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ENCED BY ROOT CEC AND COMPETING SPECIES

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Abstract approved: \_\_\_\_\_  
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The objectives of this study were to establish a suitable method for the measurement of the root cation-exchange capacity of conifer seedlings, and to examine possible influences of this root characteristic on nutrient absorption from a Bellpine soil under greenhouse conditions.

The exchange sites of fresh, excised roots were saturated with  $H^+$  by means of ten subsequent 15-second rinses in 0.1 N HCl. Each acid rinse was followed by a water rinse of equal length. This technique, together with the use of large volumes of acid and "low-salt" roots, permitted complete saturation of the root exchange sites by preventing readsorption of replaced and leaked cations. The acid which was subsequently released into a neutral 0.1 N KCl solution by these roots was titrated. Neutral pH was maintained by addition of standard KOH for up to two hours.

The titration value did not represent an accurate measurement

of the root CEC, since short titration periods prevented complete neutralization of the adsorbed acidity. Extended titration times led to the inclusion of large amounts of  $H^+$ , which are derived from various other sources within the root. This latter fraction of  $H^+$ , termed non-exchangeable, was quantitatively determined by titration of the acidity, which was liberated from Ca-saturated roots. The root CEC was measured as the difference between total and non-exchangeable acidity.

The Bellpine soil was shown to considerably reduce the root cation-exchange capacity of nursery-grown conifer seedlings. Most likely, changes in the fungus-root association, variations in the N-level, or high levels of Mn are the causes of the observed CEC decreases.

In a greenhouse experiment, incense cedar, noble fir, and two Douglas fir varieties were grown singly, in association with each other, and together with bentgrass and tall fescue. Manganese concentrations in the seedlings reached toxicity levels in many instances and induced a Fe-deficiency. The tolerance of the conifer species to high levels of Mn was correlated to their root CEC. Species with a relatively high root CEC took up more Ca; whereas, in most cases, seedlings with relatively low root CEC accumulated more K.

Increases in P uptake were paralleled by rising root CEC. These correlations, however, do not necessarily imply a causal

relationship between root CEC and nutrient absorption. Competing tree and grass species did not, in all cases, affect the nutrient uptake by the host species according to expectations from their root CEC. Other factors overshadowed possible influences of root CEC in competitive nutrient uptake.

Nutrient Uptake by Conifer Seedlings as Influenced  
by Root CEC and Competing Species

by

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# NUTRIENT UPTAKE BY CONIFER SEEDLINGS AS INFLUENCED BY ROOT CEC AND COMPETING SPECIES

## INTRODUCTION

Christmas tree production represents an important branch of the forest industry of the Pacific Northwest. To prevent excessive growth, detrimental to the production of high quality trees, plantations usually occupy land of low site index. Often, they are established on abandoned fields of high acidity and low fertility levels. As a consequence, nutrient deficiencies may occur.

In certain areas of the Willamette Valley, the trees grow excessively slow, older needles turn yellow and brown; and, in severe cases, a general pale, yellowish color decreases the value of the crop.

Low levels of K have been tentatively associated with the deficiency. The symptoms appear particularly serious where the conifers grow in association with bentgrass. The elimination of the grass has proven to be an effective tool to ease the suspected deficiency.

Bentgrass is known to be an efficient extractor of soil K. Its low root cation-exchange capacity may be related to this ability.

The root cation-exchange capacity is a plant characteristic which has been related extensively to feeding power and nutrient uptake of agricultural species. It has served as a criterion for the selection of species or varieties which were particularly adapted to

soils having certain nutrient deficiencies or toxicities.

Data on root CEC of forest tree species, and its relationship to nutrient uptake, are very limited. The present study was undertaken with the following objectives:

- 1) To develop a suitable method for the root CEC determination of conifer seedlings.
- 2) To compare root CEC values of selected conifer species.
- 3) To test, in a greenhouse experiment, the hypothesis that root CEC relations may influence nutrient uptake of conifer seedlings.

## LITERATURE REVIEW

"Differences in the ability of plants to take up cations from the soil are largely controlled by the cation-exchange capacity of the plant root and the valence of the cation" (Drake et al., 1951, p. 146). With this summary, a development culminated that had been initiated by the discovery of negative electrical charges on root surfaces by Devaux (1916) and the relation of this phenomenon to cation accumulation (Teorell, 1935; Osterhout, 1936; Brooks, 1937; Jenny and Overstreet, 1939). Later plant physiologists generally did not share this initial enthusiasm. The issue, however, is by no means dead. More recent publications (Jenny, 1966; Ando, 1967; Franklin, 1970) indicate possible new direct functions of root CEC in ion uptake.

Plant physiologists and soil scientists differ in their approach to the question whether or not CEC influences nutrient uptake. The former tend to concentrate their efforts on the actual uptake mechanism in an attempt to describe causality. If CEC and its components are directly involved in such a process is an open question. It almost certainly influences the actual availability of an ion for the plant root. This is perhaps why agronomists, who take yield data as valid answers, generally favor the idea of CEC dependence of nutrient uptake under certain conditions.

In addition, the issue also depends on the context in which a

particular investigator sees root CEC; that is, on the particular model of plant uptake mechanism and soil nutrient supply process accepted. Both shall, therefore, be outlined in the following section.

### Salt Entry into Plants

#### Apparent Free Space

As a first step in accumulation, ions and molecules enter into what is called "water space" (Cowie et al., 1949), "outer region" (Conway and Downey, 1950), "apparent free space" (Hope and Stevens, 1952), or "outer space" (Epstein, 1955). An "absorption shoulder" (Laties, 1959) appears in absorption studies as an initial rapid influx into the root tissue which, then, overshadows the slower, almost constant, irreversible and metabolically dependent absorption process.

The amount of solute uptake during this rapid influx period is partially recovered in water rinses, and, almost completely, in electrolyte solutions. The difference between the two indicates the participation of adsorption processes in this phase of accumulation, and led Briggs and Robertson (1957) to the partitioning of the Apparent Free Space (AFS) into a "Water Free Space" (WFS) and the "Donnan Free Space" (DFS). The former contains anions and cations in equivalent amounts and the same concentrations as the ambient solution.

Indiffusible anions of the cellular structure are thought to raise the cationic concentration in the latter giving rise to a Donnan system, from which anions remain more or less excluded. In essence, the AFS, thus, represents an extension of the solution environment into the root tissue, with exchange and adsorption phenomena occurring on its surfaces.

Initial difficulties in the measurement of AFS resulted in high values which implied that large fractions of the cytoplasm participated (Hope and Stevens, 1952), and the plasmalemma was very permeable. Levitt (1957) calculated corrected values of about ten percent root volume for "true free space" and accounted for this volume with interstices of the cell walls. If the interpretations of Epstein (1955) and Hylmø (1958) hold true, then, the cortical cells essentially acquire salts from the surrounding bathing solution of the cortical free space, which extends up to the stele. Others assume that ions must pass at least one, possible two, cytoplasmatic barriers located in the endodermis (Lüttge and Weigl, 1962) or the epidermis (Laties and Bud, 1964; Hendricks, 1966).

The assumed location of the Donnan Free Space (DFS), and its structural constituents, may influence CEC measurement techniques as well as the evaluation of CEC influences on uptake. Devaux (1916), and other early investigators, attribute the negative charges to the actual root surface. According to Briggs (1957), the cytoplasm

becomes the site of the DFS. Hylmö (1955) and Robertson (1958) locate the DFS in both cytoplasm and cell walls,

Most likely, however, negative charges in the cell wall create the DFS (Keller and Deuel, 1957; Bartlett, 1964; Pitman, 1965; Jenny, 1966; Hendricks, 1966; Franklin, 1969, 1970), and the plasmalemma surfaces contribute a smaller fraction (Mengel, 1968). With a two percent fraction of the root volume occupied by the DFS, it is likely that the cell walls of all cortical cells together constitute the DFS (Hendricks, 1966).

#### Nature of the Groups in the DFS

Since the DFS is located mainly in the cell walls, the constituents of this structure account for the root CEC. Cell walls of higher plants represent a cellulose framework into which other macromolecules, like hemicellulose, lignin, and pectin, are deposited (Mühlethaler, 1967). Free carboxyl groups of pectic substances furnish the bulk of the exchange groups. Keller and Deuel (1957) account for 70 to 90 percent of the total root CEC with pectin. Crooke et al. (1961) ascribe almost the entire CEC to these materials. Pectic constituents of the cell walls consist of partially methylated polygalacturonic acid which explains the CEC-uronic acid relationships established by Crooke et al. (1961) for roots and other parts of various plant species. Numerous other authors share this view

of the chemical nature of the exchange groups (Mattson, 1948; Crooke, 1958; Helmy and Elgabaly, 1958; Mitsui and Ueda, 1963a; Pitman, 1964; Marschner and Mengel, 1966; Jenny, 1966; Hendricks, 1966; Mengel, 1968; Franklin, 1969). Since cell walls contain cystein and cystin, participation of SH-groups seems possible (Mühlethaler, 1967). Phenolic OH-groups and reactive radicals of alcohols, might be involved at higher pH values (Osterhout, 1936; Mehlich, 1953; Keller and Deuel, 1957). Proteins and aminoacids of the cell membranes may contribute to the exchange complex (Teorell, 1935; Brooks, 1937; Keller and Deuel, 1957). Finally, Marschner and Mengel (1966) and Mengel (1968) assume participation of the plasmalemma via carboxyl- and phosphate radicals which parallels earlier findings by Lundegard (1945). It appears, thus, that the reactive groups causing the Donnan phenomena reside mainly in the cell walls with involvement of free radicals of the outer plasma membranes.

#### Theories on Ion Uptake Mechanisms

Monographs and reviews on salt absorption by higher plants have been published nearly annually. The difficulties of combining numerous, and often contradicting, observations become evident in the majority of them. Conclusions are rather general and cannot conceal the lack of a widely accepted model of ion accumulation. Since this accumulation occurs against osmotic gradients and

possibly against electrochemical potentials, a source of energy within the plant must be found. A model must also provide for the transportation mechanism across a membrane of limited permeability and, finally, find a way of coupling between both. Only speculations exist up to the present for the latter aspect (Hendricks, 1966).

### The Carrier Theory

The carrier theory of ion accumulation (Epstein and Hagen, 1952) assumes transport of anions and cations across the presumably impermeable membrane by a carrier that is specific to one ion or ion group. After breakdown of the ion-carrier complex in the cell interior, the ion is released and the carrier may combine with a new ion of the ambient solution. If a constant concentration and turnover rate of the carrier is assumed, its saturation with rising outside concentrations leads to a maximum uptake rate. Absorption rate and concentration in the nutrient medium are related hyperbolically. Since several carrier systems may exist for one ion, more than one maximum uptake rate may occur over a wide range of concentrations (Epstein and Hagen, 1952; Hagen and Hopkins, 1955).

The carrier theory is based on the specificity of the uptake process, on its kinetics and the analogy with enzyme reactions, and on the observed lack of a back reaction, suggesting an impermeable membrane. The carrier hypothesis has been reviewed in detail by

Epstein (1956), Bange (1962), and Fried and Broeshart (1967). Other recent reviews and individual papers seem increasingly critical (Jennings, 1963; Ulrich and Oberländer, 1964; Legett, 1968; Hiatt, 1968; Olsen, 1968). So far, no attempt to identify the carrier compound has been successful. The assumed impermeability of the plasmalemma does not agree with observed high efflux rates by various authors (Marschner, 1964; Marschner et al., 1966; Mengel and Helal, 1967; Schaedle and Jacobson, 1967; Mengel and Herwig, 1968). The stimulating effect of Ca and other bi- and trivalent ions on K and Rb uptake at low concentrations was interpreted initially as a "promotion of a reversible action between K-ions and the hydrogen form of a carrier, favouring the formation of a carrier-potassium complex" (Epstein, 1956, p. 12). This is at odds with the ideas of other researchers, who explain the phenomenon, the so-called "Viets-effect," by changes in the membrane structure and permeability induced by polyvalent cations (Handley et al., 1965; Marschner et al., 1966; Mengel and Helal, 1967; Hiatts, 1968) or, at least, not by an effect at the immediate absorption site (Jacobson et al., 1960; Marschner, 1961).

The fact that two or more isotherms are obtained for uptake rates over a wide range of concentrations was attributed to different carrier mechanisms (Epstein, 1965). For K, "system 1," effective at low concentrations, exhibits high affinity and insensitivity to

various counter-ions. In the higher concentration range, "system 2" mediates a transport that depends on the counter-ion and shows low affinity. Both systems appear as hyperbolic isotherms and, thus, support the carrier hypothesis by their maximum uptake rate. Torii and Laties (1966), however, found linear or even exponential isotherms for uptake rates in the range of system 2 for non-vacuolated tissue. This indicates an entry by diffusion across the plasmalemma. A later study by Osmund and Laties (1968) revealed that, at concentrations under one mM, the hyperbolic system 1 isotherm reflects the filling of the cytoplasm; whereas, at higher concentrations, the plasmalemma turns, to some extent, permeable to diffusion. System 2, then, reflects transport across the tonoplast into the vacuole. The two systems are assumed to operate in series. In a later response, Welch and Epstein (1969) again favor the existence of two uptake mechanisms located at the plasmalemma.

The carrier theory has focused the attention on the kinetics of the uptake process, and on phenomena of selectivity and ion interactions. The fact that it provides explanations for these observations does not necessarily constitute a proof.

#### The Electrochemical Potential Theory of Ion Uptake

The accumulation of ions against a concentration gradient does not necessarily need to be accomplished by an active, carrier mediated

process. Ion movements occur under the influence of both electrical and chemical gradients (Dainty, 1962; Jennings, 1963); and ions, accumulated in concentrations by far exceeding that of the outer solution, may be in perfect equilibrium as a result of an electrochemical potential. The Nernst equation, relating concentration gradients to electrochemical potential gradients at equilibrium conditions, may be used to decide if a measured ion distribution resulted from passive diffusion processes (Higinbotham et al., 1967). Such measurements led to the conclusion that cation movement may be passive and a result of active influx of anions. The electrochemical potential theory of ion uptake, thus, implies passive diffusion or exchange of cations as a result of electrochemical potential gradients across the plasmalemma created by an active "anion pump" (Dainty, 1962; Briggs, 1963).

Macklon and Higinbotham (1968) suggest that a change in electrochemical potential gradient precedes ion uptake. The importance of organic acids in ion accumulation, and creation of the electrochemical potential, is stressed by Hendricks (1966) and Schaedle and Jacobson (1967). Hiatt (1967, 1968) proposed a theory of salt accumulation by exchange diffusion and Donnan phenomena. Ions from the soil solution diffuse into root cells along a concentration gradient, and associate with indiffusible organic- and aminoacids of the root. A concentration gradient is, thus, maintained until

equilibrium conditions are achieved. This is supported by the observations of Mengel and Herwig (1968) that increased respiration and associated consumption of indiffusible anions, under the influence of rising temperatures, leads to increased potassium efflux.

Models of passive cation influx must provide explanations for selectivity and competition (Hendricks, 1966). Schaedle and Jacobson (1967) and Hiatt (1968) list several possibilities. Sieve effects could lead to preferential uptake of some ions over others by discrimination based on ionic radii in the hydrated or unhydrated state. Membranes contain hydrophobic constituents. The energy required for the transformation of hydrated ions into the anhydrous stage varies between ion species and could be related to discrimination. Another possibility might be specificity of chelation. File diffusion, or multiple exchange in series, is an additional, frequently assumed mechanism (Hendricks, 1966), where a small preference for one ion in an exchange reaction is raised to the power of the number of exchanges. A "chromatographically" separated ion distribution would result. Schaedle and Jacobson (1967) suggest influences of reversible shape changes of macromolecular membrane constituents as a base for ion preference. Such "sieve" effects might easily be visualized on the pathway for ion migration to the plasmalemma, as sketched by Jenny (1966).

### Membrane Structure and Ion Uptake

An assumption of passive cation entry by diffusion must also be in agreement with physical and chemical models of the plasmalemma. With a thickness of about 100 Å (Frey-Wyssling and Mühlethaler, 1965), the plasmalemma contains hydrophilic groups. Hydrophobic radicals are buried in the matrix (Branton, 1969). More specifically, a bimolecular layer of lipids, stabilized by hydrophobic interactions, is covered on both sides by electrostatically interacting proteins. Pores exist between the "lipid micelles" (Marschner and Mengel, 1966; Schoffeniels, 1967; Hiatt, 1968; Branton, 1969). Their equivalent radii are given as 4.0-4.5 Å (Schoffeniels, 1967) and 3.5-6.5 Å by Hiatt (1968). Calcium ions contract the lipid micelles vertically, thereby increasing their diameter and reducing pore size and permeability (Marschner and Mengel, 1966). The affinity of  $H^+$  for the exchange sites of these micelles exceeds that of  $Ca^{++}$  by 100 times. The hydrogen ion counteracts  $Ca^{++}$  in its effect on permeability. Influences of low pH values and rising internal H-ion concentration on efflux and net uptake can, thus, be expected.

Molecular or ionic size alone cannot sufficiently explain ionic specificity (Schoffeniels, 1967). Interactions between membrane components, solute, and solvent are suspected. Water molecules in the pores of the membrane are thought to be highly organized.

Related to the plasmalemma is a more physical possibility of ion uptake. Pinocytosis, or invagination of the plasmalemma around solute and water, has been observed for animal and, more recently, plant cells (Frey-Wyssling and Mühlethaler, 1965; Buvat, 1969).

### The Measurement of Root CEC

A method of root CEC measurement will give meaningful results only if biological characteristics, such as the location of the DFS, the nature of the exchange groups, and membrane properties, are taken into account. Basically, existing methods can be arranged in, at least, three groups: acid titration methods, direct exchange measurements, and uptake experiments, where absorption of the metabolic fraction is eliminated experimentally, or by extrapolation.

#### Measurement by Acid Titration

The value for root CEC is obtained by two steps: hydrogen saturation and subsequent titration of the adsorbed  $H^+$  with standard base in neutral salt solutions. H-roots are produced either by electro dialysis of various lengths (Mattson et al., 1949; Drake et al., 1951; Graham and Baker, 1951; Smith and Wallace, 1956a, b, c; Mouat and Walker, 1959; Morita and Aoki, 1961; Mitsui and Ueda, 1963a), or by rinses in dilute acids, a less rigorous procedure

(Williams and Coleman, 1950; Keller and Deuel, 1957; Helmy and Elgabaly, 1958; Wiersum and Bakema, 1959; Heintze, 1961; Knight et al., 1961; Crooke et al., 1964; Ando, 1967). Variations in the latter procedure include kind and strength of acid, total saturation time, and number of acid rinses applied. The titration procedures vary in their endpoints, in both pH and time. They have been performed with various bases and a variety of salt solutions. In some cases, the replaced  $H^+$  in the salt solution has been titrated without the presence of the root sample (Wiersum and Bakema, 1959; Heintze, 1961). Helmy and Elgabaly (1958) and Heintze (1961) studied the effects of various measurement variables on the obtained CEC values. The roots may be alive, or dead, even dried and milled.

