K additions was variable and the response was not related to the initial exchangeable K content of the soils. Shoot yields increased with increased additions of K (Table 5.23). At the highest level of K application all four soils showed statistically significant shoot yield increase when compared with the zero application of K. Root yields also showed apparent increases with increased K applications; however, significant root yield responses were observed only in the Long Plain soils, probably due to variability in root yield. Among the four soils studied only Long Plain and Almasippi showed significant dry matter yield increase with increased K additions. Although the dry matter yields obtained from different soils at zero K application level were different, the dry matter yields obtained from those soils at higher levels of K were quite good and comparable.

5.5.2 Potassium Uptake

The effect of K addition on percent K in the plant was variable (Table 5.24). The Lenswood and the Willowcrest soils showed an increased % K in the shoot with increased K application while the other two soils did not show any increasing trend. With minor exceptions, the % K in the roots increased with increased K additions. The total K uptake determined from shoots and roots indicated a significant response at every level of added K in all four soils. Among the four soils studied, the highest amount of K uptake was observed from the Almasippi soil at every level of K addition whereas the lowest amount of uptake was observed from the Lenswood soil. Variations in total K uptake observed in this study were not linearly related to

Table 5.23. Influence of rate of application of K as KCl on the yield of wheat at the heading stage, grown in four coarse textured soils.

Soil Series	Amount of K applied	Yield * Shoot	Root	Total Dry Matter
	mg kg^{-1}	g pot^{-1}		
Long Plain	0	12.38 a	2.22 a	14.60 a
	50	25.84 a	15.56 b	41.39 b
	100	34.56 b	26.94 c	61.50 c
	200	37.89 c	20.85 bc	58.74 c
Willowcrest	0	31.82 a	13.63 a	45.45 a
	50	34.21 ab	14.06 a	48.27 a
	100	36.41 b	16.62 a	53.03 a
	200	36.81 b	13.60 a	50.41 a
Almasippi	0	20.63 a	8.20 a	28.83 a
	50	30.97 b	9.89 a	40.86 b
	100	36.22 bc	16.12 a	52.34 bc
	200	39.25 c	17.89 a	57.14 c
Lenswood	0	27.33 a	16.55 a	43.88 a
	50	31.02 ab	16.49 a	47.51 a
	100	33.66 bc	17.55 a	51.21 a
	200	35.20 c	24.79 a	59.99 a

* Values followed by the same letter in any column for a given soil series are not significantly different at the 5% level according to Tukey's Studentized Range Test.

Table 5.24. Influence of rate of application of K as KCl on % K in the shoot and root and total K uptake of wheat at the heading stage.

Soil	Amount of K applied	K Shoot	K Root	Total K Uptake*
	mg kg^{-1}	%	%	mg pot^{-1}
Long Plain	0	3.48	0.44	450 a
	50	2.40	0.61	709 b
	100	2.19	0.56	905 c
	200	2.74	0.80	1207 d
Willowcrest	0	1.46	0.65	546 a
	50	1.76	0.85	718 b
	100	2.34	0.79	984 c
	200	2.78	0.91	1140 d
Almasippi	0	2.68	0.79	604 a
	50	2.49	0.84	846 b
	100	2.44	0.71	1000 c
	200	2.89	0.99	1303 d
Lenswood	0	1.09	0.25	338 a
	50	1.25	0.25	421 b
	100	1.59	0.28	584 c
	200	2.24	0.33	868 d

* Values followed by the same letter in any column for a given soil are not significantly different at the 5% level according to Tukey's Studentized Range Test.

total dry matter yield. However, the K uptake observed among different soils are related to the amount of exchangeable K found at the time of seeding (Fig.5.7). The relationship found between the exchangeable K at seeding and K uptake ($r^2=0.92$) was linear and is an indication of the availability of exchangeable K to the crop. The highly significant relationship observed (Fig. 5.7) in this study might also mean that measuring exchangeable K is much more important than measuring nonexchangeable or fixed K as they are in equilibrium with exchangeable K in the soil system. Therefore, measuring the exchangeable K at seeding (i.e. after addition of fertilizer) is a useful indicator of the available K to crop during that growing season. Nevertheless, from the equation (Fig. 5.7) it was evident that some available but nonexchangeable K was taken up by the plant during the growing season.

Exchangeable K has been widely used as a basis for fertilizer recommendations. Pratt (1951) found that the amount of exchangeable K before cropping was the best criterion for predicting K removal by alfalfa. However, the recent results of Richards et al. (1988) indicated that with some southern Ontario soils, the exchangeable K at seeding did not explain all the variations in K uptake by eight crops of alfalfa. The differences in observations between Richards et al. (1988) study and the present study may be that three out of four soils used in the present study originated from a similar parent material and the equilibrium between nonexchangeable and exchangeable K in these soils may have been similar. This may not be the case in Richards et al. (1988) study where soils may have originated from different parent material.

5.5.3 Availability of Fixed Potassium

The exchangeable K content increased in accordance with the amount of K added in these soils but decreased drastically during crop growth (Table 5.25). However, at the highest level of application large amount of residual K found in all four soils. In this study the relationship

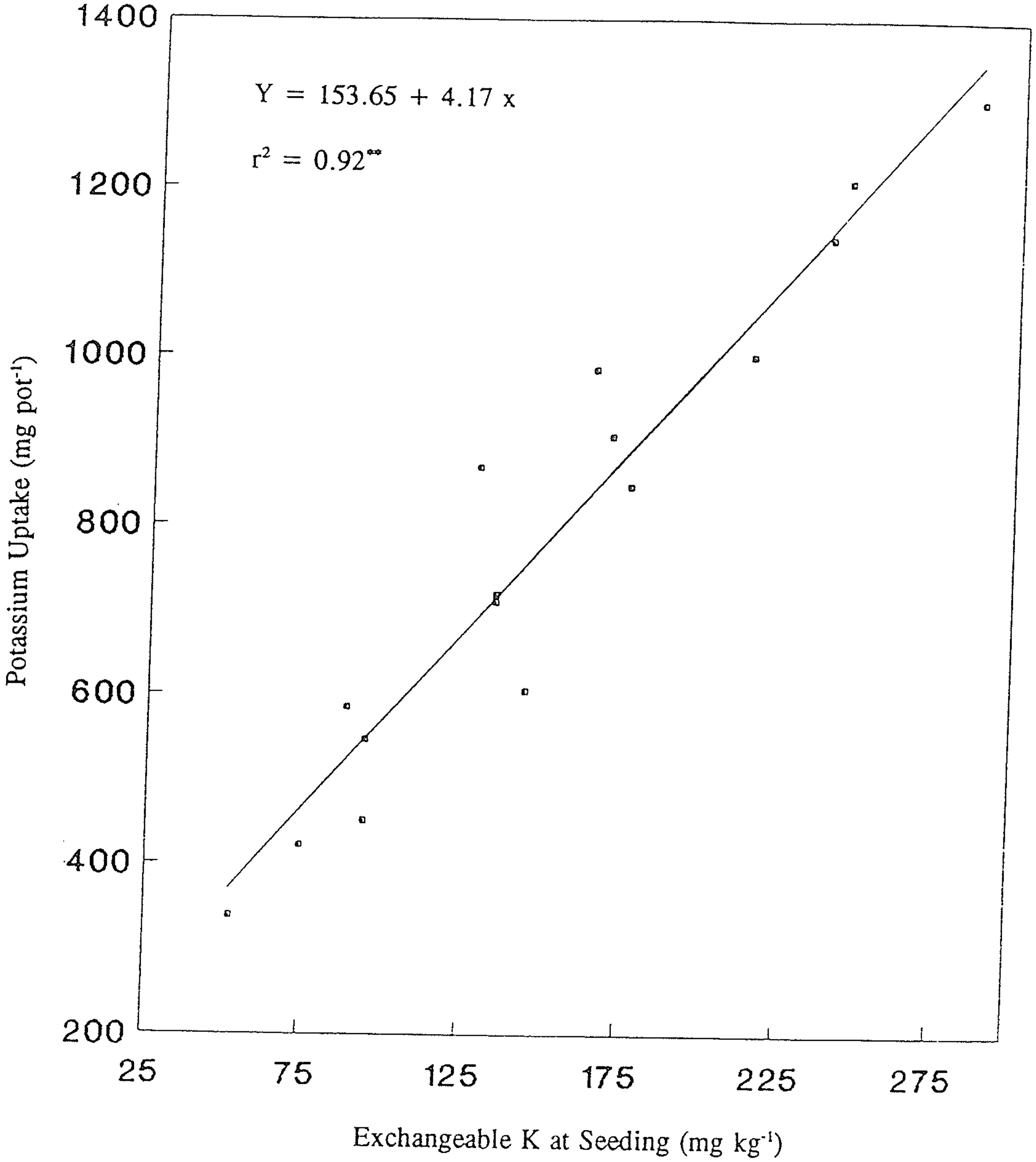


Fig. 5.7. The influence of exchangeable K on K uptake of wheat grown in four coarse textured soils.

Table 5.25. Influence of rate of application of K as KCl to four coarse textured soils on fixation of K and its recovery by wheat crop grown in pots.

Soil Series	Exch.K before trt.	K added	Exch.K at seeding	K Fixed[#]	Exch.K end of expt.	Total K Uptake[*]	Nonexch.K release[+]	Nonexch.K release beyond check trt.[@]
	mg kg^{-1}							
Long Plain	94	0	94	0	39	75	21	0
		50	134	10	36	118	20	0
		100	170	24	40	151	21	0
		200	244	54	57	201	15	0
Willowcrest	94	0	94	0	41	91	39	0
		50	134	10	48	120	34	0
		100	164	30	45	164	45	6
		200	238	56	62	190	14	0
Almasippi	144	0	144	0	49	101	6	0
		50	176	18	57	141	22	16
		100	214	30	60	167	13	7
		200	286	58	81	217	12	6
Lenswood	52	0	52	0	27	56	32	0
		50	74	28	31	70	28	0
		100	88	64	36	97	73	41
		200	128	124	39	145	55	23

[#] K Fixed = Amount of K added + Exch.K before trt - Exch.K at seeding

[+] Nonexch.K release = K uptake - (Exch.K at seeding - Exch.K end of expt.)

[@] Nonexch.K release beyond check trt. = NEK release in trt. soil - NEK rel. in check. (only positive values are recorded) observed (Fig. 5.7) between K uptake and exchangeable K at seeding ($r^2=0.92$) was comparable to the relationship observed (Fig. 5.8) between K uptake and the reduction in exchangeable K that occured during the growing season ($r^2=0.94$). Although assessment of availability of recently fixed K to growing crops was difficult, the above relationships clearly indicates that exchangeable K was the main source of K during this experiment. From Fig. 5.8 it appears that, in addition to the exchangeable K about 40[1] ppm nonexchangeable K was taken up by the plants in a pot regardless of K application rate. This amount (40 ppm) of nonexchangeable K is more or less equal to the average amount of nonexchangeable K released from all the soils studied. Therefore this nonexchangeable K could be considered as a natural release of K that occurred during the growing period as was observed by many other workers (Ayres et al. 1946; Smith and Matthews, 1957; Binnie and Barber, 1964; Richards et al., 1988). Soils have been shown to release nonexchangeable K during the growing period. In general, the amount of the nonexchangeable K release was not influenced by the amount of K added (Table 5.25). In general the amount of nonexchangeable K released was not constant among the soils studied. However, the results obtained in this type of experiment cannot be easily interpreted because of the simultaneous release of nonexchangeable K that occurred during the growing period and the lack of a distinction between the K released from the newly fixed K, previously fixed K and from the K bearing minerals. A clear distinction between these is needed for a complete interpretation. If the newly fixed K had been fully available to the crop during the growing period, at least there should be a relationship between the amount of newly fixed K and the amount of nonexchangeable K released in all four soils. With minor exception in the Lenswood, there was no relationship observed between the amount of newly fixed K and the amount of

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[1] by converting the value of intercept 242.16 (mg K /pot) to ppm

