# POTASSIUM RELEASE FROM $B_{ir}$ HORIZONS OF TWO FOREST SOILS

by

WILLIAM WALLACE BOURGEOIS

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Department Forest Resources

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We have carefully read the dissertation entitled Factors Affecting Potassium Release from $B_{ir}$ Horizons of Two Forest Soils submitted by William W. Bourgeois in partial fulfillment of the requirements of the degree of Doctor of Philosophy and recommend its acceptance. In support of this recommendation we present the following joint statement of evaluation to be filed with the dissertation.

Fundamental questions about the long time fertility of forest soils under current intensive forest practices are now being raised. These relate to the ability of a forest soil to supply essential elements under a system in which a portion of the forest crop is removed at periodic intervals by clearcutting. The total amount of elements in the soil, form of elements, available supply, and replacement sources under forest cropping systems must all be examined to understand the processes and supply practical answers.

Mr. Bourgeois has chosen to do his research in this field by examining potassium relationships of two characteristic forest soils found in western Washington. He has further localized his study of the system by selecting a specific horizon in these soils. He has employed methods previously used for soils under intensive agricultural cropping and found these to be suitable. In fact, a major contribution of his dissertation is the demonstration that these are suitable techniques to investigate some of the elemental complexities of forest soils. Chemical and thermodynamic principles which have previously been found to govern release of potassium from an agricultural soil system were also found to apply to these forest soils. The role of organic matter and sesquioxides, which are higher in these forest soils, was found to be significant in potassium release. Potassium release from forest soils of the type studied is governed by the physical, chemical and mineralogical properties of the soil solution. Particle size, minerals present, extent and nature of aggregation due to organic matter and sesquioxides all played a role in potassium release, with particle size and organic matter being more important.

Mr. Bourgeois has presented material which represents the first step in developing a more complete understanding of detailed processes involved in the cycling of an element such as potassium in a forested ecosystem. Conclusions presented are now subject to confirmation under field conditions as a prelude to using the information in developing models of ion movement in soils.

DISSERTATION READING COMMITTEE: Stanley P. Gessel

David W. Wooldridge

Dale W. Cole

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# ABSTRACT

Two forest soils were examined for their potassium release characteristics and the soil and solution factors affecting the release. Potassium was released according to exponential functions that exhibited removal of three soil potassium components (readily exchangeable, "weakly fixed", and "strongly fixed"). Soil organic matter content and particle size distribution were the principal soil factors affecting potassium release while sesquioxide content had only a minor influence. The soil organic matter was mainly in the form of clay-organic complexes that reduced the total soil exchange capacity and altered the strength of potassium adsorption. The quantity and rate of potassium released by the soil materials decreased with increasing particle size. Exchangeable potassium desorption was related to the quantity present while nonexchangeable potassium release was affected by the particle size distribution. Statistically significant predictions of potassium release from the two soils was made based on the particle size distribution and the release functions of each particle size category, provided the organic matter was removed from the soils. The solution factors that significantly affected removal of potassium were the type of cation present and the electrolyte concentration above $10^{-3}$N. Calcium and magnesium were much more effective than the other cations (Na, $NH_4$, Al, $H_3O$). The type of anion present and the solution pH had only minor influences on potassium release.

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# INTRODUCTION

The chemistry of forest soils has been considered to a greater extent since forested areas have become more intensively managed. It has been observed that due to the soil forming processes occurring on these soils there are certain chemical factors that make these soils distinctly different from many of their agricultural counterparts. Although much of the soil chemical information provided from agricultural soils has been used in forested areas, there is a trend to obtain data on forest soils comparing the information of the two soil types.

Potassium has been known as an essential and macro plant nutrient for some time. Because of its importance in plant growth a great deal of information has been gained, principally relative to agricultural soils.

Adsorbed potassium occurs in soils either as an exchangeable or nonexchangeable (fixed) form. The presence of nonexchangeable potassium allows for a slow continuous release of the element into the exchange system. In soils where potassium fixation occurs it has been shown that this release provides a continual supply of potassium for plant uptake. To accurately predict potential and continual supply of potassium for plant absorption, knowledge of the factors affecting the release of the element must be available. A considerable number of studies have dealt with this problem through the use of pure minerals such as micas and vermiculites.

The podzolic forest soils in the Northwest have not been studied intensively relative to potassium release. However, mineral cycling studies at the Allen Thompson Research site by Cole *et al.* (1967) showed that the potassium supply measured by extraction with neutral normal ammonium acetate was insufficient to support the second growth Douglas-fir stand for more than 20 years. This observation coupled with the expected longer term growth of the stand indicated release of nonexchangeable potassium. The major objective of this study was to evaluate potassium release from the selected soils and the factors reported in the literature that affect potassium release from pure minerals and agricultural soils. To fulfill this major objective the following minor objectives were considered:

1. Establish potassium release relationships relative to physical, chemical and mineralogical soil properties.
2. Evaluate the effect of particle size, organic matter and sesquioxides on K release.
3. Evaluate the effect of the type of cation and anion, electrolyte concentration and solution pH on K release.

# LITERATURE REVIEW

Release of cations from the inorganic soil fraction is primarily according to ion exchange reactions. These reactions are governed by physical and chemical components. The physical component includes the nature of the exchanger materials and their associations within the soil. The chemical component is composed of the characteristics of the exchanging solution. It is the various combinations of these two major components that govern ion exchange processes in soils.

In the case of potassium, the presence of a considerable amount of nonexchangeable potassium in certain soil types complicates and puts a greater influence on the physical component affecting ion exchange reactions. The soils where these conditions prevail contain 2:1 phyllosilicates. Consequently the potassium forms present in soils and the release of each form must be considered in explaining soil potassium relations.

## A. Ion Exchange in Soils

A number of ion exchange theories have been proposed (Bolt, 1967) all of which can be divided into five general categories based on different laws and theories:

1. emperical adsorption isotherms
2. those based on the law of mass action
3. those derived kinetically
4. those based on the Donnan equilibrium theory
5. those based on the Gouy theory

All the equations proposed to explain ion exchange based on the law of mass action, Donnan equilibrium or Gouy theory relate to Schofield's ratio law (Schofield, 1947). The equations include the concentration ratio of the adsorbed ions to solution ions, each species taken to the reciprocal of the power of its valence. Schofield's law states that "when cations in solution are in equilibrium with a large number of exchangeable ions, a change in the concentration of the solution will not disturb the equilibrium if the concentration of all monovalent ions are changed in one ratio, those of all divalent ions in the square of the ratio and those of all the trivalent ions in the cube of that ratio". From these exchange theories and laws developed the importance of the type of cation involved in the exchange, the concentration of the electrolyte in the exchanging solution, the exchange capacity of the material and the type of exchanger (Helfferich, 1962; Kelley, 1948, 1952; Mehlich, 1946; Wiklander, 1965).

### 1. Physical Component

Soil exchangers can be grouped into organic and inorganic categories. The nature of the exchanger is important in all ion exchange reactions but probably more so when "fixable" ions such as potassium, ammonium and magnesium are considered (MacLean and Brydon, 1971; Murdock and Rich, 1972). The organic material in soils is generally considered to have very little selectivity for cations in the sense of fixation (Agarwal, 1960) and consists principally of exchange sites origination from dissociation of COOH and OH groups. However there appears to be some evidence for selectivity of ions depending on the nature and abundance of the ions involved (Pratt and Grover, 1964) and the pH of the system (Bartlett and McIntosh, 1969). The inorganic fraction of the soil contains a varied mineralogical composition composed of a number of exchange sites that may or may not have preferential adsorption properties.

(a) Inorganic exchange

The ion exchange capacities of soils are almost entirely due to the silt, clay and organic matter fractions (Wiklander, 1965). However the coarser soil particles are very important in some soils (Graham, 1941) as are the iron and aluminum oxides (Mehlich, 1952). Sources of cation exchange in the inorganic soil fraction are principally due to broken bonds and isomorphous substitution (Grim, 1953; Wiklander, 1965). Broken bonds originate from the loss of a hydrogen from the hydroxyls at the edge of the mineral lattices and are of greatest importance when considering primary and kaolinitic minerals. The energies involved in this type of exchange site bonding are generally in the category of those associated with organic matter. Little if any preferential adsorption is thought to occur with these sites and they are considered as part of the readily exchangeable portion of the exchange complex. Exchange sites produced by isomorphous substitution in either the tetrahedral or octohedral layers of layer silicates make up the greatest proportion of the inorganic exchange complex in most soils. The substitution in the tetrahedral layer is usually aluminum for silicon while magnesium and ferrous iron substitute for aluminum in the octahedral layers. The substitution is governed by the ionic radii and coordination number. Isomorphous substitution in the tetrahedral layer produces a stronger bonding site than that resulting from octahedral layer substitution due to the distance of the charge origin away from the lattice edge. In podzolic soils or any soil that has free or amorphous iron and aluminum oxides a certain amount of soil exchange capacity is due to these materials. Like organic matter no ion "fixation" is associated with sesquioxides and the bonding is generally considered of the same magnitude as broken bonds and organic matter.

The exchange sites produced by isomorphous substitution in the layers adjacent to the interlayer spaces can produce localities for high specificity of particular ions. This condition is commonly associated with 2:1 and 2:2 layer silicates (micas, illites, vermiculites and chlorites). The first three minerals have a high specificity for potassium and ammonium while chlorite prefers magnesium and aluminum in interlayer spaces. The specificity is caused by the configuration of the tetrahedral layers and isomorphous substitution. This high preference for a particular ion by a mineral results in "ion fixation" or the inability of ready exchange with solution ions. Ion fixation can occur to a limited extent in minerals other than those previously mentioned (e.g. montmorillonite) due to imperfections in the crystal lattice producing localized areas exhibiting the properties of micas, chlorites, etc. Interstratified and intergrade minerals may also possess fixation abilities of one or more ions.

In soils where 2:1 minerals that possess fixation properties constitute a major portion of the exchange complex, knowledge of the release properties of both exchangeable and nonexchangeable forms must be obtained. Potassium, being one of the macronutrients required for plant growth, has received a great deal of attention resulting in a voluminous amount of literature on the subject of release into the soil solution both from pure primary and secondary minerals as well as from soil minerals and total soils (Agarwal, 1960; Bray and DeTurk, 1938; Duthion, 1968; Rich, 1968; Thomas and Hipp, 1968).

### (b) Organic exchange

Soil organic matter has long been known to contribute greatly to the exchange complex of soils. Organic colloids can have exchange capacities of 100-200 me/100g (Tisdale and Nelson, 1967) composed of exchange sites with little if any high ion specificity therefore contributing almost entirely to the exchangeable component in soils. The great diversity of constituents in soil organic matter results in variations in rates of ion release but compared to the ion bonding associated with the inorganic soil fraction the energies are lower. Relative to potassium exchange in soils where fixation occurs, the importance of organic matter is principally its effect on the exchange properties of the inorganic minerals. This effect is through clay-organic complexing which can involve as much as 98 percent of the total soil organic matter (Greenland, 1965a).

### (c) Aggregating agents and ion exchange

Aggregation of soil particles results in soil components that have ion exchange properties different from those of individual soil separates. The presence of aggregates makes explanations of processes with particular soil separates difficult, therefore the aggregating agents are usually removed before studies are conducted. To adequately relate experimental data to field conditions, the effects of aggregation on ion exchange and other processes must be known.

In acidic soils such as podzols, the principal aggregating agents are organic matter and sesquioxides. These agents have ion exchange properties of their own, which when added to individual soil separates can alter the exchange properties of the composite. However the principal effects of organic matter and sesquioxides on the ion exchange properties of podzolic B horizons are related to their alteration of the exchange properties of the individual soil particles rather than on the bulk composite. This usually occurs through the adsorption of the material onto the surfaces of the soil particles.

(i) Organic matter

Adsorption of organic molecules onto the surfaces of clays has been reviewed by Greenland (1965b) where he states that the complex formed can be due to a number of bonding mechanisms including ionic, hydrogen, van der Waals forces and other electrostatic bonding such as dipole-dipole and dipole-induced dipole. Organo-clay complex formation can be through either direct bonding or with an intermediary polyvalent cation. Most of the organo-clay complex studies have dealt with montmorillonite (Greenland, 1965a), however complex formation can occur with other minerals. Gorbunov *et al.* (1972) compared a number of inorganic materials and found that the amount of humate adsorbed occurred in the order vermiculite > montmorillonite > chlorite > muscovite > kaolinite. Although some investigators (Kodama and Schnitzer, 1971; Ross, 1971) have indicated interlayer adsorption of organic molecules, generally the complexing is associated with external surfaces (Dudas and Pawluk, 1970; Gorbunov *et al.*, 1972; Greenland, 1965b). The positioning of large organic molecules on the surfaces of clay micelles both physically and chemically block exchange sites on the particles (Greenland, 1965b), thereby altering the ion exchange system through reduction of cation exchange capacity and modification of the bonding energy distribution on the remaining available exchange sites (Bartlett and McIntosh, 1969; DeSilva and Toth, 1964; Gorbunov *et al.*, 1972; Greenland, 1965b; Kown and Ewing, 1969; Ross, 1971; Snyder *et al.*, 1969b).

(ii) Sesquioxides

Sesquioxides are present in podzolic soils as amorphous and crystalline materials, coatings on soil particles and interlayer adsorbed polymers (Carstea *et al.*, 1970a; Jackson, 1963; van Schuylenborgh, 1965). Because of their position and abundance in acid forest soils they have a significant effect on the ion exchange behavior of the soils. Adsorption of polymers or amorphous materials onto clay surfaces changes the ion bonding of adsorbed cations from a relatively strong bond to one of a weaker nature thereby allowing more ready release of adsorbed cations into the soil solution (Arshad *et al.*, 1972; Mehlich, 1952). In addition, sesquioxide coating of soil particles reduces the cation exchange capacity (Carstea *et al.*, 1970b; Singleton and Harward, 1971) which could alter the distribution of different cations on the exchange sites through ion preferences and consequently the extent of release of one ion into the soil solution in a multiple exchangeable ion situation. Although the abundance of crystalline iron and aluminum oxides and hydroxides are probably minimal in the relatively "young" soils of the temperate forests, their effect on ion exchange must be considered. Mehlich (1952) studied the release of calcium from crystalline minerals compared to montmorillonite and found that adsorbed calcium was released in the order hematite > goethite > bauxite > $Al(OH)_3$ > montmorillonite which indicated the similarity with amorphous material removal observed by Arshad *et al.* (1972). The occurrence of hydroxy-aluminum and iron polymers in interlayer positions of 2:1 minerals has been found by a number of investigators (Carstea *et al.*, 1970b; Hsu and Bates, 1964; Scott and Reed, 1962b; Singleton and Harward, 1971). Therefore when considering ion release from interlayer positions the presence or absence of interlayer polymers is of importance. Rich (1968) proposed that the interlayer polymers act as both props and blocks for and against potassium release from fixed positions. The polymers expand the interlayer spaces and allow entrance of exchange cations but their presence can also physically block ion entrance if they occur across the entire interlayer region.

## 2. Chemical Component

The transfer of potassium from the solid soil phase into the soil solution depends not only on the nature of the soil material but also on the characteristics of the solution to which the soil is subjected. The solution criteria that appear to be important in ion release are the nature of the cation and anion present in the solution and the electrolyte concentration.

### (a) Cation effect

"Many experiments have evidenced that there is no single universal order of replacing power of cations" (Wiklander, 1965) as variations occur between and within mineral types. The strength of adsorption or replacing power is generally related to the valence of the cation, ionic size in nonhydrated and hydrated conditions and the polarizability and polarizing power (Wiklander, 1965). Bonding strength increases with ionic valence and decreasing hydrated radius. The larger the ionic charge the greater neutralizing power and the smaller the hydrated ion the closer it can get to the exchange material, hence reduced dissipation of electronic bonding energy by water molecules. From a number of studies general lyotropic series can be constructed for each major clay mineral type but it should be noted that specific soils could differ to some extent from these series of relative replacing power.

| | | |
|---|---|---|
| kaolinitic | $Na<H_3O<Mg=Ca$ | (Wiklander, 1965) |
| montmorillonitic | $Na<H_3O<Mg<Ca<K<Al$ | (Foscolos, 1968; Gilbert and Laudelout, 1965) |
| illitic | $Ca<Mg<H_3O<Al<Na$ | (Barshad, 1954; Bolt *et al.*, 1963; Foscolos, 1968; Keay and Wild, 1961; Merwin and Peech, 1950; Newman, 1969; Wiklander, 1965) |

| | | |
|---|---|---|
| humus | $H_3O$<Na<K<Mg<Ca | (Wiklander, 1965) |
| sulfonic resin | Na<K<Mg<Ca | (Wiklander, 1965) |

From this list it can be seen that ion exchange materials with little or no ion adsorption specificity have relative replacing power of cations that are related to the ionic charge and hydrated ionic size. However, when ion fixation occurs to a significant extent (i.e. illitic minerals) the relationships between these two ionic properties and ion exchange are not as pronounced. As previously outlined there are physical and electrostatic factors that determine the release of fixed ions from 2:1 minerals, especially when the exchange is related exclusively to interlattice adsorption sites. The ammonium ion does not occur in the above series for illites because considerable variations were reported in the literature. The inconsistencies reported could be due either to a pH effect that will be discussed later or to the fact that the ammonium ion behaves similar to the potassium ion. Similarities in ionic size and charge allow the two ions to occur in a very stable configuration in interlayer positions. Ammonium ions can prevent the release of interlayer potassium by blockage through collapse of the lattice (Barshad, 1954). Consequently when the relative replacing power of potassium by ammonium is considered the latter ion could be placed below hydronium and sodium (Merwin and Peech, 1950) or if no collapse occurs the ion could be considered the best for releasing potassium (Barshad, 1954; Murdock and Rich, 1972). Another possibility for inconsistencies in lyotropic series in all types of exchange materials is the formation of monovalent ions from normally occurring polyvalent ions through the neutralization of one or more charges by accompanying anions (e.g. $Al(OH)_2^+$, $CaOH^+$) (Carlson and Overstreet, 1967; Coulter, 1969; Wiklander, 1965).

The percent saturation and the complementary ion present must also be considered when studying ion release (Wiklander, 1965). Percent saturation affects ion exchange through the distribution of ions on the exchange sites. Snyder *et al.* (1969) observed different ion distributions on pH-dependent and permanent exchange sites in clay suspensions. They found that the permanent charge sites preferred calcium to rubidium when there were few pH-dependent sites or when rubidium concentrations were high but at low concentrations rubidium was adsorbed more by permanent charges. Because pH-dependent exchange sites are abundant in podzolic soils due to the presence of sesquioxides and organic matter, the relative amounts of mono- and di-valent cations occupying exchange sites has an important bearing on ion release. In addition to the percent saturation of an ion the nature of the complementary ion can affect ion release (Merwin and Peech, 1950; Wiklander, 1965; Wiklander and Koulter-Andersson, 1963). Where no ion fixation occurs and the different types of adsorbed cations are of similar magnitude on the exchange complex, the ion type that will be exchanged first with the addition of an exchanging ion will be the cation adsorbed with the weakest bonding energy (Tisdale and Nelson, 1967). Inorganic colloids tend to prefer divalent cations, therefore if the exchange complex contains calcium and potassium, the exchange through addition of magnesium would be such as to release more potassium than calcium. However, when the percent saturation of an adsorbed cation becomes very low there appears to be a stronger bonding mechanism present and the complementary ion effect has a lesser influence on ion release.

### (b) Anion effect

Electrical neutrality must always be present in ion exchange systems

(Helfferich, 1962) therefore the anion component of the solution is very important. McColl and Cole (1968) and Bourgeois (1969) found significant relationships between the bicarbonate and cation concentrations of leachates from field lysimeters, indicating the importance of the anionic component in cation exchange. A limited amount of work has been done on the effect of anions on cation adsorption and desorption, however the variations due to anions has been shown (Bohorquez and Lamenca, 1969; Grim, 1953; Murdock and Rich, 1965; Richards, 1954). The reasons for differences in cation exchange with changes in the anionic nature of the solution have not been adequately identified but three possibilities have been proposed: (a) anionic modification of the exchange system, (b) effect of pH changes on the charge density of soil materials, (c) adsorption of salts by soil particles (Sommerfeldt, 1962; Thomas, 1960). Although the exact mechanism was not postulated, Sommerfeldt (1962) found that changes in the adsorptive capacity of soils occurred with the addition of different sodium salts and retention of cations varied with the type of electrolyte ($NaOH>Na_2CO_3>NaCl>Na_2SO_4$) while changes in soil pH had varying effects on cation adsorption. Additions of hydroxide and carbonate forms resulted in increased cation adsorption with increasing pH but the soil reaction had no effect when chloride forms were added. Therefore the change in the soil exchange system was not related solely to pH. McIntire *et al.* (1943) observed no pH-anion relationships in neutral soils but under acidic conditions potassium retention was lower when applied in a sulfate form compared to nitrate and chloride. Essentially no differences were observed between the latter two forms. Thomas (1960) proposed that the anionic influences on cation exchange were due to adsorption of salts by soils. The variations occurred due to differences in anion adsorptive capacity of the soils relative to the type of anion present. Anion adsorption was in the order $Cl=NO_3<SO_4<H_2PO_4$ (Thomas, 1960; Wiklander, 1965).

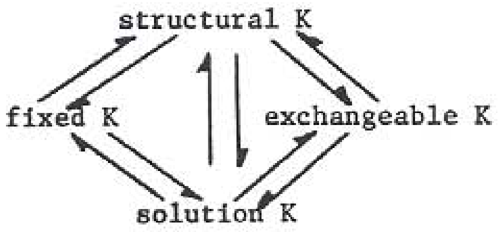
(c) Electrolyte concentration

In addition to the nature of the anions and cations in the exchanging solution, the total electrolyte concentration has been shown to play a significant role in ion exchange (Grim, 1953; Kelley, 1948). Due to the fact that the exchange mechanisms are stoichiometric reactions, generally an increase in electrolyte concentration results in increased ion exchange (Grim, 1953). Earlier ion exchange theories were presented, at which time it was pointed out that the ion concentration in solution was part of many of the theoretical exchange equations. The solution concentration is not only important in release of exchangeable potassium (Clark and Turner, 1965; Foscolos, 1968; Merwin and Peech, 1950) but also nonexchangeable forms (Bolt *et al.*, 1963; Quirk and Chute, 1968; Smith and Scott, 1966). Merwin and Peech (1950) observed that increased electrolyte concentration did result in more potassium being released but a decrease in release occurred after the electrolyte concentration exceeded 0.05N. However, this observation does not agree with those of other investigators (Clark and Turner, 1965; Quirk and Chute, 1968). Another influence that various solution concentrations have on cation desorption is the effect on the relative replacing power of cations (Clark and Turner, 1965; Foscolos, 1968; Grim, 1953). Clark and Turner (1965) found that replacing aluminum varied according to solution concentration.

| | |
|---|---|
| 0.1N | Ca>K>Na |
| 0.5N | K>Ca>Na |
| 3.0N | K>Na>Ca |

## B. Potassium in Soils

Soil potassium occurs in four basic forms all of which are in equilibrium with one another (Tisdale and Nelson, 1967). This can be diagrammatically represented as follows:



### 1. Forms of Potassium

#### (a) Structural K

Micas are generally the most important primary mineral sources of potassium, however, orthoclase and microcline can contribute significantly to plant available potassium, principally through the fine silt and clay fractions. "Well-ordered" micas in soils consist mainly of the dioctahedral muscovite and the trioctahedral biotite (Jackson, 1965), the difference being in the substitution of magnesium and ferrous iron for aluminum in the octahedral positions. These substitutions alter the crystal lattice sufficiently to provide different weathering properties, consequently variations in potassium release (Huang *et al.*, 1968). Many other micas have been identified in soils (e.g. phlogopite, paragonite) along with imperfectly ordered and intermediate weathered forms.

#### (b) Fixed K

"Fixed potassium" is a relative term associated with the nonstructural potassium that is not readily available to plants. This is primarily the interlayer potassium in 2:1 layer silicates and the principle source of native soil potassium in vermiculites, illites and interstratified montmorillonites. A fine line has developed between "fixed" and structural potassium when the micas and some illites are considered. Therefore for future discussion "fixed" potassium will refer to any interlayer forms that are not readily exchangeable with cations such as calcium and magnesium.

Illites, vermiculites and interstratified montmorillonites are the secondary mineral contributors of soil potassium (mainly "fixed"). Grim (1953) proposed the term "illite" to identify minerals that have 10 Å spacing but not well oriented enough to be called muscovite. Therefore illites are minerals that range from well-crystallized muscovite to montmorillonite. Vermiculites can generally be classified as intermediate weathering products between illites and montmorillonites. Although montmorillonites are not generally considered potassium sources, intergrades between these minerals and vermiculites can contain some interlayer regions with strong potassium preferring adsorption sites (Rich, 1964).

### (c) Exchangeable K

Exchangeable potassium is the soil fraction that is readily replaced by other cations through an ion exchange process and released into the soil solution for absorption by plants. Equilibria exist between all forms of potassium in the soil and an inbalance at any position will cause release or uptake of potassium by one or more of the components. Such an inbalance would result from plant absorption, leaching loss or change in any condition that has an effect on equilibria (e.g. soil temperature).

### 2. Interlayer Adsorption of K

The configuration of the area between two silica tetrahedral layers of 2:1 minerals produces hexagonal holes that accommodate ions of the radius of potassium (1.33 Å). The ammonium ion is of similar size and charge therefore has essentially the same reactions with the minerals. Other ions of smaller size (e.g. magnesium) could also fit into these openings between the layers but a stable coordination between the ion and its neighbours, in this case hexagonal close packing, is required. This is a very stable configuration for potassium but not for other ions such as calcium and magnesium. When hexagonal close packing occurs in the 2:1 minerals, a combination of high charge density, ionic radii, hydration energy and coordination number of the elements (Kittrick, 1966). Potassium fixation appears to occur when the electrostatic forces of attraction between the ion and mineral lattice exceed those of hydration (Foscolos, 1968; Kittrick, 1966; Wells and Norrish, 1968), and collapse of the internal space to produce a basal spacing of less than 12 Å (Agarwal, 1960). Agarwal (1960) reported that spacings less than 12 Å prevent the entrance of cations such as calcium, magnesium and sodium resulting in the internal ions becoming nonexchangeable.

### 3. Potassium Release

Potassium that is released from 2:1 clay minerals where fixation occurs originates principally from three localities; edge sites, interlattice near edge sites and interlattice sites away from edges (Addiscott and Talibudeen, 1969; Bolt *et al.*, 1963; Haylock, 1956; Newman, 1969). The edge and near edge sites are associated with the readily exchangeable potassium component of which organic matter, sesquioxides and amorphous soil fractions are members. Ion release from these adsorption sites is rapid but will continue at decreasing rates and vary in extent depending on the amount of exchangeable potassium present, the electrolyte concentration in the external solution and the nature of the exchanging ion and its accompanying anion. Once the readily exchangeable potassium has been removed, release will continue at a much reduced rate from the interlattice positions (MacLean, 1961). The release mechanisms present during this period could be mineral weathering through direct interlayer removal of potassium into the soil solution and/or redistribution of nonexchangeable potassium onto exchange sites and then desorption into the soil solution. Release from the three categories of exchange sites is associated with different bonding strengths, hence free energies of exchange (Cooper *et al.*, 1948; Gast, 1969). Van Schouwenburg and Schuffelen (1963) calculated Gapon exchange constants of 2.2, 102.3 and >2000 for the edge or planer, near edge and interlattice positions respectively. The differential release from the three types of bonded potassium resulted in exponential release curves (Newman, 1969; Quirk and Chute, 1968; Smierzchalska, 1971).

### (a) Exchangeable K release

Initial release of potassium from soil materials comes principally from the readily exchangeable component (Haylock, 1956; Addiscott and Talibudeen, 1969). The rate of ion exchange is extremely rapid (>75% within 3 seconds, Malcolm and Kennedy, 1969) although variations occur between clay mineral types due to penetration between expanded layers (Grim, 1953). Depending upon the electrolyte concentration and the amount of exchangeable potassium present, the exchangeable component of the soil could be readily exhausted. Nonexchangeable potassium provides a sink that can be drawn upon as the soil resources become depleted. This soil component is released slowly but the rate of release depends on the type of mineral containing the potassium (e.g. mica vs vermiculite), the extent of mineral weathering and the particle size within which the potassium occurs.

(b) Nonexchangeable K release

The release of nonexchangeable potassium from soil minerals is based on the exchange of interlayer potassium by ions present in the external solution. But as mentioned earlier the collapse of the mineral upon potassium fixation prevents ready exchange with these interlayer ions. Therefore the release can only occur at the edges of the interlayer space where bonding is not strong enough to maintain total lattice collapse. Rich (1968) proposed a theory on the effect of the wedge zone or the region between readily exchangeable and nonexchangeable sites. Figure 1 illustrates the regions of potassium selectivity, hence ease of exchange by external ions.

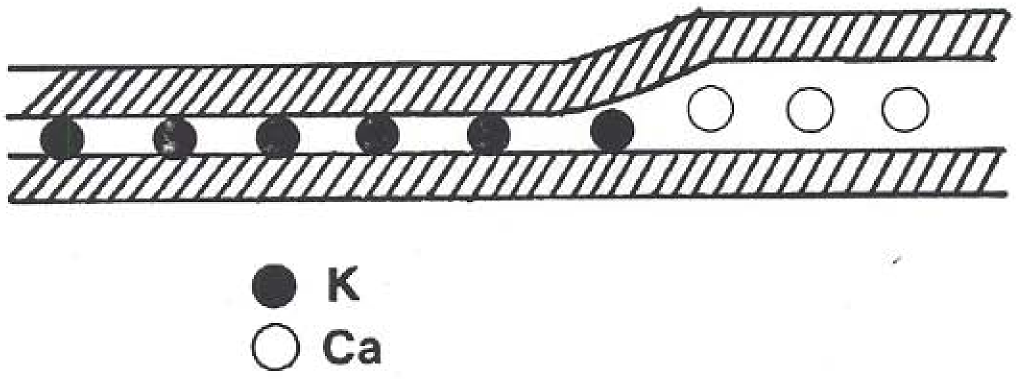


Figure 1. Diagram of a micaceous mineral wedge zone and the types of potassium adsorptive sites.

Release of potassium from the wedge zone to the soil solution is governed by a diffusion process (Keay and Wild, 1961; Mortland and Ellis, 1959; Reed and Scott, 1962). Mortland and Ellis (1959) proposed five steps that are involved in release of fixed potassium:

1. diffusion of the exchanger ion as the salt through the solution film to the particles.
2. diffusion of the exchanger ion through a hydrated interlayer space of the mineral.
3. chemical exchange of the ion for potassium ions.
4. diffusion of displaced potassium ions through the hydrated interlayer space of the mineral.
5. diffusion of the displaced potassium ions as a salt through the solution film away from the particle.

Mortland and Ellis (1959) considered potassium release to be limited by one or more of the diffusion steps and the actual ion exchange step not to be rate limiting. Keay and Wild (1961) suggested the diffusion within the particle was rate limiting. However, the ion exchange portion could be of great importance as the quantity of fixed potassium decreases, since it appears the proportion released into the soil solution is relative to the amount of interlayer potassium (MacLean, 1961; Smith and Scott, 1966). Scott (1968) reports Bassett as suggesting that as the mineral lattice layers are separated the potassium bonding becomes stronger. This could be the reason for reduced release with lower amounts of nonexchangeable potassium.

## 4. Factors Affecting K Release

Structural, fixed and exchangeable soil potassium are released into the soil solution according to physical and chemical properties of the soil and surrounding solution. Structural and fixed potassium are the forms usually associated with micas, feldspars and certain expanding 2:1 layer silicates and are not readily released through ion exchange. Small quantities of these potassium forms are released continually at low rates for long periods of time providing the soil potassium buffering capacity. The rate and extent of release depends on the soil particle size, degree of weathering, type of material involved, and soil solution characteristics.

### (a) Mineral type

Although the release of potassium from feldspars must be recognized, generally the most important mechanism for release is through ion exchange with micas, illites, vermiculites and other clay minerals (Smith *et al.*, 1968). Ion exchange in these minerals can originate at either interlayer edges or on the exterior surfaces of the minerals. Mineralogical characteristics along with the type of cation have pronounced effects on interlayer exchange and to a lesser extent with external surface exchange.

Pure minerals have principally been used to understand the mechanisms of nonexchangeable potassium release in soils. The micas have been used most because of their great importance as sources of potassium. However illites and vermiculites have also been used extensively (Rich, 1968). Although specimen minerals are excellent for examining basic mechanisms, care must be taken when extrapolating the results to soil mineral forms as indicated by qualitative and quantitative differences between specimen and soil vermiculites reported by Rhoades (1967). It has been previously mentioned that the extent and position of isomorphous substitution has an important bearing on the weatherability of 2:1 minerals hence the ease of potassium release from the micas, illites and vermiculites. Vermiculites generally release potassium more readily than the other minerals mentioned because of their lower charge density in the interlayer regions (Wentworth and Rossi, 1972). However, as differences exist between biotite and muscovite, there are variations within the vermiculitic group. Barshad (1954) reports cation exchange capacities of < 120 to > 190 me/100g for vermiculites with increases in strength of potassium bonding with increased interlayer charge. The definition of illites indicates the presence of variations in lattice characteristics hence exchange properties. In general the 2:1 minerals responsible for potassium fixation, release the element in the order vermiculite > biotite > illite > muscovite (Huang *et al.*, 1968; MacLean and Brydon, 1971; Reed and Scott, 1962; Scott, 1968; Scott and Reed, 1962(a), (b); Wentworth and Rossi, 1972).

(b) Degree of weathering

The diversity of soil potassium sources has produced varying degrees of elemental release into the soil exchange system based on the weatherability of the particular minerals. Jackson (1965) presented weathering sequences for various soil minerals among which the micas were the most readily weathered of the potassium bearing minerals and biotite the least stable of the micas. This is probably due to the octahedral substitution of iron and magnesium inducing a weaker bonding between the interlayer potassium and the silica tetrahedral layers, allowing ready cleavage between the lattice elements. The cleavage allows for interlayer entrance of other cations and exchange for the potassium, thereby releasing the element into the soil exchange system. The transformations of primary to secondary minerals in the weathering sequence occurs after muscovite in the order illite to chlorite (aluminum form) to vermiculite. Montmorillonite appears after vermiculite but the potassium bearing portions of montmorillonite would probably be positioned between these two general groups due to their intergrade configuration. The weathering sequence represents the relative ease of potassium release from the structural and "fixed" forms of the minerals. However it should be recognized that at any one time all minerals are contributing to the release of nonexchangeable potassium to the exchange system. The weathering sequence reported by Jackson (1965) has been acceptable for generalized statements (MacLean and Brydon, 1963), but variations may occur in specific studies (Leaf, 1959; Rich, 1968). Leaf (1959) observed that potassium release using N $HNO_3$ was in the order biotite > vermiculite > muscovite > microcline and Rich (1968) also placed the micas before orthoclase and microcline.

### (c) Particle size

Release of nonexchangeable potassium from soils is affected by the size of particles that are involved. Although the majority of the potassium released comes from the fine silt and clay fractions, some could originate from the coarser materials depending on the soil (MacLean and Brydon, 1963; Merwin and Peech, 1950; Rich, 1968). As the particle size increases the "effective" ion exchange surface decreases per unit weight of material, hence the exposure for elemental release decreases, all other factors being equal. However, electrostatic forces exert a great influence on release of potassium and complicate the effect of particle size. This complication makes it necessary to express the effect of size fractions on both a rate of release and amount or percent of total potassium release. The greater surface exposure and weathered edges of the clay size material results in a rapid initial release of potassium (Barshad, 1954; Doll *et al.*, 1965; Mortland and Lawton, 1961; Rich, 1968; Scott, 1968; Smith *et al.*, 1968) from the wedge zone and surface adsorbed sites, while the remaining ions are held more strongly in interlayer positions (Scott, 1968). Based on the theory of diffusion as the rate limiting step, it follows that as the particles increase in size greater distances develop between the wedge zone and the external solution through which the potassium ions must travel, thereby reducing the rate of potassium release (Reed and Scott, 1962). The rate of nonexchangeable potassium release decreases along with particle size (Doll *et al.*, 1965; MacLean and Brydon, 1963; Mortland and Lawton, 1961; Reed and Scott, 1962; Scott, 1968; Scott and Reed, 1962a; Smith *et al.*, 1968; Smith *et al.*, 1971). But the total potassium released over an extended period of time has shown to increase as the particle size increases (Smith *et al.*, 1968). However, Doll *et al.* (1965) observed that the mica fraction <0.08μ released less potassium than the 0.2-0.08μ fraction. This could be caused by the electrostatic forces involved but more work is required before the cause of the decreased release in the fine clay fraction is understood (Rich, 1968). Because of the greater release of total potassium from the silt and coarse clay materials over a long period of time, these fractions could be considered to have the greatest influence on the potassium buffering capacity of soils.

Mortland (1961) suggested that simultaneous release and fixation of potassium by one species occurs in soils due to differences in bonding between size fractions. Scott and Reed (1962a) found mixtures of biotite size fractions had potassium release characteristics intermediate between those of the extreme sized material while Smith *et al.* (1971) obtained similar curves but lower experimental values of size fraction mixtures than those calculated based on individual fraction release curves. This discrepancy between separated and mixed materials could be due to simultaneous release and fixation (Mortland, 1961) where individual size fractions behave differently when mixed compared to when separated.

(d) Solution chemistry

The solution characteristics that affect potassium release are those that influence any ion exchange reaction. The soil solution effects on potassium release from soil materials are associated mainly with exchangeable potassium. These factors are the type of cation and anion, electrolyte concentration and solution pH. The first three factors are involved in the theoretical ion exchange equations and have been discussed earlier, while the solution pH acts as a modifying agent for the other factors. The effects these factors have on potassium release depend on whether exchangeable or nonexchangeable forms are involved.

Contradictory results have been reported concerning the effect of solution pH on release of potassium from soils and clay minerals. Bolt *et al.* (1963), Coulter (1969), Keay and Wild (1961), Scott and Reed (1962b) and Smith and Scott (1966) observed no pH effect on potassium release while Huang *et al.* (1968), Krause (1965), Murdock and Rich (1965), Newman (1969), Rich (1964) and Wells and Norrish (1968) found that potassium release increased with decreasing pH. The explanation for the variation in results is unclear at this time, therefore the pH effect should be considered with each particular soil or mineral before generalizations are used.

Where a pH effect has been reported two theories have developed explaining the mechanism of potassium release from the interlayer positions. The theory that has received the most support involves the action of the hydronium ion (Haagsma and Miller, 1963; Murdock and Rich, 1965; Rich, 1964; Tucker, 1964a) while the other considers direct dissolution of the minerals (Wells and Norrish, 1968). Tucker (1964b) proposed that both mechanisms occur depending on the pH. Above pH 11 dissolution of the mineral predominates but a greater acidity ion exchange between the hydronium ion and interlayer potassium occurs. The hydronium theory is based on the similar size of the potassium and hydronium ions, therefore the latter ion can enter into the interlayer positions and exchange with the potassium. The cation exchange reaction results in a non-ionic bonding situation between the hydronium ion and the mineral lattice, which is much weaker than that occurring with the potassium ion, hence lattice collapse does not occur. This allows access of other cations such as calcium and magnesium to the interlayer positions and exchange with the potassium made accessible by interlayer expansion. Rich (1964) suggested that rather than the hydronium ion entering and participating in ion exchange with potassium, a proton transfer could occur through water films to the interlayer potassium resulting in release of the ion. The protons were thought to be produced from hydrolysis of aluminum polymers or aluminum ion itself.

The pH effect can alter the relative potassium releasing power of other cations. Murdock and Rich (1965), Rich (1964) and Rich and Black (1964) found little change in the amount of potassium released by ammonium solutions with changing pH conditions and that these solutions were able to extract more potassium than magnesium solutions. However, when the pH of magnesium solutions was lowered, comparable quantities of interlayer potassium were removed. As previously mentioned the electronic and physical configuration of interlayer potassium prevents magnesium ions from releasing this potassium. Therefore, it was postulated that a combination of hydronium and magnesium ions could release as much potassium as ammonium alone. This points out the importance of pH when considering fixed potassium and the relative releasing power of other cations. The presence of interlayer aluminum polymers blocking release of potassium must also be noted when considering pH effects.

Reduction in pH below 5 can cause release of interlayer polymers (Jackson, 1963), thereby allowing entry of cations for exchange with potassium at the wedge zone (Rich, 1964).