#### Direct Replacement Methods

Direct replacement measurements include saturation of the root exchange sites with one ion, for example, Ca, K, Ba, or Zn, and its replacement by a second, in most cases, H, Ca, Ba, or  $NH_4$ . Isotopic exchange has frequently been applied (Huffacker and Wallace, 1959; Heintze, 1961). Water rinses of various lengths between saturation and displacement prevent carry-over of excess salts. Direct exchange measurements are numerous (Williams and Coleman, 1950; Keller and Deuel, 1957; Huffacker and Wallace, 1959; Bartlett, 1964;

Vimmerstedt, 1968). Variations in this technique appear in the time provided for saturation, exchange and removal of excess salt, in the number of saturating and displacement rinses, and in the strength and kind of salt solutions used. Bartlett's method (1964) permits simultaneous measurement of cation- and anion exchange capacity.

#### Measurement by Elimination of Metabolic Uptake

Whereas metabolic absorption increases approximately linearly with time, the adsorbed fraction should remain constant after an initial rise. If, after uptake periods of varying lengths, ions in the WFS are replaced by water rinses, then, the total uptake at various times, extrapolated to zero time, should yield the adsorbed fraction as intercept. Fried et al. (1958) criticized other methods of CEC measurement on the basis of their values obtained as the intercept in uptake-time curves. Fried's results, however, are in clear contradiction to similar experimental evidence by Bange and van Gemerden (1963). Recently, Ando (1969) used basically the same concept when he proposed a new method of CEC measurement by eliminating metabolic uptake of Li under anaerobic conditions. Total Li uptake from  $N_2$ -saturated 0.1 N LiCl in 30 minutes is taken as the root CEC.

Plant and Root Environmental  
Factors Affecting CEC

Inter- and Intraspecific Differences

Root CEC determinations using various techniques have been performed for many plant species (Drake et al., 1951; Dunham et al., 1956; Crooke and Knight, 1962). Values range from few to approximately 100 meq. per 100 gram oven-dry weight. In general, monocots represent the lower range; whereas, high CEC values are given for dicots, especially legumes. Knight et al. (1961) report a range from 15.6 to 30.8 for various conifer seedlings. The values obtained by Vimmerstedt (1968) for red cedar and white pine are considerably lower.

The root surface was assumed initially as the location of the exchange complex; therefore, comparisons were thought to be valid only on a surface area basis (Smith and Wallace, 1956a). Because of the difficulties involved in accurately measuring root surface area, only a few reports express exchange capacities in these terms (Smith and Wallace, 1956a; Bell and Walker, 1957; Crooke et al., 1961; Mitsui and Ueda, 1963a). Very often, fine, fibrous roots will have a much lower CEC per unit dry-weight than coarser roots. On a unit root surface basis, these differences must be pronounced to an even greater extent (Gray et al., 1953). This does not constitute a rule

as coarser roots may be associated with lower CEC (Smith and Wallace, 1956a; McLean et al., 1956).

Intraspecific differences in root CEC appear common (Drake et al., 1951; Huffacker and Wallace, 1958; Butler et al., 1962; Mouat, 1962; Crooke et al., 1964). They may serve as a criterion for a plant breeding program, and for the selection of a certain variety adapted to a particular soil (Vose and Randall, 1962; Crooke et al., 1964).

### Age

In general, lower CEC values are reported for older roots (Dunham et al., 1956; Smith and Wallace, 1956a; McLean et al., 1956; Helmy and Elgabaly, 1958; Mouat and Walker, 1959). An exception was reported by Graham and Baker (1951). Several reasons may account for these observations. Physiologically younger parts of the root systems tend towards higher contents of pectin and uronic acids and associated increased CEC (Williams and Coleman, 1950; Smith and Wallace, 1956a; Helmy and Elgabaly, 1958; Crooke et al., 1961; Mitsui and Ueda, 1961a). These highly pectinaceous portions of the root contribute relatively more to total root CEC in younger root systems. If CEC values are expressed in terms of unit dry-weight, then, the increased dry-weight of older, coarser roots may cause an apparent decrease. Finally, CEC measurements on living roots

may be influenced by metabolism, which is particularly prevalent in the tip region of the root (Williams and Coleman, 1950).

#### CEC of Living and Dead Roots

Initial investigations by Williams and Coleman (1950) and Smith and Wallace (1956a) indicated no difference in CEC between living and dead roots. Oven-drying did not result in CEC change (Mitsui and Ueda, 1961a). Boiling, however, reduced exchange capacity (Helmy and Elgabaly, 1958), as did treatments with ether and alcohol and metabolic inhibitors (Mouat and Walker, 1959). Mengel (1961) ascribed higher CEC values after killing to rupture of metabolically maintained barriers. On the basis of more recent theories of DFS location, Crooke (1964) proposed measurements on dead and milled root tissue. No significant differences should be expected if the killing of the root does not destroy labile groups contributing to total CEC, and metabolic influences are eliminated during measurements of live root CEC (Mitsui and Ueda, 1961a).

#### Form and Availability of Nitrogen

Liani (1960b), Cunningham and Nielsen (1963), and Franklin (1966) fail to find significant CEC-nitrogen correlations. Clear increases are reported by others (McLean et al., 1956, 1957; Blanc, 1958; Helmy and Elgabaly, 1958; Huffacker and Wallace, 1958, 1959;

Heintze, 1961; Crooke and Knight, 1962; Crooke et al., 1964; Bartlett, 1964; Ando, 1969). Nitrogen-fertilizers may vary in their effect on CEC. Huffacker and Wallace (1959) obtained reductions with  $\text{NH}_4$  and urea, and observed increases with the nitrate form of N. The level of N supply may be important. Ando (1967) could raise CEC by N-treatments only up to a certain level of N. Species may vary in their response. Species with low CEC tend to show clearer effects (Smith and Wallace, 1956b; Asher and Ozanne, 1961). A response may depend on root age (McLean et al., 1956). The measurement technique may confuse the issue; the decreases following  $\text{NH}_4$ -treatment were not apparent if electro dialysis was used in the saturation process. According to Crooke et al. (1964), no relationship exists interspecifically between N-content and root CEC. It appears in intraspecific comparisons. Liani's results (1960b) do not confirm this for eucalyptus.

#### Culture Medium

Crooke et al. (1962, 1964) treat CEC as a genetic characteristic, and deny any noticeable influence of widely varying soil conditions. Marked effects of the growth medium are reflected in reports by Graham and Baker (1951), Huffacker and Wallace (1958), and Franklin (1966). Possibly, changes are more accentuated in solution cultures or artificial soils (Cunningham and Nielsen, 1963).

Growth of conifer seedlings in sandy and calcareous soils produced different root CEC (Vimmerstedt, 1968). Declining exchange capacities, due to toxic nutrient levels, are shown by Vose and Randall (1962) and Crooke and Knight (1962). Even the temperature of the growth medium may have an effect (Graham and Baker, 1951).

#### Possible Relationships of Root CEC and Nutrient Uptake

The significance of the WFS in ion accumulation is obvious. Less well established is the role of the DFS, whose exchange groups constitute the root CEC.

The cation-exchange sites may influence absorption directly in two ways: exchange adsorption in the DFS may be a first step in ion accumulation; or, the negative charges on the AFS surfaces may influence, according to Donnan laws, the composition of the solution around the carrier entities. The latter effect has been suggested by many proponents of the theory that CEC influences ionic composition of plants (Wiersum and Bakema, 1959; Knight et al., 1961; Asher and Ozanne, 1961; Ando, 1967; Mengel, 1968). Bartlett (1964, p. 351), for example, states that

It seems reasonable that the solution environment of the active exchange sites will be influenced by the presence of electrical charges in much the same way that the total root environment itself is influenced by soil cation-exchange surfaces.

The same authors also stress that these possible influences will appear only in soil solutions of very low ionic activities, and not under conditions where the soil solution contains ions in higher concentrations than necessary for a maximum uptake rate. The inequalities of ion distribution in Donnan equilibria are pronounced only in very dilute solutions. Liquid phase concentrations in most fertile soils exceed those limits (Crooke and Knight, 1962). Pitman (1964) reasons that the distance between charged surfaces of the cell wall free space determines if ionic distributions in the vicinity of active uptake sites will reflect Donnan laws. In Jenny's terms (1966), it depends on the presence of "macro-" or "microinterstices."

Exchange adsorption may or may not be the first step in ion accumulation. The solution of this problem is the key to the question whether or not the exchange sites directly influence uptake. It is also an essential component of the theory that plants, under certain conditions, may obtain part of their nutrient supply by means of direct root surface-soil colloid ion interchange. In reverse, if contact feeding (Jenny and Overstreet, 1939) becomes an established fact, then the cation-exchange sites of the root surface must, at least facultatively, supply ions for the actual uptake mechanism.

The "contact theory" is supported by findings of Jenny and Overstreet (1939), Overstreet and Dean (1951), Gonzales and Jenny (1958), and Scheuring and Overstreet (1961) that uptake is higher from

suspensions than from their equilibrium solution. Lagerwerff (1958), Olsen and Peech (1960), and Olsen (1968) propose equal uptake rates under similar experimental conditions. On the other hand, Barber (1968) has repeatedly shown that, under certain conditions, contact feeding may furnish a significant fraction in the budget of total uptake, and amounts supplied by mass flow, diffusion, and root intercept. Thus, contradicting observations make it impossible to answer our question from this aspect. Unfortunately, more direct approaches give dissenting results as well. Epstein and Hagen (1952) and Fried et al. (1958) assume an initial adsorption phase as prerequisite to absorption, but confine this to specific carrier sites. Epstein and Legett (1954, p. 791) state that, "Within rather wide limits, the rate of metabolic absorption is largely independent of the extent to which the ions occupy exchange spots on the root exchange surfaces." Equally, Lagerwerff and Peech (1961) find no significant influence of adsorption on subsequent absorption. Calcium strongly inhibits K adsorption. It may, however, favor its absorption (Marschner, 1961; Mengel, 1963; Mengel, 1968).

On the other hand, Epstein (1954), Mertz and Levitt (1961), and Wallace (1963) report possible ion uptake from the DFS. Winter's evidence (1961) of active, metabolically dependent uptake of Rb from the adsorbed state makes a strong case for possible accumulations of nutrient elements from the exchange spots that constitute

CEC.

In addition, root CEC may influence absorption more indirectly under conditions where soil supply is limiting and Donnan phenomena take place in the DFS. The effects of polyvalent ions adsorbed on exchange groups of the plasmalemma, which contribute to total root CEC (Marschner, 1968), have been mentioned. Franklin (1969, 1970) attributes increased phosphate uptake by roots, in the presence of polyvalent ions, to a more successful blocking of negative sites in the cell wall interstices, which facilitates the passing of anions through them. This effect increases with root CEC. Positive correlations between CEC and P uptake were found repeatedly (Mattson et al., 1949; Rositter and Ozanne, 1955; Drake and Steckel, 1955; Mouat and Walker, 1959; Knight et al., 1961; Asher and Ozanne, 1961). Alternative explanations may also lie in increased phosphate activities that result from the preferential adsorption of Ca by high CEC roots, or by enhanced production of organic anions that solubilize rock phosphate.

Greenhouse experiments, or field trials by agronomists and soil scientists, overwhelmingly imply a regulating influence of CEC on nutrient uptake. It is observed only under very low fertility conditions when most of the available ions exist in the adsorbed state, and plant roots have to compete with each other and/or the soil colloids.

Correlations between high or low root CEC and differential uptake of mono- and divalent ions were reported by Drake et al. (1951), Dunham et al. (1956), Drake and Campbell (1956), Liani (1961a), Heintze (1961), Morita and Aoki (1961), Mitsui and Ueda (1963b), and Aoki and Morita (1966). Mathematical relationships between root CEC values and the ratio of mono- and divalent ions in plant composition were established with varying success (Smith and Wallace, 1956a, b, c; Huffacker and Wallace, 1958; Heintze, 1961). Experiments involving intensive competition between plants of widely differing root CEC on low fertility soils confirm the assumed relationships (Gray et al., 1953; Mouat and Walker, 1959). Additional evidence comes from laboratory experiments (Elgabaly and Wiklander, 1949; Wiersum and Bakema, 1959; Morita and Aoki, 1961). In most cases, relative accumulations of K, Mg, and Ca are compared. However, in addition to the possible bearings on P uptake, relationships between root CEC and uptake have been also observed for Zn (Broda, 1965), Sr (Mouat, 1960), Al, Fe, Ti, nitrate (Butler et al., 1962; Vose and Randall, 1962; Bollard and Butler, 1966), and Mn (Vose and Randall, 1962). Crooke and Knight (1962) examined published data on mineral composition of plants in the light of their reported root CEC. Evidence against CEC-uptake relationships by Cunningham and Nielsen (1962) were

contested by Wallace (1966) on the basis of the CEC measurement technique used.

## MATERIALS AND METHODS

The study consisted of two parts: Laboratory assays were made of the root CEC's; and, the influence of root CEC on nutrient uptake was tested in a greenhouse experiment. Since species with widely differing CEC were desirable for the greenhouse study, a preliminary procedure was adopted to obtain at least relative CEC values. On the basis of these, four conifer species were selected for the uptake experiment. During the growth period, time was available for more detailed studies on the procedure for root CEC determination.

Determination of Relative Root CEC

First-year seedlings of the following conifer species were obtained from the Oregon State Forest Nursery in Elkton, Oregon:

Incense Cedar (Librocedrus decurrens Torr.)

Sierra Redwood (Sequoia gigantea (Lindl.) Decne.)

Concolor Fir (Abies concolor (Gord. and Glend.) Lindl.)

Noble Fir (Abies procera Rehd.)

Grand Fir (Abies grandis (Dougl.) Lindl.)

Ponderosa Pine (Pinus ponderosa Laws.)

Scotch Pine (Pinus sylvestris L.)

Lodgepole Pine (Pinus contorta Dougl.)

Douglas Fir (Pseudotsuga menziesii (Mirb.) Franco var.

menziesii)

Two proveniences each of the incense cedar, concolor fir, and Douglas fir were included.

The loose nursery soil offered little resistance to manual lifting, and the root systems could be recovered essentially without damage. The trees were embedded in nursery soil, transported in this form, and stored in the greenhouse from which they were removed immediately prior to CEC measurements.

The method selected for the determination of relative root CEC values closely resembled the procedure used by Helmy and Elgabaly (1958). Ten 15-second rinses in large volumes of 0.1 N HCl, interrupted by as many rinses in distilled water, were applied to saturate the exchange sites with  $H^+$ . After transfer into 0.1 N KCl, the released acidity was neutralized by additions of KOH. Total consumption of base during a titration period of ten minutes, expressed as meq. per 100 gram oven-dry root, was taken as the relative root CEC. Each measurement consisted of at least three replications. Relative root CEC in the following always refers to the titration value for H-saturated roots to pH 7 for ten minutes.

#### Greenhouse Experiment

On the basis of these preliminary CEC measurements, incense cedar (Roseburg), noble fir, and two provenances of Douglas fir, with apparently varying root CEC, were chosen for a greenhouse

study on the influence of root CEC on nutrient competition among conifer seedlings, and between conifer seedlings and grasses. The tree seedlings were provided in the described manner from the Elkton nursery.

Because of their greatly differing root CEC values established in the literature (Drake et al., 1951; Gray et al., 1953), bentgrass (Agrostis tenuis Sibth.) and tall (Alta) fescue (Festuca elatior arundinacea Schreb.) were selected. To minimize effects of different emergences from seed, bentgrass root cuttings were used; whereas, fescue was grown from seed.

Each pot contained 15 bentgrass root cuttings or 0.428 gram of tall fescue seed (1969 crop), respectively.

The soil was taken from the Tree Farm of Mr. Gary Sander's. After air-drying, the soil was sieved to remove rock fragments and organic debris, and mixed well. Each plastic pot contained 2.42 kg of air-dry soil. Twenty-five ppm N were added as  $\text{Ca}(\text{NO}_3)_2$ , except where indicated otherwise. Planting and seeding were completed by December 1st, 1969. The pots were watered with tap water and kept at approximately a 30 percent moisture level. An intermediate cutting of the grasses proved necessary to prevent shading of the trees. In a completely randomized block design, each of the 27 treatments was replicated four times.

The treatments can be arranged in four groups:

1) Nutrient uptake of trees grown singly.

Each pot contained five seedlings of a particular species after thinning.

2) Nutrient competition between tree species.

In this group, each pot contained ten seedlings, either of the same species, or five seedlings each of two competing species. Since plant density remained approximately equal, competitive advantages of one species should manifest themselves in decreased uptake of the other.

3) Nutrient uptake of trees under competition of grasses.

Five seedlings of each tree species were<sup>\*</sup> grown in combination with each grass species.

4) Effect of raised N-levels on competitive uptake.

Five seedlings of each species were again grown with each grass species, except that 100 ppm N were supplied as  $\text{Ca}(\text{NO}_3)_2$ . The experimental outlay is given in Table 1.

### Characterization of the Experimental Soil

The Christmas Tree Farm of Mr. Gary Sanders is located in the foothills of the Coast Range, a few miles south of Philomath, Oregon. With a rolling topography, the main aspect is east, and the slopes range around 15 percent. Erosion is slight, and the furrows of the abandoned field, on which the plantation was established,

Table 1. Treatments in the greenhouse experiment.

5 plants per pot, 25 ppm N	
Incense Cedar (Roseburg)	
Douglas Fir (Zone 252)	
Douglas Fir (Benton County)	
Noble Fir (Zone 662)	

5 trees per pot, 25 ppm N		5 trees per pot, 100 ppm N	
Incense Cedar (Roseburg)	Bentgrass	Incense Cedar (Roseburg)	Bentgrass
Incense Cedar (Roseburg)	Fescue	Incense Cedar (Roseburg)	Fescue
Douglas Fir (Zone 252)	Bentgrass	Douglas Fir (Zone 252)	Bentgrass
Douglas Fir (Zone 252)	Fescue	Douglas Fir (Zone 252)	Fescue
Douglas Fir (Benton County)	Bentgrass	Douglas Fir (Benton County)	Bentgrass
Douglas Fir (Benton County)	Fescue	Douglas Fir (Benton County)	Fescue
Noble Fir (Zone 662)	Bentgrass	Noble Fir (Zone 662)	Bentgrass
Noble Fir (Zone 662)	Fescue	Noble Fir (Zone 662)	Fescue

10 plants per pot, 25 ppm N	
Incense Cedar (Roseburg)	
Douglas Fir (Zone 252)	
Douglas Fir (Benton County)	
Incense Cedar - Douglas Fir (Roseburg) (Benton County)	
Douglas Fir - Douglas Fir (Zone 252) (Benton County)	

are still visible in some places.

Tree species in the adjacent forested land included Oregon white oak (Quercus garryana Dougl.), western hemlock (Tsuga heterophylla (Raf.) Sarg.), Douglas fir (Pseudotsuga menziesii (Mirb.) Franco. var. menziesii), and madrone (Arbutus menziesii Pursh).

The soil was classified as a Lithic Haploxerult, a member of the Bellpine series. The laboratory analysis of the soil included pH, free Fe oxides, cation-exchange capacity, exchangeable bases, extractable and exchangeable Al, available P, and water-soluble and exchangeable Mn.

A moisture tension curve was established in the range of zero to 15 atmospheres. The soil was air-dried, ground, and sieved prior to analysis, and stored in cardboard containers.

#### pH

The soil pH was determined with a Corning pH-meter with a glass electrode in the pasty consistence, and in a 1:10 suspension in water. A third value was obtained by measurement in 1 N KCl with a soil-solution ration of 1:10.

In each case, the mixture was stirred frequently with a glass stirring rod for 30 minutes before the measurement. After the greenhouse experiment, pH measurements were performed similarly; however, only the pH in the pasty consistence was determined.