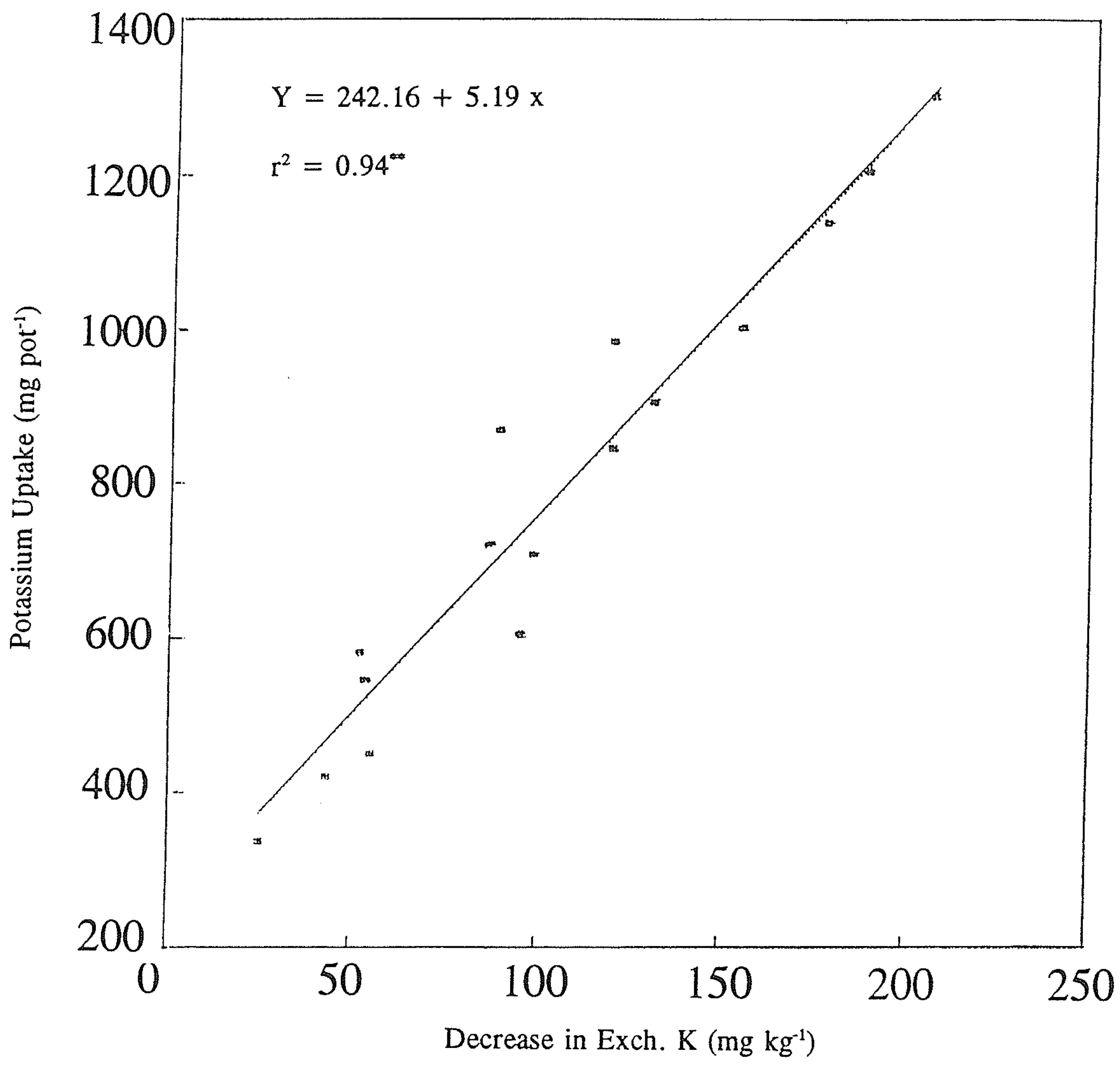


Fig. 5.8. The relationship between K uptake and decrease in exchangeable K of soils.

nonexchangeable K released. In addition, the amount of nonexchangeable K released was related neither to the amount of K added nor to the amount of K uptake.

In some instances, the nonexchangeable K release observed from the treated soils was higher than the amount released from the control treatment. However, the amount released beyond the control treatment (see Table 5.25) was not higher than the amount of K fixed in those soils indicating that a major portion of the K fixed was not available to the growing crop. All these observations and the strong relationship observed between the exchangeable K reductions and K uptake indicate that the growing crop mainly utilized the exchangeable K and thus the K fixed during the experiment would not have been a factor in K uptake to plants during the single growing season. Although there is an equilibrium existing between the fixed K and the exchangeable K in soils, in this system with perhaps a large amount of previously fixed K, adding 10 to 124 ppm (of fixed K) may not have affected the large pool of fixed K in the soil. Plants also did not utilize all the exchangeable K from the soil. At higher rates of addition more K was left unutilized. Therefore, the results from this experiment indicate that the K fixation reaction is much faster than the K release reaction and the fixed K becomes a part of "the K pool". The conversion of fixed K to available K can be a very slow process. Therefore, these data gave hardly any evidence of fixed fertilizer K being released to crops at this stage of the experiment. It is expected that continuation of intensive cropping without any further addition of fertilizer may show release of fixed K as was observed by other workers (MacLean, 1968 and Richards et al., 1988). Soils with a high fixation capacity for K may often require high rates of K fertilizer to assure sufficient amount of this nutrient for maximum production. This is certainly true when K is mixed with soil in the practice of broadcast spreading of fertilizer instead of its placement at the time of seeding.

5.5.4 Summary

Potassium application was shown to increase the crop yields in K fixing coarse textured soils. The exchangeable K content at seeding seems to be a good indicator of K uptake by crops in these coarse textured soils. The relationship observed between the reduction of exchangeable K that occurred during the growing season and K uptake indicated that a major source of K is exchangeable K. Since there was no relationship between the fixed K and the nonexchangeable K utilized by the plants, and since nonexchangeable K release was also observed in soils not treated with any potassium, it was evident that the fixed K was not readily available to the growing crop during that single growing season.

5.6 THE RELEASE OF POTASSIUM FROM NON-EXCHANGEABLE FORMS IN COARSE TEXTURED SOILS

Soil K potentially available to plants includes exchangeable, nonexchangeable and mineral K forms. Among the forms, the exchangeable K is the most readily available, since it is in direct equilibrium with the soil solution. However, soils containing little K on the exchange complex are dependent on transformations from the nonexchangeable forms to replenish the exchange or solution form upon depletion. Several workers (Pratt, 1952; Doll and Lucas, 1973; Richards et al., 1988) have observed that nonexchangeable K released during successive cropping made a significant contribution to the total K uptake by plants. Ability of soils to supply K from the nonexchangeable forms was found to be different for different soils. It was observed in the previous section that soils with the same amount of exchangeable K at seeding and with the same K fixing ability released different amounts of nonexchangeable K to wheat (see Table 5.25). According to Sparks (1980) the chemical equilibria existing between the nonexchangeable and exchangeable K forms are very complex and are dependent on the overall K status of various forms.

The purpose of this experiment was to determine the K release patterns and the changes in these patterns due to K additions for the four coarse textured soils used in the growth chamber experiment.

5.6.1 Acid Extraction - HCl Reflux Method

It is generally accepted that K in soils can be described by the following equilibrium conditions:

$$\textbf{Soil Solution K} \rightleftharpoons \textbf{Exchangeable K} \rightleftharpoons \textbf{Nonexchangeable K}$$

The portion that is nonexchangeable includes that held as fixed ions in the lattice structure of clay minerals and that which forms part of the structures of primary minerals. Attempts have been made to assess that portion of the nonexchangeable K that can become available during cropping. In this experiment, the HCl-acid reflux method proposed by Singh and Goulding (1983) was employed. The HCl reflux method is actually a modification of Haylock's (1956) and Maclean's (1961) method, in which HNO_3 was used as an extractant. In this method, the exchangeable cations are removed initially with 0.1 N HCl and then 10 successive extractions with 6.52 N HCl are made on the same soil samples. The nonexchangeable K data obtained from this method were interpreted using Haylock's concepts of 'step-K' (available to plants) and 'constant-rate K' (very slightly available to plants). The step-K corresponds to the difference between the HCl-extractable K and the constant-rate K for each successive extraction. The constant-rate K is the constant or near constant K obtained with successive extractions. In Table 5.26, the ratio between the step-K and the constant-rate K has been included. As proposed by Moss and Coulter (1964), the ratio between the step-K and the constant-rate K is a measure of 'available' K relative to further K reserve (buffer capacity) which may become available over long periods through weathering.

5.6.2 HCl - Acid Extractable K

The amount of K extracted by 0.1 N HCl and the 10 successive extractions with 6.52 N HCl are shown in Table 5.26. The values reported in column 2 (Table 5.26) are very much smaller than the values reported in column 3. These differences in values occurred due to absorption of first (6.52 N HCl) acid extract by the dry glass wool. The glass wool was used in the extraction tube to support the extraction thimble in which the soil sample was placed for successive extraction (see Section 3.12). With the second extraction (column 3), some of the extract from the previous extraction reached the receiving flask and caused the concentration to be higher than the previous extraction. Theoretically the first (6.52 N HCl) acid extract should

Table 5.26. Potassium released to HCl acid extractant from coarse textured soils and K uptake by wheat.

Soil Series	Extraction No.* 1	2	3	4	5	6	7	8	9	10	11	Total NEK Release	Step K (X)	Const. rate K (Y)	X/Y	K uptake by Wheat#
	K extracted															
	mg kg^{-1}															mg K kg^{-1}
Long Plain	138	42	72	46	32	24	22	20	18	16	16	352	192	16	12.0	75
Willowcrest	178	38	64	82	74	60	56	44	34	30	24	590	350	24	14.6	91
Almasippi	190	56	94	76	56	52	44	38	30	32	30	554	254	30	8.5	101
Lenswood	82	36	42	42	38	34	26	28	26	24	24	350	110	24	4.6	56

* Extraction 1 : 0.1 N HCl extract.
Extraction 2-11: 6.52 N HCl Extract.

Total Nonexchangeable K (NEK) extracted during successive extraction = Sum.K + 0.1 M HCl.K - 1 M NH_4OAc.K
Step K = Total Nonexchangeable K - (10 x Const. rate K)
\# Uptake from table 5.25

have been higher or equal to the subsequent extract. However, these differences would not have affected the overall pattern of K release.

The amounts of K extracted with 6.52 N HCl were largest (Table 5.26) in the first 3 extractions and declined during the next three or four extractions and then remained nearly constant in subsequent extractions (Table 5.26 and Figs. 5.9 & 5.10). This pattern was true for three soils studied with the exception of Willowcrest. Very similar patterns of K release were observed by other workers (Haylock, 1956; MacLean, 1961; Moss and Coulter, 1964; Martini and Suarez, 1977; Singh and Goulding, 1983; Richards and Bates, 1988).