# METHODS AND MATERIALS

The forest soils throughout western Washington are mainly of a podzolic nature which may or may not deploy A horizons, but always possess one or more sesquioxide accumulated horizons. The general occurrence of Bir horizons in forest soils of the area and the common abundance of roots in these horizons indicated that samples from these soil layers would be representative of much of the forested area. Two soils were selected, the Alderwood series (Typic Haplorthod) located at the A.E. Thompson research site on the Cedar River watershed (Cole and Gessel, 1968) and the Wilkeson series (Andic Glossoboric Hapludalf) located southeast of the town of Wilkeson near Mount Rainier (Anderson *et al.*, 1955). From these pedons the Bir horizons containing the majority of the plant roots (20-45 cm depth for Alderwood and 18-55 cm depth for Wilkeson) were sampled. The Alderwood soil was developed from ablation till while the Wilkeson soil originated from andesitic material. Both soils now support second growth Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco) stands with lesser vegetation consisting mainly of mosses and sword fern (*Polysticum munitum*).

## 1. Soil Characterization

Physical characterization of the two soils consisted of particle size distribution analysis by the hydrometer method (Day, 1965) after both organic matter (Luvkulich and Wiens, 1970) and sesquioxides (McKeague and Day, 1966) were removed. However to indicate the location of aggregation among the particle size fractions and the cementing agents involved in each case, the particle size distribution analysis was also performed on samples with only organic matter removed and with no treatment other than dispersion in sodium hexametaphosphate (calgon).

Chemical characterization included the pH of the soils in a 1:2 ratio of soil:0.01M $CaCl_2$ and cation exchange capacity by both normal neutral ammonium acetate (Black, 1965) and normal calcium chloride (Alexiades and Jackson, 1965). Exchangeable potassium was determined in the ammonium acetate extract using an atomic absorption spectrophotometer. Total soil potassium was obtained through acid digestion with HF, $HClO_4$, $HNO_3$ and HCl (Black, 1965) and determined on an atomic absorption spectrophotometer. Dithionite-citrate-bicarbonate extractable iron and aluminum was done according to McKeague and Day (1966) with the iron determined on an atomic absorption spectrophotometer and the aluminum by the Eriochrome cyinine RA method (Jones and Thurman, 1957).

The mineralogy of the sand, silt and clay fractions of each soil was established for soil characterization and later interpretation of the potassium release phenomena. X-ray diffraction employing Cu K $\alpha$ radiation with Ni filtration was performed following the removal of organic matter (Lavkulich and Wiens, 1970) and sesquioxides (McKeague and Day, 1966) and separation of the particle size fractions (Kittrick and Hope, 1963). The clay and fine silt fractions were homoionically saturated with magnesium and potassium before x-ray analysis.

## 2. Extent of Aggregation

The extent of aggregation by organic matter and sesquioxides and their effect on physical and mineralogical properties were evaluated in the two soils. Particle size distribution was determined on the soils using the hydrometer method (Day, 1965) following various treatments: (a) calgon dispersion, (b) removal of organic matter + calgon dispersion, (c) removal of organic matter and sesquioxides + calgon dispersion. Organic matter was removed using sodium hypochlorite (Lavkulich and Wiens, 1970) and sesquioxides using sodium dithionite-citrate-bicarbonate extration (McKeague and Day, 1966). The individual and combined influence of organic matter and sesquioxides on aggregation of the particles of the two soils were evaluated.

### 3. Particle Size Separation and Characterization

To evaluate the affects of each particle size fraction on potassium release from the total soil, a size separation procedure was required. Although dispersion with chemical reagents introduces an artificial factor, the study was designed to evaluate the factors affecting potassium release from the particle size fractions as separated by calgon dispersion. Extrapolation of the information obtained in this study to field conditions would require field experiments that were not considered as part of this investigation. No attempt was made to remove organic matter although the increase in pH due to the dispersing solution did cause some solubilization of organic material.

Separation of the particle size fractions into sand (>50μ), silt (2-50μ) and clay (>2μ) was done by sedimentation. The soils were suspended in large cylinders using sodium hexametaphosphate solution (Day, 1965) and thorough mixing with a plunger. Sedimentation was allowed until only the clay fraction remained in suspension at which time this portion was siphoned off and flocculated using N $CaCl_2$. More water was then added to the cylinder and the suspension mixed again. No further additions of dispersing solution were made unless the pH of the suspension dropped below pH8. The mixing and sedimentation procedure was continued until all the clay size material was removed. The remaining sand and silt fractions were separated by wet sieving through a 325 mm sieve. All the size fractions were dried using 95 percent ethanol, acetone and benzene (Jackson, 1969). Following the drying procedure the sand fraction was further dry sieved to remove additional fine material. It was recognized that these size fractions separated were not the same as the conventional material designations since the silt fraction contained some "clay balls" and the sand fraction some "silt and clay balls" along with adhering clay particles. However it does provide particles that represent the "active" fractions in the soil. Unless otherwise specified the sand, silt and clay fractions further referred to will represent the fractions separated in the above manner and the total soil will represent the whole soil with no separations.

Chemical and mineralogical characterization of the particle size fractions was necessary for evaluation of the exchange phenomena. The exchangeable potassium present after saturation was determined by exchange with N $CaCl_2$. This was performed on the untreated samples (no organic matter or sesquioxide removal) along with those having organic matter only and organic matter plus sesquioxides removed. The high potassium concentrations in the extracts allowed for the use of a Corning monovalent specific ion electrode for the determination of the potassium contents. The untreated potassium saturated samples were also evaluated for exchangeable potassium using neutral normal ammonium acetate as the exchanging solution. This extract was analyzed for potassium using the atomic absorption spectrophotometer. Total potassium content of all the saturated samples was found after acid digestion (Black, 1965).

X-ray analysis of the particle size fractions separated from both soils used for the equilibration studies was determined to provide a qualitative mineralogical description of the samples. Many procedures have been proposed for quantitative mineralogical evaluation of soils with none being universally accepted (Gibbs, 1967; Alexiades and Jackson, 1965). As reported later vermiculite and vermiculite-like minerals comprise a large component of the secondary mineral fraction of the Alderwood and Wilkeson soils. The relationships between vermiculite and other expanding lattice minerals of this type are well known relative to potassium fixation, hence potassium release. Therefore it was advantageous to obtain some quantitative measure of these minerals in the size fractions and total soils. An indication of the quantity of vermiculite plus vermiculite-like materials in the size fractions was obtained using the procedure of Alexiades and Jackson (1965). Based on the percentages of each size fraction in the total soil as given by the particle size distribution with no removal treatment, a quantitative estimation of the vermiculitic material in the total soils was calculated.

### 4. K Release - Equilibrating Procedure

Obviously the distribution of cations on the exchange complex of the particle size fractions was drastically altered during the separation procedure. A standard homoionically saturated exchange complex was obtained by subjecting the samples to six equilibration periods with N KCl. This was done in a 1:5, soil:KCl suspension shaken 20 minutes, centrifuged and the supernatant decanted. The saturation procedure consisted of three equilibration periods one day with the third time including an overnight sitting in N KCl followed by the additional three periods of equilibration. Following potassium saturation the soils were washed twice with each of distilled water, 95 percent ethyl alcohol, acetone and benzene in that order. This allowed for the removal of excess salt and the drying of the samples (Jackson, 1969).

Loss of water from soils has been reported to alter the distribution of potassium forms (Thomas and Hipp, 1968) by increasing the quantity of exchangeable potassium. However, Ahmad and Davis (1971) showed that either fixation or release can occur upon dehydration depending on the soil type. Soil drying by organic solvents causes fixation or release depending on the solvent (Ahmad and Davis, 1971; Bates and Scott, 1964; Dennis and Ellis, 1962). Bates and Scott (1964) observed very little change in the exchangeable potassium content after treatments with acetone and benzene and Dennis and Ellis (1962) found the same result with 95% ethanol.

Potassium release from the total soils and their fractions was approached through an "intensive leaching process". Two grams of soil were placed into a 15 ml plastic centrifuge tube with four millilitres of exchanging solution (e.g. 0.02 N $CaCl_2$). It was found that equilibration between the soil and solution was essentially complete after 20 minutes of shaking in an automatic shaker (Table 1).

Table 1. Potassium released from Alderwood soil (unsaturated) after various equilibration times.

| Time of equilibration | K released (me/100g) |
|---|---|
| 20 minutes | 0.008 |
| 30 minutes | 0.009 |
| 45 minutes | 0.010 |
| 60 minutes | 0.009 |

Following the equilibration period the suspension was centrifuged and the potassium content of the supernatant solution determined using a Corning monovalent specific ion electrode except when the exchanging solution contained a monovalent cation, in which case an atomic absorption spectrophotometer was used. The soil was then washed twice with 95 percent ethanol before the next aliquot of exchanging solution was added for the second

20 minute equilibration period. This procedure was continued until 10 equilibration periods were completed. At this point the intensive leaching was stopped since either very little potassium was being removed or the quantity being extracted was relatively constant.

### 5. Evaluation of Factors Affecting K Release

The factors considered in potassium release from the Alderwood and Wilkeson soils were divided into soil and solution components. The soil component consisted of particle size, organic matter and sesquioxides while the solution category included the effect of cation and anion type, electrolyte concentration, and solution pH.

#### (a) Soil factors

#### (i) Particle size

The sand, silt and clay fractions' effects on potassium release in the total soil were analyzed by obtaining the desorption curves for each component individually using 0.02 N $CaCl_2$ as the exchanging solution. This concentration was used to obtain a rate of potassium release that would show the required relationships within a reasonable number of equilibrations. Calcium was selected as the cation because of its low ability to become involved in adsorptive relationships other than the relatively simple forms. Having known the potassium release curves for each size fraction and the proportion of the total soil that each fraction represents, values were calculated to show the relationships to the total soil.

#### (ii) Organic matter and sesquioxides

Organic matter and sesquioxides are known to act as cementing agents and also modify the exchange complex both in the number of sites available for adsorption and the nature of the sites (Greenland, 1965b; Jackson, 1963). To evaluate the effects of these two soil components it was necessary to observe potassium release from the particle size fractions and total soils when one or both of the cementing agents were removed. Organic matter was removed using sodium hypochlorite (Lavkulich and Wiens, 1970) from all fractions. To evaluate the effects of sesquioxides on potassium exchange the removal of both organic matter and sesquioxides was necessary on another set of samples. The sesquioxide removal was done using sodium dithionite-citrate-bicarbonate (McKeague and Day, 1966). After the treatments the samples were potassium saturated and dried using the above procedure. Release curves were obtained for each size fraction of the minus organic matter and minus organic matter plus sesquioxides. Again the exchanging solution was 0.02N $CaCl_2$. The relationships between the particle size fraction desorptive curves and the total soils were compared both within and between sample treatments.

### (b) Solution characteristics

The lyotropic series is commonly used to arrange cations in order of their strength of adsorption. The relative cation positioning changes with the type of clay mineral considered. The effect of the type of cation on release of potassium from the potassium saturated particle size fractions and total soils was done using chloride as the associated anion. Calcium, magnesium, sodium, ammonium, aluminum and hydrogen were considered on the untreated total soils at a concentration of 0.02N. The effects of calcium, magnesium, sodium and hydrogen on potassium release from the particle size fractions were also studied.

Included in the solution group of factors under study relative to potassium desorption was the effect of electrolyte concentration. Again calcium chloride was used as the exchanging compound because of its relatively simple nature in ion exchange. The importance of electrolyte concentration is related to the equilibrium situation that occurs in ion exchange reactions (Bolt, 1967), therefore the amount of potassium released should be dependent on the concentration of the exchanging cation in the solution. Calcium chloride concentrations ranging from $5 \times 10^{-5}$N to $2 \times 10^{-2}$N were used to evaluate the effect of electrolyte concentration on potassium release from the untreated potassium saturated particle size fractions and total soils. These trials were not extended to the treated samples as the important relationships were found with the standard (untreated) samples. The lower concentration values were used as they represent calcium concentrations commonly found in lysimeter waters from acidic forest soils (Bourgeois and Lavkulich, 1972; Cole, unpublished data). It is recognized that much of the electrolyte range of concentration was beyond what would normally occur in the field but the trial was designed to provide basic ion exchange information.

The effects of different anions on potassium release were considered using the standard potassium saturated samples only. The compounds used were sodium forms of chloride, sulfate and bicarbonate at a concentration of 0.02N. These anionic forms were used because they are the primary anions in the natural soil solution of the soils used and provided a limited amount of complications due to fixation, etc.

The relationships between equilibrating solution pH and potassium desorption from the Alderwood and Wilkeson total soils and their particle size fractions were determined using HCl solutions. In addition to the pH 1.9 and pH 4.0 HCl solutions, $CaCl_2$, $AlCl_3$ and NaCl solutions of pH 5.6, 4.0 and 5.5 respectively were used to give additional information. The effect of cation type and electrolyte concentration were evaluated when the pH considerations were made.

# RESULTS AND DISCUSSION

## 1. Soil Characterization

### (a) Chemical properties

The selected chemical soil properties presented in Table 2 indicate the similarity of the Alderwood and Wilkeson soils. The cation exchange capacities were 19.99 and 27.49 me/100g for the Alderwood and Wilkeson soils respectively, the soil pH was 4.9 in both cases and the total and exchangeable potassium contents were comparable. Based on the particle size fractions separated by sodium hexametaphosphate dispersion, the Wilkeson silt fraction had 8.15 me/100g more cation exchange capacity than the Alderwood silt fraction while the sand and clay components of the two soils were similar. The total Wilkeson soil contained 3.05 percent sesquioxides (dithionite extractable Fe + Al) compared to 2.08 percent in the Alderwood soil. The difference was principally due to the 1.28 percent greater $R_2O_3$ (sesquioxide) content in the Wilkeson silt fraction.

### (b) Mineralogical properties

Mineralogical composition of the particle size fractions obtained from simple calgon dispersion and dispersion plus removal of cementing agents of both soils are presented in Table 3. Quartz and feldspars were in dominant amounts in all the particle size separations. Amphiboles was found in some fractions of both soils and mica was detected in trace amounts in only the Alderwood fine silt material. Chlorite, vermiculite and chlorite-vermiculite intergrades constituted the secondary mineral component of the two soils. Chlorite and vermiculite were dominant in the fine silt and clay fractions while the chlorite-vermiculite intergrades were restricted to only the clay

Table 2. Selected chemical and physical properties of the Alderwood and Wilkeson soils and their particle size fractions.

| Soil | Fraction | pH (0.01MCaCl$_2$) | C.E.C. (me/100g) | | Exch. K (me/100g) | Total K (%) | Dithionite Extracted R$_2$O$_3$ (%) | Particle Size Distribution† | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | NH$_4$OAc | CaCl$_2$* | | | | sand (%) | silt (%) | clay (%) |
| Alderwood | sand | | 18.42 | | | 0.41 | 0.80 | | | |
| | silt | | 23.55 | | | 0.34 | 2.18 | | | |
| | clay | | 145.05 | | | 0.10 | 5.73 | | | |
| | total soil | 4.86 | 19.99 | 16.50 | 0.09 | 0.39 | 2.08 | 52.2 | 45.6 | 2.2 |
| Wilkeson | sand | | 17.90 | | | 0.31 | 0.96 | | | |
| | silt | | 31.70 | | | 0.48 | 3.46 | | | |
| | clay | | 148.78 | | | 0.11 | 6.40 | | | |
| | total soil | 4.92 | 27.49 | 31.63 | 0.11 | 0.36 | 3.05 | 35.0 | 59.5 | 5.5 |

* C.E.C. determined after Alexiades and Jackson (1965) - non pH-dependent C.E.C.

† Particle size distribution determined after dispersion in calgon with no organic matter or sisquioxide treatments.

Table 3. Mineralogical properties of Alderwood and Wilkeson soils.

| | Fraction | Chlt | Vt | Chlt-Vt | Qtz | Feld. | Amph. | Mica |
|---|---|---|---|---|---|---|---|---|
| Alderwood | sand | 4 | -- | -- | 1 | 2 | 4 | -- |
| | coarse silt | -- | -- | -- | 1 | 2 | -- | -- |
| | medium silt | 3-4 | -- | -- | 1 | 1-2 | -- | -- |
| | fine silt | 1 | 1 | -- | 1 | 1 | 3 | 4 |
| | clay | 1 | 2-3 | 1 | 2 | 3 | 4 | -- |
| | sand* | -- | -- | -- | 1 | 2 | -- | -- |
| | silt* | 1 | 1 | 1 | 2-3 | 3 | 3-4 | 4 |
| | clay* | 1 | -- | 1 | 2-3 | 4 | -- | -- |
| Wilkeson | sand | -- | -- | -- | 1 | 1 | 3-4 | -- |
| | coarse silt | -- | -- | -- | 1 | 1-2 | -- | -- |
| | medium silt | 3 | -- | -- | 1 | 1-2 | -- | -- |
| | fine silt | 1 | 1 | -- | 2 | 2 | 3 | -- |
| | clay | 1 | 1 | 1 | 2 | 4 | -- | -- |
| | sand* | -- | -- | -- | 2 | 2 | 4 | -- |
| | silt* | 1 | 1 | -- | 2 | 4 | 4 | -- |
| | clay* | 1 | 4 | 2 | 2 | -- | -- | -- |

* Fractions separated by calgon dispersion only and used for equilibration studies.

Legend: Chlt = chlorite; Vt = vermiculite; Chlt-Vt = chlorite-vermiculite intergrade;
Qtz = quartz; Feld. = feldspars; Amph. = amphiboles; Mica - micas;
1 = dominant; 2 = abundant; 3 = minor; 4 = trace

size material. Trace amounts of chlorite were also detected in the medium silts of both the Alderwood and Wilkeson soils. The vermiculitic materials composed approximately 3.5 and 7.1 percent of the total Wilkeson and Alderwood soils. Greater quantities occurred in the silt and clay fractions of the Alderwood soil compared to the same Wilkeson soil fractions (Table 4). The sand fractions contained only slight amounts of these 2:1 minerals. The presence of vermiculite and chlorite-vermiculite intergrades in the soils allowed for the study of exchangeable and nonexchangeable potassium release from the soils.

Table 4. Approximate vermiculitic mineral composition of the Alderwood and Wilkeson total soils and particle size fractions (%).

| | Alderwood | Wilkeson |
|---|---|---|
| Sand | 0.2 | 0.1 |
| Silt | 14.0 | 3.6 |
| Clay | 28.3 | 24.3 |
| Total soil | 7.1 | 3.5 |

Variations in mineralogical composition were observed between the particle size fractions separated by the two methods (simple calgon dispersion and removal of cementing agents + dispersion) indicating the presence of aggregates or "clay and silt balls". Vermiculite occurred in the silt and clay fractions of both soils but the abundance of the mineral in the simple calgon dispersion separated clay material was lower than in the clay material separated after removal of cementing agents (Table 3). Also, the silt material from calgon dispersion continued to have dominant quantities of vermiculite. In the Alderwood soil a similar situation was observed when amphiboles was detected in the calgon separated silt material but not in the clay fraction separated by the standard method. These discrepancies in mineral composition of the particle size fractions obtained after different separation procedures indicated the presence of aggregation or cementation by organic matter and/or sesquioxides in the material used for the equilibration studies. Although the calgon separated sand fractions did not contain any secondary minerals based on x-ray data, cation exchange capacities of 18.42 me/100g and 17.90 me/100g for the Alderwood and Wilkeson fractions respectively indicated the presence of material other than large particle primary minerals.

### (c) Physical properties - extent of aggregation

The presence of aggregation or cementation through organic matter and sesquioxides occurred to a significant extent in both the Alderwood and Wilkeson soils. Particle size distribution was determined in both soils following three treatments: (a) calgon dispersion, (b) removal of organic matter + calgon dispersion, (c) removal of organic matter and sesquioxides + calgon dispersion (Table 5). It should be noted that the simple dispersion in calgon resulted in some loss of organic matter. Comparison of the other two removal treatments with simple dispersion showed that the clay size materials were aggregated to a considerable extent in both soils. The Alderwood clay content increased from 2.2 percent to 24.8 percent after organic matter and sesquioxide removal, while the Wilkeson soil had an increase of 28.3 percent clay. These changes in particle size distribution resulted in soil textures ranging from sandy loam to loam for the Alderwood soil and from silt loam to silty clay loam for the Wilkeson soil.

In both soils the aggregation associated with the sand fractions was caused principally by organic matter. Removal of organic material decreased the sand content by 9.2 percent and 20.0 percent in the Alderwood and Wilkeson soils respectively, while further removal of sesquioxides reduced the sand content by 5.8 percent in the Alderwood soil and had no significant effect on the Wilkeson soil. The presence of aggregation in the sand fractions explains the relatively high cation exchange capacities and indicates the presence of "silt balls" in the sand fractions used for the equilibration studies.

Table 5. Particle size distribution in Alderwood and Wilkeson soils following treatments in addition to calgon dispersion.

| Soil | Treatment | s<br>(%) | si<br>(%) | c<br>(%) |
|---|---|---|---|---|
| Alderwood | None | 52.2 | 45.6 | 2.2 |
| | -O.M. | 43.0 | 42.5 | 14.5 |
| | -O.M. & $R_2O_3$ | 37.2 | 38.0 | 24.8 |
| Wilkeson | None | 35.0 | 59.5 | 5.5 |
| | -O.M. | 15.0 | 72.2 | 12.8 |
| | -O.M. & $R_2O_3$ | 15.5 | 50.7 | 33.8 |

While organic matter appeared to be the principal aggregating agent in the sand fractions, sesquioxides had a greater effect in the silt fractions. A 3.1 percent decrease in silt content occurred in the Alderwood soil following organic matter removal but a further 4.5 percent decrease appeared after subsequent sesquioxide removal. The Wilkeson silt content increased 12.7 percent with loss of organic matter but decreased 21.5 percent following sesquioxide removal. The 12.7 percent increase was caused by the great decrease in sand content and indicated that the aggregation in the sand fraction of the Wilkeson soil was primarily connected with silt size material.

Aggregation of clay particles in the Alderwood soil involved both organic matter and sesquioxides. Organic matter removal increased the clay content 12.3 percent and following sesquioxide removal resulted in an increase of an additional 10.3 percent. In the Wilkeson soil sesquioxides played a slightly more important role in aggregation of the clay materials. The clay content increased 7.3 percent when organic matter was removed but an additional 11.3 percent increase in clay content occurred when organic matter and sesquioxides were removed. The presence of "clay and silt balls" in the materials used for the equilibration studies should be noted throughout the study since the quantities of potassium removed from the coarser fractions were higher than would be expected from pure sand and silt soil separates.

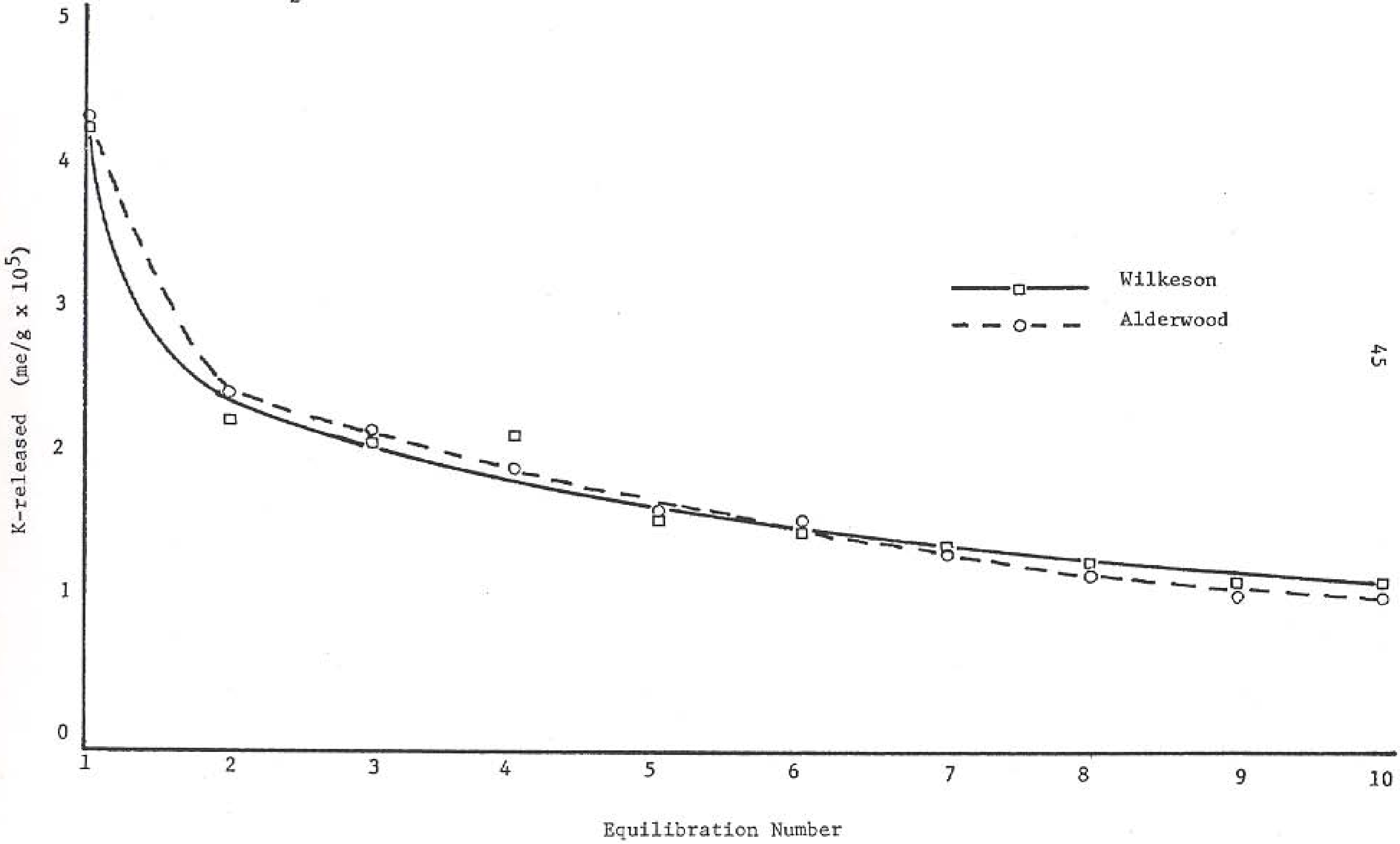
## 2. K Release Functions

### (a) Natural K release

"Natural potassium" release from the Alderwood and Wilkeson soils was according to exponential functions but did not differ significantly from each other when 0.02N $CaCl_2$ was used as the exchanging solution (Figure 2). The equations expressing these curves were $Y = 0.043\ e^{-0.175X}$ and $Y = 0.042\ e^{-0.160X}$ for the Alderwood and Wilkeson soils respectively. Exponential curves expressing potassium release from soils and minerals were also reported by Addiscott and Talibudeen (1969), Haylock (1956), MacLean and Brydon (1963) and Smierzchalska (1971).

A rapid decrease in the amounts of potassium removed from the natural soils occurred during the first two equilibrations after which potassium was released at lower and continually decreasing rates. However the exchangeable potassium content (1N $NH_4OAc$ extractable) of the soils was 0.09 me/100g and 0.11 me/100g respectively in the Alderwood and Wilkeson soils. These

Figure 2. Potassium released from Alderwood and Wilkeson total soils with no K-saturation ($CaCl_2$ exchange).



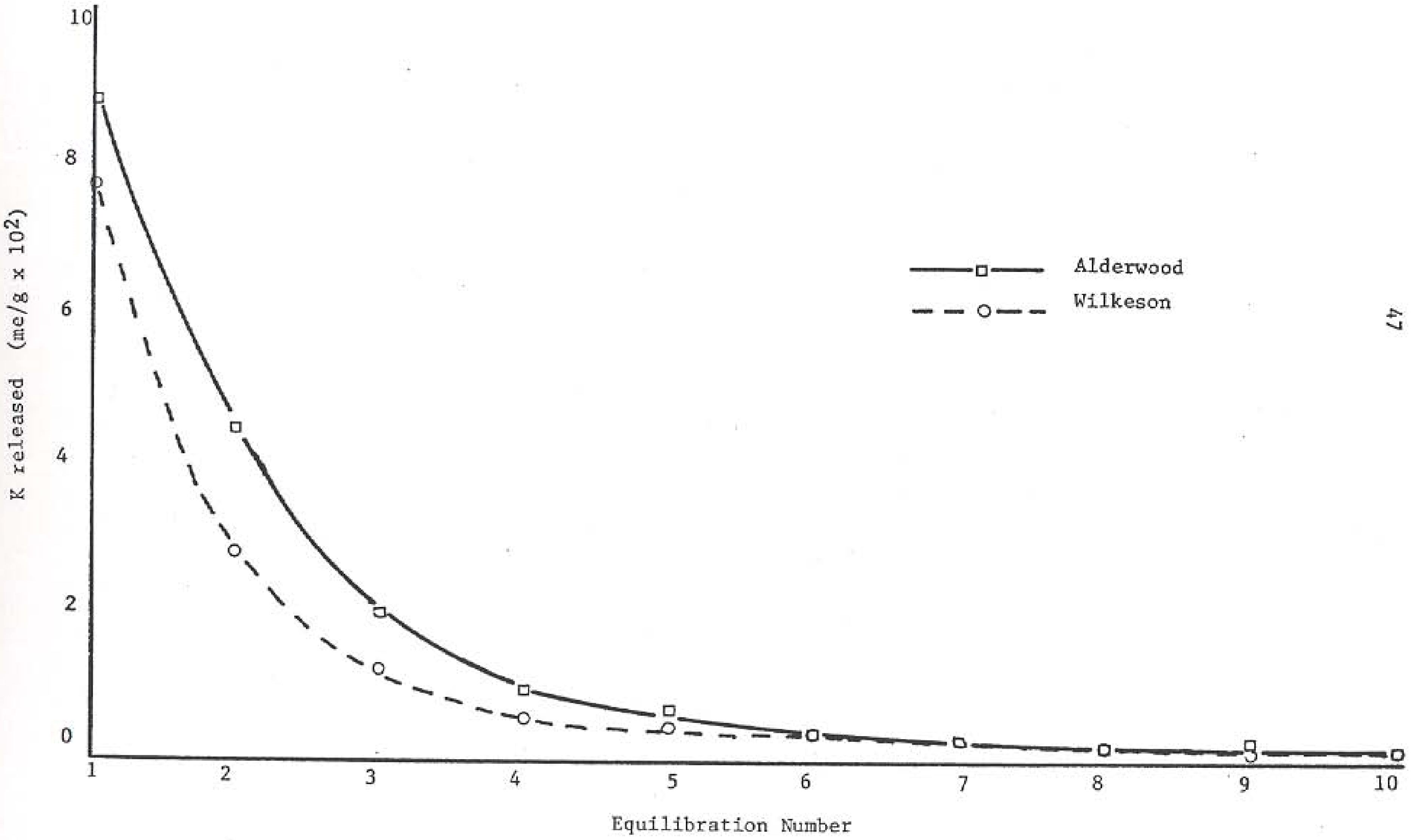
quantities were not totally released after 10 equilibrations even though the equilibrating solution (0.02N $CaCl_2$) was of sufficient strength to remove all the exchangeable forms after the first equilibration. This indicated that the potassium normally considered exchangeable was held in these soils in a way that was either nonexchangeable to divalent cations or was released slowly even when the equilibrating solution would indicate mass action exchange. The ammonium ion has been reported to remove interlayer potassium that is not available by other cations (Barshad, 1954). This was supported by the exchangeable potassium contents of the K saturated Alderwood and Wilkeson soils when 1N $NH_4OAc$ and 1N $CaCl_2$ were the equilibrating solutions (Table 6). In all cases $NH_4OAc$ accounted for more exchangeable potassium especially in the total soils where 12.79 me/100g and 13.36 me/100g occurred in the Alderwood and Wilkeson soils respectively while only 3.62 me/100g and 4.58 me/100g were extracted with N $CaCl_2$ from the same samples. If the ammonium ion removed more potassium than readily exchangeable in the K saturated and natural soils, another extracting solution (e.g. NaOAc) may be proposed for potassium characterization.

### (b) Exchangeable and nonexchangeable K release

Potassium removal from K saturated Alderwood and Wilkeson soils yielded similar exponential release curves to those for natural potassium release, although the Wilkeson soil released significantly more potassium than the Alderwood soil during the initial equilibrations with essentially the same amounts following equilibration five (Figure 3).

Haylock (1956) proposed that potassium release from soils containing minerals that "fix" potassium occurred in three steps. The first step involved rapid release of exchangeable forms followed by the removal of nonexchangeable forms that were not bonded as strongly as those in the third

Figure 3. Potassium released from Alderwood and Wilkeson untreated total soils ($CaCl_2$ exchange).



category. This third category of potassium was released slowly and was responsible for a constant release rate of the element from soils.

Figure 3 expresses the three step release of potassium from saturated samples of the two soils used in this study however when natural soil potassium was considered the release steps were not as definitive (Figure 2). The exchangeable potassium content of the K saturated soils as determined by 1N CaCl exchange was 3.62 me/100g and 4.58 me/100g for the Alderwood and Wilkeson soils respectively. These quantitites were removed from the soils in the first or second equilibration periods while the second through fifth equilibrations removed the relatively weakly held nonexchangeable soil potassium. As the nonexchangeable forms of potassium were removed by subsequent equilibrations the amounts decreased with the soil content but also with increased strength of potassium bonding. Essentially constant potassium quantities were released after the fifth equilibration, representing the third category of adsorbed potassium.

Table 6. Exchangeable potassium contents of K-saturated Alderwood and Wilkeson samples as determined by 1N $NH_4OAc$ and 1N $CaCl_2$.

| Soil | Fraction | Exchangeable K (me/100g) | |
|---|---|---|---|
| | | $NH_4OAc$ | $CaCl_2$ |
| Alderwood | sand | 19.18 | 10.43 |
| | silt | 28.65 | 24.69 |
| | clay | 122.15 | 84.51 |
| | total soil | 12.79 | 3.62 |
| Wilkeson | sand | 19.18 | 12.10 |
| | silt | 34.78 | 23.47 |
| | clay | 119.31 | 87.72 |
| | total soil | 13.36 | 4.58 |

### (c) Free energy of exchange during K release

The bonding energies involved in potassium adsorption can be represented by the change in free energy of the system when potassium is desorbed during the equilibrations (Krishnamoorthy and Overstreet, 1949; Laudelout *et al.*, 1968). Figure 4 shows the change in free energy ($\Delta G$) as calculated according to Krishnamoorthy and Overstreet (1949) with the quantities of potassium desorbed from the Wilkeson soil samples using 0.02N $MgCl_2$ as the equilibrating solution. Increasing negative $\Delta G$ depicts stronger potassium bonding hence less desorption. Three major categories of bonded potassium were separated on the curve: exchangeable, "weakly fixed" and "strongly fixed". The exchangeable and some of the "weakly fixed" forms correspond to the planer and edge face adsorption sites of van Schouwenburg and Schuffelen (1963) while most of the "weakly fixed" and all of the "strongly fixed" potassium was adsorbed on interlayer sites. Progressive decreases in $\Delta G$ corresponded to desorption of interlayer potassium farther from the mineral edges. Changes in the slope of the curve in Figure 4 were calculated using small increments of the curve. The approximate $\Delta G$ points where significant changes occurred were -750 cal/mole and -1750 cal/mole. These values should not be taken as absolute boundaries of the adsorbed potassium forms but were intended as indications of the relative $\Delta G$ that could be expected when the various forms of potassium are the contributors to soil solution potassium. Woodruff (1955) proposed that $\Delta G$ values of -2000 to -3000 cal/mole provided sufficient potassium for agricultural crop growth but deficiencies occurred when $\Delta G$ were $<-3500$ cal/mole. Although the samples used in the present study were previously potassium saturated, the $\Delta G$ values indicated that sufficient potassium would be released from "strongly fixed" sites to prevent deficiencies from occurring.

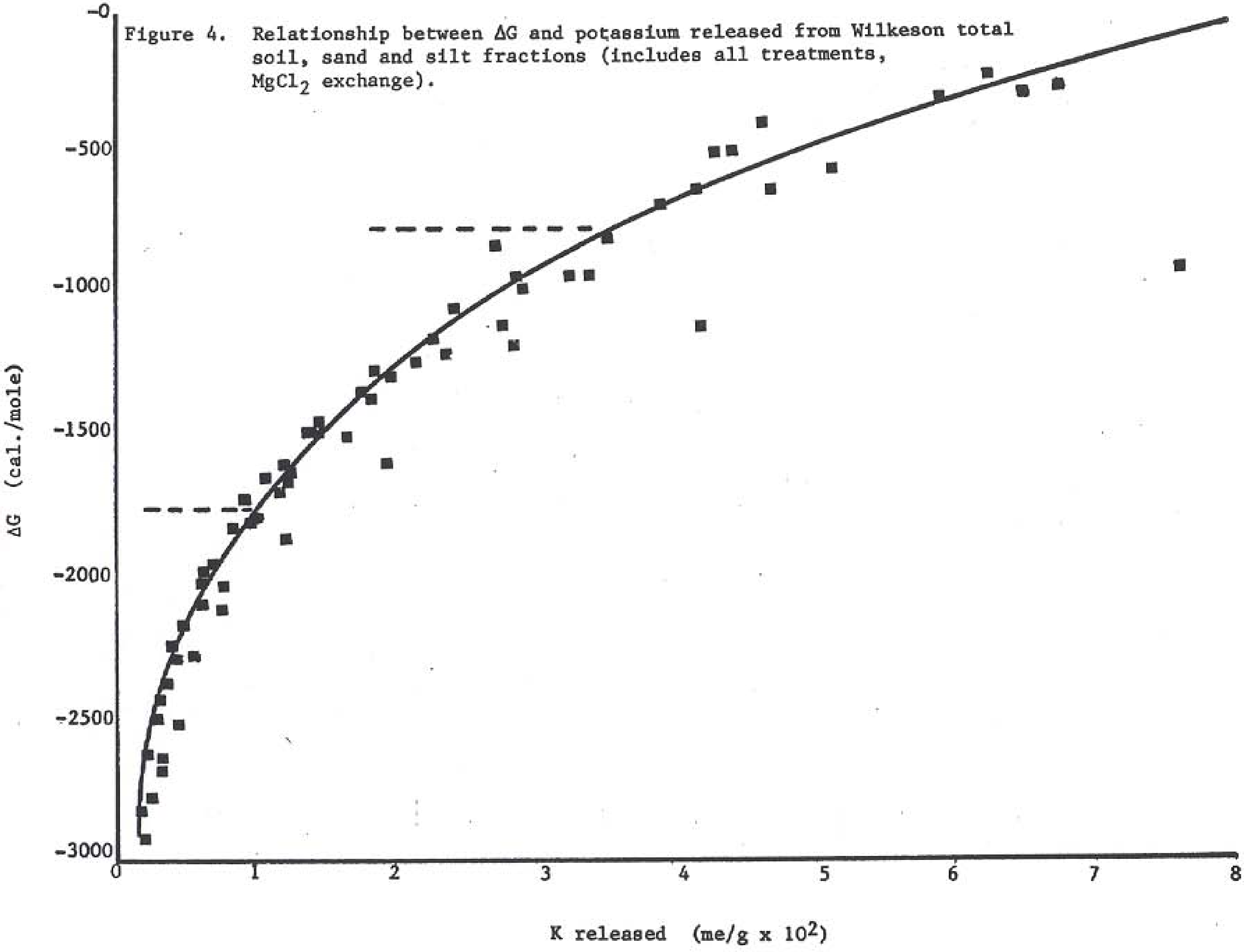


Figure 4. Relationship between ΔG and potassium released from Wilkeson total soil, sand and silt fractions (includes all treatments, $MgCl_2$ exchange).

Comparison of the equilibration period required to remove exchangeable potassium as depicted in Table 7 using $\Delta G$ values with those of Table 8 (1N $CaCl_2$ extractable potassium), discrepancies appeared especially in the silt fraction. The greater number of equilibration periods needed to remove exchangeable K based on $\Delta G$ indicated that although some adsorbed potassium was not exchangeable by 1N $CaCl_2$ it was still bonded with similar energies and consequently released with only slight decreases in $\Delta G$. Under natural soil conditions this situation would not be as prevalent because of greater differences in bonding energies associated with the forms of potassium.

### (d) Predicting equations

Equations were obtained that predicted potassium release from the K saturated Alderwood and Wilkeson total soils and particle size fractions (Table 9). The predictions were statistically significant (0.05 level). In all cases nonexchangeable potassium was released according to an exponential function. The release of exchangeable K was affected by the techniques used in the K saturation and drying procedures.

The soil drying procedure involving organic solvents used after potassium saturation (Jackson, 1969) necessitated a period of rehydration before true equilibrium was attained. During the equilibration studies with the particle size fractions of the two soils the rehydration period extended through the first two equilibrations resulting in desorption curves that did not exhibit an exclusive exponential function (Figures 5 & 6). Other than the clay fractions the total soils and particle size fractions released all their exchangeable potassium by the third equilibration period (Table 8). Consequently the abnormality in the release curves was associated with the exchangeable forms and release of nonexchangeable potassium occurred according to the exponential functions given in Table 9.