### Free Fe Oxides

Free Fe oxides were removed from duplicate samples according to the method described in detail by Jackson (1967). Fe content of the extractant was determined colorimetrically by the orthophenanthroline method (Murti et al., 1966; Jackson, 1967).

### Cation-Exchange Capacity

CEC values were obtained by two methods.

- 1) Duplicate samples of ten grams of air-dry soil were Ca-saturated by four washings in 30 ml of 0.5 N CaCl<sub>2</sub>. After the removal of excess chloride by three water washes, the sample was centrifuged twice with 0.01 N CaCl<sub>2</sub>. Ca in the system was replaced by three treatments in 0.5 N MgCl<sub>2</sub>. The combined supernatants were diluted to 100 ml, and Ca in the extract determined by atomic absorption with a Perkin Elmer 303 unit at 212 m $\mu$ . CEC was calculated after correction for the amount of 0.01 N CaCl<sub>2</sub> in the Ca-saturated soil.
- 2) CEC was determined according to the method of Alban and Kellogg (1959) by NH<sub>4</sub>-saturation in neutral 1 N NH<sub>4</sub>OAc and replacement by 0.1 N HCl.

### Exchangeable Bases

Exchangeable bases were extracted from the soil with pH 7.1  $\text{N}$   $\text{NH}_4\text{OAc}$  (Schollenberger and Dreibelbis, 1930). Ca, Mg, and K contents of the extractant were determined by means of a Perkin Elmer 303 atomic absorption unit.

### Extractable and Exchangeable Al

Extractable and KCl-exchangeable Al were determined by the procedures given by McLean (1965). Al content of the extractant was measured colorimetrically as described by Jackson (1967).

### Available P

Phosphorus, soluble in dilute acid-fluoride, was determined as described by Olsen and Dean (1965).

### Moisture Tension Curve

A moisture tension curve was established for the Bellpine soil in the range of 0 to 15 atmospheres. A hanging water column apparatus was used for tensions below 0.1 atmospheres. A pressure membrane apparatus with a cellulose-acetate membrane was applied for suctions of 5 and 15 atmospheres. In the range between, a pressure plate apparatus was used at 0.1, 0.33, 1.0, and 2.0 atmospheres.

The procedure has been outlined by Gardner (1965).

Plant Analysis and the Determination  
of Nutrient Uptake

Plant analysis was performed at the beginning and the end of the greenhouse uptake experiment for the above-ground portions of the seedlings. Ca, Mg, K, Fe, Mn, and P were included. The plant material was stored in manila envelopes, and dried in a forced-draft oven at 70°F. After grinding in a "Wiley-Mill," and a second drying period at 70°F, samples were used for plant analysis.

One gram samples of the dried and milled plant material were digested with concentrated HNO<sub>3</sub> and 70 percent perchloric acid. Fe and Mn were determined in the digest by means of a Perkin Elmer 303 atomic absorption unit. Ca, Mg, and K concentrations were measured by atomic absorption in appropriate dilutions. P concentrations were determined by the vanadomolybdophosphate-yellow colorimetric method of Jackson (1958).

During the growth period, old and newly formed tissues could be easily distinguished by a marked color difference. At the end of the greenhouse experiment, they were harvested, dried, milled, and analyzed separately, after their respective fresh and dry-weights had been determined. The exact initial shoot weight of the planted seedlings were not determined. Instead, it was assumed that the

dry-weight of the old tissue at the time of harvest closely approached this value. The inaccuracies of this procedure, due to transfer of organic and inorganic tissue constituents, were assumed to be small.

Nutrient uptake per tree was calculated in the following manner:

$$U = w_1 \cdot c_2 + w_2 c_3 - w_1 c_1$$

where:

$w_1$  = oven-dry weight of seedling tops at planting time, assumed to approach weight of old tissue at harvest time.

$w_2$  = oven-dry weight of newly formed tissue

$c_1$  = nutrient concentration at planting time

$c_2$  = nutrient concentration in old tissue at harvest time

$c_3$  = nutrient concentration in new tissue at harvest time

The use of seedlings instead of seed in the greenhouse experiment permitted not only the observation of uptake, but, also, calculations of possible losses of nutrients to the acid experiment soil, and observations on transfer and mobility of individual nutrients. The mobility of a particular element could, for example, be deducted from comparisons of initial and final concentrations in the old tissue. The interest was focused on nutritional behavior of the conifer seedlings. Nutrient uptake of grass species was not determined.

## RESULTS AND DISCUSSION

### Characterization of the Experimental Soil

The results of the chemical analysis of the experimental soil are shown in Table 2. The most prominent features are high acidity, high levels of extractable Al, and a marked difference between neutral salt CEC and the CEC value obtained with a buffered salt at pH 7. Low levels of exchangeable bases and available P characterize this soil as extremely infertile. Forest tree species, especially conifers, are known to remove nutrients very effectively, even from primary minerals. Voigt (1963) relates this effective feeding power to the cation-exchange value of their root systems. Wilde (1958) considers values of 5 meq. for exchangeable Ca and 30 ppm for exchangeable K as satisfactory for forest trees. The latter, incidentally the level found in this soil, represents the minimum requirement for the less exacting species like pine, whereas hardwoods and exacting conifers like spruce need higher levels.

The pH values and nutrient levels may have been inherently low in the parent material. Leaching and weathering during soil formation, and the continuous nutrient drain by crop removal, finally led to the abandoning of the field. The marked accumulation of K at the surface is, due, most likely, to the pump-action of the former bentgrass cover.

Table 2. Some chemical characteristics of the experimental soil.

pH	paste	4.6
	H <sub>2</sub> O, 1:10	5.0
	<u>1N</u> KCl, 1:10	4.5
CFC		<u>meq./100 gr.</u>
	neutral salt	2.5
	pH 7 <u>1N</u> NH <sub>4</sub> OAc	17.4
Ca		<u>meq./100 gr.</u>
	exchangeable	0.30
Mg		<u>meq./100 gr.</u>
	exchangeable	0.166
K		<u>meq./100 gr.</u>
	exchangeable, topsoil	0.13
	exchangeable, subsoil	0.025
	exchangeable, mixture	0.077
P		<u>ppm</u>
	soluble in dilute acid-fluoride	0.5
Mn		<u>ppm</u>
	exchangeable	5.25
	water-soluble	0.25
Al		<u>meq./100 gr.</u>
	exchangeable	3.34
	extractable	22.2
Free Fe oxides		<u>percent</u>
		2.14

The large difference in CEC obtained with a neutral or buffered salt solution is of interest. It suggests the existence of a large pH dependent charge due in part, perhaps, to organic matter but, most likely, a result of the occurrence of sesquioxide compounds and coatings that effectively block exchange sites for base adsorption. This idea is supported by a similar large difference between KCl-exchangeable and extractable Al. The low pH makes the existence of both monomeric aluminohexahydronium and aluminum polymers likely (Jackson, 1963). The mechanism, by which these hydrous oxide coatings account for a large pH-dependent charge, has been reviewed by Coleman and Thomas (1967). Basic cations must compete for the decreased "effective CEC" with strongly adsorbed exchangeable Al.

Of importance for fertilizer practice may be the fact that the experimental soil can be expected to have substantial anion retention or fixation power, due to the Al and Fe compounds and coatings. This may also, partially account for the low amounts of "available" P indicated.

Figure 1 represents a moisture tension curve for the experimental soil. Due to its texture, the soil holds large amounts of water at field capacity. However, the shallow depth limits the amount of water actually available and this may present a problem, especially for species with high moisture requirements like the true firs.

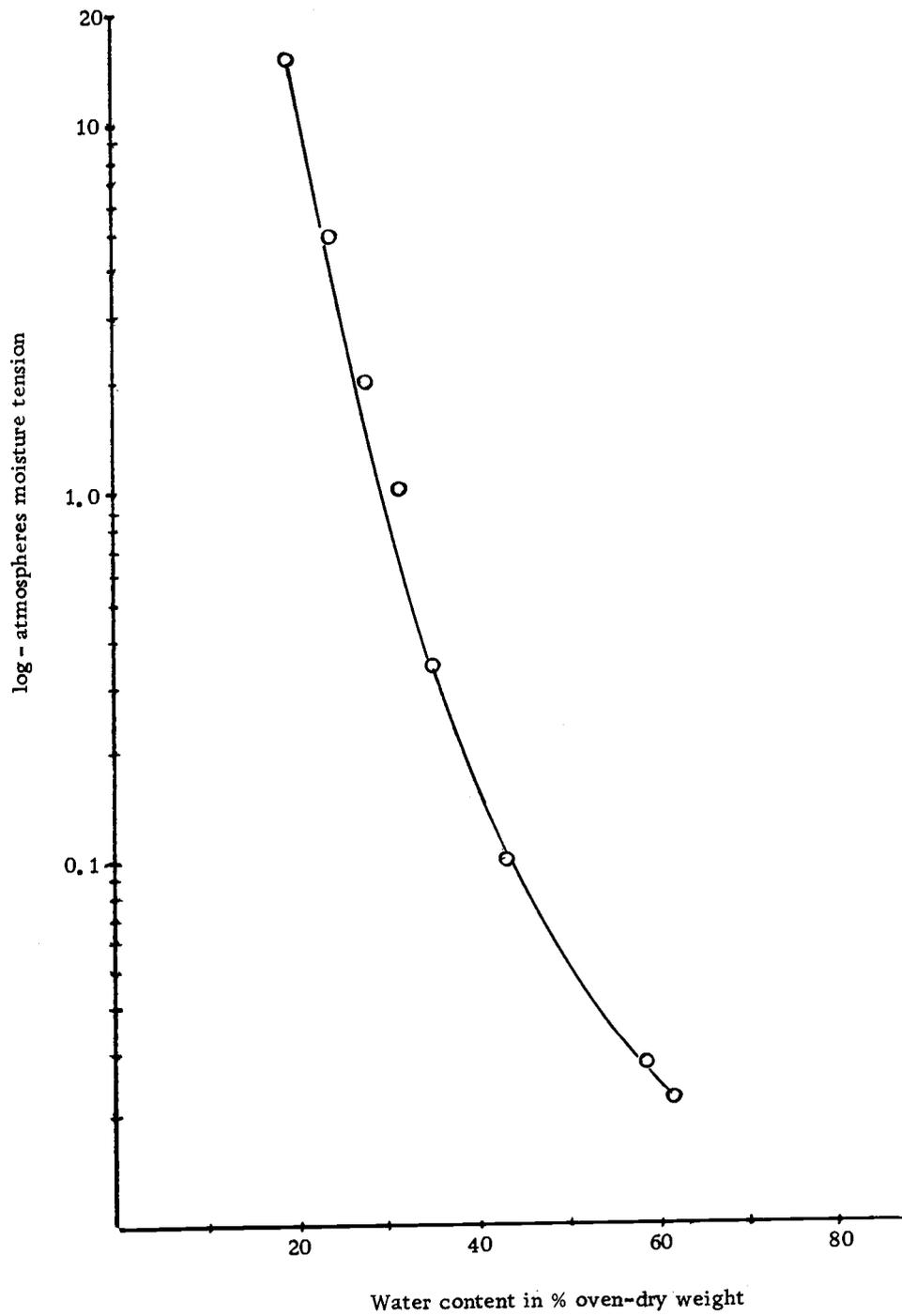


Figure 1. Water content of the experimental soil as a function of soil moisture tension.

### Relative Root CEC of Conifer Seedlings

Since at least three basic methods and many variations have been used to measure root CEC, it is not surprising that values found for the same plant species vary considerably. Plant and environment may change root CEC to a certain degree, but the bulk of these differences must be inherent in the measurement techniques applied. Although different procedures lead to different CEC values, relative differences between species seem to persist (Heintze, 1961; Bartlett, 1964; Crooke, 1964). One method may, therefore, be as good as any other, as long as only relative CEC values are the objective.

Most of the values for root CEC of forest trees have been obtained by means of acid-titration (Crooke et al., 1964). This method has been explored in detail (Helmy and Elgabaly, 1958; Heintze, 1961; Bartlett, 1964). The influence of many measurement variables is known. A modification of this technique was, therefore, applied to obtain relative CEC values for various conifer seedlings (Table 3).

It is evident that relative root CEC may vary considerably within and between species. The data are in the range of root CEC values found for agricultural species (Drake et al., 1951) and conifers (Crooke et al., 1964).

Incense cedar and Sierra redwood had finer, more fibrous roots than the other species. Within a certain species, the selection

Table 3. Relative root CEC\* of nursery grown, first-year conifer seedlings.

Species and seed source		Relative root CEC meq. / 100 gr. dry-weight
Incense Cedar	Zone 491	10.90
Incense Cedar	Zone 511	12.53
Sierra Redwood	--	14.50
Concolor Fir	Colorado	20.23
Noble Fir	Zone 662	20.60
Grand Fir	Zone 502	22.75
Ponderosa Pine	--	23.85
Scotch Pine	--	25.10
Lodgepole Pine	Zone 681	28.15
Douglas Fir	Zone 252	31.43
Concolor Fir	California	33.30
Douglas Fir	Benton County	39.39

\*The relative root CEC was arbitrarily determined as the titration value for H-roots after ten minutes.

of coarser roots leads to a decrease in root CEC, as shown for noble fir in Figure 2. The roots used in this determination were excised after the finest parts of the root systems had been used for the determination shown in Table 3. The apparent CEC of these coarse roots of only 13.3 meq. per 100 gram is, perhaps, best explained by a change in the chemical cell wall composition as the cell advances in age. Helmy and Elgabaly (1958) state that the content of pectic substances decreases from about 50 percent in young cells to 0.5 to 1.5 percent in mature tissues.

Many authors attempted to measure CEC on a surface area basis (Smith and Wallace, 1956a; Bell and Walker, 1957; Crooke et al., 1961; Mitsui and Ueda, 1963b). However, this measurement may not necessarily give a more meaningful value. The exchange sites are assumed to be distributed throughout the cortex cell walls (Pitman, 1964; Hendricks, 1966). It is not the charge density expressed on a root surface area basis, but the actual concentration of exchange sites in the DFS that determines relative adsorption of mono- and divalent ions (Ando, 1967). Crooke (1964), therefore, dries and mills the root material before H-saturation and titration. This treatment, although in agreement with the present ideas on DFS location, must necessarily expose some internal exchange sites of the root cells. Living roots were, therefore, used in this study.

A particular problem arises from the association of conifer

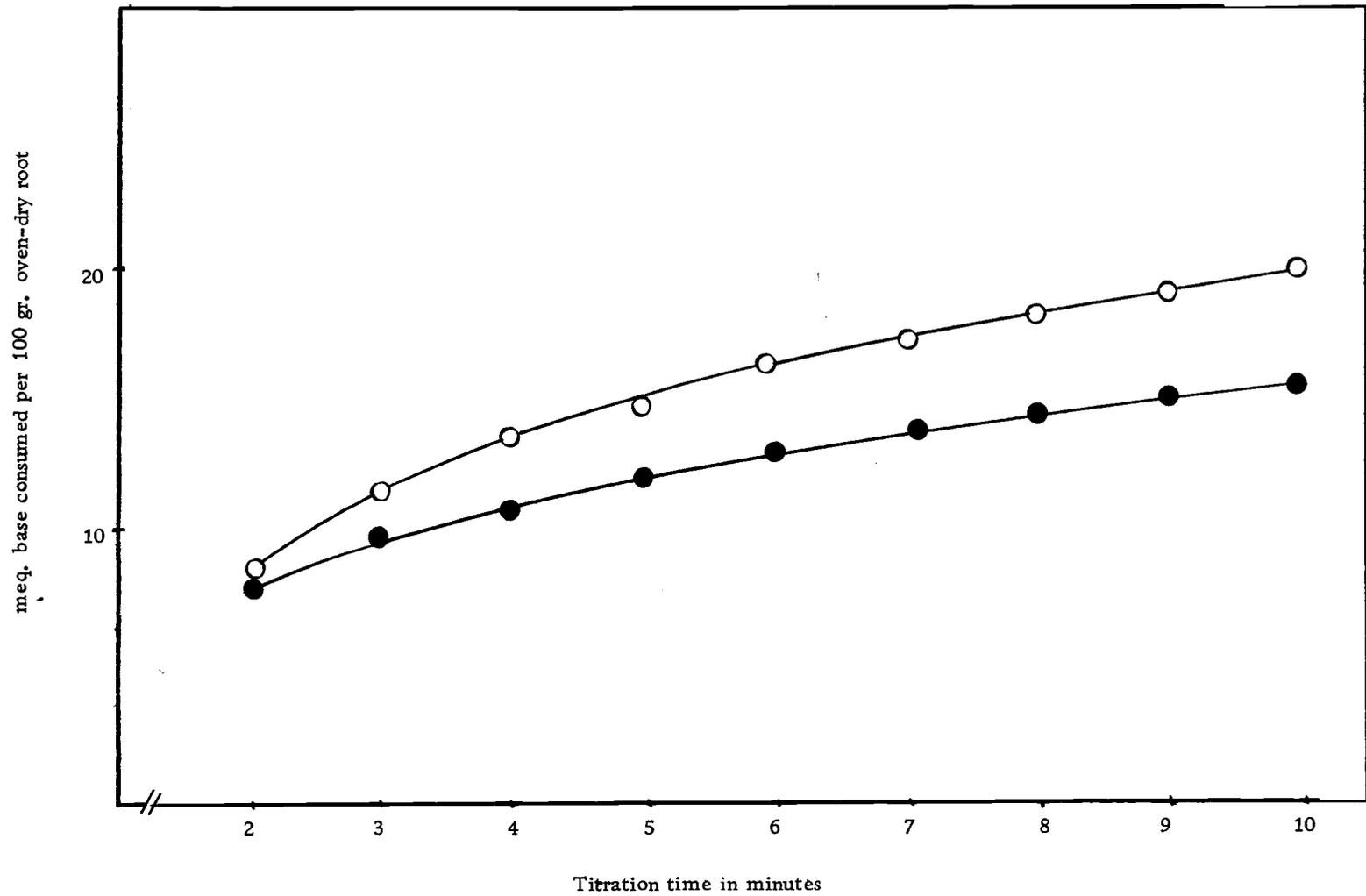


Figure 2. Titration values for H-saturated fine (○) and coarse (●) roots of noble fir.

roots with mycorrhizae. Fungus root was present during all determinations, and no attempt was made to separate root and fungus effects on CEC. Perhaps as a consequence of the less obvious nature of the endomycorrhizae, associated with many agricultural species, the literature contains no hints of possible effects of mycorrhizae on root CEC. Crooke et al. (1964), however, detected no influence of mycorrhizae on root CEC of Pinus sylvestris.

#### Studies on the Root CEC Assay

The acid titration method for root CEC determinations has been studied in many aspects and criticized in detail by various authors (Keller and Deuel, 1957; Helmy and Elgabaly, 1958; Heintze, 1961; Bartlett, 1964; Ando, 1967). The acid titration can give an accurate and meaningful CEC value only under the following conditions:

- 1) The number of charges in the DFS measured must be identical, or at least close, to the number of charges available for exchange reactions under field conditions.
- 2) The exchange complex of the root must be saturated completely with  $H^+$  during the saturation procedure.
- 3) All, and only, the  $H^+$  adsorbed during the saturation process must be replaced and neutralized during the titration.