The total amount of nonexchangeable K released during the successive extractions from the four soils, ranged from 350 mg K kg^{-1} for the Lenswood soil to 590 mg K kg^{-1} for the Willowcrest soil. According to Haylock (1956) two forms of K are extracted by the repeated extractions with N HNO_3 - one of limited solubility (constant-rate K) and the other highly soluble in 1 N HNO_3 (step-K), mostly in the first extraction. He found that only the second form was available to Italian ryegrass (Lolium Multiflora) in the course of a 15 month cropping period. The step-K and the constant-rate K values obtained in the present study for these four soils were variable. The step-K values ranged from 110 mg K kg^{-1} for the Lenswood soil to 350 mg K kg^{-1} for the Willowcrest soil, while the constant-rate K ranged from 16 mg K kg^{-1} for the Long Plain soil to 30 mg K kg^{-1} for the Almasippi soil. Neither step-K nor constant-rate K correlated well with NH_4OAc extractable K content measured at seeding from the same soils (see Table 5.25). Two soils (Long Plain and Willowcrest) with the same (NH_4OAc extractable) exchangeable K values showed differences in the amount of step-K and the constant-rate K values. This may be an indication of varying ability of soils to supply nonexchangeable K from the K pool. The results observed in this study were in agreement with those of Richards and Bates (1988). They

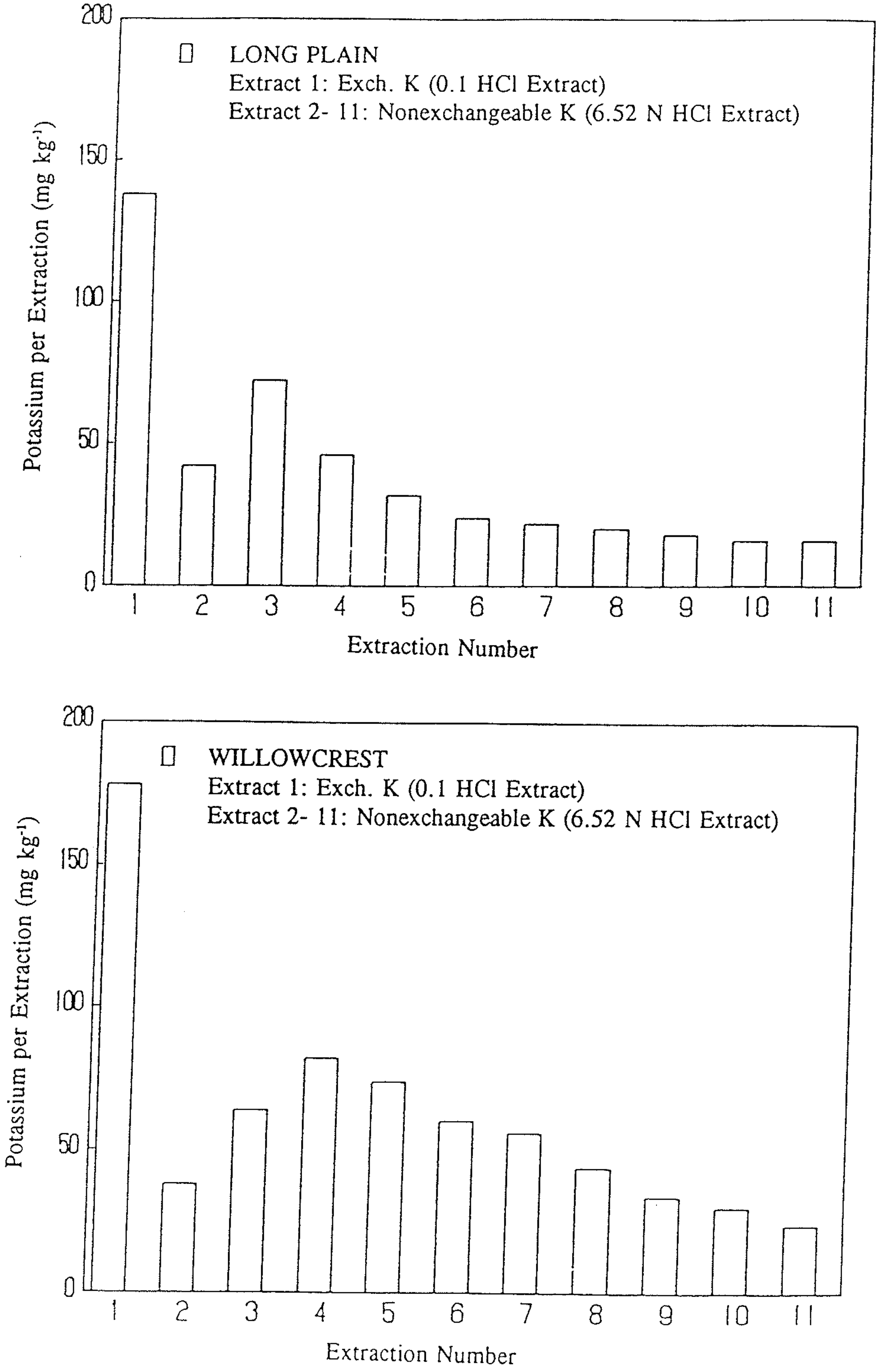
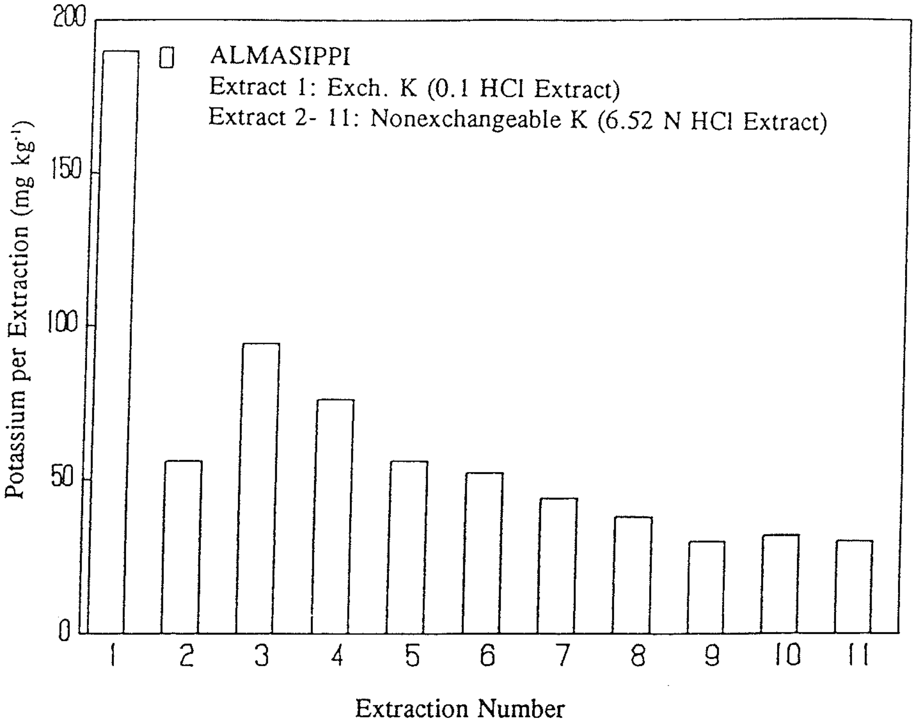


Fig. 5.9. Potassium released to HCl extractant from Long Plain and Willowcrest soils.



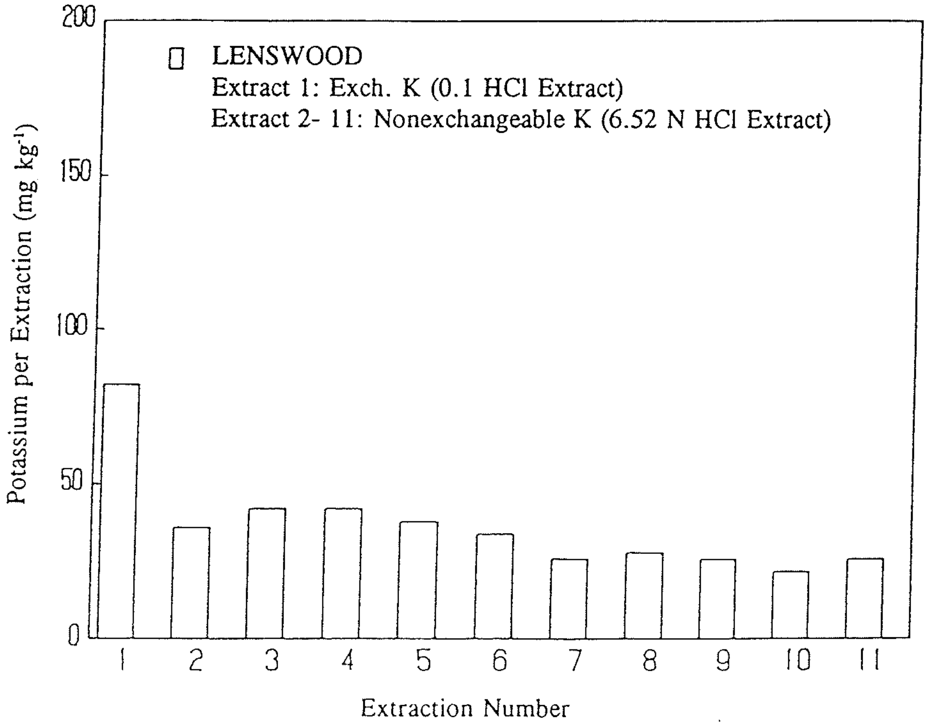


Fig. 5.10. Potassium released to HCl extractant from Almasippi and Lenswood soils.

observed that some southern Ontario soils with the same exchangeable K content released varying amounts of step-K and constant rate-K to HNO_3 extractant.

5.6.3 'Available' but Nonexchangeable K

As observed in Table 5.25, wheat extracted considerable portions of K from the nonexchangeable sources during a growing period. The nonexchangeable K removed by the crops from the four soils was not closely related to total nonexchangeable K extracted by the HCl or with the step-K. In contrast, several workers have obtained good correlations between the total nonexchangeable K extracted by HNO_3 and that (nonexchangeable K) extracted by crops in greenhouse trials (Haylock, 1956; MacLean, 1961; Moss and Coulter, 1964; Martini and Suarez, 1977; Richards and Bates, 1988). The same workers have also found a highly significant correlation between step-K and nonexchangeable K extracted by crops. However, none of the workers have found any relationship between constant-rate K extracted by HNO_3 and nonexchangeable K extracted by crops or total K uptake. In the present study lack of relationships between the K fractions extracted by HCl and crop uptake or nonexchangeable K removed by the crop was expected, since the fractions of acid extractant were mainly related with data obtained from the long term greenhouse experiments (successive cropping) by other workers instead of using the data obtained from a single cropping season as was done in this experiment. Although the results obtained from these four soils indicate that the so called 'available' but nonexchangeable fraction (step-K) is not fully immediately available to the crop, a portion of that fraction may be available to the crop beyond the exchangeable K during a single growing season. As observed by other workers, the constant-rate K was not related either to crop uptake or to the nonexchangeable K removed by the crop. In this experiment, the amount of K extracted by 0.1 N HCl (extraction No.1 of Table 5.26) was slightly higher than the amount of K extracted by 1 N NH_4OAc. However, the exchangeable K fraction extracted by 0.1 N HCl was highly correlated ($r^2 = 0.98^*$; n=4) with the crop uptake as compared to the exchangeable K extracted by NH_4OAc ($r^2 = 0.85$; n=4), indicating that a part of the K that was extracted by 0.1 N HCl was available to the crop during the single cropping period. This extra portion of K extracted by 0.1 N HCl may have been part of the step-K which was available to the crop. Although, no statistically significant relationship was found between K uptake and exchangeable K extracted by NH_4OAc or between K uptake and step-K, a multiple linear regression relating both of these parameters explained 99% of the variations observed in the crop uptake as shown below:

$$\text{Total K Uptake} = \underset{(2.42)}{26.75} + \underset{(0.044)}{0.359}\ NH_4OAc\text{-K} + \underset{(0.016)^*}{0.086}\ \text{Step-K}$$

$$R^2 = 0.99^* \quad n = 4$$

where:

Total K uptake = Total K removed by wheat in a single cropping season (at 50 days) (mg K kg^{-1} soil)

NH_4OAc-K = Exch. K (NH_4OAc extractable) (mg K kg^{-1} soil)

Step-K = Total NEK extracted by HCl - (Const.rate K x number of extractions) (mg K kg^{-1})

* Std. errors of the coefficients are given in parenthesis.

This relationship with total K uptake agrees with the findings of Richards and Bates (1988) who observed that NH_4OAc extractable K and the step-K extracted by HNO_3 together predicted the K uptake of alfalfa in some southern Ontario soils. The results observed in this experiment indicate that, though the exchangeable K values determined by NH_4OAc extracts prove to be the best of the simple extraction methods for assessing available K to the next crop (see Fig. 5.7), that value alone did not define the source of K available to crops. However, more detailed work with a large number of sample is needed to assess the contribution of the nonexchangeable form to crops from the coarse textured soils.