Table 7. Free energy changes for Wilkeson total soil, sand and silt fractions using 0.02N $MgCl_2$ as the equilibrating solution.

| Fraction | Equil. No. | Untreated ΔG(cal./mole) | Minus organic matter ΔG(cal./mole) | Minus organic matter & $R_2O_3$ ΔG(cal./mole) |
|---|---|---|---|---|
| sand | 1 | +217.3 | -543.8 | -208.8 |
| | 2 | -398.2 | -- | -636.3 |
| | 3 | -828.2 | -930.0 | -1136.9 |
| | 4 | -1503.6 | -1202.9 | -1490.2 |
| | 5 | -1646.0 | -1476.7 | -- |
| | 6 | -1703.7 | -1762.5 | -2013.6 |
| | 7 | -1954.4 | -1794.4 | -2241.8 |
| | 8 | -2160.8 | -2078.2 | -2422.1 |
| | 9 | -2378.0 | -2261.2 | -2620.5 |
| | 10 | -2493.1 | -2675.8 | -2700.6 |
| silt | 1 | --- | +757.5 | +194.9 |
| | 2 | +814.9 | --- | -- |
| | 3 | +298.9 | +213.9 | +156.8 |
| | 4 | +73.8 | -254.0 | -290.3 |
| | 5 | -490.5 | -554.5 | -498.8 |
| | 6 | -798.8 | -- | -992.5 |
| | 7 | -1050.0 | -1085.3 | -1173.8 |
| | 8 | -1264.2 | --- | -1343.2 |
| | 9 | -1465.3 | --- | -1521.8 |
| | 10 | -1634.1 | -1687.2 | -1661.1 |
| total | 1 | -931.5 | +466.8 | -236.1 |
| | 2 | -1126.9 | +127.6 | +260.9 |
| | 3 | -1594.2 | -277.1 | -217.8 |
| | 4 | -1856.6 | -634.2 | -670.0 |
| | 5 | -2103.8 | -943.4 | -978.0 |
| | 6 | -2257.2 | -1207.1 | -1275.8 |
| | 7 | -2501.0 | -1368.0 | -1457.3 |
| | 8 | -2648.1 | -1613.2 | -1647.2 |
| | 9 | -2766.9 | --- | -1806.6 |
| | 10 | -2935.4 | -2017.4 | -1981.6 |

Table 8. Number of equilibrations required to remove all exchangeable potassium from the Alderwood and Wilkeson soils using 0.02N $CaCl_2$.

| Soil | Fraction | No Treatment | | | Minus Organic Matter | | | Minus Organic Matter & $R_2O_3$ | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Exch. K* (me/g) | No. of Equil. | K-released (me/g) | Exch. K* (me/g) | No. of Equil. | K-released (me/g) | Exch. K* (me/g) | No. of Equil. | K-released (me/g) |
| Alderwood | sand | 0.1044 | 2 | 0.1058 | 0.1021 | 3 | 0.1117 | 0.0748 | 3 | 0.0803 |
| | silt | 0.1984 | 2 | 0.2118 | 0.1714 | 3 | 0.1913 | 0.1348 | 3 | 0.1622 |
| | clay | 0.5940 | 5 | 0.5834 | 0.9872 | 10 | 0.8923 | 0.9382 | 6 | 0.9962 |
| | total | 0.0303 | 1 | 0.0784 | 0.1536 | 3 | 0.1729 | 0.1169 | 2 | 0.1228 |
| Wilkeson | sand | 0.1263 | 2 | 0.1376 | 0.1173 | 3 | 0.1440 | 0.1001 | 3 | 0.1191 |
| | silt | 0.2470 | 3 | 0.2780 | 0.2637 | 3 | 0.2279 | 0.2426 | 4 | 0.2619 |
| | clay | 0.9138 | 9 | 0.9542 | 0.9828 | 10 | 0.8936 | 0.9354 | 6 | 1.0481 |
| | total | 0.0460 | 1 | 0.9000 | 0.2129 | 3 | 0.2180 | 0.2258 | 3 | 0.2343 |

* K exchangeable with N $CaCl_2$.

Table 9. Equations expressing release of nonexchangeable potassium by 0.02N $CaCl_2$ from K saturated Alderwood and Wilkeson soils and particle size fractions.

| Soil | Fraction | Treatment | Equation | $R^2$ |
|---|---|---|---|---|
| Alderwood | sand | none | $Y=0.084e^{-0.336X}$ | 0.990 |
| | | -O.M. | $Y=0.073e^{-0.385X}$ | 0.956 |
| | | -O.M. & $R_2O_3$ | $Y=0.072e^{-0.559X}$ | 0.976 |
| | silt | none | $Y=0.164e^{-0.295X}$ | 0.985 |
| | | -O.M. | $Y=0.095e^{-0.244X}$ | 0.820 |
| | | -O.M. & $R_2O_3$ | $Y=0.098e^{-0.350X}$ | 0.852 |
| | clay | none | $Y=0.163e^{-0.100X}$ | 0.708 |
| | | -O.M. | $Y=0.113e^{-0.044X}$ | 0.807 |
| | | -O.M. & $R_2O_3$ | $Y=0.226e^{-0.079X}$ | 0.890 |
| | total | none | $Y=0.201e^{-0.947X}$ | 0.994 |
| | | -O.M. | $Y=0.094e^{-0.296X}$ | 0.895 |
| | | -O.M. & $R_2O_3$ | $Y=0.100e^{-0.385X}$ | 0.880 |
| Wilkeson | sand | none | $Y=0.107e^{-0.314X}$ | 0.857 |
| | | -O.M. | $Y=0.081e^{-0.310X}$ | 0.995 |
| | | -O.M. & $R_2O_3$ | $Y=0.075e^{-0.393X}$ | 0.899 |
| | silt | none | $Y=0.136e^{-0.197X}$ | 0.917 |
| | | -O.M. | $Y=0.097e^{-0.147X}$ | 0.738 |
| | | -O.M. & $R_2O_3$ | $Y=0.102e^{-0.210X}$ | 0.858 |
| | clay | none | $Y=0.170e^{-0.100X}$ | 0.821 |
| | | -O.M. | $Y=0.112e^{-0.043X}$ | 0.762 |
| | | -O.M. & $R_2O_3$ | $Y=0.228e^{-0.075X}$ | 0.929 |
| | total | none | $Y=0.181e^{-0.702X}$ | 0.996 |
| | | -O.M. | $Y=0.106e^{-0.221X}$ | 0.855 |
| | | -O.M. & $R_2O_3$ | $Y=0.130e^{-0.307X}$ | 0.933 |

Figure 5(a). Potassium released from untreated K-saturated Alderwood size fractions ($CaCl_2$ exchange).

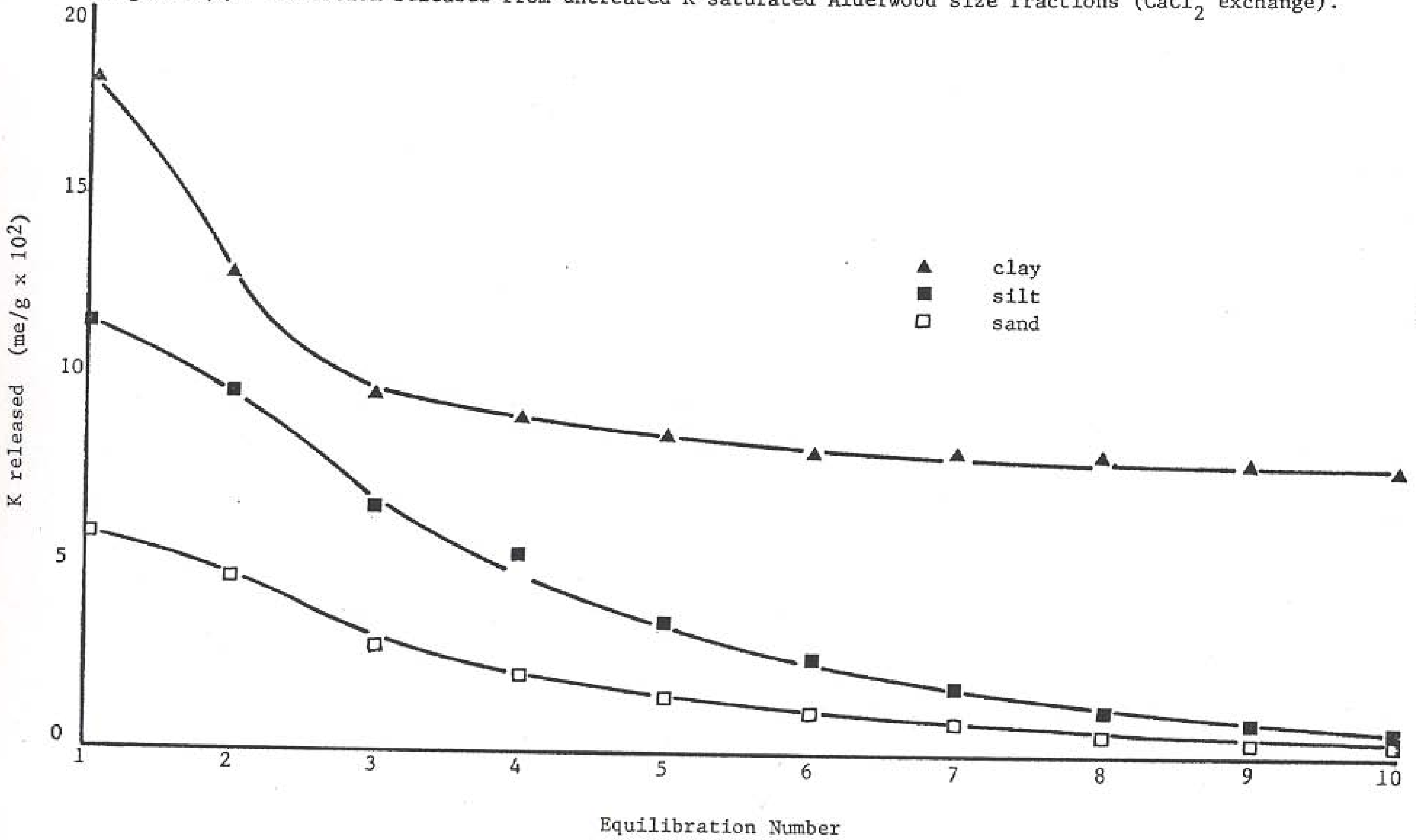


Figure 5(b). Potassium released from minus organic matter K-saturated Alderwood size fractions ($CaCl_2$ exchange).

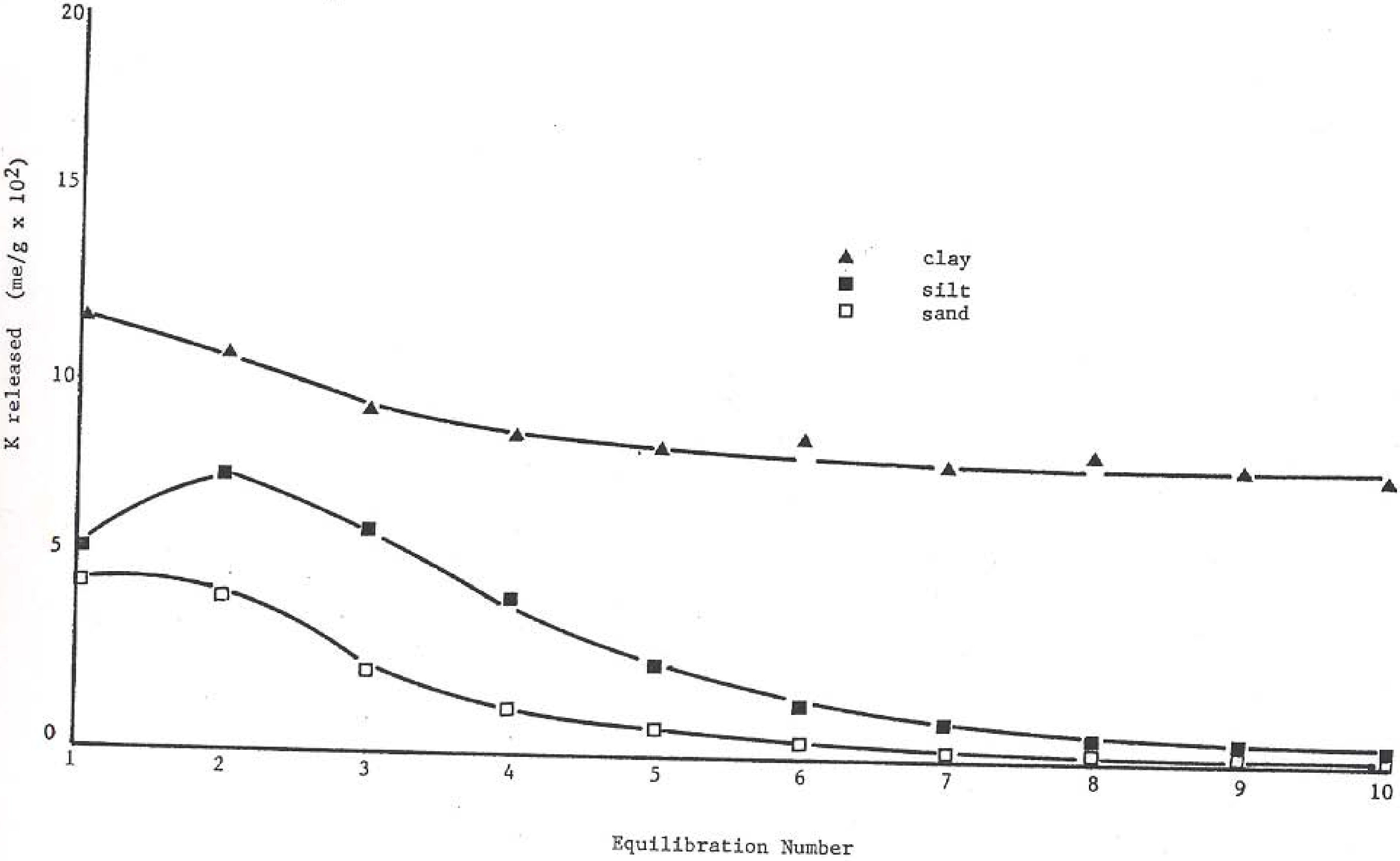


Figure 5(c). Potassium released from minus organic matter and sesquioxides K-saturated Alderwood size fractions ($CaCl_2$ exchange).

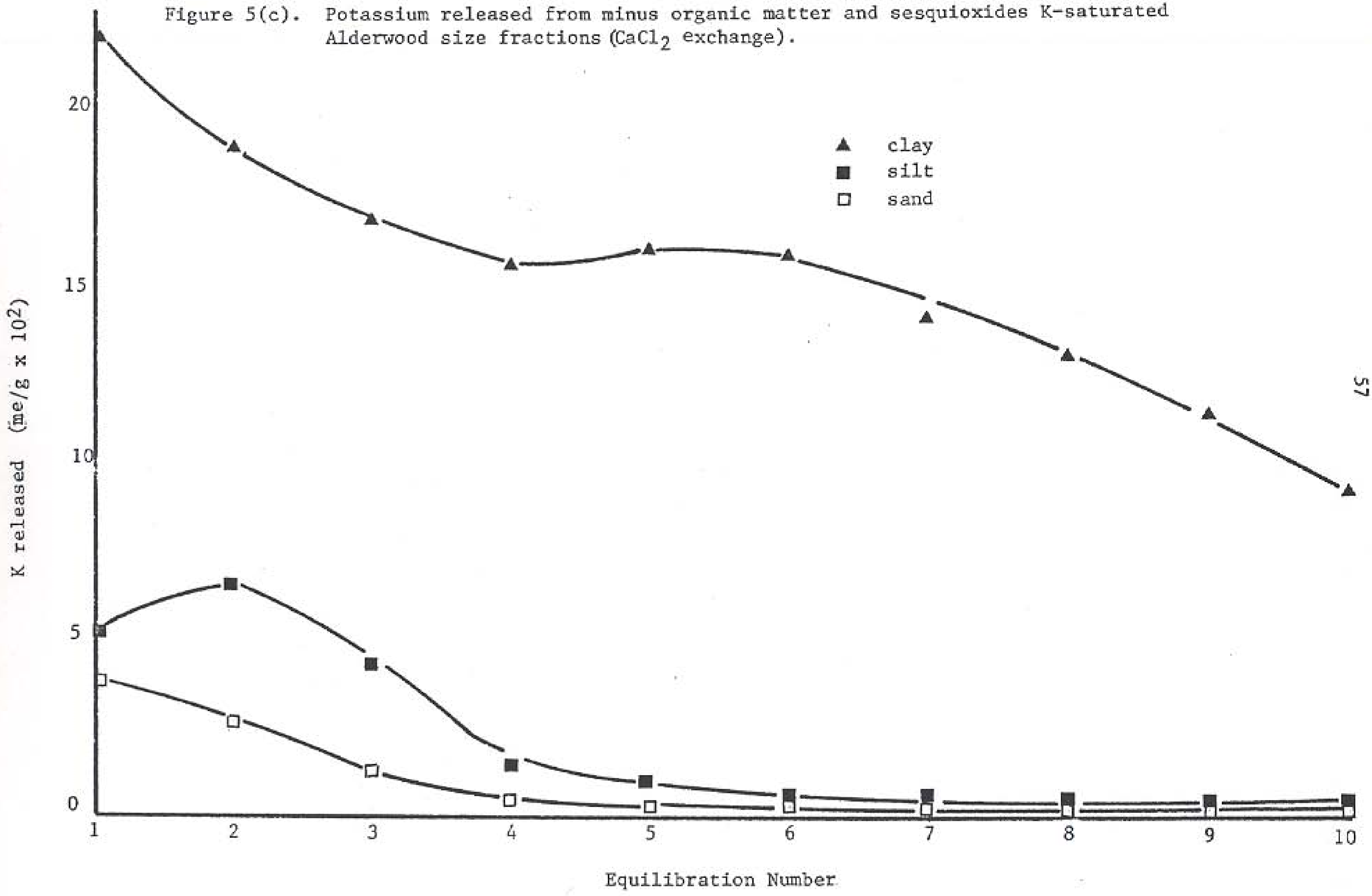


Figure 6(a). Potassium released from untreated K-saturated Wilkeson size fractions ($CaCl_2$ exchange).

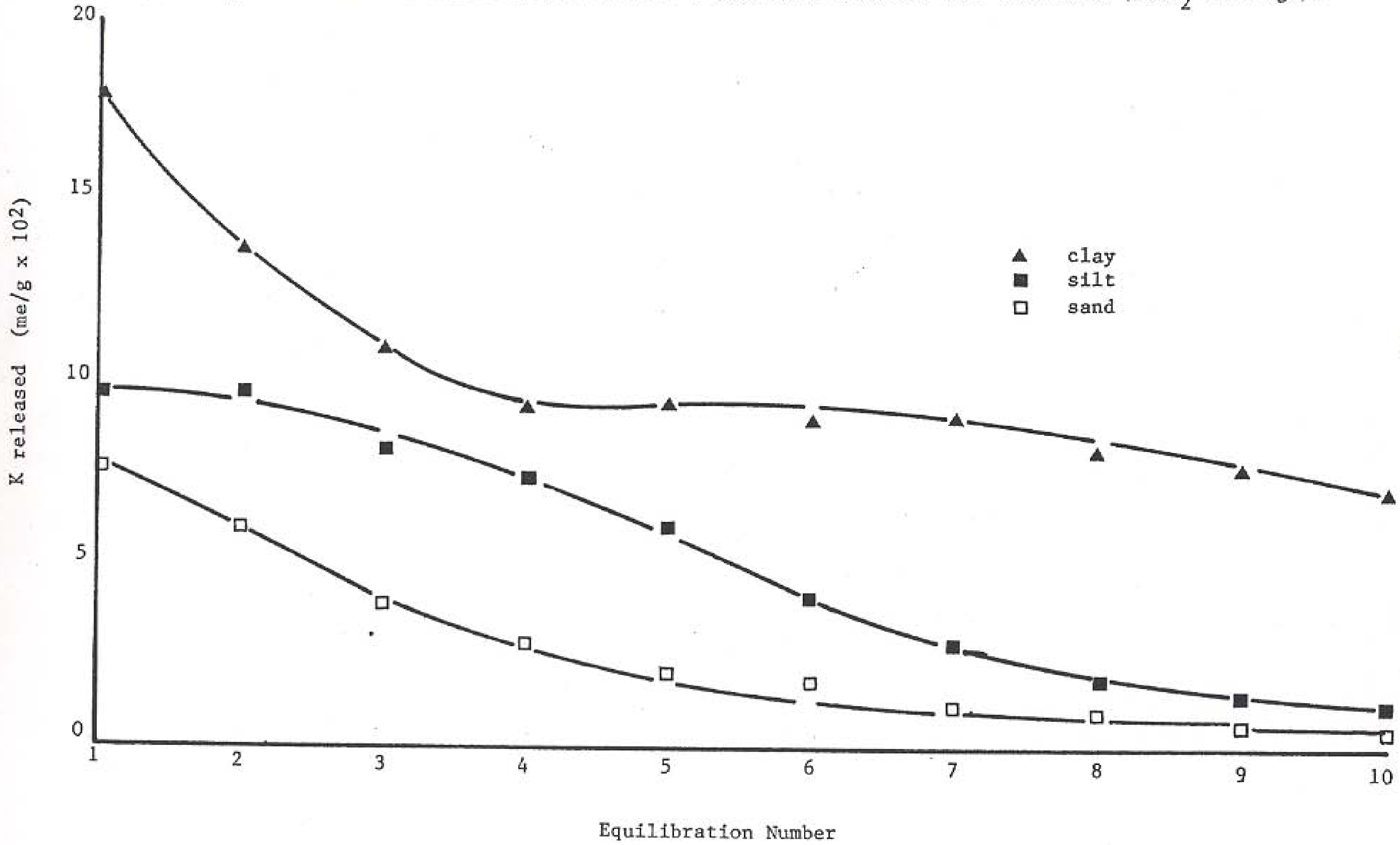


Figure 6(b). Potassium released from minus organic matter K-saturated Wilkeson size fractions ($CaCl_2$ exchange).

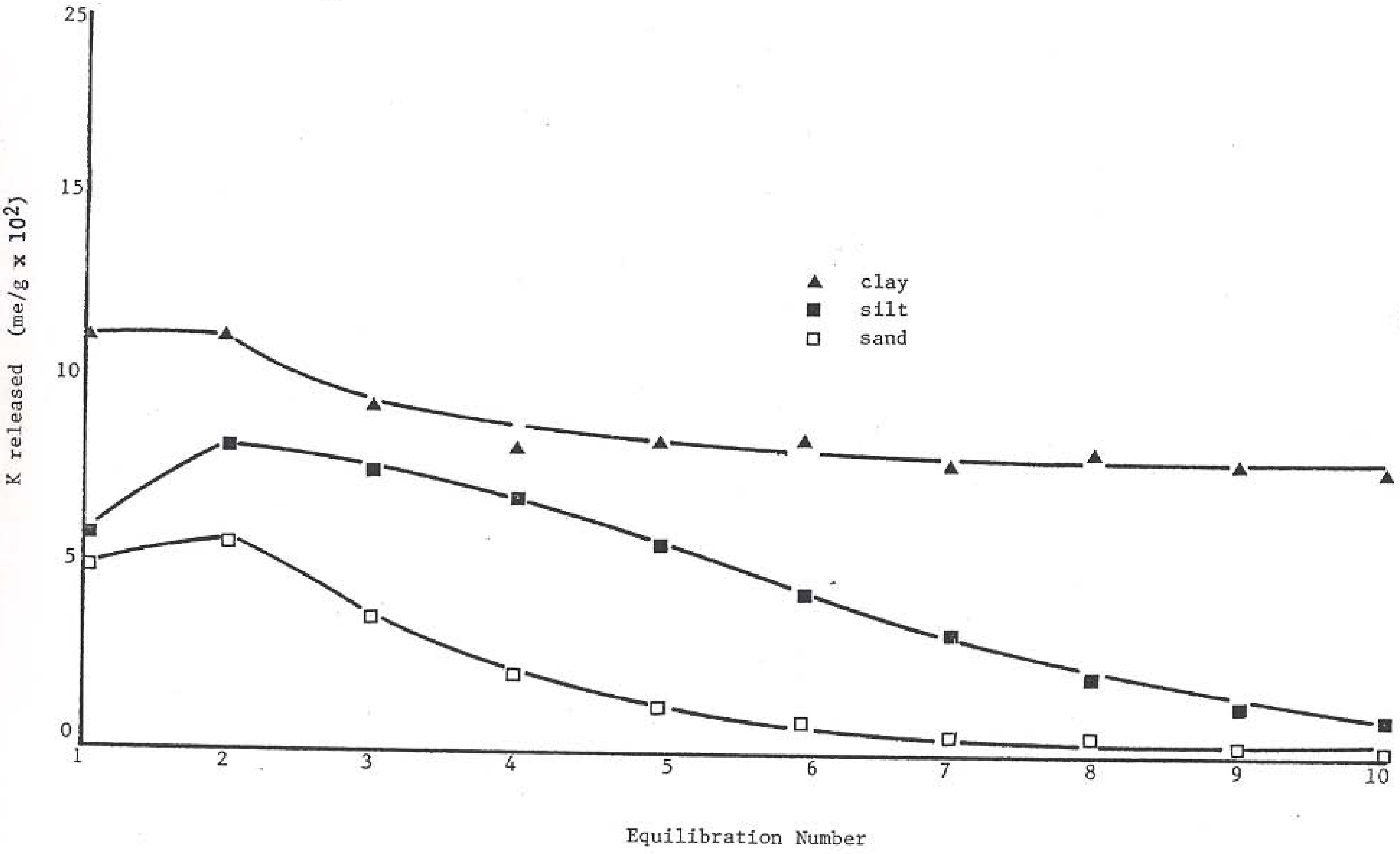
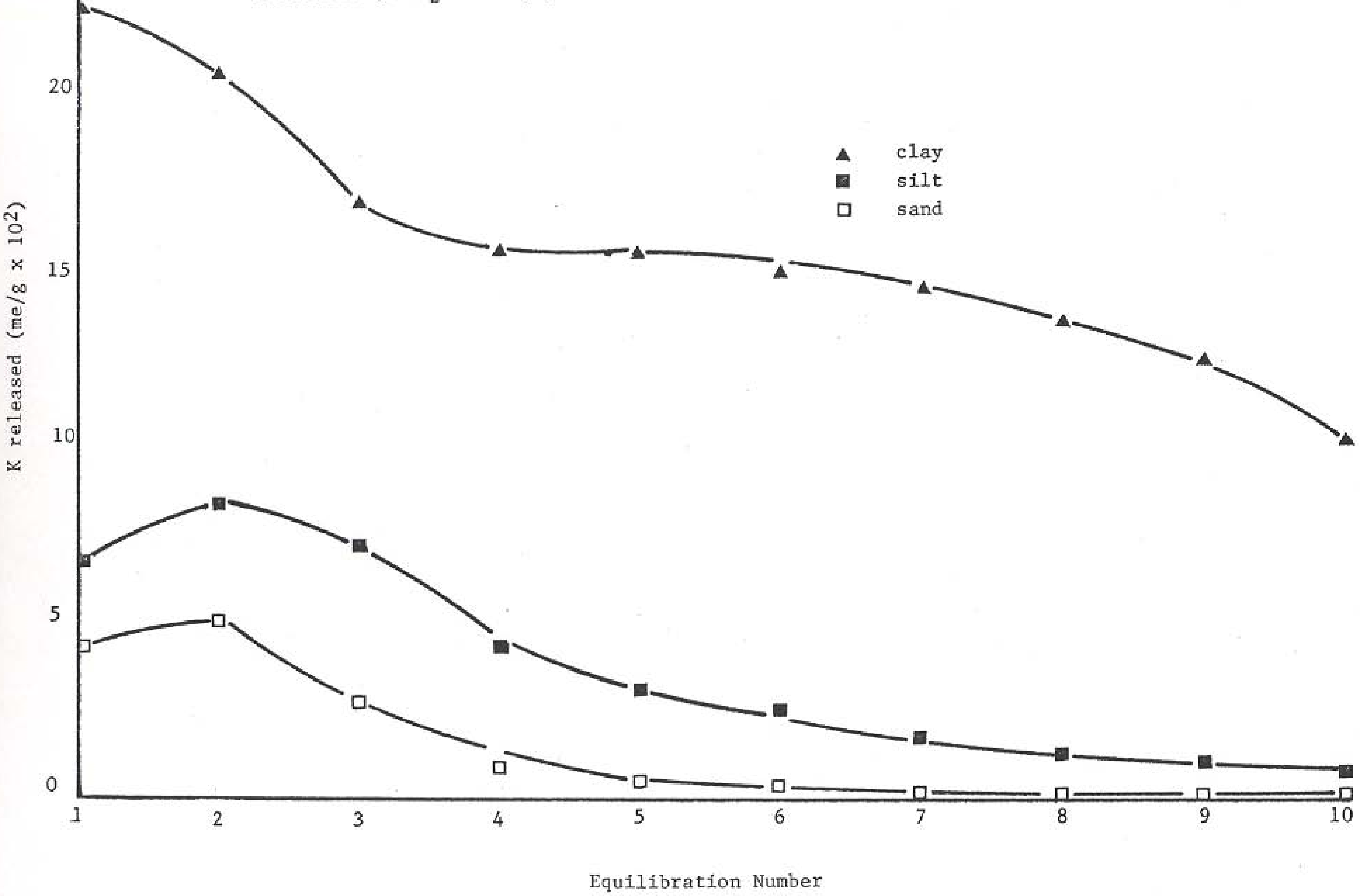


Figure 6(c). Potassium released from minus organic matter and sesquioxides K-saturated Wilkeson size fractions ($CaCl_2$ exchange).



## 3. Factors Affecting K Release

### (a) Soil factors

The principal soil factor that has been reported to affect potassium release is the particle size distribution. This has been principally connected with K release from micas where the quantity released generally increased with decreasing particle size. The effects of organic matter and sesquioxides on ion exchange prompted the evaluation of their contributions to K release.

### (i) particle size

Quantities of potassium released from the two soils using 0.02N $CaCl_2$ decreased with increasing particle size (Figure 5 & 6). Doll *et al.* (1965) and Smith *et al.* (1968) reported the same phenomenon with soil fractions as did Mortland and Lawton (1961), Reed and Scott (1962), Scott (1968), Scott and Reed (1962a) and Smith *et al.* (1971) with micas and sodium tetraphenylboron as the extracting agent. The potassium release curves of the Alderwood and Wilkeson coarser fractions exhibited increased rate of exchangeable and nonexchangeable potassium desorption with decreasing particle size (Table 10). Further increased rate of potassium desorption did not occur with the clay fractions due to the large amount of exchangeable potassium present in these samples and the relatively dilute calcium chloride solution (0.02N) used for equilibration. Equilibria occurred between the clay fractions and the $CaCl_2$ solution such that after the first 2 or 3 equilibration periods almost constant amounts of potassium were released. Increased rates of desorption could have been attained if a more concentrated equilibrating solution was used.

The clay size fractions of the two soils had similar potassium contents

Table 10. Slopes of potassium release curves for exchangeable and nonexchangeable forms in the Alderwood and Wilkeson size fractions using 0.02N $CaCl_2$ equilibrating solution.

| Soil | Fraction | Exchangeable (equilibrations 2 to 4) | | | Nonexchangeable (equilibrations 5 to 10) | | |
|---|---|---|---|---|---|---|---|
| | | Untreated | minus organic matter | minus organic matter & $R_2O_3$ | Untreated | minus organic matter | minus organic matter & $R_2O_3$ |
| Alderwood | sand | 0.0104 | 0.0067 | 0.0021 | 0.0024 | 0.0013 | 0.0004 |
| | silt | 0.0269 | 0.0215 | 0.0076 | 0.0059 | 0.0044 | 0.0015 |
| | clay | 0.0182 | 0.0107 | 0.0169 | 0.0019 | 0.0013 | 0.0080 |
| Wilkeson | sand | 0.0143 | 0.0107 | 0.0044 | 0.0033 | 0.0022 | 0.0009 |
| | silt | 0.0385 | 0.0346 | 0.0216 | 0.0098 | 0.0091 | 0.0047 |
| | clay | 0.0215 | 0.0123 | 0.0245 | 0.0044 | 0.0013 | 0.0105 |

and desorption functions. Especially with the untreated and minus organic matter samples. Potassium released from the clay fractions throughout the 10 equilibration periods was almost exclusively from exchangeable forms (Table 8). Consequently the ratios of desorbed potassium from the two soils was near the ratios of the exchangeable contents of the samples (Table 11). Desorption of exchangeable potassium from the sand and silt fractions of the two soils (equilibrations 1 to 3) had the same relationships but not as definitive as those of the clay fractions. Therefore comparisons of potassium release curves involving exchangeable forms only of other similar particle size fractions could be explained by the ratios of their exchangeable contents.

When nonexchangeable potassium forms were released from the particle size fractions, the ratios of Wilkeson:Alderwood contents released increased markedly from the ratios of the exchangeable contents (Table 11). Wilkeson sand and silt fractions contained similar or slightly higher contents of exchangeable and total potassium (Table 12) therefore they released greater quantities than the corresponding Alderwood fractions. However the differences in total potassium contents of the sand and silt fractions of the two soils were insufficient to fully explain the desorption variations. Reitemeier *et al.* (1951) and LeRoux and Rich (1969) pointed out that potassium release depended not only on the total amount of potassium present but on the stages of weathering or formation of hydrous micas. Mortland and Lawton (1961) and Smith *et al.* (1968) reported that decreased particle size yielded a more rapid rate of potassium release but the percentage of the total content released decreased. Therefore the differences in nonexchangeable potassium desorption of the Alderwood and Wilkeson particle size fractions were probably associated with variations in bonding energies.

Table 11. Ratios of potassium released from Wilkeson fractions relative to Alderwood fractions throughout the equilibration periods as related to the ratios of exchangeable potassium levels in each fraction.

| Fraction | Untreated | | Minus organic matter | | Minus organic matter & $R_2O_3$ | |
|---|---|---|---|---|---|---|
| | exch. ratio | equil. ratio | exch. ratio | equil. ratio | exch. ratio | equil. ratio |
| sand | 1.16 | 1.33 | 1.15 | 1.09 | 1.35 | 1.09 |
| | | 1.27 | | 1.36 | | 1.76 |
| | | 1.39 | | 1.54 | | 2.04 |
| | | 1.38 | | 1.60 | | 2.07 |
| | | 1.44 | | 1.66 | | 2.04 |
| | | 1.60 | | 1.72 | | 1.91 |
| | | 1.48 | | 1.54 | | 1.75 |
| | | 1.43 | | 1.43 | | 1.91 |
| | | 1.69 | | 1.64 | | 2.00 |
| | | 1.56 | | 1.69 | | 2.00 |
| silt | 0.95 | 0.97 | 1.53 | 1.06 | 1.80 | 1.23 |
| | | 1.02 | | 1.10 | | 1.24 |
| | | 1.06 | | 1.25 | | 1.65 |
| | | 1.43 | | 1.61 | | 2.86 |
| | | 1.71 | | 2.21 | | 3.16 |
| | | 1.57 | | 2.77 | | 4.40 |
| | | 1.66 | | 2.72 | | 4.23 |
| | | 1.69 | | 3.06 | | 3.80 |
| | | 1.66 | | 2.98 | | 3.86 |
| | | 1.93 | | 3.08 | | 3.63 |
| clay | 1.04 | 0.99 | 0.99 | 0.96 | 1.00 | 1.00 |
| | | 1.06 | | 1.04 | | 1.07 |
| | | 1.14 | | 1.01 | | 0.98 |
| | | 1.02 | | 0.98 | | 0.99 |
| | | 1.09 | | 1.02 | | 1.16 |
| | | 1.11 | | 0.99 | | 0.93 |
| | | 1.11 | | 0.96 | | 1.01 |
| | | 1.02 | | 1.01 | | 1.04 |
| | | 0.97 | | 0.99 | | 1.09 |
| | | 0.95 | | 1.03 | | 1.10 |

Table 12. Exchangeable (me/100g) and total (%) potassium in K-saturated Alderwood and Wilkeson soils and fractions.

| | Fraction | No treatment | | Minus organic matter | | Minus organic matter & $R_2O_3$ | |
|---|---|---|---|---|---|---|---|
| | | Exch. | Total | Exch. | Total | Exch. | Total |
| Alderwood | sand | 10.43 | 0.76 | 10.21 | 0.74 | 7.48 | 0.66 |
| | silt | 24.69 | 0.98 | 17.14 | 0.91 | 13.48 | 0.95 |
| | clay | 84.51 | 1.99 | 98.72 | 1.99 | 93.82 | 3.62 |
| | total | 3.62 | 0.53 | 15.36 | 0.77 | 11.69 | 0.81 |
| Wilkeson | sand | 12.10 | 0.70 | 11.73 | 0.78 | 10.01 | 0.66 |
| | silt | 23.47 | 1.09 | 26.37 | 1.06 | 24.26 | 1.13 |
| | clay | 87.72 | 1.78 | 98.28 | 1.75 | 93.54 | 3.41 |
| | total | 4.58 | 0.48 | 21.29 | 0.87 | 22.58 | 1.14 |

Separation of the physical components (sand, silt, clay) from the total soil provided an opportunity to observe the release of potassium from the fractions relative to each other and the total soil. Theoretically the amount of potassium released by the sum of the particle size fractions relative to their content in the total soil should equal the quantity released by the total soil, provided no alteration occurred during particle size separation and the fractions behaved the same when separated as when combined. Doll *et al.* (1965) attributed deviations of experimental from calculated potassium release between particle size fractions and total soils to simultaneous fixation and release as proposed by Mortland (1961). However Smith *et al.* (1971) reported good relationships between calculated and determined potassium release from a mixture of biotite size fractions and Scott and Reed (1962a) found that mixtures of particle size fractions yielded quantities of potassium intermediate between the extremes of the size fractions used. Also it appeared that each particle released potassium at a rate unaffected by the presence of others.

Comparisons of potassium release from the sand, silt and clay fractions with the total soils were performed using both 0.02N $CaCl_2$ and $MgCl_2$ equilibrating solutions ($MgCl_2$ figures in Appendix). For each equilibration period the sum of potassium desorbed from the three particle size fractions of each soil were considered relative to the quantity released from the total soil during the appropriate equilibration period. The sum of potassium contributions from each particle size fraction was calculated from the percentage of each fraction in the total soil, determined by simple calgon dispersion (Table 2), and the quantities of potassium released from each fraction. The simple calgon dispersion particle size distribution values were used because it was this method that yielded the particle size fractions for the equilibration studies.

Prediction of potassium desorption from the total soils by the release from the particle size fractions varied with the forms of potassium being released and the treatment to which the soils and particle size fractions were subjected before equilibration (Figure 7). Other than the untreated samples, the desorption of exchangeable potassium as calculated from the sum of the fractions was less than that released by the total soils. Nonexchangeable potassium release from the total soils was more satisfactorily predicted than the release of exchangeable forms by the calculated sum of particle size fraction release values. The sum of particle size fraction desorption values were slightly higher than the total soil experimental values which was similar to the soil results reported by Smith *et al.* (1971). However comparison of the calculated values with the experimental values for nonexchangeable potassium release showed that only the untreated samples had statistically significant differences (Table 13).

Table 13. Student's "t" values for potassium released from total Alderwood and Wilkeson soils compared to calculated release from size fractions based on individual release curves and percentages of each size in total soils (0.02N $CaCl_2$ equilibrating solution).

| Soil | Treatment | "t" value | |
|---|---|---|---|
| Alderwood | none | 3.208 | * |
| | -O.M. | -0.128 | N.S. |
| | -O.M. & $R_2O_3$ | -0.527 | N.S. |
| Wilkeson | none | -3.748 | ** |
| | -O.M. | -0.787 | N.S. |
| | -O.M. & $R_2O_3$ | -1.369 | N.S. |

* significant at 0.05 level.

** significant at 0.01 level.

N.S. not significant.

Figure 7(a). K release from treated and untreated Alderwood total soil compared to the calculated release based on particle size fraction release (0.02N $CaCl_2$ equilibrating solution).