### Influence of Soil pH on Root CEC under Field Conditions

Since the exchange complex constituting the DFS comprises numerous groups of varying acidic strengths, such as pectic carboxyl groups, phenolic and alcoholic OH-groups, phosphate groups, and reactive radicals of aminoacids, the negative charge of the root is, to some extent, pH-dependent. The titration to pH 7 is, therefore, arbitrary and may lead to dissociation of acidic groups that do not normally participate in exchange reactions in acid soils. However, it must be remembered that the pH measured for the bulk soil may not necessarily correspond to the pH at the root surface, which may be higher or lower (Jackson, 1967). Therefore, a titration of the roots to the pH of a particular soil would, possibly, be as arbitrary. Moreover, from titration curves established by Williams and Coleman (1950) and Helmy and Elgabaly (1958), a rather strong acid nature of the H-root follows. This means that the slope of the titration curve between pH 5 and pH 7 is rather steep. Variations in soil pH in this range may affect the CEC only to a small extent.

Acid rinses during the saturation period led to a loss of detectable amounts of aminocacids from the root tissue (Bartlett, 1964). This does not necessarily indicate an alteration of the exchange complex. The leakage of organic acids from the cell interior, under the influence of high acidity, has been observed by numerous authors

(Rains et al., 1964; Marschner et al., 1966; Marschner and Mengel, 1966; Mengel and Helal, 1967). On the other hand, the groups that create the cation-exchange capacity are thought to be very stable. They can be destroyed only by strong physicochemical methods (Mitsui and Ueda, 1963a; Pitman, 1964; Frey-Wyssling and Mühlethaler, 1965). It is, therefore, doubtful if the rather mild rinses in 0.1 N HCl sufficiently alter the exchange complex so that significant deviations from the CEC under field conditions occur. Most likely, it can be assumed that the number of exchange groups, available for exchange reactions at pH 7, closely approach the availability of exchange sites under field conditions.

#### Influences of Saturation Time and Base Release on the Root CEC Measurement

Incomplete saturation of the root exchange complex may be the result of too short, or too long, saturation periods. Helmy and Elgabaly (1958) obtained increases in the titration value when they applied increasing numbers of acid rinses. A similar trend became obvious in the present study. Figure 3 shows the titration curves obtained after the roots had been subjected to two, four, six, eight, and ten acid rinses. Although no statistical analysis was applied, it is obvious that the bulk of the exchange sites are saturated with  $H^+$  after four to six rinses.

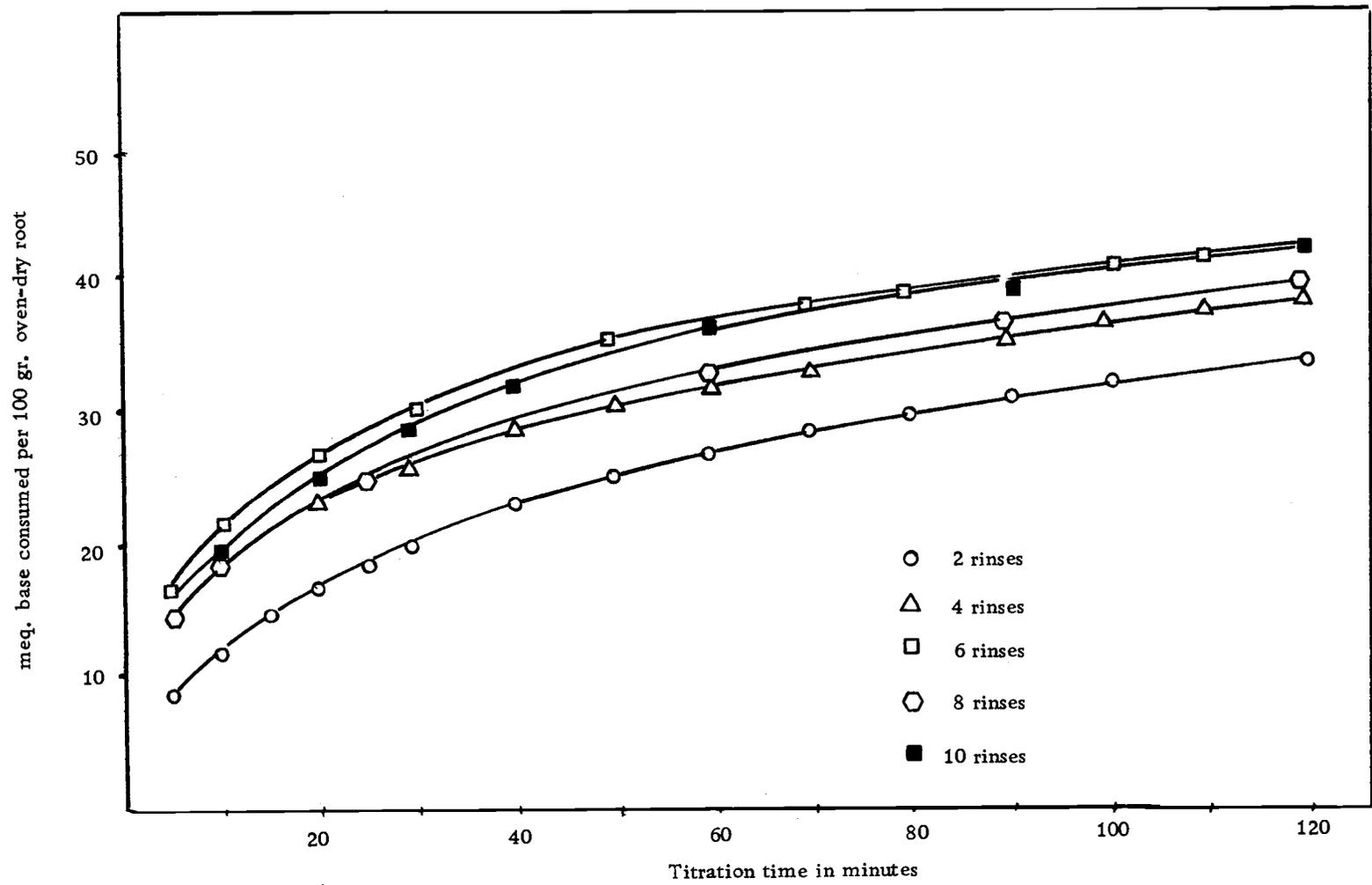


Figure 3. Titration values for excised roots of noble fir in 0.1 N KCl after the indicated number of prior acid rinses.

Uninterrupted, long saturation procedures may also prevent complete saturation by readsorption of basic cations that had been replaced from the root exchange sites or leaked from the interior of the root cells. Crooke (1958), for example, obtained a higher root CEC after two five-minute rinses than after one ten-minute acid rinse. Ando (1967) found rather heavy and equally high cation losses from excised barley roots in subsequent acid rinses. He concluded that complete saturation of the roots with  $H^+$  was impossible by acid washings due to readsorption.

To minimize these readsorption effects, ten subsequent short-time rinses in large volumes of acid were used in this study. The amounts of cations released to individual rinses decreased rapidly to very small values (Table 4). In the light of the small root samples and the large acid volumes used, it appears reasonable to assume that readsorption did not present a problem in the attempt to completely saturate the roots with  $H^+$ .

The same data (Table 4) are presented graphically in Figure 4. It is evident that the amount of cations released from the root, under the influence of 0.1 N HCl, is a function of the number of acid rinses applied. The liberation of cations occurs in two phases: After a rapid initial release, basic cations are liberated in a slower process that is a nearly linear function of time.

The initial steep rise, most likely, reflects the desorption of

Table 4. Basic cations released by excised roots of noble fir during H-saturation into individual acid rinses.

Number of rinses*	Ca	Mg meq./100 gr. oven-dry weight	K
1	5.60	2.49	1.50
2	1.62	0.46	0.64
3	0.67	0.22	0.46
4	0.45	0.14	0.38
5	0.37	0.11	0.30
6	0.70	0.09	0.25
7	0.37	0.08	0.25
8	0.44	0.08	0.26
9	0.38	0.07	0.17
10	0.60	0.07	0.21
water**	1.20	0.14	0.52

\*each rinse represents the combined acid and subsequent water rinse.

\*\*amounts of cations lost from the roots during ten water rinses subsequent to saturation.

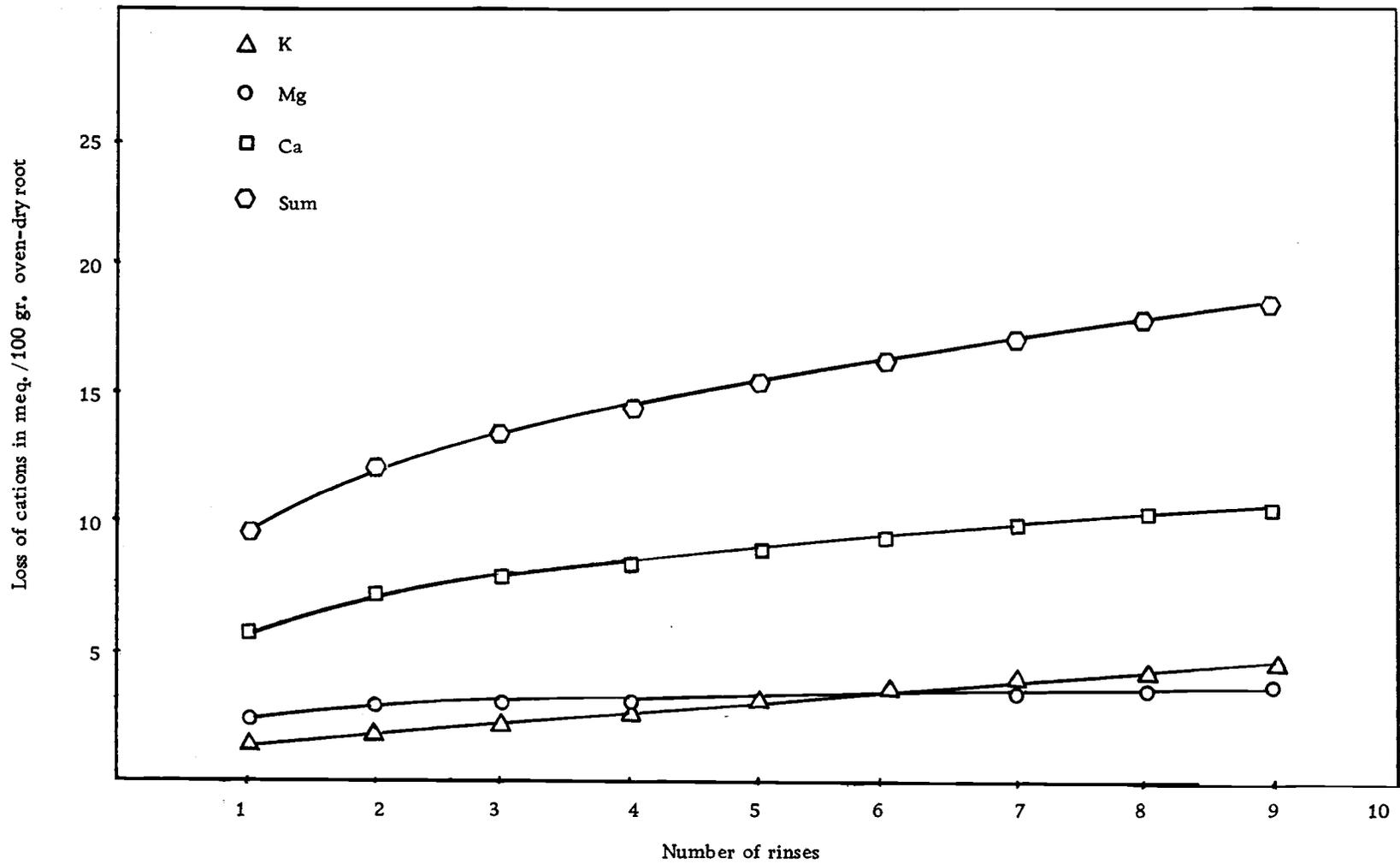


Figure 4. Release of basic cations from excised roots of noble fir as a function of the number of acid rinses.

native bases from the root exchange sites. This is substantiated by the observed concurrent rises in the titration value (Figure 3). The second phase of the desorption curve is not paralleled by increases in adsorbed acidity, as measured by the titration value, and, therefore, represents not a release by exchange reactions, but a leakage of bases from the cell interior. Bases, particularly K, have been observed to leak from the root cells, especially from "high-salt roots," or under conditions where the membrane exchange sites hold large amounts of  $H^+$  (Jenny and Overstreet, 1939; McLean and Baker, 1953; Rains et al., 1964; Marschner, 1964; Marschner and Mengel, 1966; Marschner et al., 1966; Franklin, 1966; Mengel and Helal, 1967; Mengel and Herwig, 1968).

The curves for the liberation of individual basic cations from the root reflect the valence effect in their initial phase. It takes three rinses to remove the adsorbed  $Ca^{++}$ , whereas, only two are necessary for  $Mg^{++}$ . The curve for K-release extrapolates to near zero, which indicates that K-release is almost entirely due to leakage, and no significant adsorbed fraction existed. Several authors have shown that divalent ions effectively suppress adsorption of K and other monovalent ion species (Marschner, 1961, 1968; Bange and Van Gernerden, 1963; Ando, 1967). That complete saturation with  $H^+$  is likely after only four to six acid rinses is also illustrated in Figure 5, which shows the amounts of Ca and Mg released

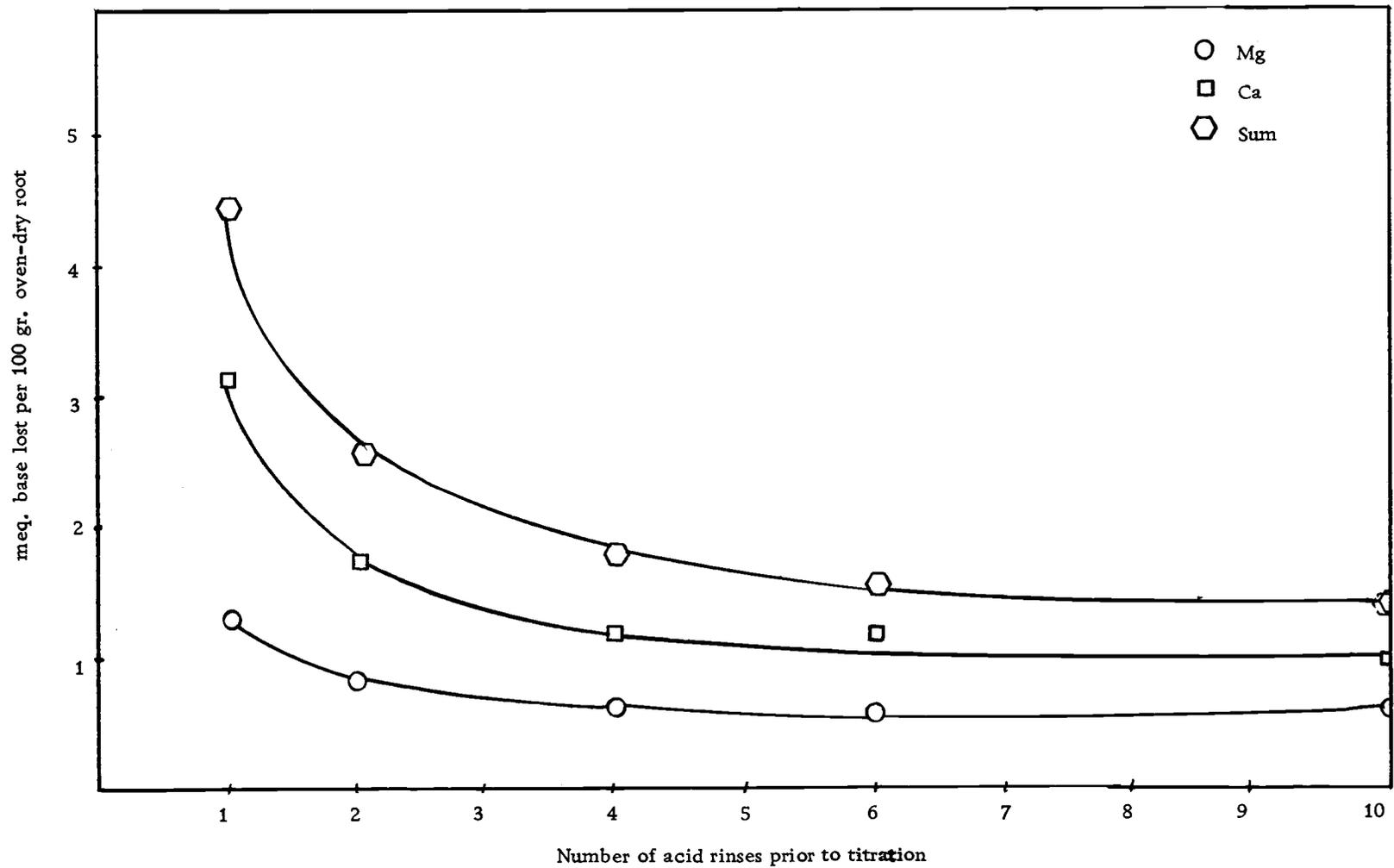


Figure 5. Loss of Ca and Mg into 0.1 N KCl during the titration of excised roots of noble fir as a function of the number of prior acid rinses.

into the 0.1 N KCl solution during titration as a function of the number of prior acid rinses.

The data in Figure 4 do not necessarily reflect generally valid relations. The experiment was carried out on plants that had grown under extremely crowded conditions, and in a relatively small volume of nursery soil during the greenhouse storage. Somewhat different data were obtained when the desorption experiment was repeated with noble fir seedlings, which had been freshly provided from the nursery (Figure 6). Whereas little difference occurred in the release patterns of Ca and Mg, the roots contained a more substantial adsorbed fraction of K. They released K from the cell interior at a much higher rate.

In summary, it can be concluded that complete H-saturation of the root exchange groups during the saturation procedure can be assumed after ten 15-second rinses in 0.1 N HCl, especially if leakage from the cell interior is minimized by the use of "low-salt roots."