Many workers have used strong acid extracts, especially the step-K as a measure of the K supplying power of soils (Haylock, 1956; MacLean, 1961; Moss and Coulter, 1964; Acquaye, 1973; Martini and Suarez, 1977; Richards and Bates, 1988). Some other workers have obtained close correlations between the amount of clay and the K supplying power of some Canadian soils (Smith and Matthews, 1957; McEwen and Matthews, 1958; MacLean, 1961; Al-Kanani et al., 1984). In this investigation, there was no such close relationships observed between clay content of soils and the step-K extracted by HCl (see Table 3.6). Any relationship between clay content and K supplying power may also depend on the type of clay minerals. In this study, the first three soils (The Long Plain, Willowcrest, Almasippi) showed similarities in their composition of clay minerals and the last sample had more vermiculite than the other three soils (see Section 5.2.2). Therefore a lack of relationship between clay content and K supplying power of soil may be due to variations in clay mineralogical compositions of soils used in this study.

5.6.4. Effect of K Additions on Nonexchangeable K Release to Acid Extractant

The step-K is usually equated to K fixed from fertilizer and other sources (Moss and Coulter, 1964; Singh and Goulding, 1983). In other words, this K can be considered as that involved in the fixation process. According to Martin and Sparks (1985), the nonexchangeable K is solely derived from the K held in the wedge positions of illites and vermiculites. According to Metson et al. (1956), the constant-rate K is considered as the K dissolved from the primary minerals of the silt and sand, and from the more inaccessible surfaces of the hydrous micas. Therefore, when fertilizer is added to a soil one would expect an increase in exchangeable and step K but none in the constant-rate K. Table 5.27 illustrates the distribution of step-K and

Table 5.27. Potassium released to HCl extractant from coarse textured soils treated with various amounts of K as KCl.

Added K	Exch.K (0.1 N HCl Exr)	Fixed K	Step K (X)	Increased Step-K	Constant rate K (Y)	X/Y	Total K recovd.#
	mg K kg^{-1}						mg K kg^{-1}
Long Plain:							
0	138	0	192	0	16	12.0	446
400	482	56	284	92	16	17.7	920
1000	894	244	390	198	14	27.8	1380
Willowcrest:							
0	178	0	350	0	24	14.6	684
400	482	96	363	13	26	14.0	1084
1000	904	274	418	68	28	14.9	1552
Almasippi:							
0	190	0	254	0	30	8.5	698
400	502	88	267	13	28	9.5	1038
1000	908	282	416	162	24	17.3	1524
Lenswood:							
0	82	0	110	0	24	4.6	402
400	286	196	94	-16	22	4.3	566
1000	668	414	274	164	20	13.7	1112

Total K recovered = Sum.K + 0.1 N HCl.K (see Appendix D.1)

constant-rate K for four soils before and after additions of two rates (400 and 1000 mg kg^{-1}) of K fertilizers (details given in Appendix D).

In general, increasing K additions increased the exchangeable K content (0.1 N HCl extractable) of the soils. With the exception of the Lenswood soil, the values obtained for exchangeable K are comparable among the soils studied. All the soils have shown an increased step-K content with increased K additions while the constant-rate K content was unaffected. Different soils have been shown to contain more or less a constant value for constant-rate K. At the 1000 mg K kg^{-1} addition, the step-K ranged from 274 mg K kg^{-1} for the Lenswood soil to 418 mg K kg^{-1} from the Willowcrest soil, while the constant-rate K ranged from 14 for the Long Plain soil to 28 for the Willowcrest soil. The results observed by Moss and Coulter (1964) and Richards and Bates (1988) have also shown that K additions increased the step-K content of the soils. The ratio between the step-K and the constant-rate K was also shown to increase with increased K additions, indicating that the buffer capacity of the soil to supply K has increased in these soils.

The amount of K fixation against 0.1 N HCl extraction, as calculated by the differences between the amount of K added plus the amount of exchangeable K extracted from untreated soil and the exchangeable K extracted from the treated soil was shown to increase with increased K additions in all four soils. In other words, not all of the added K was recovered as HCl exchangeable K from these soils and the amount not recoverable has increased with increased K additions. Though the step-K has increased generally with increased K additions, with a minor exception in the Lenswood soil, the increased step-K due to K addition was always less than the amount of K fixed by the corresponding soils (compare column 3 with column 5 of Table 5.27), indicating that not all of the fixed K was recovered as step-K. Though the fixed K at 400 mg K kg^{-1} application level was fully recovered as step-K from the Long Plain soil, the K fixed at the highest level was not fully recovered from any of the soils studied. Specifically, the (Lenswood) soil with a high vermiculite content showed more resistance to K release than the other three soils studied.

These results seem to suggest that though the increases in step-K beyond the initial level are due to new K fixation, all the fixed K is not fully represented by the amount of step-K present in the soil, indicating that part of the fixed K cannot be easily recovered from the soils. This may have occurred due to the transformation of clay minerals during the K fixation process as observed by others (Barshad, 1948; Jackson et al., 1952; Sawhney, 1967 b; Ross et al., 1985; Ross et al., 1989). The recoverability of K from the different soils may also be related to the type of minerals present in the soil. Kittrick (1966) studied the mechanisms of ion fixation by vermiculite. He noted that the process of ion fixation by vermiculite involves irreversible contractions. Removal of K from mica like minerals (specially dioctahedral) is usually difficult by acid extractions (Ross and Kodama, 1970). In addition, it should be kept in mind that the amount of exchangeable K extracted by 0.1 N HCl was always higher than the amount of exchangeable K extracted by 1 N NH_4OAc from the same soil. Hence the real amount of K fixed against 1 N NH_4OAc would have been much larger than the amount observed in this experiment.

5.6.5 Summary

Soils have varying ability to supply K from nonexchangeable sources. The step-K and the constant-rate K values obtained were shown to be different for four different soils. The Willowcrest soil had the largest amount of step-K among the four soils studied. Neither the step-K nor the constant-rate K correlated well with the NH_4OAc extractable K content measured at seeding. The nonexchangeable K removed by one crop of wheat in the growth chamber experiment was not related to any of those components extracted by HCl such as the total nonexchangeable K, step-K or constant-rate K.

Adding K to K fixing soils increased the step-K content but not the constant-rate K; however, the increased step-K due to K additions has not equated to that of K fixed. This indicates that part of the fixed K is not recoverable. The recoverability of added K from K fixing soils may be related to the clay mineralogical composition of the soils.

CHAPTER 6

GENERAL DISCUSSION

The amount of K fixation in coarse textured soils was shown to be highly variable. Soils with 10% or less clay fixed fairly large amounts of K from the added source on air-drying. At 100 mg K kg^{-1} application rate, the K fixation for 22 surface soil samples ranged from 16 to 84% of the applied K. In general, K fixation increased with increased application rate in all the soil samples studied. The magnitude of K fixation observed in these soil samples is comparable to the magnitude of the K fixation observed by other workers with some Canadian soils (MacLean, 1962; Richards, 1985). However, the methods used by those workers, included either several wetting and drying cycles, or oven-drying, or both, following K additions. All these wetting and drying treatments and oven-drying the soil at 70 or 105 C have been shown to increase the amount of K fixation beyond the amount of K fixation that could be expected from air-drying alone (Attoe 1946, Cook and Hutcheson, 1960).

The soil samples from the subsurface and C horizons also were shown to fix as much K as the surface soil samples. In all the profile samples, the organic matter content either decreased or was present in insignificant amount with increasing depth of the soil. In a Willowcrest soil profile, although the clay and silt content of the soil decreased with increasing depth, the amount of K fixation was not greatly affected by these changes, indicating that either the K fixing ability of those silt and clay have increased with increasing depth or the increased sand content was responsible for maintaining the K fixation at the same level throughout the profile.

The clay mineralogy of the high fixing surface soils was dominated by vermiculites in coarse clay, fine silt and coarse silt fractions, whereas the other soils which fixed intermediate amounts, did not show any particular clay mineral as a major mineral in any of those fractions. The soils that originated from a similar parent material (Almasippi association) showed very similar clay mineralogical patterns in all the size fractions. The fine clay fractions of all soils consisted of montmorillonite as a major clay mineral, while the coarse clay fractions consisted of four clay minerals namely: montmorillorite, vermiculite, illite and kaolinite. The fine silt and coarse silt fractions showed vermiculite, illite and kaolinite as components of clay minerals. Among the clay minerals observed in these soils, the vermiculite, illite and montmorillonites have been shown to fix K under both wet and dry conditions (Raney and Hoover, 1946; Stanford, 1947; Demumbrum and Hoover, 1958). It has been shown by many workers (e.g. Arifin and Tan, 1973) that the K fixing capacity of different clay minerals are different and their fixing capacities are higher when they are mixed with other minerals (Demumbrum and Hoover, 1958). From this it is clear that K fixation cannot be related to a single clay mineral type as the other clay minerals also have been shown to fix added K. This may in part explain the reason why the % K fixation at constant rate of K addition in these soils was not very closely related to the amount of clay in the soils. However, in some Canadian soils, MacLean (1962) has found a positive relationship between the % K fixation and the % clay content of the soils. Another reason for not obtaining a close relationship between clay content and K fixation may be due to the K fixation in the silt and sand fractions as observed in the preliminary experiments. However, amounts of silt and sand were also not directly related to the amount of K fixation.

A simple linear regression analyses of 22 surface soils relating fixation and CEC showed a significant positive relationship ($r^2 = 0.61$). Since CEC represents all exchange sites including all potential (mineral) K fixing sites, this characteristic may be a good indication of the K fixing ability of these soils. Since not only clay and silt, but also sand fractions are responsible for K fixation, the CEC may represent all the fixing sites in these soils. However, part of the CEC originates from organic matter, this portion of CEC has to be taken into account when considering any close relationship with CEC. Many workers have also found a close positive relationship between CEC and K fixation (Martin et al., 1945; Ataga, 1973). Some other workers have observed that the magnitude of the reduction of CEC following K fixation is equal to the amount of K fixed in soils (Martin et al., 1945; Coffman and Fannings, 1974).

Among the surface soils studied, all the calcareous soils fixed more K than non-calcareous soils at each level of added K. However, the amount of $CaCO_3$ present in each soil was not directly related to the amount of K fixation. Addition of $CaCO_3$ to a non-calcareous soil increased K fixation. Similar observations were made by other workers (Wiklander, 1950; MacLean, 1962). The effect of $CaCO_3$ on K fixation in these soils may be in part due to the high pH. A significant linear relationship observed between pH of the surface soils and K fixation ($r^2 = 0.32^{**}$) reinforces this conclusion. The other effect of $CaCO_3$ may be in part due to the effect of Ca and Mg ions. Because of higher Ca and Mg saturation in the calcareous than non-calcareous soils in the present study, there was a possibility that some of the potential K fixing sites may have been occupied by Ca and Mg ions in these soils. Since Ca ions are not fixed by the clay minerals (Joffe and Levine, 1947) and K ions have higher selectivity than the Ca ions (Rich, 1964; Rich and Black, 1964), adding K to Ca enriched calcareous soils may have fixed more K than the non-calcareous soils. A close relationship ($r^2 = 0.41^{**}$) observed between the exchangeable Ca and K fixation in these soils may be one of the reasons for this behavior. In particular in the first batch of surface soil samples in which nearly 50% of the samples were calcareous, a very close relationship ($r^2 = 0.72^{**}$) between Ca and K fixation was shown. However, in general, soils used in the present study were high in exchangeable Ca and the exchangeable Ca may have merely reflected the CEC of the soil. When soils used in the present study were grouped on the basis of the presence and absence of $CaCO_3$, results indicated that calcareous soils contained more clay and silt (could be partly $CaCO_3$) than non-calcareous soils. In addition, CEC and pH were higher and K-saturation was lower than in non-calcareous soils. However, all of the above characteristics were shown to relate to K fixation in these coarse textured soils.

Although no direct relationship was observed between K fixation and exchangeable K of soils, when the exchangeable K was combined with CEC of soils (i.e. K-Saturation), the relationship was evident indicating that there was a close relationship existing between the exchangeable K of the soil and K fixation. Soils with higher K-saturation fixed less K than the soils with lower K-saturation.