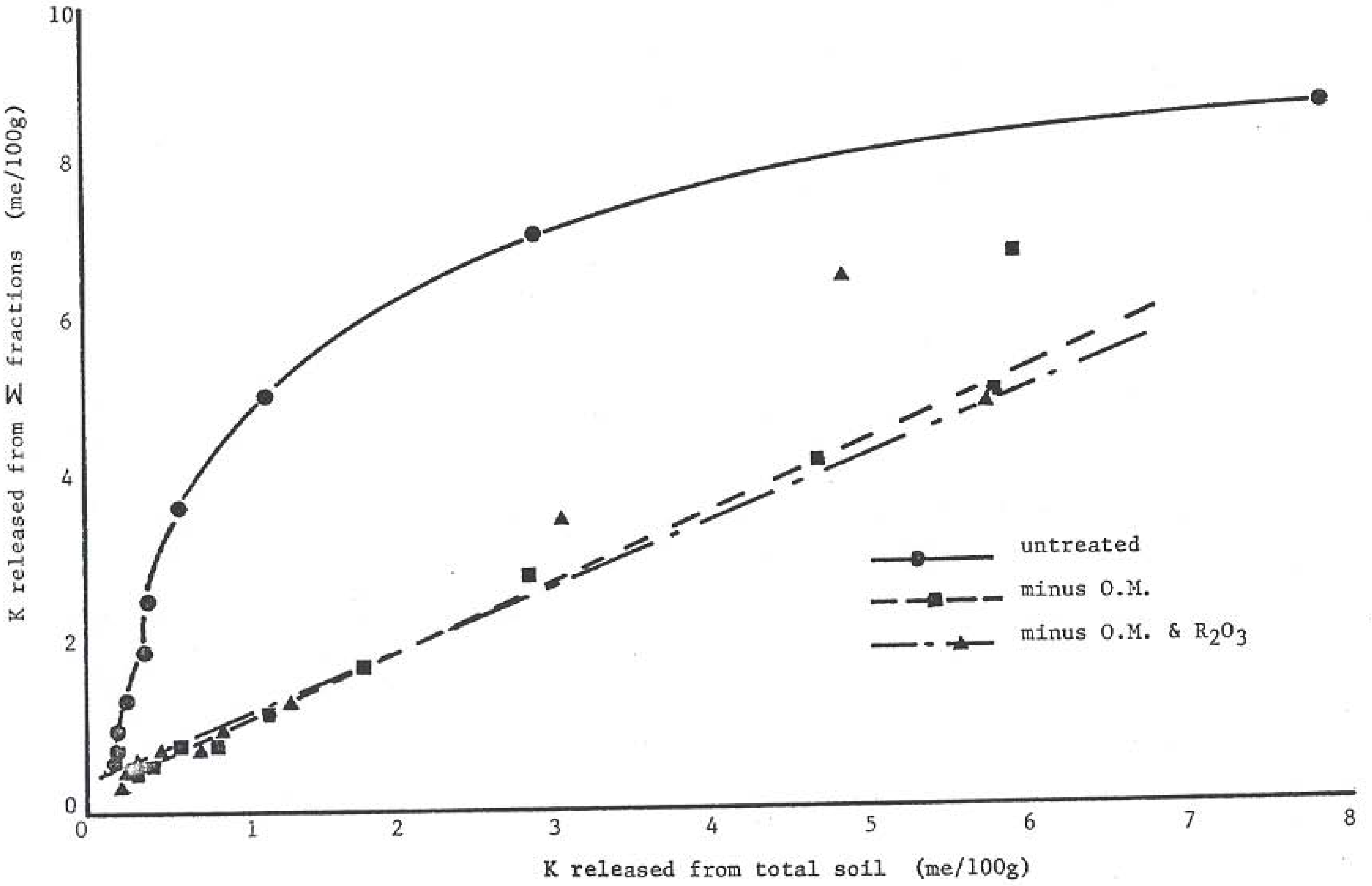
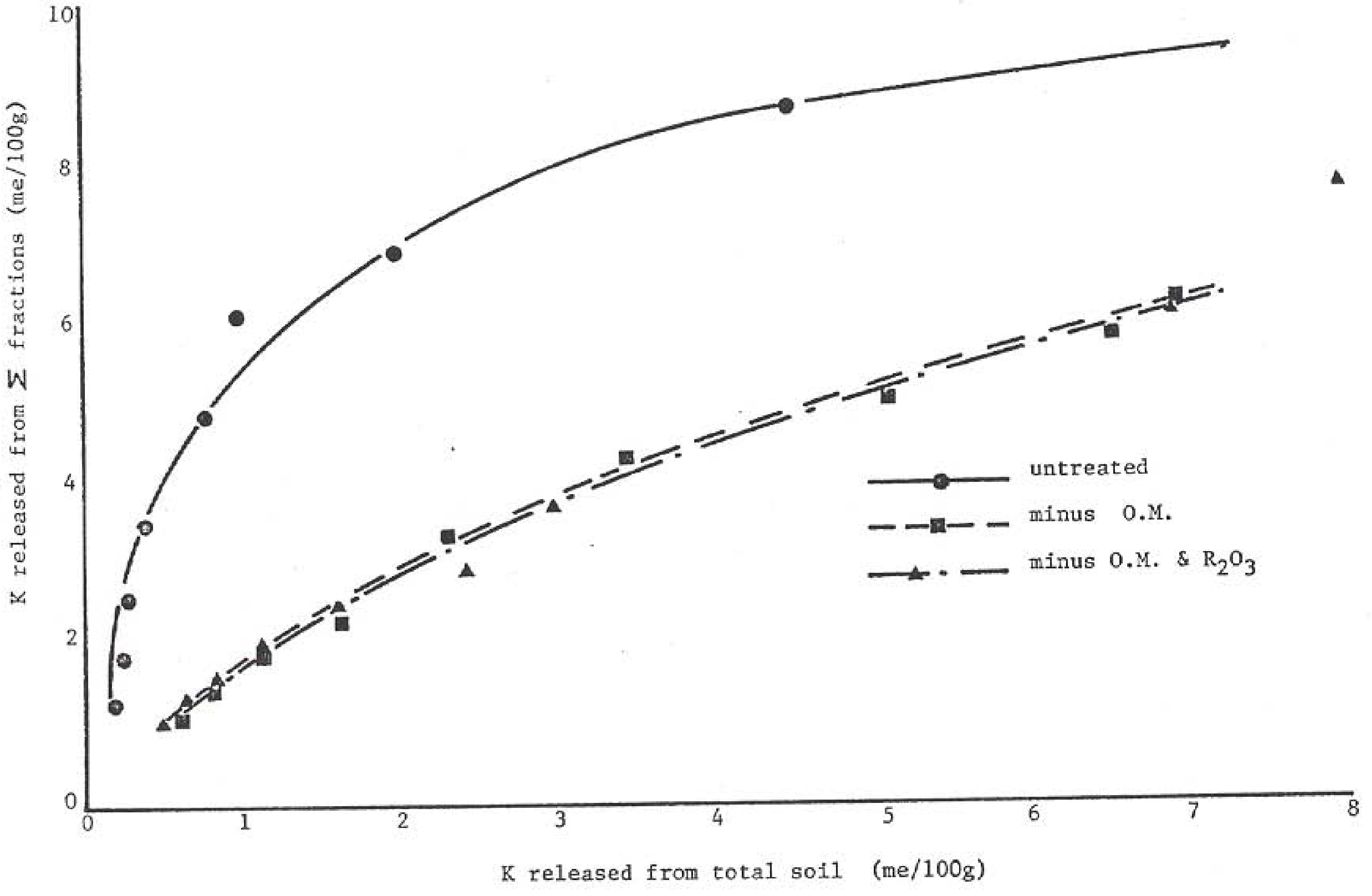


Figure 7(b). K release from treated and untreated Wilkeson total soil compared to the calculated release based on particle size fraction release (0.02N $CaCl_2$ equilibrating solution).



The strong deviations of the observed potassium release curves from the theoretical (1:1 relationship) in the untreated samples was due to the soil organic material. Calgon dispersion removed a certain amount of organic matter and sodium hydroxide slightly more (Table 14), thereby providing the total soil with the characteristics which gave more accurate predictions of potassium release than when no organic matter was removed (Figure 8). Removal of the entire organic fraction of the total soil and its particle size fractions using sodium hypochlorite reduced the prediction error especially relative to release of nonexchangeable potassium (Figure 9). Extraction of sesquioxides and organic matter did not provide conditions for significantly better total soil desorption predictions by the sum of the particle size fractions' potassium release (Figure 9). The small error in total soil potassium release prediction indicated that the release of nonexchangeable potassium from the Alderwood and Wilkeson soils was a function of the particle size distribution and its relationships provided the organic material was removed.

Table 14. Exchangeable potassium (me/100g) and % carbon in K-saturated Alderwood and Wilkeson soils after various treatments.

| | Untreated | | Ultrasonics | | Calgon | | 0.5MNaOH | | NaOCl | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Exch K | %C | Exch K | %C | Exch K | %C | Exch K | %C | Exch K | %C |
| Alderwood | 3.62 | 3.65 | 4.21 | 3.61 | 11.56 | 3.56 | 14.07 | 2.93 | 15.36 | -- |
| Wilkeson | 4.58 | 3.70 | 5.42 | 3.63 | 12.98 | 3.32 | 16.24 | 3.32 | 21.29 | -- |

(ii) organic matter

Soil organic material has generally been considered to have high cation exchange capacities and relatively weak exchangeable cation bonding (Buckman and Brady, 1961). However when this material is complexed with inorganic soil particles, reductions in the sum of inorganic and organic

Figure 8(a). Nonexchangeable K release from various treated Alderwood total soil compared to calculated release based on particle size fraction release (0.02N $MgCl_2$ equilibrating solution).

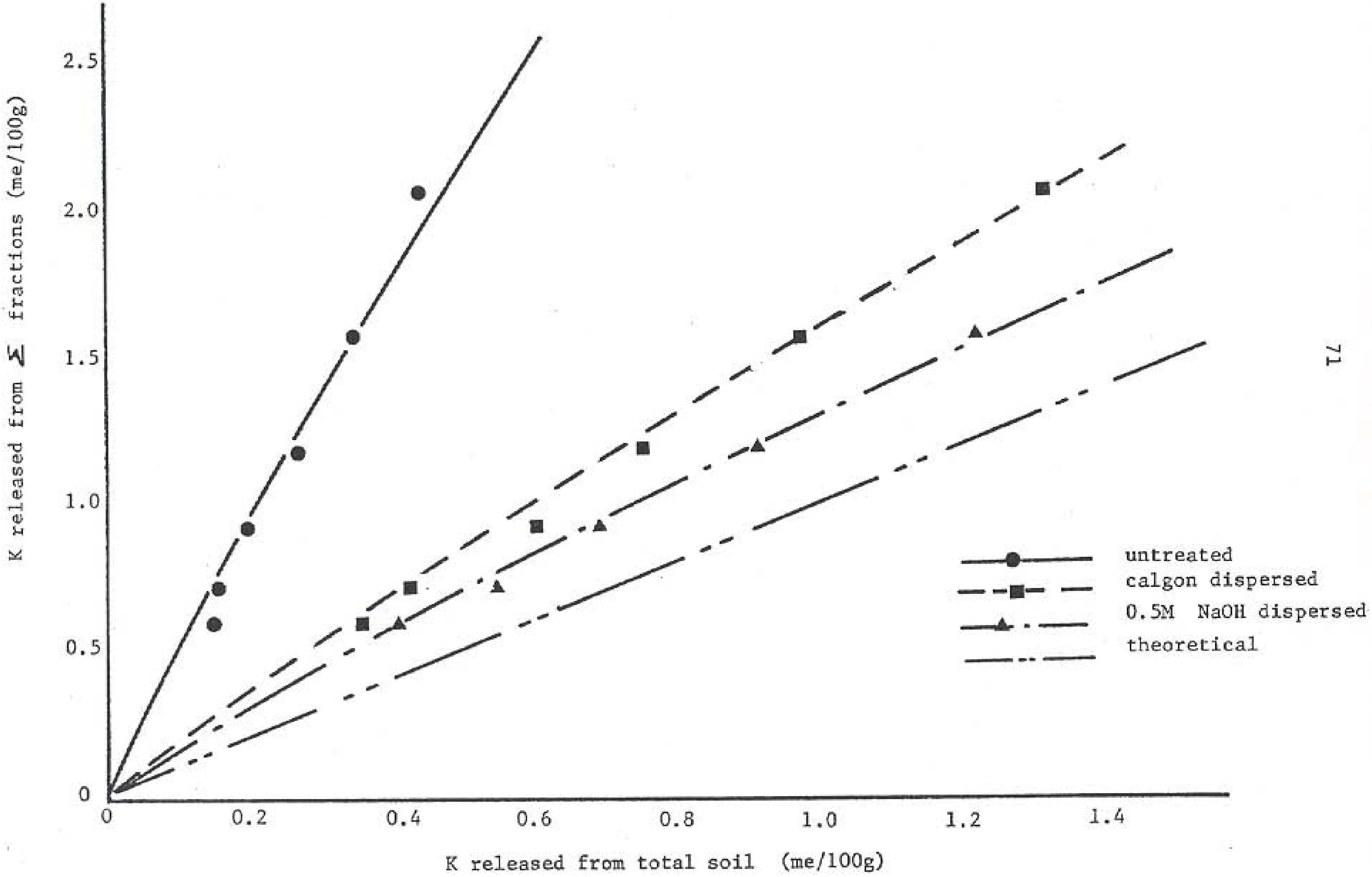


Figure 8(b). Nonexchangeable K release from various treated Wilkeson total soil compared to calculated release based on particle size fraction release (0.02N $MgCl_2$ equilibrating solution).

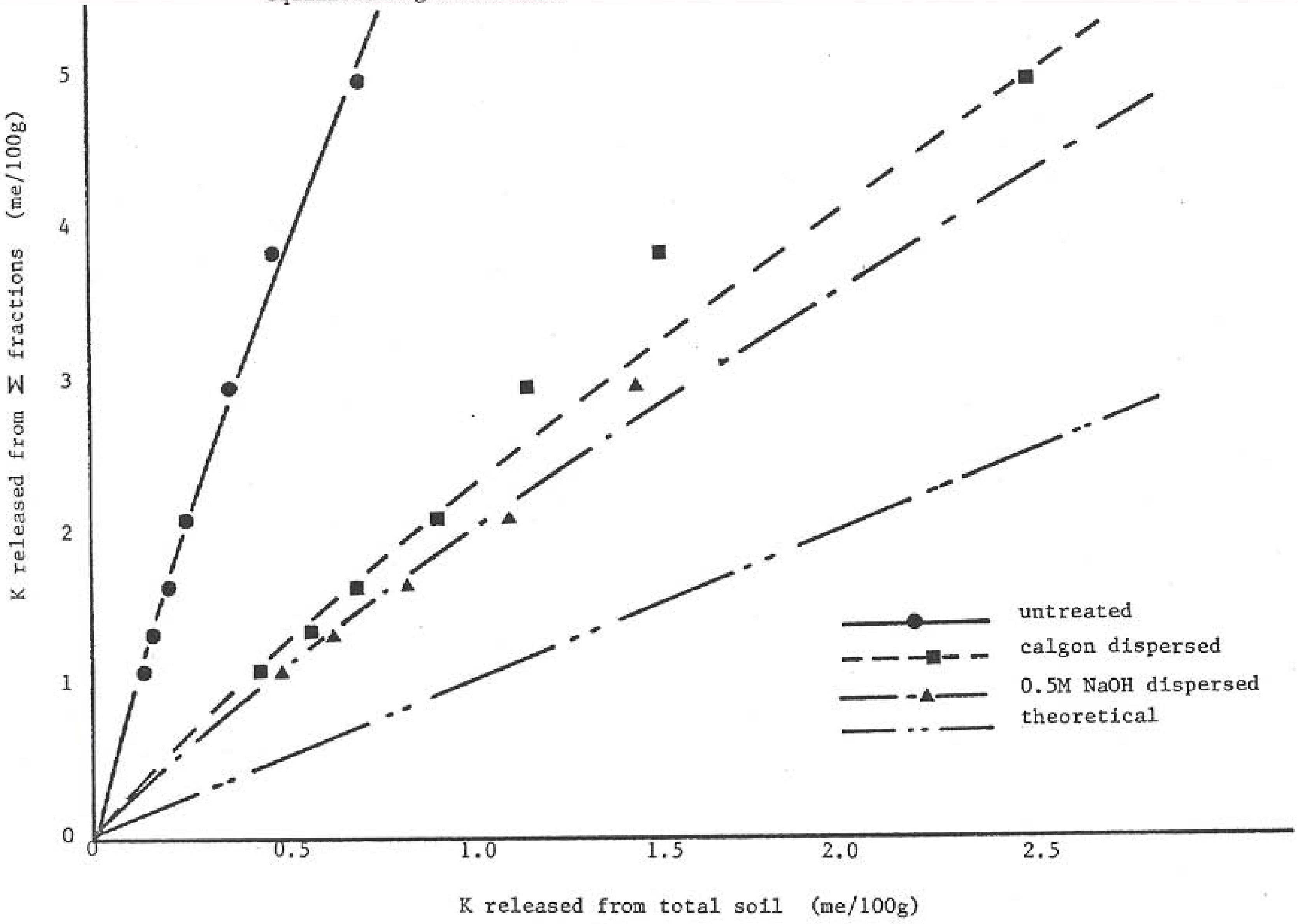


Figure 9(a). Nonexchangeable potassium release from treated and untreated Alderwood total soil compared to calculated release based on particle size fraction release (0.02N $CaCl_2$ equilibrating solution).

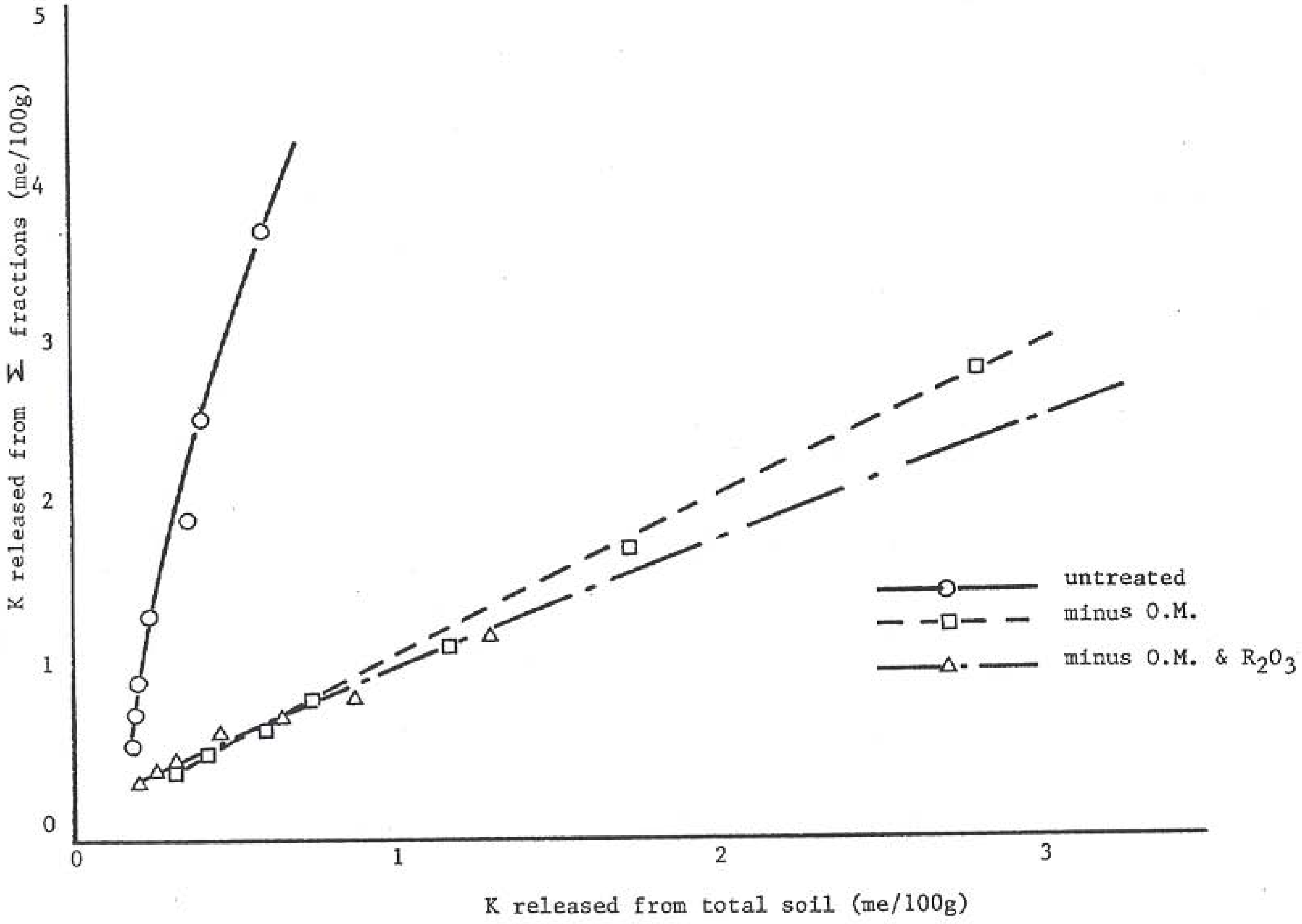
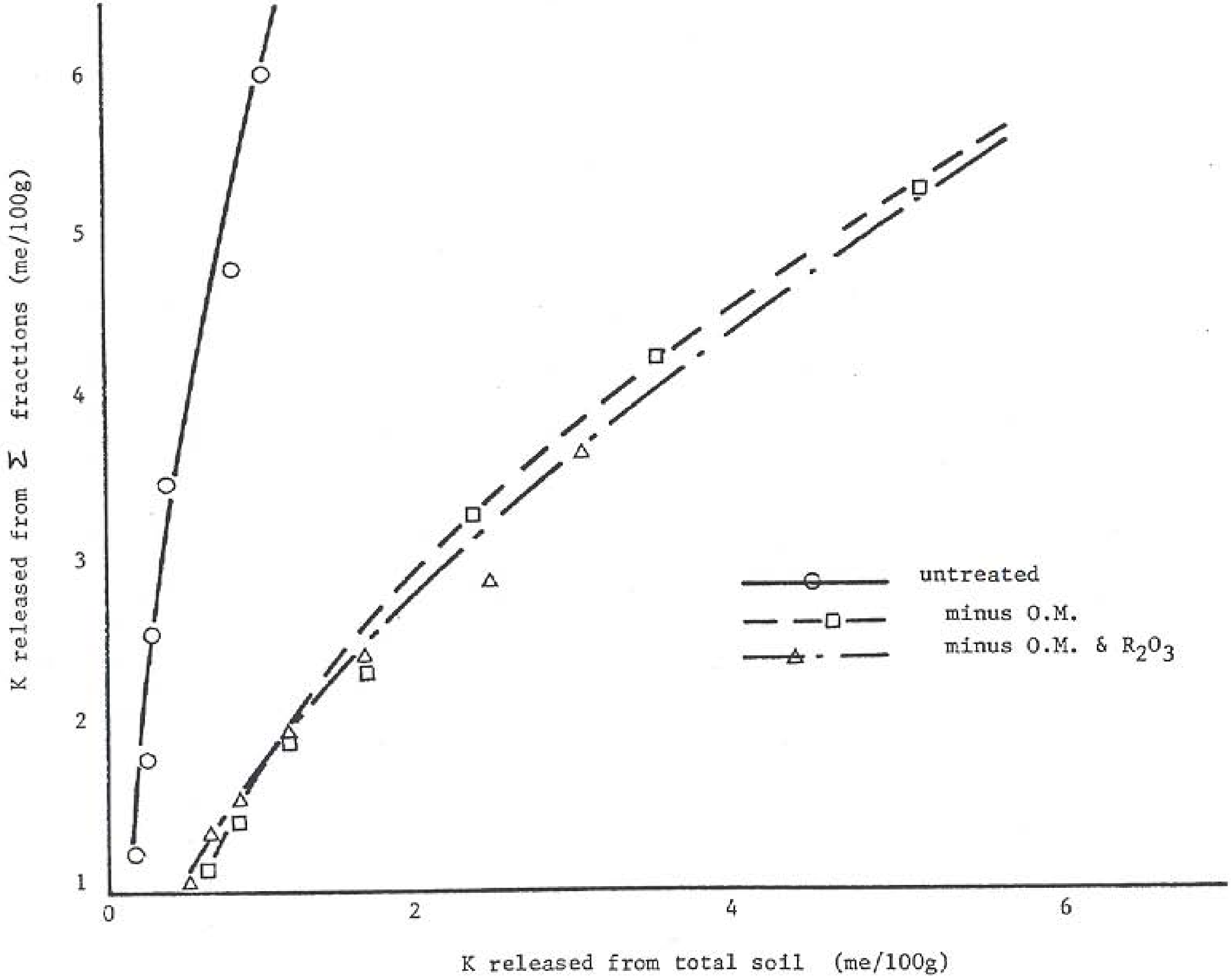


Figure 9(b). Nonexchangeable potassium release from treated and untreated Wilkeson total soil compared to calculated release based on particle size fraction release (0.02N $CaCl_2$ equilibrating solution).



exchange capacities can occur (DeSilva and Toth, 1964; Gorbunov *et al.*, 1972; Greenland, 1965b). Greenland (1965b) and Gorbunov *et al.* (1972) attributed the decrease in C.E.C. to physical and chemical blockage of some organic matter COOH groups and inorganic exchange sites. Most of the inorganic-organic soil fraction complexing is associated with the clay fraction (Greenland, 1965a) and more precisely the 0.2 to 0.08μ fraction (Dudas and Pawluk, 1970). Schlichte (1968) reported increased cation exchange capacities of the Everett soil series when the organic matter was removed and since this soil type commonly occurs adjacent to the Alderwood soil it was not unexpected to find increased exchangeable potassium contents in the total Alderwood and Wilkeson soils after NaOCl treatment (Table 12). Increasing amounts of organic material was removed from these soils by different treatments (ultrasonics <calgon <0.5M NaOH<NaOCl) resulting in increased quantities of exchangeable potassium following K saturation (Table 14).

The exchange capacities of the particle size fractions also changed after NaOCl treatment. The Alderwood clay fraction exchangeable potassium content increased 14.21 me/100g and the Wilkeson fraction 10.56 me/100g. The exchangeable potassium content of the Wilkeson silt fraction increased slightly (2.90 me/100g) but the Alderwood silt fraction and both sand fractions remained relatively constant (Table 12). This supports Greenland's statement that organic complexing is primarily associated with clay fractions. The decrease in organic carbon in the coarser particle fractions was due to loss of "free" organic matter which possessed 7.55 me/100g and 0.22 me/100g in the Alderwood silt and sand fractions respectively and 0.37 me/100g in the Wilkeson sand fraction. These values were based on the decreases in exchangeable potassium contents of these fractions after NaOCl treatment.

The effects of organic material on the exchange properties of the Alderwood and Wilkeson soils and particle size fractions were expressed in the potassium release curves. The K saturated sand fractions, without organic matter, released lower quantities of potassium than the samples not treated with NaOCl (Figure 10). Potassium release from the untreated and minus organic matter Alderwood sand fraction differed only slightly when the average coefficient of variation for the 10 equilibration periods (20.8%) was considered. An average coefficient of variation in potassium release from the Wilkeson sand fraction (13.8%) did not account for all the variation in desorption due to organic matter removal, therefore sodium hypochlorite treatment of this fraction resulted in reduced quantities of potassium desorbed.

Differences in potassium release also existed between the untreated and minus organic matter silt fraction samples of the Alderwood soil (Figure 11). Release of nonexchangeable potassium from the silt fraction was not significantly affected by organic matter removed but release of exchangeable forms were lower in samples without organic material. This reduction was associated with a decreased exchangeable content and increased bonding energies involving adsorbed potassium. The increased bonding energies were indicated by the number of equilibration periods required to remove the exchangeable potassium forms. In the untreated silt fraction 0.2369 me/g exchangeable potassium was released after the second equilibration, but three equilibration periods were required to remove the 0.1714 me/g exchangeable content from the minus organic matter samples.

The Wilkeson minus organic matter silt fraction released less potassium throughout the 10 equilibration periods than the untreated samples even when the 8.3% average coefficient of variation in potassium desorption was

Figure 10(a). Potassium release from K-saturated Alderwood sand fraction after various treatments ($CaCl_2$ exchange).

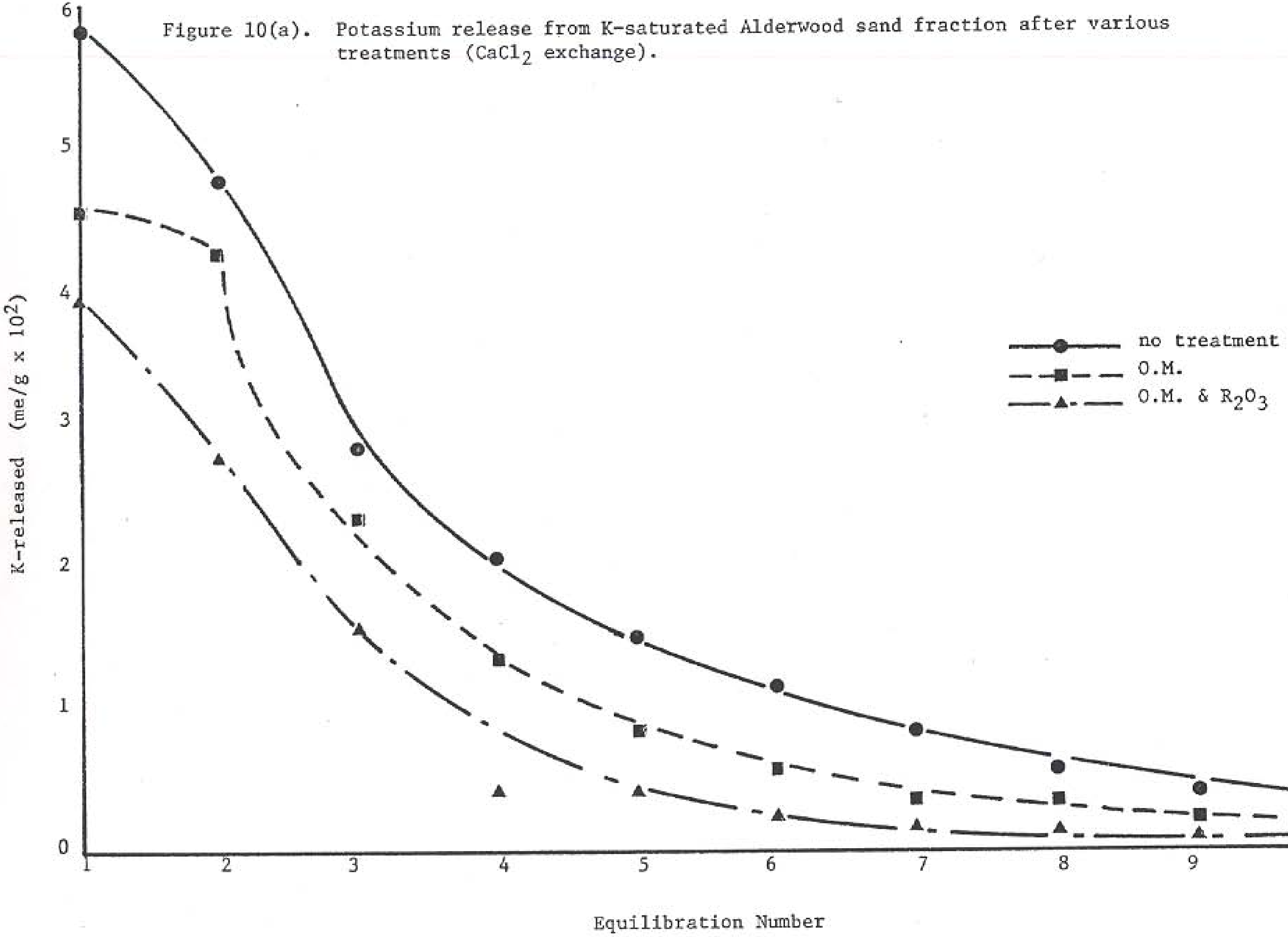


Figure 10(b). Potassium release from K-saturated Wilkeson sand fraction after various treatments ($CaCl_2$ exchange).

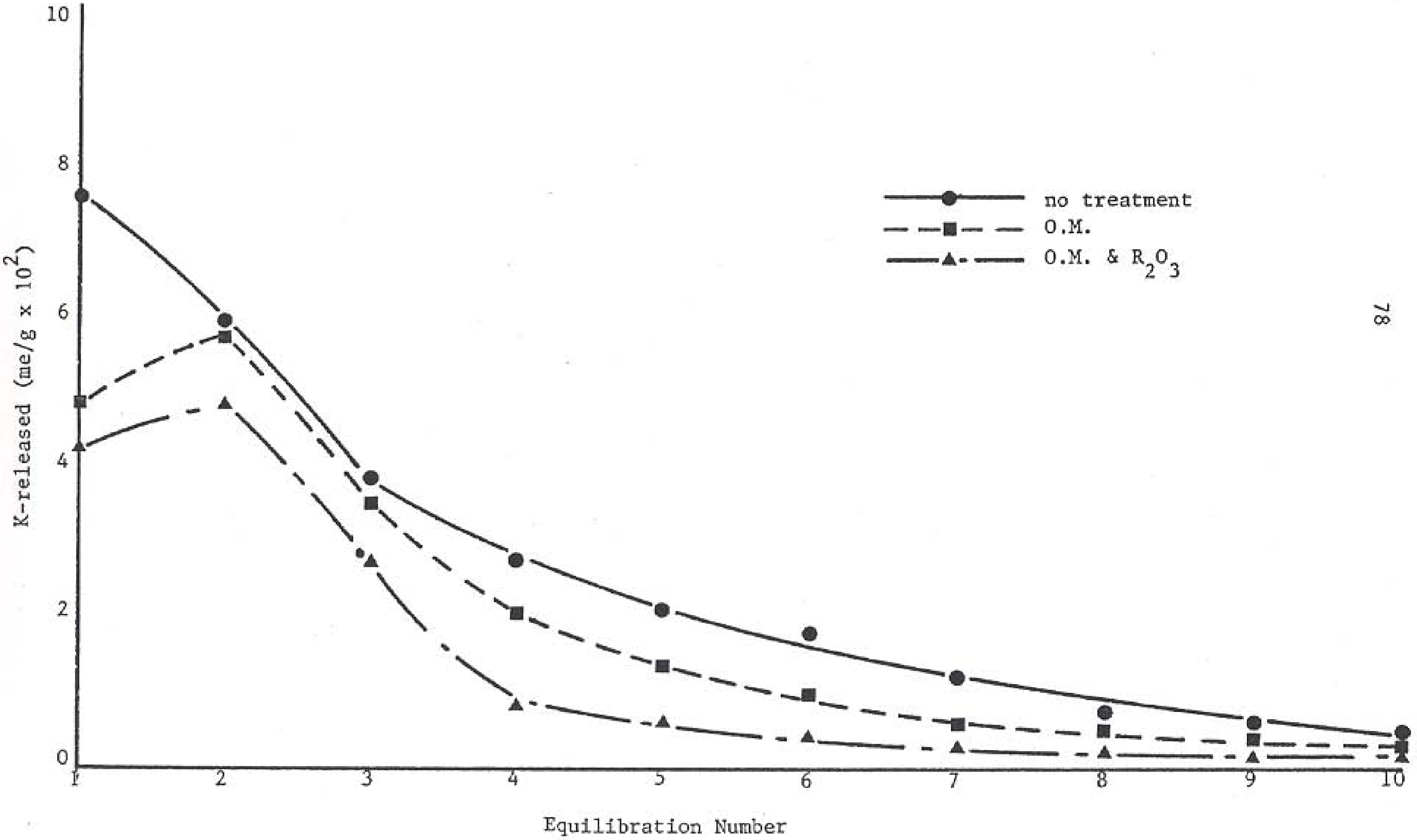


Figure 11 (a). Potassium release from K-saturated Alderwood silt fraction after various treatments ($CaCl_2$ exchange).

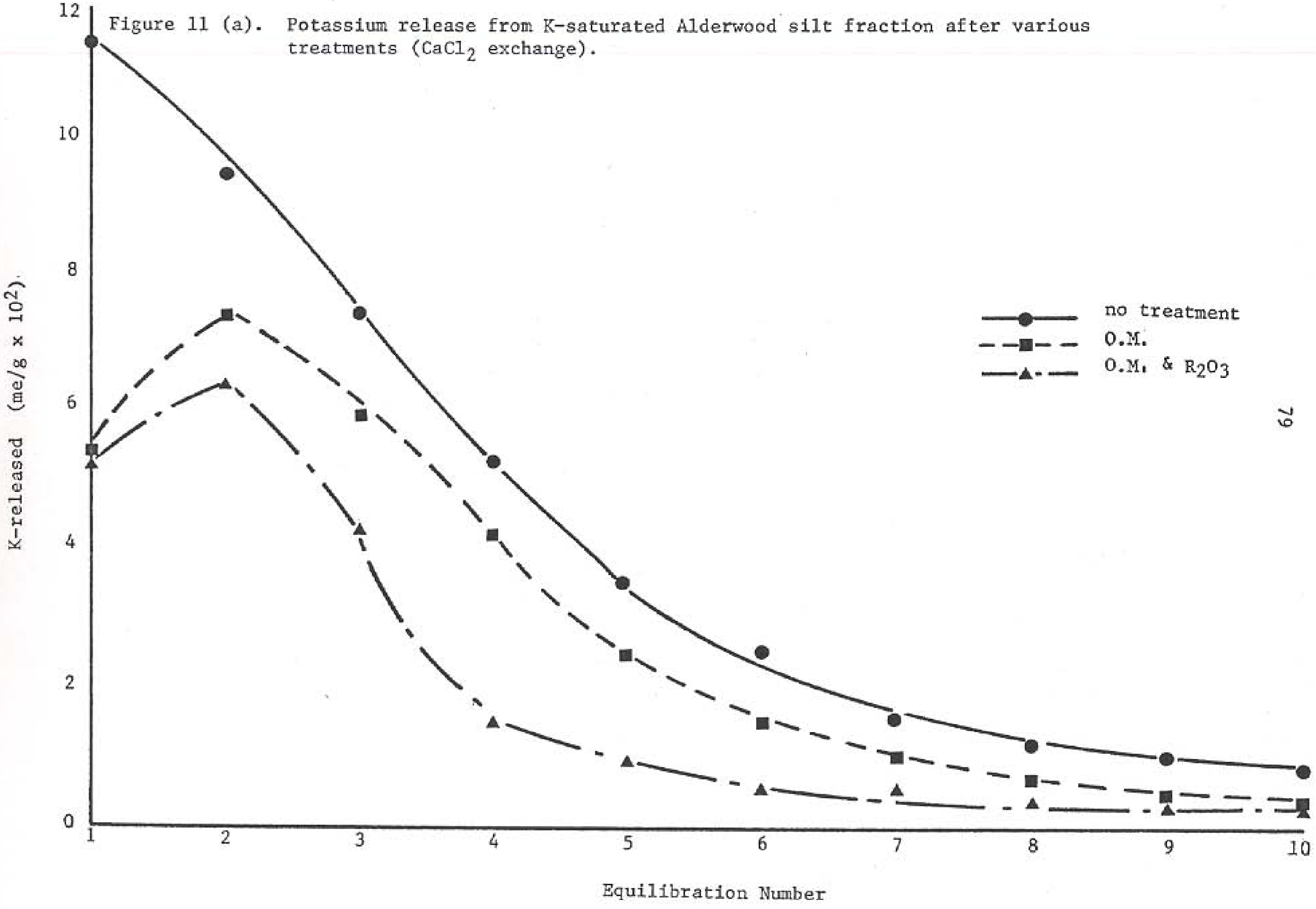
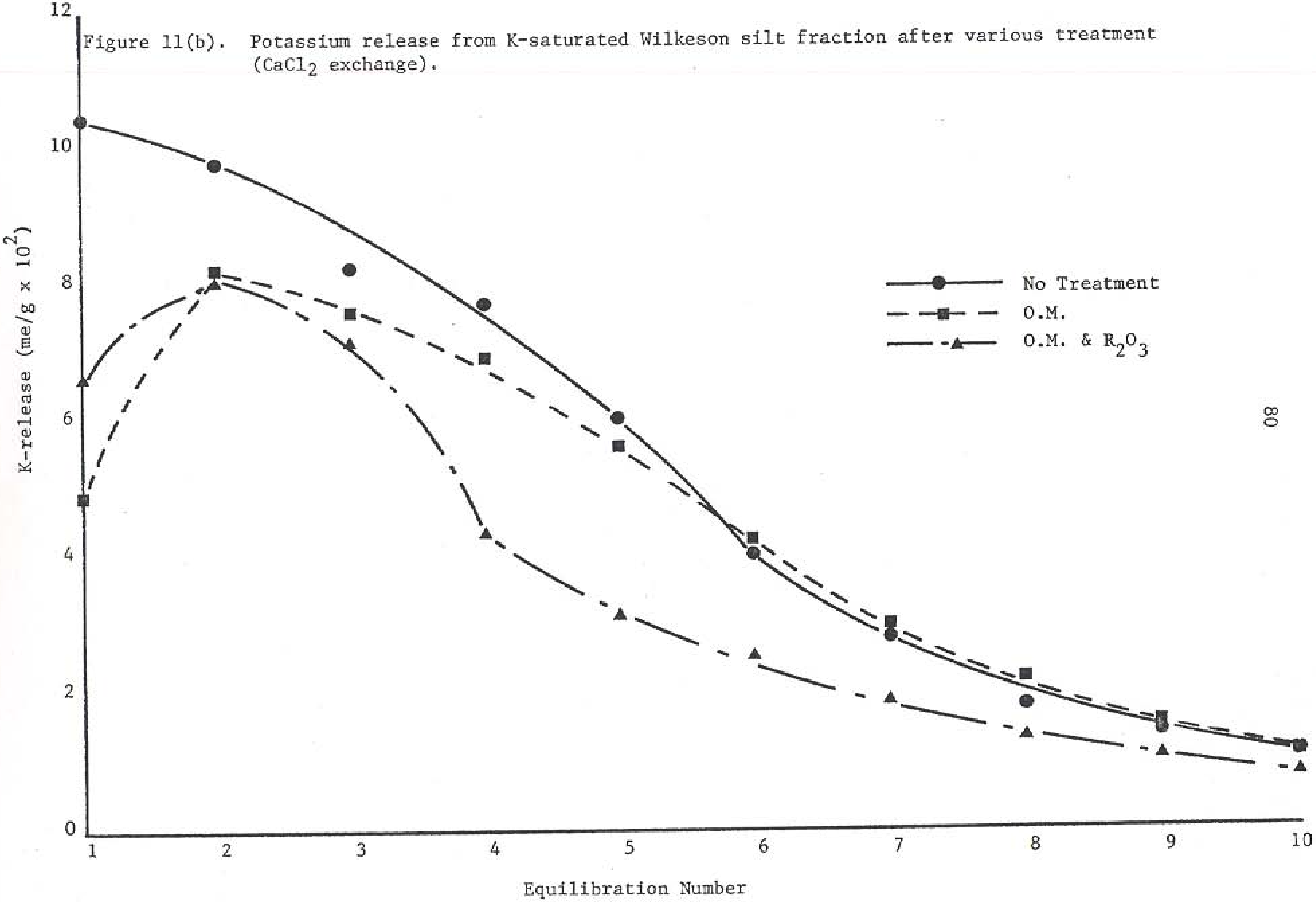


Figure 11(b). Potassium release from K-saturated Wilkeson silt fraction after various treatment ($CaCl_2$ exchange).



considered (Figure 11). As in the case of the Alderwood silt fraction there was evidence to indicate the bonding of exchangeable potassium in the samples without organic material was stronger than in the untreated samples. Desorption of 0.2470 me/g of potassium (exchangeable potassium content of untreated Wilkeson silt fraction) occurred between the second and third equilibrations while it required three to four periods to release the same amount of potassium from the minus organic matter silt samples even though more total exchangeable potassium was present. The reason for the slower potassium release following organic matter removal was the increased bonding strength associated with adsorption sites released by NaOCl treatment.