#### Influence of Non-exchangeable Acidity on the Root CEC Measurement

The acidity, adsorbed on the exchange sites during the saturation, can be completely neutralized during the titration. The question is; Is only the  $H^+$ , adsorbed during the H-saturation, neutralized and measured during the titration? This obviously is not the case

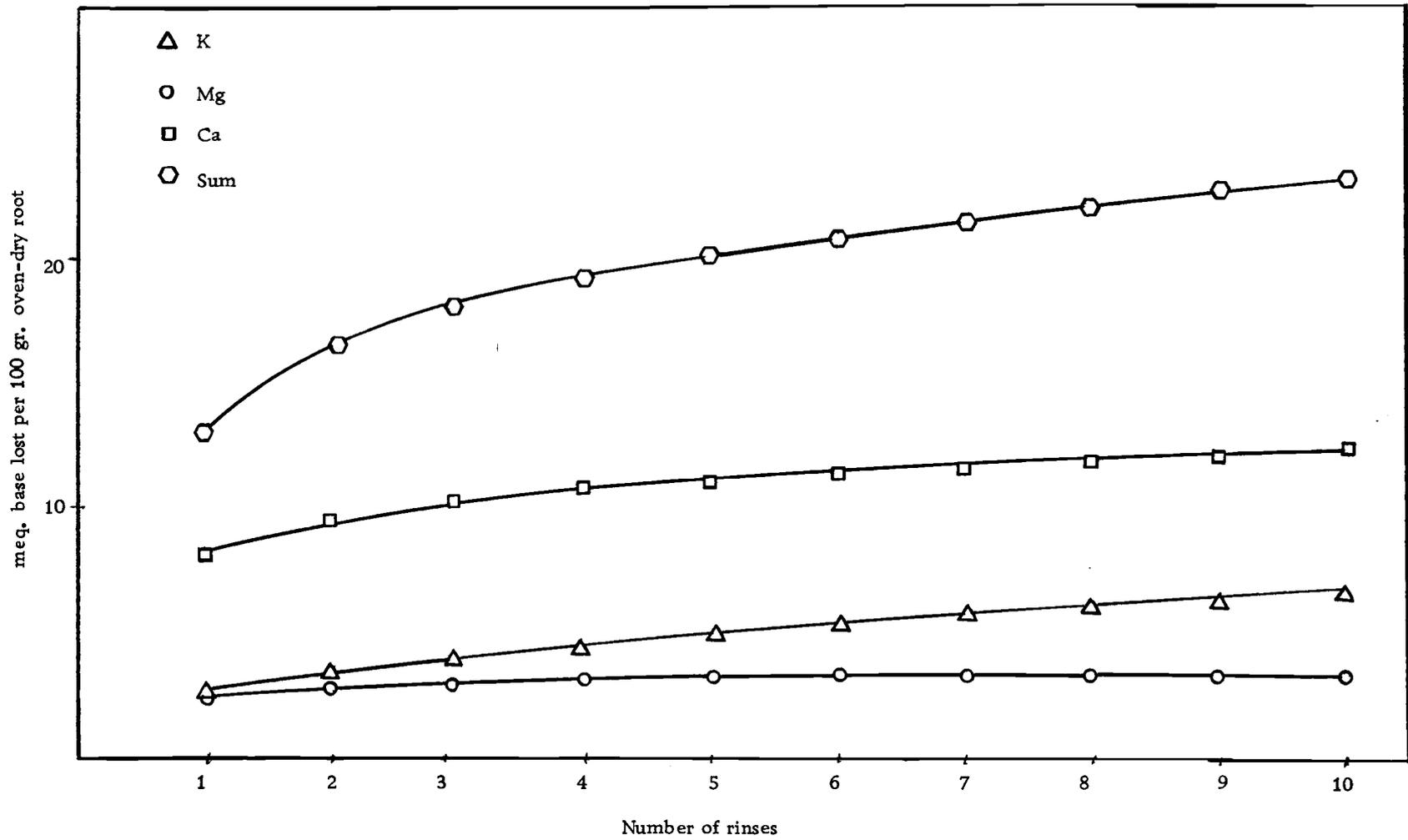


Figure 6. Release of basic cations from excised "high-salt" roots of noble fir as a function of the number of acid rinses.

during conventional titrations, as shown by the continuous acidic drift. It is hard to visualize that the replacement of the  $H^+$ , adsorbed during the relatively short saturation process, should continue for such long periods. Several other mechanisms have, therefore, been suggested: Mouat and Walker (1959) and Heintze (1961) assume metabolic uptake of  $K^+$  with concurrent release of  $H^+$ . Smith and Wallace (1956a), Helmy and Elgabaly (1958), and Mitsui and Ueda (1963a) assume slow release of  $H^+$  by dissociation of acid groups of different acidic strengths and location. Keller and Deuel (1957), Heintze (1961), and Franklin (1966) attribute the acidic drift to slow saponification of methylated carboxyl groups of the pectic acids during the titration. Most likely, simple release of  $H^+$  and organic acids from the cell interior, which is due to leakage, contributes significant amounts of acidity.

If, during the titration, it were possible to separate between  $H^+$ , adsorbed to the exchange sites of the DFS, and the acidity released from these various other sources, then an exact CEC value could be determined by the acid titration method. An attempt was made to isolate the acidity released by the various mechanisms. Hydrogen, which is not released by the exchange spots of the DFS, but derived from these other sources listed above, will be called non-exchangeable acidity.

Even fresh roots of noble fir, merely washed free of soil

particles by distilled water, exhibit the acidic drift (Figure 7), if they are titrated in 0.1 N KCl and maintained at pH 7. However, the base consumption during the titration by these untreated roots cannot be attributed to the release of non-exchangeable acidity alone. The root CEC cannot be expected to be entirely base saturated; and, roots are known to contain native, adsorbed  $H^+$  (Williams and Coleman, 1950). The titration curve for untreated roots, therefore, reflects neutralization of both native adsorbed and non-exchangeable  $H^+$ . Hydrogen-ions have a 100-fold stronger affinity for the exchange sites of the plasmalemma than even the divalent, strongly adsorbed  $Ca^{++}$ . To remove native, adsorbed  $H^+$ , the roots were, therefore, shaken for 60 minutes in large volumes of 0.1 N  $CaCl_2$ .

Figure 7 indicates that even these Ca-saturated roots show the acidic drift. But since the titration curve represents a straight line through the origin, it can be assumed that the  $CaCl_2$ -treatment succeeded in removing the adsorbed, native H; and, that the titration curve for Ca-saturated roots reflects only the neutralization of non-exchangeable acidity.

If this fraction can be isolated, then it should be possible to determine correct CEC values by subtraction of the non-exchangeable acidity from the total acidity released during the titration of H-saturated roots. Figure 8 depicts such a root CEC determination for noble fir. As already indicated by parallel slopes of the titration

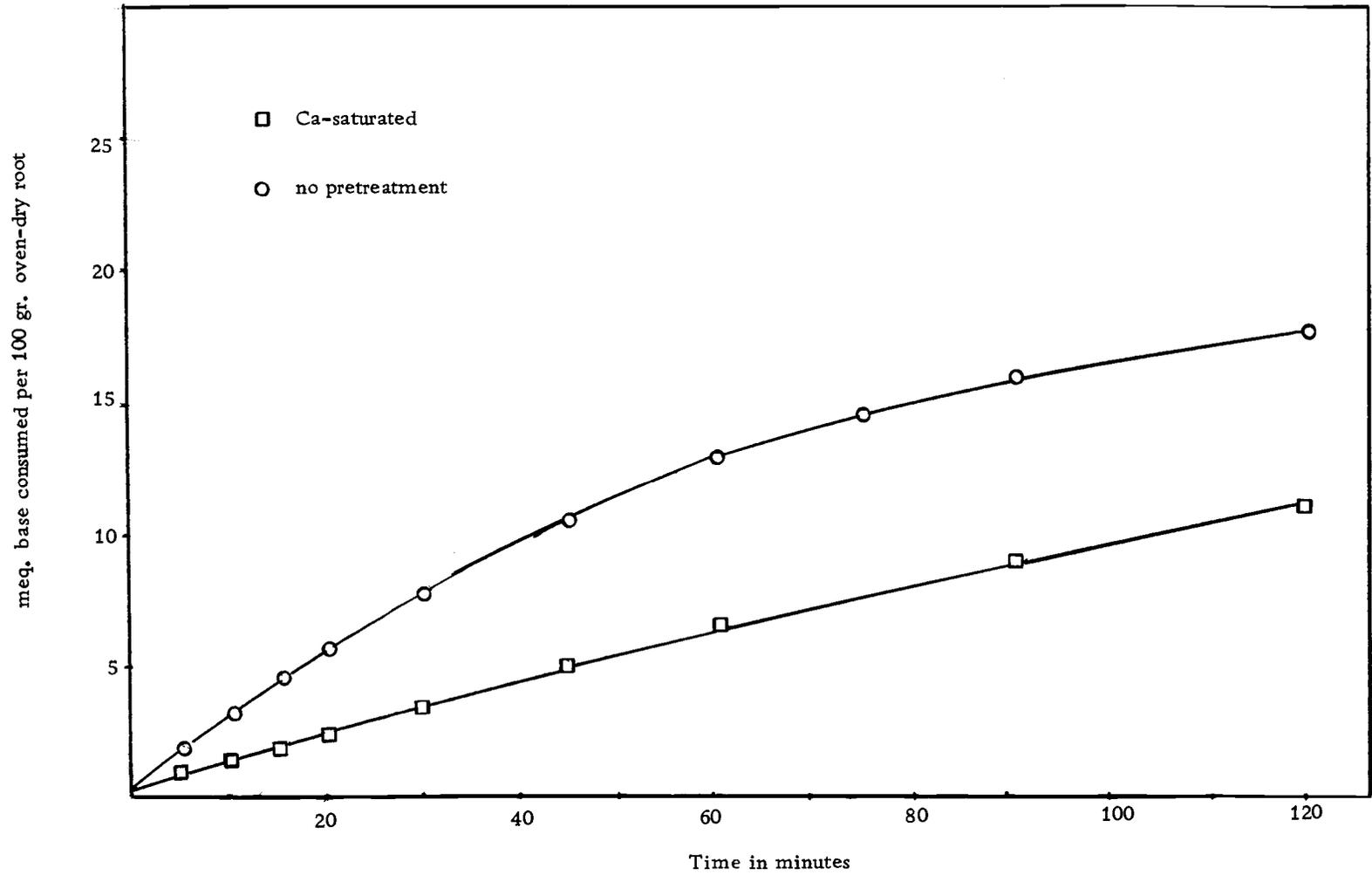


Figure 7. Titration values for excised roots of noble fir without pretreatment and after Ca-saturation of the exchange sites.

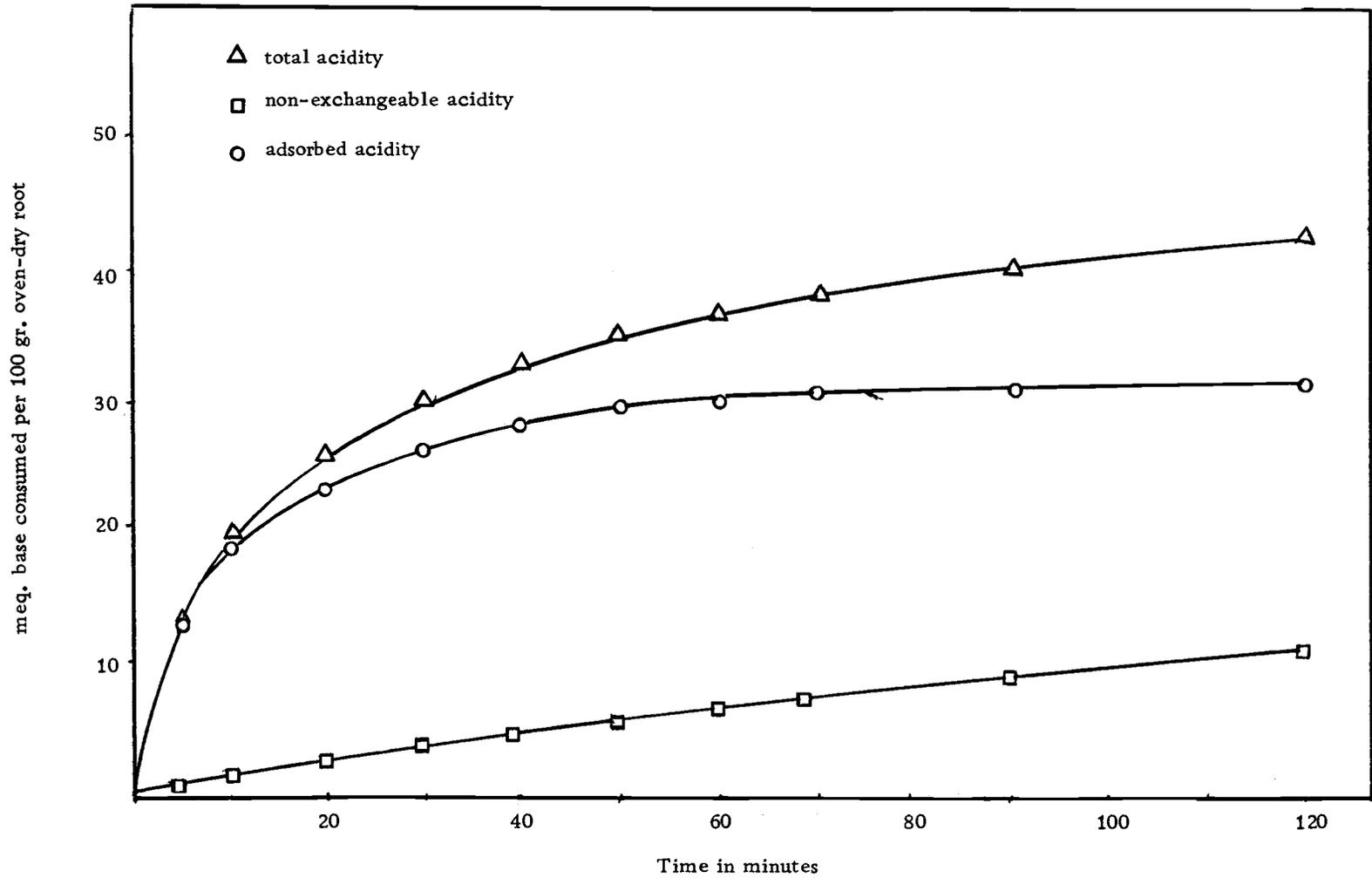


Figure 8. Root CEC of noble fir determined in KCl by titration with KOH.

curve for Ca-saturated roots, and by the second phase of the titration curve for H-saturated roots, subtraction leads to a constant value after 60 minutes. It is proposed that this value is an accurate measurement of the root CEC, and represents only the neutralization of adsorbed acidity.

An underlying assumption is that the acidic drift, caused by release of non-exchangeable acidity, is equal for initially Ca-saturated roots, and for samples with an initial H-saturation of the exchange complex. This assumption may introduce a slight inaccuracy. Calcium has been shown to curb efflux of organic acids and bases in contrast to adsorbed  $H^+$ , which, together with an increasing fraction of  $K^+$ , occupies the exchange sites of the roots in 0.1 N KCl (Marschner, 1964; Mengel and Helal, 1967). Where this occurs, the curve for the titration of adsorbed acidity, obtained by subtraction, will not culminate at a constant CEC value. From the results of this study, it is assumed, however, that the errors so introduced are very small and negligible.

From Figure 8, it follows that the neutralization of the adsorbed acidity may take as long as 60 minutes. This may seem astonishing considering the fact that only a few 15-second acid rinses attained complete H-saturation of the root CEC. It indicates the strong affinity of  $H^+$  for the exchange sites (Marschner and Günther, 1964). The  $K^+$  of the replacing KCl-solution is, obviously, not very

effective in removing adsorbed  $H^+$ . Presumably, a divalent ion like Ba would remove the adsorbed  $H^+$  faster; whereas, longer periods would be necessary if Li was used as the replacing cation. This valence effect is confirmed in Figure 9 and Figure 10. When the H-saturated roots of noble fir are titrated with standard LiOH in 0.1 N LiCl, the culmination of the titration curve for adsorbed  $H^+$  does not occur before 90 minutes. The root CEC value obtained by the use of LiCl and LiOH, however, agrees very well with the value obtained after titration with KOH in KCl.

When 0.1 N  $BaCl_2$  and standard  $Ba(OH)_2$  are used in the titration, the maximum value of the neutralization curve for adsorbed  $H^+$  is attained at approximately 50 minutes. However, there is also a distinct decrease in the root CEC value which presently cannot be explained.

The dilemma in using conventional CEC measurements by the acid titration method becomes obvious. If short titration periods are chosen, then the release of non-exchangeable acidity from the root is negligible; but, only a fraction of the adsorbed  $H^+$ , which balances the root CEC, is included in the titration value. Long titration periods may lead to the neutralization of most, if not all, of the adsorbed, exchangeable  $H^+$ . However, substantial amounts of non-exchangeable acidity from sources other than the DFS increase the apparent CEC value.

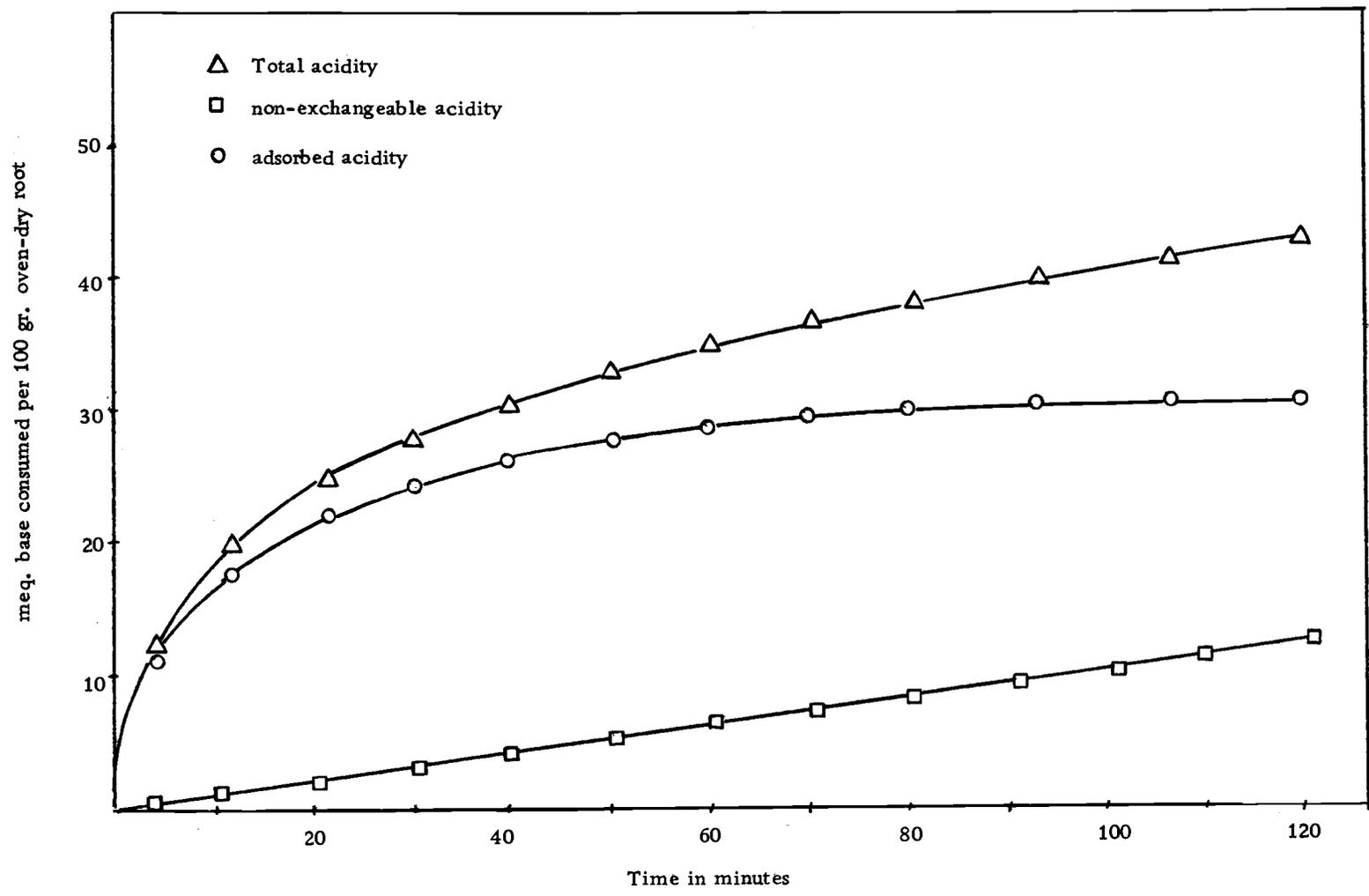


Figure 9. Root CEC of noble fir determined in LiCl by titration with LiOH.