It has also been shown in this study that leaching the soils with solutions containing large hydrated cations such as Ca, Mg and Na increased K fixation. Leaching the soil with these hydrated cations drastically reduced the exchangeable K content of the soils and thus causing lower K-saturation than before. As observed by other workers (Wiklander, 1950; Jackson and During, 1979) leaching the soils with hydrated cations would have also caused some of the fixed or nonexchangeable K from the wedge zone and interlayers to escape, leaving the clay minerals in an expanded state. When K-depleted, and partially weathered minerals are supplied with K, more K would possibly be fixed by these soils.

Potassium fixation in these surface and subsurface samples increases with increased K additions while the % fixation decreases. This pattern of fixation indicated that there should be a maximum value for K fixation in a given soil. Since this pattern resembles the Langmuir type of adsorption model, the K fixation process can be considered as a concentration dependent surface phenomena. Potassium fixing capacity (maximum) estimated by using the Langmuir model was highly variable among the soils studied. The magnitude of the K fixing capacity estimated by this method for each soil was comparable to the amount of K fixation observed at the highest level of K application. The K fixation capacity estimated by these methods is an indication of the total number of K fixing sites present in a unit weight of soil when there is no previous fixation.

It has been shown from this study that the amount of K fixation from a given amount of applied K is dependent on the amount of previously fixed K in the soil. When K fixing soils are supplied with large amounts of K, part of the fixing capacity will be satisfied, and the subsequent fixation from a new addition will depend on the amount of previously fixed K in that soil. Continuous addition of K to a K fixing soil, provided there was no heavy depletion of K involved, should eventually satisfy all the fixing sites and lead to a non-fixing state or saturation point. Additions of K to a K fixing soil, while increasing the amount of fixed K will increase the exchangeable K content of the soil. Soils with high exchangeable K contents were shown to fix less added K than soils with low exchangeable K. These observations made from the experiment on the effect of previously fixed K on subsequent fixation helps to confirm that the K fixation process is a rapid one, reaching an equilibrium state very quickly. An experiment conducted to study the effect of incubation time on K fixation indicated that at a given level of K application, a maximum amount of fixation is attained within three days of incubation.

A growth chamber experiment conducted to study the availability of fixed K to wheat indicated that the fixed K was not readily available to the crop during that growing season. However, nonexchangeable K was extracted by the crop from all treated and non-treated soils during the growing season. Since the amount of nonexchangeable K extracted by the crop was neither related to the amount fixed by the soil nor the amount added, it was evident that the amount of added K that was fixed by the soil had little or no effect on the release of nonexchangeable K during the growing season. The reason for this may be that the soils which fixed the least amount of added K most probably had a large amount of previously fixed K in the system and a little amount of newly fixed K may not have affected the large pool of fixed K.

The non-exchangeable K release to HCl extraction has shown to contain two forms of K; one highly soluble (step-K) and the other less soluble (constant-rate K) as observed by other workers (Haylock, 1956; Moss and Coulter, 1964; Singh and Goulding, 1983). Soils with the same amount of initial exchangeable K were shown to contain variable amounts of step-K and constant-rate K, indicating that each soil has its own K supplying capacity from the non-exchangeable sources. The step-K estimated by the HCl extraction method was not directly related to either the total amount of K removed or the total amount of nonexchangeable K removed by wheat in the growth chamber experiment. However, other workers have confirmed the existence of a very good relationship between the step-K and the nonexchangeable K extracted by the crop during several successive cropping (Haylock, 1956; MacLean, 1961; Moss and Coulter, 1964; Richards and Bates, 1988). Since the step-K represents the long-term supply of nonexchangeable K (Moss and Coulter, 1964), the lack of a relationship between step-K and K uptake obtained from the single cropping data was not unexpected. Although the step-K measured in this study was not directly related to crop uptake, a multiple regression relating NH_4OAc extractable K at seeding and step-K as independent variables explained 99% of the variations observed in the K uptake among the four soils studied. This relationship indicated the availability of a portion of the step-K during the single cropping season.

The step-K extracted from the K treated soils was shown to increase with increased K addition in these soils as observed by other workers (Moss and Coulter, 1964; Richards and Bates, 1988). However, the amount of step-K increase due to K additions in these soils was not equated to the amount of K fixed from the added K. The amount of step-K was always less than the total amount of K fixed against 0.1 N HCl. This observation leads one to believe that part of the fixed K was not easily extractable by HCl and may have undergone some mineralogical transformation following K additions as was observed by other workers (Barshad, 1948; Jackson et al., 1952; Ross et al., 1985; Ross et al., 1989). This was especially true for a soil with high vermiculite content in which the major portion of the added K was not recovered by strong HCl-extraction. Since the fixed K was not fully recoverable by the strong acid, it is reasonable to believe that a portion of the fixed K may not be easily recoverable by growing plants even in the long run.

CHAPTER 7

SUMMARY AND CONCLUSIONS

Potassium fixation studies indicated that K fixation was the major reason that an Almasippi soil required large amounts of broadcast K to attain a maximum crop yield in the field. The K fixation studies further indicated that some coarse textured soils had a large capacity to fix added K and part of that was fixed by the sand fractions. However, the total contribution of sand fractions toward K fixation was very small as compared with clay plus silt fractions of those soils.

Potassium fixation studies using 22 coarse textured surface soil samples indicated that K fixation values are highly variable among the soils. In general, the amount of K fixation increased and the % K fixation decreased with increased K additions. The amount of K fixed in the sub-surface soil was generally comparable with surface soils.

Clay mineralogical analyses of surface soils indicated that the high fixing soils contained vermiculite as a major component of the coarse clay, fine silt and coarse silt fractions of the soils whereas the low fixing soils contained montmorillonite and illite as major components of the coarse clay and illite and kaolinite as major components of the fine and coarse silt fractions. Soil samples from the Almasippi association believed to have originated from similar parent material were shown to contain mainly montmorillonite in the fine clay fractions and montmorillonite, vermiculite, illite and kaolinites in the coarse clay fractions. The fine and coarse silt fractions consisted mainly of vermiculite, illite and kaolinites. No major differences in clay mineralogy were observed among the Almassipi soils studied. From this finding it appears that variations in K fixation observed among the nine Almasippi soils were not due to one type of clay mineral. All the clay minerals except kaolinite may have been involved in the K fixation process.

Although clay, silt and sand fractions were responsible for K fixation in these soils, the percentage of none of these fractions was correlated closely with the observed K fixation. However, CEC and % K-saturation of the soil were closely related to the observed K fixation values, indicating that CEC and the amount of exchangeable K in the soil may reflect the amount of subsequent fixation of the soil. Although exchangeable Ca, exchangeable Mg and organic carbon were positively related to K fixation their role in K fixation was not clear. Their relationship to K fixation may be merely a reflection of their relationship with the CEC of the soil.

Among the surface soils studied, all the calcareous soils fixed more K than the non-calcareous soils. The effect of $CaCO_3$ on K fixation may be in part due to higher pH values and in part due to increased Ca ions in the exchange complex. In addition, the calcareous soils also had higher clay, silt and CEC and lower K-saturation than the non-calcareous soils. Addition of $CaCO_3$ to a non-calcareous soil also resulted in increased K fixation.

Potassium fixation behavior was shown to be an equilibrium process, indicating that there is an equilibrium existing between the exchangeable K and fixed K in the soil. At a given level of K application, a maximum amount of fixation is attained within a short period of three days, indicating that K fixation is a very quick process. A study on the effect of previous application of K on the residual capacity to fix K from subsequent sources indicated that a soil which received a large dose of K previously, fixed only a small amount from the subsequent application. Since the fixation of K approached a limiting value with increased K application, it would be possible to say that the fixation is dependent on the existence of a limited number of fixing sites found in the soil minerals. Because of this unique capacity for fixation, any depletion of K from the soil complex would lead to high fixation of K from the subsequent application. A study on the effect of leaching on K fixation indicated that leaching a soil with solutions containing large hydrated cations such as Ca, Mg and Na increased K fixation. Depletion of soil K (i.e. lowering the K-saturation) by these large hydrated cations may be a reason for the increased K fixation. It was evident from the above studies that the % K-saturation of the soil was one of the factors that affected K fixation. Simple linear regression analyses also indicated a significant negative relationship between K fixation and % K-saturation of soils.

The potassium fixation patterns observed in these soils showed increased K fixation and decreased % K fixation with increased K additions. From this behavior, it was evident that a maximum value for fixed K was being approached with increased additions of K. This type of pattern for K fixation resembled the Langmuir type of adsorption isotherm, indicating that K fixation can be considered as a surface phenomena. The K fixation capacity estimated for different soils by using the Langmuir model was shown to be highly variable among the soils studied. The K fixation capacity of a soil is an indication of the total number of K fixing sites in a unit weight of soil.

A growth chamber experiment conducted to study the availability of fixed K to wheat indicated that the fixed K at any level of K addition was not readily available to the crop during a single growing season. Although some nonexchangeable K was available to the crop during the growing season, the amount of added K fixed had little or no effect on the release of nonexchangeable K.

The nonexchangeable K released to an acid extractant showed that soils have varying abilities to supply K from the nonexchangeable sources. From the same experiment it was evident that, though adding K to a K fixing soil increased the so called ‘step-K’ pool, it was not possible to extract all of the nonexchangeable K as step-K by this process. The portion that was not extractable as step-K may not be available to the crops even in the long run. Soils with a high capacity for K fixation may require high rates of K fertilizer to assure an adequate supply of this nutrient for maximum crop production. This is particularly true when K is mixed with the soil, as may occur in the practice of broadcast spreading of fertilizer.

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Appendix A

Table A.1. Cation exchange capacity, exchangeable calcium and percentage K saturation of 22 coarse textured surface soils.

	Soil Series	Soil No.	C.E.C	Exch.Ca[#]	K Saturation
			cmol$_c$ kg^{-1}		%
1.	Elm Creek	RWL7	13.06	9.6	3.83
2.	Almasippi	SC 357	28.30	18.9	0.63
3.	Long Plain	SC 315	20.50	15.4	0.49
4.	St.Claude	SC 297	36.40	10.9	0.55
5.	Lenswood	STA 90	32.80	23.1	0.30
6.	Almasippi	WBN 66	14.20	8.6	2.11
7.	Willowcrest	WBN 41	9.90	6.8	4.04
8.	Long Plain	GY 1	4.60	3.6	4.35
9.	St.Claude	GY 14	20.80	4.9	1.68
10.	Willowcrest	GY 50	13.28	8.9	2.71
11.	Stockton	BRA 1	17.90	13.8	1.12
12.	Pine Ridge	STA 24	2.70	1.4	7.41
13.	Poppleton	STA 33	36.30	20.1	2.20
14.	Silver Creek	SWR 7	8.30	5.0	3.61
15.	Sevick	SWR 53	27.60	20.9	2.17
16.	Gilbert	SWR 57	18.90	18.0	2.17
17.	Craigford	SWR 77	23.30	16.8	1.72
18.	Stockton	TWN-HAL 13	11.40	5.4	1.75
19.	Dobbin	SC 369	10.50	6.3	3.81
20.	Long Plain	PGW 189	22.00	18.6	1.36
21.	Willowcrest	PGW 195	12.80	10.4	3.91
22.	Lauder	TWN SOU 1	9.80	5.7	1.02

[#] For calcareous soils exchangeable Ca values were estimated by subtracting the total exchangeable cations from the soil CEC.