The organic matter effects in the clay fractions were essentially the same as those in the silt fractions and did not differ significantly between soils. Removal of organic material increased the exchangeable potassium content following K saturation by 0.0690 me/g and 0.3922 me/g in the Wilkeson and Alderwood clay fractions respectively. In both cases the increased exchangeable contents were associated with bonding sites of increased energies. This was represented by lower amounts of potassium exchanged in the minus organic matter samples, expecially during the first two equilibration periods (Figure 12). The Alderwood untreated clay fraction released 0.5834 me/g of potassium within five equilibration periods while six periods were required to remove 0.5732 me/g from the minus organic matter samples. Similar results were obtained from the Wilkeson clay fractions when 0.8722 me/g of potassium was released from the untreated samples compared to 0.7355 me/g from those without the organic material (both after 8 equilibration periods). When the average coefficient of variation (10%) in potassium release during each equilibration period was considered, very little difference occurred between the treated and untreated clay fractions of the two soils after the initial potassium desorption (equilibrations 1 and 2).

Figure 12(a). Potassium release from K-saturated Alderwood clay fraction after various treatments ($CaCl_2$ exchange).

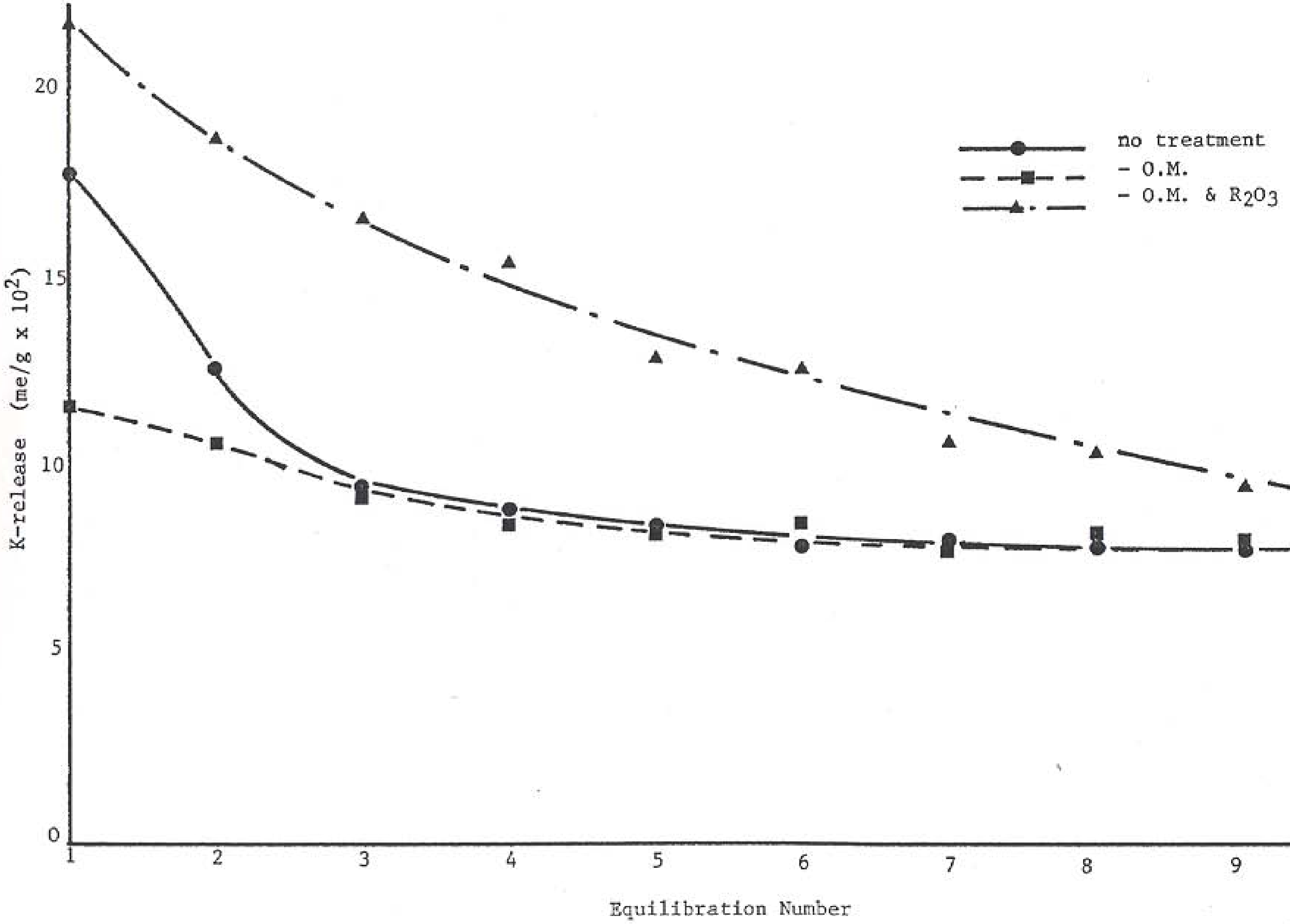
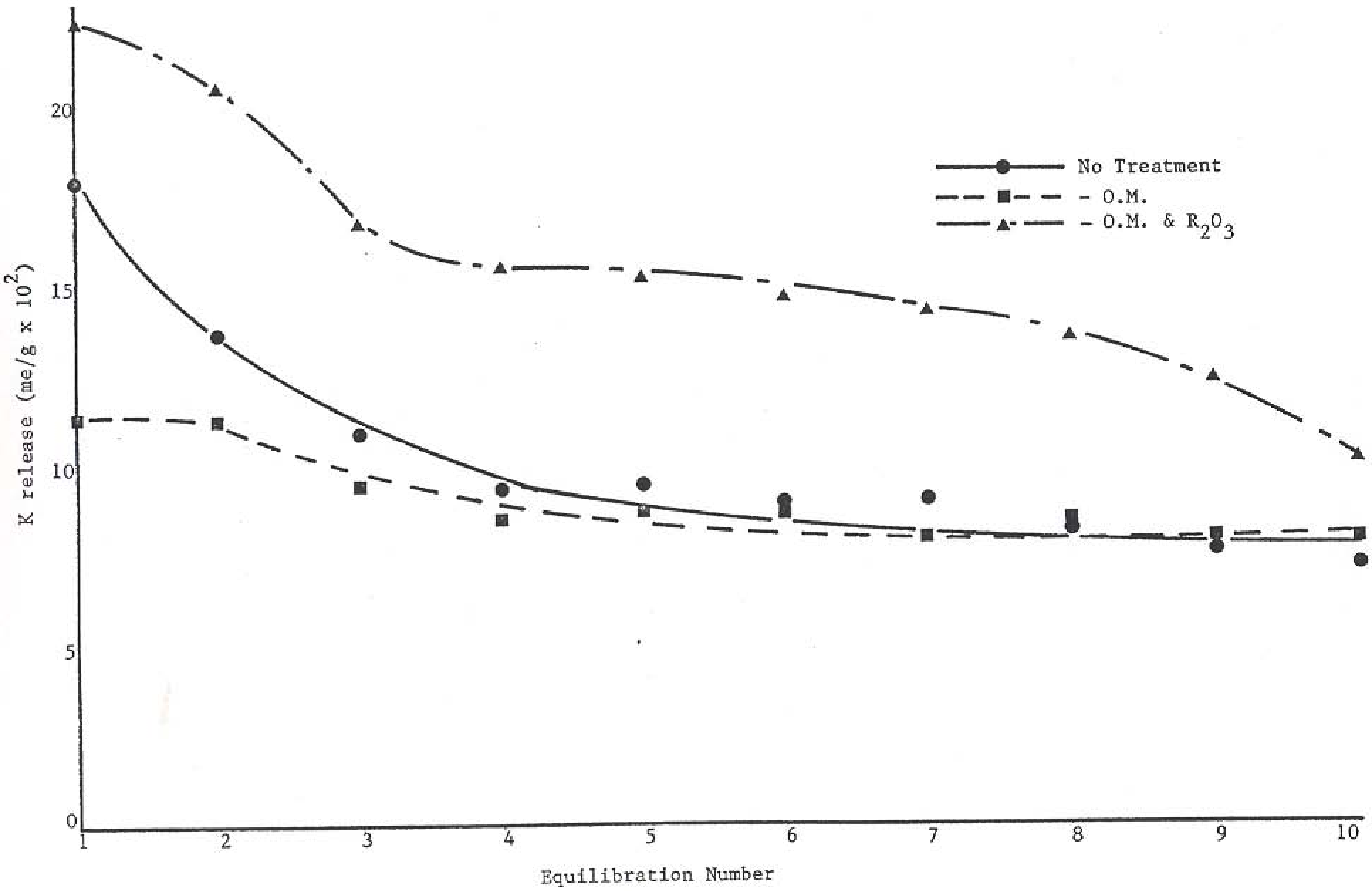


Figure 12(b). Potassium release from K-saturated Wilkeson clay fraction after various treatments ($CaCl_2$ exchange).



Consequently the organic matter effect was principally associated with the exchange sites that responded during the first equilibrations.

The Alderwood and Wilkeson total soils exhibited the greater organic matter effects on potassium desorption than the particle size fractions. Increases of 0.1233 me/g and 0.1669 me/g exchangeable potassium occurred in the Alderwood and Wilkeson soils respectively following organic matter removal and K saturation. The increases in exchangeable potassium did not significantly alter the rate of desorption from the soils (Figure 13) but the quantities released were considerably higher. Although bonding energies were indicated in the exchange sites released by organic matter removal from the individual particle size fractions, this effect was not prevalent in the total soils. This could have been due to masking by the large increases in exchangeable potassium.

### (iii) sesquioxides ($R_2O_3$)

Sesquioxides occur in soils both as surface coatings on soil particles and interlayer adsorbed polymers in expansible layer silicates (Jackson, 1963). Adsorption of sesquioxides onto soil particles in these ways can significantly alter the cation exchange character of the soil. Although iron and aluminum polymers possess some cation exchange capacity (Jackson, 1963) their greatest effect on the ion exchange system is through blockage of surface and interlayer exchange sites. Mehlich (1952) observed differences in calcium release from various types of iron and aluminum compounts (hematite > goethite > bauxite > $Al\ (OH)_3$ > montmorillonite) and removal of iron and aluminum oxides from soils reduced the rate of calcium desorption. The differential release of calcium was attributed to sesquioxide blockage of exchange sites that had stronger bonding energies than those associated with the iron and aluminum materials.

Figure 13(a). Potassium release from K-saturated Alderwood total soil after various treatments ($CaCl_2$ exchange).

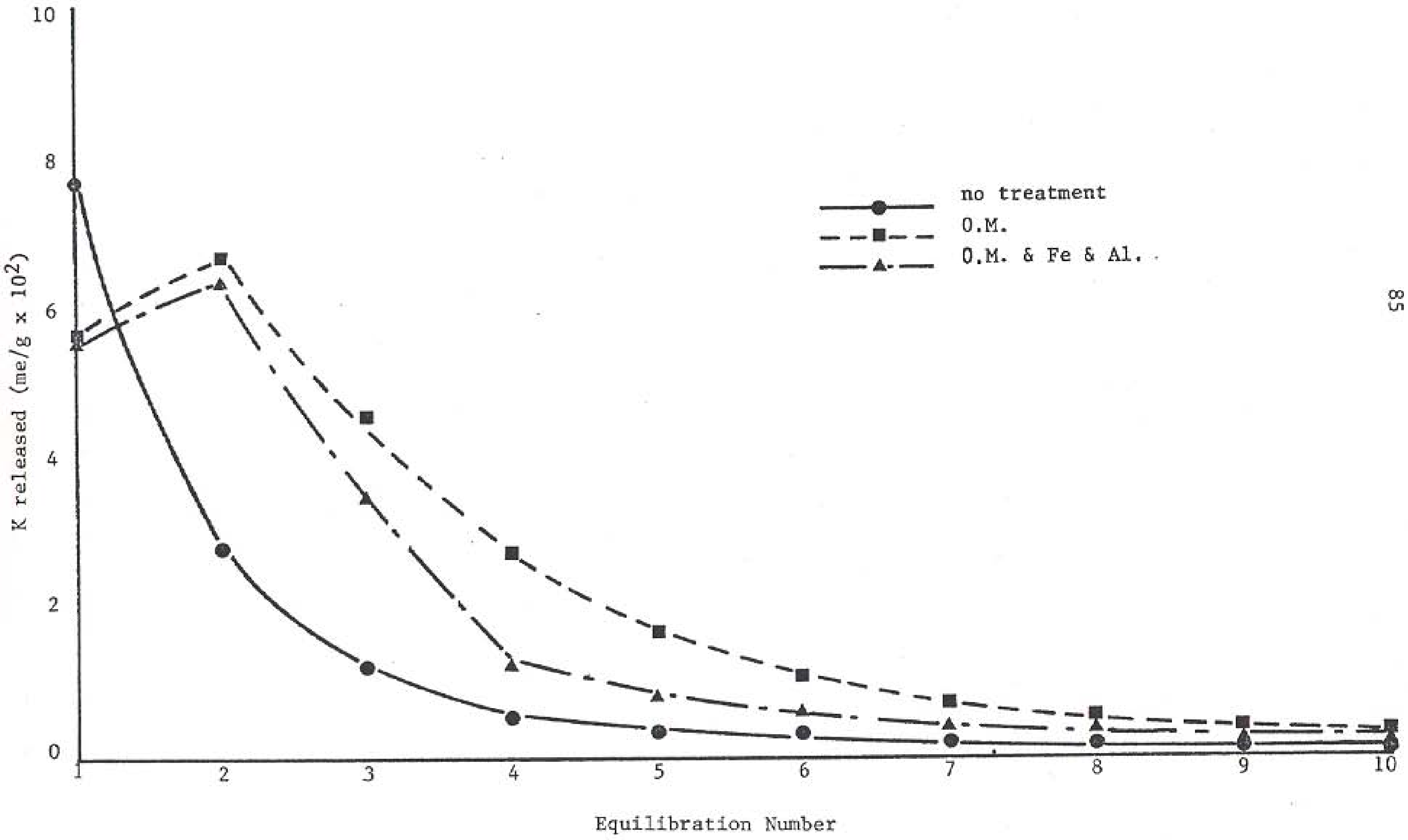
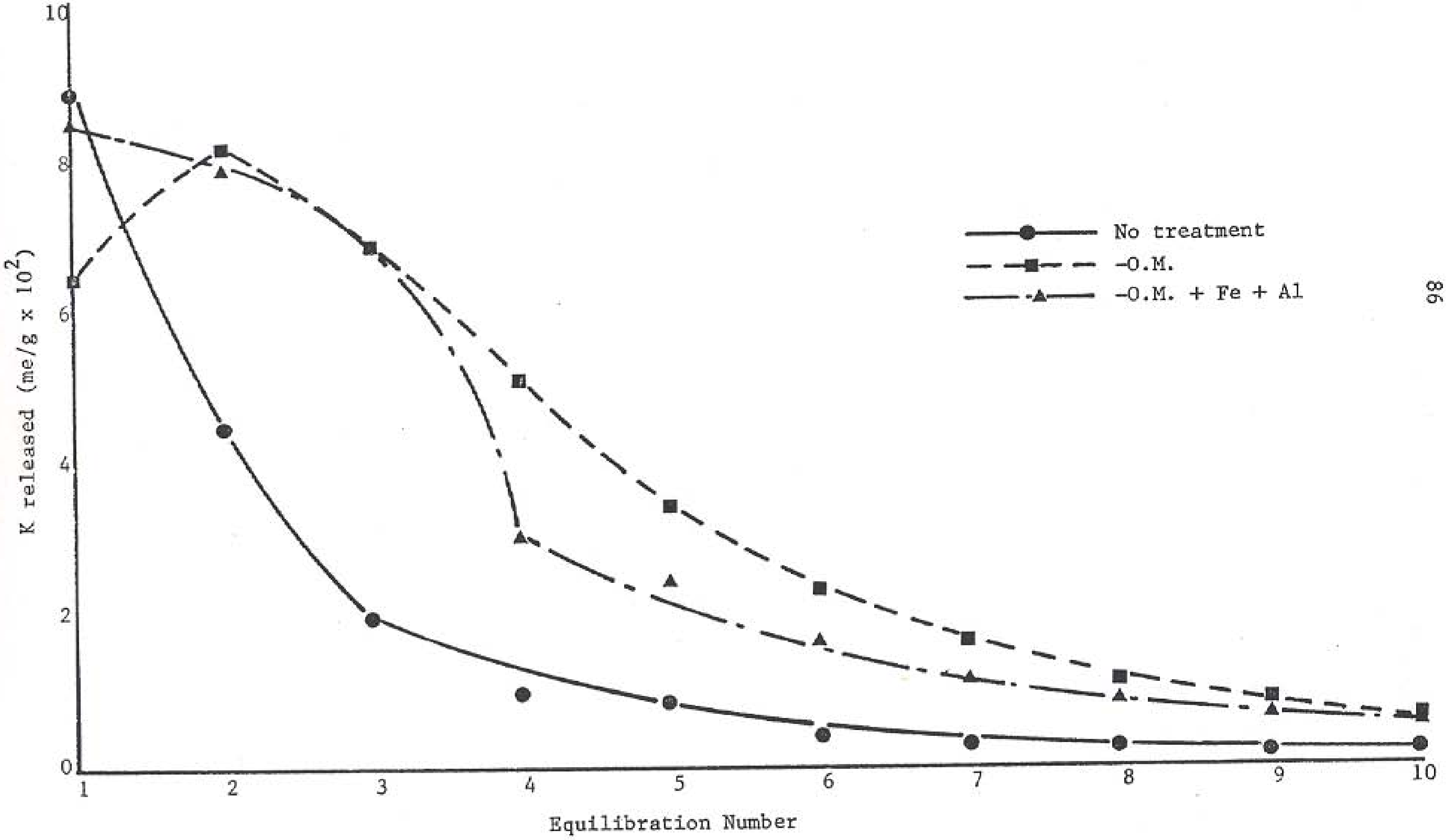


Figure 13(b). Potassium release from K-saturated Wilkeson total soil after various treatments ($CaCl_2$ exchange).



X-ray analysis of expandable clay minerals has indicated the presence of hydroxy polymers in interlayer positions (Jackson, 1963) which affect covering can also occur thereby reducing the cation exchange capacity of the materials (Carstea *et al.*, 1970b; Dixon and Jackson, 1962; Singleton and Harward, 1971).

Potassium saturated Alderwood and Wilkeson particle size fractions with the untreated and minus organic matter samples (Table 12). This discrepancy with the previous investigators' findings of increased exchange capacity following sodium dithionite treatment was a result of the fixation of potassium by the released interlayer exchange sites. Other than the sand fractions decreased exchangeable contents (Table 15). The increases in total potassium could result in potential fixation ranging from 4.68 me/100g (Alderwood silt) to 47.20 me/100g (Wilkeson clay). The decreases in both exchangeable and total contents of the sand fractions could be due partially to loss of exchange capacity associated sand and silt fractions following sesquioxide removal could have been caused by the polymers coating soil particles but not blocking exchange sites.

The Alderwood and Wilkeson total soils both indicated increased potassium fixation after sesquioxides were removed (Table 15)[illegible]ease in exchangeable and an increase in total potassium after $R_2O_3$ removal. The Alderwood total soil had a potential of 4.69 me/100g fixed potassium. Although the total potassium of

Table 15. Changes in exchangeable and total potassium and the potential K fixation between -O.M. and -O.M. and $R_2O_3$ samples in Alderwood and Wilkeson size fractions and total soils (me/100 g).

| | Alderwood | | | | Wilkeson | | | |
|---|---|---|---|---|---|---|---|---|
| | sand | silt | clay | total soil | sand | silt | clay | total soil |
| Exch. K | -2.73 | -3.66 | -4.90 | -3.67 | -1.72 | -2.11 | -4.74 | +1.29 |
| Total K | -2.04 | +1.02 | -41.69 | +1.02 | -3.06 | +1.79 | +42.46 | +6.90 |
| Potential fixed K | - | 4.68 | 46.59 | 4.69 | - | 3.90 | 47.20 | 5.61 |

the Wilkeson total soil increased in the minus $R_2O_3$ samples (6.90 me/100g) so did the exchangeable content (1.29 me/100g) indicating slightly more sesquioxide coating of soil particles than in the Alderwood soil. The increases in total and exchangeable potassium provided a potential of 5.61 me/100g fixed potassium.

Potassium desorption as influenced by sesquioxide removal was expressed by the comparison of the minus organic matter and minus organic matter and sesquioxide samples. The sand and silt fractions of both soils released the least amount of total potassium when the organic matter and sesquioxides were removed (Figures 10 & 11) but the rate of exchangeable potassium desorption was higher than in the minus organic matter samples with the exception of the Alderwood sand fraction. The increased rate of exchangeable potassium release did not indicate exchangeable adsorption sites having increased bonding energies as proposed by Mehlich (1952). Ionic equilibria considerations could have caused the increased rate of potassium desorption since the amount of potassium released would be a function of the quantity of exchangeable forms. The minus $R_2O_3$ samples had less exchangeable potassium but the equilibrating solution remained the same in all sample equilibrations. Therefore the removal of the readily exchangeable potassium was completed more rapidly when larger quantities were present.

Release of nonexchangeable potassium from the minus sesquioxide sand and silt fractions was at a lower rate compared to the samples with only organic matter removed, with the exception of the Wilkeson silt fraction. Stronger ionic bonding and potassium fixation were indicated when the total potassium content increased but the rates and quantities of potassium released decreased. The fixation component could have accounted for the discrepancy between the results of this study and that of Mehlich (1952) relative to bonding energies associated with adsorption sites released by $R_2O_3$ removal. The presence of potassium fixation was supported by increased negative changes in free energy as shown by the Wilkeson samples (Table 7) and the x-ray diffractograms of the Alderwood and Wilkeson samples (Figures 14 & 15). X-ray analysis of the silt, clay and total soil samples before and after the 10 equilibration periods showed differential collapse of the 2:1 layer silicates after heating at 300°C. Greater collapse occurred in the unequilibrated samples due to the presence of considerable interlayer potassium. The smallest degree of difference in lattice collapse occurred in the clay fractions where only small amounts of interlayer potassium were replaced by the magnesium. The differences in potassium release from the minus organic matter and minus organic matter and sesquioxide sample were becoming less by the tenth equilibration period (Figures 10 & 11). Projecting these desorption curves one could see that once the native "fixed" potassium was reached the effects of organic matter and $R_2O_3$ would be negligible.

The clay fractions had the greatest amount of potential "fixable" potassium following organic matter and sesquioxide removal with 46.59 me/100g and 47.20 me/100g for the Alderwood and Wilkeson fractions respectively. It appeared from these values that sesquioxides consisted of surface coatings and interlayer polymers associated with the clay particles. The adsorption sites made available by sesquioxide removal did not appear to have significantly greater bonding energies. Decreases of only 4.90 me/100g and 4.74 me/100g exchangeable potassium in the Alderwood and Wilkeson fractions respectively occurred when sesquioxides were removed in addition to organic matter. However all the exchangeable potassium was removed from the clay fractions within six equilibration periods and at greater rates than from the minus organic matter only samples. The rate of nonexchangeable potassium desorption did not differ significantly from that of the exchangeable forms. The lack of more strongly held fixable potassium following sesquioxide

Figure 14(a). X-ray diffractograms of Alderwood silt and clay K-saturated samples ($R_2O_3$ and organic matter removed) before and after 10 equilibrations with 0.02N $MgCl_2$ (samples heated to 300°C before x-ray analysis).

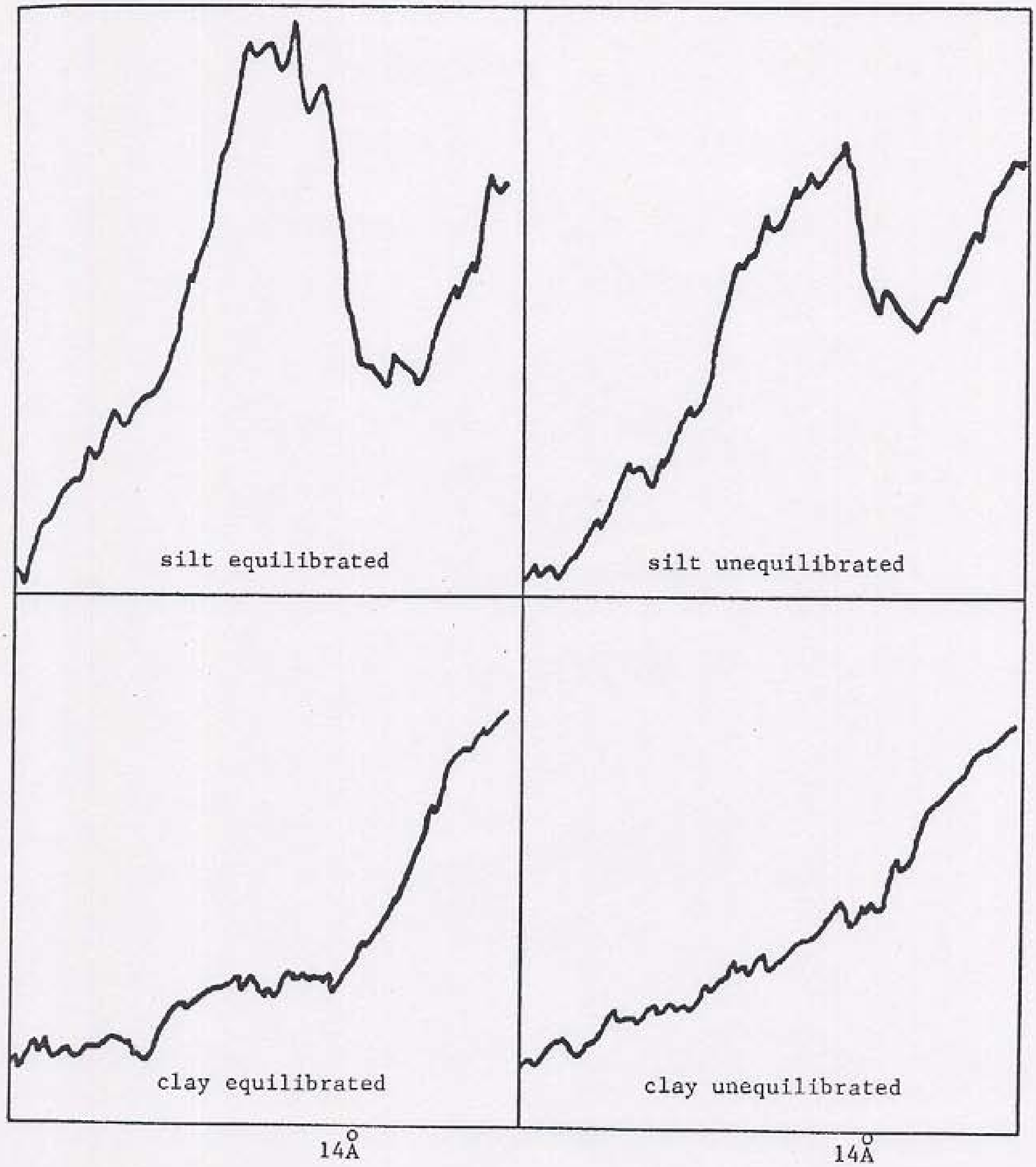


Figure 14(b). X-ray diffractograms of Wilkeson silt and clay K-saturated samples ($R_2O_3$ and organic matter removed) before and after 10 equilibrations with 0.02 N $MgCl_2$ (samples heated to 300°C before x-ray analysis).

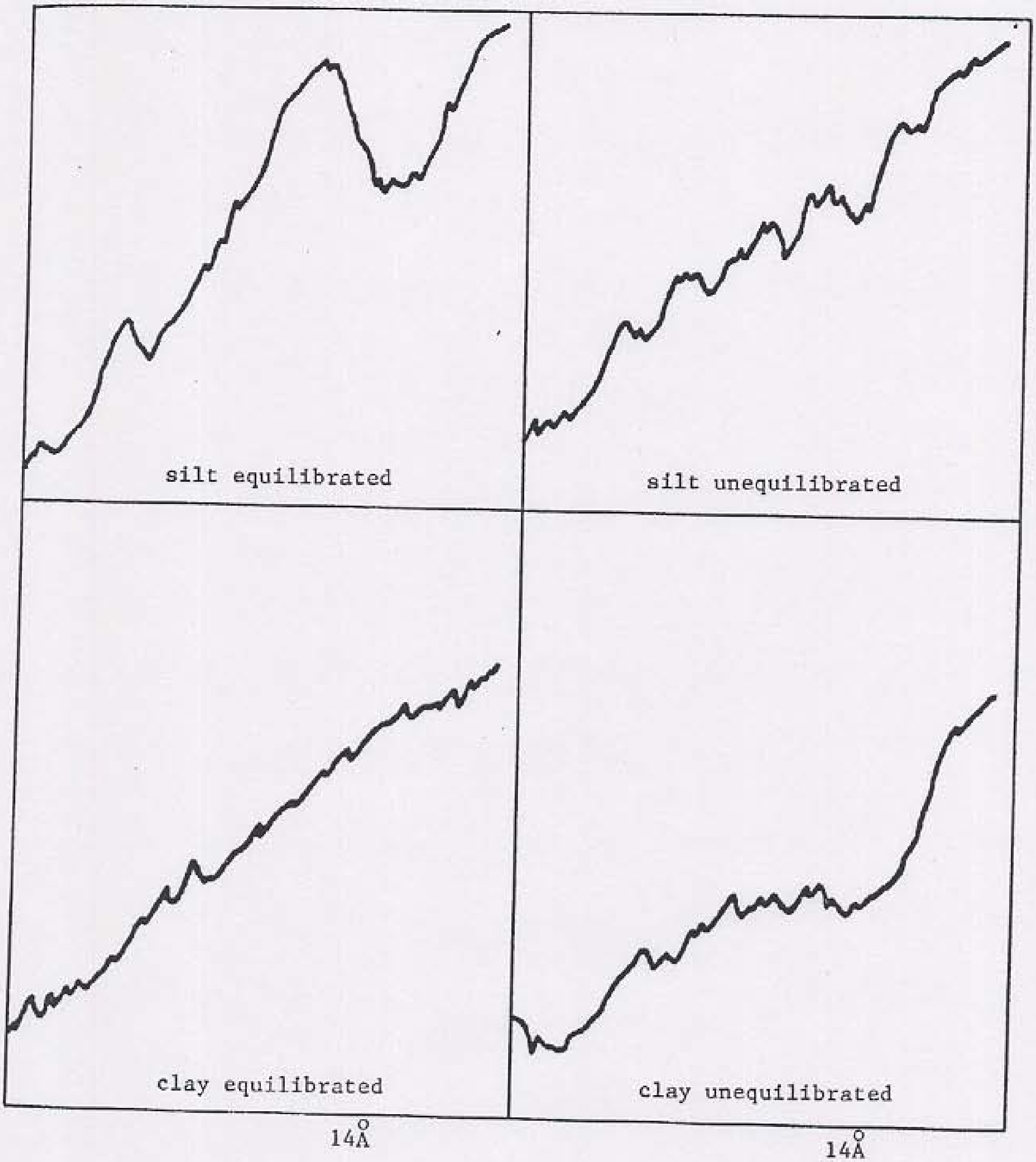
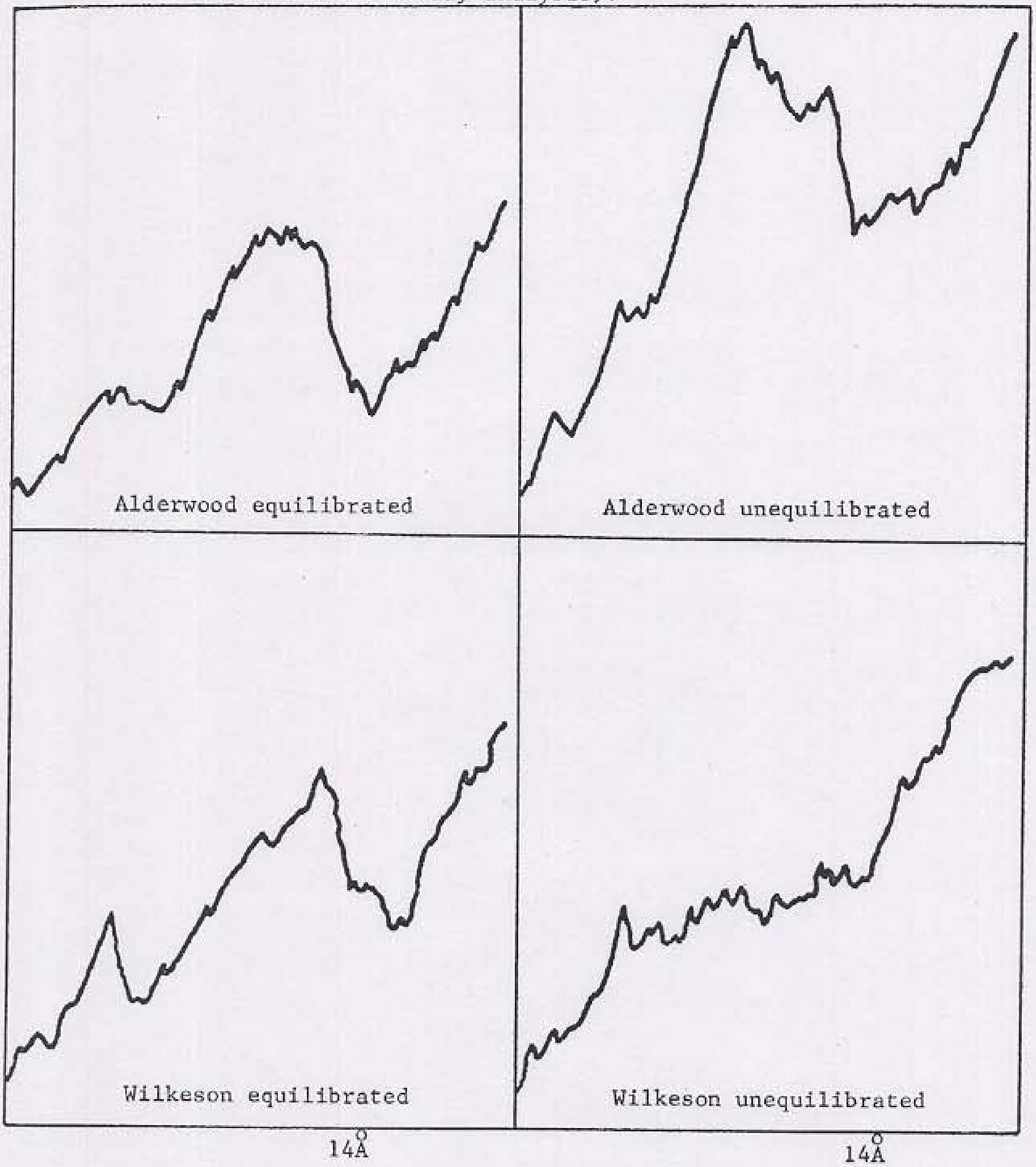


Figure 15. X-ray diffractograms of Alderwood and Wilkeson K-saturated total soil samples ($R_2O_3$ and organic matter removed) before and after 10 equilibrations with 0.02N $MgCl_2$ (samples heated to 300°C before x-ray analysis).



removal may have been due to the short period of time between potassium saturation and equilibration (Agarwal, 1960).

Alderwood and Wilkeson total soils exhibited potassium release retationships similar to those of the sand and silt fractions (Figure 13) since these fractions constituted the major components of the total soils. In both soils the amount of potassium released was less from the samples without sesquioxides compared to those minus organic matter only. Again the exchangeable potassium was desorbed more readily from the samples without sesquioxides but the nonexchangeable forms were released at a lower rate than the minus organic matter samples. Potential potassium fixation increased to 4.69 me/100g and 5.61 me/100g for the Alderwood and Wilkeson total soils respectively following $R_2O_3$ removal. Slightly stronger bonding energies were involved in the adsorption of nonexchangeable potassium in the minus $R_2O_3$ total soil samples as indicated by the changes in free energy (Table 7).