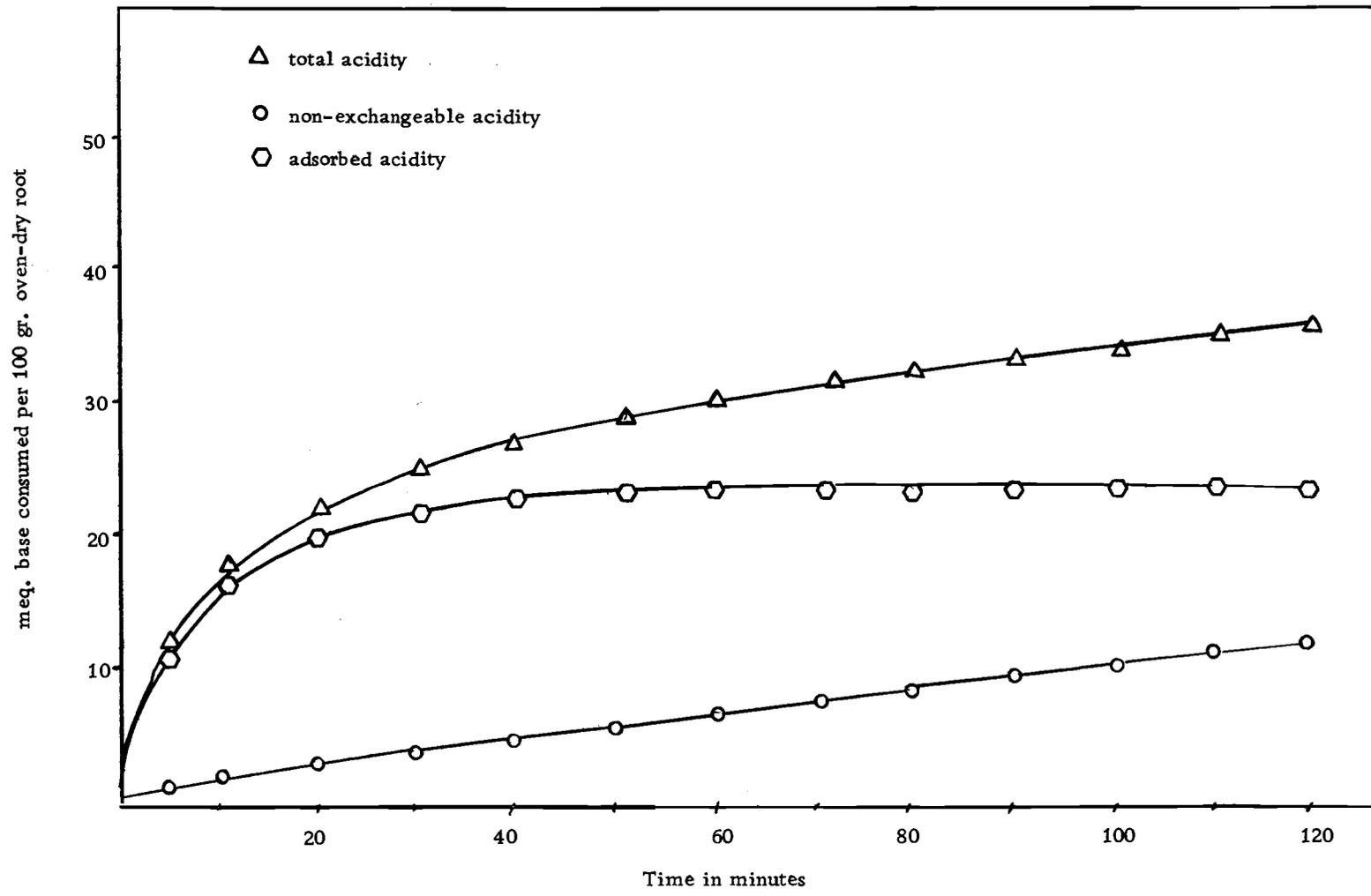


Figure 10. Root CEC of noble fir determined in  $BaCl_2$  by titration with  $Ba(OH)_2$ .

### The Measurement of Root CEC of Conifer Seedlings

It appears that the acid titration method can provide a good measurement of the root CEC of conifers only if readsorption of basic cations during the saturation period is prevented, and if  $H^+$ , adsorbed to the exchange groups of the DFS during the saturation, can be separated during the titration from non-exchangeable  $H^+$ . The following method for the determination of root CEC of conifer seedlings is proposed:

- 1) Washing: Roots of intact seedlings are washed free of adhering soil particles under running tapwater. Fine roots of comparable lengths and morphology are excised and subjected to further washings in distilled water until the rinses are completely clear. Adhering water is removed between sheets of blotting paper. Three grams of root material are transferred to a "teabag," made from plastic flyscreen, and rinsed again in distilled water.
- 2) Saturation: The roots are subjected to ten 15-second rinses in 200 ml of 0.1 N HCl. Each acid rinse is immediately followed by a 15-second rinse in 200 ml of distilled water. Ten additional 15-second rinses in 100 ml of distilled water follow to remove excess acid. Fresh volumes of acid and water must be employed for each rinse.
- 3) Titration of total acidity: The H-saturated root sample is immediately transferred into 60 ml of agitated 0.1 N KCl, and titrated to pH 7 by addition of standard KOH. The normality

of the latter should be approximately 0.01 N. Base is added whenever necessary to maintain pH 7 for approximately two hours. The roots are removed from the 0.1 N KCl solution, rinsed again in distilled water, and dried for 24 hours at 70° F.

- 4) Determination of non-exchangeable acidity: After having been washed as outlined, a second three-gram root sample is Ca-saturated for 60 minutes in several large volumes of agitated 0.1 N CaCl<sub>2</sub>. The roots are rinsed free of excess CaCl<sub>2</sub>, blotted gently, and then titrated as indicated above.
- 5) Determination of root CEC: The amounts of base consumed by Ca- and H-saturated roots are expressed in terms of 100 gram oven-dry root and plotted as a function of time. By subtraction of the titration values for Ca-saturated roots from the respective titration values for H-saturated roots, the neutralization curve for acidity adsorbed in the DFS is obtained. The culmination of this curve in a constant value is the root CEC.

#### Effects of the Bellpine Soil on Root CEC

At the end of the greenhouse experiment, the proposed method for determination of root CEC was used on the four conifer species. Titration curves for the H- and Ca-saturated roots, and the resulting neutralization curve for adsorbed acidity, are given in Figures, 11, 12, 13, and 14. The resulting CEC values are compiled in Table 5.

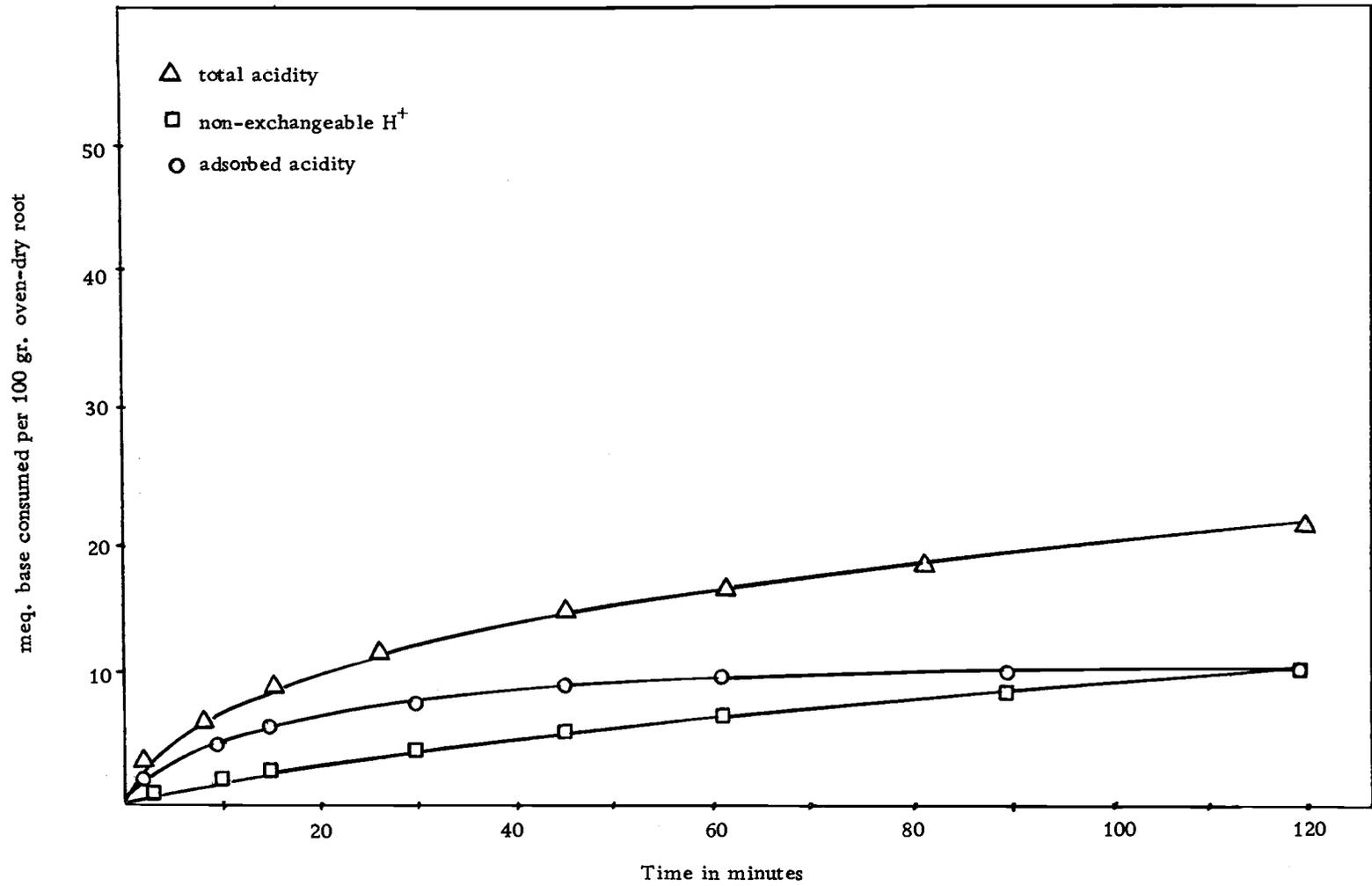


Figure 11. Root CEC of incense cedar (Roseburg) after growth in Bellpine soil.

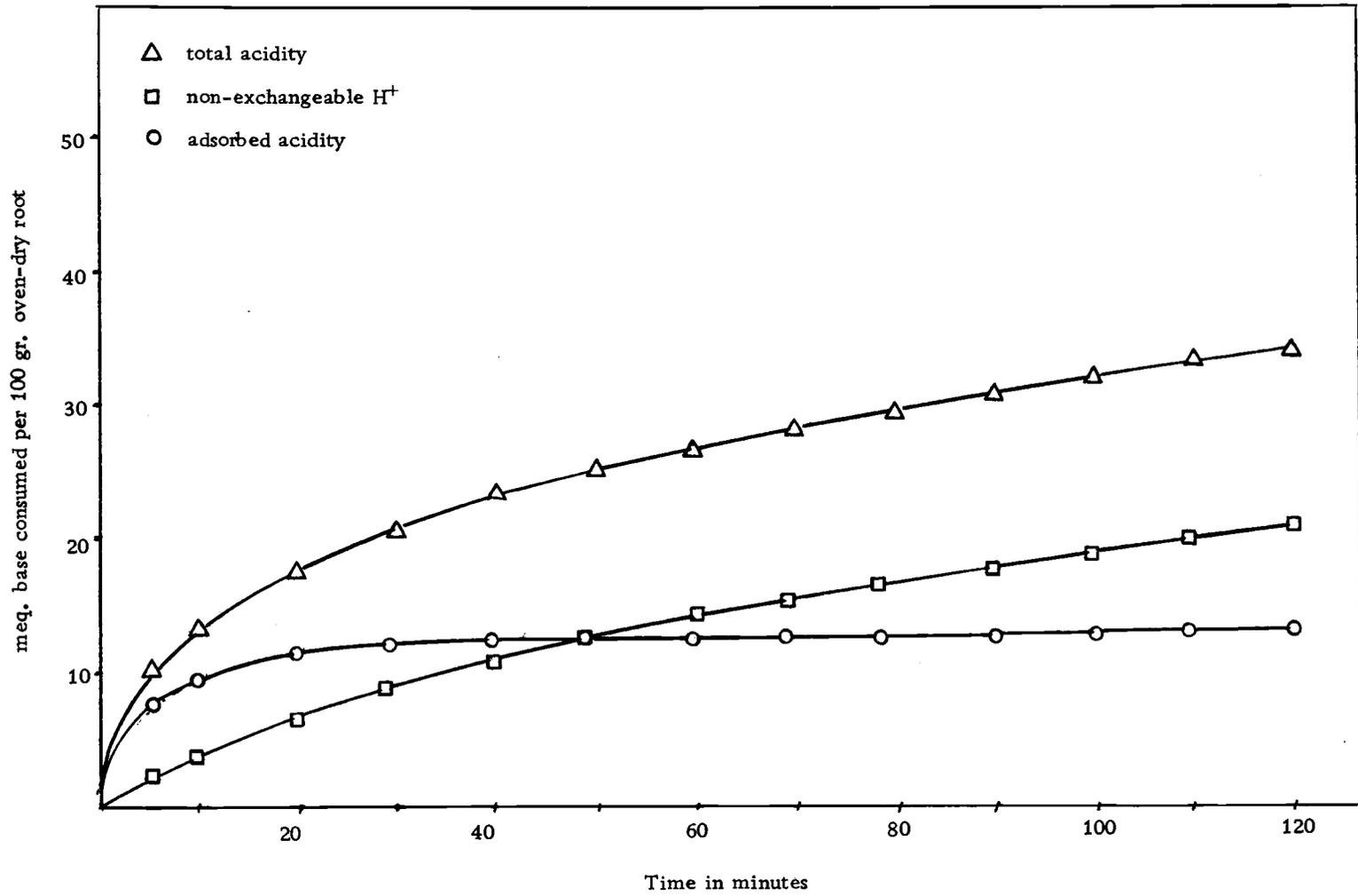


Figure 12. Root CEC of Douglas fir (Zone 252) after growth in Bellpine soil.

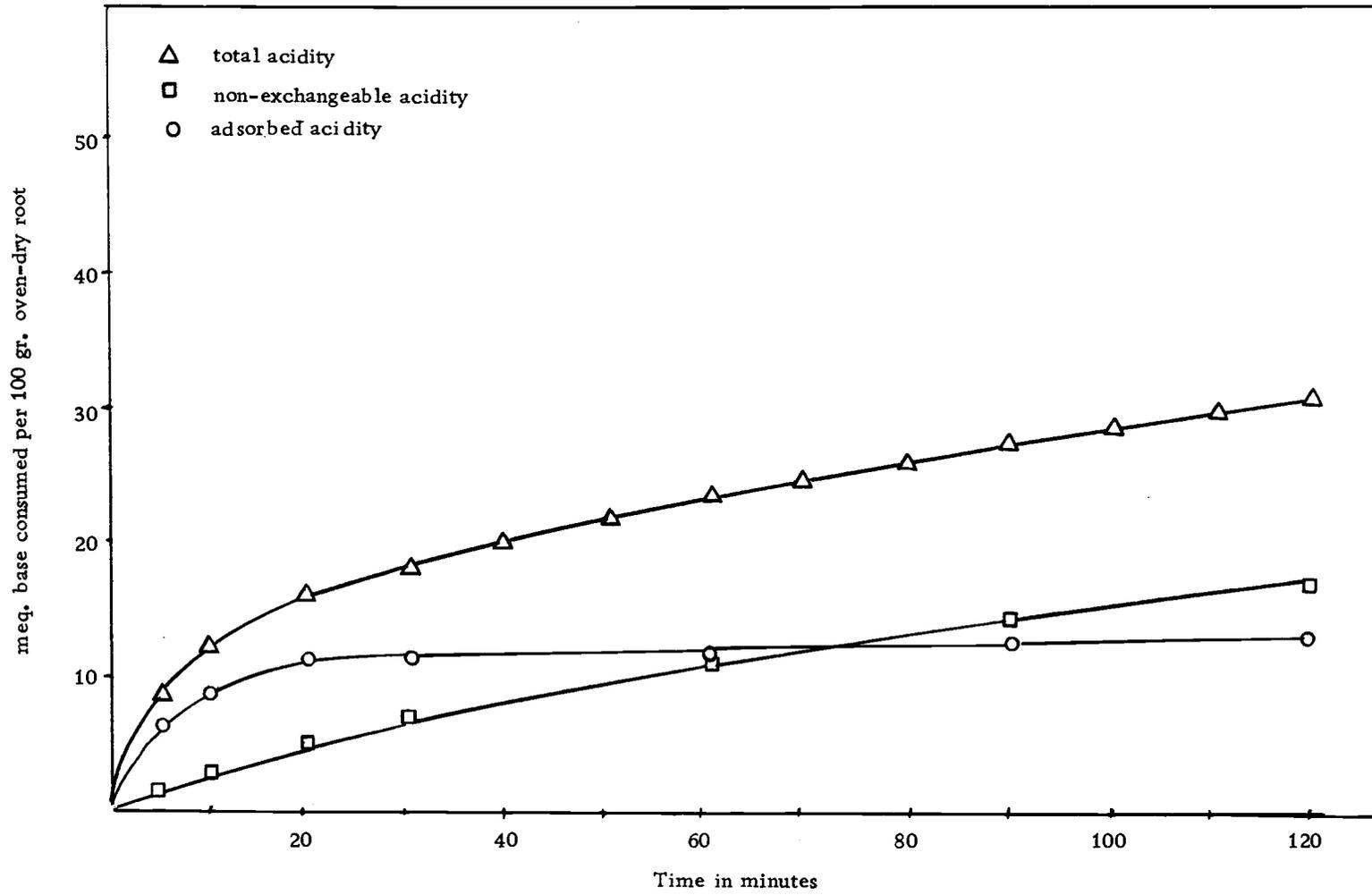


Figure 13. Root CEC of Douglas fir (Benton County) after growth in Bellpine soil.