Appendix B-1

(A)

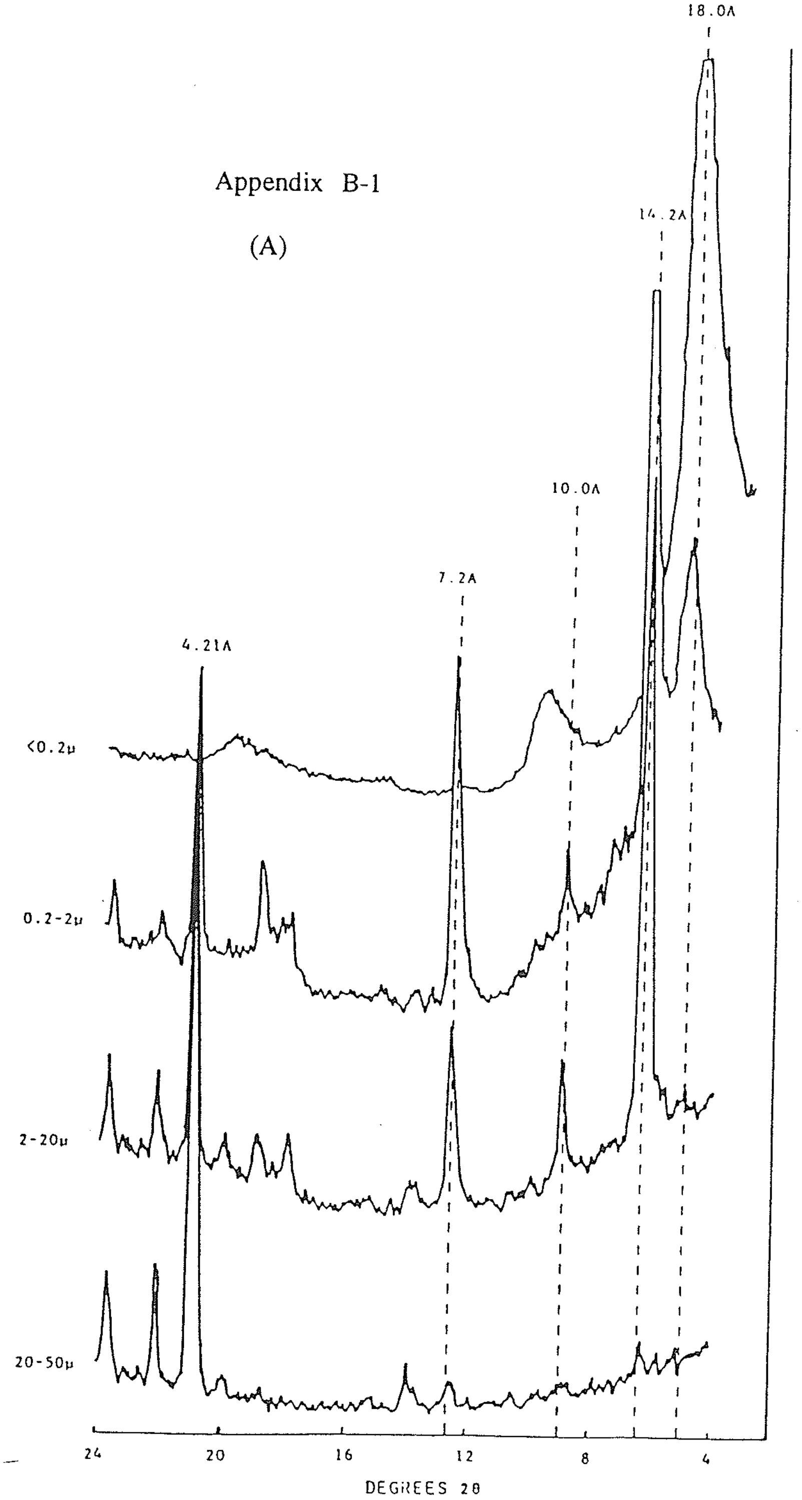

Fig. B-1-A. X-ray diffraction pattern of Mg-saturated and glycerated samples for various sized fractions of Almasippi soil.

Appendix B-1

(B)

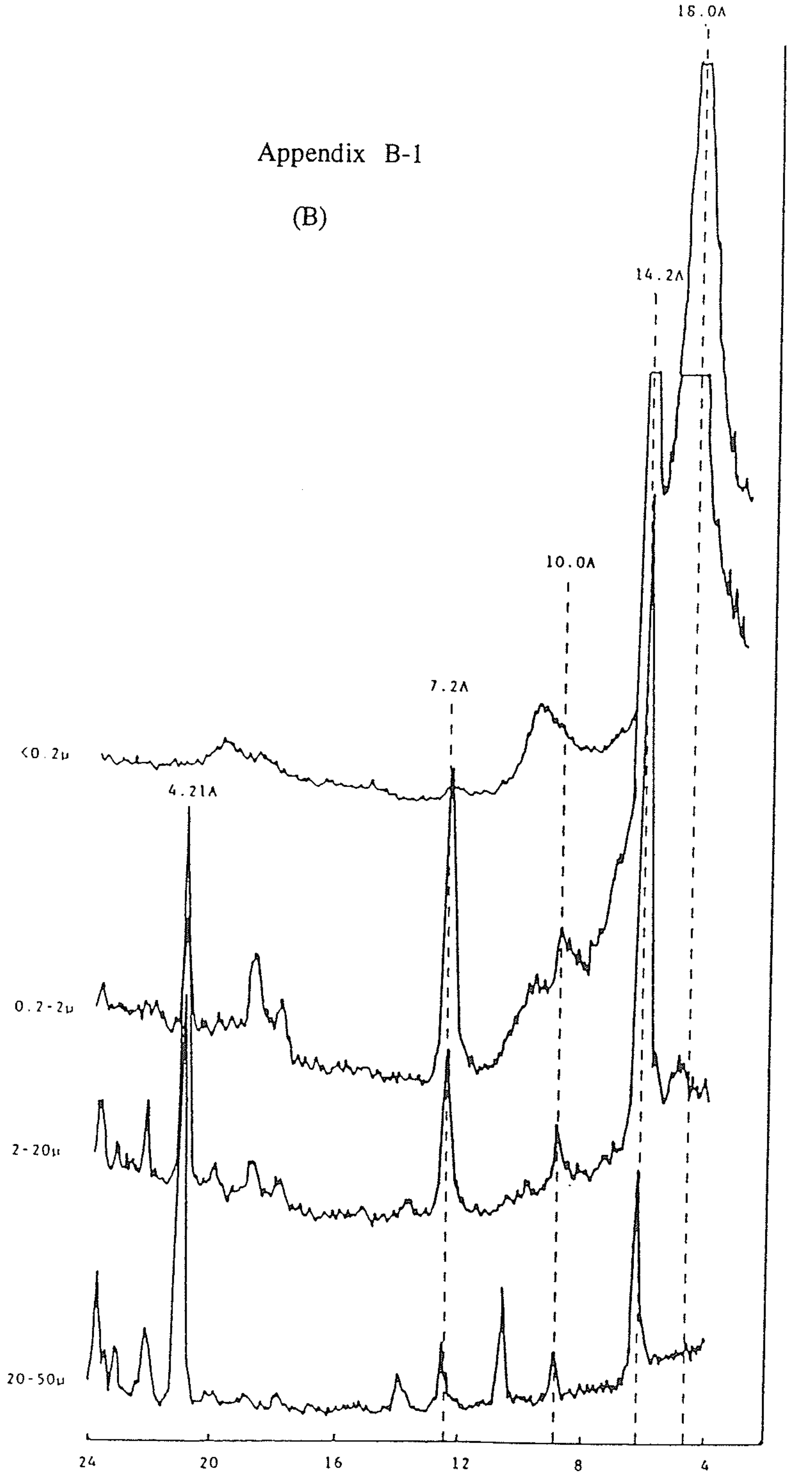

Fig. B-1-B. X-ray diffraction pattern of Mg-saturated and glycerated samples for various sized fractions of Lenswood soil.

Appendix B-1

(C)

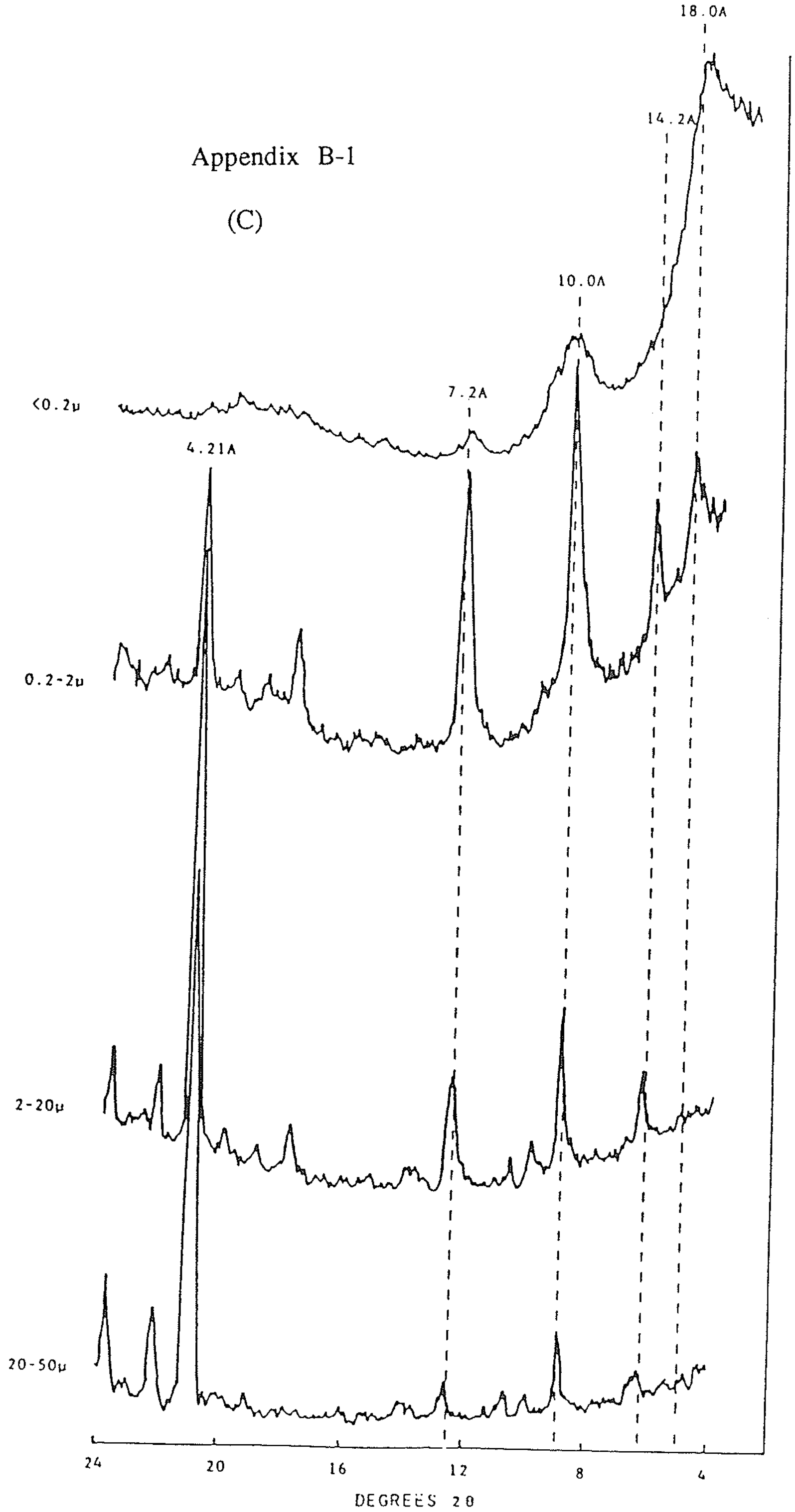

Fig. B-1-C. X-ray diffraction pattern of Mg-saturated and glycerated samples for various sized fractions of Rignold soil.