### (b) Solution characteristics

#### (i) cation type

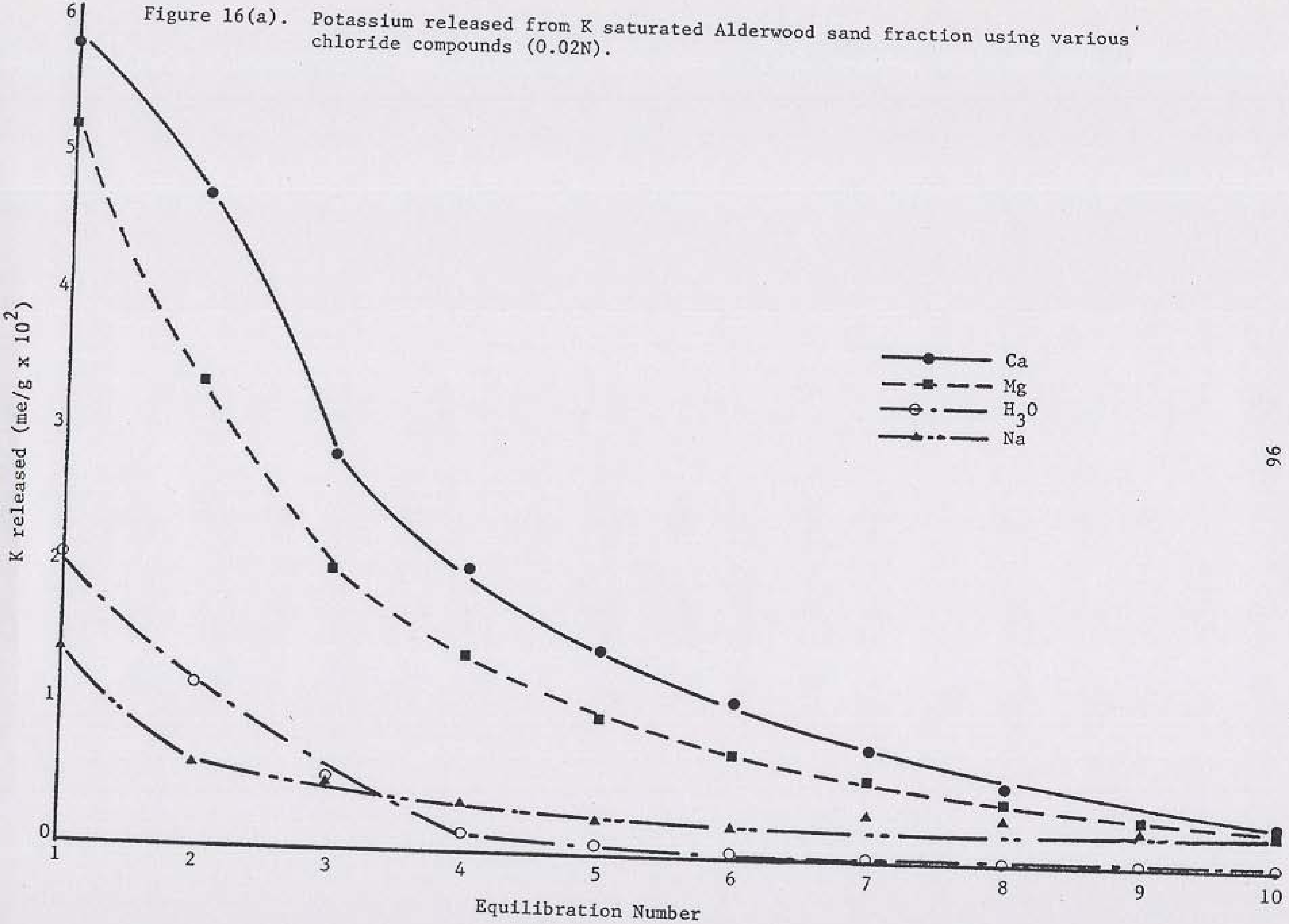
Ion release or exchange from soil particles has shown to be affected by the type of cation present in the equilibrating solution (Bolt, 1967; Helfferich, 1962; Wiklander, 1965). The importance of knowing the relative replacing abilities of one cation for another is obvious when mineral cycling abilities of one cation for another is obvious when mineral cycling and ion release studies are considered. Foscolos (1968) reported variations in relative replacing powers of cations depending on the clay mineral considered and as explained earlier the release of potassium from certain 2:1 clay minerals is affected by cation size. Consequently the release of potassium from the Alderwood and Wilkeson soils and particle size fractions by different cations was important for further ion release studies.

The cations considered for the particle size fractions and total soils were calcium, magnesium and sodium since these were the major cations present in lysimeter leachates (Bourgeois and Lavkulich, 1972; Cole, unpublished data). Aluminum, ammonium and hydronium ions were also considered for the total soils so as to provide an approximate lyotropic series for the soils. The effect of cation type on potassium release was reported on the untreated potassium saturated samples only, since the relationships held true for the samples without sesquioxides and/or organic matter.

Calcium and magnesium had similar potassium replacing abilities in all samples and were more efficient than sodium. These results agreed with the general replacing power sequence proposed by Kelley (1952). In the particle size fractions of both soils calcium desorbed slightly more potassium than did magnesium (Figures 16 & 17) especially when the average coefficients of variation were considered (Table 16). However the consistently higher quantities of potassium released by calcium cannot be ignored, therefore calcium was considered slightly more efficient than magnesium in desorbing potassium.

Calcium and magnesium were both able to remove all the exchangeable potassium from the samples (except the clay fractions) within 3 equilibration periods. Although the hydrated ionic sizes of calcium and magnesium were 9.6 Å and 10.8 Å respectively (Grim, 1953) they were able to remove nonexchangeable potassium from all particle size fractions. The pH of the equilibrating solutions was 5.6 consequently a considerable concentration of hydronium ions was present. Rich and Black (1964) suggested that cations larger than the potassium ion can release interlayer potassium through the action of hydronium ions. They reported magnesium releasing as much interlayer potassium as did ammonium ions when the pH of the magnesium solution was lowered below neutral.

Figure 16(a). Potassium released from K saturated Alderwood sand fraction using various chloride compounds (0.02N).



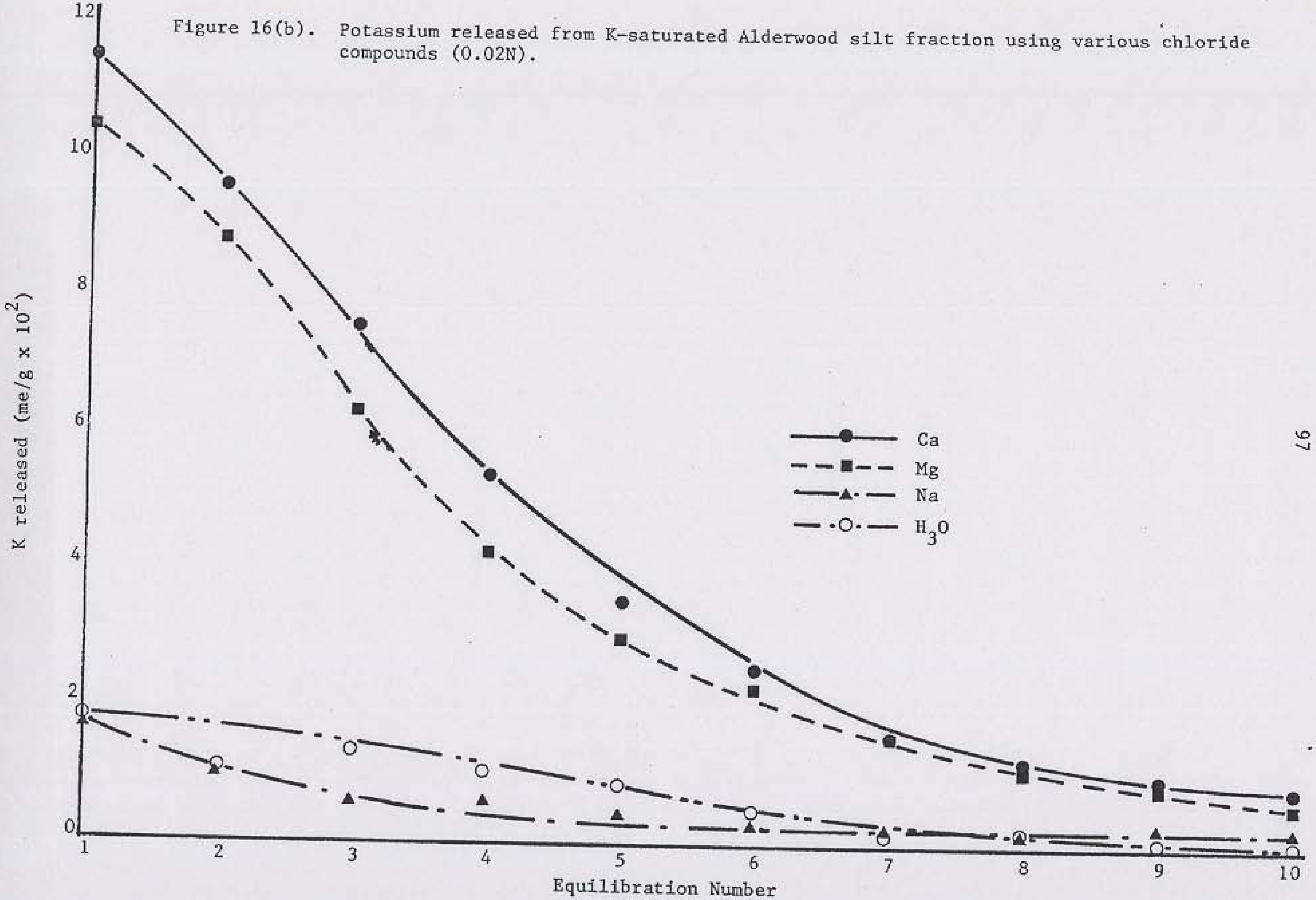


Figure 16(b). Potassium released from K-saturated Alderwood silt fraction using various chloride compounds (0.02N).

Figure 16(c). Potassium released from K-saturated Alderwood clay fractions using various chloride compounds (0.02 N).

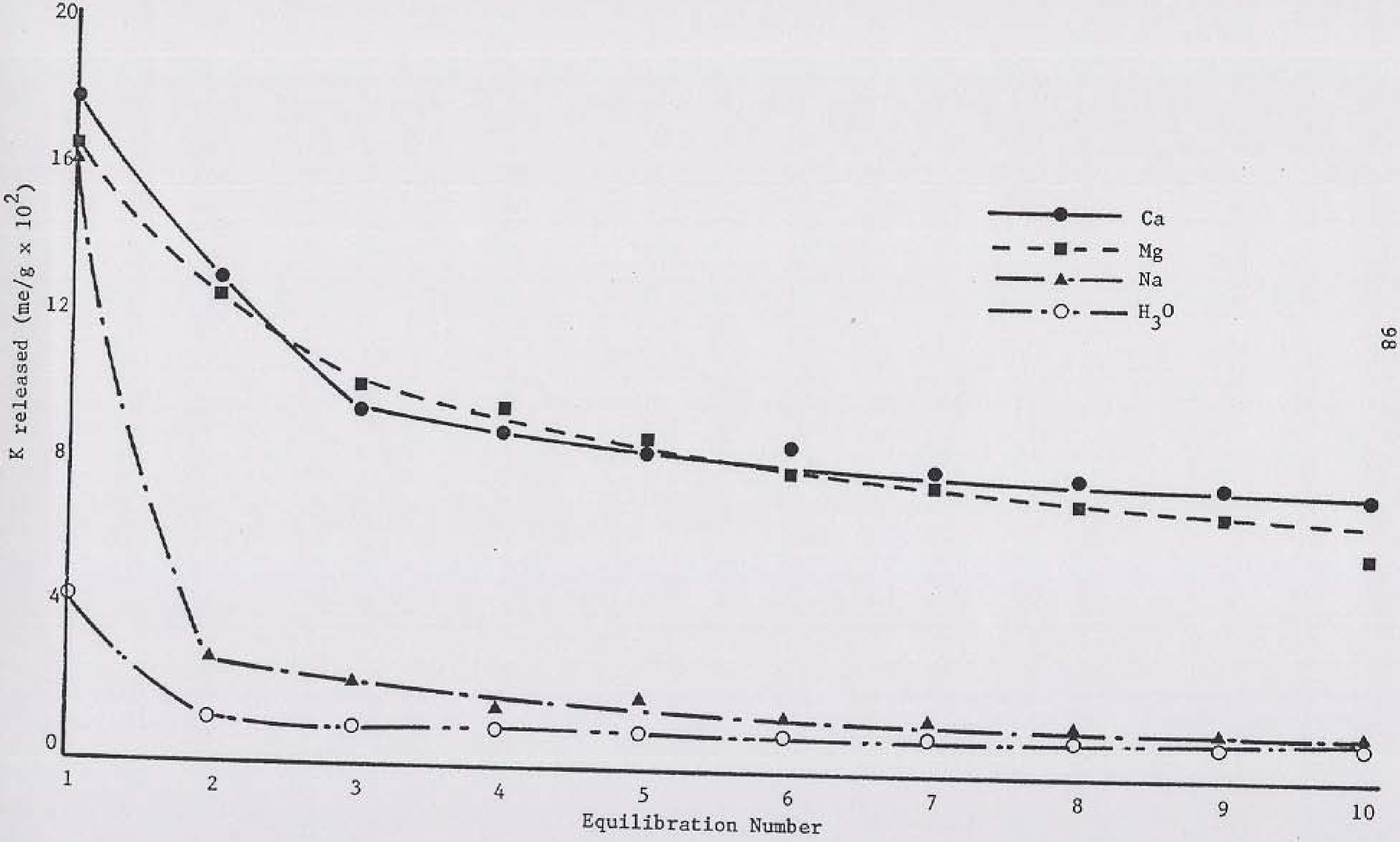
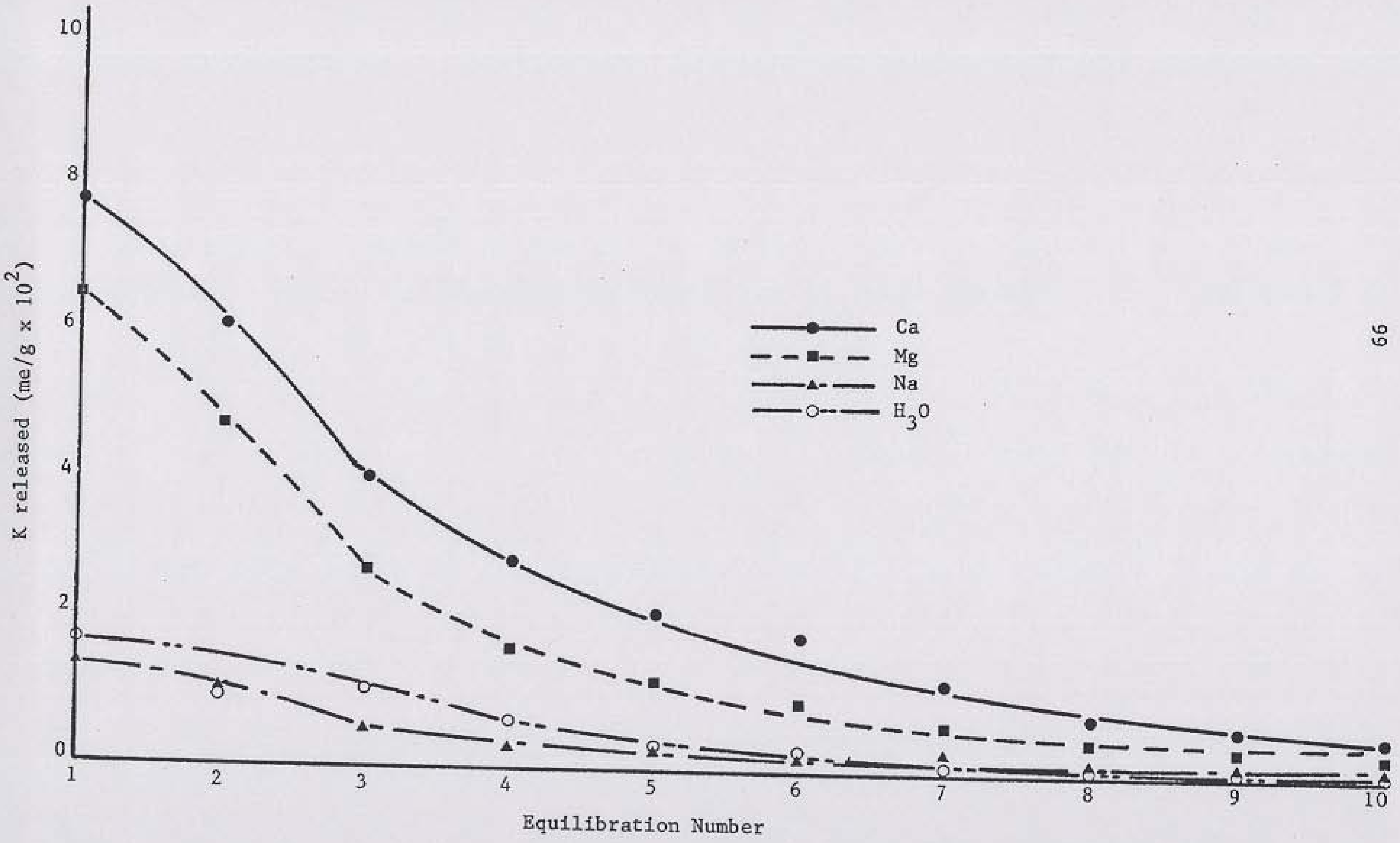


Figure 17(a). Potassium released from K-saturated Wilkeson sand fraction using various chloride compounds (0.02N).



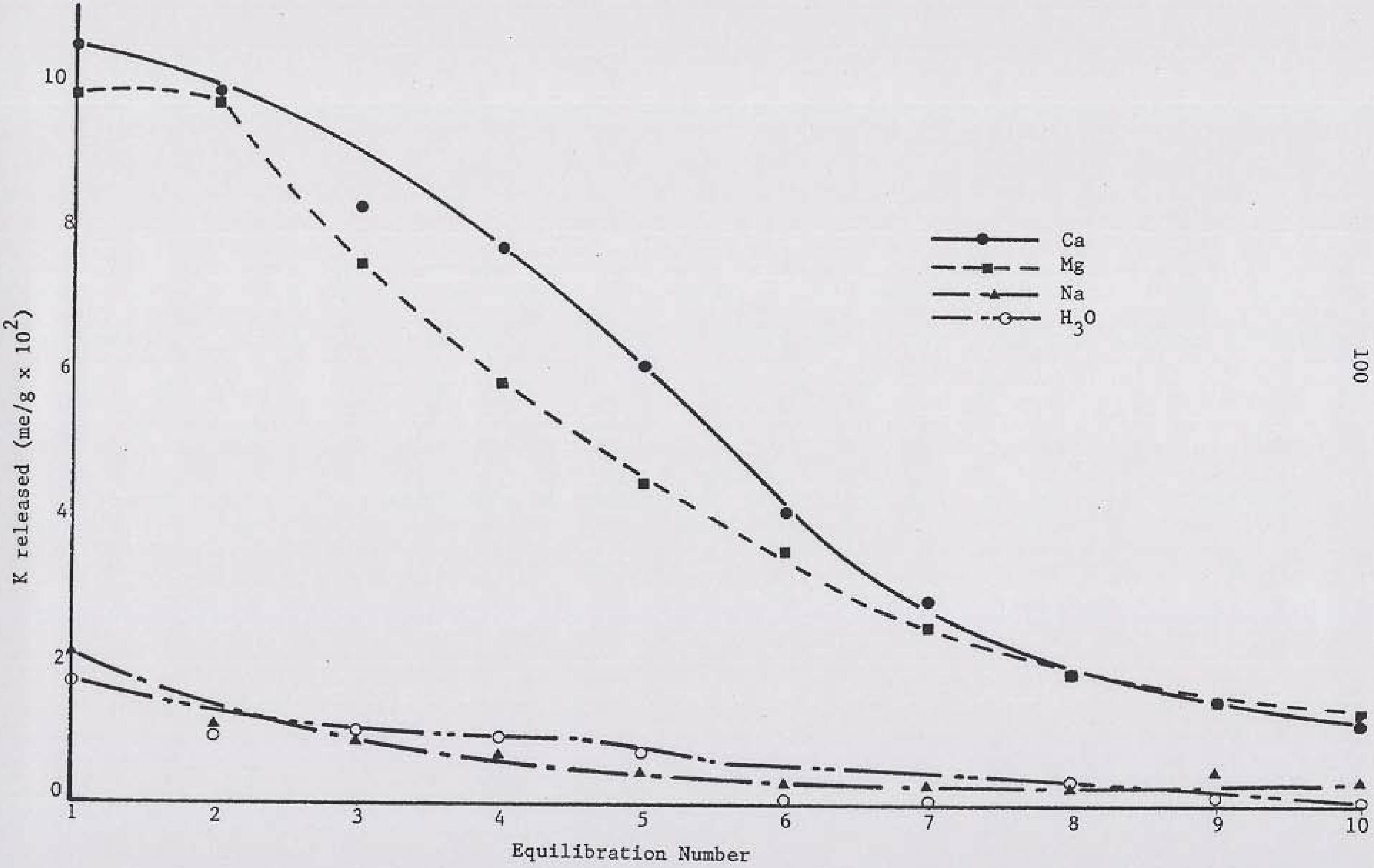


Figure 17(b). Potassium released from K-saturated Wilkeson silt fraction using various chloride compounds (0.02N).

Figure 17(c). Potassium released from K-saturated Wilkeson clay fraction using various chloride compounds (0.02N).

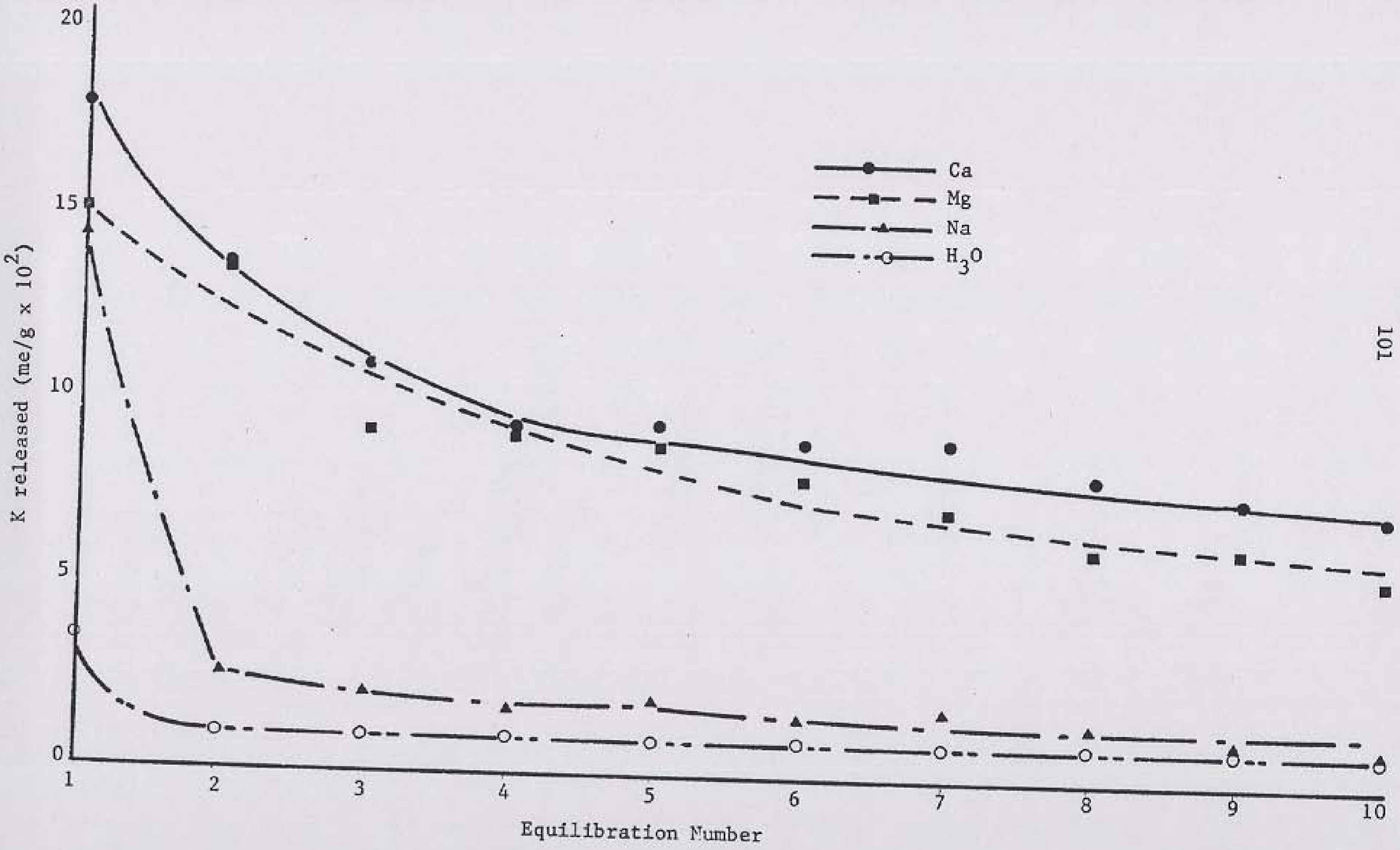


Table 16. Average coefficients of variation in potassium release and ratios of potassium released by various cations relative to calcium over 10 equilibration periods.
(0.02N concentrations were used.)

| Soil | Fraction | Ca/Mg | Ca/Na | Ca/$H_3O$ | Ca/Al | Ca/$NH_4$ | C.V.(%) |
|---|---|---|---|---|---|---|---|
| Alderwood | sand | 1.3 | 4.1 | 15.1 | | | 20.8 |
| | silt | 1.1 | 7.5 | 8.4 | | | 8.1 |
| | clay | 1.0 | 4.9 | 8.7 | | | 9.8 |
| | total | 1.0 | 4.4 | 10.4 | 1.7 | 5.5 | 13.7 |
| Wilkeson | sand | 1.7 | 6.9 | 8.1 | | | 13.8 |
| | silt | 1.1 | 7.0 | 21.6 | | | 8.3 |
| | clay | 1.2 | 5.3 | 8.2 | | | 9.6 |
| | total | 0.8 | 5.2 | 11.0 | 1.9 | 8.5 | 16.0 |

Sodium was much less efficient than calcium at removing potassium from the samples (Table 16). The differences were such that 0.02N NaCl was not able to desorb all the exchangeable potassium even after 10 equilibration periods. The potassium desorption curves (Figures 16 & 17) showed significant decreases in potassium release during the first 3 equilibrations but very little change in the final 7 periods indicating that the soil particles preferred potassium to sodium. A similar rapid decrease in potassium exchanged by sodium was observed by Merwin and Peech (1950) but sodium also replaced more potassium than did calcium and magnesium.

The hydronium ion was the least efficient of all the cations considered in releasing potassium (Figures 16 & 17). The pH of the 0.02 N HCl equilibrating solution was 1.9 which could have caused release of aluminum hydroxy cations (e.g. $Al\ (OH)_2^+$) (Jackson, 1963) which acted as the exchanging ion rather than $H_3O^+$. Therefore it was not the hydronium ion but an aluminum hydroxy cation that was compared with the other cations. After 2 or 3 equilibrations, problems with soil dispersion were encountered in the potassium release technique. This could probably have been the result of the large hydroxy cation increasing the zeta potential of the soil particles. The lower quantities of potassium removed by 0.02N HCl was not a result of aluminum hydroxy polymer blockage of interlayer potassium as indicated by Rich and Black (1964). As in the case of sodium release of potassium, all the exchangeable forms were not removed after 10 equilibrations, therefore nonexchangeable potassium was not directly involved in the potassium release.

An approximate lyotropic series was established for the Alderwood and Wilkeson total soils using 0.02N chloride solutions. Figure 18 shows the release of potassium by the various electrolytes ($Ca{=}Mg{>}Na{>}NH_4{>}\ H_3O$). Although the quantities of potassium released by each cation type varied between soil, the general order of replacing ability was the same. Foscolos

Figure 18(a). Potassium release from untreated K-saturated Alderwood total soil using 0.02N electrolyte concentrations.

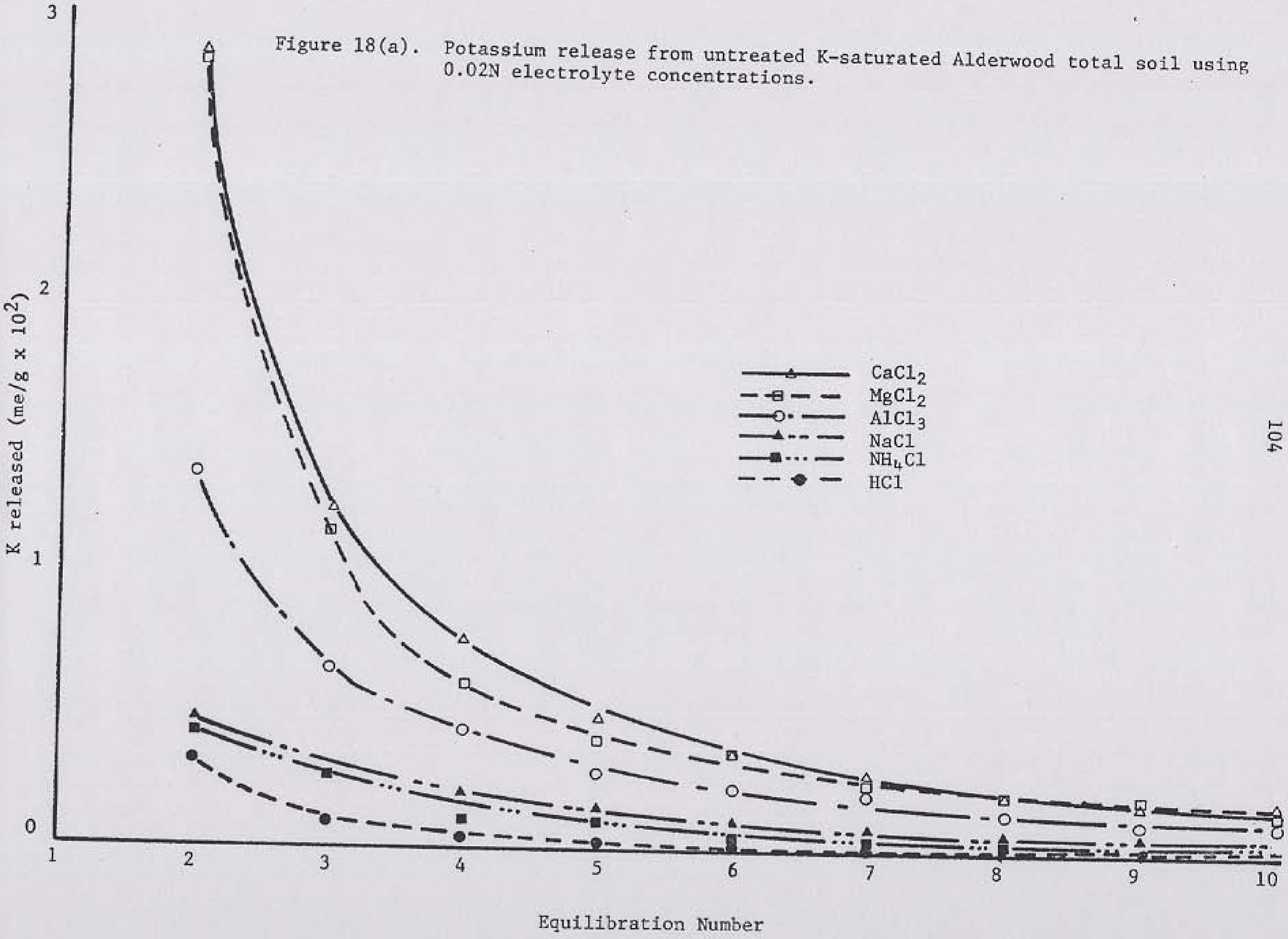
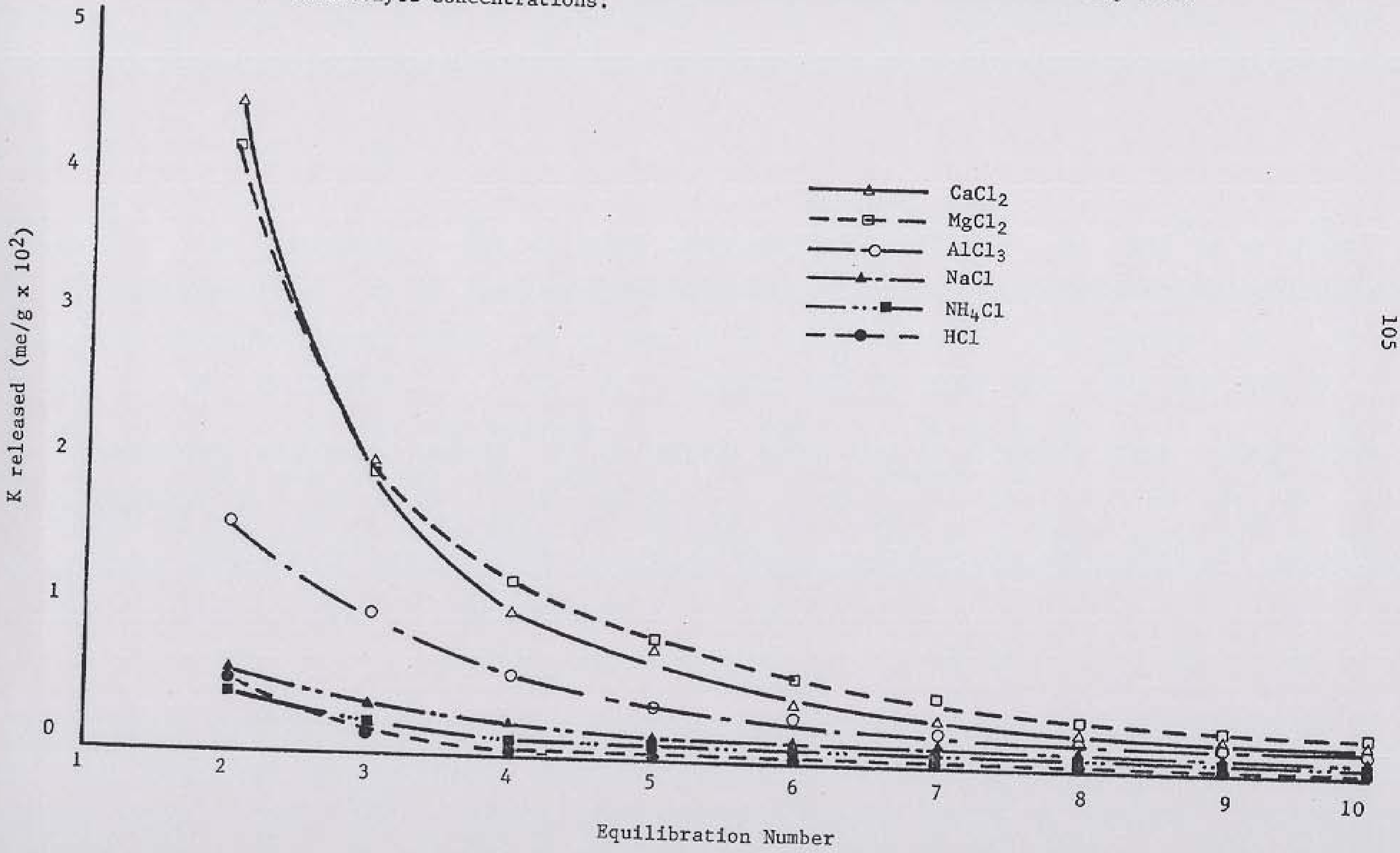


Figure 18(b). Potassium release from untreated K-saturated Wilkeson total soil using 0.02N electrolyte concentrations.



(1968) reported a similar sequence using vermiculite ($Mg>Ca>H_3O>Al>Na$). The low positioning of aluminum and hydronium in the lyotropic series could possibly have been due to $Al(OH)_2^+$ exchange rather than $Al^{+3}$ and $H_3O^+$. Ionic size and charge factors have been reported as reasons for aluminum and hydronium being high on the relative replacing sequence (Grim, 1953; Wiklander, 1965), however the presence of aluminum hydroxy cations would reduce the emphasis of these two criteria. Adsorption of incompletely dissociated metal hydroxide ions in soils has been suggested by Bower and Truog (1940), Carlson and Overstreet (1967), Coulter (1969) and Wiklander (1965). Another discrepancy observed in the release of potassium was the positioning of $NH_4$. The ionic size and charge of the ammonium ion are similar to those of potassium, therefore $NH_4$ is generally positioned below K but above Na in the lyotropic series; (Gilbert and Laudelout, 1965; Grim, 1953; Kelley, 1948; Wiklander, 1965). All the exchangeable potassium was not removed from either of the soils through the 10 equilibration periods so the effectiveness of $NH_4$ on releasing nonexchangeable potassium was not of consideration. The preference of the soils for ammonium ion appeared lower than both potassium and sodium. The potassium ion could be placed between magnesium and aluminum for a complete lyotropic series for the Alderwood and Wilkeson total soils.

### (ii) anion type

Electrical neutrality must always be maintained in any ion exchange reaction, therefore cation desorption is dependent upon the amount of anionic charges present in the soil solution. Thomas (1960) suggested that the desorption of cations was related to the strength of anion adsorption such that as soil preference for an anion increases the extent of cation desorption decreases. The relative strength of anion adsorption is pH dependent but the pH effect varies with anion type (Wiklander, 1965). Wiklander (1965) reported

Cl adsorption increasing from 0.3 me/100g at pH 6.7 to 4.4 me/100g at pH 5.0 while $SO_4$ adsorption increased from 2.0 me/100g to 10.5 me/100g in the same pH range.

Potassium desorption from the particle size fractions of the two soils varied with the type of sodium compound used in the exchanging solution. In all the particle size fractions sodium chloride released less potassium than either sodium bicarbonate or sodium sulfate (Figures 19 & 20). However the relative effectiveness of these latter two electrolytes in desorbing potassium varied with the soil type. In the Alderwood particle size fraction samples the bicarbonate anion was more effective than sulfate while the reverse was true in the Wilkeson fractions. Sodium bicarbonate removed an average of 15%, 31% and 11% more potassium from the Alderwood sand, silt and clay fractions respectively than did sodium chloride. The Wilkeson sand and silt fractions released 34% and 17% more potassium respectively when subjected to the bicarbonate compound compared to sodium chloride. Over the 10 equilibration periods essentially the same amount of potassium was removed from the Wilkeson clay fraction by sodium bicarbonate and sodium chloride.

No reference to the effects of bicarbonate ion on cation exchange or the position of the ion relative to other anions in adsorptive bonding were found. However Sommerfeldt (1962) reported carbonate ion to be less effective than chloride and sulfate in desorbing cations. The importance of the bicarbonate anion in ion movement in soils has been indicated by the compositions of lysimeter waters. Bourgeois (1969) and McColl and Cole (1968) observed strong relationships between cation and bicarbonate concentrations in leachates.

The greatest increases in potassium released by sulfate over chloride were in the Wilkeson particle size fractions, especially the sand and silt fractions where 72% more potassium was removed. Sodium sulfate removed 16% more potassium from the Wilkeson clay fraction than did the chloride form,

Figure 19(a). Potassium release from untreated K-saturated Alderwood sand fraction using various Na compounds (0.02N).

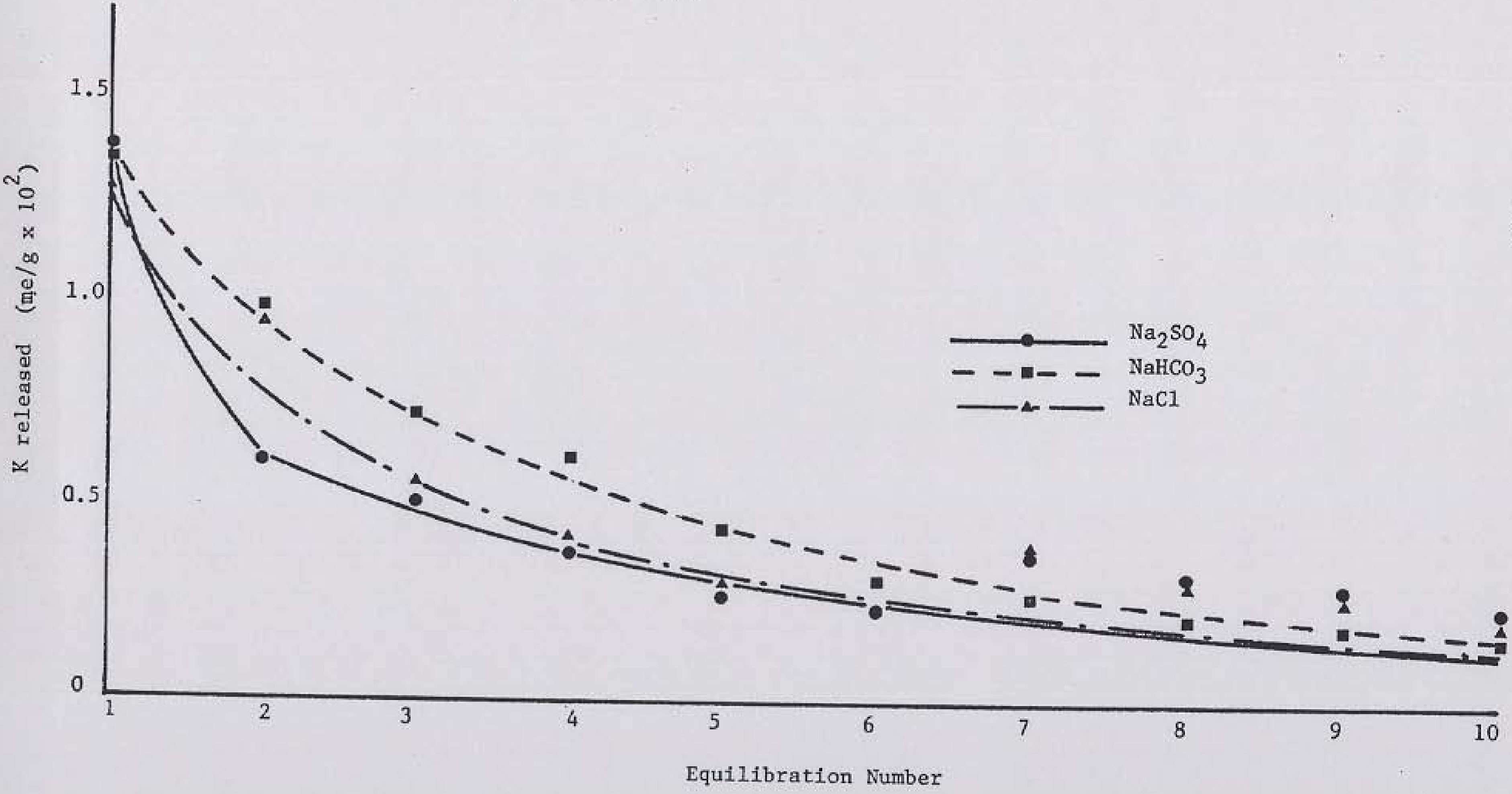


Figure 19(b). Potassium release from untreated K-saturated Alderwood silt fraction using various Na compounds (0.02N).