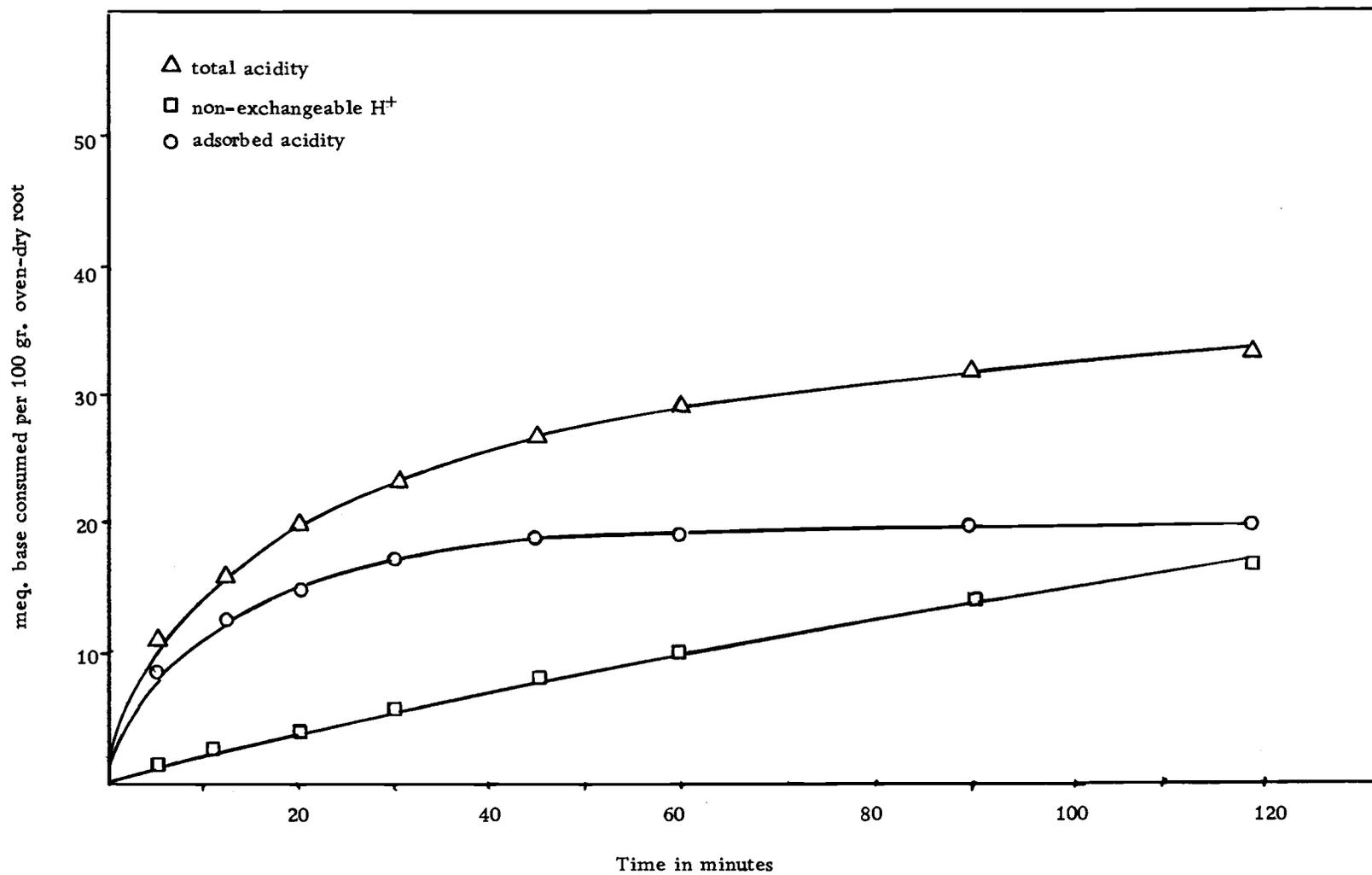


Figure 14. Root CEC of noble fir after growth in Bellpine soil.

Table 5. Root CEC of first-year conifer seedlings after growth in Bellpine soil.

Species and seed source	Root CEC meq./100 gr. dry-weight
Incense Cedar (Roseburg)	10.00
Noble Fir (Zone 662)	19.00
Douglas Fir (Zone 252)	12.50
Douglas Fir (Benton County)	12.50

Table 6. Relative root CEC\* of first-year conifer seedlings before and after growth in Bellpine soil.

Species and seed source	Relative root CEC before                  after meq./100 gr. dry-weight	
Incense Cedar (Roseburg)	10.90	7.10
Noble Fir (Zone 662)	20.60	14.50
Douglas Fir (Zone 252)	31.43	11.50
Douglas Fir (Benton County)	39.39	13.30

\*The relative root CEC was arbitrarily determined as the titration value of H-roots after ten minutes.

There is reason to believe that these values do not represent a characteristic CEC, and that the Bellpine soil influences the root CEC of conifers. Table 6 compares relative root CEC before and after the greenhouse experiment. A decrease is obvious in all cases. It is particularly pronounced for the Douglas firs, and marked for noble fir. There was only a slight reduction for incense cedar. Most likely, this reduction of the relative CEC will be paralleled by a similar decrease in the root CEC, as measured by elimination of non-exchangeable acidity. To test this, fresh noble fir seedlings were provided from the nursery and grown in the greenhouse for eight weeks, both in the nursery soil and in the acid Bellpine soil.

Figure 15 shows that the root CEC of noble fir did, indeed, decrease considerably in the Bellpine soil. This is at odds with the observations by Crooke et al. (1962) that root CEC is, to a large extent, independent of soil type. Theoretically, the following reasons could account for the observed decreases:

- 1) Root CEC decreases for older plant parts. However, this possibility can be ruled out. It is not the age of the plant, but the physiological age of the rootlets used for the CEC determination that is important. Only the finest parts of the root system, including a few inches of the tip region, were used in all determinations. In addition, the roots used in the measurement, depicted in Figure 15, were of equal age.

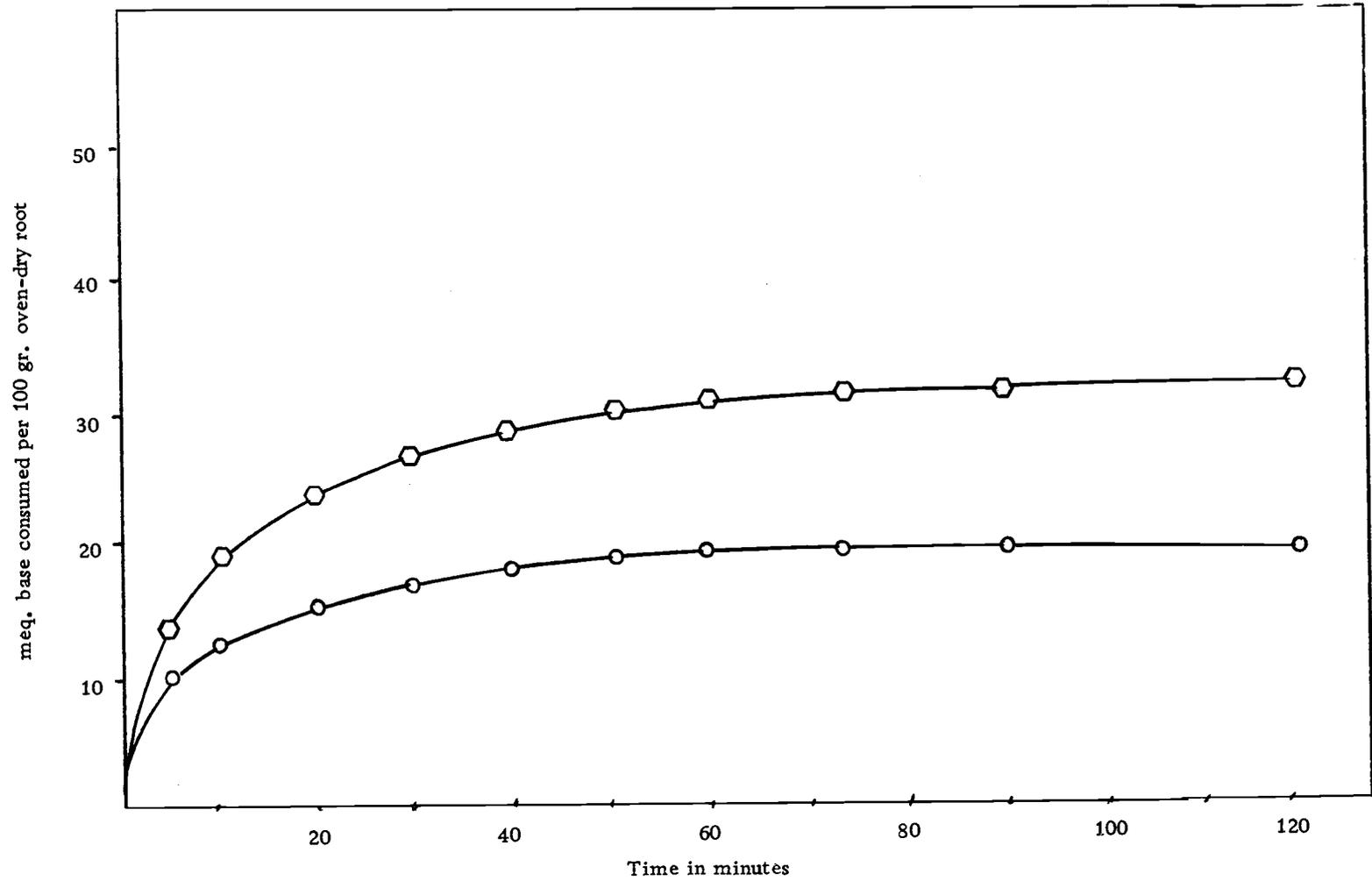


Figure 15. Root CEC of noble fir after growth in nursery soil (○) and Bellpine soil (◻).

- 2) The plant may, in adaptation and response to a particular nutritional problem, change its root CEC. Such a case was observed by Wiersum and Bakema (1959). However, these authors observed only small changes; and, therefore, this possibility seems rather remote.
- 3) Root CEC may be positively correlated to the N-content of the growth medium. Although 25 ppm N were supplied as  $\text{Ca}(\text{NO}_3)_2$ , this possibility cannot be excluded.
- 4) If mycorrhizae influence root CEC, then a change in the fungus-root association could account for the decrease. The roots of all species, especially the Douglas firs, showed mycorrhizae before and after the experiment. Up to the present time, no influence of mycorrhizae on root CEC has been detected (Crooke et al., 1964), but the possibility should definitely be considered.
- 5) Heavy metal toxicity may increase or reduce root CEC (Crooke, 1958). Manganese toxicity usually results in decreases. Since very high levels of Mn were found in the tops of all seedlings, this seems particularly attractive as a possible cause for the root CEC decrease observed. It is not clear whether the reduction is only apparent, or due to an actual decrease in the number of exchange sites. Heavy metals can be held very tightly by exchange groups of organic materials (Heintze,

1957). The relatively weak acid rinses may, therefore, fail to remove all of the adsorbed Mn from the exchange complex (Crooke, 1958; Wallace, 1966).

Low soil-N levels, mycorrhizal changes, and high levels of manganese may, therefore, singly or in combination, account for the decreases of root CEC of conifer seedlings in the Bellpine soil. The decrease may be real, or only apparent; therefore, it appears very difficult to predict its effects on nutrient uptake.

Nutrient Uptake of Conifer Seedlings in Relation  
to Root CEC and Competing Species

Hypothesis

If root CEC is related to the nutrient absorption by forest trees, then, based on results of studies involving agricultural species, the following effects can be anticipated:

- 1) Under competition, nutrient uptake by a host conifer species will be, within limits, a function of its own root CEC and the root CEC of a competing species. Under otherwise equal conditions, conifer species with relatively low root CEC will extract monovalent ions more efficiently from the soil; whereas, species with a relatively high root CEC will feed with greater success for polyvalent ions. Correspondingly, uptake of divalent ions by a particular conifer species will be depressed to a greater extent if the competing species has a relatively high root CEC. In contrast, the uptake of monovalent ions will be reduced to a greater extent if the competitor has a relatively low root CEC.
- 2) Conifer species with relatively high root CEC will, under certain conditions, extract more P from the soil than species with a relatively low root CEC.

To examine a possible role of root CEC in the mineral nutrition of

conifer seedlings, this hypothesis was tested in a greenhouse experiment.

### General Uptake Patterns

During their five-month growth period in the acid Bellpine soil, the nutrient content of all seedlings did not increase. A net increase in the total nutrient content was observed only for Ca and Mn. In many instances, net losses of K, Mg, and P occurred. In the light of the high acidity of the Bellpine soil, these losses are not surprising. They parallel earlier observations in this study where leaking of some nutrients occurred following mild acid rinses and H-saturation of membrane exchange sites. According to Marschner (1964), this efflux is rather rapid; it occurs during the "planting shock" and proceeds until a certain equilibrium is attained. Re-uptake may be initiated upon the formation of new tissues (Marschner et al., 1966).

Similar losses of P from seeds and plants to certain P-fixing soils, characterized by an abundance of sequioxide compounds and coatings, were reported by Michail and Marschner (1958) and Fried and Broeshart (1967). Loss of bases from intact plants and excised roots, under the influence of H-saturated clays, were noted by Jenny and Overstreet (1939). Armson (1963) describes losses of K to the soil from white spruce seedlings.

The magnitude of both uptake and losses was strongly affected by the initial size of the planted seedlings. These values varied considerably, especially interspecifically, between the relatively smaller firs and the taller incense cedars. By means of analysis of covariance, the measured uptake values were adjusted for differences in initial seedling weight; and, the effects of root CEC of host and competing species on nutrient uptake by the conifers were isolated.

The values in Tables 7 and 8 were obtained from the actual uptake data by separate analysis of covariance for firs and cedars. Hence, treatment comparisons, which illustrate the effects of competing tree and grass species, are valid only within a certain host species or seed source; and, the adjusted mean uptake values closely resemble the values actually measured. A common analysis of covariance was, then, performed for all conifer species. Due to the larger corrections for initial seedling weight in this analysis, adjusted values deviate to a greater degree from the measurements. They permit, however, comparisons of equal treatments where only the host species varies, and, thus, an evaluation of the influence of the root CEC of the conifer seedlings themselves on their nutrient uptake.

Table 7. Mean adjusted uptake of basic cations by conifer seedlings as a function of competing grass species.

Competing grass species	N level	Host Conifer Species (5 plants per pot)			
		Incense Cedar	Noble Fir	Douglas Fir	
				Zone 252	Benton County
	ppm			Uptake of Ca in $\mu\text{g}$ per tree	
none	25	1803.76	1041.30	963.41	-
Bentgrass	25	1426.51	890.79	1175.67	857.56
Fescue	25	1747.94	700.08	804.32	992.53
Bentgrass	100	4131.92	1151.38	1843.61	2733.50
Fescue	100	3633.29	1213.20	1097.76	2345.37
				Uptake of Mg in $\mu\text{g}$ per tree	
none	25	25.92	276.90	87.31	-
Bentgrass	25	-195.12	87.57	80.26	469.12
Fescue	25	-157.13	94.68	58.63	307.75
Bentgrass	100	105.31	153.94	149.33	511.12
Fescue	100	-39.70	248.03	131.28	332.34
				Uptake of K in $\mu\text{g}$ per tree	
none	25	1271.84	282.55	1004.41	-
Bentgrass	25	-2505.44	-798.33	312.30	-504.68
Fescue	25	-1529.26	-594.83	118.03	582.02
Bentgrass	100	-757.49	-308.31	556.02	-554.82
Fescue	100	-3056.72	-764.90	421.48	172.86
Incense Cedar:			Noble and Douglas Firs:		
LSD (5%) Ca: 1500	fCa : 4.677		LSD (5%) Ca : 467	fCa : 8.378**	
LSD (5%) Mg: 284	fMg : 1.675		LSD (5%) Mg : 124	fMg : 6.144**	
LSD (5%) K : 3085	fK : 2.387		LSD (5%) K : 691	fK : 5.081**	

Table 8. Mean adjusted uptake of basic cations by conifer seedlings as a function of associated tree species.

Associated Tree Species (5 plants per pot)	Host Conifer Species (5 plants per pot)		
	Incense Cedar	Douglas Fir	
		Zone 252	Benton County
		Uptake of Ca in $\mu\text{g}$ per tree	
Incense Cedar	1244.95	-	1115.97
Dougl. Fir (Zone 252)	-	1112.84	910.19
Dougl. Fir (Benton County)	2560.99	673.71	984.36
		Uptake of Mg in $\mu\text{g}$ per tree	
Incense Cedar	-292.03	-	229.00
Dougl. Fir (Zone 252)	-	238.69	249.49
Dougl. Fir (Benton County)	-145.65	162.72	345.35
		Uptake of K in $\mu\text{g}$ per tree	
Incense Cedar	84.20	-	100.63
Dougl. Fir (Zone 252)	-	494.99	171.42
Dougl. Fir (Benton County)	-2888.80	302.75	1010.96

for LSD and f values see Table 7

Uptake of Basic Cations in Relation to the  
Root CEC of the Competitors

The mean adjusted uptake values for the seedlings, under the influence of tree and grass competitors with widely varying root CEC, are shown in Tables 7 and 8. Based on the stated hypothesis, we expect that, among the grass species, fescue will reduce the uptake of divalent ions by the host conifers to a greater extent than bentgrass. Table 7 indicates that this by no means occurs in all instances; and that, in some treatments, the association with fescue actually led to a higher uptake rate of Ca and/or Mg.

We must also anticipate that bentgrass, as the competing species, curbs uptake of K by the conifers to a greater extent than fescue. Again, this was not observed in most cases. Douglas fir (Zone 252), for example, attained higher uptake rates of K in the company of bentgrass at both levels of N. Since its Ca uptake varies in a parallel fashion, it was, most likely, not the differential root CEC of the grasses, but simply the greater vigor of the fescue that led to these results. In the ideal case, the uptake of mono- and divalent ions should be contrarily affected by the competing grasses. Table 7 indicates that this occurs distinctively only for Douglas fir (Benton County). For this species, competition of bentgrass reduces K uptake at both levels of N to a greater degree than fescue, and, simultaneously, permits a higher uptake of divalent ions. This

indicates the possibility that, here, root CEC might actually have been involved in the competition for mono- and divalent ions.

In the case of inter- and intraspecific nutrient competition among conifers, we expect that Douglas fir (Benton County) greatly reduces uptake of divalent ions by the host species. Correspondingly, we anticipate reductions in the K absorption by the host conifers under competition by incense cedar. Table 8 indicates that the opposite occurs in the interspecific competition between incense cedar and Douglas fir (Benton County). The Douglas fir actually stimulates Ca and Mg uptake by the cedars, while it greatly reduces their K absorption. This phenomenon cannot be explained by the root CEC concept. On the other hand, the uptake of Ca and Mg by Douglas fir (Zone 252) is, in agreement with the hypothesis, considerably reduced under the competition of Douglas fir (Benton County); whereas, K uptake by the latter variety is strongly curbed with the introduction of Douglas fir (Zone 252). It is also noticeable that the tall incense cedars had no effect on Ca uptake by Douglas fir (Benton County).

In the overall picture, it appears that the relative uptake rates of mono- and divalent ions by the host conifers were affected by competition in agreement with the hypothesis only in the case of Douglas fir (Benton County). However, the reliability of the technique to

trace the preferential uptake of a particular nutrient by a competing species, with the help of the reduced absorption of this nutrient by the host species, will certainly be influenced by the mobility of the nutrient in the soil, the intensity of the competition, and the growth period involved.

The results indicate that, in some cases, the root CEC of a competing species may be of influence in the nutrient absorption by a host species. They strongly suggest, however, that other determinants, perhaps integrated in the greater vigor of one competitor, may be of overriding importance. In addition, it must be remembered that two species do not compete for only one nutrient. They may interact with a variety of chemical, physical, and soil biological determinants of nutrient absorption. It seems very unlikely that, in the evaluation of the effects of different competing species on the nutrient uptake by a host species, root CEC can be assumed to be the only variable.