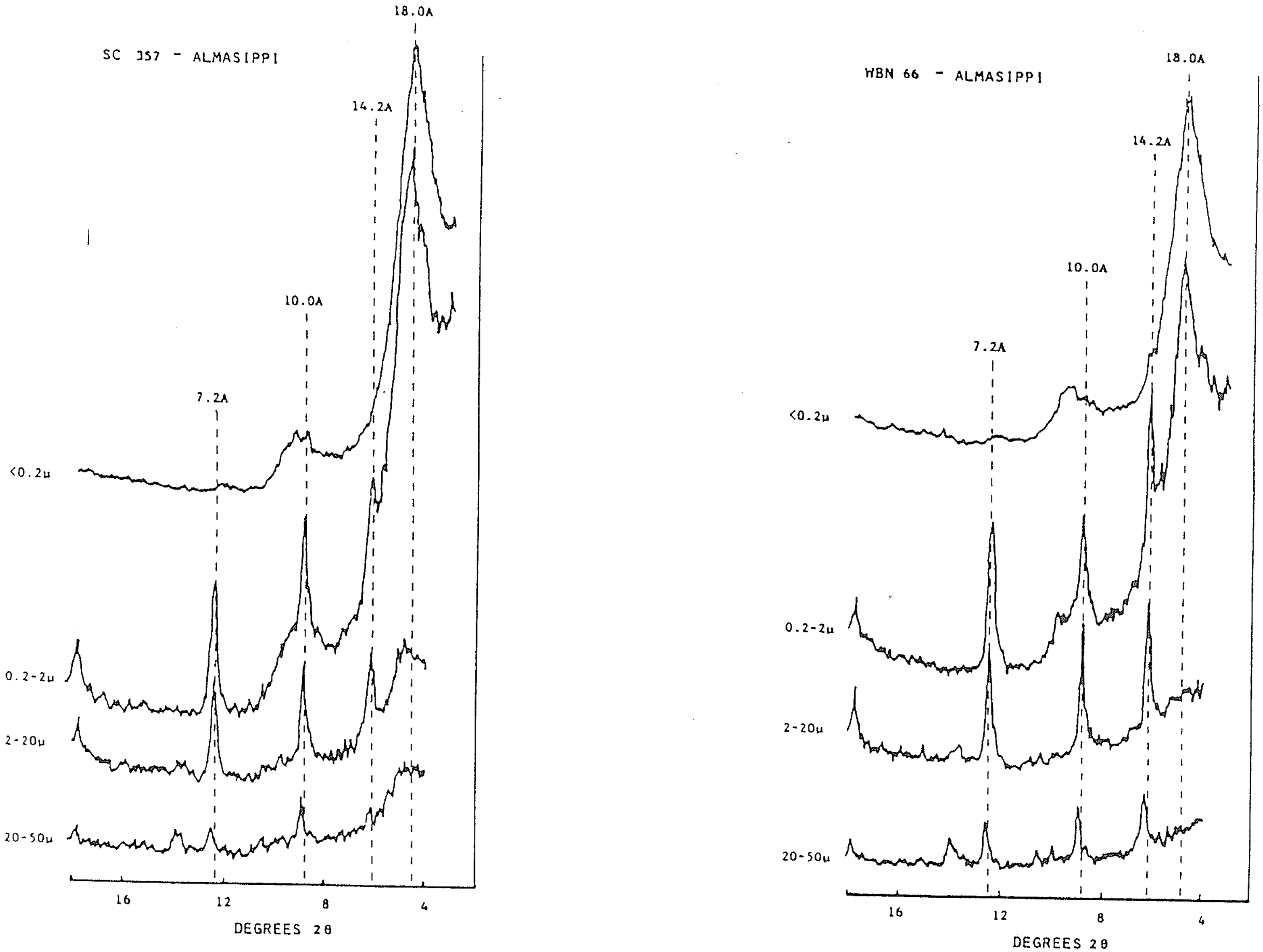

Fig. B-2-A. X-ray diffraction pattern of Mg-saturated and glycerated samples for various sized fractions of Almasippi soils.

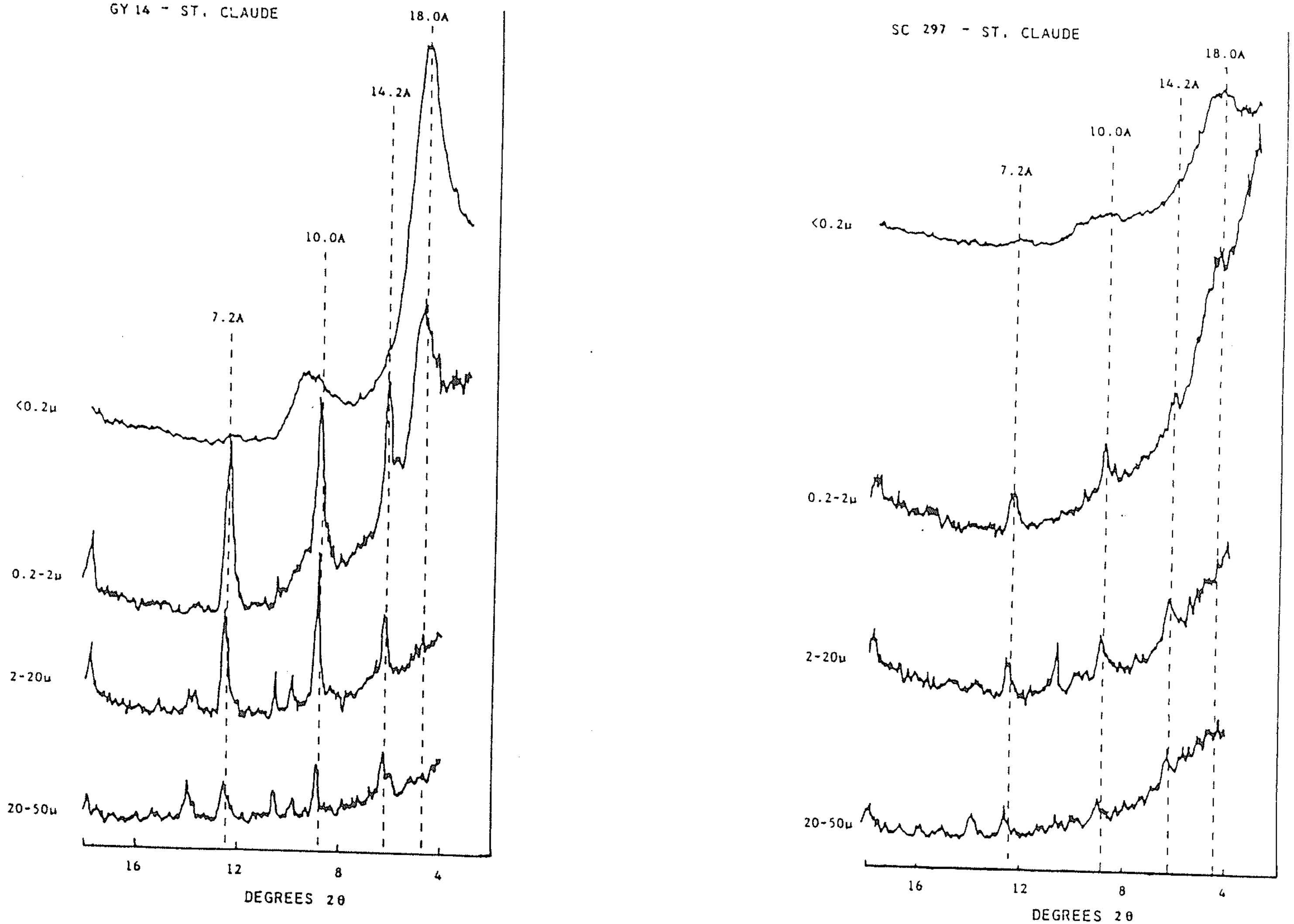

Fig. B-2-B. X-ray diffraction pattern of Mg-saturated and glycerated samples for various sized fractions of St.Claude soils.

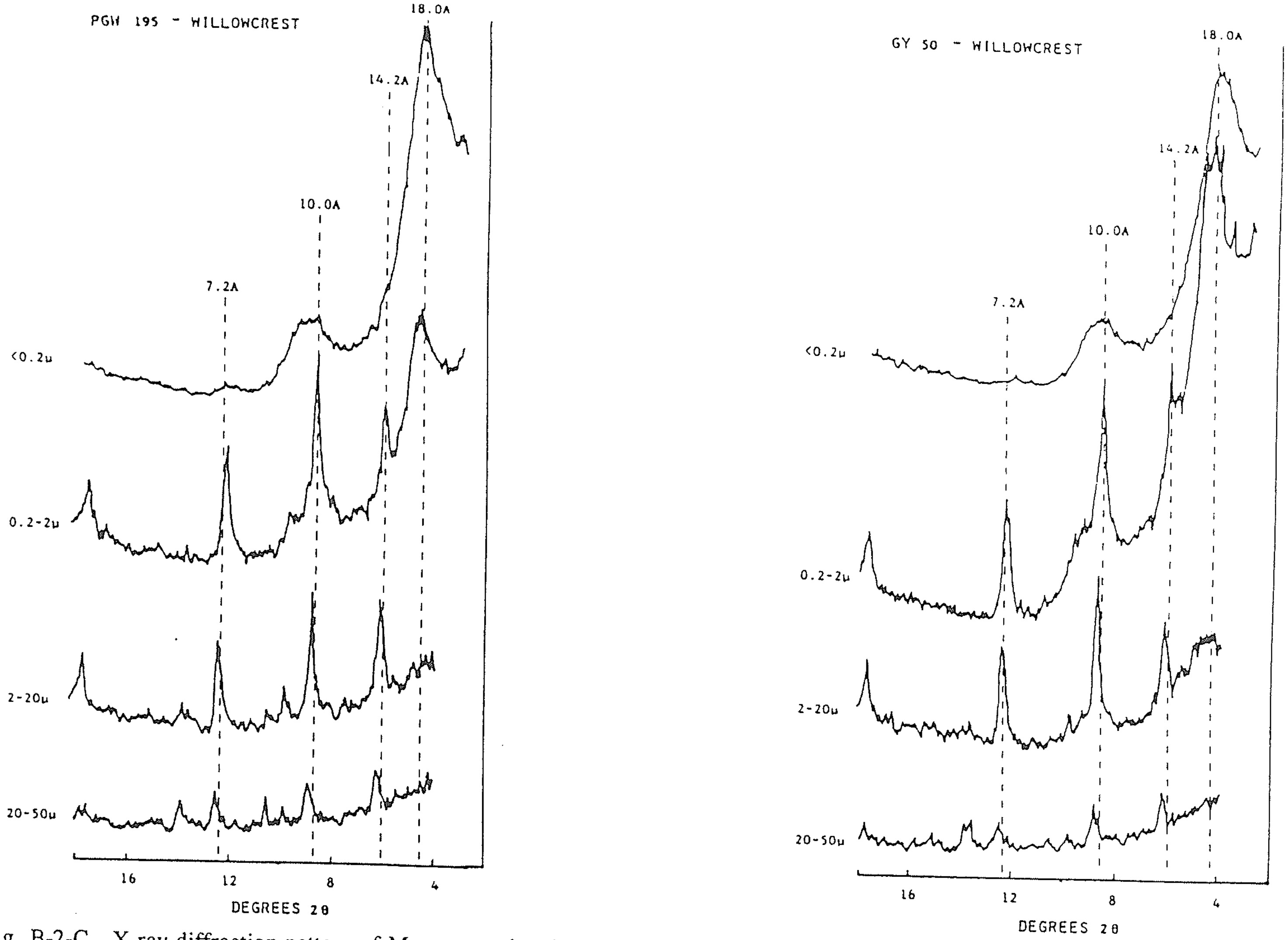

Fig. B-2-C. X-ray diffraction pattern of Mg-saturated and glycerated samples for various sized fractions of Willowcrest soils.