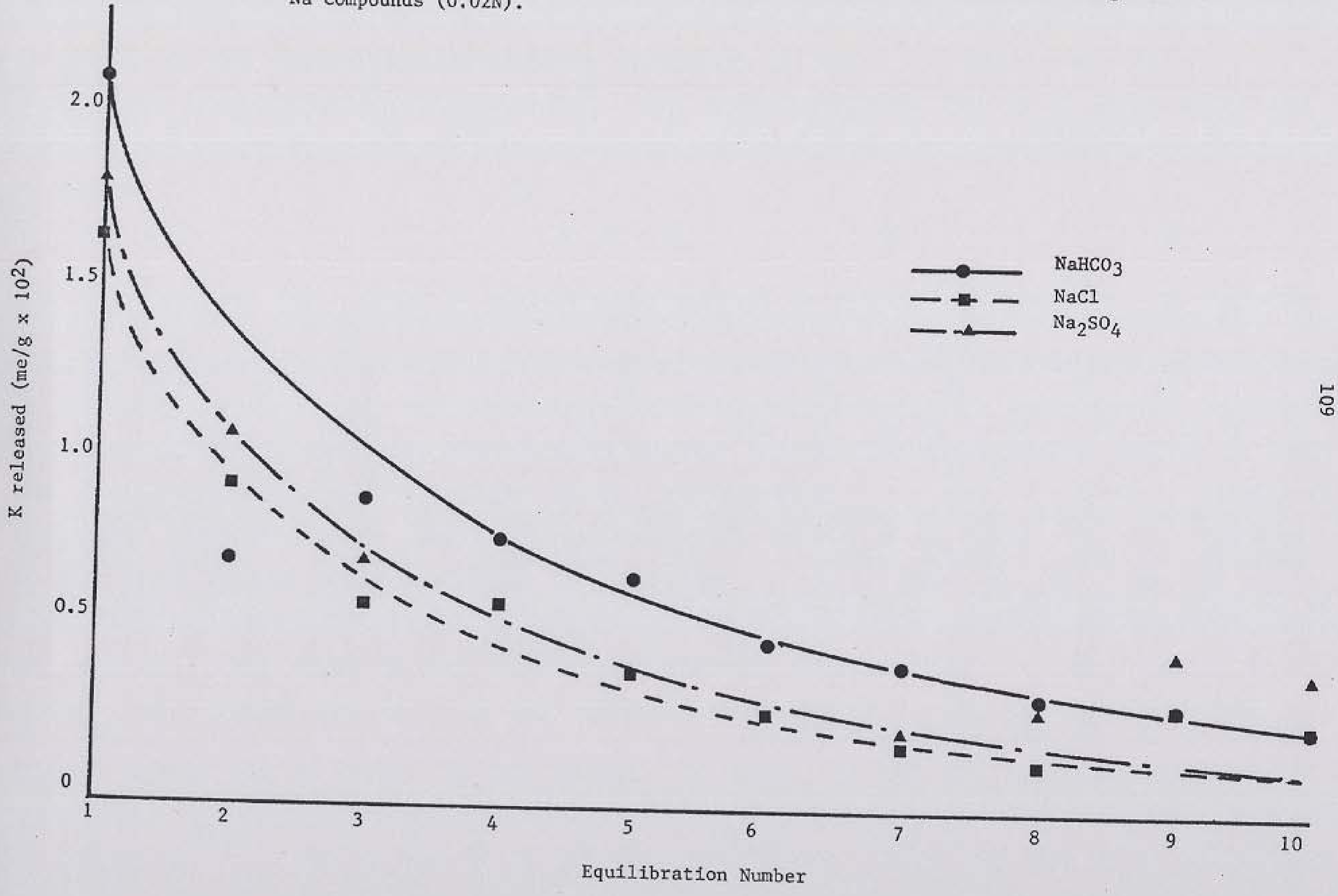


Figure 19(c). Potassium release from untreated K-saturated Alderwood clay fraction using various Na compounds (0.02N).

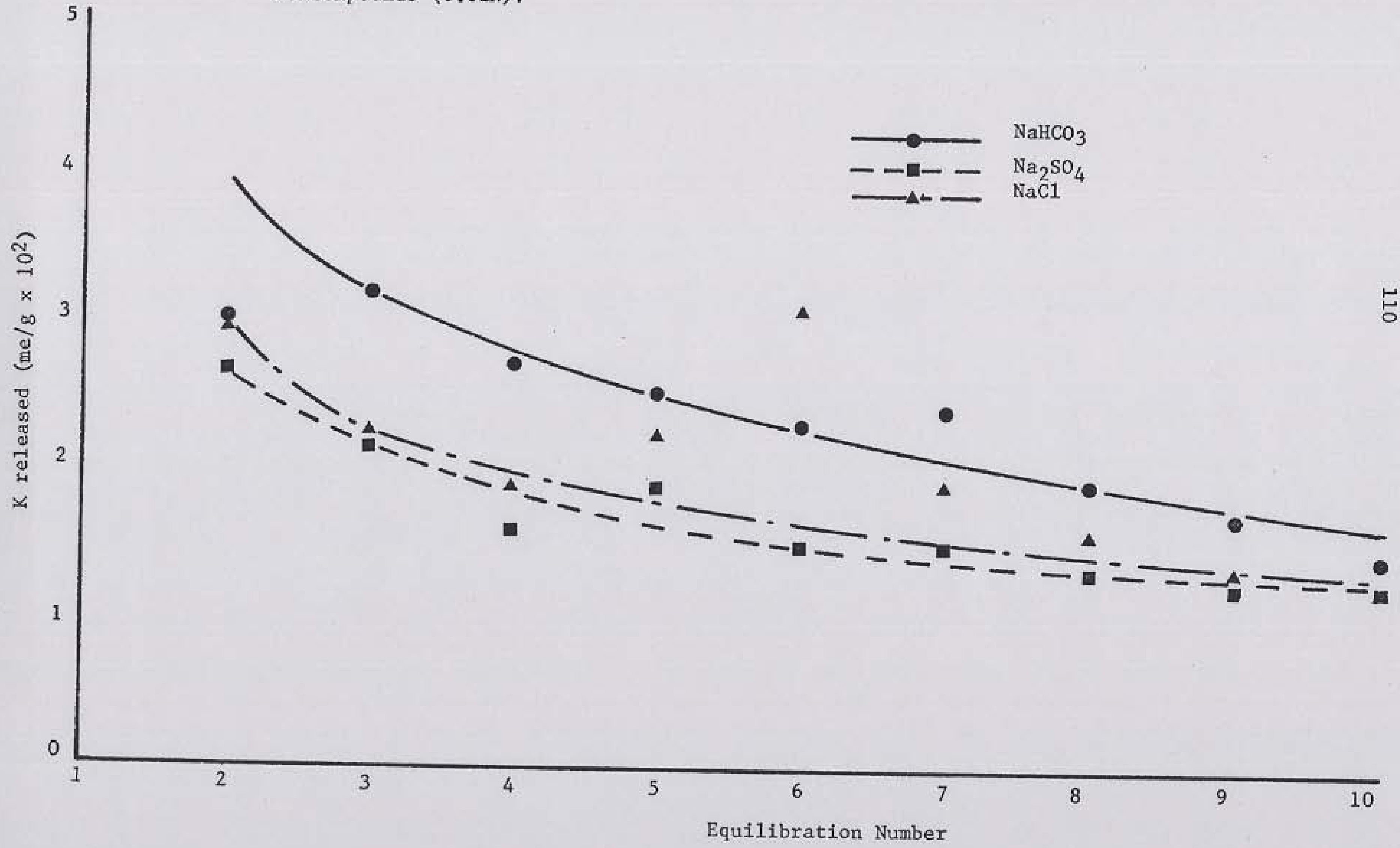


Figure 20(a). Potassium release from untreated K-saturated Wilkeson sand fraction using various Na compounds (0.02N).

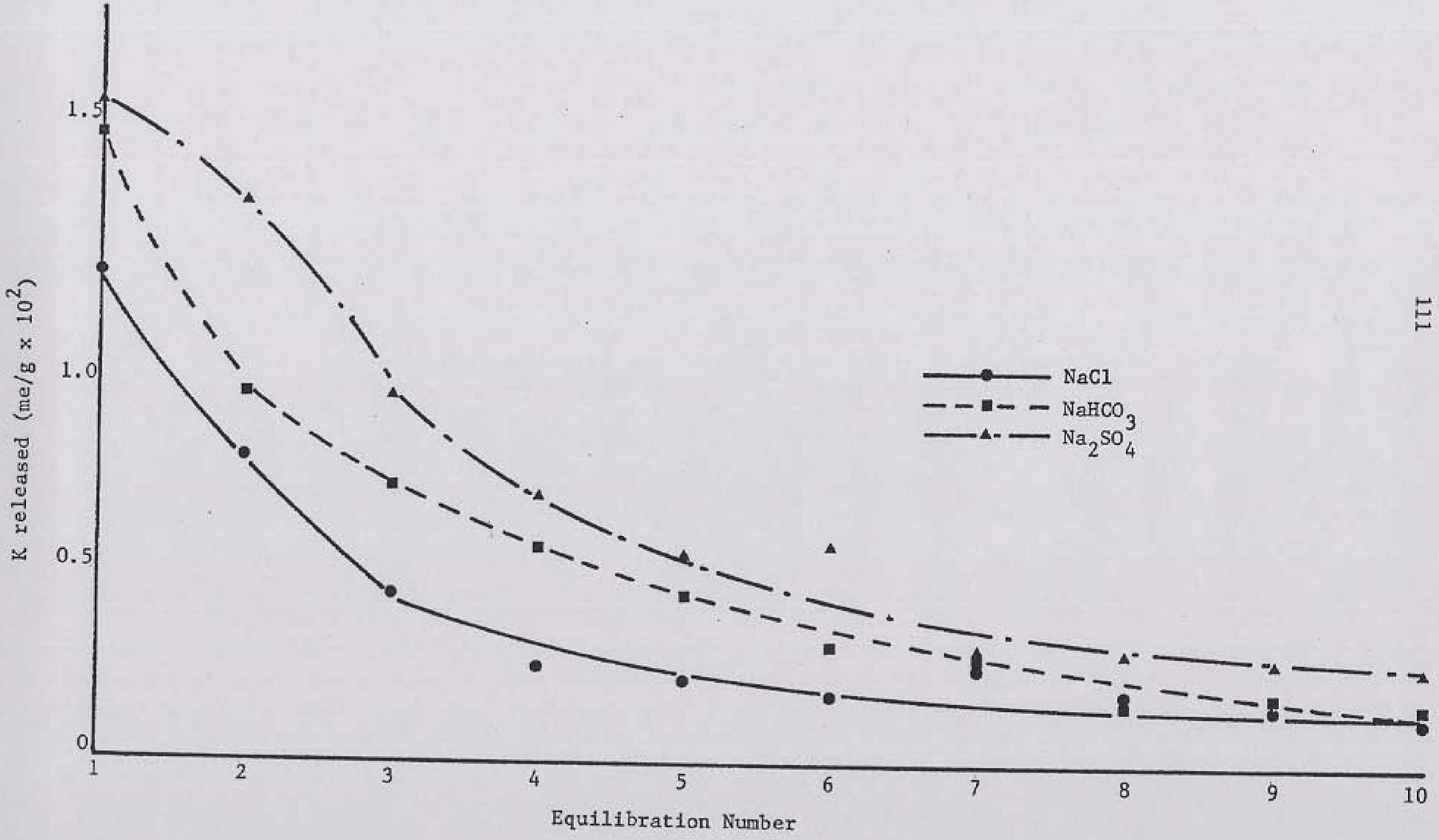


Figure 20(b). Potassium release from untreated K-saturated Wilkeson silt fraction using various Na compounds (0.02N).

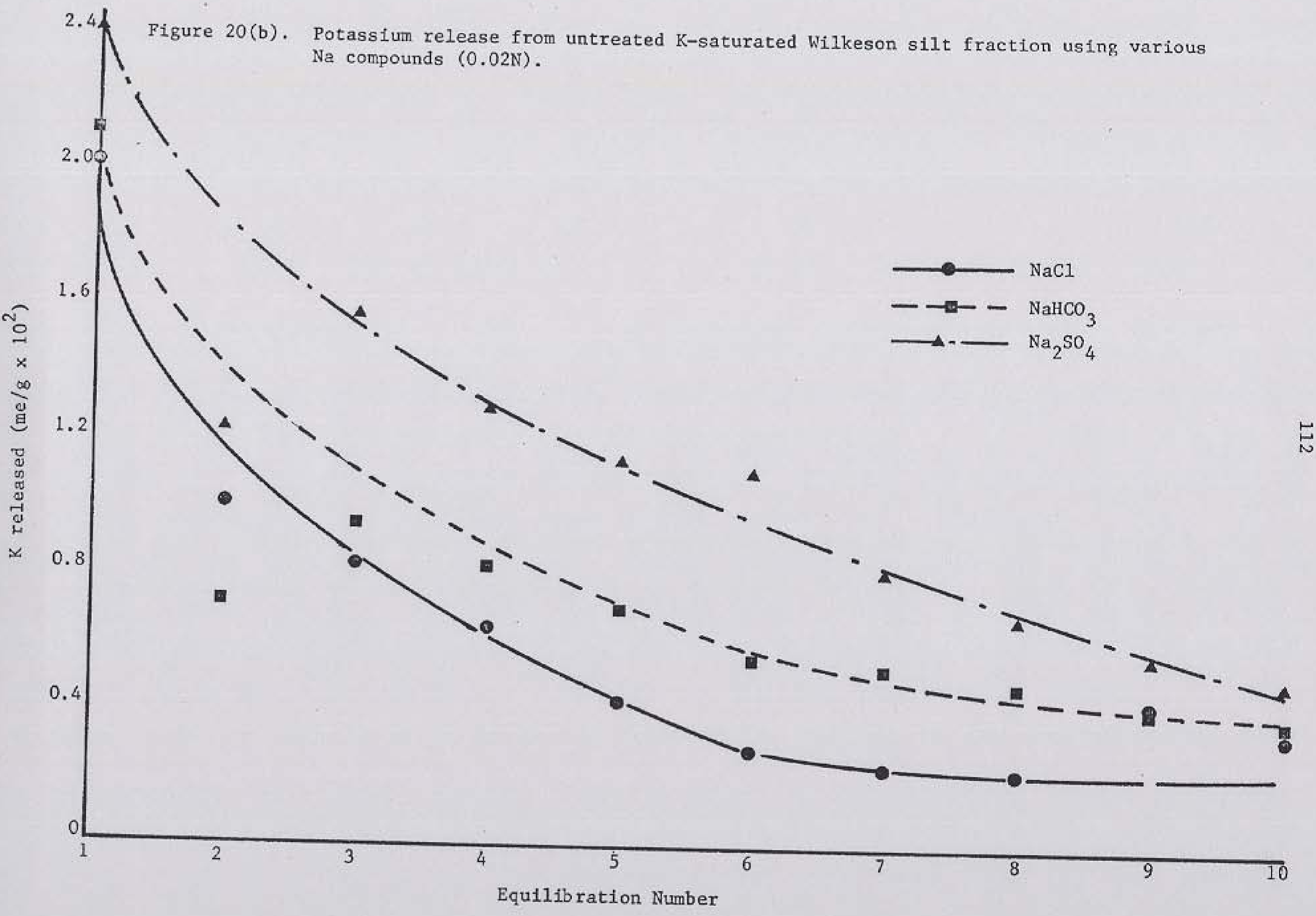
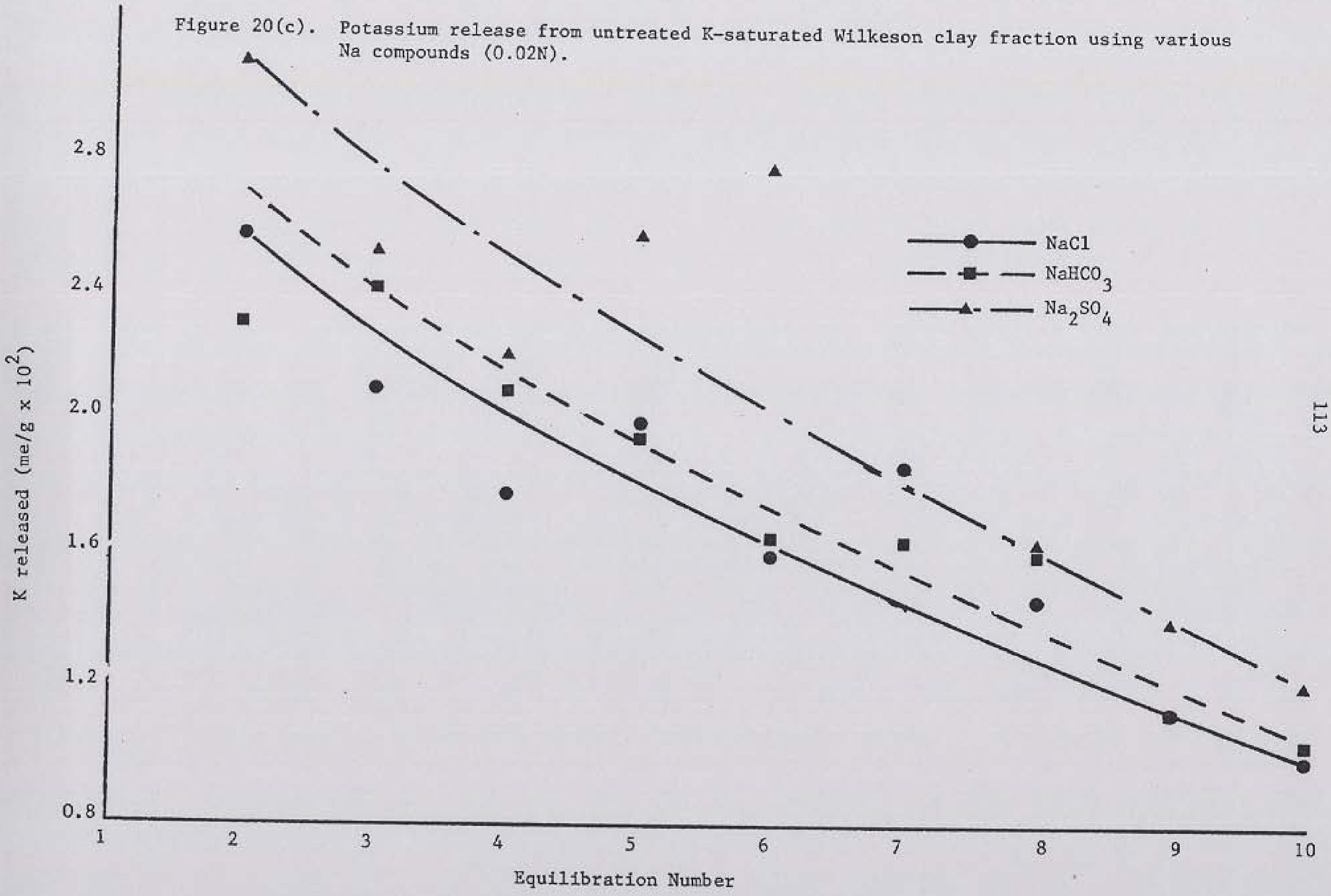


Figure 20(c). Potassium release from untreated K-saturated Wilkeson clay fraction using various Na compounds (0.02N).



which was comparable to the 6%, 18% and 17% increases in the Alderwood sand, silt and clay fractions respectively. The larger amounts of potassium released by the sulfate over chloride compound of sodium agreed with the results reported by Ayres and Hagihara (1953), Berg and Thomas (1959), MacIntire *et al.* (1943), Sommerfeldt (1962), Thomas (1960) and Wiklander (1965).

The Alderwood and Wilkeson total soils were essentially the same relative to potassium release by the three different sodium solutions (Figure 21) as the order of release was $SO_4$>Cl>$HCO_3$. Sodium sulfate extracted more potassium from both soils than the chloride solution while 79% and 140% more potassium was released by the Alderwood and Wilkeson soils respectively when sodium chloride was used rather than sodium bicarbonate.

### (iii) electrolyte concentration

Ion exchange is based on equilibria between ions in the exchanging solution and those on the exchanger material (Helfferich, 1962). The theoretical ion exchange equations proposed for soils include ratios of the ion concentrations in solution to those adsorbed on the soil particles (Bolt, 1967). It is generally considered that increasing the ionic concentration of the solution phase will result in increased ion exchange by mass action, Donnon equilibria or Gouy theory mechanisms (Kelley, 1948; Wiklander, 1965). Concentration effects on ion exchange appear to be more prevalent at concentration changes below 1N (Clark and Turner, 1965). Merwin and Peech (1950) found that potassium desorption from soil fractions increased with solution concentration to 0.05N after which decreased potassium exchange occurred and Keay and Wild (1961) reported no concentration effect on potassium exchange between 1.0N and 2.0N solution concentrations. However increases in ion exchange with solutions greater than 1N have been reported (Bolt *et al.*,

Figure 21(a). Potassium release from untreated K-saturated Alderwood total soil using various Na compounds (0.02N).

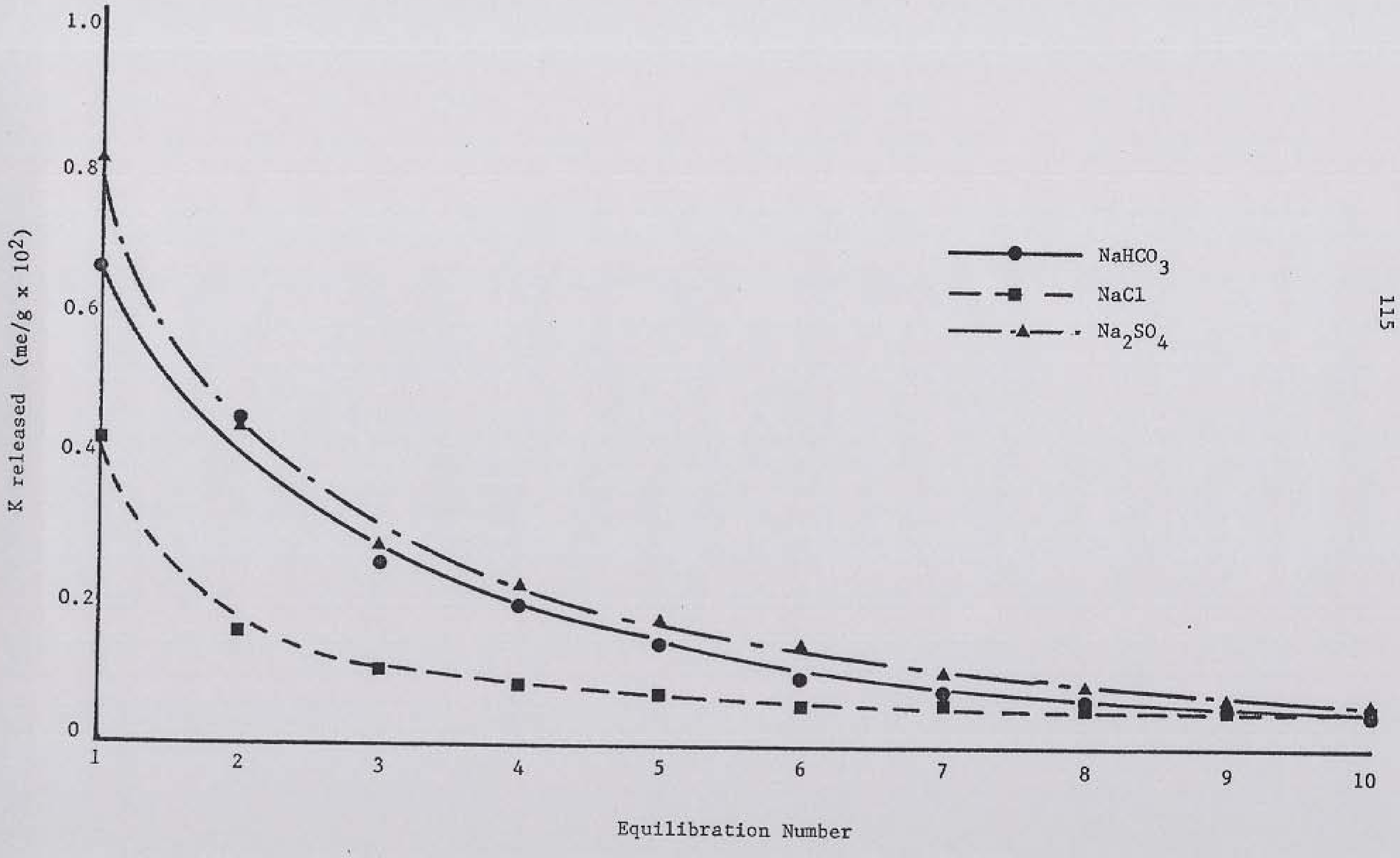
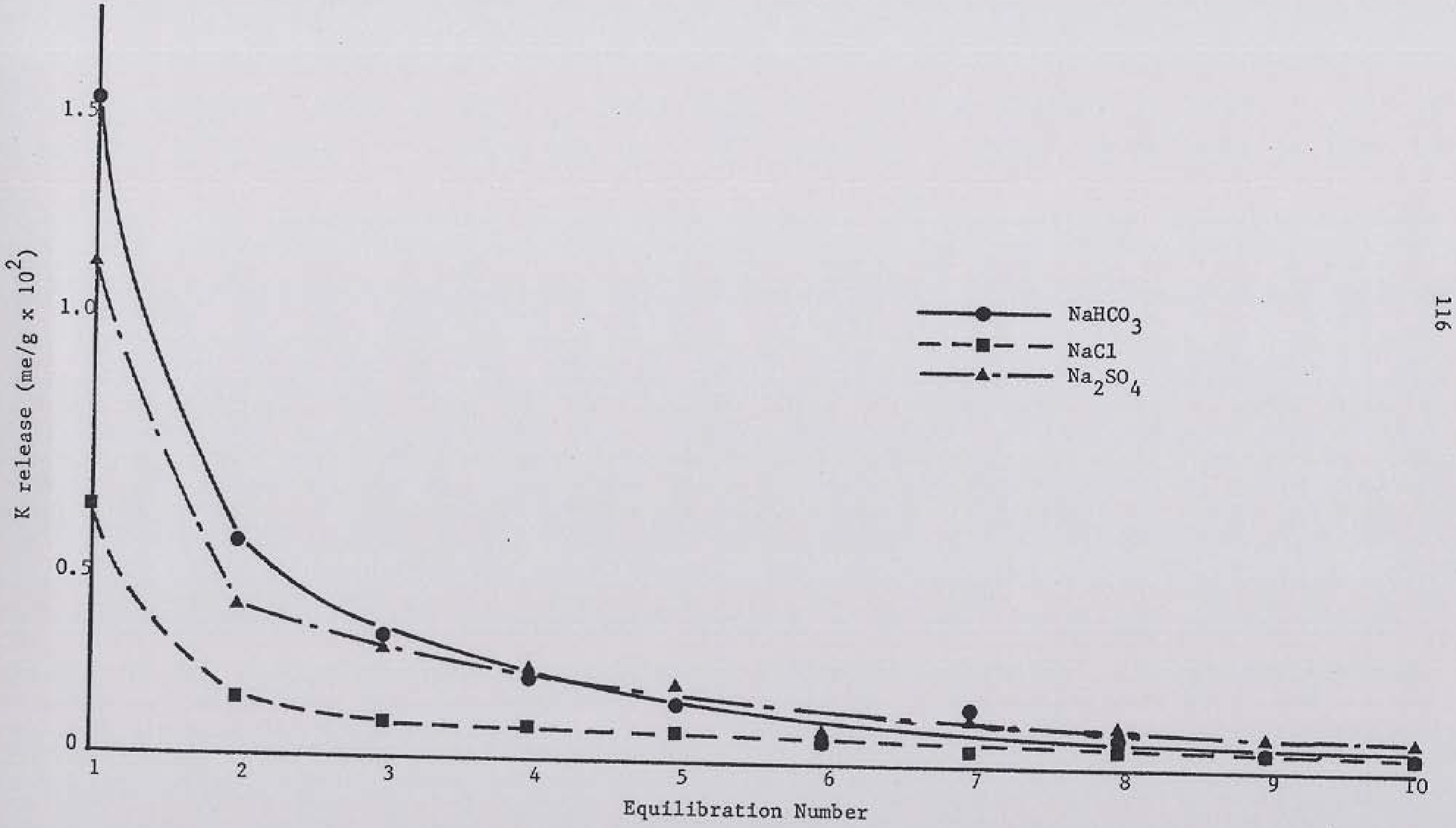


Figure 21(b). Potassium release from untreated K-saturated Wilkeson total soil using various Na compounds (0.02N).



1963; Clark and Turner, 1965; Quirk and Chute, 1968).

The Alderwood and Wilkeson soils and their particle size fractions exhibited increased release of potassium with increases in calcium chloride solution concentration (Table 17). The concentration effect was complicated at each equilibration period with the presence of nonexchangeable potassium forms. When all the exchangeable potassium was removed within the first 3 equilibration periods (e.g. 0.02N $CaCl_2$) the subsequent equilibrations yielded functions expressing increased and then decreased potassium release with increasing electrolyte concentration (Table 17). However the decrease was associated with the presence of nonexchangeable versus exchangeable potassium and not the electrolyte concentration. The total quantity of potassium removed from the samples after 10 equilibrations increased with calcium chloride concentration (Figure 22).

Although these results agreed with the literature, the important portion of the curves relative to ion exchange in soils under natural conditions was at the lowest solution concentrations. When ion concentrations in leachates collected by lysimeters were used as indications of soil solution concentrations available for potassium release, the values were less than $3 \times 10^{-5}$N (Cole, unpublished data). Comparing the potassium released over the 10 equilibration periods for the $5 \times 10^{-5}$N and $5 \times 10^{-4}$N calcium chloride solutions only slight increases (<8%) were obtained in the clay fractions and total soils with the higher electrolyte concentration (Table 18). The Alderwood sand fraction had the greatest increase in potassium removed 48.2% by these two electrolyte concentrations while the silt and Wilkeson sand fractions had increases ranging from 14.9% to 21.1%.

Table 17. Potassium released from Alderwood and Wilkeson total soils and particle size fractions by various calcium chloride concentrations (N).

| Fraction | Equil. No. | Alderwood (me/100 g) | | | | | | Wilkeson (me/100 g) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $5\times10^{-5}$ | $5\times10^{-4}$ | $10^{-3}$ | $5\times10^{-3}$ | $10^{-2}$ | $2\times10^{-2}$ | $5\times10^{-5}$ | $5\times10^{-4}$ | $10^{-3}$ | $5\times10^{-3}$ | $10^{-2}$ | $2\times10^{-2}$ |
| Sand | 1 | 0.78 | 0.83 | 0.89 | 1.69 | 2.40 | 5.82 | 1.50 | 1.35 | 1.54 | 2.05 | 3.07 | 7.72 |
| | 2 | 0.37 | 0.53 | 0.67 | 1.90 | 3.63 | 4.76 | 0.60 | 0.66 | 0.82 | 2.10 | 3.79 | 6.04 |
| | 3 | 0.25 | 0.42 | 0.51 | 1.77 | 2.92 | 2.86 | 0.39 | 0.47 | 0.64 | 1.81 | 3.68 | 3.98 |
| | 4 | 0.23 | 0.35 | 0.50 | 1.73 | 2.26 | 2.08 | 0.30 | 0.38 | 0.46 | 1.85 | 2.65 | 2.86 |
| | 5 | 0.23 | 0.35 | 0.47 | 1.60 | 1.63 | 1.50 | 0.35 | 0.43 | 0.54 | 1.96 | 2.10 | 2.16 |
| | 6 | 0.19 | 0.35 | 0.46 | 1.51 | 1.27 | 1.16 | 0.29 | 0.40 | 0.54 | 1.94 | 1.96 | 1.86 |
| | 7 | 0.18 | 0.32 | 0.42 | 1.24 | 0.80 | 0.84 | 0.24 | 0.35 | 0.57 | 1.59 | 1.17 | 1.24 |
| | 8 | 0.17 | 0.30 | 0.41 | 1.02 | 0.56 | 0.56 | 0.23 | 0.34 | 0.52 | 1.45 | 0.94 | 0.80 |
| | 9 | 0.16 | 0.29 | 0.42 | 0.88 | 0.45 | 0.38 | 0.22 | 0.32 | 0.43 | 1.23 | 0.71 | 0.64 |
| | 10 | 0.18 | 0.32 | 0.43 | 0.89 | 0.47 | 0.32 | 0.24 | 0.31 | 0.45 | 0.95 | 0.51 | 0.50 |
| | total | 2.74 | 4.06 | 5.18 | 14.23 | 16.39 | 20.28 | 4.36 | 5.01 | 6.51 | 16.93 | 20.48 | 27.80 |
| Silt | 1 | 1.71 | 1.71 | 1.79 | 2.66 | 3.58 | 11.54 | 1.99 | 2.18 | 1.95 | 2.86 | 4.04 | 9.74 |
| | 2 | 0.76 | 1.04 | 1.15 | 2.69 | 4.86 | 9.64 | 0.93 | 1.06 | 1.17 | 2.84 | 4.83 | 9.80 |
| | 3 | 0.61 | 0.69 | 0.80 | 2.45 | 4.45 | 7.58 | 0.56 | 0.70 | 0.86 | 2.46 | 4.45 | 8.26 |
| | 4 | 0.63 | 0.65 | 0.76 | 2.25 | 4.19 | 5.38 | 0.46 | 0.58 | 0.74 | 2.43 | 4.60 | 7.70 |
| | 5 | 0.52 | 0.59 | 0.73 | 2.20 | 4.76 | 3.54 | 0.40 | 0.55 | 0.65 | 2.30 | 4.14 | 6.06 |
| | 6 | 0.45 | 0.55 | 0.68 | 2.05 | 3.78 | 2.56 | 0.40 | 0.46 | 0.63 | 2.25 | 4.32 | 4.02 |
| | 7 | 0.38 | 0.51 | 0.66 | 2.03 | 3.25 | 1.70 | 0.37 | 0.49 | 0.65 | 2.20 | 4.19 | 2.82 |
| | 8 | 0.38 | 0.50 | 0.65 | 2.04 | 2.92 | 1.08 | 0.34 | 0.46 | 0.61 | 2.16 | 3.84 | 1.82 |
| | 9 | 0.36 | 0.46 | 0.63 | 2.02 | 2.13 | 0.88 | 0.32 | 0.45 | 0.58 | 2.05 | 3.45 | 1.46 |
| | 10 | 0.34 | 0.46 | 0.62 | 2.30 | 1.88 | 0.60 | 0.35 | 0.48 | 0.62 | 2.35 | 3.16 | 1.16 |
| | total | 6.14 | 7.16 | 8.47 | 22.69 | 35.80 | 44.50 | 6.12 | 7.41 | 8.46 | 23.90 | 41.02 | 52.84 |

(continued)

Table 17. Potassium released from Alderwood and Wilkeson total soils and particle size fractions by various calcium chloride concentrations (N). (concluded)

| Fraction | Equil. No. | Alderwood (me/100 g) | | | | | | Wilkeson (me/100 g) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $5x10^{-5}$ | $5x10^{-4}$ | $10^{-3}$ | $5x10^{-3}$ | $10^{-2}$ | $2x10^{-2}$ | $5x10^{-5}$ | $5x10^{-4}$ | $10^{-3}$ | $5x10^{-3}$ | $10^{-1}$ | $2x10^{-2}$ |
| Clay | 1 | 11.15 | 11.61 | 11.05 | 11.75 | 13.25 | 18.06 | 7.98 | 8.49 | 8.11 | 8.90 | 11.05 | 17.94 |
| | 2 | 9.17 | 8.90 | 8.06 | 14.12 | 14.27 | 12.82 | 6.22 | 6.42 | 5.68 | 8.43 | 12.28 | 13.64 |
| | 3 | 5.78 | 5.99 | 6.94 | 10.84 | 10.36 | 9.62 | 4.04 | 4.14 | 4.14 | 7.47 | 8.98 | 10.92 |
| | 4 | 4.19 | 4.67 | 4.73 | 7.81 | 9.44 | 9.18 | 3.46 | 2.76 | 3.07 | 6.09 | 8.13 | 9.34 |
| | 5 | 3.99 | 4.35 | 4.47 | 6.70 | 9.40 | 8.66 | 2.49 | 2.49 | 2.87 | 5.20 | 8.06 | 9.48 |
| | 6 | 3.89 | 4.28 | 4.49 | 7.07 | 9.05 | 8,19 | 2.17 | 2.39 | 2.73 | 5.85 | 7.75 | 9.02 |
| | 7 | 3.43 | 4.04 | 4.48 | 7.32 | 8.90 | 8.20 | 1.93 | 2.30 | 2.63 | 5.83 | 7.66 | 9.12 |
| | 8 | 3.49 | 3.97 | 4.04 | 7.26 | 8.67 | 8.10 | 1.87 | 2.21 | 2.61 | 5.63 | 7.52 | 8.26 |
| | 9 | 3.70 | 4.19 | 4.34 | 7.29 | 9.44 | 7.94 | 1.84 | 2.27 | 2.61 | 5.83 | 7.66 | 7.70 |
| | 10 | 3.19 | 4.02 | 3.79 | 7.32 | 7.90 | 7.70 | 1.85 | 2.27 | 2.74 | 5.94 | 7.71 | 7.28 |
| | total | 51.98 | 56.02 | 56.39 | 87.48 | 100.67 | 98.38 | 33.85 | 35.73 | 37.19 | 65.17 | 86.80 | 102.70 |
| Total soil | 1 | 2.56 | 2.45 | 2.50 | 2.43 | 2.66 | 7.84 | 3.76 | 3.78 | 3.86 | 4.08 | 3.73 | 9.00 |
| | 2 | 1.35 | 1.33 | 1.27 | 1.37 | 1.43 | 2.88 | 2.34 | 2.45 | 2.52 | 2.55 | 2.51 | 4.50 |
| | 3 | 0.55 | 0.70 | 0.73 | 0.72 | 0.76 | 1.14 | 1.36 | 1.22 | 1.34 | 0.70 | 1.17 | 2.00 |
| | 4 | 0.32 | 0.43 | 0.48 | 0.47 | 0.46 | 0.60 | 0.82 | 0.73 | 0.80 | 0.73 | 0.69 | 1.00 |
| | 5 | -- | 0.33 | 0.38 | 0.31 | 0.31 | 0.40 | 0.53 | 0.57 | 0.50 | 0.48 | 0.44 | 0.80 |
| | 6 | 0.42 | 0.26 | 0.29 | 0.24 | 0.23 | 0.36 | 0.42 | 0.43 | 0.41 | 0.34 | 0.34 | 0.40 |
| | 7 | 0.22 | 0.22 | 0.23 | 0.17 | 0.18 | 0.24 | 0.29 | 0.32 | 0.29 | 0.22 | 0.24 | 0.30 |
| | 8 | 0.14 | 0.20 | 0.19 | 0.14 | 0.14 | 0.20 | 0.21 | 0.26 | 0.23 | 0.19 | 0.18 | 0.26 |
| | 9 | 0.10 | 0.18 | 0.16 | 0.11 | 0.12 | 0.20 | 0.16 | 0.18 | 0.17 | 0.15 | 0.13 | -- |
| | 10 | 0.09 | 0.17 | 0.13 | 0.09 | 0.08 | 0.18 | 0.14 | 0.17 | 0.15 | 0.14 | 0.14 | 0.20 |
| | total | 5.75 | 6.27 | 6.36 | 6.05 | 6.37 | 13.90 | 10.03 | 10.11 | 10.27 | 9.58 | 9.57 | 18.46 |

Figure 22(a). Total potassium released from Alderwood total soil and particle size fractions after 10 equilibration periods using various calcium chloride solutions.