#### Uptake of Bases in Relation to the Root CEC of the Host Conifer Species

In Figures 16 and 17, average uptake values for different conifer species from comparable treatments were plotted as a function of their relative root CEC. Seemingly, a relatively low root CEC represented an advantage in the accumulation of monovalent ions. Thus, incense

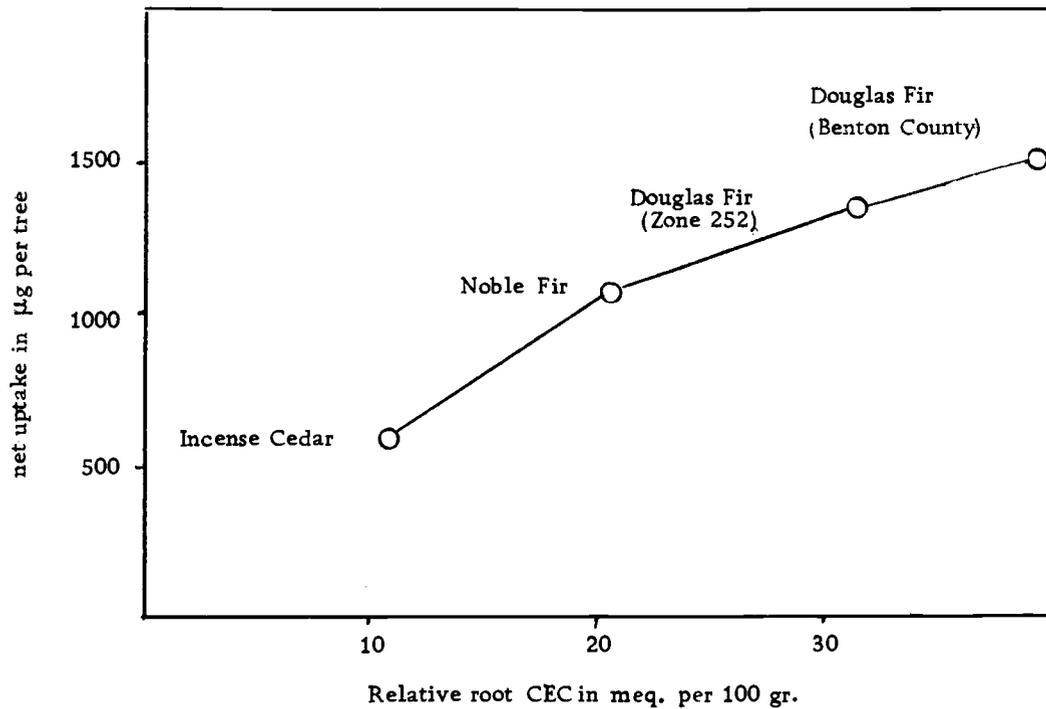


Figure 16. Average uptake of Ca by conifer seedlings under grass competition as a function of relative root CEC at 25 ppm N.

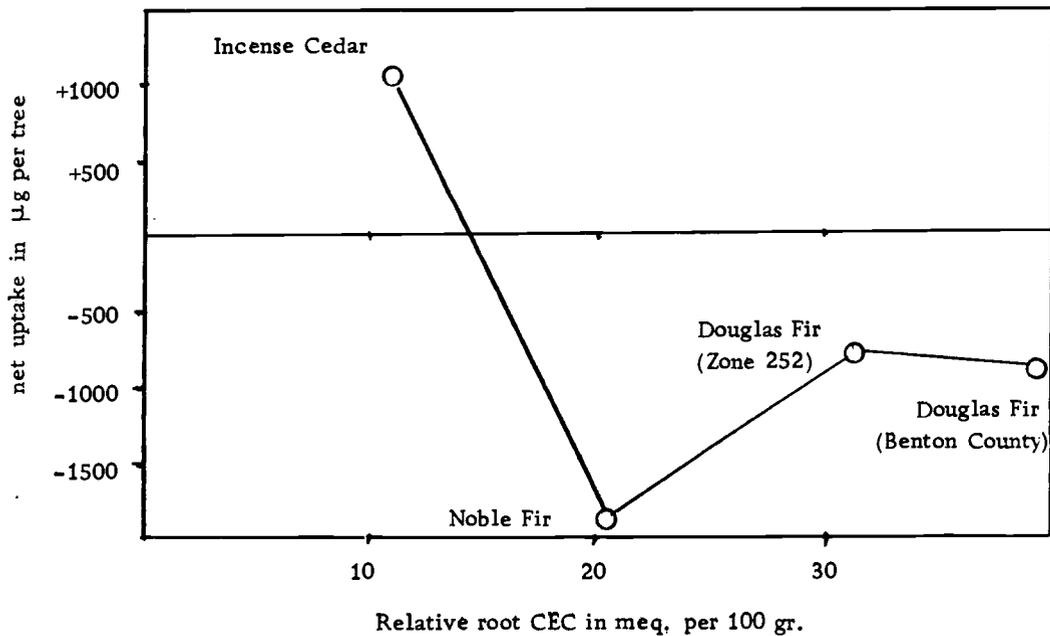


Figure 17. Average uptake of K by conifer seedlings under grass competition as a function of relative root CEC.

cedar succeeded in the uptake of relatively high amounts of K. Intra-specifically, the Douglas fir with the lower root CEC absorbed more K than the high CEC variety. The K uptake by noble fir does not correspond to its relative root CEC. As described earlier, the root CEC of this species, when measured after the growth period and the changes induced by the Bellpine soil, actually exceeded all other species. This phenomenon could possibly account for the irregularity. In contrast, uptake of Ca from the experimental soil was favored by a relatively high root CEC; and, rising CEC values were paralleled by similar increases in Ca absorption.

In the interpretation of these data, it must be remembered that a correlation between two characteristics does not necessarily imply a causal relationship. Hence, it cannot necessarily be concluded that it was actually the root CEC that caused the differential absorption of mono- and divalent ions by the conifers. However, the observed relationships support earlier findings by numerous other investigators and, in general, agree well with the hypothesis.

#### Root CEC and the Uptake of P

In contrast to other ions, the movement of P in the soil is rather restricted. A particularly pronounced immobility can be expected in the Bellpine soil with its low pH, high clay content, and the abundance of sesquioxide compounds. Theoretically, under

conditions of very intensive competition, a competing species might decrease P uptake by the conifers by feeding on the same source of P. On the other hand, stimulating effects of high CEC species on P uptake of inefficient feeders with low CEC have been reported (Drake and Steckel, 1955). Hence, no pronounced effect of competing species on P uptake by the conifers was anticipated, and no particular trend was obvious. Neither soil pH (Table 9) nor competing grass or tree species seemed to produce any consistent effect.

Averages of all adjusted treatment means are plotted as a function of root CEC in Figure 18. In agreement with the hypothesis, P uptake seems to increase with root CEC.

#### Root CEC and the Uptake of Mn

Kramer and Kozlowski (1960, p. 228) and Berger and Pratt (1963) regard Fe concentrations in plant tissues under 80 to 100 ppm as deficient. In this experiment, Fe concentrations ranged from 40 to 100 ppm in the newly formed tissues, which indicates that most conifers were not able to take up sufficient Fe from the Bellpine soil. The deficiency was also manifested in a typical, more or less pronounced chlorosis in the new tissue and browning of mature leaves. Figure 20, which also indicates the range of Fe concentrations encountered, depicts, in essence, the dilution of a small, available amount of Fe with an increasing amount of new incense

Table 9. Soil pH in the pots after harvest.

Competing Species	N- level	Incense Cedar	Noble Fir	(Zone 252)	Douglas Fir (Benton County)
	ppm N		Soil pH <sup>+</sup>		
none	25	4.90	4.83	4.65	4.80
Bentgrass	25	5.05	5.20	5.00	4.90
Bentgrass	100	5.19	4.95	4.90	5.00
Fescue	25	5.03	5.10	5.10	5.01
Fescue	100	5.25	4.90	4.82	4.85
Incense Cedar	25	5.10	--	--	5.01
Douglas Fir (Zone 252)	25	--	--	4.85	5.10
Douglas Fir (Benton County)	25	5.01	--	5.10	5.05

<sup>+</sup> pH was measured in the pasty consistence on a composite sample of four replications.

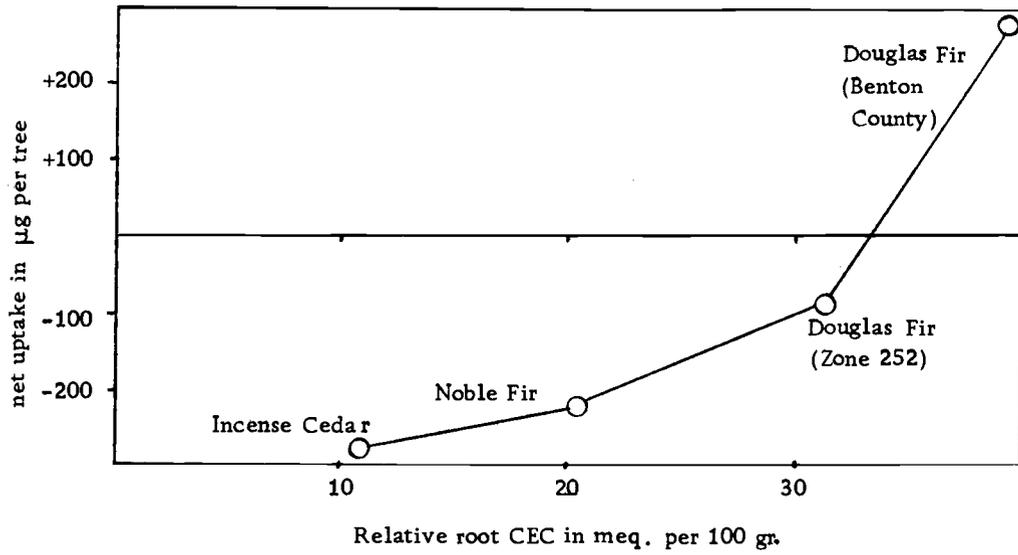


Figure 18. Average uptake of P by conifer seedlings as a function of relative root CEC.

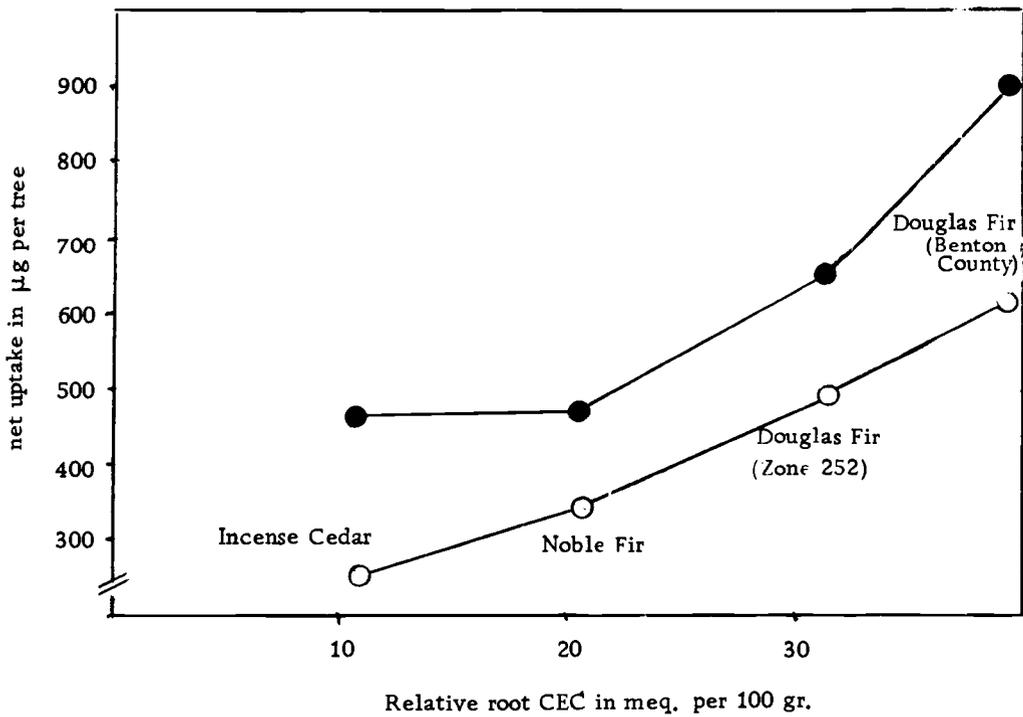


Figure 19. Average uptake of Mn by conifer seedlings under grass competition as a function of relative root CEC at 25 ppm N (O) and 100 ppm N (●).

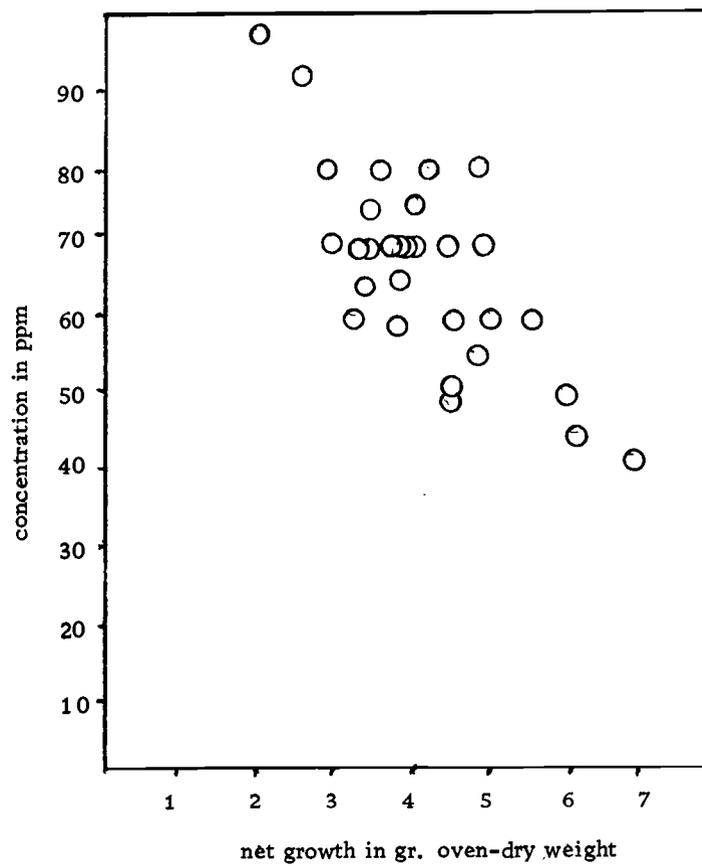


Figure 20. Concentrations of Fe in newly formed tissue of incense cedar as a function of new growth.

cedar tissue.

Iron deficiencies have been reported for conifers on calcareous soils (Berger and Pratt, 1963). They are less likely to be encountered on acid soils, and are usually induced by an overabundance of other heavy metals such as manganese, copper, or nickel. It is proposed that Mn induced the deficiency in this experiment. In most plants, Mn toxicities occur above 800 ppm (Berger and Pratt, 1963). Manganese concentrations reached over 1000 ppm in this study. In Figure 19, the average Mn uptake by the conifers from comparable treatments was related to the relative root CEC. An almost linear increase of Mn uptake with root CEC is obvious at 25 ppm N. The higher level of  $\text{Ca}(\text{NO}_3)_2$  stimulated accumulation of Mn. The fact that this response is not caused by higher acidity is demonstrated in Table 9, which indicates that the higher level of  $\text{Ca}(\text{NO}_3)_2$  did not produce a significantly lower pH. Similarly, Table 9 shows that the greater resistance of the low CEC species cannot be explained by differential changes in the soil pH, one of the prime determinants of Mn availability.

A low root CEC has repeatedly been related to inter- and intraspecific variations in the resistance to Mn toxicities and high levels of other metals (Vose and Randall, 1962; Bollard and Butler, 1966). The greater tolerance of incense cedar to toxic amounts of Mn, and the higher susceptibility of noble and Douglas firs, are in

agreement with these observations. Again, however, it must be stated that Mn absorption is regulated by numerous other determinants, each of which could have produced similar results. The data, therefore, do not constitute a proof that tolerance to Mn and low root CEC are causally related.

Greenhouse conditions, with their high temperatures and high light intensities, have been observed to raise Mn levels in plants and to induce Fe chlorosis (Jackson, 1967). Hence, it becomes difficult to evaluate the possible significance of the observed imbalance of Mn and Fe to growth and color of conifers in Christmas tree plantations on the Bellpine soil. The levels of exchangeable and water soluble Mn found in the Bellpine soil (Table 2) are not excessive. The analysis was, however, performed on air-dried soil. In addition, it is often observed that only poor correlations exist between these measures for Mn availability and observed toxicities. The easily reducible or "active Mn" (Scheffer and Schachtschabel, 1966, p. 319), which was not determined, may give a better estimate. The high acidity of the Bellpine soil, and the pronounced Mn coatings found on rock fragments in the subsoil, indicate that the Mn levels may be high.

The deficiency symptoms of conifers in the field, consisting of a pale, chlorotic appearance and dying of older needles, were similar to those observed in the greenhouse. Low levels of other

bases, especially K (Black, 1968, p. 348), may enhance Fe deficiencies. Mn toxicities are cumulative. Plants are affected to a greater degree the longer they grow (Bollard and Butler, 1966). This could explain the concentration of severe deficiency symptoms on the inner branches and needles of mature Douglas firs which were observed on the Bellpine soil.

## SUMMARY AND CONCLUSION

The mineral nutrition of conifer seedlings on an infertile Bell-pine soil was studied in a greenhouse experiment, and related to the cation-exchange capacity of the seedlings and their tree and grass competitors.

Relative root CEC was determined by H-saturation of fresh, excised roots in repeated, mild acid rinses, and subsequent titration in a neutral salt solution. There were large inter- and intraspecific differences among the conifers. This method for the determination of root CEC can give valid results only on a relative scale. It was shown that an arbitrary endpoint in time must be chosen, and that more  $H^+$  than that which is adsorbed in the Donnan Free Space is included in the titration. A method was, therefore, devised to eliminate both difficulties.

Even untreated roots consume base and release  $H^+$ , not only from exchange sites, but also from various other sources. After Ca-saturation of the roots, this latter fraction was isolated and termed non-exchangeable.

Subtraction of the non-exchangeable acidity from the total acidity, measured during the titration of H-saturated roots, led to a constant value, which represented only adsorbed acidity and equals the root CEC. It was concluded that this value closely approaches

the concentration of exchange sites available under field conditions.

Growth in the Bellpine soil decreased the root CEC of all tested conifer species. Reasons for this reduction were discussed.

The possible role of root CEC in the nutrient uptake of conifer seedlings was examined in a greenhouse experiment, for which the infertile Bellpine soil represented a suitable growth medium. In many treatments, the planted conifer seedlings actually lost K, Mg, and P to the experimental soil.

Competing grass and tree species rarely affected the nutrient uptake of the conifers according to expectations from the Donnan Law. It was concluded that, although root CEC may be one of the determinants of successful nutrient accumulation in competition, other factors will often be of overriding importance.

There was evidence, however, that conifers with a relatively high root CEC took up divalent ions and P preferentially from the Bellpine soil. In contrast, incense cedar, which had the lowest CEC, was a relatively more efficient feeder for soil K and proved to be more resistant to a Mn induced Fe deficiency, which occurred in the greenhouse experiment.

Other factors besides root CEC may, however, have influenced nutrient uptake and could have led to similar results. The relations between mycorrhizae and root CEC should be investigated. The results of this study do not necessarily constitute a proof of the

hypothesis that root CEC may be one of the determinants in the mineral nutrition of conifer seedlings, although they often indicate a relationship between root CEC and nutrient uptake.

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