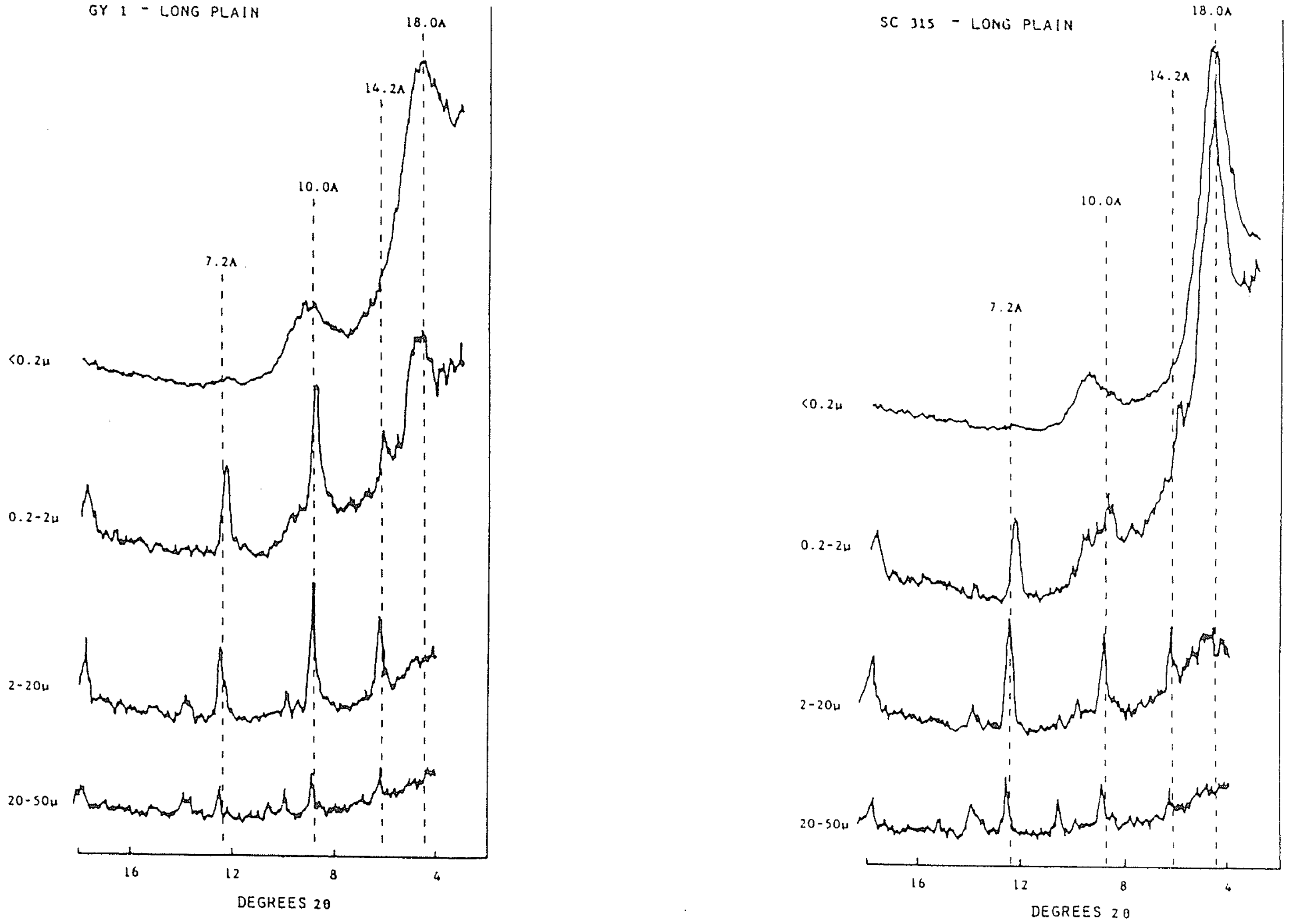

Fig. B-2-D. X-ray diffraction pattern of Mg-saturated and glycerated samples for various sized fractions of Long Plain soils

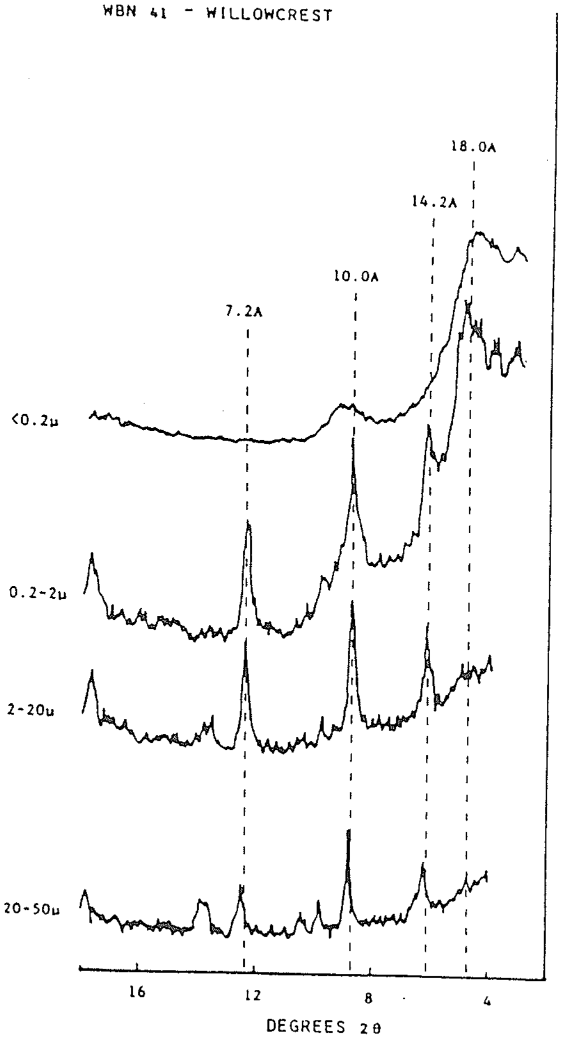

Fig. B-2-E. X-ray diffraction pattern of Mg-saturated and glycerated samples for various sized fractions of Willowcrest soil.

Appendix C.1

Methods of Finding Previously Fixed Potassium

Method I. Iterative (Search) Technique:

The computer programme used for this method:

```
 10 INPUT "SOIL NUMBER:-";Q$
 20 FOR E = 1 TO 6
 30 PRINT E;: INPUT "Input the values of C and y";C(E),Y(E)
 40 NEXT E
 50 LPRINT :LPRINT TAB(18);Q$:LPRINT
 60 LPRINT " Xo";TAB(10)"R Square";TAB(25)"Intercept";TAB(38);"Slope"
 70 LPRINT :FOR Z=1 TO 48:LPRINT "*";:NEXT Z :LPRINT
 80 FOR X = 0 TO 500
 90 FOR G = 1 TO 6
100 I(G) = Y(G) + X
110 J(G) = C(G)/I(G)
120 NEXT G
130 S=0:SUMX=0:SUMY=0:SUMXSQ=0:SUMYSQ=0:SUMXY=0
140 FOR N = 1 TO 6
150 S=S+1
160 SUMX=SUMX + C(N)
170 SUMXSQ=SUMXSQ + C(N)*C(N)
180 SUMY=SUMY + J(N)
200 SUMXY=SUMXY + C(N)*J(N)
210 SUMYSQ=SUMYSQ + J(N)*J(N)
220 NEXT N
230 DENOMX=S*SUMXSQ-SUMX*SUMX
240 DENOMY=S*SUMYSQ-SUMY*SUMY
250 A=(SUMXSQ*SUMY-SUMXY*SUMX)/DENOMX
260 B=(S*SUMXY-SUMX*SUMY)/DENOMX
270 R=(B*B) *DENOMX/DENOMY
280 LPRINT X;:LPRINT USING "########.#####";R,A,B
290 NEXT X
```

Appendix C-2

METHOD II. Multiple Regression Method:

Derivation:

$$\frac{C}{Y} = \frac{1}{S} C + \frac{1}{K S} \tag{6}$$

and $Y = y_1 + X_o$

$$C = \frac{1}{S} Y C + \frac{1}{K S} Y$$

$$= \frac{1}{S} C (y_1 + X_o) + \frac{1}{K S} (y_1 + X_o)$$

$$= \frac{1}{S} C y_1 + \frac{1}{S} C X_o + \frac{1}{K S} y_1 + \frac{X_o}{K S}$$

$$C - \frac{1}{C} C X_o = \frac{1}{S} C y_1 + \frac{1}{K S} y_1 + \frac{X_o}{K S}$$

$$(1 - \frac{1}{S} X_o) C = \frac{1}{S} C y_1 + \frac{1}{K S} y_1 + \frac{X_o}{K S}$$

$$(\frac{S - X_o}{S}) C = \frac{1}{S} C y_1 + \frac{1}{K S} y_1 + \frac{X_o}{K S}$$

Multiplying both sides by S

$$(S - X_o) C = C y_1 + \frac{1}{K} y_1 + \frac{X_o}{K}$$

$$C = (\frac{1}{S - X_o}) C y_1 + \frac{1}{K (S - X_o)} y_1 + \frac{X_o}{K (S - X_o)}$$

$$C = A_0 (C\ y_1) + A_1 (y_1) + A_2 \qquad (7)$$

Where;

$$A_0 = \frac{1}{S - X_o}$$

$$A_1 = \frac{1}{K\ (S - X_o)}$$

$$A_2 = \frac{X_o}{K\ (S - X_o)}$$

By using the equation (7) and doing by multiple regression of C on C y_1 and y_1 coefficients A_0, A_1, and A_2 would be found. With known values of A_0, A_1, and A_2; S, K, and X_o could be found.

$$\frac{A_0}{A_1} = \frac{1}{(S - X_o)} \times \frac{K\ (S - X_o)}{1} = K \qquad (8)$$

$$\frac{A_1}{A_2} = \frac{1}{K\ (S - X_o)} \times \frac{K\ (S - X_o)}{X_o} = \frac{1}{X_o} \qquad (9)$$

$$A_0 = \frac{1}{(S - X_o)}\ ; \quad S = (\frac{1}{A_0} + X_o) \qquad (10)$$

Appendix C-3

Potassium Fixation Isotherm

Example: Method of Calculation I

Soil No.	Added K	C	y1	Xo	Y	C/Y
	mg kg^{-1}	μg mL^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	g mL^{-1}
RWL 7	0	5.90		278	278	0.021223
	50	7.65	15		293	0.026109
	100	9.50	28		306	0.031045
	200	13.60	46		324	0.041975
	400	21.25	93		371	0.057277
	1000	46.35	191		469	0.098827

Regression Output:

Constant	0.013264
Std Err of Y Est	0.003195
R Squared	0.990198
No. of Observations	6
Degrees of Freedom	4
X Coefficient(s)	0.001888
Std Err of Coef.	0.000093

Fixation Max. = 1/Slope = 529.54

Equilibrium Const. = 1/(Intercept*Maximum)

= 0.1424

Appendix C-4

Potassium Fixation Isotherm

Example: Method of Calculation II

Soil No.	C	y1	Cy1	X_o	Y	C/Y
	μg mL^{-1}	mg kg^{-1}		mg kg^{-1}	mg kg^{-1}	g mL^{-1}
RWL-7	5.90	0	0	43.39	43.39	0.135976
	7.65	15	114.75		58.39	0.131015
	9.50	28	266.00		71.39	0.133071
	13.60	46	625.60		89.39	0.152142
	21.25	93	1976.25		136.39	0.155803
	46.35	191	8852.85		234.39	0.197747

Regression Output:

Constant	5.736047	
Std Err of Y Est	0.512572	
R Squared	0.999318	
No. of Observations	6	
Degrees of Freedom	3	
X Coefficient(s)	0.132198	0.001734
Std Err of Coef.	0.012241	0.000251

A_o/A_1	0.013117	K
A_2/A_1	43.38961	X_o
$(1/A_o+X_o)$	620.0638	S

Appendix D

Table D.1. Potassium released to HCl acid extractant from four coarse textured soil treated with two levels of K as KCl (Soil samples from growth chamber expt.)

K added	Extraction No.*											Step K (X)	Const. rate K (Y)
	1	2	3	4	5	6	7	8	9	10	11		
						K extracted							
						mg kg^{-1}							
Long Plain:													
400	482	64	66	66	52	42	52	42	22	16	16	284	16
1000	894	110	102	68	46	40	32	26	28	20	14	390	14
Willowcrest:													
400	482	44	46	64	60	90	90	82	60	40	26	363	26
1000	904	100	134	114	42	46	58	36	30	30	28	418	28
Almasippi:													
400	502	48	102	58	66	78	46	56	34	20	28	267	28
1000	908	118	108	70	68	68	46	42	44	28	24	416	24
Lenswood:													
400	286	50	34	32	40	22	16	22	22	20	22	94	22
1000	668	114	70	46	46	34	34	28	28	24	20	274	20

* Extraction 1 : 0.1 N HCl extract. (Exch. K)
Extraction 2-11: 6.52 N HCl Extract. (Nonexchangeable K)

Total Nonexchangeable K (NEK) = Sum.K + 0.1 M HCl.K - 1 M NH_4OAc.K

Step K = Total Nonexchangeable K - (10 x Const. rate K)