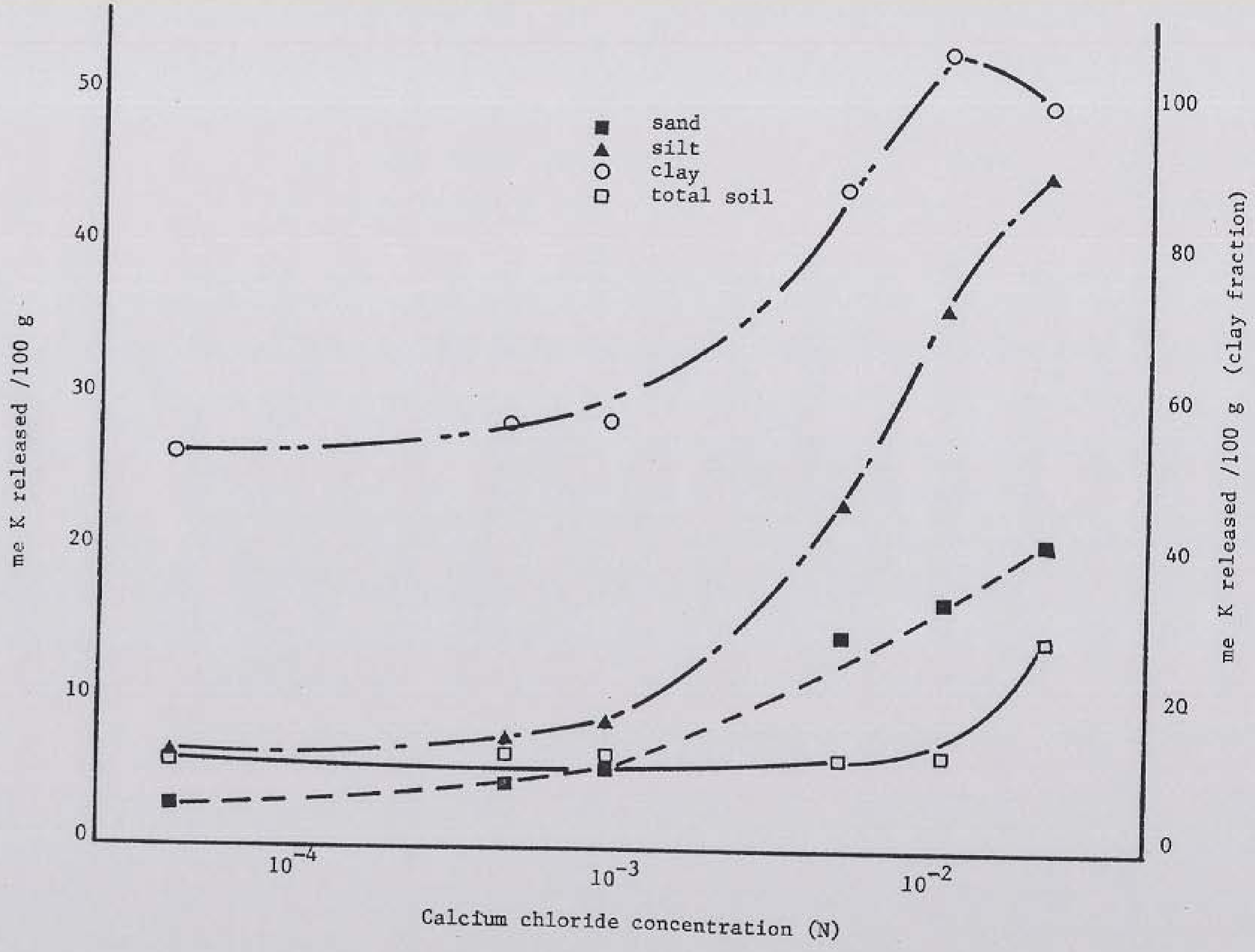


Figure 22(b). Total potassium released from Wilkeson total soil and particle size fractions after 10 equilibration periods using various calcium chloride solutions.

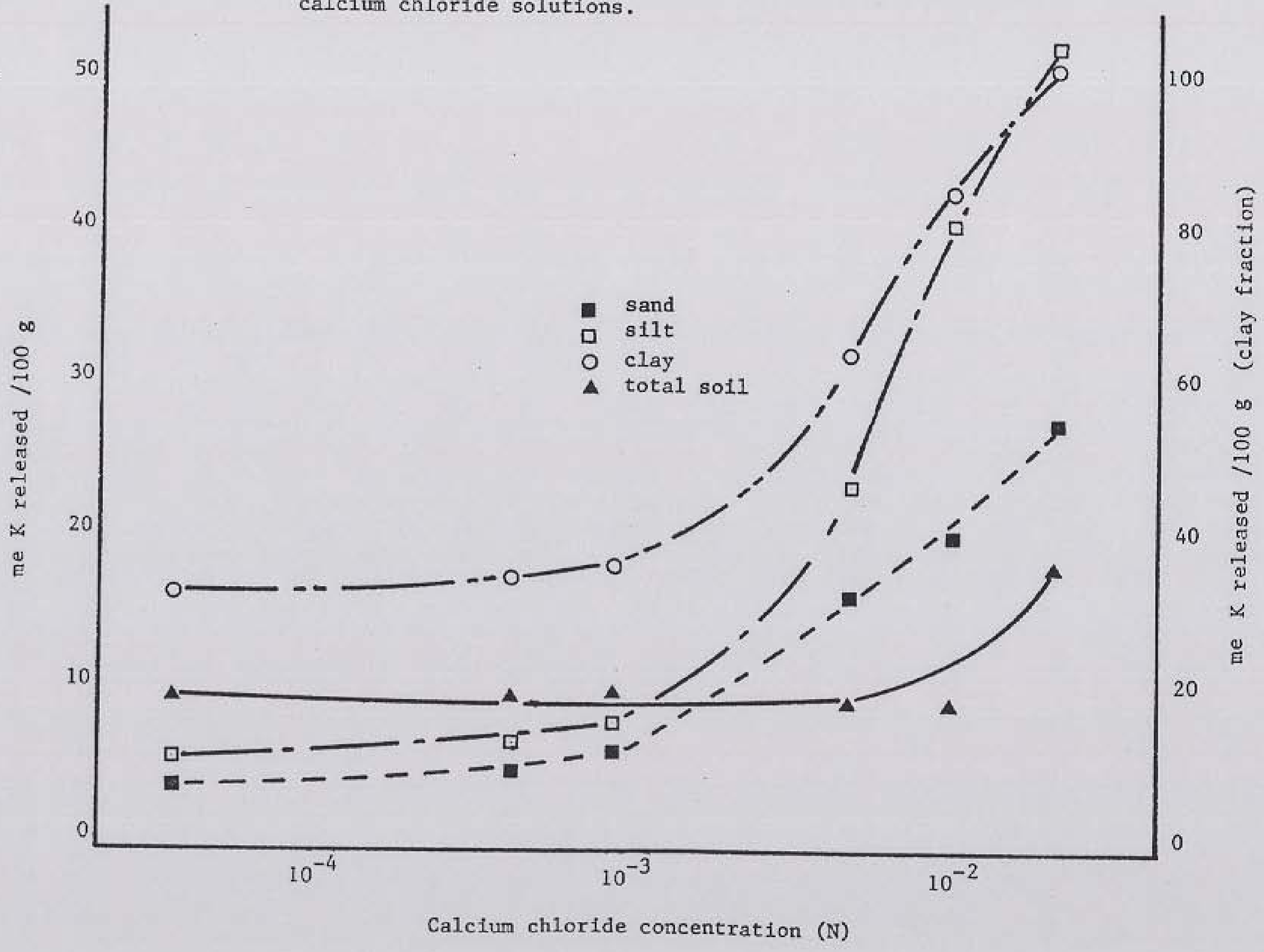


Table 18. Percent increase in total potassium released after 10 equilibration periods from Alderwood and Wilkeson total soils and particle size fractions by $5 \times 10^{-4}$N over $5 \times 10^{-5}$N $CaCl_2$.

| Soil | Fraction | Percent increase K released |
|---|---|---|
| Alderwood | sand | 49.2 |
| | silt | 16.6 |
| | clay | 7.8 |
| | total soil | 9.0 |
| Wilkeson | sand | 14.9 |
| | silt | 21.1 |
| | clay | 5.6 |
| | total soil | 0.8 |

### (iv) solution pH

As mentioned in the literature review contradictory results have been reported on the pH effects on potassium release. In some instances no pH effect was found (Coulter, 1969; Smith and Scott, 1966; Wells and Norrish, 1968) while in others decreasing the equilibrating solution pH increased potassium release (Huang *et al.*, 1968; Newman, 1969; Rich, 1964; Rich and Black, 1964).

Other than the Wilkeson total soil and the clay fractions, the total potassium removed after 10 equilibration periods increased with decreasing solution pH (Table 19). The reasons for the opposite response observed with the clay fractions and the Wilkeson total soil were unclear. Although it appeared that potassium desorption increased with hydrogen ion concentration, the importance of this factor may have been limited. The quantity of potassium removed from the sand fractions by HCl solutions of pH 1.9 was 3.8 times

Table 19. Potassium released from Alderwood and Wilkeson total soils and particle size fractions under different solution pH conditions (HCl extractions) (me/g)

| Soil | Equilibration No. | Sand | | Silt | | Clay | | Total soil | |
|---|---|---|---|---|---|---|---|---|---|
| | | pH 1.9 | pH 4.0 | pH 1.9 | pH 4.0 | pH 1.9 | pH 4.0 | pH 1.9 | pH 4.0 |
| Alderwood | 1 | 0.0210 | 0.0023 | 0.0166 | 0.0056 | 0.0440 | 0.0921 | 0.0159 | 0.0072 |
| | 2 | 0.0119 | 0.0007 | 0.0100 | 0.0011 | 0.0110 | 0.0491 | 0.0032 | 0.0022 |
| | 3 | 0.0050 | 0.0010 | 0.0134 | 0.0008 | 0.0092 | 0.0466 | 0.0010 | 0.0008 |
| | 4 | 0.0014 | 0.0008 | 0.0114 | 0.0006 | 0.0100 | 0.0302 | 0.0004 | 0.0003 |
| | 5 | 0.0009 | 0.0007 | 0.0083 | 0.0005 | 0.0092 | 0.0269 | 0.0011 | 0.0004 |
| | 6 | 0.0007 | 0.0024 | 0.0046 | 0.0014 | 0.0100 | 0.0274 | 0.0006 | 0.0003 |
| | 7 | 0.0004 | 0.0009 | 0.0018 | 0.0006 | 0.0100 | 0.0187 | 0.0003 | 0.0003 |
| | 8 | 0.0003 | 0.0006 | 0.0013 | 0.0011 | 0.0100 | 0.0128 | 0.0002 | 0.0003 |
| | 9 | 0.0002 | 0.0006 | 0.0006 | 0.0009 | 0.0082 | 0.0102 | 0.0001 | 0.0002 |
| | 10 | 0.0001 | 0.0009 | 0.0004 | 0.0013 | 0.0092 | 0.0082 | 0.0001 | 0.0002 |
| | total | 0.0419 | 0.0109 | 0.0684 | 0.0139 | 0.1292 | 0.3112 | 0.0228 | 0.0122 |
| Wilkeson | 1 | 0.0166 | 0.0047 | 0.0166 | 0.0084 | 0.0353 | 0.1262 | 0.0119 | 0.0162 |
| | 2 | 0.0092 | 0.0008 | 0.0092 | 0.0017 | 0.0092 | 0.0450 | 0.0051 | 0.0123 |
| | 3 | 0.0104 | 0.0006 | 0.0100 | 0.0008 | 0.0100 | 0.0463 | 0.0015 | 0.0031 |
| | 4 | 0.0064 | 0.0011 | 0.0092 | 0.0006 | 0.0100 | 0.0335 | 0.0005 | 0.0019 |
| | 5 | 0.0036 | 0.0009 | 0.0072 | 0.0005 | 0.0092 | 0.0279 | 0.0008 | 0.0012 |
| | 6 | 0.0027 | 0.0014 | 0.0005 | 0.0015 | 0.0100 | 0.0279 | 0.0004 | 0.0008 |
| | 7 | 0.0013 | 0.0013 | 0.0005 | 0.0008 | 0.0100 | 0.0205 | 0.0003 | 0.0006 |
| | 8 | 0.0007 | 0.0010 | 0.0027 | 0.0011 | 0.0100 | 0.0143 | 0.0002 | 0.0004 |
| | 9 | 0.0006 | 0.0008 | 0.0018 | 0.0010 | 0.0100 | 0.0136 | 0.0002 | 0.0003 |
| | 10 | 0.0003 | 0.0010 | 0.0005 | 0.0009 | 0.0092 | 0.0100 | 0.0001 | 0.0002 |
| | total | 0.0518 | 0.0136 | 0.0582 | 0.0173 | 0.1229 | 0.3653 | 0.0210 | 0.0370 |

greater than that removed by pH 4.0 HCl solutions. However when 0.02N $CaCl_2$ (pH 5.6) was used as the equilibrating solution versus 0.02N HCl (pH 1.9), 4.8 and 5.4 times more potassium were released from the Alderwood and Wilkeson sand fractions respectively by the $CaCl_2$ solution. Similar results were obtained for all the particle size fractions and total soils (Table 20).

When the solution pH was constant (pH 4.0) but the electrolyte was $AlCl_3$ rather than HCl, 5.0 and 1.9 times more potassium were removed by the former solution from the Alderwood and Wilkeson total soils respectively. The concentration difference of 0.02N ($AlCl_3$) and 5 x $10^{-5}$N (HCl) did not account for all the variation in potassium removed. The Alderwood total soil released 6.11 me/100g to 0.02N $AlCl_3$ solutions while only 2.28 me/100g to 0.02N HCl and 1.22 me/100g to 5 x $10^{-5}$N HCl solutions. Therefore the effect of cation type accounted for 3.83 me/100g and the electrolyte concentration plus cation effects for 4.89 me/100g. Hence the electrolyte concentration affect was responsible for only 1.06 me/100g compared to the 3.83 me/100g for the cation type only. In the Wilkeson total soil the concentration differences accounted for 1.60 me/100g while the $Al^{+3}$ ion released 5.00 me/100g more potassium than the $H_3O^+$ ion. When 0.02N NaCl (pH 5.5) was used as the equilibrating electrolyte 6.6 and 5.7 times less potassium were released respectively from the Alderwood and Wilkeson total soils relative to 0.02N $CaCl_2$ (pH 5.6) released potassium. Because the hydronium ion was relatively inefficient compared to other cations at desorbing exchangeable potassium from the Alderwood and Wilkeson total soils it was concluded that the effect of equilibrating solution pH on potassium desorption was relatively insignificant compared to the effects of cation type and electrolyte concentration.

Table 20. Ratios of total potassium released from 10 equilibration periods using electrolyte solutions of various pH.

| Soil | Fraction | $\frac{\text{HCl (pH 1.9)}}{\text{HCl (pH 4.0)}}$ | $\frac{\text{CaCl}_2\text{ (pH 5.5)}}{\text{HCl (pH 1.9)}}$ | $\frac{\text{AlCl}_3\text{ (pH 4.0)}}{\text{HCl (pH 4.0)}}$ | $\frac{\text{NaCl (pH 5.5)}}{\text{HCl (pH 1.9)}}$ |
|---|---|---|---|---|---|
| Alderwood | sand | 3.8 | 4.8 | | |
| | silt | 4.9 | 6.5 | | |
| | clay | -0.4* | 8.2 | | |
| | total soil | 1.9 | 6.1 | 5.0 | 1.9 |
| Wilkeson | sand | 3.8 | 5.4 | | |
| | silt | 3.4 | 9.1 | | |
| | clay | -0.4* | 8.4 | | |
| | total soil | -0.6* | 8.8 | 1.9 | 1.5 |

* pH 1.9 K released < pH 4.0 K released.

# CONCLUSIONS

From the data collected on potassium release from the Alderwood and Wilkeson soils, the following conclusions appear warranted:

1. The presence of structural, fixed and exchangeable potassium forms in the Alderwood and Wilkeson soils resulted in release of soil potassium from these soils according to exponential functions. Potassium release from K saturated samples was in accordance with the three steps proposed by Haylock (1956), including an initial rapid release of readily exchangeable potassium followed by a slower release of "weakly fixed" forms and concluded by a phase of continued slow release of almost constant quantities of "strongly fixed" potassium. The three steps were characterized by change in free energy ($\Delta G > -750$ cal/mole while the "weakly fixed" forms had $\Delta G$ between $-750$ cal/mole and $-1750$ cal/mole and the "strongly fixed" forms with $\Delta G < -1750$ cal/mole).
2. The quantity of potassium released by the soil materials decreased as the particle size increased but the rate of release increased in the order sand < silt < clay. Therefore, although the fine clay sized material provided a significant component of the initial rapidly released potassium, the coarse clay, silt and sand fractions were responsible for the soil potassium buffering capacity. The coarser particle size fractions could be the components responsible for the continual release of small quantities of potassium in forest soils that are not accounted for in the neutral normal ammonium acetate extraction technique used for available soil potassium characterization.

3. Desorption of exchangeable potassium from the soil materials was according to the relative quantity of exchangeable potassium present. A possibility may exist that release of exchangeable potassium forms from soils similar to the Alderwood and Wilkeson soils could be predicted using the release data obtained in this study and the quantities of exchangeable potassium present in other soils.

4. Nonexchangeable potassium release from the Alderwood and Wilkeson soils was associated with the particle size distribution. Statistically significant predictions of potassium desorption from the total soils were obtained based on the potassium released from each particle size fraction and the percentage of the fraction present in the total soils. Organic matter affected the predictions to the extent that statistically significant differences were obtained from the calculated potassium released versus the experimental quantities released from the total soils. However, sesquioxides did not significantly affect the predictions. It appeared that future mathematical modeling of potassium release from forest soils must consider the significant affects of the soil organic fraction.

5. Aggregation through bonding by organic matter and sesquioxides occurred in both soils and involved all three particle size fractions. Organic matter was the more important cementing agent in the sand fractions while sesquioxide bonding predominated in the silt fractions. The two cementing agents had essentially the same impact on aggregation in the clay fractions. Removal of organic matter and sesquioxides increased the percent clay

in the Alderwood and Wilkeson soils by 22.4% and 28.3% respectively and decreased the sand contents 15.0% and 19.5%. These changes in particle size distribution resulted in the Alderwood soil texture changing from sandy loam to loam and the Wilkeson texture from silt loam to silty clay loam. Sesquioxide cementation was slightly greater than organic matter bonding in the Wilkeson particle size fractions but the Alderwood fractions had the opposite situation. The aggregation significantly affected the ion exchange characteristics of the soils in addition to the particle size distribution.

6. Soil organic matter had significant effects on potassium release, especially relative to the exchangeable forms. Organo-mineral complexing was present in the two soils and reduced the exchange capacity of the inorganic soil fraction. It also increased the rates and quantities of potassium released from the soil fractions. This reflected the increased bonding energies that were possessed by the exchange sites released by the removal of the complexed organic matter. The organo-mineral complexing was primarily associated with the silt and clay fractions but the complexing effects were very prevalent in the total Alderwood and Wilkeson soils.

7. Removal of sesquioxides from the soils reduced the exchangeable potassium contents through increased potassium fixation by the released interlayer adsorptive sites. Potential increases in potassium fixation ranged from 3.90 me/100g to 47.20 me/100g with no significant increase in fixation by the sand fractions. The Alderwood and Wilkeson total soils had 4.69 and 5.61 me/100g potentially increased fixed potassium respectively. Release of exchangeable potassium forms was lower in magnitude but at higher

rates when $R_2O_3$ were removed. This did not indicate the increased bonding energies of the released exchange sites as reported by Mehlich (1952), however this could have been due to the fixed potassium component. Increased bonding energies associated with the nonexchangeable potassium forms were indicated by the lower quantities of potassium released. The effects of $R_2O_3$ appeared to be restricted to the added potassium and not to the naturally occurring nonexchangeable forms.

8. Removal of potassium from the Alderwood and Wilkeson soils and their particle size fractions was affected by the type of cation present in the exchanging solution. Calcium was the most efficient cation but only slightly higher than magnesium. The pH of the equilibrating solution enhanced the efficiency of these two cations, especially relative to the removal of nonexchangeable forms. This agrees with the findings of Rich and Black (1964). The efficiency of the other cations relative to the removal of exchangeable potassium was in the order $Al > Na > NH_4 > H_3O$. An approximate lyotropic series for the Alderwood and Wilkeson soils was constructed ($Ca \geq Mg > Al > K > Na > NH_4 > H_3O$).

9. The anionic effects on potassium release varied between the particle size fractions of the two soils. The efficiency order of potassium removal was $HCO_3 > SO_4 > Cl$ in the Alderwood particle size fractions while the Wilkeson fractions had the order $SO_4 > HCO_3 > Cl$. The total soils had an efficiency order of $SO_4 > Cl > HCO_3$. In the particle size fractions, the bicarbonate anion removed 11 to 34 percent more potassium and the sulfate anion 6 to 72 percent more than the chloride anion.

10. Potassium release from the Alderwood and Wilkeson soils and particle size fractions increased with equilibrating electrolyte solution concentration. The greatest increases occurred at concentrations greater than $10^{-3}N$. In the concentration range commonly found in lysimeter leachates ($5 \times 10^{-5}N$ to $5 \times 10^{-4}N$) <10% increases in potassium were removed from the Alderwood and Wilkeson total soils. Increases in potassium desorption from the particle size fractions ranged from 5.6% to 48.2%. Electrolyte concentration would not be a significant factor in potassium release from forest soils under natural conditions.
11. The effect of equilibrating solution pH on the release of exchangeable potassium from the Alderwood and Wilkeson soils was relatively insignificant compared to the effects of cation type and electrolyte concentration. This could have been due to the relative ineffectiveness of the hydronium or $Al(OH)_2^+$ ion compared to other cations in desorbing exchangeable potassium.

## SUMMARY

Potassium release from forest soils of the Alderwood and Wilkeson type will be governed by the physical, chemical and mineralogical properties of the soils and the chemical properties of the soil solution. The most important soil properties were the particle size distribution, soil mineralogy, extent and nature of aggregation due to organic matter and sesquioxides, organic matter content and to a lesser extent the sesquioxide content. The most important soil solution characteristic was the type of cation present.

Nonexchangeable potassium was present in the two forest soils and may be the principal source of the element for plant absorption. This could be the reason for continual growth of the Douglas-fir stand at Cedar River beyond the 20 year limit indicated by the data of Cole *et al.* (1967). Determination of the exchangeable potassium content using ammonium acetate provided higher values than when calcium chloride was used. Release of natural potassium was according to exponential functions but indicated that all the exchangeable potassium predicted by the ammonium acetate procedure was not of the readily exchangeable form. These findings indicated that a different extraction method is necessary for evaluating the readily available potassium content of these forest soils.

Relative to potassium release functions and soil factors affecting the release, the relationships reported for agricultural soils are also present in these forest soils. Potassium release was according to the three steps proposed by Haylock (1956) and the rate of release increased as the particle size decreased. Sesquioxides influenced the release of the element but this was primarily through their effect on particle surface ion exchange properties. Where interlayer adsorption occurred the sesquioxides acted as props rather than blocks thereby making interlayer removal of potassium more efficient.

The organic matter in the two forest soils had a great influence on the ion exchange relationships. The presence of organo-clay complexes either as individual particles or as aggregates significantly reduced the ion exchange capacity of the soils and altered the adsorption energy of the exchange system. In addition the organic material provided the greatest interference on modeling potassium release from the soils based on release from the individual particle size fractions. It appears that to accurately model potassium release from forest soils knowledge of the organic matter influence in each soil is essential.

The solution characteristics that have been reported to affect ion exchange in soils had varied effects on the two forest soils used in this study. The type of cation had the greatest influence on potassium release with $Ca \geq Mg > Na > NH_4 > H_3O$. The anionic effects were variable and required further work before definite conclusions could be made. Although greater amounts of potassium were released as the electrolyte concentration increased there were only minor increases when concentrations in the range usually found in forest soils were considered. Potassium release increased with decreasing solution pH but this effect was minor when compared with the effects of cation type.

Generally, potassium release from the Alderwood and Wilkeson forest soils was according to that reported for agricultural soils and pure minerals. However, factors such as the soil organic matter and type of cation appeared to have greater influences in the forest soils. The determination of readily available potassium in these soils must be reconsidered.

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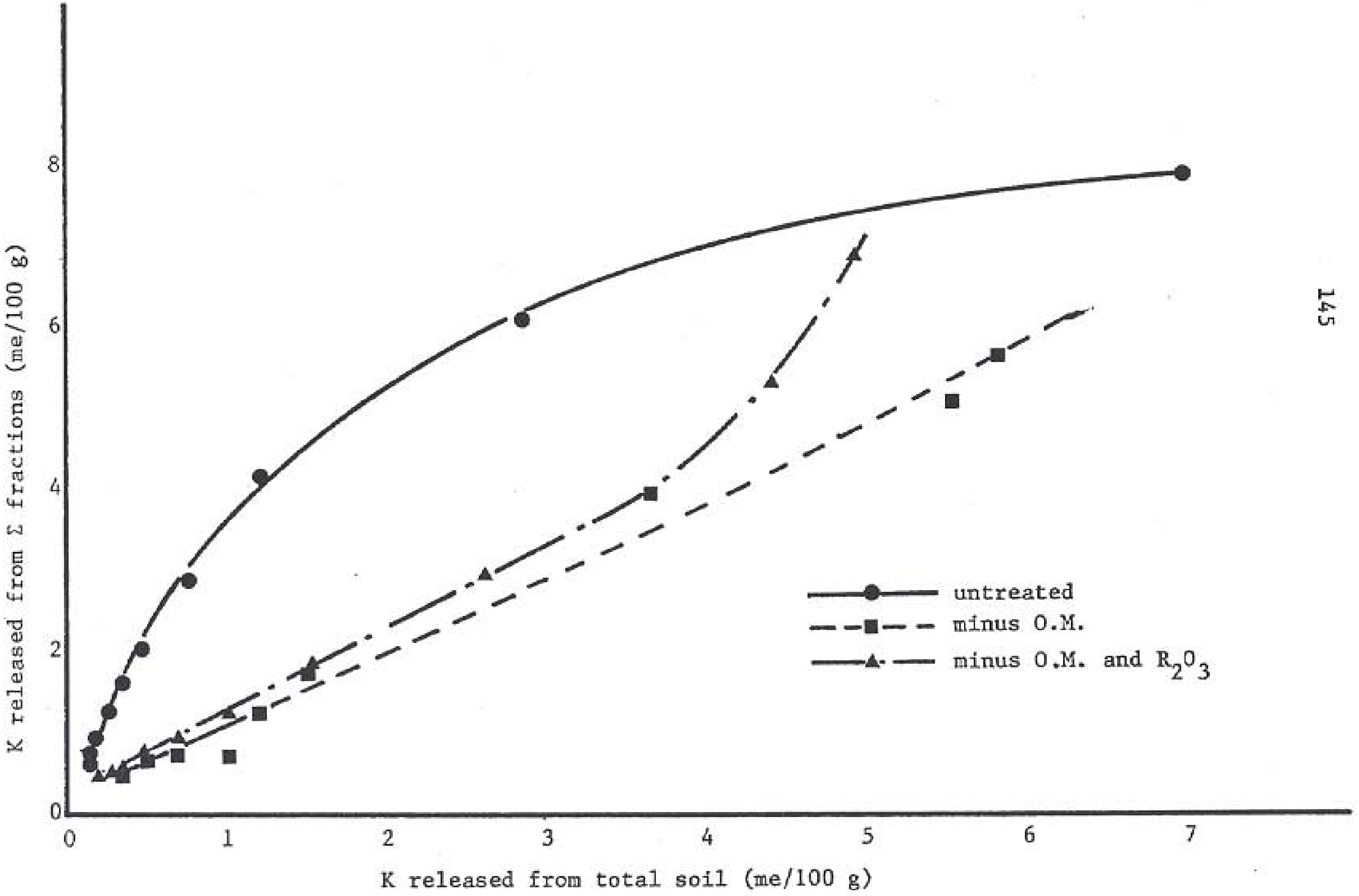
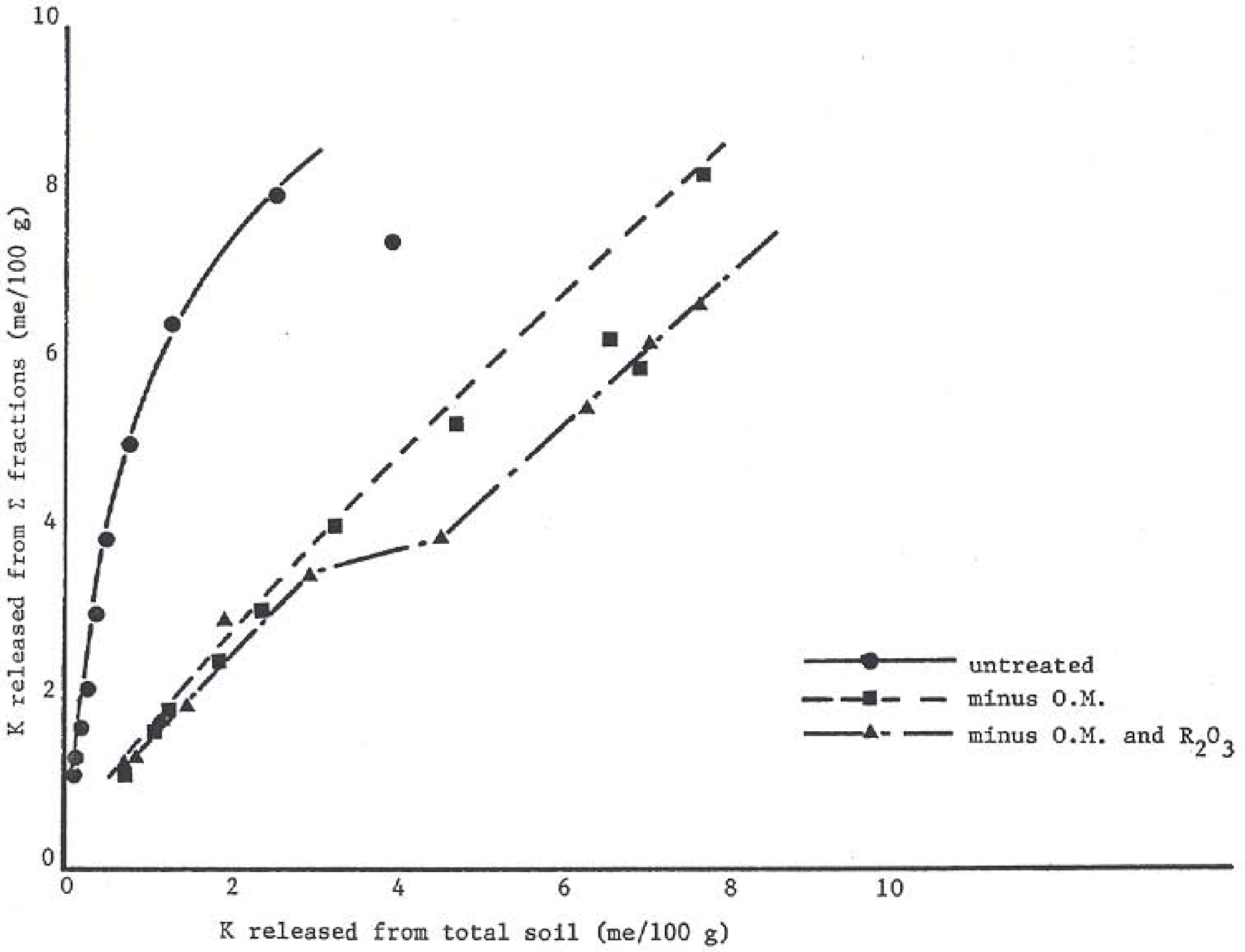
# APPENDIX

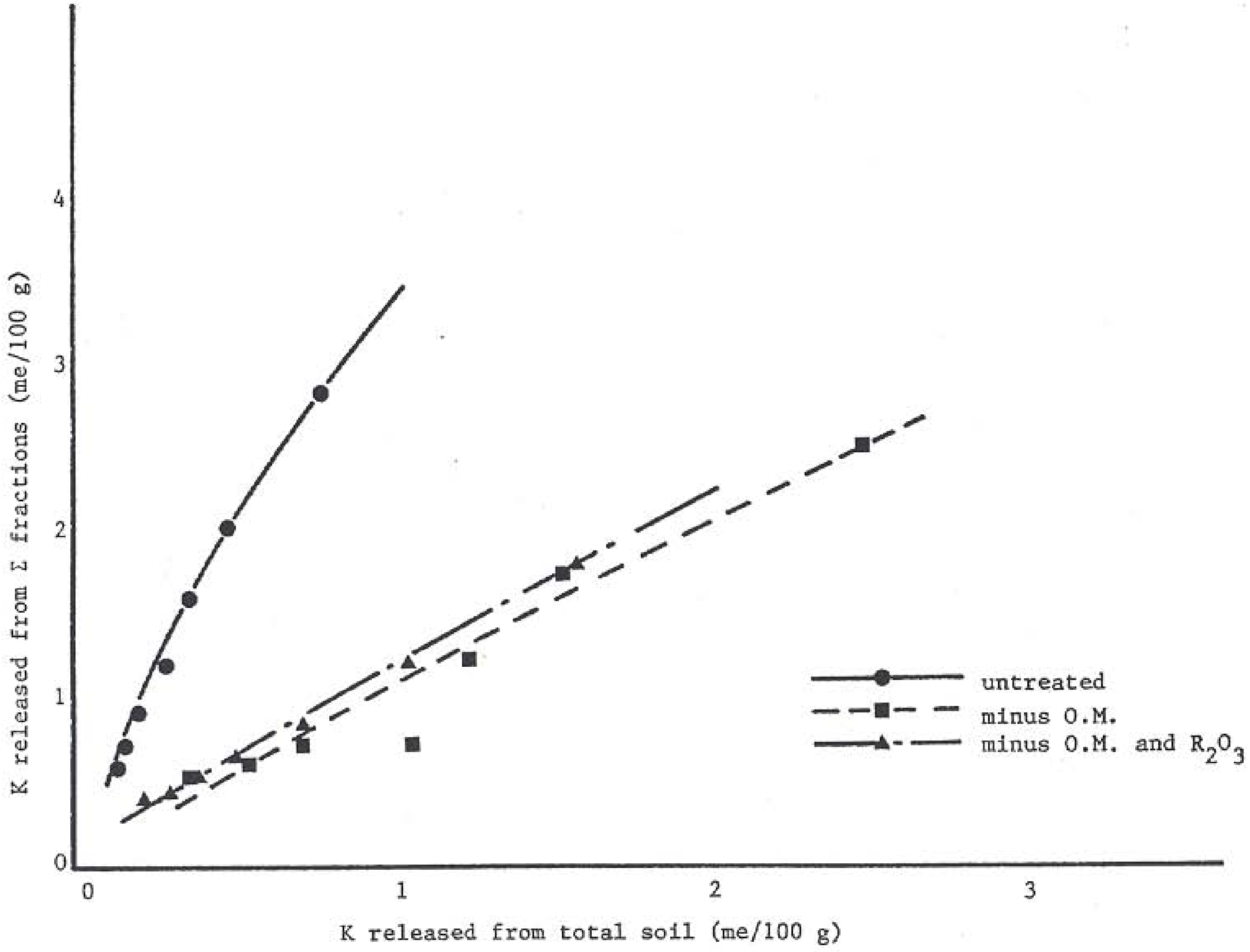
K release from treated and untreated Alderwood total soil compared to the calculated release based on particle size fraction release (0.02N $MgCl_2$ equilibrating solution)



K release from treated and untreated Wilkeson total soil compared to the calculated release based on particle size fraction release (0.02N $MgCl_2$ equilibrating solution).

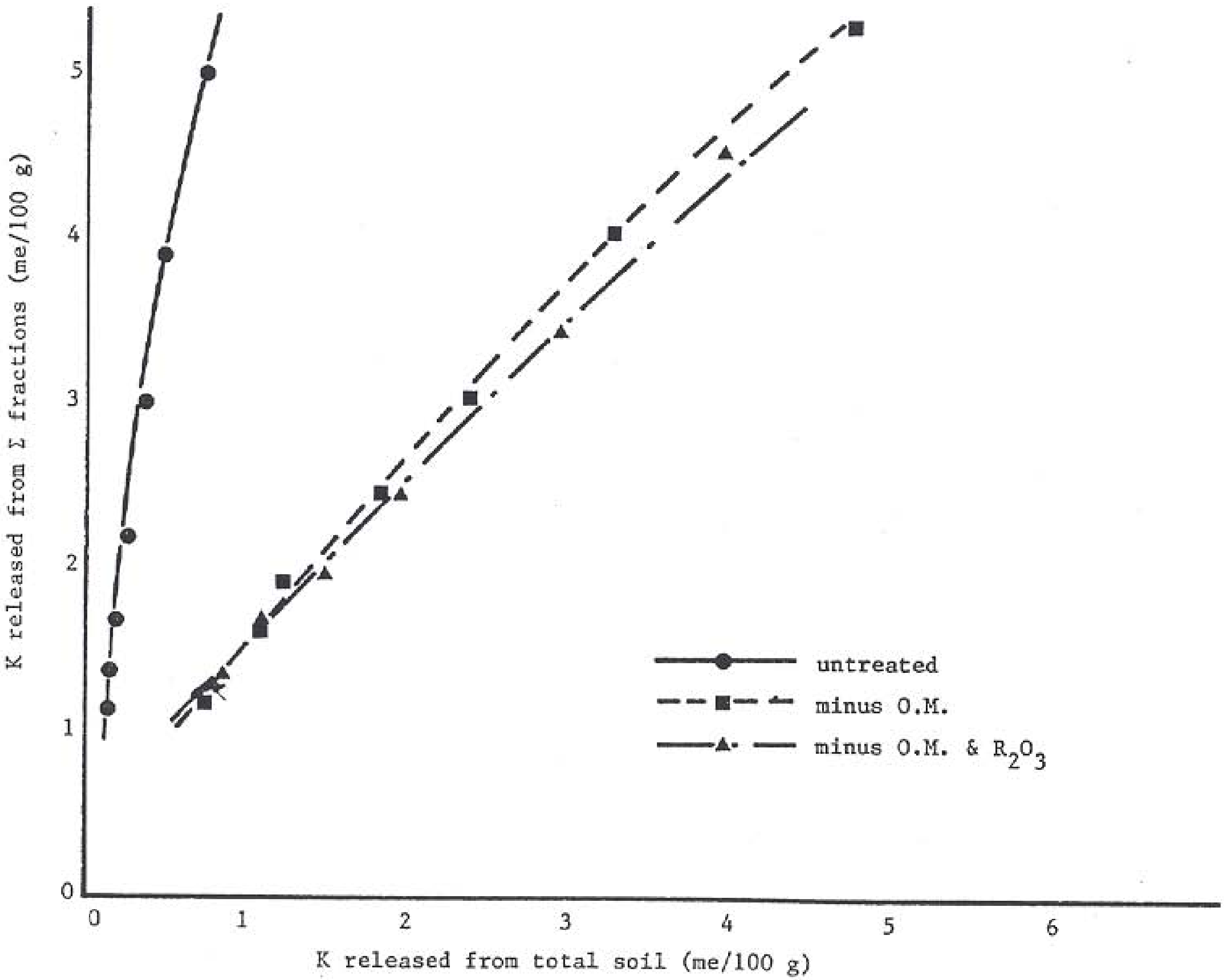


Nonexchangeable potassium release from treated and untreated Alderwood total soil compared to calculated release based on particle size fraction release (0.02N $MgCl_2$ equilibrating solution).



Nonexchangeable potassium release from treated and untreated Wilkeson total soil compared to calculated release based on particle size fraction release

(0.02N $MgCl_2$ equilibrating solution)



# VITA

Name: William Wallace Bourgeois

Born: November 18, 1943; Vancouver, British Columbia, Canada

Parents: Gaston P. and Elizabeth S. Bourgeois

Education: 1961: Graduated Kitsilano High School, Vancouver, B.C., Canada

1965: Bachelor of Scientific Agriculture, University of British Columbia, Vancouver, B.C.

1969: Master of Science (Soil Science), University of British Columbia, Vancouver, B.C.

1973: Doctor of Philosophy (Forest Soils), University of Washington, Seattle, Washington, U.S.A.